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FULL PAPER

Hexakis(trialkylsilyl)cyclotrisilanes and photochemical generation of bis(trialkylsilyl)silylenes

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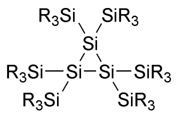
Received 4th September 2001, Accepted 23rd January 2002
First published as an Advance Article on the web 8th March 2002

Hexakis(trialkylsilyl)cyclotrisilanes **1a** (trialkylsilyl = *tert*-butyldimethylsilyl) and **1b** (trialkylsilyl = diisopropylmethylsilyl) were synthesized by the reductive coupling of the corresponding 2,2-dibromotrisilanes. Their molecular structures were confirmed by X-ray crystallography. In the absence of trapping reagents, photolysis of cyclotrisilanes **1a** and **1b** gave the corresponding stable tetrakis(trialkylsilyl)disilenes quantitatively. Irradiation of cyclotrisilanes **1a** and **1b** in (*Z*)-2-butene and (*E*)-2-butene afforded exclusively the corresponding (*Z*)- and (*E*)-2,3-dimethyl-1-silacyclopropanes, respectively. Stereospecific formation of the cycloadducts indicates that the bis(trialkylsilyl)silylenes generated from cyclotrisilanes **1a** and **1b** would be singlets in the ground state.

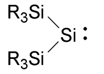
Introduction

One of the most intriguing research aims in the chemistry of silicon divalent species (silylenes)[1] is the generation of triplet silylenes and the investigation of their properties. Although a number of theoretical and experimental studies have been devoted to the design and generation of the triplet silylenes, they have never been observed so far even as the excited triplet silylenes.[2,3] On the basis of the previous studies, a promising strategy for the triplet silylenes has been suggested to be the introduction of sterically bulky σ-donating and/or π-accepting substituents on the central silicon atom. The bulky substituents widen the apex angle and cause a decrease in the HOMO(n)–LUMO(3pπ) gap in the ground state singlet silylenes. The σ-donating and π-accepting substituents will elevate HOMO(n) and lower LUMO(3pπ) orbital levels, respectively, and hence, decrease the HOMO–LUMO gap. One of the prospective substituents for triplet silylenes will therefore be sterically bulky trialkylsilyl groups. In their theoretical paper, Grev, Schaefer and Gaspar have stated "a winning strategy for the experimental design of a triplet ground-state silylene is to produce, by whatever means, a bis(trialkylsilyl)silylene with alkyl being somewhat larger than methyl".[2a] More recently, Apeloig *et al.* have shown theoretically that $(^tBu_3Si)_2Si$: has a triplet state multiplicity in the ground state with a singlet–triplet energy difference (ΔE_{ST}) of -7.1 kcal mol^{-1} at the BLYP/DZVP-ECP level.[2b] Experimentally, Gaspar *et al.* have recently generated $(^iPr_3Si)_2Si$: by the photolysis of $(^iPr_3Si)_3SiH$ and found the silylene adds to (*Z*)- and (*E*)-2-butenes to afford stereospecifically the corresponding (*Z*)-and (*E*)-2,3-dimethylsilacyclopropanes, respectively.[3]

During the course of our study on silyl-substituted silylenes[4] and disilenes,[5] we have independently investigated the reactivity of bis(trialkylsilyl)silylenes generated by photolysis of the corresponding hexakis(trialkylsilyl)cyclotrisilanes. Since the chemistry of cyclotrisilanes has attracted much attention over the past two decades because of their unique physical and chemical properties arising from the highly-strained three-membered ring structure,[6] we first discuss the synthesis and structure of novel hexakis(trialkylsilyl)cyclotrisilanes **1a** and **1b**, and then, the photolysis of these compounds affording the corresponding bis(trialkylsilyl)silylenes **2a** and **2b**. Stereospecific addition of **2a** and **2b** toward (*E*)- and (*Z*)-2-butenes indicates that these silylenes are singlets in the ground state, being consistent with the results of the high-level calculations by Apeloig *et al.*[2b]



1a (R_3Si = $^tBuMe_2Si$)
1b (R_3Si = $^iPr_2MeSi$)

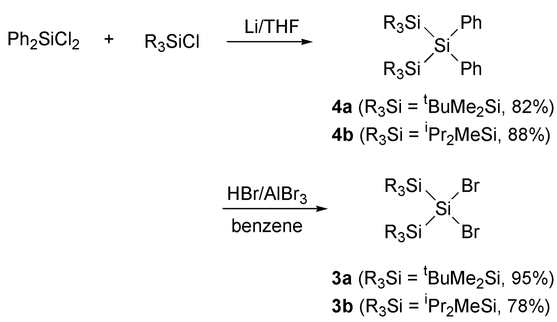


2a (R_3Si = $^tBuMe_2Si$)
2b (R_3Si = $^iPr_2MeSi$)

Results and discussion

Syntheses of hexakis(trialkylsilyl)cyclotrisilanes

Prerequisite compounds for the synthesis of cyclotrisilanes **1a** and **1b**, 2,2-dibromohexaalkyltrisilanes **3a** and **3b** were prepared according to the method shown in Scheme 1. Treatment of a mixture of dichlorodiphenylsilane and a trialkylchlorosilane with lithium powder in THF gave the corresponding 2,2-diphenyltrisilane; **4a** (82% yield, R_3Si = $^tBuMe_2Si$) and **4b** (88% yield, R_3Si = $^iPr_2MeSi$).[7] Bromodephenylation of **4a** and **4b** with dry hydrogen bromide in the presence of a catalytic amount of aluminium bromide provided **3a** (95% yield) and **3b** (78% yield), respectively.



4a (R_3Si = $^tBuMe_2Si$, 82%)
4b (R_3Si = $^iPr_2MeSi$, 88%)

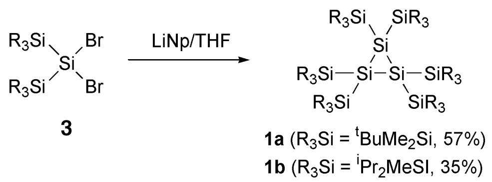
3a (R_3Si = $^tBuMe_2Si$, 95%)
3b (R_3Si = $^iPr_2MeSi$, 78%)

Scheme 1

Cyclotrisilanes **1a** and **1b** were prepared by the reductive dehalogenation of the corresponding 2,2-dibromotrisilanes **3a**

DOI: 10.1039/b107905k

and **3b** with lithium naphthalenide in 57 and 35% yields, respectively [eqn. (1)].[9]



(1)

Cyclotrisilanes **1a** and **1b** are both quite stable to oxygen, water and alcohols in the solid state in contrast to hexakis(triethylsilyl)cyclotrisilane **1c**[8b] and hexakis(trimethylsilyl)cyclotrisilane **1d**.[10] Cyclotrisilanes **1a** and **1b** were stored for more than three years without any decomposition. Protection of the three-membered ring by bulky *tert*-butyldimethylsilyl and diisopropylmethylsilyl groups would be responsible for the high stability of **1a** and **1b**.

Molecular structure of cyclotrisilanes 1a and 1b in the solid state

Single crystals of **1a** and **1b** suitable for X-ray crystallographic analysis were obtained by recrystallization from *p*-xylene and hexane, respectively. Cyclotrisilanes **1a** and **1b** are almost equilateral triangles, although they have no crystallographic *C*3 axis perpendicular to the cyclotrisilane ring. In a single crystal of **1a** two structures, shown in Fig. 1, were found at the same site with a ratio of 63 : 37. These two structures are enantiomeric and overlap with each other through 180° rotation about the *C*3 axis of the cyclotrisilane ring followed by reflection in a plane perpendicular to the axis. The asymmetric units of **1b** contain two crystallographically independent molecules. In the single crystal of **1a**, one molecule of *p*-xylene was incorporated for each cyclotrisilane in the lattice; no solvent was incorporated in the crystal of **1b**. Figs. 1 and 2 show ORTEP drawings of **1a** and **1b** and their selected bond lengths and angles are summarized in Table 1.

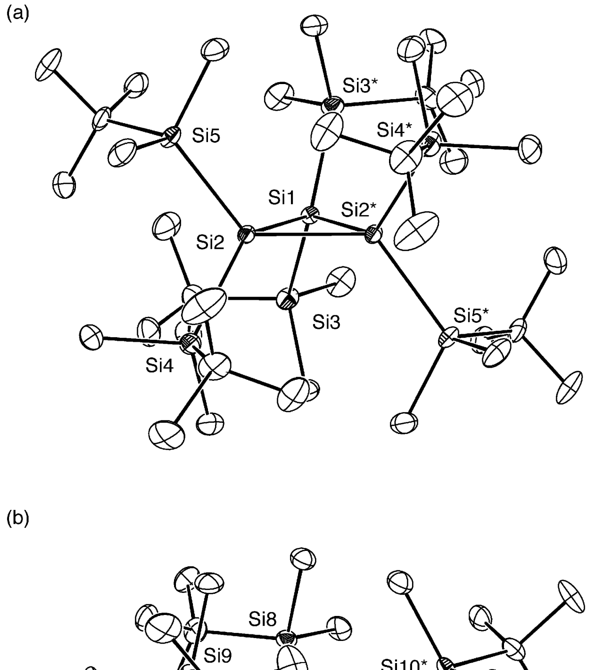


Fig. 1 ORTEP[21] drawings of cyclotrisilane **1a**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Two structures with 63 and 37% site occupancies are shown in (a) and (b), respectively.

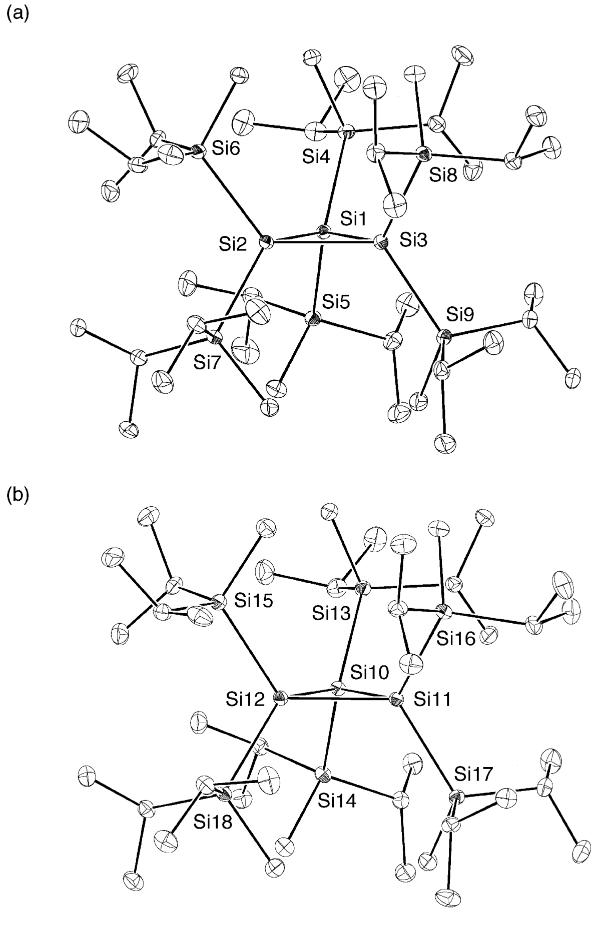


Fig. 2 ORTEP drawings of cyclotrisilane **1b**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. The two crystallographically independent molecules in the asymmetric unit are shown in (a) and (b).

The averaged length of the endocyclic Si–Si bonds is 2.420 Å for **1a** and 2.390 Å for **1b**, both of which are much longer than that for hexakis(trimethylsilyl)cyclotrisilane **1d** [2.357 Å (av.)];[10] the severe steric repulsion between two vicinal bulky trialkylsilyl substituents would be responsible for the larger endocyclic Si–Si bond distances in **1a** and **1b**. In addition, the Si(ring)–Si(substituent) bond lengths and Si(ring)–Si(ring)–Si(substituent) angles for **1a** and **1b** are significantly larger than those for **1d**, probably due to the same reason; the bond lengths are 2.423–2.439, 2.387–2.412 and 2.3575(6) Å and the angles are 125.70–127.30°, 121.78–126.47° and 121.17–122.50° for **1a**, **1b** and **1d**,[10] respectively.

UV spectra of cyclotrisilanes 1a and 1b

Cyclotrisilanes **1a** and **1b** show two major absorption bands in their UV-vis spectra (Fig. 3); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 264 (6.0×10^4) and 372 (1.3×10^3) for **1a** and 255 (6.1×10^4) and 349 (1.3×10^3) for **1b**. The band maxima at around 350 nm for **1a** and **1b** are found at much longer wavelengths than those for peralkylcyclotrisilanes and less hindered hexakis(triethylsilyl)cyclotrisilane **1c**; the λ_{max}/nm values are 310, 323, 328, 340 and 335 for [(neopentyl)$_2$Si]$_3$,[11a] (^{i}Pr$_2$Si)$_3$,[6c] [(diethylmethyl)$_2$Si]$_3$,[11b]

Table 1 Selected bond lengths (Å) and angles (°) for cyclotrisilanes **1a** and **1b**

Cyclotrisilane **1a** ($R_3Si = {}^tBuMe_2Si$)			
Si(1)–Si(2)	2.4227(12)	Si(2)–Si(2*)	2.4183(15)
Si(1)–Si(3)	2.4354(11)	Si(2)–Si(4)	2.4333(12)
Si(2)–Si(5)	2.4263(11)	Si(6)–Si(7)	2.423(2)
Si(7)–Si(7*)	2.418(2)	Si(6)–Si(8)	2.4301(18)
Si(7)–Si(9)	2.4389(19)	Si(7)–Si(10)	2.4244(18)
Si(2)–Si(1)–Si(2*)	59.88(5)	Si(1)–Si(2)–Si(2*)	60.06(2)
Si(3)–Si(1)–Si(3*)	107.41(7)	Si(2)–Si(1)–Si(3)	114.93(3)
Si(2)–Si(1)–Si(3*)	127.17(3)	Si(4)–Si(2)–Si(5)	107.83(4)
Si(1)–Si(2)–Si(4)	127.05(4)	Si(1)–Si(2)–Si(5)	114.61(4)
Si(2*)–Si(2)–Si(4)	115.78(5)	Si(2*)–Si(2)–Si(5)	125.84(5)
Si(7)–Si(6)–Si(7*)	59.86(7)	Si(6)–Si(7)–Si(*7)	60.07(4)
Si(8)–Si(6)–Si(8*)	107.28(11)	Si(7)–Si(6)–Si(8)	114.94(5)
Si(7)–Si(6)–Si(8*)	127.30(5)	Si(9)–Si(7)–Si(10)	107.96(7)
Si(6)–Si(7)–Si(9)	126.78(7)	Si(6)–Si(7)–Si(10)	114.64(6)
Si(7*)–Si(7)–Si(9)	115.90(8)	Si(7*)–Si(7)–Si(10)	125.70(9)
Cyclotrisilane **1b** ($R_3Si = {}^iPr_2MeSi$)			
Si(1)–Si(2)	2.3892(8)	Si(1)–Si(3)	2.3957(8)
Si(2)–Si(3)	2.3871(9)	Si(1)–Si(4)	2.4111(8)
Si(1)–Si(5)	2.3973(8)	Si(2)–Si(6)	2.3918(8)
Si(2)–Si(7)	2.3997(8)	Si(3)–Si(8)	2.3962(8)
Si(3)–Si(9)	2.4007(8)	Si(10)–Si(11)	2.3902(8)
Si(10)–Si(12)	2.3835(9)	Si(11)–Si(12)	2.3932(8)
Si(10)–Si(13)	2.4118(8)	Si(10)–Si(14)	2.3936(8)
Si(11)–Si(16)	2.4018(8)	Si(11)–Si(17)	2.3987(8)
Si(12)–Si(15)	2.3967(8)	Si(12)–Si(18)	2.4092(8)
Si(2)–Si(1)–Si(3)	59.85(2)	Si(1)–Si(2)–Si(3)	60.21(2)
Si(1)–Si(3)–Si(2)	59.94(2)	Si(2)–Si(1)–Si(4)	124.88(3)
Si(2)–Si(1)–Si(5)	116.39(3)	Si(3)–Si(1)–Si(4)	112.15(3)
Si(3)–Si(1)–Si(5)	122.76(3)	Si(4)–Si(1)–Si(5)	111.87(3)
Si(1)–Si(2)–Si(6)	110.53(3)	Si(1)–Si(2)–Si(7)	126.47(3)
Si(3)–Si(2)–Si(6)	126.27(3)	Si(3)–Si(2)–Si(7)	116.61(3)
Si(6)–Si(2)–Si(7)	109.73(3)	Si(1)–Si(3)–Si(8)	124.43(3)
Si(1)–Si(3)–Si(9)	116.47(3)	Si(2)–Si(3)–Si(8)	112.19(3)
Si(2)–Si(3)–Si(9)	123.26(3)	Si(8)–Si(3)–Si(9)	111.79(3)
Si(11)–Si(10)–Si(12)	60.18(2)	Si(10)–Si(11)–Si(12)	59.77(2)
Si(10)–Si(12)–Si(11)	60.05(2)	Si(11)–Si(10)–Si(13)	112.09(3)
Si(11)–Si(10)–Si(14)	123.92(3)	Si(12)–Si(10)–Si(13)	125.65(3)
Si(12)–Si(10) Si(14)	116.00(3)	Si(13)–Si(10)–Si(14)	110.97(3)
Si(10)–Si(11)–Si(16)	117.19(3)	Si(10)–Si(11)–Si(17)	125.19(3)
Si(12)–Si(11)–Si(16)	121.78(3)	Si(12)–Si(11)–Si(17)	113.52(3)
Si(16)–Si(11)–Si(17)	110.85(3)	Si(10)–Si(12)–Si(15)	110.56(3)
Si(10)–Si(12)–Si(18)	124.74(3)	Si(11)–Si(12)–Si(15)	122.81(3)
Si(11)–Si(12)–Si(18)	118.57(3)	Si(15)–Si(12)–Si(18)	111.45(3)

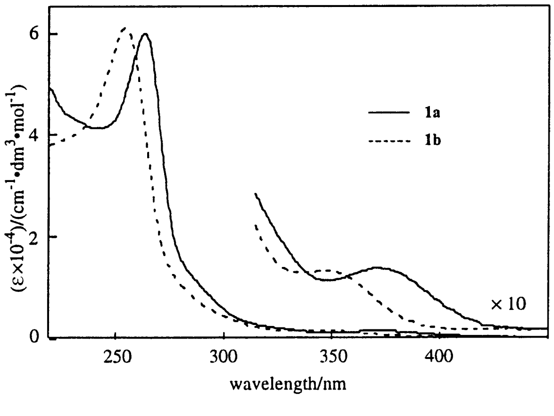


Fig. 3 UV-vis spectra of hexakis(trialkylsilyl)cyclotrisilanes **1a** ($R_3Si = {}^tBuMe_2Si$) and **1b** ($R_3Si = {}^iPr_2MeSi$) in hexane at rt.

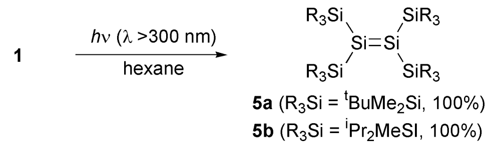
$({}^tBu_2Si)_3$[11c] and **1c**.[8b] Elongation of the ring Si–Si bonds due to steric repulsion between the bulky trialkylsilyl substituents as well as the electron-donating effects of the trialkylsilyl substituents may decrease the HOMO–LUMO gap in a cyclotrisilane and lead to a red shift of the $\sigma \longrightarrow \sigma^*$ transition.[12,13]

^{29}Si NMR spectra

The ^{29}Si resonances due to the endocyclic silicon nuclei in **1a** and **1b** are observed at −156.5 and −148.6 ppm, respectively, which are more deshielded than that of **1c** (−174 ppm).[8b] The ^{29}Si resonances for these hexakis(trialkylsilyl)cyclotrisilanes appear at very high field compared to those of known hexa-alkyl- and hexaaryl-cyclotrisilanes,[6c] although the reason remains unclear.[12,14] The lower field ^{29}Si resonances in **1a** and **1b** than that in **1c**[8b] would be attributed to the widening of the Si(substituent)–Si(ring)–Si(substituent) angles[15] and elongation of the ring Si–Si bond, which lower the $\sigma \longrightarrow \pi^*$ transition energies.

Photochemical generation of bis(trialkylsilyl)silylenes from 1a and 1b

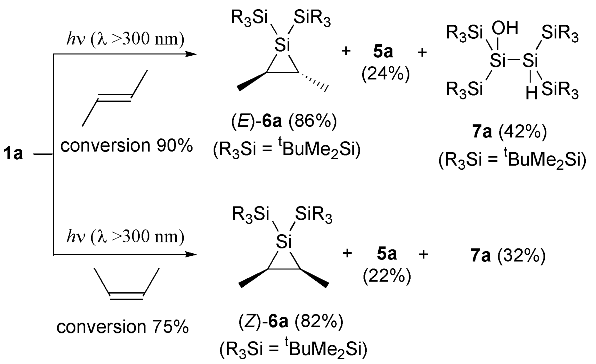
Photolysis of hexakis(trialkylsilyl)cyclotrisilanes to give the corresponding silylene and disilene was first reported by Matsumoto, Sakamoto and Nagai.[8b] As we have previously reported,[5a] irradiation of hexane solutions of **1a** and **1b** with a high-pressure mercury arc lamp in the absence of any trapping reagent at room temperature gave isolable disilenes **5a** and **5b**, respectively, in quantitative yields [eqn. (2)]. Monitor-



(2)

ing the photolysis of **1a** and **1b** in benzene-d_6 by NMR spectroscopy proved quantitative formation of **5a** and **5b**; no other products were observed by NMR spectroscopy during the photoreaction.

The intermediate bis(trialkylsilyl)silylenes **2a** and **2b** were trapped by 2-butenes to give the corresponding silacyclopropanes in a stereospecific *syn*-addition manner.[3,16] Typically, photolysis of **1a** in (*E*)-2-butene at room temperature in an NMR tube with a high-pressure mercury arc lamp gave the corresponding silacyclopropane, (*E*)-1,1-bis(*tert*-butyldimethylsilyl)-2,3-dimethylsilirane [(*E*)-**6a**] as a sole silylene adduct in 86% yield together with the corresponding disilene **5a** (24%) and its hydrate **7a** (42%) (Scheme 2).[17,18] On the other hand, photolysis of **1a** in (*Z*)-2-butene gave exclusively the (*Z*)-adduct, (*Z*)-1,1-bis(*tert*-butyldimethylsilyl)-2,3-dimethylsilirane [(*Z*)-**6a**] (82%) together with **5a** (22%) and **7a** (32%). Similar stereospecific retention during addition of the starting olefin was observed in the photolysis of **1b** in (*E*)- and (*Z*)-2-butenes giving (*E*)- and (*Z*)-**6b**, respectively. Photolysis of cyclotrisilanes **1a** and **1b** in a 3-methylpentane matrix at 77 K gave no evidence for the generation of the corresponding bis(trialkylsilyl)silylenes; in matrices, a facile recombination of the initial photoproducts, bis(trialkylsilyl)silylene and tetrakis(trialkylsilyl)disilene, may take place.



Scheme 2

The stereospecific *syn*-addition of both bis(*tert*-butyldimethylsilyl)silylene **2a** and bis(diisopropylmethylsilyl)silylene **2b** is indicative that they are singlets in the ground state, being consistent with the theoretical results for **2a**,[2b] which is a singlet in the ground state with a singlet–triplet energy difference of 1.5 kcal mol^{-1} at the BLYP/DZVP-ECP level, while Gaspar *et al.* pointed out that triplet silylenes possibly undergo stereospecific *syn*-addition to olefins.[3c,19]

Experimental

All operations were performed in oven- or flame-dried glassware under an atmosphere of dry nitrogen or argon. All solvents were distilled from appropriate drying agents before use. ^1H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (59 MHz) NMR were recorded on a Bruker AC300P NMR spectrometer. ^1H and ^{13}C NMR chemical shifts were referenced to residual ^1H and ^{13}C of the solvents; chloroform-*d* (^1H δ 7.24 and ^{13}C δ 77.0), benzene-d_6 (^1H δ 7.15 and ^{13}C δ 128.0). ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm. Mass spectra and high resolution mass spectral data were obtained on a JEOL JMS MS-600W mass spectrometer. UV-visible spectra were recorded on a Milton Roy SP3000 spectrometer. GC analysis was conducted using a Shimadzu 8A gas chromatograph (Silicon SE-30 1 m glass column with 5 mm o.d.).

Lithium powder, magnesium, cuprous cyanide, 2-chloropropane, (*E*)-2-butene, (*Z*)-2-butene, trichloromethylsilane, dichlorodiphenylsilane, *tert*-butylchlorodimethylsilane were commercially available and used as supplied.

Preparations

Chlorodiisopropylmethylsilane.[20] To a THF (200 cm^3) solution of isopropylmagnesium chloride [prepared by the reaction of isopropyl chloride (83.2 g, 1.06 mol) with magnesium (24.3 g, 1.00 mol)] in the presence of cuprous cyanide (0.5 g, 5.6 mmol), was added trichloromethylsilane (72.2 g, 0.48 mol) with stirring. After completion of the exothermic reaction, the mixture was refluxed for an hour. The THF was then distilled off and diethyl ether (1000 cm^3) was introduced. After the resulting salt was removed by filtration, the solvent was distilled off. The title compound (44.2 g, 0.27 mol) was obtained in 56% yield after distillation from the residual oil; bp 72 °C/45 Torr.

1,3-Di(*tert*-butyl)-1,1,3,3-tetramethyl-2,2-diphenyltrisilane 4a. To a suspension of lithium powder (2.12 g, 305 mmol) in THF (200 cm^3) was added a mixture of dichlorodiphenylsilane (14.9 g, 58.9 mmol) and *tert*-butylchlorodimethylsilane (26.6 g, 177 mmol) in THF (80 cm^3) at 0 °C under sonication. After about 80% of the lithium was consumed, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then hydrolyzed with water. The organic layer was dried over anhydrous sodium sulfate and then the solvent was distilled off. The title compound (20.0 g, 48.5 mmol) was obtained in 82% yield by Kugelrohr distillation. **4a**: a colorless oil; bp 85 °C/ 0.02 Torr; δ_H ($CDCl_3$) 0.23 (12 H, s, 4 SiMe), 0.65 (18 H, s, 2 ^{t}Bu), 7.26–7.32 (6 H, m, Ph), 7.60–7.65 (4 H, m, Ph); δ_C ($CDCl_3$) −3.2 (SiMe), 19.4 (*C*Me$_3$), 27.8 (C*Me*$_3$), 127.6, 128.1, 136.5, 136.6 (Ph); δ_{Si} ($CDCl_3$) −41.4 ($SiPh_2$), −5.73 ($^tBuMe_2Si$); *m*/*z* 412 (0.9, M^+), 355 (23), 167 (37), 149 (100); HRMS found, 412.2435. $C_{24}H_{40}Si_3$ requires 412.2438.

1,1,3,3-Tetraisopropyl-1,3-dimethyl-2,2-diphenyltrisilane 4b. The title compound (3.87 g, 8.80 mmol, 88%) was prepared following to the same method as for **4a** using lithium powder (0.367 g, 52.8 mmol), dichlorodiphenylsilane (2.543 g, 10.1 mmol) and chlorodiisopropylmethylsilane (5.055 g, 30.7 mmol). **4b**: a colorless oil; bp 120 °C/0.02 Torr; δ_H ($CDCl_3$) 0.21 (6 H, s, 2 SiMe), 0.89 (12 H, d, *J* 7.1 Hz, 4 CH_3), 0.91 (12 H, d, *J* 7.1 Hz, 4 CH_3), 0.95–1.20 (4 H, m, 4 CH), 7.25–7.31 (6 H, m, Ph), 7.56–7.62 (4 H, m, Ph); δ_C ($CDCl_3$) −6.4 ($SiCH_3$), 13.6 (*CH*Me$_2$), 19.2 (CH*Me*$_2$), 19.7 (CH*Me*$_2$), 127.5, 128.0, 136.5, 137.1 (Ph); δ_{Si} ($CDCl_3$) −3.88 ($^iPr_2MeSi$), −39.0 ($SiPh_2$); *m*/*z* 440 (16, M^+), 269 (63), 234 (58), 227 (81), 59 (100); HRMS found, 440.2747. $C_{26}H_{44}Si_3$ requires 440.2751.

2,2-Dibromo-1,3-di(*tert*-butyl)-1,1,3,3-tetramethyltrisilane 3a. To a mixture of **4a** (12.0 g, 29.0 mmol) and a catalytic amount of anhydrous aluminium bromide in benzene (100 cm^3) was introduced dry hydrogen bromide gas until the exothermic reaction was complete. Acetone (0.5 cm^3) was added and then the resulting acetone–aluminium bromide complex was removed by decantation. After solvent was distilled off, the title compound (11.5 g, 27.6 mmol, 95%) was obtained by distillation under reduced pressure. **3a**: a colorless oil; bp 80 °C/0.02 Torr; δ_H ($CDCl_3$) 0.29 (12 H, s, 4 SiMe), 1.08 (18 H, s, ^{t}Bu); δ_C ($CDCl_3$) −5.9 (SiMe), 19.1 (*C*Me$_3$), 28.0 (C*Me*$_3$); δ_{Si} ($CDCl_3$) 1.0 ($^tBuMe_2Si$), 23.4 ($SiBr_2$); *m*/*z* 418 [2, $M^+(^{79}Br^{81}Br)$], 224 (9), 222 (9), 115 (14), 73 (100); HRMS found, 416.0026. $C_{12}H_{30}Si_3{}^{79}Br_2$ requires 416.0022.

2,2-Dibromo-1,3-dimethyl-1,1,3,3-tetraisopropyltrisilane 3b. The title compound (13.4 g, 30.0 mmol, 78%) was prepared from **4b** (16.9 g, 38.5 mmol) according to the same method as for the preparation of **3a**. **3b**: a colorless oil; 90 °C/0.02 Torr; δ_H ($CDCl_3$) 0.24 (6 H, s, 2 SiMe), 1.12 (12 H, d, *J* 6.7 Hz, 4 CH_3), 1.14 (12 H, d, *J* 7.4 Hz, 4 CH_3), 1.27–1.42 (4 H, m, 4 CH); δ_C ($CDCl_3$) −8.9 (SiMe), 12.8 (*C*HMe$_2$), 19.0, 19.3 (CH*Me*$_2$); δ_{Si} (CDCl$_3$) 0.71 (^{i}Pr$_2$MeSi), 24.7 (SiBr); *m*/*z* 448 [2, M$^+$(^{81}Br^{81}Br)], 446 (4), 444 (2), 129 (100), 73 (66), 59 (91); HRMS found, 444.0337. $C_{14}H_{34}Si_3{}^{79}Br_2$ requires 444.0335.

Hexakis(*tert*-butyldimethylsilyl)cyclotrisilane 1a. To a suspension of lithium naphthalenide [prepared by mixing lithium (250 mg, 36.0 mmol) and naphthalene (5.310 g, 41.4 mmol) in THF (80 cm^3)] was added a solution of 2,2-dibromotrisilane **3a** (6.55 g, 15.7 mmol) in THF (20 cm^3) at −78 °C. Warming the mixture to room temperature and then stirring overnight gave a dark red solution. The resulting mixture was hydrolyzed, and then washed with water and brine. The organic layer was dried over anhydrous sodium sulfate. After removal of solvent and washing the resulting solid with ethanol, pale yellow microcrystals of the title compound (2.310 g, 2.98 mmol) were obtained in 57% yield. **1a**: light yellow crystals; mp 191 °C (Found: C, 55.75; H, 11.82%. $C_{36}H_{90}Si_9$ requires C, 55.73; H, 11.69%); δ_{H} (C$_6$D$_6$) 0.47 (36 H, s, 12 SiMe), 1.20 (54 H, s, ^{t}Bu); δ_{C} (C$_6$D$_6$) 3.4 (SiMe), 22.3 (*C*Me$_3$), 30.4 (C*Me*$_3$); δ_{Si} (THF-*d*$_8$) −156.5 (ring Si), 8.05 (^{t}BuMe$_2$Si); *m*/*z* (%) 774 (0.02, M$^+$), 716 (0.1), 73 (100), 59 (8); λ_{max}/nm (hexane) 264 (ε/dm^3 mol^{-1} cm^{-1} 6.0 × 10^4), 372 (1.3 × 10^3).

Hexakis(diisopropylmethylsilyl)cyclotrisilane 1b. To a suspension of lithium naphthalenide [prepared by mixing lithium (73 mg, 10.5 mmol), naphthalene (1.36 g, 10.6 mmol) in THF (30 cm^3)] was added a solution of **3b** (1.74 g, 3.91 mmol) in THF (10 cm^3) at −78 °C. Similar work-up as described above gave the title compound (395 mg, 1.38 mmol, 35%) as colorless crystals. **1b**: colorless crystals; mp 221 °C (Found: C, 58.85; H, 12.17%. $C_{42}H_{102}Si_9$ requires C, 58.66; H, 11.95%); δ_{H} (CDCl$_3$) 0.16 (18 H, s, 6 SiMe), 1.04 (36 H, d, *J* 7.4 Hz, 6 CHMe$_2$), 1.10 (36 H, d, *J* 7.4 Hz, 6 CHMe$_2$), 1.39 (12 H, sept, *J* 7.4 Hz, 12 C*H*Me$_2$); δ_{C} (CDCl$_3$) −4.2 (Me), 16.4 (C*H*Me$_2$), 19.5, 20.7 (CH*Me*$_2$); δ_{Si} (CDCl$_3$) −148.6 (ring Si), 10.8 (^{i}Pr$_2$MeSi); *m*/*z* 858 (16.4, M$^+$), 815 (16.8), 615 (55.5), 557 (100); λ_{max}/nm (hexane) 255 (ε/dm^3 mol^{-1} cm^{-1} 6.1 × 10^4), 349 (1.3 × 10^3).

X-Ray crystal structures of cyclotrisilanes 1a and 1b

Single crystals of **1a** and **1b** suitable for X-ray diffraction study were obtained by recrystallization from *p*-xylene and hexane, respectively. X-Ray data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation (λ 0.71073 Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997).

Crystal data for 1a. $C_{36}H_{90}Si_9{\cdot}C_8H_{10}$, M = 882.04, monoclinic, a = 18.223(2), b = 15.815(2), c = 11.7534(4) Å, β = 123.9562(7)°, V = 2809.7(5) Å^3, T = 150 K, space group $C2$ (no. 5), Z = 2, μ(Mo-Kα) = 2.4 cm^{-1}, 13441 reflections measured, 6579 unique (R_{int} = 0.023). The final $R1$ and $wR2$ values were 0.0372 [$I > 2\sigma(I)$] and 0.0978 (for all data), respectively.

Crystal data for 1b. $C_{42}H_{102}Si_9$, M = 860.05, triclinic, a = 11.3299(5), b = 22.755(1), c = 24.229(1) Å, α = 64.743(3), β = 77.141(3), γ = 89.051(2)°, V = 5485.9(5) Å^3, T = 150 K, space group $P\bar{1}$ (no. 2), Z = 4, μ(Mo-Kα) = 2.4 cm^{-1}, 31145 reflections measured, 17805 unique (R_{int} = 0.045). The final $R1$ and $wR2$ values were 0.050 [for $I > 2\sigma(I)$] and 0.104 (for all data), respectively.

CCDC reference numbers 170529 and 170530.

See http://www.rsc.org/suppdata/dt/b1/b107905k/ for crystallographic data in CIF or other electronic format.

Photoreactions of cyclotrisilanes 1a and 1b

Photolysis in the absence of trapping agents. In an argon atmosphere, cyclotrisilane **1a** (50 mg, 0.065 mmol) and degassed hexane (6 cm^3) were placed in a Pyrex Schlenk tube. The resulting suspension was irradiated with a high-pressure mercury lamp (500 W) for a day at room temperature. The precipitated **1a** was gradually dissolved as the reaction proceeded and the solution changed from light yellow to orange. Evaporation of the solvent gave the corresponding tetrasilyldisilene **5a** as a light orange solid. NMR analysis showed the complete consumption of **1a** without any other noticeable products. Similarly, photolysis of **1b** in hexane gave tetrasilyldisilene **5b** quantitatively.

Photolysis of cyclotrisilane 1a in (*E*)-2-butene. Cyclotrisilane **1a** (10.0 mg, 1.28 × 10^{-5} mol) and degassed (*E*)-2-butene (6 cm^3) were placed in an NMR tube equipped with a stopcock. The resulting suspension was then irradiated with a high-pressure mercury lamp for 3 hours at room temperature. The remaining solid **1a** dissolved and the color changed to reddish orange as the reaction proceeded. After evaporation of excess (*E*)-2-butene, the residual solid was dissolved in dry benzene-*d*$_6$, and the NMR tube was sealed. The ^{1}H, ^{13}C and ^{29}Si NMR spectra showed 90% conversion of **1a**. The mixture included (*E*)-1,1-bis(*tert*-butyldimethylsilyl)-2,3-dimethylsilirane **6a** (3.1 mg, 9.9 × 10^{-6} mol, 86%), tetrakis(*tert*-butyldimethylsilyl)disilene **5a** (1.4 mg, 2.8 × 10^{-6} mol, 24%), and its hydrate **7a** (2.6 mg, 4.8 × 10^{-6} mol, 42%).[9,18] The yields were determined by comparison of the ^{1}H NMR integrals to those of the methyl protons of 1,2,4,5-tetramethylbenzene (2.9 mg, 0.022 mmol), which was added to the mixture after photolysis. Within the limits of the ^{1}H NMR measurements, only (*E*)-silirane formed. (*E*)-**6a**; δ_{H} (C$_6$D$_6$) 0.12 (6 H, s, SiMe), 0.18 (6 H, s, SiMe), 0.72–0.82 (2 H, m, C*H*Me), 1.01 (18 H, s, ^{t}Bu), 1.48–1.51 (6 H, m, CH*Me*); δ_{C} NMR (C$_6$D$_6$) −1.8 (SiMe), −1.7 (SiMe), 18.8 (Si*C*Me$_3$), 18.9 (ring C), 19.8 (ring Me), 27.9 (C*Me*$_3$); δ_{Si} NMR (C$_6$D$_6$) −144.1 (ring Si), 2.8 (^{t}BuMe$_2$Si); HRMS found, 314.2277. $C_{16}H_{38}Si_3$ requires 314.2281.

Photolysis of cyclotrisilane 1a in (*Z*)-2-butene. Following the same procedure used for the reaction of **1a** in (*E*)-2-butene, photolysis of **1a** (10.0 mg, 1.28 × 10^{-5} mol) was carried out in (*Z*)-2-butene. The NMR spectra of the reaction mixture showed that the photolysis conversion was 75% and the mixture included (*Z*)-1,1-bis(*tert*-butyldimethylsilyl)-2,3-dimethylsilirane (*Z*)-**6a** (2.5 mg, 7.9 × 10^{-6} mol mmol, 82%), disilene **5a** (1.1 mg, 2.1 × 10^{-6} mol, 22%), and its hydrate **7a** (1.7 mg, 3.2 × 10^{-6} mol mmol, 33%). (*Z*)-**6a**: δ_{H} (C$_6$D$_6$) 0.07 (6 H, s, 2 SiCH$_3$), 0.20 (6 H, s, 2 SiCH$_3$), 0.98 (9 H, s, ^{t}Bu), 1.01 (9 H, s, ^{t}Bu), 1.25–1.30 (2 H, m, 2 CH), 1.43–1.45 (6 H, m, 2 CH$_3$); δ_{C} (C$_6$D$_6$) −3.4, −0.8 (SiMe), 13.1 (ring C), 13.2 (ring Me), 19.4, 20.6 (Si*C*Me$_3$), 27.86, 27.89 (SiC*Me*$_3$); δ_{Si} (C$_6$D$_6$) −154.5 (ring Si), 0.6, 4.5 (^{t}BuMe$_2$Si); *m*/*z* 314 (71.4, M$^+$), 258 (96.7), 141 (39.8), 84 (100); HRMS found, 314.2314. $C_{16}H_{38}Si_3$ requires 314.2281.

Photolysis of cyclotrisilane 1b in (*E*)-2-butene. Following the same procedure used for the photolysis of **1a** in 2-butenes, photolysis of **1b** (10.0 mg, 1.16 × 10^{-5} mol mmol) was carried out in (*E*)-2-butene. The NMR spectra of the reaction mixture showed that the photolysis conversion was 68% and the mixture included (*E*)-1,1-bis(diisopropylmethylsilyl)-2,3-dimethylsilirane (*E*)-**6b** (2.2 mg, 6.4 × 10^{-6} mol, 81%), tetrakis(diisoproprylmethylsilyl)disilene **5b** (0.81 mg, 1.4 × 10^{-6} mol, 18%) and its hydrate **7b** (2.6 mg, 4.4 × 10^{-6} mol, 56%).[9,18] (*E*)-**6b**: δ_{H} (C$_6$D$_6$) 0.05 (6 H, s, 2 SiMe), 0.68–0.72 (2H, m, 2 C*H*Me), 0.92–1.10 (4H, m, 4 C*H*Me$_2$), 1.04–1.14 (24 H, m, 4 CH*Me*$_2$), 1.47–1.50 (6 H, m, 2 CH*Me*); δ_{C} (C$_6$D$_6$) −6.9 (SiMe), 14.0 (Si*C*HMe$_2$), 18.3 (ring C), 18.5 (ring Me), 18.7 (SiCH*Me*$_2$);

δ_{Si} (C_6D_6) −147.8 (ring Si), 7.2 ($^iPr_2MeSi$); *m*/*z* 342 (33.2, M^+), 286 (100), 160 (35.6), 73 (22.1); HRMS found, 342.2590. $C_{18}H_{42}Si_3$ requires 342.2594.

Photolysis of cyclotrisilane 1b in (*Z*)-2-butene. Following the same procedure used for the photolysis of **1a** in 2-butenes, photolysis of **1b** (10.0 mg, 1.16×10^{-5} mol) was carried out in (*Z*)-2-butene. The NMR spectra of the reaction mixture showed that the photolysis conversion was 81% and the mixture included (*Z*)-1,1-bis(diisopropylmethylsilyl)-2,3-dimethylsilirane (*Z*)-**6b** (1.9 mg, 5.6×10^{-6} mol, 60%), a trace amount of disilene **5b** (<1%), and its hydrate **7b** (3.1 mg, 5.2×10^{-6} mol, 55%). (*Z*)-**6b**: δ_H (C_6D_6) −0.03 (3 H, s, $SiCH_3$), 0.10 (3 H, s, $SiCH_3$), 0.90–1.01 (4 H, m, 4 $CHMe_2$), 1.05–1.13 (24 H, m, 4 $CHMe_2$), 1.33–1.40 (2 H, m, 2 *CH*Me), 1.43–1.45 (6 H, m, 2 CH*Me*); δ_C (C_6D_6) −8.2, −6.1 (SiMe), 12.4, 13.2 (Si*C*HMe$_2$), 17.0 (ring Me), 18.5 (ring C), 18.8, 19.8 (SiCH*Me*$_2$); δ_{Si} (C_6D_6) −158.1 (ring Si), 4.7, 9.4 ($^iPr_2MeSi$); *m*/*z* 342 (30.6, M^+), 286 (100), 160 (40.1), 73 (31.3); HRMS found, 342.2621. $C_{18}H_{42}Si_3$ requires 342.2594.

Acknowledgements

This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (Grants-in-Aid for Scientific Research (B) No. 11440185 (M. K. and T. I.) and Encouragement of Young Scientists No. 12740336 (T. I.)).

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