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Headline Articles

Bimolecular Reactions of Tetrakis(trialkylsilyl)disilenes with Various Reagents

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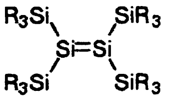
Versatile reaction modes of tetrasilyldisilenes with various reagents have been disclosed. Typically, tetrakis(*t*-butyldimethylsilyl)disilene **1b** reacts with 1-alkenes and a 1-alkyne having allylic hydrogens to afford the corresponding ene-addition products, while a reaction of **1b** with styrene gives the [2+2] cycloaddition product. In contrast to tetra-*t*-butyldisilene and tetramesityldisilene, a reaction of **1b** with a 1,3-butadiene gives quantitatively the [4+2] cycloaddition product. In accord with the biradical nature of disilene as predicted theoretically, tetrasilyldisilene **1b** reacts with haloalkanes to provide the corresponding 2,3-dichlorotetrasilane or 2-alkyl-3-chlorotetrasilane probably via radical mechanisms. Facile nucleophilic additions of water, methanol, and methyllithium to **1b** are indicative of the high electrophilicity of **1b**.

Although a number of bimolecular reactions of both transient and isolable disilenes (silicon–silicon doubly-bonded compounds) have been reported,[1)] substituent effects on the modes, rates, and mechanisms of the reactions have rarely been discussed.[2)] Studies of the substituent effects will be crucial to the systematic understanding of the characteristics of group-14 double bonds, including C=C bonds. We have recently isolated several tetrakis(trialkylsilyl)disilenes (**1a**—**c**) and revealed their unusually long Si=Si bond distances,[3a)] striking dependence of the electronic spectra on the alkyl-substituents,[3a)] very low-field ^{29}Si NMR resonances of the unsaturated silicon nuclei,[3b)] and facile rotation around the Si=Si bonds (Chart 1).[3c)] Remarkable electronic effects of trialkylsilyl substituents would be responsible for these structural characteristics. Whereas reaction modes among **1a**—**1c** have been found to be different in several reactions due to the steric effects of the trialkylsilyl substituents, the present study has been focussed on the various bimolecular reactions of **1b** as a typical tetrasilyldisilene. Tetrasilyldisilene **1b** behaved as an electrophile to hydroxylic and organometallic reagents, a biradicalloid to haloalkanes, and a 2π system for electrocyclic reactions with alkenes and a 1,3-diene. Unique reaction modes of **1b** are demonstrated and discussed in comparison with those reported previously for typical isolable disilenes such as tetra-*t*-butyldisilene and tetramesityldisilene.[1)]

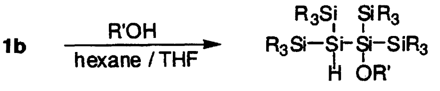


1a, R_3Si = *i*-Pr_2MeSi;
1b, R_3Si = *t*-$BuMe_2Si$;
1c, R_3Si = *i*-Pr_3Si.

Chart 1.

Results and Discussion

Reactions of 1b with Water and Methanol. The reaction mode and reactivity of tetrasilyldisilene **1b** toward water and methanol are similar to those of other known disilenes.[1)] Thus, disilene **1b** reacted rapidly with water at 0 °C to give the corresponding 2-hydroxytetrasilane **2** (Eq. 1). A reaction of **1b** with methanol at 50 °C afforded 2-methoxytetrasilane **3** together with water-adduct **2**, even when methanol is rigorously dried. Since the rate-determining step of the reaction is proposed to be a nucleophilic addition of the alcoholic oxygen to the unsaturated silicon,[4,5)] this much lower reactivity of methanol suggests that the steric hindrance at the transition state for the reaction with methanol is severer than that for the water addition.



(1)

2, 75% (R_3Si = *t*-$BuMe_2Si$, R'=H)
3, 66% (R_3Si = *t*-$BuMe_2Si$, R'=Me)

Reaction of 1b with Methyllithium. When a THF solution of **1b** was treated with excess methyllithium at 0 °C, the orange solution turned to pale orange. Hydrolysis of the solution gave the corresponding 2-methyltetrasilane **5**,

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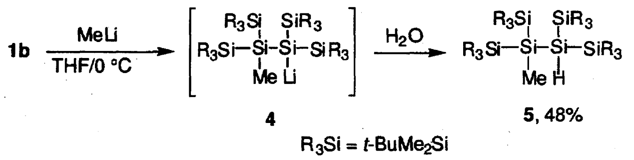
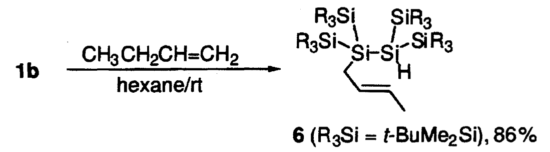
indicating the formation of silyllithium **4** as an intermediate (Eq. 2).[6]



(2)

No similar reactions of tetra-*t*-butyldisilene and tetramesityldisilene have been reported; these disilenes are suggested to be less electrophilic than disilene **1b**.

Ene Reactions with 1-Alkenes and a 1-Alkyne. Disilene **1b** reacted with various alkenes having allylic hydrogens quite smoothly to afford the corresponding ene-addition products in high yields. Typically, a reaction of **1b** with 1-butene below -15 °C in the dark gave ene-addition product **6** in 86% yield (Eq. 3). The stereochemistry of **6** was determined to be *trans*, on the basis of the ^3J value between the two olefinic protons (see Experimental); no other isomer was detected in the reaction mixture.

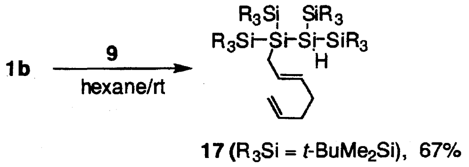


(3)

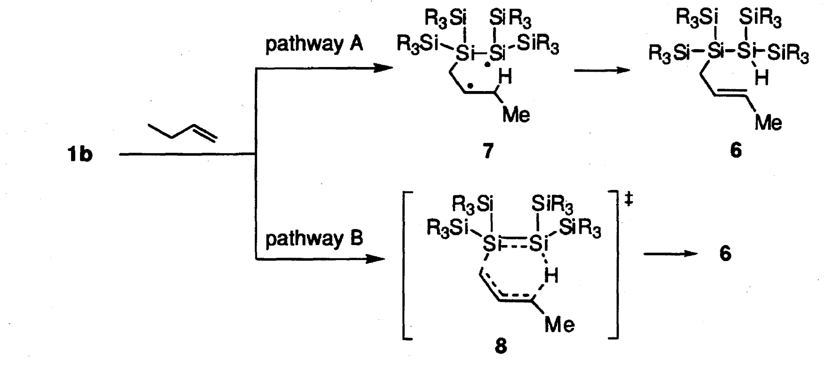
The following two pathways can be envisaged to explain the result (Scheme 1): (1) the initial addition of **1b** to an olefin giving the corresponding 1,3-biradical **7**, followed by the intramolecular abstraction of a β-hydrogen giving **6** (pathway A) and (2) the concerted ene addition of an alkene to disilene **1b** through a cyclic transition state like **8** (pathway B). Both these pathways can explain the *trans* arrangement about the double bond in **6**, since they proceed via six-membered cyclic transition states.

In order to distinguish these two pathways, reactions of disilene **1b** with 1,6-heptadiene (**9**) and vinylcyclopropane (**10**) as radical clocks[7] were investigated. If a reaction of **1b** with an alkene proceeds via pathway A, reactions of **1b** with **9** and **10** should give biradical intermediates **11** and **12**, respectively, which will undergo facile rearrangement to cyclic isomers **13** and **14** to give final addition products **15** and **16**, respectively (Scheme 2); related intramolecular rearrangements from 2-hexa-5-enyl and 1-cyclopropylethyl radicals are reported to occur very quickly with the first-order rate constants of 1.0×10^5 s^{-1} [8] and 1.3×10^8 s^{-1} [9] respectively, at 298 °C.

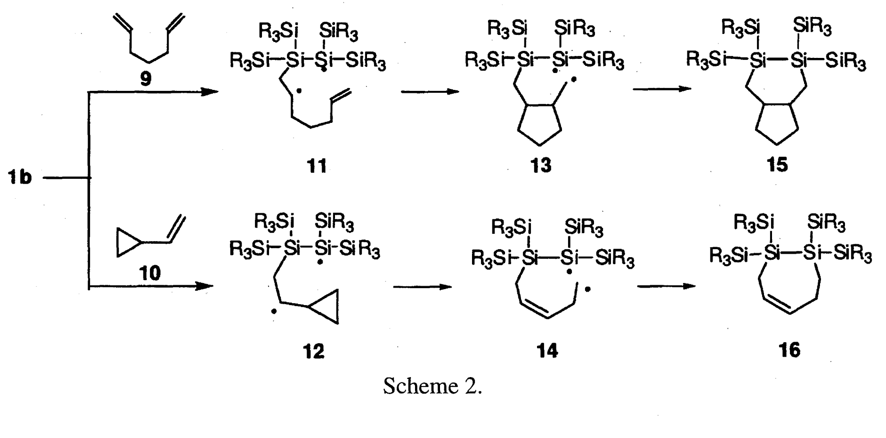
In reality, disilene **1b** reacted with **9** at room temperature to afford 2-(2,6-heptadienyl)tetrasilane **17** (the (*E*)-isomer) in a moderate yield without any cyclic products such as **15** (Eq. 4). The reaction of **1b** with vinylcyclopropane was remarkably slow at room temperature to give a complex mixture, in which neither an expected cyclic disilane **16** nor the corresponding ene addition product was detected (Eq. 5).



(4)



Scheme 1.

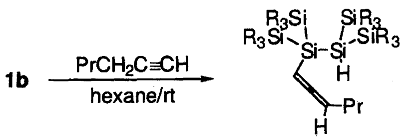


Scheme 2.

$$\mathbf{1b} \xrightarrow[\text{very slow}]{\mathbf{10}\text{/hexane/rt}} \text{A Complex Mixture} \qquad (5)$$

These results indicate that reactions of disilene **1b** with alkenes proceed via the concerted pathway (pathway B) rather than the radical addition pathway (pathway A). In addition, the result shown in Eq. 5 is compatible with the expected low reactivity of vinylcyclopropane as an ene reagent.[10)]

Disilene **1b** reacted with a 1-alkyne in a similar ene-addition manner, giving the corresponding 2-allenyltetrasilane as shown in Eq. 6.



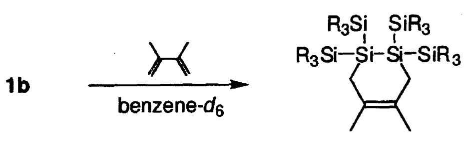
(6)

18 (R_3Si = *t*-$BuMe_2Si$), 20%

To the best of our knowledge, the present results constitute the first examples of the concerted ene reactions of disilenes with simple olefins. It has been reported that tetramesityldisilene does not undergo ene reaction with a 1-alkene and a 1-alkyne,[11)] while a pyrolysis of tetramesityldisilene affords a benzosilacyclobutene derivative, which may be produced via an intramolecular ene addition reaction.[12)] Photochemically-generated transient disilenes have been reported to react with 2,3-dimethyl-1,3-butadiene giving ene addition products but in low yields; [4+2] cycloadditions occur competitively.[13)]

The enhanced reactivities of tetrasilyldisilene **1b** toward the terminal alkenes and alkyne suggest that the energy level of the π-type LUMO in **1b** is significantly lowered compared with those in tetra-*t*-butyldisilene and tetramesityldisilene.[14)]

The Diels–Alder Additions of 1b with 2,3-Dimethyl-1,3-butadiene. As shown in Eq. 7, **1b** underwent readily the Diels–Alder type cycloaddition with 2,3-dimethyl-1,3-butadiene at room temperature to give quantitatively the corresponding 4,5-disilacyclohexene **19**.[16)]

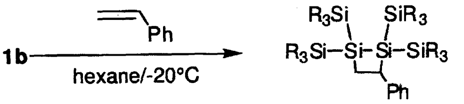


(7)

19 (R_3Si = *t*-$BuMe_2Si$), quantitatively

Although many isolable disilenes have been known to undergo [4+2] reactions with heterodienes such as benzil,[17,18a,18b)] benzoyl chloride,[19)] acrylamine,[18c)] and 1,4-diazabutadiene,[18d)] no [4+2] addition of the disilenes to 1,3-butadienes has been reported. A reaction of tetra-*t*-butyldisilene with 2,3-dimethyl-1,3-butadiene has been reported to afford ene addition products predominantly together with a small amount of the Diels–Alder adduct (vide supra).[13)] The reason for the higher reactivity of **1b** toward a 1,3-diene than that of tetramesityldisilene may be ascribed to the lower-lying π-LUMO in **1b**, as invoked for the ene-additions of **1b**.

The [2+2] Cycloaddition with Styrene. Tetrasilyldisilene **1b** was found also to react with styrene very rapidly at −20 °C to give the corresponding 1,2-disilacyclobutane **20** (Eq. 8).



(8)

20 (R_3Si = *t*-$BuMe_2Si$), 84%

Recently, the [2+2] cycloadditions of isolable disilenes with olefins have been reported by Weidenbruch et al.[20,21)] and Baines et al.[22)] Although these cycloadditions have been considered to proceed through a biradical intermediate, mechanistic details have not been investigated so far. Taking into account the results of the reactions of **1b** with the radical clocks as mentioned above, the reaction of **1b** with styrene may not proceed via a simple radical addition pathway. Since the concerted [2+2] cycloadditions of olefins are known to be allowed between an electron-deficient olefin and an electron-rich olefin,[23)] the present [2+2] reaction of **1b** may proceed through a concerted pathway. Further studies will be needed to establish the mechanism of the [2+2] cycloadditions of disilenes with styrene.

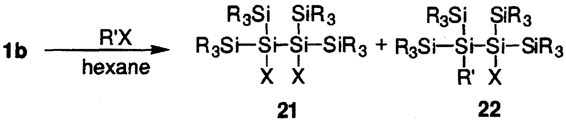
While the [2+2] cycloaddition reaction of tetramesityldisilene with phenylacetylene has been reported,[24)] a reaction of **1b** with phenylacetylene proceeded slowly but gave a complex product mixture without formation of the corresponding [2+2] adduct.

Reaction of 1b with Haloalkanes. Although there is no precedent for the direct reaction of a C=C double bond with a haloalkane, disilene **1b** reacted very smoothly with various haloalkanes in the dark. Thus, reactions of **1b** with carbon tetrachloride and carbon tetrabromide at −50 °C in the dark gave the corresponding 2,3-dihalotetrasilane **21a** (X = Cl) and **21b** (X = Br) in high yields. Reactions of **1b** with chloroform and dichloromethane gave readily the corresponding 1,2-adducts of the alkyl halides: 2-chloro-3-(dichloromethyl)tetrasilane **22c** and 2-chloro-3-(chloromethyl)tetrasilane **22d**, respectively, at lower temperatures than room temperature. Similarly, treatment of **1b** with bromomethane provided 2-bromo-3-methyltetrasilane **22e** at −30 °C. The results of these reactions are summarized in Table 1.

Table 1. Reactions of Disilene **1b** with Various Haloalkanes

Haloalkane	Temp	Yield/%[a,b)]	
	°C	**21**	**22**
CCl_4	−50	83 (**21a**)	—
CBr_4	−65	90 (**21b**)	—
$CHCl_3$	−50→r.t.	—	78 (**22c**)
CH_2Cl_2	−50→r.t.	—	85 (**22d**)
CH_3Br	−30	—	95 (**22e**)

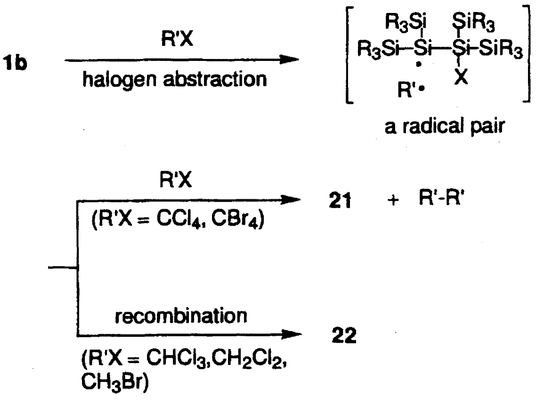
a) Numbering of the product is shown in parentheses. b) Yield was determined by NMR spectroscopy.



(9)

R_3Si = *t*-BuMe$_2$Si

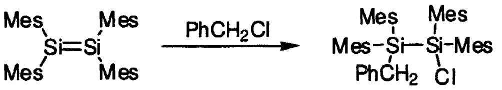
21a, X = Cl; **21b**, X = Br.
22c, R' = CHCl$_2$, X = Cl; **22d**, R' = CH$_2$Cl, X = Cl;
22e, R' = CH$_3$, X = Br.



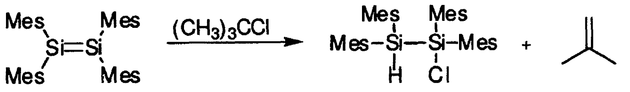
Scheme 3.

The reactions of tetrasilyldisilene **1b** with haloalkanes can be understood by a radical mechanism as shown in Scheme 3: tetrasilyldisilene **1b** abstracts initially a halogen atom from an alkyl halide to form a pair of the corresponding β-halodisilanyl radical and alkyl radical. When chloroform, dichloromethane, and bromomethane are used as alkyl halides, recombination of the radical pair in the cage gives the corresponding adducts. During reactions of **1b** with carbon tetrachloride and carbon tetrabromide, the facile halogen abstraction of the β-halodisilanyl radical takes place to give the corresponding 1,2-dihalodisilane derivative; the competitive reaction of the β-halodisilanyl radical with trihalomethyl radical in the cage may be prevented because of the steric hindrance.[25] The reactivities of **1b** toward alkyl halides are comparable qualitatively to those of triethylsilyl radical; the rate constant for halogen abstraction of triethylsilyl radical decreases in the order: $CCl_4 > (CH_3Br) > CHCl_3 > CH_2Cl_2$.[26] It is possible, however, that single-electron transfer from disilene to alkyl halides giving the radical ion pair, followed by the halide transfer, produces a pair of the β-halodisilanyl radical and the haloalkyl radical.

As precedents for the reaction of disilenes with alkyl halides, reactions of tetramesityldisilene with benzyl chloride and 2-chloro-2-methylpropane have been reported, but the reaction mechanisms have not been taken into consideration (Eqs. 10 and 11).[22,27]



(10)



(11)

On the basis of the theoretical calculations, Teramae has proposed that disilene will have a weak but significant singlet biradical character in the trans bent conformation.[28] Our experimental results as well as the previous works[22] are compatible with the predicted biradical character of disilenes in general. A study of the mechanistic details is now under way.[15]

Experimental

General. ^1H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (59 MHz) NMR spectra were recorded on a Bruker AC-300P FT NMR spectrometer. Mass spectra were obtained on either a JEOL JMS D-300, a JEOL JMS D-100s, or a JEOL JMS-600W mass spectrometer. GLC analysis was conducted using a Shimadzu 8A gas chromatograph (5% or 15%/Celite545, 1.5 m). Preparative GPC was performed on JAI LC-908 and LC-08 gel permeation chromatographs.

Materials. Tetrasilyldisilene **1b**[3a] and vinylcyclopropane[29] were prepared according to the reported procedure. THF, hexane, and benzene-d_6 were dried over a potassium mirror and then distilled prior to use by using a vacuum line. Commercially available carbon tetrachloride, chloroform, dichloromethane, 1-chloropropane, bromomethane, 1-butene, 1-hexyne, 1,6-heptadiene, styrene, and 2,3-dimethyl-1,3-butadiene were dried over calcium hydride overnight in the dark and then distilled prior to use by using a vacuum line. Carbon tetrabromide was sublimed under reduced pressure prior to use.

Procedures for Reactions of 1b with Various Reagents. All reactions were performed under argon or nitrogen in a standard vacuum system unless otherwise noted. All the reactions were carried out in the dark to exclude possible reactions through the excited state of **1b**. Typically, to a hexane solution of disilene **1b** in a schlenk test tube equipped with a magnetic stirrer bar, a pertinent reagent was introduced through a vacuum line. The reaction mixture was stirred at −50 °C, then allowed to warm to room temperature until the color of disilene **1b** disappeared. The volatile components were removed in vacuo. The products were purified by gel permeation chromatography. The yields were determined by ^1H NMR spectroscopy using 1,2,4,5-tetramethylbenzene as an internal standard.

Reaction with Water. In a schlenk tube equipped with a magnetic stirrer bar, tetrasilyldisilene **1b** (39.6 mg, 7.66×10^{-5} mol) and deoxygenated dry hexane (3.5 ml) were placed. Then, a THF (10 ml) solution of water (11.2 mg, 6.22×10^{-4} mol) was added to the mixture at room temperature. The orange color of the solution disappeared completely within 30 min. Removal of the solvent in vacuo and then recrystallization from hexane gave 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2-hydroxy-1,1,4,4-tetramethyltetrasilane **2** (30.6 mg, 5.72×10^{-5} mol, 75%) as an off-white solid. **2:** A colorless solid; mp 91 °C; ^1H NMR (C_6D_6) $\delta = 0.25$ (s, 6 H, SiMe), 0.29 (s, 6 H, SiMe), 0.31 (s, 13 H, $\mathrm{Si\underline{Me}}$+$\mathrm{Si{-}O\underline{H}}$), 1.03 (s, 18 H, *t*-Bu), 1.12 (s, 18 H, *t*-Bu), 3.39 (s, 1 H, SiH); ^{13}C NMR (C_6D_6) $\delta = -3.3, -3.0, -2.0, -1.1, -0.7$ ($\mathrm{Si\underline{C}H_3}$), 18.7, 20.1 ($\mathrm{\underline{C}(CH_3)_3}$), 27.5, 28.3 ($\mathrm{C(\underline{C}H_3)_3}$); ^{29}Si NMR (CD_2Cl_2, 223 K) $\delta = -121.9$ ($\mathrm{\underline{Si}{-}H}$), −7.0, −5.6, −0.2, 2.8 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)), 14.3 ($\mathrm{\underline{Si}{-}OH}$); MS (EI, 14 eV) *m*/*z* (%) 532 (M^+-2; 25.3), 419 (M^+-115; 19.8), 402 (14.2), 275 (100). Anal. Calcd for $(C_{24}H_{62}OSi_6)_2\cdot H_2O$: C, 52.96; H, 11.67%. Found: C, 52.79; H, 11.73%.

Reaction with Methanol. To a THF (5 ml) solution of tetrasilyldisilene **1b** (104 mg, 2.61×10^{-5} mol) in a schlenk tube equipped with a magnetic stirrer bar, methanol (326 mg, 1.02×10^{-2} mol) was added at room temperature. The orange color of the solution disappeared completely within 90 min at 40 °C. Removal of the solvent in vacuo gave an off-white solid, which contained 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2-methoxy-1,1,4,4-tetramethyltetrasilane **3** and **2** in 66 and 22% yields, respectively. Separation of these two compounds by GPC, HPLC, and recrystallization has failed. **3**: ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta=0.28$ (s, 6 H, SiMe), 0.31 (s, 12 H, SiMe), 0.34 (s, 6 H, SiMe), 1.07 (s, 18 H, *t*-Bu), 1.13 (s, 18 H, *t*-Bu), 3.26 (s, 3H, OMe), 3.48 (s, 1 H, SiH); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta=-2.3$, -2.1, -0.7 ($\mathrm{Si\underline{C}H_3}$), 19.2, 19.7 ($\mathrm{\underline{C}(CH_3)_3}$), 27.7, 28.4 ($\mathrm{C(\underline{C}H_3)_3}$), 55.2 ($\mathrm{O\underline{C}H_3}$); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta=-122.3$ ($\mathrm{\underline{Si}H}$), -4.3, 2.2 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)), 18.1 ($\mathrm{\underline{Si}OMe}$); MS (EI, 70 eV) *m*/*z* (%) 548 (M$^+$; 2.1), 533 (8.8), 491 (5.6), 433 (23.9), 402 (17.4), 289 (100), 73 (93.8). HRMS Calcd for $\mathrm{C_{25}H_{64}OSi_6}$: M, 548.3573. Found: *m*/*z* 548.3545.

Reaction with Methyllithium. In a schlenk tube equipped with a glass-covered stirrer bar, tetrasilyldisilene **1b** (50.7 mg, 9.80×10^{-5} mol) and THF (2.5 ml) were placed. When methyllithium in THF (1.3 mol dm^{-3}, 0.60 ml, 5.2×10^{-4} mol) was added to the mixture at 0 °C, the solution changed immediately from dark orange to light yellow. After the mixture was stirred at room temperature for 1 h, an excess amount of water was added. The organic layer was extracted by hexane, neutralized, washed with water and brine, and then dried over anhydrous magnesium sulfate. After the solvent was removed in vacuo, a pale yellow oil was obtained. The resulting oil was subjected to GPC to give pure 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-1,1,2,4,4-pentamethyltetrasilane **5** (25.3 mg, 4.74×10^{-5} mol, 48%). **5:** Colorless crystals; mp 113—114 °C; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta=0.13$ (s, 6 H, SiMe), 0.16 (s, 6 H, SiMe), 0.19 (s, 12 H, SiMe), 0.44 (s, 3 H, $\mathrm{Si\underline{Me}{-}SiH}$), 0.92 (s, 18 H, *t*-Bu), 0.95 (s, 18 H, *t*-Bu), 3.05 (s, 1 H, SiH); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta=-120.1$ ($\mathrm{\underline{Si}{-}H}$), -76.4 ($\mathrm{\underline{Si}{-}Me}$), -1.9, 1.8 ($\mathrm{\underline{Si}Me_2}$-(*t*-Bu)); MS (EI, 14 eV) *m*/*z* (%) 532 (M$^+$; 4.5), 475 (M$^+-57$; 22), 416 (M$^+-116$; 100). HRMS Calcd for $\mathrm{C_{25}H_{64}Si_6}$: M, 532.3624. Found: *m*/*z* 532.3594.

Reaction with 1-Butene. A reaction of **1b** (54.2 mg, 1.05×10^{-5} mol) with 1-butene (0.5 ml) in hexane (3 ml) proceeded readily below -15 °C to give the (*E*)-isomer of 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2-(2-butenyl)-1,1,4,4-tetramethyltetrasilane (**6**, 51.8 mg, 9.03×10^{-5} mol, 86%) together with a small amount of **2**. **6:** A colorless oil; ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta=0.17$ (s, 12 H, SiMe), 0.19 (s, 6 H, SiMe), 0.23 (s, 6 H, SiMe), 0.95 (s, 18 H, *t*-Bu), 0.96 (s, 18 H, *t*-Bu), 1.57 (dd, $J=6.3$ Hz, $J=1.0$ Hz, 3 H, $\mathrm{CH_3}$), 1.97 (d, $J=7.3$ Hz, 2 H, $\mathrm{SiC\underline{H_2}CH{=}}$), 3.42 (s, 1 H, SiH), 5.25 (qd, $J=14.8$ Hz, $J=6.3$ Hz, 1 H, $\mathrm{CH_3C\underline{H}{=}}$), 5.47 (td, $J=14.8$ Hz, $J=7.3$ Hz, 1 H, $\mathrm{CH_3CH{=}C\underline{H}}$); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=-1.6$, -1.5, -0.8, 0.3 ($\mathrm{Si\underline{C}H_3}$), 17.8 ($\mathrm{\underline{C}H_3CH{=}}$), 19.2 ($\mathrm{\underline{C}(CH_3)_3}$), 19.3 ($\mathrm{Si\underline{C}H_2CH{=}}$), 20.0 ($\mathrm{\underline{C}(CH_3)_3}$), 27.8, 28.5 ($\mathrm{C(\underline{C}H_3)_3}$), 123.5, 131.0 ($\mathrm{\underline{C}H{=}}$); ^{29}Si NMR ($\mathrm{CDCl_3}$) $\delta=-121.8$ ($\mathrm{\underline{Si}H}$), -69.4 ($\mathrm{\underline{Si}CH_2}$), -0.5, 1.9 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)); MS (EI, 14 eV) *m*/*z* (%) 572 (M$^+$; 0.4), 456 (45.5), 399 (32.5), 340 (100). HRMS Calcd for $\mathrm{C_{28}H_{68}Si_6}$: M, 572.3937. Found: *m*/*z* 572.3932. The *trans* arrangement about the double bond is evident from the ^3J values of 14.8 Hz between two olefinic protons. No other diastereomers were formed in the reaction mixture.

Reaction with 1,6-Heptadiene (9). A reaction of **1b** (55.9 mg, 1.08×10^{-4} mol) with **9** (0.3 ml) proceeded at room temperature. After the reaction mixture was stirred for 2 d in the dark, ^{1}H NMR indicated the existence of only two products; 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2-((*E*)-2,6-heptadienyl)-1,1,4,4-tetramethyltetrasilane **17** (44.5 mg, 7.25×10^{-5} mol, 67%) together with **2** (8.8 mg, 1.64×10^{-5} mol, 15%). No other products such as **15** were obtained. **17:** A colorless oil; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta=0.323$ (s, 6 H, SiMe), 0.329 (s, 6 H, SiMe), 0.332 (s, 6 H, SiMe), 0.37 (s, 6 H, SiMe), 1.07 (s, 18 H, *t*-Bu), 1.08 (s, 18 H, *t*-Bu), 2.14 (m, 4 H, C(4)$\mathrm{H_2}$, C(5)$\mathrm{H_2}$), 2.24 (d, $J=7.5$ Hz, 2 H, C(1)$\mathrm{H_2}$), 5.00 (dd, $J=10$ Hz, $J=2.1$ Hz, 1 H, C(7)H), 5.05 (dd, $J=17.0$ Hz, $J=2.1$ Hz, 1 H, C(7)H), 5.45 (dm, $J=15.0$ Hz, 1 H, C(3)H), 5.76 (dt, $J=15.0$ Hz, $J=7.5$ Hz, 1 H, C(2)H), 5.81 (ddm, $J=17.0$ Hz, $J=10.0$ Hz, 1 H, C(6)H); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta=-1.2$, -1.0, -0.5, 0.6 ($\mathrm{Si\underline{C}H_3}$), 19.4 ($\mathrm{\underline{C}(CH_3)_3}$), 19.9 (Si–C(1)), 20.2 ($\mathrm{\underline{C}(CH_3)_3}$), 28.0, 28.7 ($\mathrm{C(\underline{C}H_3)_3}$), 32.7, 34.1 (C(4), C(5)), 114.9 (C(7)), 129.1, 130.4, 138.4 (C(2), C(3), C(6)); ^{29}Si NMR $\delta=-121.2$ ($\mathrm{\underline{Si}H}$), -68.9 ($\mathrm{\underline{Si}(SiR_3)_2}$), -0.1, 2.4 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)); MS (EI, 70 eV) *m*/*z* (%) 612 (M$^+$; 0.7)), 497 (12.3), 381 (57.9), 353 (61.7), 323 (54.3), 73 (100). HRMS Calcd for $\mathrm{C_{31}H_{72}Si_6}$: M, 612.4249. Found: *m*/*z* 612.4211.

Reaction with Vinylcyclopropane (10). A reaction of **1b** (50.4 mg, 9.75×10^{-5} mol) with vinylcyclopropane (80 mg) in hexane (2.5 ml) was carried out at room temperature in the dark for 3 d. Removal of the volatile components in vacuo gave a pale yellow oil. While the mass spectrometric analysis of the oil indicated the existence of vinylcyclopropane adducts of **1b** in addition to **2**, the ^{1}H NMR spectrum was too complicated to be analyzed. An attempted separation of the adducts using GPC (eluent $\mathrm{CHCl_3}$) failed.

Reaction with 1-Hexyne. The reaction of **1b** (101 mg, 1.95×10^{-4} mol) with 1-hexyne (342 mg, 4.16×10^{-3} mol) completed within 12 h at room temperature affording 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2-(1,2-hexadienyl)-1,1,4,4-tetramethyltetrasilane **18** as a major product. Pure **18** (23.2 mg, 3.87×10^{-5} mol, 20%) was obtained by GPC ($\mathrm{CHCl_3}$). **18:** A colorless oil; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta=0.31$ (s, 3 H, SiMe), 0.34 (s, 3 H, SiMe), 0.37—0.39 (m, 12 H, SiMe), 0.88 (t, $J=7.3$ Hz, 3 H, C(6)$\mathrm{H_3}$), 1.06 (s, 18 H, *t*-Bu), 1.11 (s, 9 H, *t*-Bu), 1.12 (s, 9 H, *t*-Bu), 1.38 (m, 2 H, C(5)$\mathrm{H_2}$), 2.08 (m, 2 H, C(4)$\mathrm{H_2}$), 4.75 (dt, $J=7.4$, 7.2 Hz, 1 H, $\mathrm{PrC\underline{H}}$), 5.44 (dt, $J=7.4$, 3.5 Hz, 1 H, $\mathrm{SiC\underline{H}}$); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta=-1.9$, -1.7, -1.5, -0.8, -0.1, 0.1 ($\mathrm{Si\underline{C}H_3}$), 14.0 ($\mathrm{\underline{C}(6)H_3}$), 19.2, 20.1, 20.3 ($\mathrm{\underline{C}(CH_3)_3}$), 23.6 (C(4 or 5)$\mathrm{H_2}$), 27.9, 28.6 ($\mathrm{C(\underline{C}H_3)_3}$), 30.7 ($\underline{\mathrm{C}}$(4 or 5)$\mathrm{H_2}$), 80.7, 84.6 ($\underline{\mathrm{C}}$(1 or 3)H), 210.8 ($\mathrm{CH{=}\underline{C}{=}CH}$); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta=-118.9$ ($\mathrm{\underline{Si}{-}H}$), -78.7 ($\mathrm{\underline{Si}CH}$), 0.3, 0.9, 2.1, 2.2 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)); MS (EI, 14 eV) *m*/*z* (%) 598 (1.1), 541 (35.7), 482 (50.2), 425 (100), 366 (29.3).

Reaction with Styrene. A reaction of **1b** (50.2 mg, 6.47×10^{-5} mol) with styrene (0.5 ml) was completed within 2 h below -20 °C to give 1,1,2,2-tetrakis(*t*-butyldimethylsilyl)-3-phenyl-1,2-disilacyclobutane **20** (33.7 mg, 5.43×10^{-5} mol, 84%) together with **2**. Pure **20** (16.6 mg, 2.67×10^{-5} mol, 41%) was obtained by GPC. **20:** A colorless oil; ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta=0.04$ (s, 3H, Me), 0.25 (s, 3 H, SiMe), 0.26 (s, 3 H, SiMe), 0.30—0.32 (m, 9 H, SiMe), 0.42 (s, 3 H, SiMe), 0.49 (s, 3 H, SiMe), 0.65 (s, 9 H, *t*-Bu), 0.98 (s, 9 H, *t*-Bu), 0.99 (s, 9 H, *t*-Bu), 1.01 (s, 9 H, *t*-Bu), 1.70 (dd, $J=6.2$, 12.6 Hz, 1 H, $\mathrm{C\underline{H}Ph}$), 2.23 (dd, $J=12.6$, 15.3 Hz, 1 H, CH), 3.68 (dd, $J=6.2$, 15.3 Hz, 1 H, CH), 6.97—7.02 (m, 1 H, PhH(*p*)), 7.10—7.12 (m, 2 H, PhH(*o*)), 7.15—7.21 (m, 2 H, Ph(*m*)); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=-1.0$, 0.1, 0.3, 0.4, 0.5, 0.6, 0.9, 1.0 ($\mathrm{SiCH_3}$), 17.8 ($\mathrm{CH_2}$), 19.1, 19.5, 20.6 ($\mathrm{\underline{C}(CH_3)_3}$), 28.4, 29.0, 29.3, 29.4 ($\mathrm{C(\underline{C}H_3)_3}$), 35.5 ($\mathrm{\underline{C}HPh}$), 124.0, 126.3, 128.0, 148.0; ^{29}Si NMR ($\mathrm{CDCl_3}$) $\delta=-58.6$ ($\mathrm{\underline{Si}CH_2}$), -27.8 ($\mathrm{\underline{Si}CHPh}$), -0.1, 0.6, 2.7, 4.2 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)); MS (EI, 14 eV) *m*/*z* (%) 620 (M$^+$; 27.7), 505 (53.8), 449 (100), 274 (65.3), 258 (29.1).

Reaction with 2,3-Dimethylbutadiene. A reaction of **1b** (25 mg, 3.23×10^{-5} mol) with an excess amount of 2,3-dimethyl-1,3-butadiene (0.1 ml) in $\mathrm{C_6D_6}$ (0.5 ml) was carried out in a Young's NMR tube at room temperature to give 4,4,5,5-tetrakis(*t*-butyldimethylsilyl)-1,2-dimethyl-4,5-disilacyclohexene **19** quantitatively. **19:** A colorless oil; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta = 0.33$ (s, 12 H, SiMe), 0.34 (s, 12 H, SiMe), 1.06 (s, 36 H, *t*-Bu), 1.75 (s, 6 H, $\mathrm{CH_3}$), 2.05 (s, 4 H, $\mathrm{CH_2}$); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta = -0.5$, 0.1 ($\mathrm{Si\underline{C}H_3}$), 20.0 ($\mathrm{CH_2}$), 20.4 ($\mathrm{Si\underline{C}(CH_3)_3}$), 26.3 ($\mathrm{CH_3}$), 28.9 ($\mathrm{SiC(\underline{C}H_3)_3}$), 127.9 (C=C); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta = -74.6$ ($\mathrm{\underline{Si}(SiMe_2(}$*t*-Bu)), -1.1 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)); MS (EI, 20 eV) *m*/*z* (%) 598 ($\mathrm{M^+}$; 0.3), 483 (100) 367 (21.5), 73 (24.2). HRMS Calcd for $\mathrm{C_{30}H_{70}Si_6}$: M, 598.4093. Found: *m*/*z* 598.4099.

Reaction with $\mathrm{CCl_4}$. When $\mathrm{CCl_4}$ (0.5 ml) was introduced to **1b** (22.9 mg, 4.43×10^{-5} mol) in hexane (1.0 ml) at -50 °C through a vacuum line, the orange color of the solution of **1b** disappeared immediately. 1,4-Di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2,3-dichloro-1,1,4,4-tetramethyltetrasilane **21a** (3.69×10^{-5} mol, 83%) was obtained as colorless crystals. **21a:** Mp 133 °C; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta = 0.35$ (s, 12 H, SiMe), 0.36 (s, 12 H, SiMe), 1.13 (s, 36 H, *t*-Bu); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta = -1.9$, -1.3 ($\mathrm{Si\underline{C}H_3}$), 20.7 ($\mathrm{\underline{C}(CH_3)_3}$), 28.3 ($\mathrm{C(\underline{C}H_3)_3}$); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta = 1.2$ ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)), 7.9 ($\mathrm{\underline{Si}Cl}$); MS (EI, 14 eV) *m*/*z* (%) 571 ($\mathrm{M^+}-15$; 1.8), 529 ($\mathrm{M^+}-57$; 3.6), 436 (100). HRMS Calcd for $\mathrm{C_{23}H_{57}Cl_2Si_6}$: ($\mathrm{M^+}-15$), 571.2452. Found: *m*/*z* 571.2455.

Reaction with $\mathrm{CBr_4}$. When a solution of $\mathrm{CBr_4}$ (78.3 mg, 2.36×10^{-4} mol) in hexane (3.0 ml) was introduced to **1b** (50.2 mg, 9.71×10^{-5} mol) in hexane (2.5 ml) at -65 °C, the orange color of **1b** disappeared immediately. After removal of the volatile components, the ^{1}H NMR analysis of the residue indicated the production of 2,3-dibromo-1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-1,1,4,4-tetramethyltetrasilane **21b** in 90% yield (59.1 mg, 8.74×10^{-5} mol). Pure **21b** (24.2 mg, 3.57×10^{-5} mol, 37%) was obtained by recrystallization from hexane at -30 °C. **21b:** Colorless crystals; mp 153 °C; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta = 0.38$ (s, 12 H, SiMe), 0.40 (s, 12 H, SiMe), 1.14 (s, 36 H, *t*-Bu); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta = -1.2$, -0.8 ($\mathrm{Si\underline{C}H_3}$), 21.0 ($\mathrm{\underline{C}(CH_3)_3}$), 28.6 ($\mathrm{C(\underline{C}H_3)_3}$); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta = -7.9$ ($\mathrm{\underline{Si}Br}$), 1.1 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)); MS (EI, 14 eV) *m*/*z* (%) 661 ($\mathrm{M^+(^{79}Br^{81}Br)}-15$; 0.3), 619 ($\mathrm{M^+}-57$; 1.6), 482 ($\mathrm{M^+}-194$; 100). Anal. Calcd for $\mathrm{C_{24}H_{60}Br_2Si_6}$: C, 42.57; H, 8.93%. Found: C, 42.63; H, 8.70%.

Reaction with $\mathrm{CHCl_3}$. The reaction of **1b** (33.5 mg, 6.48×10^{-5} mol) with $\mathrm{CHCl_3}$ (0.5 ml) in hexane occurred gradually at about 0 °C to give 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2-chloro-3-(dichloromethyl)-1,1,4,4-tetramethyltetrasilane **22c** (32.0 mg, 5.03×10^{-5} mol, 77%). **22c:** Colorless crystals; mp 169—170 °C; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta = 0.30$ (s, 6 H, SiMe), 0.38 (s, 6 H, SiMe), 0.39 (s, 6 H, SiMe), 0.47 (s, 6 H, SiMe), 1.11 (s, 18 H, *t*-Bu), 1.19 (s, 18 H, *t*-Bu), 6.28 (s, 1 H, $\mathrm{\underline{C}HCl_2}$); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta = -0.9$, -0.2, 0.4, 0.6 ($\mathrm{SiCH_3}$), 20.5, 22.0 ($\mathrm{\underline{C}(CH_3)_3}$), 28.5, 28.8 ($\mathrm{C(\underline{C}H_3)_3}$), 64.8 ($\mathrm{\underline{C}HCl_2}$); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta = -24.4$ ($\mathrm{\underline{Si}CHCl_2}$), 0.2 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)), 2.8 ($\mathrm{\underline{Si}Cl}$), 3.4 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)); MS (EI, 14 eV) *m*/*z* (%) 619 ($\mathrm{M^+}-15$; 5.7), 577 ($\mathrm{M^+}-57$; 36.8), 519 ($\mathrm{M^+}-115$; 100). Anal. Calcd for $\mathrm{C_{25}H_{61}Cl_3Si_6}$: C, 47.17; H, 9.66%. Found: C, 47.13; H, 9.38%.

Reaction with $\mathrm{CH_2Cl_2}$. Disilene **1b** (39.4 mg, 7.61×10^{-5} mol) reacted with $\mathrm{CH_2Cl_2}$ (0.5 ml) slowly at room temperature in hexane (1.0 ml), giving 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2-chloro-3-(chloromethyl)-1,1,4,4-tetramethyltetrasilane **22d** (39.1 mg, 6.49×10^{-5} mol, 85%). **22d:** Colorless crystals; mp 145—147 °C; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta = 0.29$ (s, 6 H, SiMe), 0.33 (s, 6 H, SiMe), 0.36 (s, 6 H, SiMe), 0.42 (s, 6 H, SiMe), 1.09 (s, 18 H, *t*-Bu), 1.11 (s, 18 H, *t*-Bu), 3.72 (s, 2 H, $\mathrm{C\underline{H_2}Cl}$); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta = -1.6$, -0.9, 0.3 ($\mathrm{Si\underline{C}H_3}$), 20.2, 21.0 ($\mathrm{\underline{C}(CH_3)_3}$), 28.4, 28.6 ($\mathrm{C(\underline{C}H_3)_3}$), 31.1 ($\mathrm{\underline{C}H_2Cl}$); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta = -48.2$ ($\mathrm{\underline{Si}CH_2Cl}$), 0.8, 1.4 ($\mathrm{SiMe_2}$(*t*-Bu)), 4.9 ($\mathrm{\underline{Si}Cl}$); MS (EI, 14 eV) *m*/*z* (%) 585 ($\mathrm{M^+}-15$; 2.1), 543 ($\mathrm{M^+}-57$; 9.9), 485 ($\mathrm{M^+}-115$; 100), 450 ($\mathrm{M^+}-150$; 22.5). Anal. Calcd for $\mathrm{C_{25}H_{62}Cl_2Si_6}$: C, 49.87; H, 10.37%. Found: C, 50.14; H, 10.24%.

Reaction with $\mathrm{CH_3Br}$. A facile reaction of **1b** (41.3 mg, 7.98×10^{-5} mol) with bromomethane (0.5 ml) occurred at -30 °C to give 1,4-di-*t*-butyl-2,3-bis(*t*-butyldimethylsilyl)-2-bromo-1,1,3,4,4-pentamethyltetrasilane **22e** (46.4 mg, 7.58×10^{-5} mol, 95%). **22e:** A colorless solid; ^{1}H NMR ($\mathrm{C_6D_6}$) $\delta = 0.31$ (s, 6 H, SiMe), 0.32 (s, 6 H, SiMe), 0.37 (s, 6 H, SiMe), 0.38 (s, 6 H, SiMe), 0.79 (s, 3 H, Si–Me), 1.05 (s, 18 H, *t*-Bu), 1.13 (s, 18 H, *t*-Bu); ^{13}C NMR ($\mathrm{C_6D_6}$) $\delta = -2.5$, -1.3, -1.0, -0.7, -0.0 ($\mathrm{Si\underline{C}H_3}$), 20.5, 20.9 ($\mathrm{\underline{C}(CH_3)_3}$), 28.6, 28.7 ($\mathrm{C(\underline{C}H_3)_3}$); ^{29}Si NMR ($\mathrm{C_6D_6}$) $\delta = -60.6$ ($\mathrm{\underline{Si}CH_3}$), -5.8 ($\mathrm{\underline{Si}Br}$), -0.6, -0.2 ($\mathrm{\underline{Si}Me_2}$(*t*-Bu)); MS (EI, 20 eV) *m*/*z* (%) 610 (1.2, $\mathrm{M^+(^{79}Br)}$; 1.2), 612 ($\mathrm{M^+(^{81}Br)}$; 1.2), 553 (4.6), 555 (3.8), 416 (100), 303 (16.8), 273 (30.6), 217 (27.8), 73 (39.3). Anal. Calcd for $\mathrm{C_{25}H_{63}BrSi_6}$: C, 49.05; H, 10.37%. Found: C, 49.15; H, 10.54%.

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11) a) A. D. Fanta, D. J. DeYoung, J. Beltzner, and R. West, *Organometallics*, **10**, 3466 (1991); b) D. J. DeYoung and R. West, *Chem. Lett.*, **1986**, 883.

12) M. J. Fink, D. J. Young, J. Michl, and R. West, *J. Am. Chem. Soc.*, **105**, 1070 (1983).

13) For reactions of transient disilenes with 2,3-dimethyl-1,3-butadiene, see: a) S. Masamune, S. Murakami, and H. Tobita, *Organometallics*, **2**, 1464 (1983); b) H. Sakurai, Y. Nakadaira, and H. Sakaba, *Organometallics*, **2**, 1484 (1983).

14) In order to obtain the experimental evidence for the low-lying LUMO in tetrasilyldisilenes, the detailed electrochemical study will be required. A preliminary study has shown that the reduction potentials of tetrasilyldisilenes **1a**—**1c** are lower than those of tetraryldisilenes reported so far.$^{15)}$

15) T. Ishima, T. Iwamoto, M. Ichinohe, and M. Kira, to be published.

16) Apparently, the Diels–Alder type reactions are influenced by the steric hindrance around Si=Si double bond. Whereas **1a** as well as **1b** reacted with 2,3-dimethyl-1,3-butadiene to provide the corresponding [4+2] cycloadduct quantitatively, **1c** did not react with the diene.

17) For reactions of tetramesityldisilene with benzil, see: a) P. Boudjouk, B.-H. Han, and K. R. Anderson, *J. Am. Chem. Soc.*, **104**, 4992 (1982); b) P. Boudjouk, *Nachr. Chem. Tech. Lab.*, **31**, 798 (1983).

18) [4+2] reactions of tetra-*t*-butyldisilene: a) M. Weidenbruch, A. Schäfer, and K.-L. Thom, *Z. Naturforsch. B*, **38**, 1695 (1983); b) A. Schäfer, M. Weidenbruch, and S. Pohl, *J. Organomet. Chem.*, **282**, 305 (1985); c) M. Weidenbruch, H. Piel, A. Lesch, K. Peters, and H. G. von Schnering, *J. Organomet. Chem.*, **454**, 35 (1993); d) M. Weidenbruch, A. Lesch, and K. Peters, *J. Organomet. Chem.*, **407**, 31 (1991).

19) A. D. Fanta, J. Beltzner, D. R. Powell, and R. West, *Organometallics*, **12**, 2177 (1993).

20) Reactions of tetra-*t*-butyldisilene with a C=C bond in pyridine and isobenzofuran, see: a) M. Weidenbruch, B. Flintjer, S. Pohl, D. Haase, and J. Martens, *J. Organomet. Chem.*, **338**, C1, (1988); b) M. Weidenbruch, A. Lesch, K. Peters, and H. G. von Schnering, *J. Organomet. Chem.*, **423**, 329 (1992).

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22) C. E. Dixon, J. A. Cooke, and K. M. Bains, *Organometallics*, **16**, 5437 (1997).

23) N. D. Epiotis, *J. Am. Chem. Soc.*, **94**, 1924 (1972).

24) It has not been fully understood whether [2+2] reactions of disilenes with terminal acetylenes proceed through a biradical intermediate or a zwitterionic intermediate. D. J. DeYoung, M. J. Fink, and R. West, *Main Group Met. Chem.*, **1**, 19 (1987), and references cited therein.

25) The product distribution of reactions of tetrasilyldisilenes with haloalkanes depends also on the steric bulkiness of the silyl substituents. Disilene **1a** reacted readily with haloalkanes to give the corresponding adducts in a similar manner to disilene **1b**. Thus, treatment of **1a** with CCl_4 gave the corresponding 2,3-dichlorotetrasilane, while the reactions of **1a** with $CHCl_3$ and CH_2Cl_2 gave the corresponding 2-chloro-3-halomethyltetrasilanes. On the other hands, the reactions of tetrasilyldisilene **1c** having bulky triisopropylsilyl substituents with CCl_4, $CHCl_3$, and CH_2Cl_2 afforded only the correspoding 2,3-dichlorotetrasilane. The steric hindrance of **1c** may prevent the recombination of the intermediary β-halosilyl radical and haloalkyl radical in the cage.

26) a) C. Chatgilialoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, **104**, 5123 (1982); b) C. Chatgilialoglu, *Chem. Rev.*, **95**, 1229 (1995), and references cited therein.

27) During the course of the mechanistic study,$^{15)}$ it has been found that **1b** reacts with benzyl chloride to afford the corresponding 2-chloro-3-benzyltetrasilane quantitatively, while the reaction of **1b** with 2-chloro-2-methylpropane gives a complex mixture composed of **21a**, isobutene, isobutane, and other unidentified products. The details will be reported elsewhere.

28) a) H. Teramae, *J. Am. Chem. Soc.*, **109**, 4140 (1987); b) Teramae has also found by ab initio MO calculations that the diradical character of tetrasilyldimetallenes is larger than that of tetrahydrodimetallenes; a private communication.

29) W. Fischetti and R. F. Heck, *J. Organomet. Chem.*, **293**, 391 (1985).