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Review

Stable cyclic and acyclic persilyldisilenes

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Abstract

Synthesis, structure, and reactions of persilylated cyclic and acyclic disilenes that we have synthesized are described in detail. Due to the remarkable electronic and steric effects of trialkylsilyl substituents, tetrakis(trialkylsilyl)disilenes (RR′Si=SiRR′: R, R′ = *i*-Pr_2MeSi (**1a**), *t*-$BuMe_2Si$ (**1b**), *i*-Pr_3Si (**1c**); R = *i*-Pr_2MeSi, R′ = *t*-$BuMe_2Si$ (**1d**)) showed interesting features in the geometry around Si=Si bond, electronic spectra, ^{29}Si-NMR resonances of the unsaturated silicon nuclei, *E*,*Z*-isomerization, reduction by alkali metals, and various bimolecular reactions with alcohols, alkyl lithium, alkenes, alkynes, and haloalkanes. As the first cyclooligosilenes, 1-tris(*t*-butyldimethylsilyl)silyl-2,3,3-tris(*t*-butyldimethylsilyl)cyclotrisilene (**2**) and hexakis(*t*-butyldimethylsilyl)cyclotetrasilene (**3**) were synthesized typically by the reduction of the corresponding tris(trialkylsilyl)silyltrihalosilane with potassium graphite in THF and with sodium in toluene, respectively. Photochemical conversion of **3** to the corresponding bicyclo[1.1.0]butane (**9**) and its thermal reversion to **3**, as well as photochemical isomerization of **2** to **9** were observed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tetrasilyldisilene; Cyclotrisilene; Cyclotetrasilene; X-ray structure; UV–vis spectra; ^{29}Si-NMR; Cyclic voltammetry; Isomerization; Addition

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1. Introduction

The chemistry of stable disilenes has been the subject of extensive studies since the first isolation of tetramesityldisilene in 1981 by West et al. [1,2]. Whereas significant modification of the structure and reactivity of disilenes is expected to be caused by the substituents, most of the isolated disilenes have been the tetraaryl-substituted disilenes; very few experimental studies have been devoted to the substituent effects. We have been interested in the substituent effects of trialkylsilyl groups on the geometry, electronic structure, and reactivity of disilenes because of the expected unique electronic effects. Tetrakis(trialkylsilyl)disilenes made by the dimerization of the corresponding disilylsilylenes, whose singlet-triplet energy differences have been shown theoretically to be much smaller than those of dialkyl- and diarylsilylenes [3,4], should have higher planarity around the Si=Si bonds than tetraalkyl- and tetraaryldisilenes, according to the theory of Trinquier et al. [5]. Actually, theoretical calculations have shown that silyl substituents increase the Si=Si bond dissociation energy and that tetrasilyldisilene is planar around the Si=Si bond, while the parent disilene has the *trans*-bent structure [6] (Chart 1).

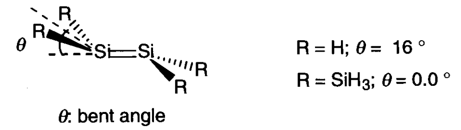

Chart 1.

The existence of a variety of structural types such as cycloalkenes, conjugated polyenes, cumulenes, and aromatic compounds is responsible for the rich chemistry of C=C double bonds. In contrast, various types of the silicon analogues of alkenes are still missing and remain to be actively investigated.

We have recently isolated several tetrakis(trialkylsilyl)disilenes (**1a**–**1d**) [7], persilylated cyclotrisilene **2**, R_3Si = *t*-$BuMe_2Si$ [8a] and cyclotetrasilene **3**, R_3Si = *t*-

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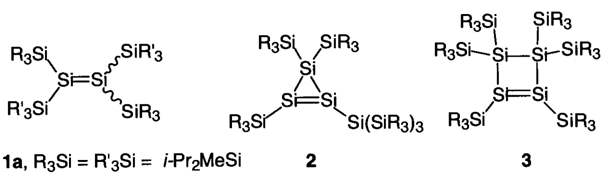
BuMe$_2$Si [8b], and related compounds. In this account, synthesis, structure, and reactivities of persilylated cyclic and acyclic disilenes that we have synthesized are described in detail; due to the remarkable electronic and steric effects of trialkylsilyl substituents, these disilenes showed interesting features in the Si=Si bond distances, electronic spectra, ^{29}Si-NMR resonances of the unsaturated silicon nuclei, and *E*,*Z*-isomerization and other reactions (Chart 2).



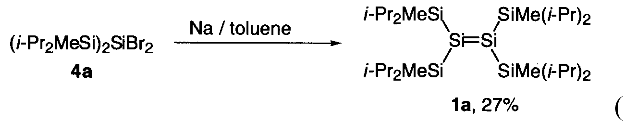
1a, $R_3Si = R'_3Si$ = *i*-Pr$_2$MeSi
1b, $R_3Si = R'_3Si$ = *t*-BuMe$_2$Si
1c, $R_3Si = R'_3Si$ = *i*-Pr$_3$Si
1d, R_3Si = *i*-Pr$_2$MeSi, R'_3Si = *t*-BuMe$_2$Si

Chart 2.

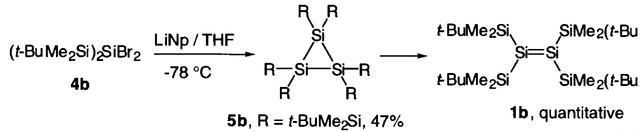
Prior to our first isolation of tetrakis(trialkylsilyl)disilenes in 1994 [7a], (*E*) and (*Z*)-1,2-bis(2,4,6-triisopropylphenyl)-1,2-bis(trimethylsilyl)disilenes had been prepared by West et al. as the first stable silyl-substituted disilenes [9]. Matsumoto and Nagai found that photolysis of hexakis(triethylsilyl)cyclotrisilane gave the corresponding disilene, tetrakis(triethylsilyl)disilene, which was marginally stable in solution [10]. Chemistry of stable cyclooligosilenes has also been very actively investigated by other research groups. Wiberg et al. reported that the novel cyclotetrasilene, 1,2,3,4-tetrakis-(tri-*tert*-butylsilyl)-1,2-diiodo-3,4-cyclotetrasilene was obtained by a simple reaction of tetrakis(tri-*tert*-butylsilyl)tetrahedrane with iodine [11]. Weidenbruch et al. have isolated several chalcogenated tetrasilacyclopentenes [12]. Sekiguchi et al. have isolated a stable cyclotrisilene very recently [13].

2. Synthesis

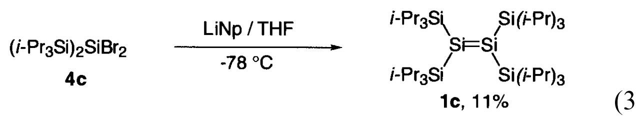
Tetrakis(trialkylsilyl)disilenes (**1a**–**1d**) with bulky trialkylsilyl substituents have been synthesized via reductive coupling of the corresponding 2,2-dihalotrisilanes and isolated as thermally stable solids (Eqs. (1)–(4)) [7]. The reaction conditions of the reductive coupling depends on the substituents on silicon. Disilene (**1a**) was prepared by refluxing a mixture of bis(diisopropylmethylsilyl)dibromosilane (**4a**) and sodium in toluene for 6 h in 27% yield (Eq. (1)). Tetrakis(triisopropylsilyl)disilene (**1c**) was obtained in 11% yield by reductive coupling of bis(triisoopropylsilyl)dibromosilane (**4c**) with lithium naphthalenide (LiNp) in THF at −78°C (Eq. (3)). The same reduction of bis(*tert*-butyldimethylsilyl)dibromosilane (**4b**) as above gave the corresponding cyclotrisilane (**5b**) in 47%, which is converted to **1b** by photolysis (Eq. (2)).



(1)

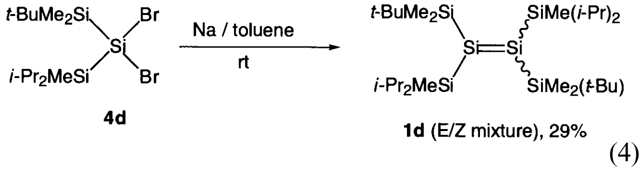


(2)



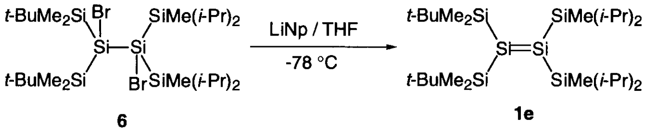
(3)

Reductive coupling of 1-*t*-butyl-2,2-dibromo-3,3-diisopropyl-1,1,3-trimethyltrisilane (**4d**) with sodium in toluene led to a 2:1 mixture of tetrasilyldisilenes (*E*)- and (*Z*)-**1d** in 29% yield (Eq. (4)) [7b]. The major isomer was tentatively assigned as (*E*)-**1d** on the basis of its NMR spectral features. Recrystallization from hexane at low temperature gave (*E*)-**1d** as air-sensitive orange crystals.



(4)

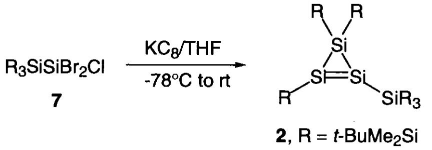
Disilene **1e**, an isomer of (*E*)- and (Z)-**1d**, was prepared according to Eq. (5) and identified by NMR spectroscopy but several attempts to isolate **1e** as pure crystals failed because of the easy isomerization to a mixture of (*E*)- and (*Z*)-**1d** at room temperature (vide infra) [7b].



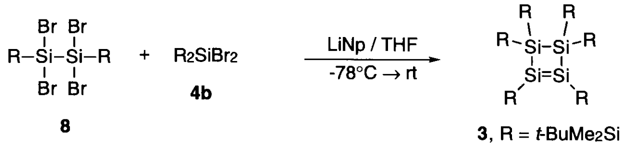
(5)

Disilenes **1a**–**1d** were highly air- and moisture-sensitive in solution, but survived for a day under exposure to air in the solid state.

The first stable cyclotrisilene (**2**) [8a] and cyclotetrasilene (**3**) [8b] were synthesized as shown in Eqs. (6)–(8).



(6)

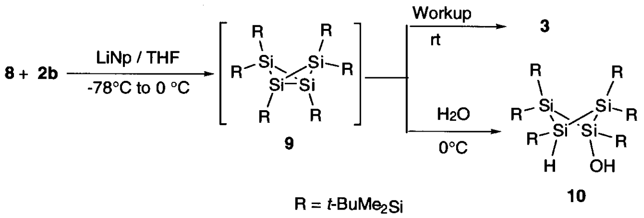


(7)

$$\mathbf{7} \xrightarrow[\text{toluene}]{\text{Na}} \mathbf{3} \qquad (8)$$

Cyclotrisilene (**2**) was obtained by the reduction of tris(trialkylsilyl)silyldibromochlorosilane (**7**) using a suspension of KC_8 in THF at − 78°C in 65% yield together with tris(*tert*-butyldimethylsilyl)chlorosilane as a sole byproduct as determined by NMR (Eq. (6)) [8a].

Cyclotetrasilene (**3**) was first synthesized by reductive coupling of the corresponding 2,2,3,3-tetrabromotetrasilane (**8**) and 2,2-dibromotrisilane (**4b**) using lithium naphthalenide in THF at − 78°C in 13.6% yield (Eq. (6)). It was recently found that the initial product of the reductive coupling is not **3** but the corresponding bicyclo[1.1.0]tetrasilane (**9**), which isomerizes to **3** during work-up at room temperature (vide infra for the isomerization mechanism) [14]. Neither **3** nor its hydrolysis products were formed in significant yields, when the reductive coupling was carried out at − 78°C and then the reaction mixture was hydrolyzed at 0°C ; instead, the hydrolysis product of **9**, 1-hydroxyhexasilylcyclotetrasilane (**10**), was obtained in 12% yield (Eq. (9)).

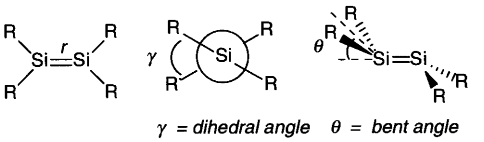


(9)

Interestingly, the reduction of tris(trialkylsilyl)silyldibromochlorosilane (**6**) using sodium in toluene at room temperature afforded cyclotetrasilene **3** in 66% yield (Eq. (8)); the method constitutes an improved synthesis for **3** [8a].

Cyclooligosilenes **2** and **3** were air-sensitive similar to other tetrasilyldisilenes; the characteristic color disappeared immediately when the samples in solution were exposed to air.

Table 1
Comparison of structural parameters among disilenes [a]



Disilene	r (Å)	γ (°)	δ (°)
1a	2.228(2)	0	5.4(0)
1b	2.202(1)	8.9(1)	0.1(0)
1c	2.251(1)	0	10.2(0)
(*E*)-**1d**	2.196(3)	0	0.65(0)
Tetramesityldisilene [b]	2.143	3	13

[a] Standard deviation is shown in parentheses.
[b] Ref. [2f].

3. Structural characteristics

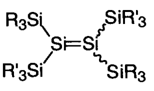
3.1. X-ray structures

The molecular structures of **1a**–**1c** [7a], (*E*)-**1d** [7b], and **3** [8b] were determined by single-crystal X-ray diffraction studies. Important structural parameters for these disilenes are summarized in Table 1. The structural arrangement around the Si=Si bonds of acyclic tetrasilyldisilenes depended significantly on the alkyl-substituents at the saturated silicons. Both **1a** and **1c** were *trans*-bent around the Si=Si bonds with the bent angles (θ) of 5.4° and 10.2°, respectively, while in **1b**, there was twist ($\gamma = 8.9°$) of the double bond without bending. The Si=Si bond distances for **1a**–**1c** were ca. 0.1 Å longer than those for hitherto known disilenes (2.14–2.16 Å) [2f, 15]. Severe steric repulsion between trialkylsilyl groups could be responsible for the deformation from planarity and elongation of the Si=Si bond distances found in **1a**–**1c**. Disilene (*E*)-**1d** has the highest planarity around silicon–silicon double bond with the bent angle of 0.65°, no twisting, and the shortest Si=Si bond distance (2.196 Å) among the acyclic tetrasilyldisilenes [7b].

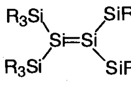
These results imply that tetrasilyldisilenes should be planar around Si=Si bond as predicted by theoretical calculations [6], if there is no significant steric crowding between substituents. However, it is also suggested that the potential energy surfaces are rather shallow not only for twisting and bending but also stretching of the double-bond; the double bond of disilene would be referred to a soft double bond compared with a hard double bond of a simple olefin. Whereas the deformation mode, *trans*-bent or twist, depends also on the shape of the trialkylsilyl substituents, the degree of the steric repulsion between geminal and vicinal trialkylsilyl substituents is larger in the following order; **1c** > **1b** > **1a** > (*E*)-**1d**.

The Si=Si bond length (Si1–Si2) in cyclotetrasilene (**3**) is 2.174 Å [8b], which is rather shorter than those of acyclic tetrasilyldisilenes **1a**–**1c**, and (*E*)-**1d** (2.196–2.251 Å) (Chart 3) [7]. The Si3–Si4 single bond is unusually long (2.450 Å). The four-membered ring is not planar but folded with the out-of-plane angles of ca. 37°. The arrangement around the Si=Si bond is a little *trans*-bent ($\theta = 13°$), where bent angle θ is defined as an angle between the R–Si1–Si4 (or R–Si2–Si3) plane and the Si1–Si2 bond. The twist angle γ between two $Si(sp^3)$–$Si(Sp^2)$–$Si(Sp^3)$ planes is 12.3°. Steric repulsion between vicinal *t*-$BuMe_2Si$ groups on Si3 and Si4 would be the major reason for the folding of the four-membered ring, the long Si3–Si4 bond, and also for the deformation around the soft Si=Si bond.

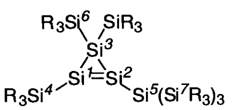
Table 2
^{29}Si-NMR chemical shifts for cyclic and acyclic tetrasilyldisilenes ^{a}fl



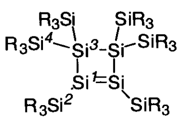
1a – 1d



1e



2



3

Disilene	δ(Si)			
	Si$_u$ ^{a}	Si$_s$ ^{a}	Others	Ref.
1a	$+144.5$	$+11.7$		[7a]
1b	$+142.1$	$+6.0$		[7a]
1c	$+154.5$	$+16.4$		[7a]
(E)-**1d**	$+141.8$	$+6.7, +10.4$		[7b]
(Z)-**1d**	$+141.9$	$+6.0, +10.8$		[7b]
1e	131.3, 156.2	$+5.6, +11.3$		[7b]
2	$+81.9$ (Si^1), $+99.8$ (Si^2)	-117.2(Si^5), -105.7 (Si^3), $+14.0$(Si^4)	$+0.4$ (Si^6), $+6.4$ (Si^7)	[8a]
3	$+160.4$	-71.4 (Si^3), 5.0(Si^2)	1.5 (Si^4)	[8b]

^{a} Si$_u$, unsaturated silicon; Si$_s$, saturated silicon connected with the unsaturated silicon.

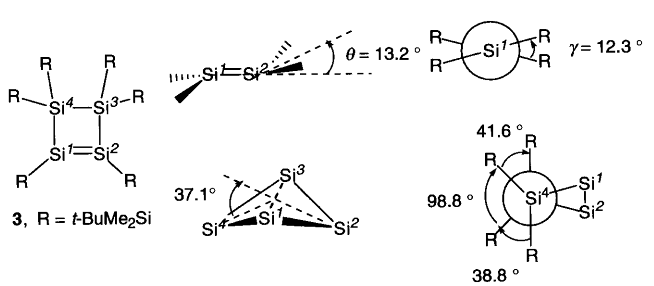


Chart 3.

3.2. ^{29}Si-NMR spectra

The ^{29}Si resonances for the unsaturated silicons (δ(Si$_u$)) in **1a**–**1c** and (E)- and (Z)-**1d** appeared at remarkably lower fields than those for known other disilenes (Table 2), which are falling between δ $+49$ and $+98$ [2f]; the resonances for **1a**, **1b**, **1c**, (E)-**1d**, and (Z)-**1d** are observed at δ 144.5, 142.1, 154.5, 141.8, and 141.9, respectively. Unusually low-field resonances of Si$_u$ may be compared with the corresponding ^{13}C resonances for tetrakis(trimethylsilyl)ethylenes (δ_C 195.3) and related silylethylenes, which appear at much lower fields than that of the parent ethylene (δ_C 122.8) [16]. Interestingly, the ^{29}Si resonances due to Si$_u$ of **1e** appears at δ 131.3 and 156.2, which are remarkably up- and downfield shifted from that of **1d** (δ 142). The large separation of the two ^{29}Si resonances observed for **1e** (δ 131.3 and 156.2) imply a significant difference of the geometries around two tricoordinate silicons.

The ^{29}Si-NMR chemical shift tensors of various disilenes including tetrasilyldisilenes were determined by solid state NMR spectroscopy [17]. Whereas various disilenes show significant deshielding along one principal axis (δ_{11} in Fig. 1), for tetrasilyldisilenes this deshielding is extreme. The deshielding in the δ_{11} direction can be related to the low σ–π^* transition energy for these tetrasilyldisilenes, which is rationalized by higher-lying σ orbital levels of Si=Si bonds in tetrasilyldisilenes compared with those in tetraaryldisilenes.

While the δ(Si$_u$) value of the unsaturated silicon atoms in cyclotetrasilene (**3**) is a little lower (δ 160.4) than those for the acyclic tetrasilyldisilenes [8b], the δ(Si$_u$) values of cyclotrisilene (**2**) are significantly higher than those for the acyclic disilenes [8a]; δ $+81.9$ (t-BuMe$_2$Si–Si=) and $+99.8$ ppm ((t-BuMe$_2$Si)$_3$Si–Si=). The tendency of the δ(Si$_u$) values among **1b**, **2**, and **3** is quite parallel to that of the chemical shifts of the unsaturated carbons (δ(C$_u$)) among ethylene, cyclopropene, and cyclobutene [18]; the high-field shift of δ(Si$_u$) of **8** and δ(C$_u$) of cyclopropene would have the same origin. These resonances are well reproduced by GIAO calculations (GIAO/B3LYP/6-311 + G(2df,p)//HF/6-31G(d)) for the model compounds as shown in Table 3 [17,19].

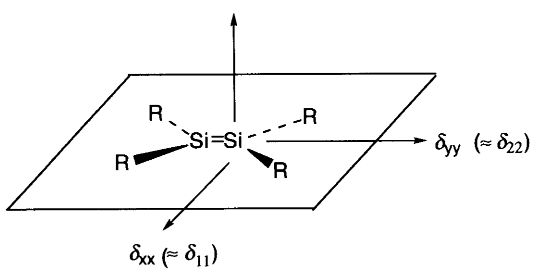
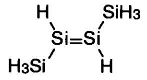
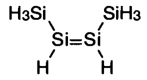
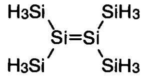
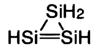
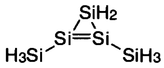
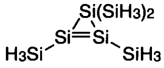
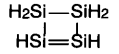
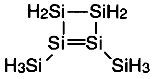
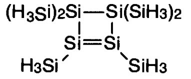


Fig. 1. Approximate orientation of the principal shielding tensor components in disilenes.

Table 3
Calculated chemical shift tensors relative to tetramethylsilane[a]

Disilene		δ_{iso}[b]	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$[c]	ref.
$H_2Si{=}SiH_2$	D_{2h}	65.9	294.8	-15.1	-81.8	376.6	17
	C_{2h}	109.3	399.3	12.2	-83.7	483.0	17
	C_{2v}	109.2	403.7	10.6	-86.6	490.3	19
	D_{2h}	147.5	447.0	96.4	-100.8	444.8	17
	C_{2v}	23.8	266.7	-51.4	-143.8	410.5	19
	C_{2v}	103.2	445.2	47.3	-183.1	628.3	19
	C_{2v}	104.8	457.8	28.1	-171.5	629.3	19
	C_{2v}	112.1	345.5	1.93	-11.1	356.6	19
	C_{2v}	187.9	484.1	80.0	-0.5	484.6	19
	C_{2v}	183.4	456.2	85.4	8.6	447.6	19

a) GIAO/B3LYP/6-311+G(2df,p)//HF/6-31G(d).
b) $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.
c) $\Delta\delta = \delta_{11} - \delta_{33}$.

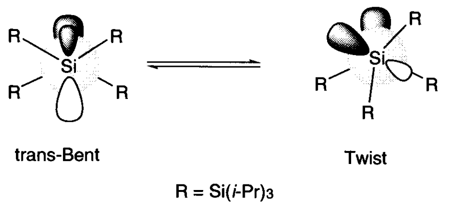
Table 4
UV absorption maxima of acyclic and cyclic tetrasilyldisilenes

Disilene	λ_{max} (nm) (ε)
1a	410 (7700), 355 (1400), 290 (2000)
1b	420 (2800), 360 (1900), 290 (2600)
1c	480 (2200), 425 (1600), 370 (2700), 295 (6300)
2	482 (2600), 398 (1300), 310 (7700, sh)
3	465 (6800), 359 (1100), 308 (4100, sh)

3.3. UV spectra

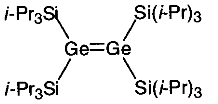
Acyclic disilenes **1a**–**1d** are yellow to light orange in the solid state. Expectedly, the UV–vis spectra of these disilenes in KBr pellets are similar to one another with the band maxima at around 420 nm. However, disilenes **1a**–**1c** are quite different in color in solution; the extraordinary color change from yellow in the solid state to dark red in hexane solution is observed for the most crowded **1c**. As expected from the *soft* Si=Si bonds, these disilenes may be forced to the nearly planar geometry in the solid states due to the lattice energy, while the disilenes would be relaxed in solution to take the most stable molecular geometry.

The absorption maxima for various tetrasilyldisilenes at 298 K in hydrocarbon solution are listed in Table 4. Since the π–π* transition bands appear at around 400 nm for the known tetraaryldisilenes [2f], the band maxima at 412 and 424 nm for **1a** and **1b**, respectively, are assigned to the π–π* transition band of the disilenes with *trans*-bent geometry; the band-width for **1b** is however much larger than that for **1a**. Disilene **1c** shows a unique broad band at around 480 nm together with the bands at 425, 370, and 295 nm; the latter three bands are assigned to the *trans*-bent conformation, since the corresponding bands are found in **1a** and **1b**. The existence of the broad 480 nm band in **1c** suggests the contribution of the several conformations including a twist form in solution to relieve steric strain (Eq. (10)).



(10)

It is interesting to compare the UV spectral feature of **1c** with that of a germanium analog, tetrakis(trisopropylsilyl)digermene (**11c**) [20]. While a similar spectral feature is observed between **1c** and **11c** at room temperatures, **11c** shows a remarkable thermochromism to give the intense typical π–π* band at around 420 nm at 77 K in 3-methylpentane. Since the thermochromic behavior of **11c** has similarity with the classical thermochromic olefins like bianthrones [21], the behavior would be attributed to a thermal equilibrium between the bent and twist conformations around the double bond. On the other hand, the absorption spectrum of **1c** shows five discrete bands in the region of 250–600 nm at 77 K; apparently the broad 480 nm band at room temperature split into two bands with the maxima of 460 and 570 nm. Larger steric congestion in **1c** may even increase the population of the twist conformations at low temperatures [22] (Chart 4).



11c

Chart 4.

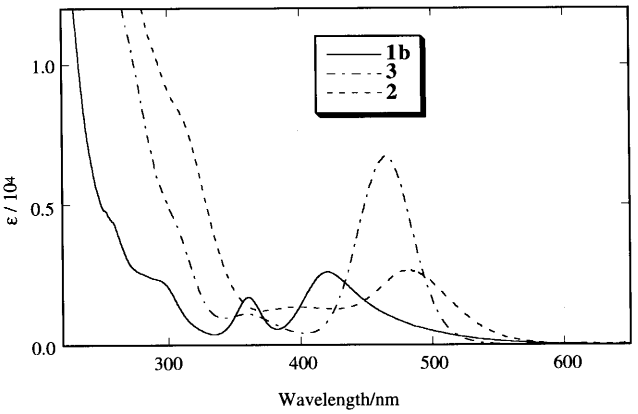


Fig. 2. UV spectra of disilenes **1b**, **2**, and **3** in 3-methylpentane at room temperature.

Table 5
Peak potentials of disilenes determined by cyclic voltammetry [a,b]

Disilene	Ep(Ox.) (V)	Ep(Red.) (V)
1a	+0.88	−1.82, −2.41
1c	+0.70	−1.70, −2.56
3	+0.44	−2.12
$Mes_2Si{=}SiMes_2$	+0.44 (0.38) [c]	−2.12 (−2.12) [c]
$Tip_2Si{=}SiTip_2$	0.56, +1.32	−2.66

[a] Potentials were measured versus Ag | Ag^+ at room temperature in THF containing 0.1 M $[Bu_4N]^+[PF_6]^-$. The ferrocene/ferricinium ion couple was measured at +0.61 V in this system.

[b] Unless otherwise noted, data were taken from Ref. [23].

[c] Data in parentheses were taken from Ref. [24].

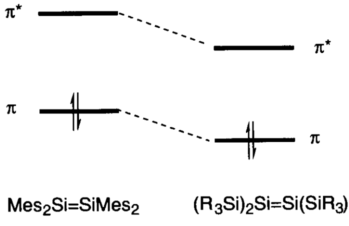


Fig. 3. Schematic representation of the relative energy levels of the frontier orbitals of tetrasilyldisilenes and tetraaryldisilenes

Cyclooligosilenes **2** and **3** showed characteristic π–π* bands at 465 and 482 nm with ε values of 6800 and 2600, respectively (Table 4). UV–vis spectra of **1b**, **2**, and **3** are compared in Fig. 2. The maxima are red-shifted from that of the corresponding tetrasilyldisilene **1b** (λ_{max} 424 nm), while the extent is larger in **2** due to the greater ring strain. The π–π* band maximum of **2** appeared at much longer wavelength with larger absorption coefficient than tetrakis(di-*tert*-butylmethylsilyl)cyclotrisilene (λ_{max} 466, ε 440) reported by Sekiguchi et al. [13], suggesting significant σ(Si–Si)–π(Si=Si) conjugation in **2**.

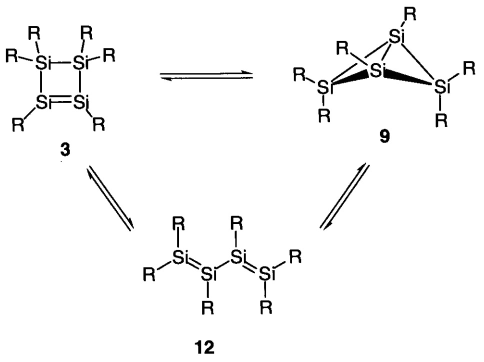
3.4. Cyclic voltammetry

Oxidation and reduction potentials of several tetrasilyldisilenes were measured by cyclic voltammetry [23]. Since both reduction and oxidation of these tetrasilyldisilenes were irreversible similarly to those of tetraaryldisilenes [2f,24], the peak potentials were compared in Table 5. Interestingly, the oxidation potentials of **1a** and **1c** are significantly higher than those of tetramesityldisilene, while the reduction potentials of **1a** and **1c** are lower. It is suggested both HOMO and LUMO of tetrasilyldisilenes are lower in energy than those of tetramesityldisilene as shown in Fig. 3. In addition to the steric reasons, the difference of the frontier orbital levels may characterize the reactivity differences between tetraaryldisilenes and tetrasilyldisilenes (vide infra).

4. Reactions

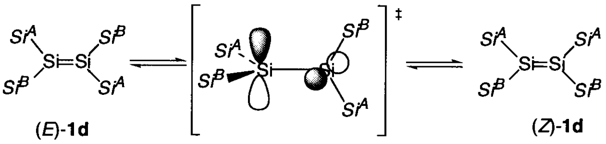
4.1. E–Z isomerization

Whereas *E*–*Z* isomerization in stable tetraaryl- and diaryldialkyldisilenes are known to occur with the activation energies ranging from 24 to 31 kcal mol^{-1} [2f], the *E*–*Z* isomerization in tetrasilyldisilene **1d** was found to occur much more easily. Thus, the ^{29}Si-NMR spec-

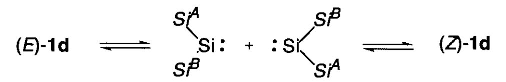


Scheme 1.

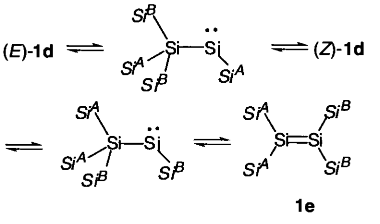
trum of a mixture of (*E*)-**1d** and (*Z*)-**1d** was remarkably dependent on the temperature. Two pairs of signals due to *i*-Pr$_2$MeSi (Si^A) and *t*-BuMe$_2$Si (Si^B) groups, which are observed independently at 273 K, coalesce at 308 K (for Si^A) and 303 K (for Si^B) to give two sharp singlets at temperatures higher than 330 K, indicating that facile isomerization between (*E*)- and (*Z*)-**1d** occurs even at room temperature. There are two possible mechanisms for the *E*–*Z* isomerization other than simple rotation around the central Si–Si bond (Eq. (11)): (1) the dissociation–recombination mechanism between the disilene and the corresponding silylenes (Eq. (12)) and (2) the repeated disilene–disilanylsilylene rearrangement (Eq. (13)).



(11)



(12)

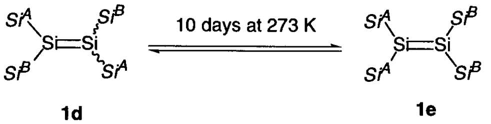


(13)

The dissociation–recombination pathway is known for a tetraaryldisilene [15,25] but the process in the tetrakis(trialkylsilyl)disilenes is eliminated by the cross-experiments; heating **1e** or a mixture of **1a** and **1b** at 40°C gave no cross products. The disilene–disilanylsilylene rearrangement is also known to occur between the transient hexamethyltrisilene and the corresponding trisilane-1,1-diyl at 200°C [26]. Although during this process, it is expected to give **1e**, the dynamic NMR experiment has shown that the isomerization occurs only between *E* and *Z* isomers of **1d**; the signals due to **1e** remain sharp between 0 and 50°C . The *E*,*Z*-isomerization of **1d** observed by the dynamic ^{29}Si-NMR then must occur through the rotation around the Si=Si double bond. The barrier to the *E*–*Z* isomerization in **1d** was estimated to be ca. 15 kcal mol^{-1} at the coalescence temperatures. The major reason for the low barrier for the silyl-substituted disilenes may be ascribed to the effective σ–π conjugation in the transition state of the isomerization as invoked in the relatively low rotational barrier in tetrasilylethylenes [27]. Thus, in the twisted transition structure (Eq. 11), the π-orbital on an unsaturated silicon can interact with the σ and σ^* orbitals between the neighboring unsaturated silicon and the substituent silicons, which leads to the stabilization of the transition structure. The stabilization energy will be much larger than those expected for tetraaryldisilenes, where σ and σ^* orbitals of an Si–C$_{Ar}$ type are involved in the σ–π conjugation; the energy levels of σ(Si–Si) and σ^*(Si–Si) orbitals are known to be higher and lower than those of σ(Si–C) and σ^*(Si–C) orbitals, respectively, and hence, closer to the energy level of 3p–orbital of silicon [28].

4.2. Dyotropic isomerization

Significant increase of the ^{29}Si-NMR signals due to **1e** was observed during repeated NMR experiments for an *E*, *Z*-mixture of **1d**, suggesting another isomerization pathway of **1d** in addition to the *E*–*Z* isomerization (Eq. 11). When a mixture of (*E*)- and (*Z*)-**1d** in toluene-d_8 was kept for 10 days at 278 K, structural isomer **1e** was formed and an equilibrium was established among these three isomers with the ratio of (*E*)-**1d**:(*Z*)-**1d**:**1e** = 2:1:1 (Eq. (14)). The structure of **1e** was confirmed by comparing the NMR spectra with those of the authentic disilene **1e**. Although similar isomerization has been known for dimesityl(dixylyl)disilene, 70 days are needed at 298 K to attain equilibrium [29]. The formal dyotropic isomerization between **1d** and **1e** may involve the disilene–disilanylsilylene rearrangement shown in Eq. (13).



(14)

4.3. Cyclotetrasilene–bicyclo[1.1.0]tetrasilane isomerization

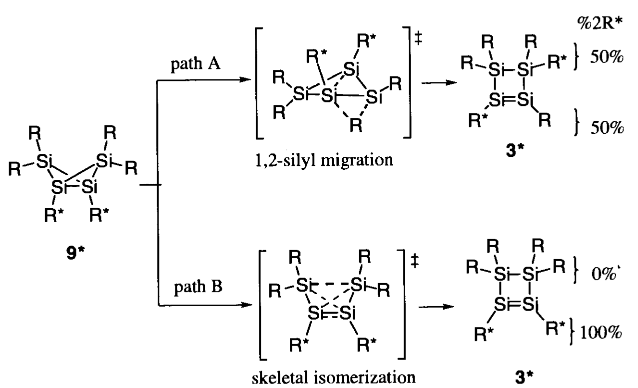
The thermal and photochemical pathways involved in the interconversion among **3**, tetrasilabicyclo-[1.1.0]butane (**9**), and tetrasila-1,3-butadiene (**12**) may constitute an interesting chemistry as the silicon version of the well-studied electrocyclic interconversion of C$_4$H$_6$ (cyclobutene, bicyclobutane, and butadiene).

Actually, we found facile photochemical conversion of **3** to **9** and its thermal reversion to **3**, while no evidence was obtained for **12** (Scheme 1).

Photolysis of **3** in 3-methylpentane with a high-pressure Hg arc lamp ($\lambda > 420$ nm) at 288 K afforded a 1:9 mixture of **3** and **9** at the photostationary state. Leaving the photolysate for 12 h in the dark at room temperature, **3** was reproduced quantitatively.

The photochemical conversion of **3** to **9** and the thermal reversion were repeated more than ten times without appreciable side reactions. The present results indicate that **3** is thermodynamically more stable than **9**, in contrast to a previous experimental study of a tetrasilabicyclo[1.1.0]butane [30] and a theoretical study of parent Si_4H_6 [31].

The first-order rates and the activation parameters for the thermal isomerization of **3**–**9** were determined: $k = 5.67 \times 10^{-5}$ s^{-1} at 288 K, $\Delta H^{\ddagger} = 16.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -20.8$ cal mol^{-1} K^{-1} The large negative $\Delta S^{\ddagger}$ value suggests that the transition-state structure of the thermal isomerization would be significantly restricted, and therefore, any multi-step mechanisms involving bond-cleavage at the rate-determining step may be eliminated from the possible mechanisms. There are two plausible pathways for the isomerization of **3** to **9** as shown in Scheme 2: a concerted or a step-wise isomerization involving 1,2-silyl migration accompanied by cleavage of the central Si–Si bond of **9** (path A) and a concerted skeletal isomerization (path B). By labeling the two R groups (R = *t*-BuMe$_2$Si) on bridgehead silicons of **9** by two R* groups (R* = *t*-Bu(CD$_3$)$_2$Si), the two pathways A and B will be discriminated. Thus, if the isomerization occurs via path A, one of the two R* groups will be found on the unsaturated silicon atoms (USi) of **3**, while the other at the saturated ring silicon atoms (SSi); the distribution of two R* groups over four-membered ring (%2R*) should be 50% at USi and 50% at SSi. On the other hand, in case of skeletal isomerization (path B), the %2R* should be 100% at USi.



Scheme 2.

Table 6
ESR parameters of tetrakis(trialkylsilyl)disilene anion radicals and related radicals

Radical	a(Si$_\alpha$)/mT	a(Si$_\beta$)/mT	*g*
12a	3.18	0.25	2.0063
12b	2.92	–	2.0058
12c	2.45	–	2.0062
[Mes$_2$Si=SiMes$_2$]$^{\bullet}$ [a,b]	4.96	–	2.0031
[*t*-Bu$_2$Si=Si(Bu-*t*)$_2$]$^{\bullet}$ [a]	3.36	–	2.0035
(Me$_3$Si)$_3$Si$^{\bullet}$ [c]	6.5	0.62	2.0050
Me$_3$Si$^{\bullet}$ [c]	18.3	–	2.0031

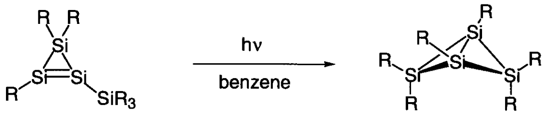
[a] Ref. [35].

[b] Mes = 2,4,6-trimethylphenyl.

[c] Ref. [37].

The thermal isomerization from **9** to **3** was confirmed to proceed via 1,2-silyl migration using the labeled compounds, although the analysis was complicated by the incomplete labeling. The thermal isomerization may occur through a concerted dyotropic-type rearrangement [32] or via the intermediary formation of a tetrasilacyclobutane-1,3-diyl diradical followed by the 1,2-silyl migration to the radical center [33]. By similar labeling experiments, the photochemical isomerization of **3** to **9** was also found to occur via 1,2-silyl migration.

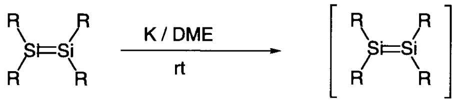
Interestingly, photolysis of **2** in benzene at low temperatures caused isomerization to the corresponding bicyclobutane (**9**) via the 1,2-silyl migration (Eq. (15)) [34].



2, R = *t*-BuMe$_2$Si **9** (15)

4.4. Reduction by alkali metals

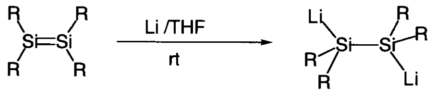
Radical ions of stable disilenes have been sparsely investigated so far. Weidenbruch et al. have first reported ESR spectra of tetra-*tert*-butyldisilene and tetramesityldisilene anion radicals, which were generated during reduction of the corresponding 1,2-dichlorodisilanes but not by direct reduction of the corresponding disilenes with alkali metal [35]. Reduction of **1a**–**1c** by potassium in dimethoxyethane at room temperature gave the corresponding disilene radical anions **12a**–**12c**, whose structures were characterized by ESR spectroscopy [36]. The ESR parameters of **12a**–**12c** are summarized in Table 6 with those of the pertinent reference radicals. The hyperfine coupling constants for the unsaturated silicons (a(Si$_\alpha$)) were 2.45–3.18 mT, which are comparable to a half of that of tris(trimethylsilyl)silyl radical (a(Si$_\alpha$) = 6.5 mT) [37], suggesting that radical anions **12a**–**12c** have nearly planar geometry (Eq. (16)).



1a – **1c**

12a, R = *i*-Pr$_2$MeSi;
12b, R = *t*-BuMe$_2$Si;
12c, R = *i*-Pr$_3$Si. (16)

Reduction of **1a** and **1b** with lithium in THF gave the corresponding 1,2-dilithiated tetrasilyldisilenes in quantitative yields. The dilithodisilanes are rather stable and isolable as white powder (Eq. (17)) [38].



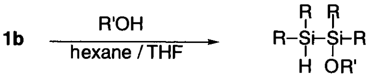
1a, 1b **13a**, R = *i*-Pr$_2$MeSi; **13b**, R = *t*-BuMe$_2$Si. (17)

4.5. Bimolecular reactions

Although a number of bimolecular reactions of both transient and isolable disilenes have been reported [2], substituent effects on the modes, rates, and mechanisms of the reactions have rarely been discussed. Comparison of the reactions of tetrasilyldisilenes with those of known stable disilenes should contribute to the proper understanding of the chemistry of silicon–silicon double bonds.

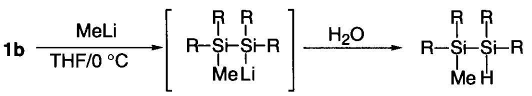
4.5.1. Reactions with various nucleophiles

The reaction mode and reactivity of tetrasilyldisilene (**1b**) toward water and methanol are similar to those of other known disilenes [2]. Thus, disilene **1b** reacted rapidly with water at 0°C to give the corresponding 2-hydroxytetrasilane (**14**) (Eq. 22). A reaction of **1b** with methanol at 50°C afforded 2-methoxytetrasilane **15** together with water-adduct **14**, even when methanol is rigorously dried [7b].



14, 75% (R = *t*-BuMe$_2$Si, R'=H)
15, 66% (R = *t*-BuMe$_2$Si, R'=Me) (18)

When a THF solution of **1b** was treated with excess methyllithium at 0°C , the orange solution turned pale orange. Hydrolysis of the solution gave the corresponding 2-methyltetrasilane (**17**), indicating the formation of silyllithium (**16**) as an intermediate (Eq. (19)).

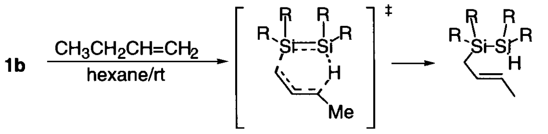


16 **17**, 48%
R = *t*-BuMe$_2$Si (19)

No similar reactions of tetra-*tert*-butyldisilene and tetramesityldisilene with alkyl metals have been reported; these disilenes are suggested to be less electrophilic than disilene **1b**. A similar reaction has been proposed to occur during the reactions of branched chlorooligosilanes with methyl lithium [39].

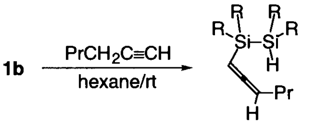
4.5.2. Ene reactions with 1-alkene and 1-alkyne

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 **18** with *trans* stereochemistry around the C=C bond; no other isomer was detected in the reaction mixture (Eq. (20)). The concerted ene addition of an alkene to disilene **1b** through a cyclic transition state like **19** was evidenced by the experiments using 1,6-heptadiene and vinylcyclopropane as radical clocks.



19 **18** (R = *t*-BuMe$_2$Si), 86% (20)

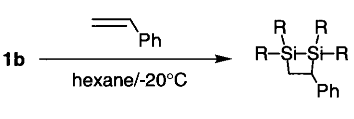
Disilene **1b** reacted with a 1-alkyne in a similar ene-addition manner, giving the corresponding 2-allenyltetrasilane as shown in Eq. (21).



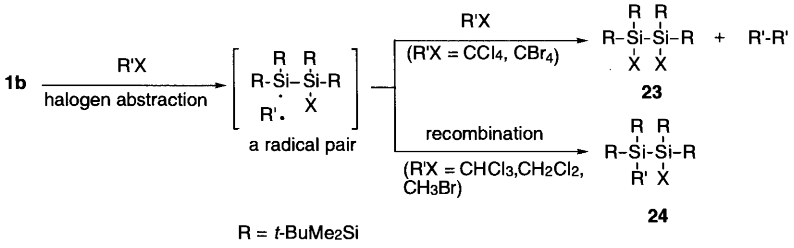
20 (R = *t*-BuMe$_2$Si), 20% (21)

In contrast, it has been reported that tetramesityldisilene does not undergo ene reaction with a 1-alkene and a 1-alkyne [40], while a pyrolysis of tetramesityldisilene affords a benzosilacyclobutene derivative [41], which may be produced via an intramolecular ene addition reaction. 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 [42]. The reason for the enhanced reactivities of tetrasilyldisilene **1b** toward the terminal alkenes and alkyne may be attributed to the fact that the energy level of the π-type LUMO in a tetrakis(trialkylsilyl)disilene is significantly lowered compared with those in tetra-*tert*-butyldisilene and tetramesityldisilene as suggested by the reduction potential (vide supra).

The reaction of **1b** with styrene occurred very rapidly at − 20°C to give the corresponding 1,2-disilacyclobutane **21** (Eq. (22)). The [2 + 2] cycloadditions of isolable disilenes with olefins have been reported by Weidenbruch et al. [43a–c] and Baines et al. [43d]. Although these cycloadditions have been considered to proceed through a biradical intermediate, further studies will be needed to establish the mechanism.



21 (R = *t*-BuMe$_2$Si), 84% (22)

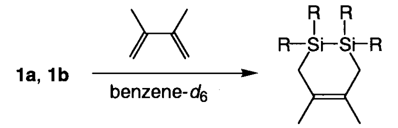


Scheme 3.

While the [2 + 2] cycloaddition reaction of tetramesityldisilene with phenylacetylene has been reported [44], a reaction of **1b** with phenylacetylene proceeded slowly but gave a complex product mixture without formation of the corresponding [2 + 2] adduct.

4.5.3. *The Diels–Alder additions with 2,3-dimethyl-1,3-butadiene*

As shown in Eq. (23), **1a** and **1b** readily underwent the Diels–Alder type cycloadditions with 2,3-dimethyl-1,3-butadiene at room temperature to give quantitatively the corresponding 4,5-disilacyclohexene **22a** and **22b**, respectively. Highly sterically crowded disilene **1c** did not react with the diene.



22a (R = i-Pr2MeSi)
22b (R = t-BuMe2Si),
quantitatively (23)

Although many isolable disilenes have been known to undergo [4 + 2] reactions with heterodienes such as benzil [45], benzoyl chloride [46], acrylamine [47a], and 1,4-diazabutadiene [47b], no [4 + 2] addition of the disilenes to 1,3-butadienes has been reported. A reaction of tetra-*tert*-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) [42]. 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**.

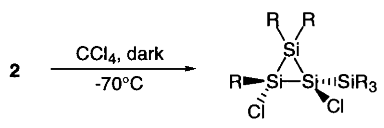
4.5.4. *Reactions of **1b** with haloalkanes*

Although there is no precedent for the direct reaction of a C=C double bond with a haloalkane, tetramesityldisilene has been known to react with benzyl chloride and 2-chloro-2-methylpropane [46].

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 (**23a**) (X = Cl) and **23b** (X = Br) in high yields. Reactions of **1b** with chloroform, dichloromethane, and bromomethane gave readily the corresponding 1,2-adducts of the alkyl halides (**24**).

The reactions of tetrasilyldisilene **1b** with haloalkanes can be understood by a radical mechanism as shown in Scheme 3: disilene **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 the 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. The reactivities of **1b** toward alkyl halides are parallel to those of triethylsilyl radical; the rate constant for halogen abstraction of triethylsilyl radical decreases in the order: $CCl_4 > (CH_3Br) > CHCl_3 > CH_2Cl_2$ [48]. As suggested by the oxidation potentials of tetrasilyldisilenes, initial electron transfer from tetrasilyldisilene to haloalkane is highly endothermic and hence unlikely. It is interesting to note that 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 [49].

The reaction of cyclotrisilene **2** with an excess amount of carbon tetrachloride completed within 1 min even at − 70°C to afford the corresponding *trans*-1,2-dichloro-1-tris(*tert*-butyldimethylsilyl)silyl-2,3,3-tris(*tert*-butyldimethylsilyl)cyclotrisilane **25** quantitatively without cleavage of the Si–Si single bonds in the ring (Eq. (24)). The X-ray analysis of a single crystal of **25** disclosed that the two chlorine atoms were arranged in a *trans* fashion.



25 (24)

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