Synthesis and reactions of polythiadisilabicyclo[k. l. m]alkanes

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Abstract

The reaction of tris(trimethylsilyl)methylsilane ($TsiSiH_3$) with elemental sulfur afforded 1,3-bis{tris(trimethylsilyl)methyl}-2,4,5,6,7,8-hexathia-1,3-disilabicyclo[3.2.1]octane (6), 1,3-bis{tris(trimethylsilyl)methyl}-2,4,5,6,7-pentathia-1,3-disilabicyclo[2.2.1]heptane (b5), and 1,3-bis{tris(trimethylsilyl)methyl}-2,4,5,6-tetrathia-1,3-disilabicyclo[2.1.1]hexane (4) in 12%, 12%, and 22% yields respectively. Structures of these compounds were confirmed by X-ray diffraction analysis. 1,3-Bis{tris(trimethylsilyl)methyl}-2,4,5-trithia[1.1.1]pentane (3) was obtained by photolysis of 4 in the presence of trimethylphosphine, quantitatively. The distance between the bridgehead silicon atoms of 2.407 Å in 3 lies in the range of common Si–Si single bonds.

Keywords: Silicon; Sulfur; Bicyclo [k.l.m]alkanes; Polysulfide

1. Introduction

There has currently been considerable interest in the chemistry of Group IV propellanes (1a) and bicyclo[1.1.1]pentanes (1b) in view of the nature of the bridgehead bonds [1–3]. Pentasila[1.1.1]propellane has not been isolated as yet, although a derivative of bicyclo[1.1.1]pentasilane [4] has been synthesized. According to both calculations and experiments, M–M distances in [1.1.1]propellanes (M = C, Si, Ge, Sn, Y = CH_2, SiH_2, GeH_2, SnH_2) are much shorter than those in bicyclo[1.1.1]pentanes except for the tin analogue [2–7]. Theoretically, substitution of electronegative groups (e.g. O, CH_2) at the peripheral positions should stabilize the central M–M interaction for M = Si [5e]. Therefore, the structures of [1.1.1]propellanes of the type M_2Y_3 (M = Si, Ge, Sn; Y = O, S, Se) (1a) and the corresponding bicyclo[1.1.1]pentanes $H_2M_2Y_3$ (1b) are very similar [6].

According to theoretical studies, trioxadisilabicyclo-[1.1.1]pentane (2) is predicted to have a short distance between the bridgehead silicon atoms of only 2.069 Å [5], which is shorter than that of silicon–silicon double

bond. The corresponding distance in the sulfur analogue, trithiadisilabicyclo[1.1.1]pentane, has been predicted to be 2.363 Å [6], which corresponds to a Si–Si single bond. However, neither the attractive compound 2 nor its chalcogen analogue has been experimentally observed prior to our studies [8,9]. We have succeeded in synthesizing and determining the structure of 1,3-bis-substituted 2,4,5-trithia-1,3-disilabicyclo[1.1.1]-pentane by taking advantage of an excellent steric protection group, tris(trimethylsilyl)methyl (denoted as Tsi hereafter) by means of photodesulfurization of polythiadisilabicyclo[k.l.m]alkanes [9]. Herein, we report the first full detail of the synthesis, structures and reactions of polythiadisilabicyclo[k.l.m]alkanes.

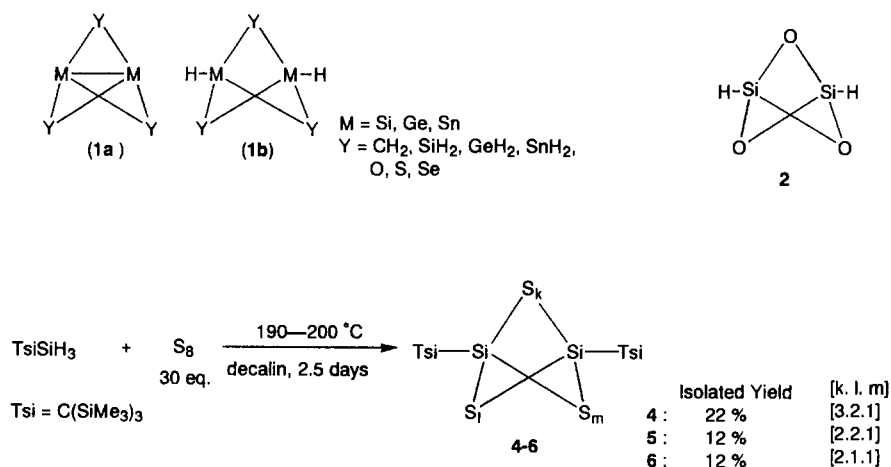## 2. Results and discussion

2.1. Synthesis of polythiadisilabicyclo[k.l.m.]alkanes

A decalin solution of trisylsilane {tris(trimethylsilyl)-methylsilane = $TsiSiH_3$} and 30 equivalents of elemental sulfur were heated at 190–200°C for 2.5 days. Chromatographic separation afforded $(TsiSi)_2S_4$ (4), $(TsiSi)_2S_5$ (5), and $(TsiSi)_2S_6$ (6) as yellow solids in 22%, 12%, and 12% yields respectively, which are stable towards air and moisture (Scheme 1). There are three possible structures for 6 as shown in Fig. 1, which

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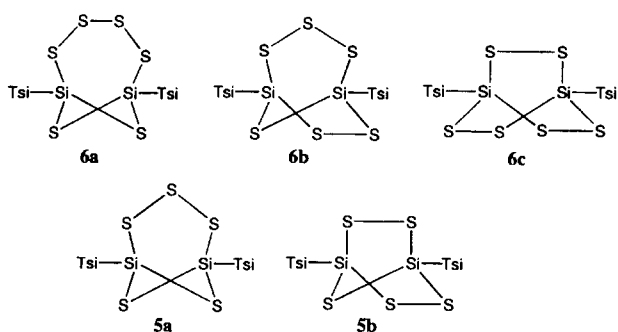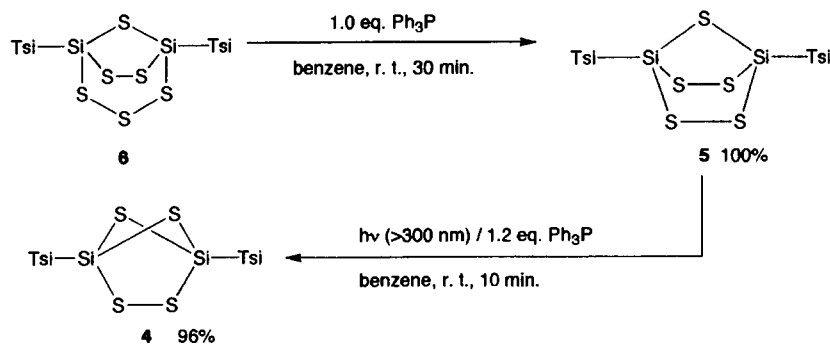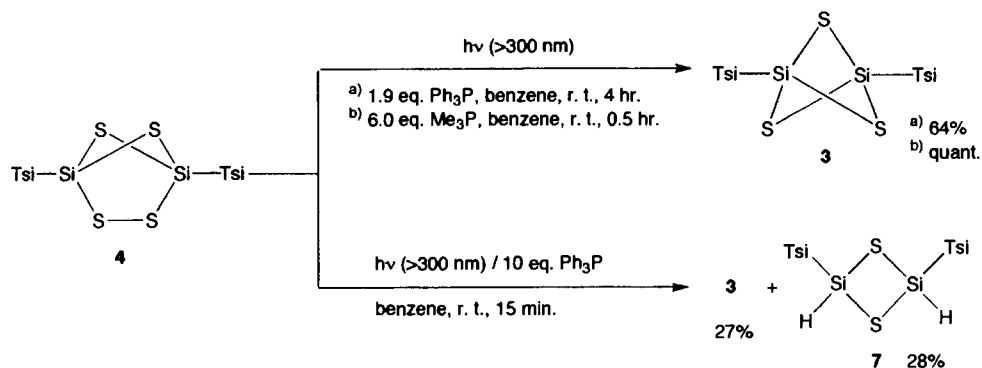
M = Si, Ge, Sn
Y = CH₂, SiH₂, GeH₂, SnH₂,
O, S, Se

(1a) **(1b)** **2**

Scheme 1.

TsiSiH₃ + S₈ $\xrightarrow[\text{30 eq. decalin, 2.5 days}]{190—200\ °C}$

Tsi = C(SiMe₃)₃

	Isolated Yield	[k. l. m]
4 :	22 %	[3.2.1]
5 :	12 %	[2.2.1]
6 :	12 %	[2.1.1]

4-6

Scheme 1.

6a   **6b**   **6c**

5a   **5b**

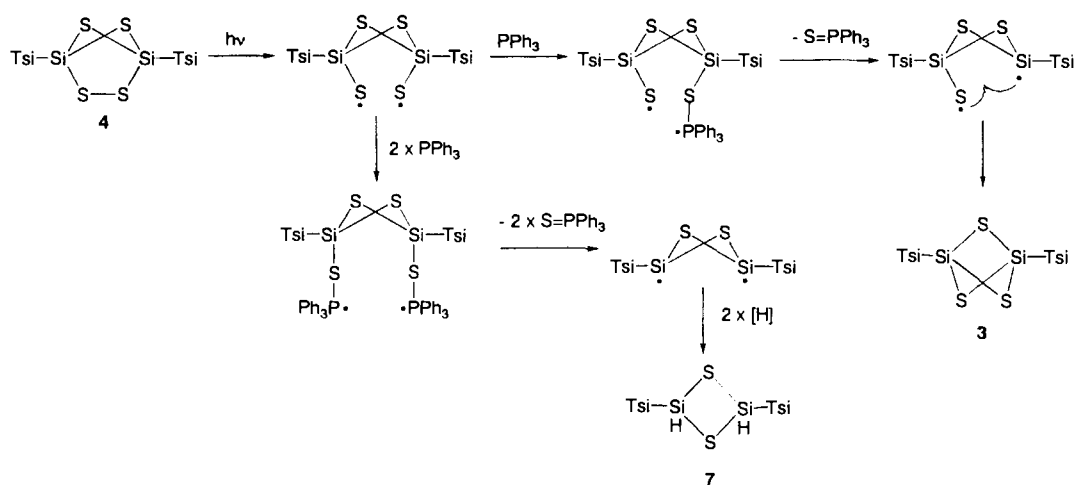Fig. 1. Possible structures of compounds **5** and **6**.

are **6a**, **6b**, and **6c**. Compound **5** has two possible structures, **5a** and **5b** (Fig. 1). Unfortunately, these structures could not be distinguished by means of NMR and other spectroscopic methods. However, the structures of polythiadisilabicyclo[$k.l.m$]alkanes **6**, **5**, and **4** were confirmed by X-ray structure analysis to be 2,4,5,6,7,8-hexathia-1,3-disilabicyclo[3.2.1]octane, 2,4,5,6,7-pentathia-1,3-disilabicyclo[2.2.1]heptane, and 2,4,5,6-tetrathia-1,3-disilabicyclo[2.1.1]hexane respectively.

$\xrightarrow[\text{benzene, r. t., 30 min.}]{1.0\ \text{eq. Ph}_3\text{P}}$

6   **5 100%**

$\xleftarrow[\text{benzene, r. t., 10 min.}]{hv\ (>300\ nm)\ /\ 1.2\ \text{eq. Ph}_3\text{P}}$

4 96%

Scheme 2.

$\xrightarrow{hv\ (>300\ nm)}$
a) 1.9 eq. Ph₃P, benzene, r. t., 4 hr.
b) 6.0 eq. Me₃P, benzene, r. t., 0.5 hr.

3   a) 64%   b) quant.

4

$\xrightarrow[\text{benzene, r. t., 15 min.}]{hv\ (>300\ nm)\ /\ 10\ \text{eq. Ph}_3\text{P}}$

3 +

27%   **7 28%**

Scheme 3.

Scheme 4.

(1)

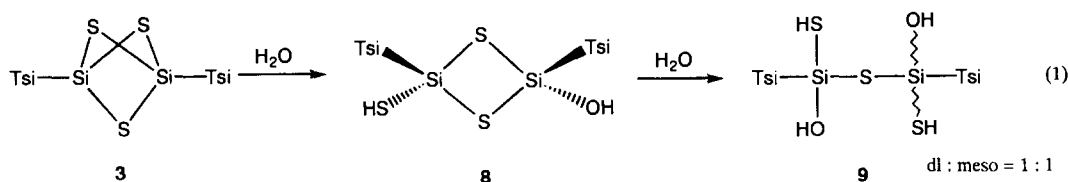dl : meso = 1 : 1

2.2. Desulfurization of polythiadisilabicyclo[k.l.m.]alkanes

Desulfurization reactions of polythiadisilabicyclo[k.l.m]alkanes are summarized in Scheme 2. When reacted with PPh_3, 6 was quantitatively converted into 5. The reaction of 5 with PPh_3 in benzene at 70°C for 1 day resulted in no observable reaction. In contrast, it is well-known that photolysis of disulfide generates thiyl radicals, which are effectively quenched by a trivalent phosphorus compound and eliminate sulfur [10]. Further desulfurization of 5 was achieved by irradiation with a high pressure Hg lamp ($h\nu > 300$ nm) in the presence of 1.2 equivalents of triphenylphosphine in benzene for 10 min to give 4 in 96% yield. When 4 was irradiated in

the presence of 1.9 equivalents of triphenylphosphine for 4 h, 2,4,5-trithia-1,3-disilabicyclo[1.1.1]pentane (3) was obtained in 64% yield. When 4 was subjected to photolysis in the presence of a ten-fold excess of PPh_3, cyclodisilthiane 7 and 3 could be isolated in 28% and 27% yields respectively, while independently, 3 did not further react under identical conditions (Scheme 3). Desulfurization of 4 in d_8-toluene afforded d_1- or d_2-cyclodisilthiane and cyclodisilthiane 7 (11% yield, D : H = 35 : 65) along with 3 (29% yield). This suggested that proton sources for the formation of 7 are methyl groups of solvent and substituents of compound 4.

The most likely initial step of the photochemical desulfurization of 4 is the S–S bond cleavage. Trapping of the resulting thiyl biradical by one or two molecules

Table 1
^1H, ^{13}C, and ^{29}Si NMR spectral data of 6, 5, 4, 3, 4Se and 3Se

	6 [a]	5 [a]	4 [a]	3 [a,b]	4Se [c]	3Se [b,d]
^1H NMR	0.35	0.35	0.37	0.45	0.40	0.45
^{13}C NMR	5.5 (q)	5.2 (q)	5.1 (q)	4.3 (q)	5.1 (q)	4.3 (q)
	6.0 (s)	6.0 (s)	6.5 (s)	6.9 (s)	6.0 (s)	5.8 (s)
^{29}Si NMR	0.1 (SiMe$_3$)	0.6 (SiMe$_3$)	0.8 (SiMe$_3$)	1.0 (SiMe$_3$)	0.8 (SiMe$_3$)	0.6 (SiMe$_3$)
	46.4 (Si–S)	37.3 (Si–S)	25.7 (Si–S)	5.8 (Si–S)	–7.5 (Si–Se)	–59.0 (Si–Se)

[a] See Ref. [9]. [b] D_6-Benzene was used as a solvent. [c] 4Se is selenium analogue of 4; see Ref. [11]. [d] 3Se is selenium analogue of 3; see Ref. [8].

of PPh$_3$ would then lead to the formation of **3** and **7** as shown in Scheme 4.

By the irradiation in the presence of trimethylphosphine, **4** was quantitatively converted into **3**. Separation by gel-permeation liquid chromatography followed by recrystallization from benzene, afforded **3** as white crystals. The structure of **3** was unequivocally determined by single crystal X-ray diffraction analysis. The compound **3** is thermally quite stable (about 300°C) but slowly hydrolyzed by moisture to provide 1,3-bis{tris(trimethylsilyl)methyl}-1-hydroxy-3-mercaptocyclodisilthiane **8** (Eq. (1)), which was further hydrolyzed to 1,3-bis{tris(trimethylsilyl)methyl}1-3-dihydroxy-1,3-dimercaptosulfide **9** (Eq. (1)).

2.3. NMR spectra of polythiadisilabicyclo[k.l.m]alkanes (6, 5, 4, and 3)

^{1}H, ^{13}C, and ^{29}Si NMR spectral data of **6, 5, 4** and **3** are shown in Table 1. ^{13}C NMR data of methyl carbon in **3, 4, 5**, and **6** are 4.3, 5.1, 5.2, and 5.5 ppm, which are in order of the steric repulsion of the two Tsi

groups. Interestingly, compounds **4Se** and **3Se**, which are selenium analogues of **4** and **3** respectively, show the same chemical shifts of a methyl carbon in the Tsi group as those of **4** and **3** respectively. ^{29}Si NMR data of the bridgehead silicons in **6, 5, 4**, and **3** are 46.4, 37.3, 25.7, and 5.8 ppm, which are in order of the strain of silthiane rings. In contrast, those of **4Se** [11] and **3Se** [8] are −7.5 and −59.0 ppm respectively. The difference of the bridgehead silicon's chemical shift between **3** and **3Se** is derived from the stereo-compression effect between the peripheral atoms [12].

2.4. UV spectra of polythiadisilabicyclo[k.l.m]alkanes (6, 5, 4, and 3)

Although the absorption maximum of polysulfides in the UV–vis spectrum is shifted to longer wavelengths with the number of sulfur atoms [13], that of cyclic polysulfides is shifted to shorter wavelengths with the number of ring atoms [14]. The smaller dihedral angle of cyclic polysulfide is responsible for the increasing ring strain. Typical cyclic disulfides, tetramethylene

Table 2
Summary of crystal data collection for **5, 4**, and **3**

	5	4	3
Formula	C$_{20}$H$_{54}$Si$_8$S$_5$	C$_{20}$H$_{54}$Si$_8$S$_4$	C$_{20}$H$_{54}$Si$_8$S$_3$
Fw	679.66	647.60	615.53
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/a$	$P\bar{1}$	$P2_1/c$
a (Å)	27.279(1)	9.000(3)	15.369(1)
b (Å)	8.972(1)	15.419(6)	13.159(1)
c (Å)	30.871(2)	26.315(8)	17.672(2)
α (deg)		94.10(2)	
β (deg)	92.32(22)	99.79(2)	91.51(1)
γ (deg)		89.98(2)	
V (Å^3)	7549.8	3589.1	3572.6
Z	8	4	4
D (calcd) (g cm^{-3})	1.20	1.20	1.14
Crystal size (mm^3)	0.20 × 0.40 × 0.60	0.60 × 0.50 × 0.20	0.50 × 0.50 × 0.40
Color; habit	yellow, rod	pale yellow, rod	white, rod
$F(000)$ (e)	2928	1400	1336
μ (Mo Kα) (cm^{-1})	5.6	5.3	4.7
Radiation	Mo Kα	Mo Kα	Mo Kα
(Graphite monochromator)	λ = 0.71073 Å	λ = 0.70930 Å	λ = 0.71073 Å
Temperature (°C)	23 ± 1	23 ± 1	23 ± 1
Diffractometer	CAD4	CAD4	CAD4
Scan	ω–2θ	ω–2θ	ω–2θ
Scan range (θ) (deg)	52.6	50.0	50.0
hkl range			
No. of unique reflections	16301	7802	6557
No. of observed reflections ($F_0^2 \geq 3\sigma(F_0^2)$)	8001	6105	5200
No. of refined parameters	622	631	307
R	0.078	0.054	0.036
R_w	0.091	0.077	0.037
(shift/error)$_{max}$	1.35σ	0.06σ	0.23σ
$\Delta\rho$fin (max/min) (e Å^3)	1.23(11) −0.14(0)	0.61(10) −0.33(0)	0.39(4) −0.07(0)

disulfide and trimethylene disulfide have C–S–S–C dihedral angles of 60° and 27° and absorption maxima at 286 and 330 nm respectively [14]. Interestingly, **4** has a Si–S–S–Si dihedral angle of 0° and an absorption maximum at 366 nm. Compound **5** also has small Si–S–S–Si dihedral angles, 11° and 19°, and an absorption maximum at 375 nm. The longer wavelength of 375 nm in **5** than **4** is due to the through space interaction between the intramolecular two disulfides. A remarkable S · · · S interaction of 2-S3 was observed at 290 nm (ε 38) in the electronic spectrum. That the weak but definite absorption at 290 nm was assigned as originating from the S · · · S interaction of **3** was based on the following two reasons. Firstly, cyclodisilthiane **7** does not have a definite absorption around 290 nm. This suggests that the absorption of 290 nm in **3** is not derived from a Si–S bond. Secondly the selenium analogue, $(TsiSi)_2Se_3$, displays an absorption band at 365 nm (ε 33) [15]. Moreover, $(TsiGe)_2Se_3$ also exhibits an absorption maximum in the same region (365 nm). It was concluded that the absorption at 365 nm was derived from a Se · · · Se interaction [12].

2.5. X-ray analysis of polythiadisilabicyclo[k.l.m]alkanes (6, 5, 4, and 3)

Single-crystal X-ray diffraction structure analyses were undertaken to determine the unequivocal molecular structure of **6** [16] **5**, **4**, and **3**. Crystal data of **5**, **4**, and **3** and summarized in Table 2. Compound **5** crystallized with two independent molecules in a crystal unit. An ORTEP drawing of **5** (molecule 1) is shown in Fig. 2. Interatomic distances (Å) and angles (degree) for molecule 1 with the corresponding values for molecule 2 are listed in Tables 3 and 4 respectively. The Si atoms of the $C(SiMe_3)_3$ group in molecule 2 were disordered equally between two sets of sites (Si(41, 42, 43) and Si(44, 45, 46)), whereas the positions of the carbon atoms are identical for both sets, and refinement of occupancies of Si(41, 42, 43) and Si(44, 45, 46) sug-
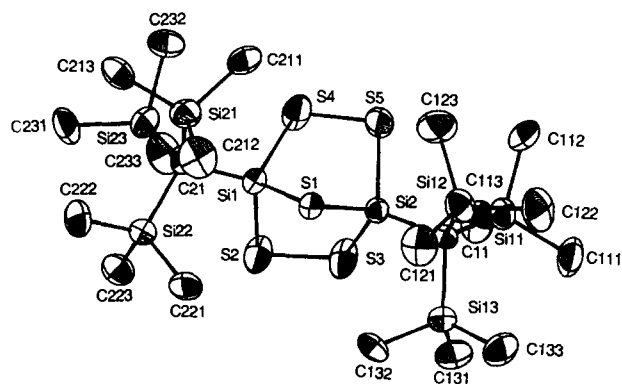
Table 3
Selected bond lengths (Å) of **5**

Molecule 1		Molecule 2	
S1–Si1	2.139(3)	S6–Si3	2.129(3)
S1–Si2	2.128(3)	S6–Si4	2.126(4)
S2–S3	2.043(4)	S7–S8	2.034(5)
S2–Si1	2.160(4)	S7–Si3	2.151(4)
S3–Si2	2.160(4)	S8–Si4	2.149(4)
S4–S5	2.040(4)	S9–S10	2.021(4)
S4–Si1	2.161(4)	S9–Si4	2.174(4)
S5–Si2	2.168(4)	S10–Si3	2.176(4)
Si1–C21	1.846(8)	Si3–C31	1.855(9)
Si2–C11	1.861(9)	Si4–C41	1.845(9)
Si11–C11	1.930(9)	Si31–C31	1.920(9)
Si11–C111	1.90(1)	Si31–C311	1.89(1)
Si11–C112	1.89(1)	Si31–C312	1.90(1)
Si11–C113	1.91(1)	Si31–C313	1.90(1)
Si12–C11	1.921(9)	Si32–C31	1.955(9)
Si12–C121	1.90(1)	Si32–C321	1.89(1)
Si12–C122	1.91(1)	Si32–C322	1.90(1)
Si12–C123	1.92(1)	Si32–C323	1.91(1)
Si13–C11	1.930(9)	Si33–C31	1.932(9)
Si13–C131	1.91(1)	Si33–C331	1.91(1)
Si13–C132	1.90(1)	Si33–C332	1.90(1)
Si13–C133	1.91(1)	Si33–C333	1.88(1)
Si21–C21	1.931(9)	Si41–C41	1.94(1)
Si21–C211	1.89(1)	Si41–C411	1.88(1)
Si21–C212	1.91(1)	Si41–C412	1.95(1)
Si21–C213	1.91(1)	Si41–C413	2.05(1)
Si22–C21	1.935(9)	Si42–C41	1.85(1)
Si22–C221	1.89(1)	Si42–C421	2.03(2)
Si22–C222	1.90(1)	Si42–C422	2.00(1)
Si22–C223	1.92(1)	Si42–C423	1.95(1)
Si23–C21	1.936(9)	Si43–C41	1.94(1)
Si23–C231	1.89(1)	Si43–C431	2.03(1)
Si23–C232	1.92(1)	Si43–C432	1.90(2)
Si23–C233	1.90(1)	Si43–C433	1.93(1)
		Si44–C41	1.94(1)
		Si44–C411	1.92(1)
		Si44–C412	1.92(1)
		Si44–C432	2.09(1)
		Si45–C41	1.93(1)
		Si45–C422	1.98(2)
		Si45–C431	1.89(1)
		Si45–C433	2.06(1)
		Si46–C41	2.02(1)
		Si46–C413	2.03(1)
		Si46–C421	1.91(1)
		Si46–C423	1.92(1)

Fig. 2. ORTEP drawing of **5**.

gested that these should be in the ratio of 1 : 1. Each of the five-membered rings in the bicyclo[2.2.1]heptane skeleton is a half-chair conformation, and the (Si–S–S–Si) torsion angles are 11–19°: (Si1–S2–S3–Si2, 19.28°; Si1–S4–S5–Si2, 16.74° in molecule 1; Si3–S7–S8–Si4; 11.81°; Si4–S9–S10–Si3, 11.28° in molecule 2). Compound **4** crystallized with two independent molecules in a crystal unit. An ORTEP drawing of **4** (molecule 1) is shown in Fig. 3. Interatomic distances (Å) and angles (degree) for molecule 1 with the corresponding values

Table 4
Selected bond angles (deg) of **5**

Molecule 1		Molecule 2	
Si1–S1–Si2	89.2(1)	S3–S6–Si4	89.5(1)
S3–S2–Si1	98.2(2)	S8–S7–Si3	100.2(2)
S2–S3–Si2	105.0(2)	S7–S8–Si14	104.8(2)
S5–S4–Si1	104.9(2)	S10–S9–Si4	100.3(2)
S4–S5–Si2	98.9(2)	S9–S10–Si3	104.8(2)
S1–Si1–S2	101.5(1)	S6–Si3–S7	103.1(1)
S1–Si1–S4	105.1(1)	S6–Si3–S10	104.4(2)
S1–Si1–C21	116.4(3)	S6–Si3–C31	116.1(3)
S2–Si1–S4	106.4(1)	S7–Si3–S10	105.3(2)
S2–Si1–C21	113.3(3)	S7–Si3–C31	114.5(3)
S4–Si1–C21	113.1(3)	S10–Si3–C31	112.3(3)
S1–Si2–S3	105.6(1)	S6–Si4–S8	105.3(2)
S1–Si2–S5	101.7(1)	S6–Si4–S9	102.4(2)
S1–Si2–C11	116.4(3)	S6–Si4–C41	115.9(3)
S3–Si2–S5	104.5(2)	S8–Si4–S9	104.9(2)
S3–Si2–C11	113.6(3)	S8–Si4–C41	115.3(3)
S5–Si2–C11	113.7(3)	S9–Si4–C41	111.8(3)
C11–Si11–C111	112.3(5)	C31–Si31–C311	112.8(5)
C11–Si11–C112	112.3(5)	C31–Si31–C312	112.6(5)
C11–Si11–C113	111.7(4)	C31–Si31–C313	111.8(5)
C111–Si11–C112	105.6(5)	C311–Si31–C312	106.7(5)
C111–Si11–C113	107.1(5)	C311–Si31–C313	106.5(5)
C112–Si11–C113	107.4(6)	C312–Si31–C313	105.9(6)
C11–Si12–C121	112.0(5)	C31–Si32–C321	113.6(4)
C11–Si12–C122	111.7(5)	C31–Si32–C322	113.1(5)
C11–Si12–C123	112.2(5)	C31–Si32–C323	111.1(5)
C121–Si12–C122	107.2(5)	C321–Si32–C322	106.5(6)
C121–Si12–C123	106.2(6)	C321–Si32–C323	106.3(5)
C122–Si12–C123	107.3(6)	C322–Si32–C323	105.7(5)
C11–Si13–C131	113.1(5)	C31–Si33–C331	112.2(5)
C11–Si11–C132	113.2(4)	C31–Si33–C332	111.7(5)
C11–Si11–C133	110.6(5)	C31–Si33–C333	113.2(5)
C131–Si11–C132	107.0(5)	C331–Si33–C332	107.1(6)
C131–Si11–C133	105.1(5)	C331–Si33–C333	106.6(6)
C132–Si11–C133	107.3(6)	C332–Si33–C333	105.6(6)
C21–Si21–C211	113.4(4)	C41–Si41–C411	114.8(5)
C21–Si21–C212	112.1(5)	C41–Si41–C412	110.2(5)
C21–Si21–C213	111.7(5)	C41–Si41–C413	106.6(5)
C211–Si21–C212	105.4(5)	C411–Si41–C412	103.9(6)
C211–Si21–C213	107.3(5)	C411–Si41–C413	111.7(6)
C212–Si21–C213	106.5(5)	C412–Si41–C413	109.6(6)
C21–Si22–C221	114.3(4)	C41–Si42–C421	109.4(6)
C21–Si22–C222	111.9(5)	C41–Si42–C422	110.7(6)
C21–Si22–C223	111.3(5)	C41–Si42–C423	113.3(5)
C2A–Si6A–C61A	112.5(5)	C2B–Si6B–C61B	112.4(4)
C2A–Si6A–C62A	111.3(4)	C2B–Si6B–C62B	111.4(5)
C2A–Si6A–C63A	111.8(5)	C2B–Si6B–C63B	111.9(4)
C61A–Si6A–C62A	106.9(5)	C61B–Si6B–C62B	106.5(5)
C61A–Si6A–C63A	106.4(5)	C61B–Si6B–C63B	106.4(6)
C62A–Si6A–C63A	107.6(5)	C62B–Si6B–C63B	108.0(5)
C2A–Si7A–C71A	112.9(5)	C2B–Si7B–C71B	113.0(5)
C2A–Si7A–C72A	111.6(5)	C2B–Si7B–C72B	111.8(5)
C2A–Si7A–C73A	112.5(5)	C2B–Si7B–C73B	112.7(4)
C71A–Si7A–C72A	106.6(6)	C71B–Si7B–C72B	106.4(5)
C71A–Si7A–C73A	106.8(6)	C71B–Si7B–C73B	106.7(6)
C72A–Si7A–C73A	106.1(5)	C72B–Si7B–C73B	105.7(5)
C2A–Si8A–C81A	110.8(4)	C2B–Si8B–C81B	110.9(4)
C2A–Si8A–C82A	113.6(4)	C2B–Si8B–C82B	113.1(4)
C2A–Si8A–C83A	111.6(4)	C2B–Si8B–C83B	111.4(5)
C81A–Si8A–C82A	106.6(5)	C81B–Si8B–C82B	106.9(6)
C81A–Si8A–C83A	107.2(5)	C81B–Si8B–C83B	107.2(5)
C82A–Si8A–C83A	106.7(5)	C82B–Si8B–C83B	107.0(5)

Table 4 (continued)

Molecule 1		Molecule 2	
Si1A–C1A–Si3A	108.4(4)	Si1B–C1B–Si3B	108.3(4)
Si1A–C1A–Si4A	108.5(4)	Si1B–C1B–Si4B	108.5(5)
Si1A–C1A–Si5A	109.9(5)	Si1B–C1B–Si5B	109.6(4)
Si3A–C1A–Si4A	110.8(5)	Si3B–C1B–Si4B	110.9(5)
Si3A–C1A–Si5A	110.1(5)	Si3B–C1B–Si5B	110.3(5)
Si3C–C1A–Si4C	111.9(6)	Si3D–C1B–Si4D	111.8(5)
Si3C–C1A–Si5C	108.3(5)	Si3D–C1B–Si5D	108.7(5)
Si4A–C1A–Si5A	109.3(5)	Si4B–C1B–Si5B	109.2(4)
Si4C–C1A–Si5C	111.4(5)	Si4D–C1B–Si5D	111.5(5)
Si2A–C2A–Si6A	107.6(5)	Si2B–C2B–Si6B	107.8(4)
Si2A–C2A–Si7A	109.0(4)	Si2B–C2B–Si7B	108.8(4)
Si2A–C2A–Si8A	108.9(4)	Si2B–C2B–Si8B	108.8(5)
Si6A–C2A–Si7A	111.5(4)	Si6B–C2B–Si7B	111.5(5)
Si6A–C2A–Si8A	109.6(4)	Si6B–C2B–Si8B	109.8(4)
Si7A–C2A–Si8A	110.2(5)	Si7B–C2B–Si8B	110.0(4)

for molecule 2 are listed in Tables 5 and 6 respectively. Both independent molecules of **4** are essentially identical structurally. The Si atoms of the $C(SiMe_3)_3$ group were disordered equally between two sets of sites (Si(3A, 4A, 5A) and Si(3C, 4C, 5C) in molecule 1 and Si(3B, 4B, 5B) and Si(3D, 4D, 5D) in molecule 2), whereas the positions of the carbon atoms are identical for both sets, and refinement of occupancies of Si(3A, 4A, 5A) and Si(3C, 4C, 5C) in molecule 1 and Si(3B, 4B, 5B) and Si(3D, 4D, 5D) in molecule 2 suggested that these should be in the ratio of 3:2 in each molecule. The five-membered ring in the bicyclo[2.1.1]-hexane skeleton is an envelope conformation, and the torsion angles are Si1A–S3A–S4A–Si2A = 0.08° and Si1B–S3B–S4B–Si2B = 0.05°. An ORTEP drawing of **3** is shown in Fig. 4. Interatomic bond lengths (Å), and angles (degree) are listed in Tables 7 and 8 respectively. The Si atoms of the $C(SiMe_3)_3$ group were disordered equally between two sets of sites (Si(21, 22, 23) and Si(31, 32, 33)) whereas the positions of the carbon atoms are identical for both sets. The refinement of occupancies of Si(21, 22, 23) and Si(31, 32, 33) suggested that these should be in the ratio of 3:1.

The structure of **3** is in good agreement with the results of the quantum chemical calculation [6], which is
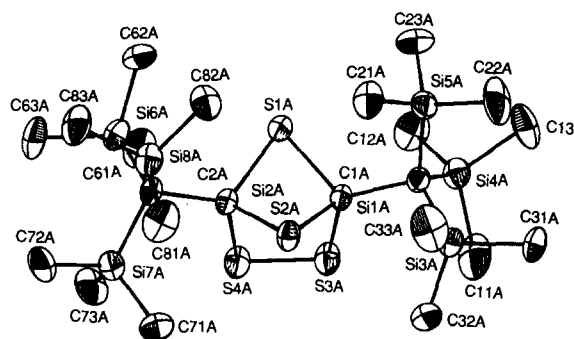

Fig. 3. ORTEP drawing of **4**.

Table 5
Selected bond lengths (Å) of 4

Molecule 1		Molecule 2	
S1A–Si1A	2.160(4)	S1B–Si1B	2.161(4)
S1A–Si2A	2.162(3)	S1B–Si2B	2.160(3)
S2A–Si1A	2.161(4)	S2B–Si1B	2.161(3)
S2A–Si2A	2.162(3)	S2B–Si2B	2.161(4)
S3A–S4A	2.094(4)	S3B–S4B	2.096(4)
S3A–Si1A	2.172(3)	S3B–Si1B	2.172(4)
S4A–Si2A	2.180(3)	S4B–Si2B	2.178(3)
Si1A–C1A	1.847(9)	Si1B–C1B	1.848(9)
Si2A–C2A	1.85(1)	Si2B–C2B	1.851(9)
Si3A–C1A	1.94(1)	Si3B–C1B	1.93(1)
Si3A–C31A	1.96(1)	Si3B–C31B	1.96(1)
Si3A–C32A	1.89(1)	Si3B–C32B	1.89(1)
Si3A–C33A	1.99(1)	Si3B–C33B	1.99(1)
Si3C–C1A	1.96(1)	Si3D–C1B	1.95(1)
Si3C–C–11A	2.07(1)	Si3D–C11B	2.08(1)
Si3C–C31A	1.97(1)	Si3D–C31B	1.96(1)
Si3C–C32A	1.89(1)	Si3D–C32B	1.89(1)
Si4A–C1A	1.94(1)	Si4B–C1B	1.940(9)
Si4A–C11A	2.02(1)	Si4B–C11B	2.01(1)
Si4A–C12A	1.90(1)	Si4B–C12B	1.90(1)
Si4A–C13A	1.92(1)	Si4B–C13B	1.92(1)
Si4C–C1A	1.89(1)	Si4D–C1B	1.90(1)
Si4C–C12A	1.91(1)	Si4D–C12B	1.91(1)
Si4C–C13A	2.00(1)	Si4D–C13B	1.99(1)
Si4C–C23A	2.07(2)	Si4D–C23B	2.07(2)
Si5A–C1A	1.945(9)	Si5B–C1B	1.94(1)
Si5A–C21A	1.92(1)	Si5B–C21B	1.92(1)
Si5A–C22A	1.94(1)	Si5B–C22B	1.94(1)
Si5A–C23A	1.96(1)	Si5B–C23B	1.97(1)
Si5C–C1A	1.96(1)	Si5D–C1B	1.95(1)
Si5C–C21A	1.89(1)	Si5D–C21B	1.90(1)
Si5C–C22A	2.03(1)	Si5D–C22B	2.02(1)
Si5C–C33A	2.02(1)	Si5D–C33B	2.02(1)
Si6A–C2A	1.951(9)	Si6B–C2B	1.945(9)
Si6A–C61A	1.89(1)	Si6B–C61B	1.89(1)
Si6A–C62A	1.89(1)	Si6B–C62B	1.89(1)
Si6A–C63A	1.90(1)	Si6B–C63B	1.90(1)
Si7A–C2A	1.917(8)	Si7B–C2B	1.920(9)
Si7A–C71A	1.90(1)	Si7B–C71B	1.90(1)
Si7A–C72A	1.90(1)	Si7B–C72B	1.90(1)
Si7A–C73A	1.91(1)	Si7B–C73B	1.90(1)
Si8A–C2A	1.939(9)	Si8B–C2B	1.940(9)
Si8A–C81A	1.92(1)	Si8B–C81B	1.92(1)
Si8A–C82A	1.90(1)	Si8B–C82B	1.89(1)
Si8A–C83A	1.90(1)	Si8B–C83B	1.90(1)
C221–Si22–C222	106.0(5)	C421–Si42–C422	111.4(7)
C221–Si22–C223	105.9(5)	C421–Si42–C423	98.9(6)
C222–Si22–C223	106.8(5)	C422–Si42–C423	112.5(7)
C21–Si23–C231	112.5(4)	C41–Si43–C431	105.3(5)
C21–Si23–C232	111.5(5)	C41–Si43–C432	112.0(6)
C21–Si23–C233	112.5(5)	C41–Si43–C433	109.8(5)
C231–Si23–C232	107.7(5)	C431–Si43–C432	112.0(6)
C231–Si23–C233	106.2(5)	C431–Si43–C433	101.4(6)
C232–Si23–C233	106.1(6)	C432–Si43–C433	115.5(7)
Si2–C11–Si11	107.6(4)	C41–Si44–C411	113.0(6)
Si2–C11–Si12	109.1(4)	C41–Si44–C412	111.5(5)
Si2–C11–Si13	108.2(4)	C41–Si44–C432	104.3(6)
Si11–C11–Si12	111.3(4)	C411–Si44–C412	103.4(6)
Si11–C11–Si13	108.9(4)	C411–Si44–C432	111.8(6)
Si12–C11–Si13	110.7(4)	C412–Si44–C432	113.1(6)
Si11–C21–Si21	109.0(4)	C41–Si45–C422	108.4(6)
Si1–C21–Si22	108.2(4)	C41–Si45–C431	111.5(6)

Table 5 (continued)

Molecule 1		Molecule 2	
Si1–C21–Si23	109.4(4)	C41–Si45–C433	104.9(5)
Si21–C21–Si22	110.0(4)	C422–Si45–C431	118.3(6)
Si21–C21–Si23	110.4(4)	C422–Si45–C433	111.1(6)
Si22–C21–Si23	109.9(4)	C431–Si45–C433	101.7(6)
		C41–Si46–C413	104.6(5)
		C41–Si46–C421	107.4(6)
		C41–Si46–C423	107.7(6)
		C413–Si46–C421	116.7(8)
		C413–Si46–C423	115.5(7)
		C421–Si46–C423	104.4(7)
		Si3–C31–Si31	108.9(4)
		Si3–C31–Si32	107.6(4)
		Si3–C31–Si33	109.3(4)
		Si31–C31–Si32	109.6(4)
		Si31–C31–Si33	111.8(4)
		Si32–C31–Si33	109.5(4)
		Si4–C41–Si41	107.7(5)
		Si4–C41–Si42	108.4(5)
		Si4–C41–Si43	107.8(5)
		Si4–C41–Si44	110.0(5)
		Si4–C41–Si45	112.9(5)
		Si4–C41–Si46	109.5(5)
		Si41–C41–Si42	113.1(5)
		Si41–C41–Si43	106.9(5)
		Si42–C41–Si43	112.8(5)
		Si44–C41–Si45	110.6(5)
		Si44–C41–Si46	106.5(5)
		Si45–C41–Si46	107.2(5)

reported by Gordon et al., as shown in Table 9. The bicyclo[1.1.1]pentane skeleton is constructed from three cyclobutanes (dihedral angles of each cyclobutane are 120.40°, 119.75° and 118.85°, av. 120.0°). The nonbonding Si · · · Si distances of 5, 4, and 3 are 3.00, 2.66 and 2.407 Å. The Si–S–Si angles of 5, 4, and 3 are 89.2, 75.9 (av.) and 67.08° (av.). Considering the common Si–S–Si angles (ca. 82°) [17] in cyclodisilthianes, these Si–S–Si values of 4 and 3 are extremely sharp. Especially, in 3 the acute Si–S–Si angles (66.88(3)°, 66.98(3)° and 67.27(4)°) can be regarded as angles of three-membered ring compounds rather than of normal four-membered ring compounds. One of the features of 3 is the very short S · · · S distance, 3.15 Å, which is within the sum of the van der Waals radii of sulfur (3.70 Å). Interestingly, the bridgehead Si · · · Si distance of 2.407 Å lies within the range of common Si–Si single bond lengths (2.23–2.70 Å) [18], and is ca. 0.1 Å shorter than that of its selenium analogue (2.515 Å) [8]. This value is very short relative to that of the cyclodisilthianes (2.78–2.83 Å) [17]. This unusual shortening of the Si · · · Si distance is caused by the difference in electronegativity between the peripheral sulfur atom and the bridgehead silicon atom. Actually, no such shortening is observed in the corresponding silicon analogue, bicyclo[1.1.1]pentasilane (Si · · · Si; 2.92 Å) [19]. The repulsion between sulfur atoms affects the shortening of

Table 6
Selected bond angles (deg) of 4

| Molecule 1		Molecule 2	
Si1A-S1A-Si2A	75.9(1)	Si1B-S1B-Si2B	75.9(1)
Si1A-S2A-Si2A	75.9(1)	Si1B-S2B-Si2B	75.9(1)
S4A-S3A-Si1A	97.4(1)	S4B-S3B-Si1B	97.2(1)
S3A-S4A-Si2A	97.5(1)	S3B-S4B-Si2B	97.6(1)
S1A-Si1A-S2A	94.1(1)	S1B-Si1B-S2B	94.1(1)
S1A-Si1A-S3A	102.4(1)	S1B-Si1B-S3B	102.3(1)
S1A-Si1A-C1A	120.0(3)	S1B-Si1B-C1B	120.2(3)
S2A-Si1A-S3A	102.4(1)	S2B-Si1B-S3B	102.4(1)
S2A-Si1A-C1A	120.8(3)	S2B-Si1B-C1B	120.9(3)
S3A-Si1A-C1A	113.6(3)	S3B-Si1B-C1B	113.4(3)
S1A-Si2A-S2A	94.0(1)	S1B-Si2B-S2B	94.1(1)
S1A-Si2A-S4A	102.0(1)	S1B-Si2B-S4B	101.9(1)
S1A-Si2A-C2A	121.4(3)	S1B-Si2B-C2B	121.3(3)
S2A-Si2A-S4A	102.1(1)	S2B-Si2B-S4B	102.1(1)
S2A-Si2A-C2A	120.1(3)	S2B-Si2B-C2B	120.2(3)
S4A-Si2A-C2A	113.6(3)	S4B-Si2B-C2B	113.6(3)
C1A-Si3A-C31A	109.8(5)	C1B-Si3B-C31B	109.5(5)
C1A-Si3A-C32A	112.6(5)	C1B-Si3B-C32B	112.8(5)
C1A-Si3A-C33A	107.5(5)	C1B-Si3B-C33B	107.7(5)
C31A-Si3A-C32A	104.2(6)	C31B-Si3B-C32B	104.2(5)
C31A-Si3A-C33A	113.3(6)	C31B-Si3B-C33B	113.5(6)
C32A-Si3A-C33A	109.5(6)	C32B-Si3B-C33B	109.3(5)
C1A-Si3C-C11A	103.7(6)	C1B-Si3D-C11B	103.4(6)
C1A-Si3C-C31A	108.6(5)	C1B-Si3D-C31B	108.5(6)
C1A-Si3C-C32A	111.8(6)	C1B-Si3D-C32B	111.8(5)
C11A-Si3C-C31A	114.1(7)	C11B-Si3D-C31B	114.0(6)
C11A-Si3C-C32A	115.1(6)	C11B-Si3D-C32B	115.4(6)
C31A-Si3C-C32A	103.7(6)	C31B-Si3D-C32B	103.7(6)
C1A-Si4A-C11A	106.3(5)	C1B-Si4B-C11B	106.6(5)
C1A-Si4A-C12A	111.8(5)	C1B-Si4B-C12B	111.9(5)
C1A-Si4A-C13A	110.1(5)	C1B-Si4B-C13B	110.0(5)
C11A-Si4A-C12A	113.7(5)	C11B-Si4B-C12B	113.2(6)
C11A-Si4A-C13A	111.4(6)	C11B-Si4B-C13B	111.4(6)
C12A-Si4A-C13A	103.6(6)	C12B-Si4B-C13B	103.9(6)
C1A-Si4C-C12A	113.6(5)	C1B-Si4D-C12B	113.6(6)
C1A-Si4C-C13A	109.0(6)	C1B-Si4D-C13B	108.6(6)
C1A-Si4C-C23A	106.0(6)	C1B-Si4D-C23B	106.1(5)
C12A-Si4C-C13A	100.7(7)	C12B-Si4D-C13B	100.9(6)
C12A-Si4C-C23A	113.0(6)	C12B-Si4D-C23B	112.7(6)
C13A-Si4C-C23A	114.7(6)	C13B-Si4D-C23B	115.1(7)
C1A-Si5A-C21A	111.4(5)	C1B-Si5B-C21B	111.4(5)
C1A-Si5A-C22A	110.0(6)	C1B-Si5B-C22B	109.6(6)
C1A-Si5A-C23A	108.3(5)	C1B-Si5B-C23B	108.4(6)
C21A-Si5A-C22A	102.9(5)	C21B-Si5B-C22B	102.8(5)
C21A-Si5A-C23A	111.4(6)	C21B-Si5B-C23B	111.4(6)
C22A-Si5A-C23A	112.8(6)	C22B-Si5B-C23B	113.2(6)
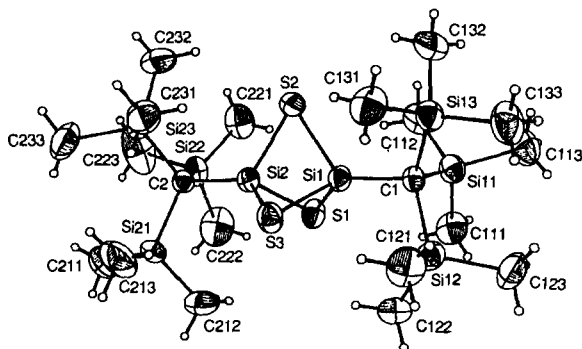
Fig. 4. ORTEP drawing of 3.

Si · · · Si distance of 3. Thus the unusual short Si · · · Si distance is due to geometrical factors, caused by a tug-of-war between the three Si-S-Si and six S-Si-S angles.

3. Experimental section

3.1. General consideration

All manipulations were performed using standard Schlenk techniques under an argon atmosphere. Solvents were dried over sodium benzophenone ketyl, distilled, and degassed prior to use. The reagents used in this study were purchased from commercial sources and purified, dried and degassed as necessary. Preparative gel-permeation liquid chromatography (GPC) was carried out on LC-908 on JAIGEL 1H and 2H column (Japan Analytical Industry, styrene–divinylbenzene copolymer, pore size 25 Å) with toluene as solvent. NMR spectra were run on either a Bruker AC-400 or AC-300 spectrometer at 400 and 300 MHz respectively. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances which were calibrated against tetramethylsilane. ^{29}Si NMR spectra were referenced to external tetramethylsilane. Infrared spectra were recorded on a Jasco FT/IR-5000 using KBr tablet. UV spectra were carried out on a Jasco Ubest-55 spectrometer. Mass spectra (EI) and high-resolution mass spectra were obtained on a Jeol JMS SX102A mass spectrometer. Infrared spectra were recorded on a FT-IR using a KBr tablet. Elemental analyses were carried out on a

Table 7
Selected bond lengths (Å) of 3

S1-Si1	2.174(1)	Si21-C212	1.841(4)
S1-Si2	2.171(1)	Si21-C213	1.914(4)
S2-Si1	2.181(1)	Si22-C2	1.959(3)
S2-Si2	2.186(1)	Si22-C221	1.862(4)
S3-Si1	2.182(1)	Si22-C222	1.876(5)
S3-Si2	2.180(1)	Si22-C223	1.913(5)
Si1 · · · Si2	2.407(1)	Si23-C2	1.890(3)
Si1-C1	1.838(3)	Si23-C231	1.909(4)
Si2-C2	1.833(3)	Si23-C232	1.906(4)
Si11-C1	1.934(3)	Si23-C233	1.896(4)
Si11-C111	1.871(4)	Si31-C2	1.852(4)
Si11-C112	1.872(4)	Si31-C211	1.901(5)
Si11-C113	1.863(4)	Si31-C212	1.952(6)
Si12-C1	1.931(3)	Si31-C222	2.250(6)
Si12-C121	1.871(3)	Si32-C2	1.913(5)
Si12-C122	1.870(3)	Si32-C221	2.024(5)
Si12-C123	1.870(3)	Si32-C223	2.085(6)
Si13-C1	1.931(3)	Si32-C232	1.940(5)
Si13-C131	1.864(3)	Si33-C2	2.042(4)
Si13-C132	1.860(3)	Si33-C213	2.082(5)
Si13-C133	1.875(4)	Si33-C231	1.803(5)
Si21-C2	1.930(3)	Si33-C233	2.048(5)
Si21-C211	1.879(4)		

Perkin Elmer 2400 by the Chemical Analytical Center of the University of Tsukuba. Tris(trimethylsilyl)methylsilane was prepared as described in the literature [20]. All melting points are uncorrected.

3.2. Reaction of TsiSiH₃ with elemental sulfur

A mixture of TsiSiH₃ (500 mg, 1.9 mmol), S₈ (2.0 g, 63 mmol), and 3 ml of decalin was heated at 190°C for 60 hr. After removal of the solvents in vacuo, the residue was dissolved in CH_2Cl_2. After filtration and removal of the solvent under reduced pressure, the

Table 8
Selected bond angles (deg) of 3

Si1–S1–Si2	67.27(4)	C2–Si22–C223	108.4(2)
Si1–S2–Si2	66.88(3)	C221–Si22–C222	109.8(2)
Si1–S3–Si2	66.98(3)	C221–Si22–C223	104.9(2)
S1–Si1–S2	92.68(4)	C222–Si22–C223	110.9(2)
S1–Si1–S3	92.77(4)	C2–Si23–C231	111.5(1)
S1–Si1–Si2	56.30(3)	C2–Si23–C232	111.5(1)
S1–Si1–Cl	122.21(9)	C2–Si23–C233	111.4(2)
S2–Si1–S3	91.87(4)	C231–Si23–C232	106.6(2)
S2–Si1–Si2	56.66(3)	C231–Si23–C233	105.2(2)
S2–Si1–Cl	124.68(9)	C232–Si23–C233	110.4(2)
S3–2Si1–Si2	56.49(3)	C2–Si31–C211	113.4(2)
S3–Si1–Cl	123.67(9)	C2–Si31–C212	111.6(2)
S1–Si2–S2	92.63(4)	C2–Si31–C222	100.8(2)
S1–Si2–S3	92.89(4)	C211–Si31–C212	100.8(2)
S1–Si2–Si1	56.43(3)	C211–Si31–C222	120.5(3)
S1–Si2–C2	122.40(9)	C212–Si31–C222	110.0(2)
S2–Si2–S3	91.76(4)	C2–Si32–C221	106.3(2)
S2–Si2–Si1	56.46(3)	C2–Si32–C223	103.4(2)
S2–Si2–C2	124.15(9)	C2–Si32–C232	109.1(2)
S3–Si2–Si1	56.53(3)	C221–Si32–C223	93.5(2)
S3–Si2–C2	124.03(9)	C221–Si32–C232	117.8(2)
Cl–Si11–C111	112.7(1)	C223–Si32–C232	124.4(3)
Cl–Si11–C112	111.6(1)	C2–Si33–C213	98.7(2)
Cl–Si11–C113	111.8(1)	C2–Si33–C231	109.3(2)
C111–Si11–C112	105.7(2)	C2–Si33–C233	99.7(2)
C111–Si11–C113	107.0(2)	C213–Si33–C231	123.2(2)
C112–Si11–C113	107.7(2)	C213–Si33–C233	119.7(2)
Cl–Si12–C121	112.3(1)	C231–Si33–C233	103.2(2)
Cl–Si12–C122	112.8(1)	Si2–C2–Si33	106.0(2)
Cl–Si12–C123	111.0(1)	Si21–C2–Si22	110.2(1)
C121–Si12–C122	105.8(2)	Si21–C2–Si23	112.1(1)
C121–Si12–C123	107.5(2)	Si22–C2–Si23	111.4(1)
C122–Si12–C123	107.1(2)	Si1–Cl–Si11	107.6(1)
Cl–Si13–C131	112.2(1)	Si1–Cl–Si12	107.2(1)
Cl–Si13–C132	111.7(1)	Si1–Cl–Si13	107.9(1)
Cl–Si13–C133	111.8(1)	Si11–Cl–Si12	111.2(1)
C131–Si13–C132	106.1(2)	Si11–Cl–Si13	111.4(1)
C131–Si13–C133	107.2(2)	Si12–Cl–Si13	111.4(1)
C132–Si13–C133	107.6(2)	Si2–C2–Si21	107.7(1)
C2–Si21–C211	111.0(1)	Si2–C2–Si22	106.3(1)
C2–Si21–C212	113.1(1)	Si2–C2–Si23	108.9(1)
C2–Si21–C213	109.0(1)	Si2–C2–Si31	110.8(2)
C211–Si21–C212	105.9(2)	Si2–C2–Si32	108.1(2)
C211–Si21–C213	110.2(2)	Si31–C2–Si32	115.3(2)
C212–Si21–C213	107.6(2)	Si31–C2–Si33	108.9(2)
C2–Si22–C221	111.1(1)	Si32–C2–Si33	107.2(2)
C2–Si22–C222	111.5(1)		

Table 9
Experimental (3) and calculated (10) bond lengths (Å) and angles (deg) of 2,4,5-trithia-1,3-disilabicyclo[1.1.1]pentane (3, 10)
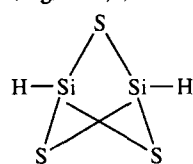
	3 [a]	10 [b]
Si---Si	2.407	2.363
Si–S	2.171–2.186	2.176
Si–S–Si	66.89–67.28	65.8
Si–Si–S	56.28–56.65	57.1

[a] Single crystal X-ray diffraction data. [b] See Ref. [6b].

residue was charged on silica-gel column chromatography (eluent; n-hexane–CH_2Cl_2). The resulting yellow solid was purified by GPC (eluent; toluene) and preparative TLC to give 4 [9], 5 [9], and 6 [9] in 22% (138 mg), 12% (77 mg), and 12% (85 mg) yield respectively.

3.3. Desulfurization of 6 with PPh₃

A benzene (5 ml) solution of 6 (108 mg, 0.13 mmol) and triphenylphosphine (51 mg, 0.19 mmol) was stirred for 30 min. After removal of the solvent, the residue was separated by silica-gel column chromatography (eluent; n-hexane–CH_2Cl_2) to give 5 (105 mg, quant.).

3.4. Desulfurization of 5 with PPh₃ under irradiation

A d_6-benzene (400 μl) solution of 5 (13 mg, 0.019 mmol) and triphenylphosphine (6.3 mg, 0.024 mmol) in a NMR tube was irradiated by a high-pressure Hg lamp at room temperature. The reaction was monitored by ¹H and ¹³C NMR. After 10 min, the solvent was removed in vacuo, and the residue was separated by preparative TLC to afford 4 (11.5 mg, 96% yield).

3.5. Desulfurization of 4 with PPh₃ under irradiation

A benzene (20 ml) solution of 4 (129 mg, 0.20 mmol) and triphenylphosphine (80 mg, 0.31 mmol) in a Pyrex glass tube was irradiated by a high-pressure Hg lamp for 2 h at room temperature. After removal of the solvent, the residue was separated by GPC (eluent; toluene) to give 3 [9] (78.6 mg, 64% yield).

3.6. Desulfurization of 4 with excess amount of PPh₃ under irradiation

(a) In benzene: a benzene (3.5 ml) solution of 4 (42 mg, 0.065 mmol) and triphenylphosphine (172 mg, 0.66

mmol) in a Pyrex glass tube was irradiated by a high-pressure Hg lamp for 15 min at room temperature. After removal of the solvent, the residue was separated by GPC (eluent; toluene) to afford **3** (10.6 mg) and **7** [9] (10.4 mg) in 27% and 28% yields respectively.

(b) *In toluene*: a d_8-toluene (400 μl) solution of **4** (17 mg, 0.026 mmol) and triphenylphosphine (67 mg, 0.26 mmol) in an NMR tube was irradiated by a high-pressure Hg lamp at room temperature. The reaction was monitored by ^{1}H and ^{13}C NMR. After 60 min, the solvent was removed in vacuo and the residue was separated by GPC (eluent; toluene) to afford **3** and d_1_ and d_2 – **7** in 29% and 11% (H:D = 65:35) yields, respectively.

3.7. Desulfurization of 4 with PMe₃ under irradiation

A d_6-benzene (400 μl) solution of **4** (12 mg, 0.018 mmol) and PMe₃ (1.0 M THF solution, 130 μl, 0.13 mmol) in a NMR tube was irradiated by a high-pressure Hg lamp at room temperature. The reaction was monitored by ^{1}H and ^{13}C NMR. After 20 min, **4** was completely consumed. After removal of the solvents and excess of PMe₃ in vacuo, the residue was separated by GPC (eluent; toluene) to give **3** (11 mg, quant.).

3.8. Hydrolysis of 3

A benzene solution of **3** was hydrolyzed by moisture in air to yield **8**, quantitatively. A benzene solution of **8** [9] was further hydrolyzed by moisture in air to give **9**, quantitatively. For **9**: white crystals, m.p. 255–256°C, ^{1}H NMR (300 MHz, C_6D_6): δ 0.45 (s, 27H × 2), 1.20 (s, 1H), 1.77 (s, 1H), 3.40 (s, 1H), 4.80 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ 5.3 (q), 5.4 (q), 10.2 (s), 10.5 (s); ^{29}Si NMR (59 MHz, C_6D_6): δ – 1.5 (SiMe₃), – 1.4 (SiMe₃); MS, m/z 650 (M^+); Exact mass, Calc. for $C_{20}H_{58}O_2Si_8S_3$: m/z 650.1753. Found m/z 650.1742.

3.9. Crystal and experimental data for 5, 4, and 3 [21]

Yellow crystals of **5**, pale yellow crystals of **4**, and colorless crystals of **3** obtained from recrystallization from benzene, were used for X-ray analyses. Crystal data and data collection parameters and results of the analyses are listed in Table 2. Diffraction measurements were made on an Enraf–Nonius CAD4 computer-controlled Kappa axis diffractometer by using graphite monochromatized Mo K α radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least squares routines. All data processing was performed on a Micro VAX3100 computer by using the MolEN structure-solving program obtained

from Enraf–Nonius Corp., Delft, Netherlands. The ω-2θ scan technique was adopted by varying the ω scan width as a function of θ (ω scan width; 0.4 + 0.620 tan θ for **5**, 0.6 + 0.350 tan θ for **4**, 0.6 + 0.550 tan θ for **3**). All intensities were corrected for Lorentz and polarization factors as well as decay correction. An empirical absorption correction based on a series of ψ-scan was also applied to the data. Neutral-atom scattering factors were calculated by the standard procedures [22a]. An anomalous dispersion correction was applied to all non-hydrogen atoms [22b]. Full-matrix least-squares refinements minimized the function $\Sigma w(|F_o| - |F_c|)^2$, $w = 1$.

Compound **5** crystallized in the monoclinic crystal system. The space group $P2_1/a$ was identified uniquely on the basis of the systematic absences observed during the collection of the data ($h0l$, $h = 2n$, $0k0$, $k = 2n$). The structure was solved by a combination of direct methods (MULTAN 80) and difference Fourier syntheses. Hydrogen atoms were not included in the calculation.

Compound **4** crystallized in the triclinic crystal system. There were no systematic absences; the space group was determined to be $P\bar{1}$. The structure was solved by a combination of direct methods (MULTAN 80) and difference Fourier syntheses. Hydrogen atoms were not included in the calculation.

Compound **3** crystallized in the monoclinic crystal system. From the systematic absences of $h0l$, $l = 2n$, $0k0$, $k = 2n$, and from subsequent least squares refinement, the space group was determined to be $P2_1/c$. The structure was solved by a combination of direct methods (MULTAN 80) and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. Some of hydrogen atoms (33 atoms) were found in the D-Fourier map and the others (21 atoms) were located by calculation. Disordered hydrogen atoms attached to nine carbon atoms connected to Si(31, 32, 33) were not included.

Refinement was performed by the full-matrix least squares method with 622 (for **5**), 631 (for **4**), and 307 (for **3**) variable parameters (anisotropic thermal parameters for non-hydrogen atoms, where the positions and thermal parameters for hydrogen atoms were not refined). The molecular structures with atomic labelling schemes and the bond lengths and angles are given in Figs. 2–4 and Tables 2–8.

4. Supplementary material available

Detailed information of the X-ray crystal analysis of **5** and **4** (138 pages). Ordering information is given on any current masthead page.

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