

Chapter 1

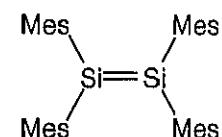
**Synthesis, Crystal Structure, and Reactivity of Cyclotrisilene:
A Three-Membered Ring Compound with a Si=Si Double Bond**

Summary

The reductive dehalogenation of di-*tert*-butyl(methyl)silyl-substituted dibromosilane (**1**) and tribromosilane (**2**) derivatives with sodium metal in toluene produced tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene (**3**) which has an endocyclic Si=Si double bond. The molecular structure of **3** was confirmed by X-ray crystallography. The cyclotrisilene was reacted with carbon tetrachloride or 1,2-dibromoethane to give the corresponding dihalocyclotrisilane derivatives. The crystal structure of 1,2-dichloro-1,2,3,3-tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilane (**4a**) showed a *trans* arrangement of the two chlorine atoms in the three-membered system.

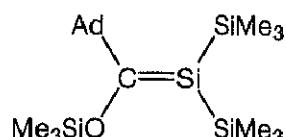
Introduction

The synthesis of several compounds with double bonds involving silicon or germanium has been accomplished,¹ following the discovery of Mes₂Si=SiMes₂ (Mes = 2,4,6-trimethylphenyl)² and (Me₃Si)₂Si=C(OSiMe₃)Ad (Ad = 1-Adamantyl).³ Since then, there has been explosive growth in the area of unsaturated compounds of heavier Group 14 elements.¹ In 1996 the first compounds with endocyclic Si–Si double bonds were reported by Kira et al.,⁴ and two years later by Wiberg et al. from the reaction of tetrakis(*tri-tert*-butylsilyl)tetrasilatetrahedrane with iodine.⁵



Mes = 2,4,6-trimethylphenyl

R. West (1981)

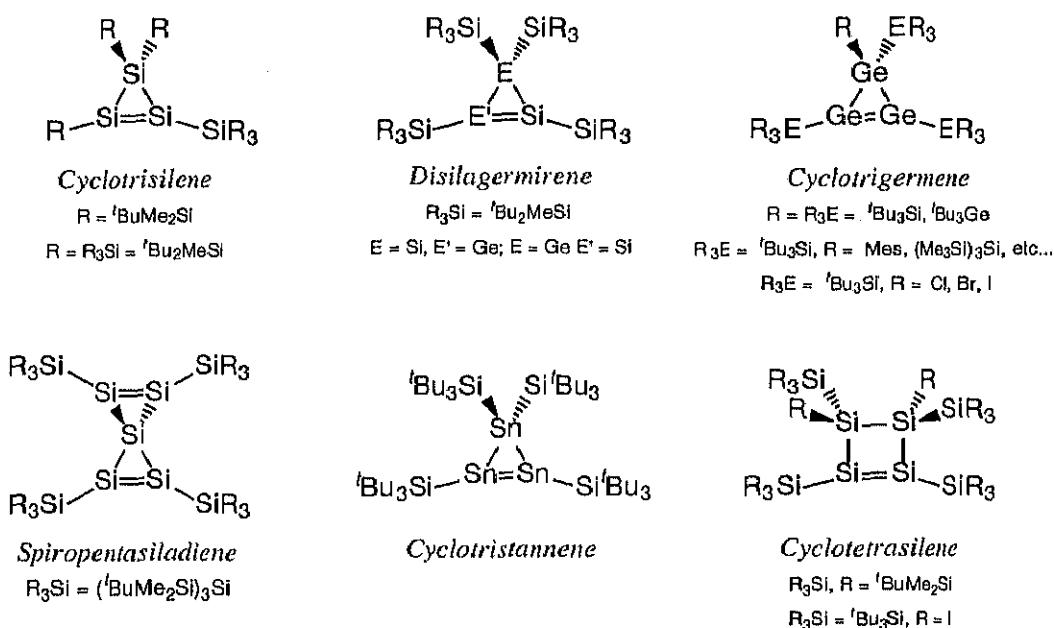


Ad = 1-adamantyl

A. G. Brook (1981)

In 1995, Sekiguchi et al. reported the first successful synthesis of cyclotrigermene derivatives which has a endocyclic Ge-Ge double bond in the three-membered ring skeleton, and their structural characterization by X-ray crystallography.⁶ Sekiguchi et al. have demonstrated the formation of cyclotrigermenylum ion, a free germyl cation with a 2π -electron system, by the oxidation of cyclotrigermenes with trityl tetraarylbrates (trityl = triphenylmethy)⁷ and have also shown that cyclotrigermenylum ion is a good precursor of cyclotrigermenes which have unsymmetrical substituents.⁸ In 1999, Wiberg et al. reported tin analogue of cyclopropene by the reaction of dichlorostannylene with 'Bu₃SiNa.⁹ Cyclotrisilene (R₄Si₃), analogous to cyclopropene (R₄C₃) and cyclotrigermene (R₄Ge₃), is a very intriguing molecule as it contains a three-membered unsaturated ring. While our work was in progress we learned that Kira et al. had synthesized asymmetrically substituted cyclotrisilene 1-tris(*tert*-butyldimethylsilyl)silyl-2,3,3-tris(*tert*-butyldimethylsilyl)cyclotrisi-

lene by a reduction of 1,1-dibromo-3-*tert*-butyl-2,2-bis(*tert*-butyldimethylsilyl)-1-chloro-3,3-dimethyltrisilane with KC_8 .^{10a} Very recently, structural analysis of the cyclotrisilene was finally reported.^{10b} Kira et al. have also found an interesting compound, spiro-pentasiladiene derivative as a minor product of the same reaction system.¹¹



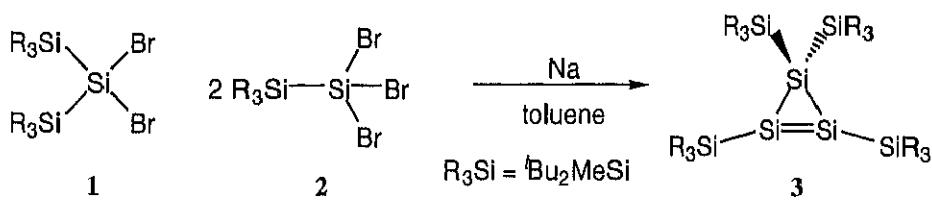
In this chapter, synthesis and characterization of symmetrically substituted cyclotrisilene and the first crystal structure of a cyclotrisilene derivative by X-ray crystallography. The unique reactivities of the cyclotrisilene with haloalkanes, phenylacetylene, and GeCl_2 dioxane are also discussed.

Results and Discussion

Synthesis of Cyclotrisilene

For the synthesis of strained molecules, such as cyclotrisilene and cyclotrigermene, it is prime importance to choose an appropriate protecting group. The stabilization of heavier Main Group element multiple bonds has been largely achieved by using sterically demanding substituents. Theoretical calculations to examine the electronic factor of substituents indicate that electropositive substituents such as silyl groups are likely to reduce the strain considerably within three-membered rings formed by Group 14 elements.¹² Thus, the author has chosen the di-*tert*-butyl(methyl)silyl group for the protection of the cyclotrisilene ring skeleton.

The reductive condensation of one molar amount of 2,2-dibromo-1,1,3,3-tetra-*tert*-butyl-1,3-dimethyltrisilane **1** and two molar amount of 2,2,2-tribromo-1,1-di-*tert*-butyl-1-methyldisilane **2** with sodium in toluene led to the immediate formation of a dark red solution. The reaction was followed by gas chromatography, and **2** was disappearing within three hours. The reaction mixture was recrystallized from hexane to give pure tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene **3** as air- and moisture sensitive red-orange crystals in 9.1% yield (Scheme 1-1). The mechanism of the formation of **3** is obscure, although the *t*Bu₂MeSi group is essential to the formation of the cyclotrisilene ring. A short reaction time is crucial for the successful isolation of **3**. Prolonged reaction may result in over-reduction. The cyclotrisilene **3** is air and moisture sensitive, and the color disappears immediately when a solution is exposed to the air. However, **3** was thermally stable and melts at 207 °C without decomposition.



Scheme 1-1

The structure of **3** was determined by MS and ^1H , ^{13}C , and ^{29}Si NMR spectroscopy. The NMR data on the structure of **3** in benzene- d_6 indicate a highly symmetrical structure. Thus, in the ^1H and ^{13}C NMR spectra of **3** in benzene- d_6 , only two kinds of signals arising from ' Bu_2MeSi ' groups are observed (see experimental section). The ^{29}Si NMR spectrum showed signals at $\delta = -127.3$, 7.9, 27.1, and 97.7. The signal at lowest field ($\delta = 97.7$) is assigned to the unsaturated silicon atoms of ' $\text{Bu}_2\text{MeSi-Si=}$ ', and the signal at high field ($\delta = 127.3$) can be assigned to the saturated skeletal silicon atom of $(\text{Bu}_2\text{MeSi})_2\text{Si}$. The mass spectrum showed no molecular ion peaks, but showed a very weak peak at m/z 655 [$\text{M}^+ - \text{Bu}$] and relatively intense peaks in the mass range of m/z 555-560, which are in agreement with the formula $\text{C}_{27}\text{H}_{63}\text{Si}_6$. The latter peaks are attributable to the tris[di-*tert*-butyl (methyl)silyl]cyclotrisilene cation by loss of a ' Bu_2MeSi ' group.

Molecular Structure of Cyclotrisilene **3**

Recrystallization of **3** from hexane at -10 °C afforded red-orange cubes suitable for a single-crystal X-ray diffraction study. The molecular structure and selected structural parameter are shown in Figure 1-1.¹³ The crystal structure shows that, crystallographically, the molecule has no symmetry. The geometry around Si=Si double bond is not planar, as determined by sum of the bond angles of the unsaturated silicon atoms (357.5° for Si1 and 358.1° for Si2). The cyclotrisilene has a twisted Si=Si double bond probably as a consequence of the eclipsed arrangement of the two ' Bu_2MeSi ' groups attached to the unsaturated silicon atoms, whereas the ' Bu_3Si '-substituted cyclotrigermene has a planar Ge=Ge double bond. The torsional angle of Si4-Si1-Si2-Si5 is 31.9(2)°. The Si=Si bond length is 2.138(2) Å, which is similar to those of the known three-membered ring disilenes, 1-disilagermirene (2.146(1) Å)¹⁴, asymmetrically substituted cyclotrisilene (2.132(2) Å)^{10b}, and tetrakis(*tert*-butyldimethylsilyl)spiropentasiladiene (2.186(3) Å).¹¹ The Si-Si single bond

lengths in **3**, especially the bond distances between the saturated silicon atom in the three-membered ring and substituents (2.401(3) Å for Si3-Si6 and 2.403(3) Å for Si3-Si7), are somewhat longer than the normal Si-Si bond length (2.34 Å). The three-membered ring is almost an isosceles triangle with bon angle of 61.8(1), 63.3(1), and 53.9(1).

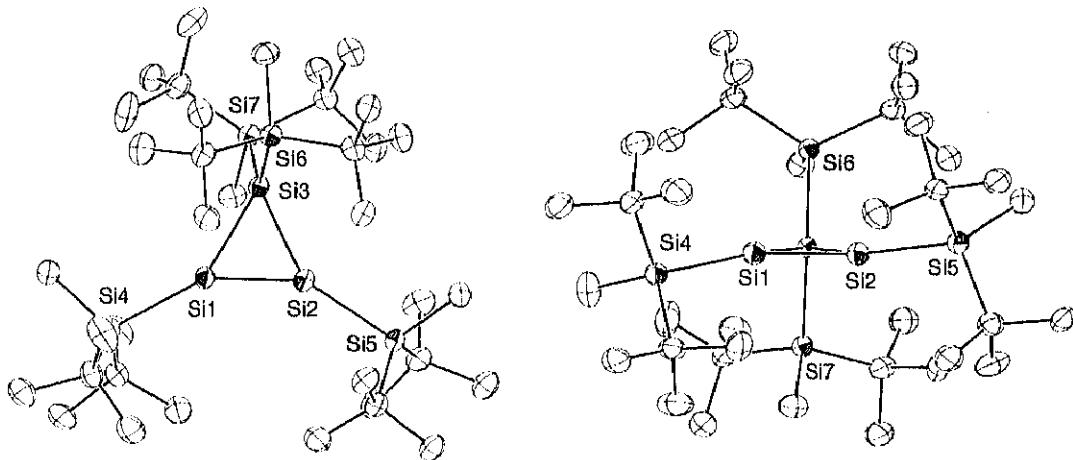


Figure 1-1. ORTEP drawings of **3** (left; top view, right; side view).

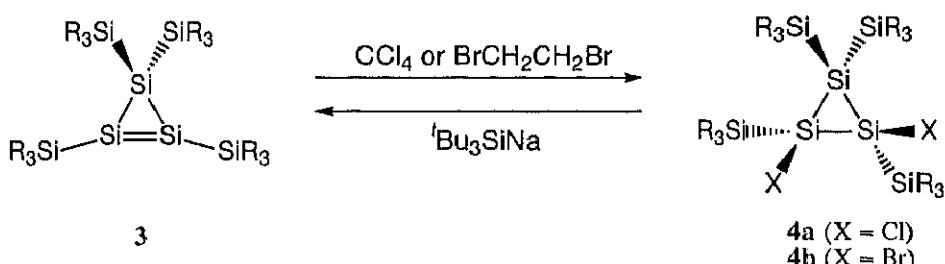
Reactivity of Cyclotrisilene **3**

Cyclotrisilene is expected to exhibit an enhanced reactivity arising from the combination of highly reactive Si-Si double bond and highly strained three-membered ring skeleton in one molecule, which gives an access to the novel cyclic and bicyclic compounds by the addition and cycloaddition reaction.¹⁵ Then, the reactivity of cyclotrisilene **3** toward haloalkanes, phenylacetylene, and GeCl₂ dioxane complex were investigated.

Reaction of Cyclotrisilene with Haloalkanes

The reaction of the cyclotrisilene **3** with excess carbon tetrachloride results in the formation of the corresponding dichloroadduct in an almost quantitative yield, without any side products (Scheme 1-2). This reaction proceeded immediately, even low temperature, and during the reaction, the color of the reaction mixture changed from red-orange to yellow,

at which time NMR spectra showed the absence of the starting material. Evaporation of excess CCl_4 left a yellow residue, which was found to be practically pure dichlorocyclotrisilane **4a**. The reaction of **3** with 1,2-dibromoethane yielded the corresponding dibromocyclotrisilane **4b**. Of the two possible stereoisomers, only one was formed in the reaction of **3** with CCl_4 or 1,2-dibromoethane. These new compounds were isolated as air stable yellow crystals. The structures of **4a,b** were established on the basis of spectral data, elemental analysis, and X-ray crystallography.



Scheme 1-2

For compounds **4a** and **4b**, ^1H and ^{13}C NMR spectra showed the existence of two sets of signals from the different methyl groups and four the diastereotopic *tert*-butyl groups. This indicates that the two halogen atoms are in *trans* fashion relative each other. ^{29}Si NMR spectrum revealed four resonances for **4a** and **4b**, from which the two upfield signals belong to the endocyclic silicon atoms, and the others belong to the silyl substituents.

The crystal structure of 1,2-dichloro-1,2,3,3-tetrakis[di-*tert*-butyl(methyl)silyl]-cyclotrisilane (**4a**) was determined by X-ray analysis, as shown Figure 1-2. The crystal structure data confirms that the two chlorine atoms are arranged in a *trans* configuration to each other, which is in agreement with the previously established *trans* geometry from the NMR data. Such geometry may be caused by the proposed radical mechanism¹⁶ and the relative stability of the products. The endocyclic Si-Si bond length of 2.4223(8) Å for Si1-Si2 is 4% longer than a normal Si-Si single bond length (2.34 Å). The bond length of 2.338(1) Å for Si2-Si2' lies in a normal region. The two $'\text{Bu}_2\text{MeSi}$ groups attached to Si2

and Si2' atoms occupy the less hindered pseudo-equatorial positions, whereas the two chlorine atoms occupy the pseudo-axial positions, as determined by the angles between the three-membered ring plane and the Si–R vector ($R = {^t}\text{Bu}_2\text{MeSi}$ and Cl): 130.2° for ${^t}\text{Bu}_2\text{MeSi}$, and 102.9° for Cl. This geometry causes an elongation of Si–Cl bond (2.1171(7) Å) relative to the average value of 2.05 Å.¹⁷

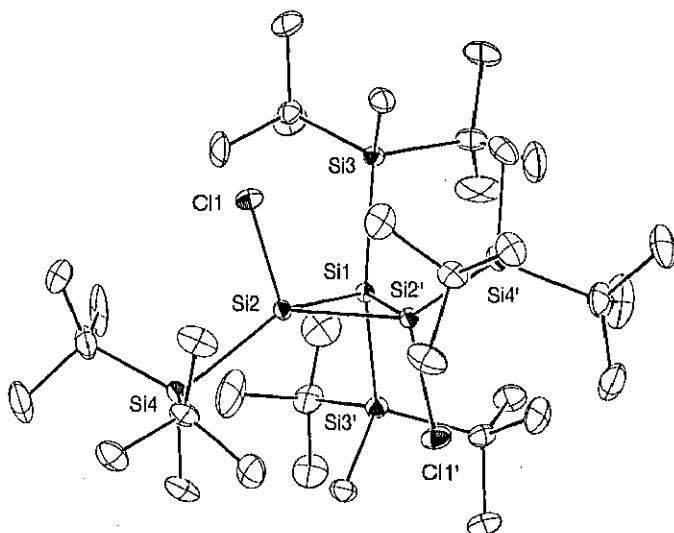
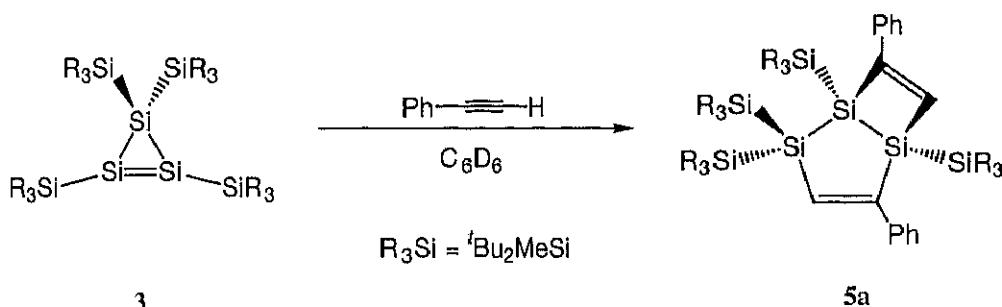


Figure 1–2. ORTEP drawing of *trans*-dichlorocyclotrisilane **4a**.

It is interesting that the reaction of the dihalocyclotrisilanes, **4a** and **4b**, with $'\text{Bu}_3\text{SiNa}$ produced quantitatively the corresponding starting cyclotrisilene **3** (Scheme 1-3). The reactions proceeded very quickly and cleanly without the formation of any side products, except for $'\text{Bu}_3\text{SiCl}$ (or $'\text{Bu}_3\text{SiBr}$), $'\text{Bu}_3\text{SiSi}'\text{Bu}_3$. The reaction was easily monitored visually, by the change in color from yellow due to the compounds **4a** and **4b**, to an intense red, characteristic for **3**. It is likely that the reaction pathway includes an electron-transfer step with a halogen-sodium exchange to form an anionic intermediate, which then quickly undergoes elimination of NaX to form the final cyclotrisilene **3**. Therefore, such dihalocyclotrisilane can be considered as an unusual but convenient and very effective source for the preparation of cyclotrisilene.

Reaction of Cyclotrisilene with Phenylacetylenes

Cyclotrisilene **3** was allowed to react with excess phenylacetylene in benzene-*d*₆ at room temperature. The red-orange color of **3** disappeared within 15 hours to give a 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene derivative **5a** in a 65% yield (Scheme 1-3). No reaction occurred with trimethylsilylacetylene, bis(trimethylsilylacetylene), or diphenylacetylene, and a complicated reaction mixture was formed with 1-hexyne.



Scheme 1-3

The structure of **5a** was determined by mass spectrometry, NMR spectra, and X-ray crystallography. The mass spectrum of **5a** showed a very weak parent ion at 916, with fragmentation peaks at 859 ($\text{M}^+ - \text{'Bu}$) and at 759 ($\text{M}^+ - \text{SiMe}'\text{Bu}_2$). The ¹H NMR spectrum showed two olefinic protons at 7.42 and 7.89 ppm, as well as peaks indicating the presence of four different $'\text{Bu}_2\text{MeSi}$ groups, and two phenyl groups. The ¹³C and ²⁹Si NMR spectra were also consistent with the structure being a 1:2 adduct of **5a** with phenylacetylene. As shown Figure 1-3, compound **5a** has a bicyclo[3.2.0]hepta-3,6-diene skeleton, the formation of which can be explained by the consecutive addition of one molecule of phenylacetylene to the Si=Si double bond of **5a**, and by insertion of a second molecule of phenylacetylene into the Si-Si single bond in the resulting cyclotrisilane ring. The cycloaddition reaction of acetylenes with a Si=Si double bond to give the disilacyclobutene derivative is well known,¹⁸ but the insertion of C-C multiple bonds in to a Si-Si single bond at ambient temperature without the use of a catalyst has not been reported.

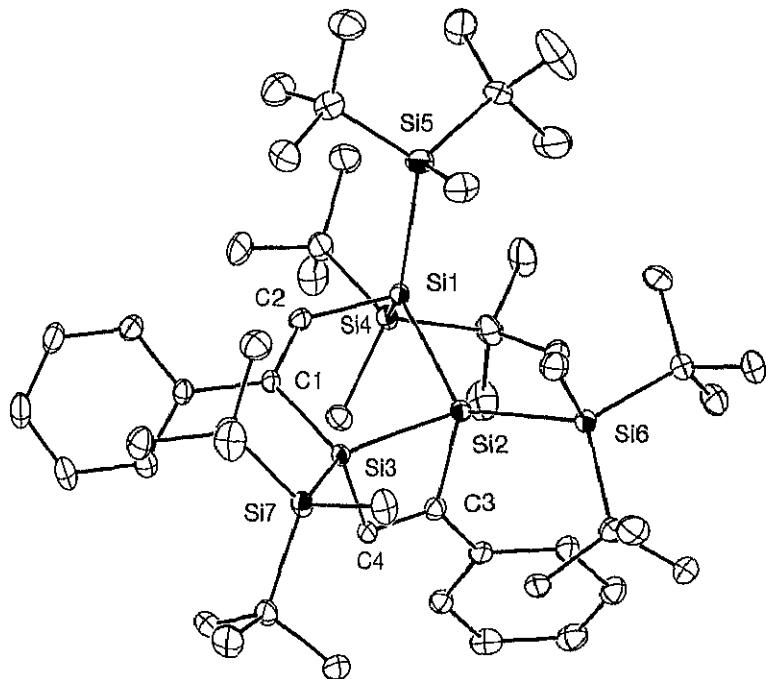


Figure 1-3. ORTEP drawing of **5a**.

The formation of **5** was quite interesting for me, and prompted the author to investigate its formation mechanism. Under the same conditions as above, deuterium-labeled cyclotrisilane, **3-d₆**, which was prepared by the reductive condensation of [¹Bu₂(CD₃)-Si]₂SiBr₂ **1-d₆** with sodium, in which the CH₃ groups in the di-*tert*-butyl(methyl)-silyl substituents on the saturated silicon atom were replaced a CD₃ group, was reacted with phenylacetylene to give **5A-d₆** and **5B-d₆** in 1:1 molar ratio. In the ¹H NMR spectrum of the mixture of **5A-d₆** and **5B-d₆**, the signal at 0.67 ppm assigned to a methyl group on Si6 completely disappeared, and the relative intensities of two signals at 0.16 and 0.51 ppm, assigned to the methyl groups on Si4 and Si5, were half the magnitude to those of **5a** (Figure 1-4). This result indicates that **5a** is not formed via a simple [2+2] cycloaddition and insertion process. A more likely mechanism is as follows. First, the phenylacetylene undergoes cycloaddition to the Si=Si double bond of **3-d₆** to form the 1,4,5-trisilabicyclo[2.1.0]pent-2-ene derivative **6-d₆**, which then isomerizes to the 1,2,3-trisilacyclopenta-3,5-diene derivative **7-d₆**, which has a conjugated Si=C-C=Si system in a five-membered ring.

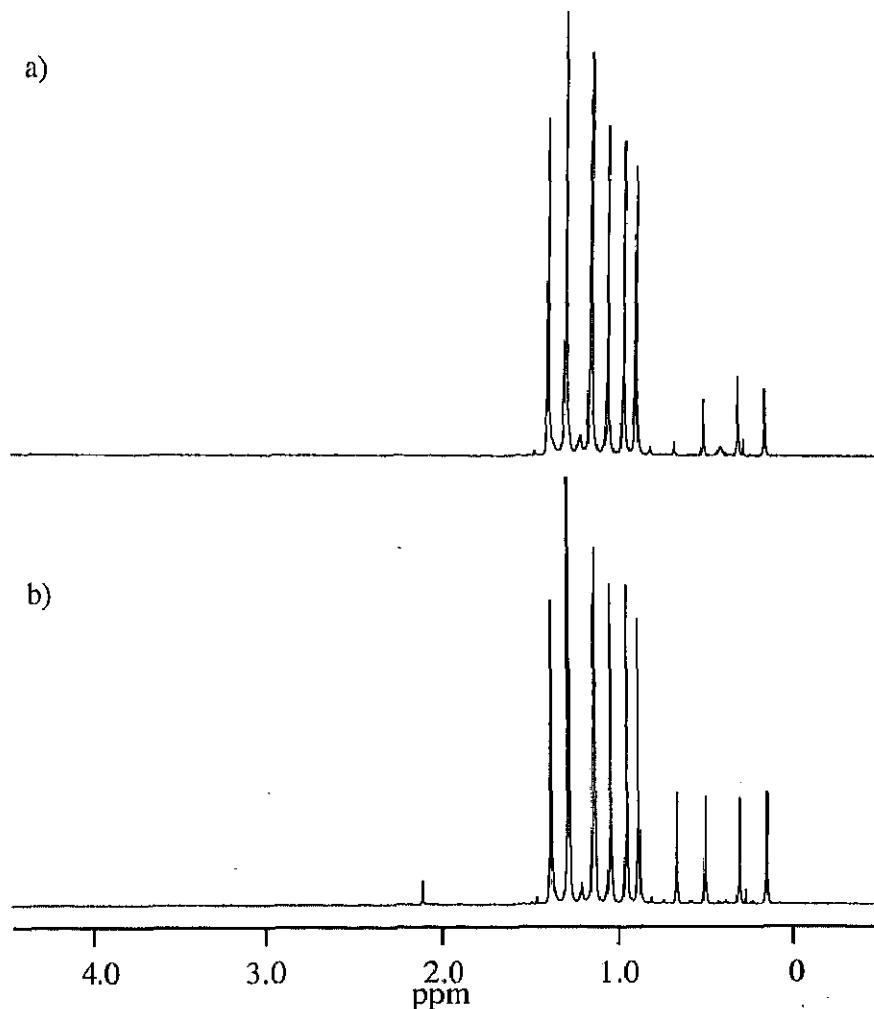
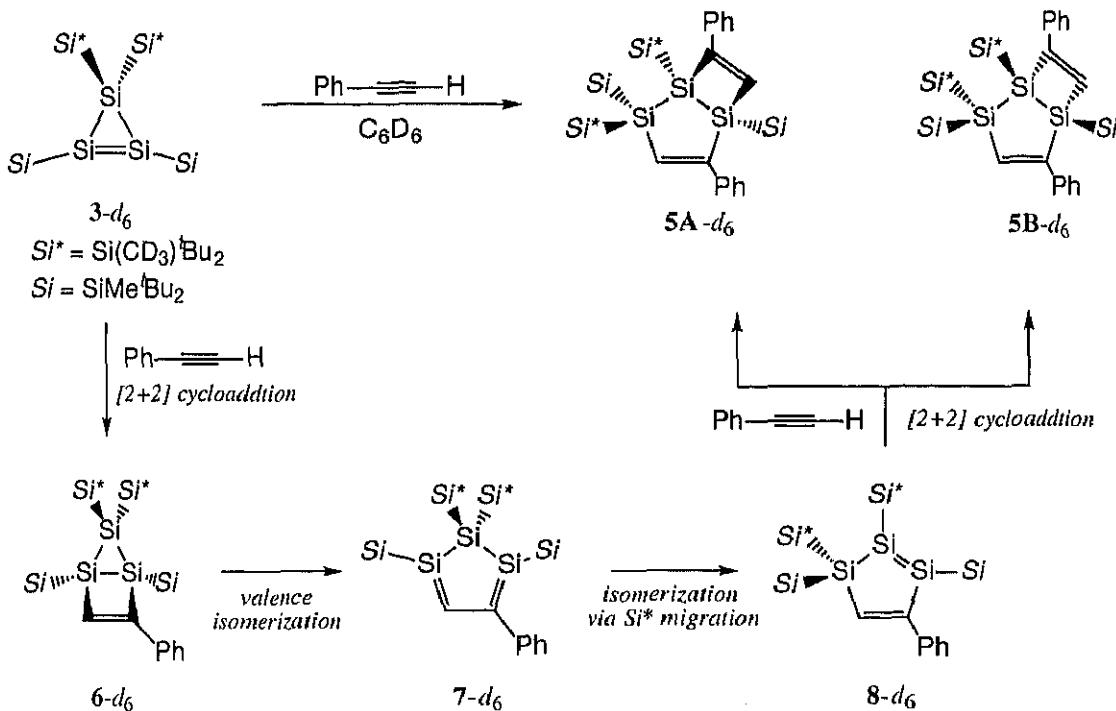


Figure 1-4. ^1H NMR spectra of 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene
a) **5A-*d*₆** and **5B-*d*₆** in benzene-*d*₆; **5a** in benzene-*d*₆.

Secondly, one $'\text{Bu}_2(\text{CD}_3)\text{Si}$ group on a saturated silicon atom migrate to an unsaturated silicon atom to give the 1,2,3-trisilacyclopenta-2,4-diene derivative **8-*d*₆**, which has a Si=Si-C=C system in a five-membered ring. Finally, the silole intermediate **8-*d*₆**, is trapped by phenylacetylene *via* a [2+2] cycloaddition across the Si=Si double bond to afford a mixture of **5A-*d*₆** and **5B-*d*₆** (Scheme 1-4). However, the silole intermediate **7** and **8** were not observed in monitoring the reaction of **3** with phenylacetylene using NMR spectroscopy, which probably due to their high reactivity. Even with equimolar quantity of phenylacetylene, the product **5a** was formed together with unreacted **3**.



Scheme 1-4

To have better understanding of the isomerization **6** to **8**, theoretical calculations on the parent system (**6-H** to **8-H**) were carried out at the B3LYP/6-31G(d) level, and all isomers **6-H** - **8-H** were found as energy minimum geometries. The bicyclic structure **6-H** was the most unfavorable, probably due to the highly strained three- and four-membered bicyclic structure, and the silole **7-H** and **8-H** were more stable by 1.0 and 13.1 kcal/mol relative to **6-H**, respectively. The conrotatory isomerization of **6-H** to **7-H** may be unfavorable because of the fixed bicyclic structure of **6-H**. The last compound consequently isomerizes by the migration of the hydrogen atoms to give the thermodynamically most stable silole structure **8-H**, with a Si=Si-C=C system.

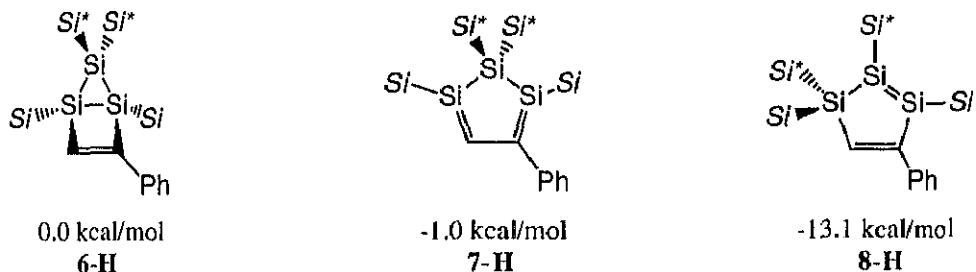
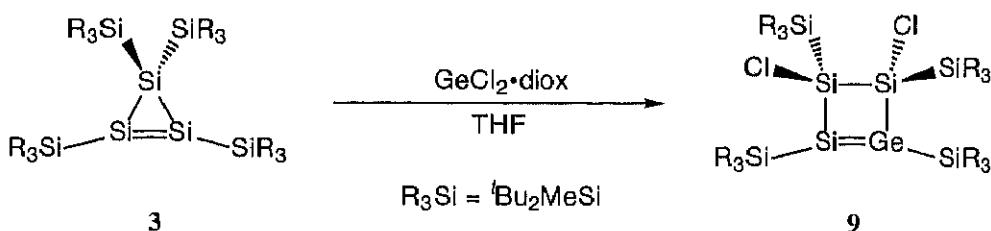


Chart 1-1. Relative energies of $\text{Si}_3\text{C}_2\text{H}_5$ isomers (B3LYP/6-31G(d)).

Reaction of Cyclotrisilene with GeCl₂ dioxane

Sekiguchi et. al reported the unexpected formation of Δ^3 -1,2,3,4-disiladigermetene derivative by the reactions of 1- and 2-disilagermirene with GeCl₂ dioxane.¹⁹

The reaction of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene **3** with equimolar amount of GeCl₂ dioxane in oxygen-free, dry THF at room temperature led to the formation of a yellow solution within 30 minutes. After the solvent was removed, the residue was recrystallized from hexane to afford yellow crystals of *trans*-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-1,2,3-trisila-4-germacyclobutene **9** in 97% yield (Scheme 1-5).

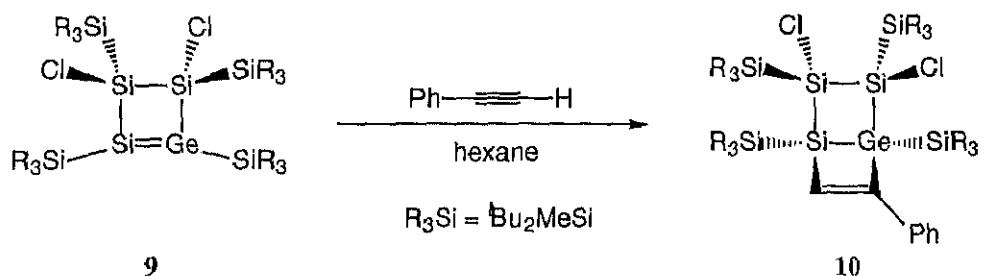


Scheme 1-5

The structure of **9** was determined by mass spectrometry and by ¹H, ¹³C, and ²⁹Si NMR spectroscopy as well as product analysis of phenylacetylene adduct of **9**. In the ¹H and ¹³C NMR spectra of **9** in benzene-*d*₆, four kinds of signals arising from ¹Bu₂MeSi groups are observed. The ²⁹Si NMR showed seven signals at $\delta = 0.1, 4.8, 17.0, 17.9, 26.1, 37.4$, and 149.4 . The signal at lowest field ($\delta = 149.4$) is assigned to unsaturated silicon atom in the four-membered ring skeleton, which is similar to the chemical shifts of unsaturated silicon atoms in the cyclotetrasilene derivatives.^{4,5}

Baines et al. reported that acyclic germasilene readily react with phenylacetylene to produce the corresponding silagermacyclobutene derivative via a regioselective [2+2] cycloaddition.²⁰ Expectedly, reaction of **9** with excess of phenylacetylene in hexane at room temperature produced the corresponding bicyclic compound of *trans*-3,4-dichloro-1,2,3,4-

tetrakis[di-*tert*-butyl(methyl)silyl]-5-phenyl-1,2,3-trisila-4-germabicyclo[2.2.0]hex-5-ene **10** in 87% yield as only one isomer.



Scheme 1-5

The structure of **10** was determined by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy as well as X-ray crystallography. The X-ray structure of **10** disclosed that the two chlorine atoms were arranged in a *trans* configuration as shown Figure 1-4. The formation of **10** from **9** confirms that **9** has a four-membered ring structure and the existence of endocyclic silicon-germanium double bond.

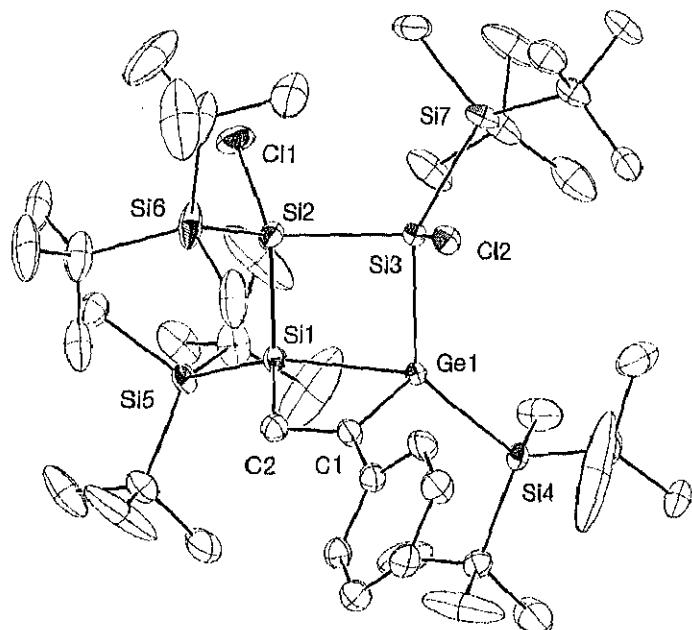
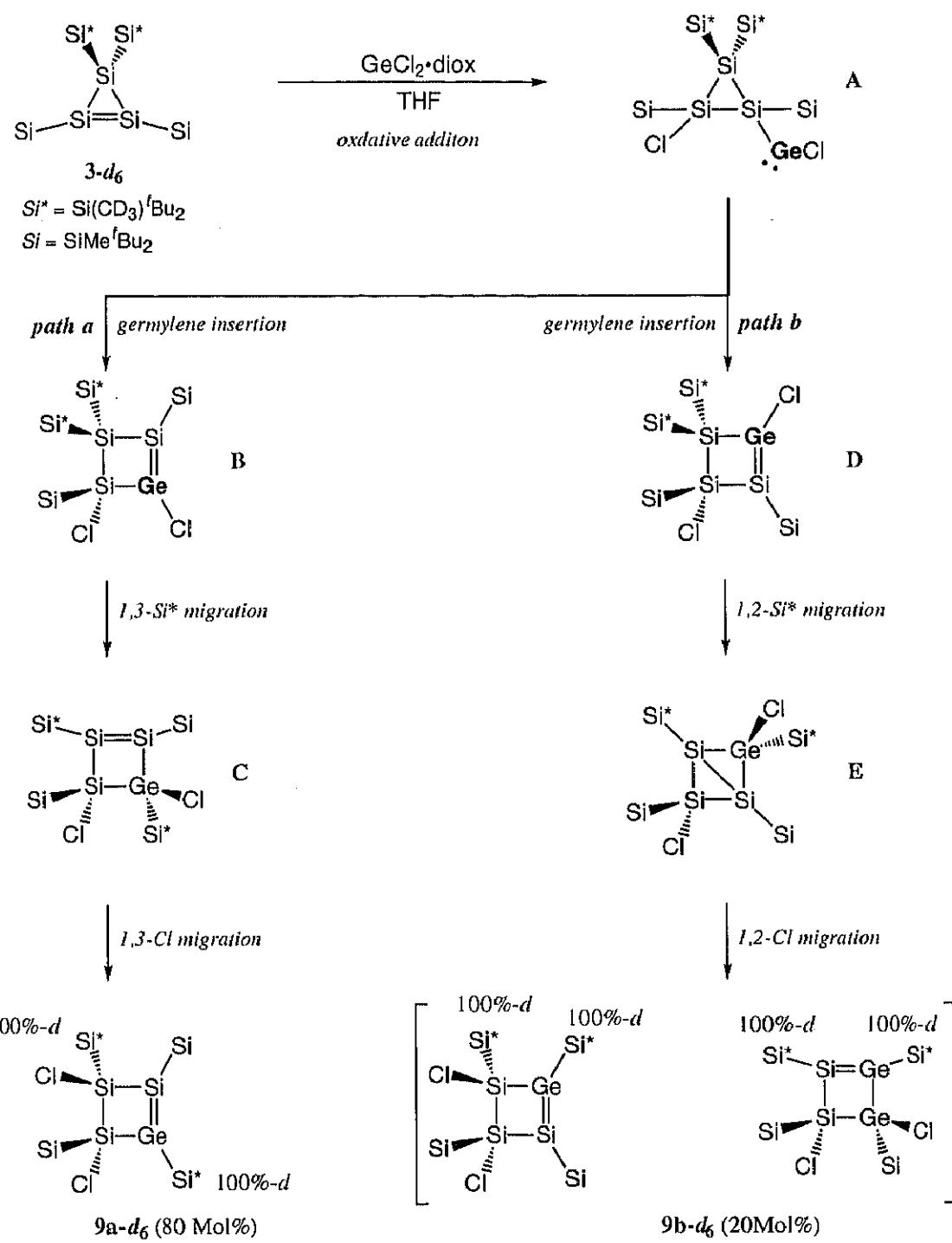


Figure 1–4. ORTEP drawing of **10**.

The formation of **9** was quite interesting, and the reaction of deuterium-labeled cyclotrisilene **3-d₆** with GeCl₂ dioxane was examined to investigate formation mechanism of **9**. Treatment of **3-d₆** with GeCl₂ dioxane produced **9a-d₆** and **9b-d₆** in a 4:1 molar ratio. This result indicates that **9** is probably formed through two pathways. A major process is as follows. In the first step, it is reasonable to assume that GeCl₂ dioxane undergoes oxidative addition across the Si=Si double bond to produce chlorogermylene **A** (Scheme 1-6). The resulting **A** then may quickly undergo intramolecular insertion into the Si–Si(Cl) bond to form compound **B** with a Si=Ge bond. The latter then possibly rearranges to compound **C** with a Si=Si bond: the driving force for such an isomerization may be the presence of the highly electronegative and π -donating Cl substituents on the sp^2 -Ge atom in **B**, which is known to be a destabilizing factor for E=E bonds.²¹ Final 1,3-Cl migration from Ge to Si atom would complete this reaction sequence, resulting in the isomerization to form the final trisilagermetene **9** (path a). Another pathway is similar to the formation of disiladigermetene by the reaction of disilagermirene with GeCl₂,dioxane.¹⁹ Thus, the divalent germanium center of **A** undergoes intramolecular insertion into the Si–Si(Si₂) bond to form compound **D** with a Si=Ge bond. The later then possibly rearranges to bicyclo[1.1.0]butane **E** via a 1,2-silyl migration. Finally, 1,2-Cl migration from Ge to Si atom occurred to give compound **9** (path b).



Scheme 1-6

Conclusion

Tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene (**3**) was obtained by the reductive condensation of dibromosilane (**1**) and tribromosilane (**2**) derivatives with sodium metal in toluene. The X-ray structure of **3** showed that it has a trans-bent geometry around silicon–silicon double bond. The cyclotrisilene has unique reactivities arising from the combination of highly reactive silicon–silicon double bond and highly strained three-membered ring in one molecule. Thus, reaction toward haloalkenes such as carbon tetrachloride produce the corresponding dihalocyclotrisilanes which could easily go back to the cyclotrisilene by the reduction with $'\text{Bu}_3\text{SiNa}$. The reactions of the cyclotrisilene with phenylacetylene and GeCl_2 dioxane produced unusual ring expanded compounds, 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene and trisilagermacyclobutene derivative with endocyclic $\text{Ge}=\text{Si}$ double bond, respectively.

Experimental Section

General procedure

All reactions involving air-sensitive compounds were carried out under argon atmosphere using high-vacuum line and standard Schlenk techniques and dry, oxygen-free solvents. $'\text{BuLi}$ (1.7 M solution in pentane) and MeLi (1.5 M solution in diethyl ether) were purchased from Aldrich, dichlorosilane was from Tokyo Teisan Co., and dichloromethylsilane was presented by Shin-Etsu Co. $'\text{Bu}_2\text{MeSiBr}$ was synthesized by the bromination of $'\text{Bu}_2\text{MeSiH}$ ²² with Br_2 in CH_2Cl_2 according to the literature procedure.²³ $'\text{Bu}_2\text{MeSiF}$ was prepared by the reaction of $'\text{Bu}_2\text{SiF}_2$ ²⁴ with MeLi in Et_2O .²⁵ Ph_3SiLi was prepared from the reaction of chlorotriphenylsilane²⁶ with Li in THF.²⁷ NMR spectra were recorded on a Brüker AC-300FT NMR spectrometer (^1H NMR at 300.13 MHz; ^{13}C NMR at 75.47 MHz; ^{29}Si NMR at 59.63 MHz). Mass spectra were obtained on a JEOL JMS SX-102 instrument (EI, 70 eV). UV spectra were recorded on a Shimadzu UV-3150 UV-visible spectrophotometer in hexane. Elemental analyses were performed at the Analytical Centers of Tsukuba University (Tsukuba, Japan) and Tohoku University (Sendai, Japan).

Preparation of $'\text{Bu}_2\text{MeSiNa}$

A mixture of $'\text{Bu}_2\text{MeSiBr}$ (2.23 g, 9.4 mmol) and sodium (28 mmol) in heptane (100 mL) was refluxed for 12 h to form the greenish-brown suspension. Excess sodium and sodium bromide was removed by decantation followed by filtration through a glass filter under argon. The residual solid was washed with dry hexane (50 mL). The combined solution was evaporated in a vacuum to furnish a brown solid. This crude material, containing an impurity of $('\text{Bu}_2\text{MeSi})_2$ (~10%), was used in the next reactions without further purification. The pure compound can be obtained by recrystallization from hexane as a bright yellow powder (0.90 g, 5.0 mmol, 54%): ^1H NMR (C_6D_6 , δ) 0.01 (s, 3 H), 1.16

(s, 18 H); ^{13}C (C_6D_6 , δ) 0.3, 21.1, 32.0; ^{29}Si NMR (C_6D_6 , δ) 13.8.

Preparation of $(^{\text{'}}\text{Bu}_2\text{MeSi})_2\text{SiH}_2$

A solution of H_2SiCl_2 (4.9 g, 49 mmol) in hexane was added at -10 °C to a solution of freshly prepared $'\text{Bu}_2\text{MeSiNa}$ [from $'\text{Bu}_2\text{MeSiBr}$ (99 mmol) and Na (478 mmol)] in heptane. The mixture was allowed to warm to room temperature and stirred for 1 h. Sodium bromide was filtered off, and the mixture was concentrated in a vacuum. $(^{\text{'}}\text{Bu}_2\text{MeSi})_2\text{SiH}_2$ was isolated by Kugelrohr distillation under reduced pressure as a colorless solid (14.8 g, 43 mmol, 88%). bp 100-120 °C/0.1 mmHg.; ^1H NMR (C_6D_6 , δ) 0.12 (s, 6 H), 1.08 (s, 36 H), 3.12 (s, 2 H); ^{13}C NMR (C_6D_6 , δ) -6.2, 20.1, 29.1; ^{29}Si NMR (C_6D_6 , δ) -120.5, 10.4; MS (m/z, relative intensity) 344 (M^+ , 5), 329 ($\text{M}^+ - \text{Me}$, 3), 287 ($\text{M}^+ - '\text{Bu}$, 41), 157 ($\text{SiMe}'\text{Bu}_2$, 100); HRMS calcd for $\text{C}_{18}\text{H}_{44}\text{Si}_3$ 344.2751, found 344.2735.

Preparation of $(^{\text{'}}\text{Bu}_2\text{MeSi})_2\text{SiBr}_2$ **1**

A solution of Br_2 (8.1 g, 51 mmol) in dichloromethane (25 mL) was added dropwise at -30 °C to a solution of $(^{\text{'}}\text{Bu}_2\text{MeSi})_2\text{SiH}_2$ (8.0 g, 23 mmol) in dichloromethane (25 mL). After being stirred for 1 h, the mixture was evaporated in a vacuum. $(^{\text{'}}\text{Bu}_2\text{MeSi})_2\text{SiBr}_2$ (**1**) was isolated by Kugelrohr distillation as a colorless solid (11.2 g, 96%). bp 180-200 °C/0.1 mmHg, mp 63-64 °C; ^1H NMR (C_6D_6 , δ) 0.28 (s, 6 H), 1.20 (s, 36 H); ^{13}C NMR (C_6D_6 , δ) -5.9, 23.1, 31.1; ^{29}Si NMR (C_6D_6 , δ) 7.6, 22.3; MS (m/z, relative intensity) 500 (M^+ , 11), 443 ($\text{M}^+ - '\text{Bu}$, 8); HRMS calcd for $\text{C}_{18}\text{H}_{42}\text{Br}_2\text{Si}_3$ 500.0961, found 500.0961.

Preparation of $'\text{Bu}_2\text{MeSiSiPh}_3$

A solution of $'\text{Bu}_2\text{MeSiF}$ (17.5 g, 99 mmol) in THF (50 mL) was added to the

solution of Ph₃SiLi [prepared from Ph₃SiCl (29.8 g, 101 mmol) and lithium (6.0g, 865 mmol)] in THF (250 mL). After addition of ¹Bu₂MeSiF, then the reaction mixture was heated under reflux for 1 week. After cooling to room temperature, aqueous hydrochloric acid was slowly added to the reactants. The aqueous phase was extracted with Et₂O (100 mL x 3) and combined organic solutions were dried with sodium sulfate and concentrated on a rotary evaporator. The solid precipitate was recrystallized from EtOH to furnish colorless crystals of ¹Bu₂MeSiSiPh₃ (22.2 g, 54%). bp 180-200 °C/0.1 mmHg: ¹H NMR (CDCl₃, δ) 0.40 (s, 3 H), 0.91 (s, 18 H); ¹³C NMR (CDCl₃, δ) -5.1, 21.4, 29.9, 127.6, 128.7, 136.9, 137.2; ²⁹Si NMR (CDCl₃, δ) -20.7, 0.8; MS (*m/z*, relative intensity) 416 (M⁺, 0.4), 359 (M⁺ - ¹Bu, 14), 259 (13), 73 (100).

Preparation of ¹Bu₂MeSiSiBr₃ 2

A mixture of ¹Bu₂MeSiSiPh₃ (11.3 g, 27 mmol), catalytic amount of AlBr₃, and 120 mL of benzene is placed in a 200-mL, three-necked, round bottom flask equipped with a gas inlet tube. Dry hydrogen bromide gas is passed into the vigorously stirred mixture. The process of the reaction was monitored by gas chromatography. If the conversion was not complete, additional AlBr₃ was added and passage of HBr was continued. All solids are removed by filtration through Celite, after changing the solvent to hexane, and the mixture was concentrated in a vacuum. ¹Bu₂MeSiSiBr₃ (**2**) was isolated by Kugelrohr distillation as a colorless solid (11.2 g, 90%). bp 80-100 °C/0.1 mmHg, mp xx-xx °C: ¹H NMR (C₆D₆, δ) 0.11 (s, 3 H), 1.06 (s, 18 H); ¹³C NMR (C₆D₆, δ) -8.3, 21.8, 29.2; ²⁹Si NMR (C₆D₆, δ) -7.5, 21.8; MS (*m/z*, relative intensity) 367 (M⁺ - ¹Bu, 0.5), 326 (1.1), 139 (14), 73 (100).

Synthesis of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene 3

A mixture of **1** (1.01 g, 2.01 mmol) and **2** (1.78 g, 4.19 mmol) in toluene (10 mL) was added to a dispersion of sodium (0.95 g, 41.3 mmol) in toluene (10 mL) at room temperature. The reaction was followed by gas chromatography, with **2** disappearing after three hours. At this time 44% of **1** remained. The resulting salts and excess sodium were removed by filtration, and then the solvent was removed in vacuo to give a dark red solid, which contained cyclotrisilene **3** in 34% yield based on the amount of **1** that had reacted. Pure **3** (130 mg, 9.1%) was obtained as air-sensitive red-orange crystals by recrystallization of the reaction mixture from hexane. mp 207-209 °C; ¹H NMR (C₆D₆, δ) 0.42 (s, 6 H), 0.47 (s, 6 H), 1.20 (s, 36 H), 1.29 (s, 36 H); ¹³C NMR (C₆D₆, δ) -4.7, -2.5, 22.2, 23.2, 29.9, 31.2; ²⁹Si NMR (C₆D₆, δ) -127.3, 7.9, 27.1, 97.7; MS (m/z, relative intensity) 655 (M⁺ - ¹Bu, 0.2), 555 (M⁺ - SiMe¹Bu₂, 8.6), 73 (100), 59 (11); UV/Vis (hexane): λ_{max}/nm (ε) 466 (440), 297 (sh, 1490), 259 (3610), 223 (7490).

X-ray Crystal Structure Determination of 3

A single crystal of **3** for X-ray diffraction was grown from a hexane solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71070 \text{ \AA}$). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement are summarized in Table 1-1a. The final atomic parameters, the bond length, the bond angles, and torsional angles of **3** are listed in Table 1-1b, Table 1-1c, and Table 1-1d, respectively.

Table 1-1a. Crystal data and structure refinement for 3.

Experimental

Compound maxus

Crystal data

$C_{36}H_{84}Si_7$	$D_m = 1.018 \text{ Mg m}^{-3}$
$M_r = 713.67$	X-ray radiation
Monoclinic	$\lambda = 0.71073 \text{ \AA}$
$P2_1/c$	Cell parameters from all reflections
$a = 24.063 (4) \text{ \AA}$	$\theta = 1-41.07^\circ$
$b = 11.629 (2) \text{ \AA}$	$\mu = 0.227 \text{ mm}^{-1}$
$c = 17.715 (3) \text{ \AA}$	$T = 120 \text{ K}$
$\beta = 110.435 (1)^\circ$	Cube
$V = 4645 (2) \text{ \AA}^3$	$0.5 \times 0.35 \times 0.15 \text{ mm}$
$Z = 4$	Red
$D_x = 1.018 \text{ Mg m}^{-3}$	Crystal source: Local laboratory

Data collection

DIP Image plate diffractometer	$[I > 3.00 \text{ sigma}(I)]$
Absorption correction:	$\theta_{\max} = 26.75^\circ$
none	$h = -31 \rightarrow 29$
8796 measured reflections	$k = -15 \rightarrow 0$
8473 independent reflections	$l = 0 \rightarrow 23$
4291 observed reflections	

Refinement

Refinement on F	$(\Delta/\sigma)_{\max} = 0.0947$
$R = 0.071$	$\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
$wR = 0.136$	$\Delta\rho_{\min} = -0.49 \text{ e \AA}^{-3}$
$S = 2.499$	Extinction correction: None
4291 reflections	Atomic scattering factors from
388 parameters	<i>D. Waasmaier&A. Kirfel, Acta Cryst. 1995, A51, 416-431</i>
H-atom parameters not refined	
Count statistics	

Data collection: DIP Image plate. Data reduction: maXus. Program(s) used to solve structure: maXus. Program(s) used to refine structure: maXus. Molecular graphics: maXus. Software used to prepare material for publication: maXus.

Table 1-1b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	Ueq
Si1	0.22030(8)	0.0691(2)	0.25410(9)	0.0410(9)
Si2	0.21440(8)	-0.0650(2)	0.16910(9)	0.0418(9)
Si3	0.31020(7)	0.0000(2)	0.24520(9)	0.0365(9)
Si4	0.16940(8)	0.2166(2)	0.2959(1)	0.042(1)
Si5	0.15370(8)	-0.2074(2)	0.08420(9)	0.0399(9)
Si6	0.34980(8)	0.1313(2)	0.17230(9)	0.0396(9)
Si7	0.37300(8)	-0.1216(2)	0.35010(9)	0.0400(9)
C1	0.2265(3)	0.3253(7)	0.3519(4)	0.067(5)
C2	0.1153(3)	0.2863(6)	0.2006(3)	0.049(4)
C3	0.1518(4)	0.3529(7)	0.1600(5)	0.078(5)
C4	0.0734(3)	0.3692(6)	0.2207(4)	0.060(4)
C5	0.0782(3)	0.1961(7)	0.1399(3)	0.063(4)
C6	0.1338(3)	0.1557(6)	0.3682(3)	0.052(4)
C7	0.1804(4)	0.0787(7)	0.4299(4)	0.082(6)
C8	0.0792(3)	0.0826(7)	0.3264(4)	0.071(5)
C9	0.1174(3)	0.2525(7)	0.4159(4)	0.065(5)
C10	0.2019(3)	-0.3362(6)	0.0862(4)	0.052(4)
C11	0.124(3)	-0.1493(6)	-0.0234(4)	0.049(4)
C12	0.1748(3)	-0.0987(7)	-0.0446(4)	0.068(5)
C13	0.0966(3)	-0.2481(6)	-0.0834(4)	0.058(4)
C14	0.0763(3)	-0.0567(7)	-0.0531(4)	0.061(4)
C15	0.0963(3)	-0.2500(5)	0.1310(3)	0.045(3)
C16	0.1286(3)	-0.3058(6)	0.2131(3)	0.059(4)
C17	0.0607(3)	-0.1471(7)	0.1445(4)	0.067(5)
C18	0.0527(3)	-0.3395(6)	0.0780(4)	0.056(4)
C19	0.2828(3)	0.2135(6)	0.1062(4)	0.054(4)
C20	0.4009(3)	0.2442(6)	0.2406(3)	0.052(4)
C21	0.3810(5)	0.2703(8)	0.3109(5)	0.106(7)
C22	0.4016(3)	0.3577(6)	0.1959(4)	0.058(4)
C23	0.4666(4)	0.2047(7)	0.2739(4)	0.074(5)
C24	0.3814(3)	0.0556(6)	0.0995(3)	0.044(3)
C25	0.4331(3)	-0.0256(6)	0.1407(4)	0.066(5)
C26	0.3315(3)	-0.0172(6)	0.0419(4)	0.062(4)
C27	0.4016(3)	0.1428(6)	0.0492(4)	0.057(4)
C28	0.4533(3)	-0.3058(6)	0.3674(4)	0.055(4)
C29	0.3621(3)	-0.3058(6)	0.4514(3)	0.048(4)
C30	0.3651(4)	0.0423(6)	0.4630(4)	0.063(4)
C31	0.4105(3)	-0.1429(7)	0.5230(3)	0.062(5)
C32	0.3021(3)	-0.1311(7)	0.4524(4)	0.063(5)
C33	0.3621(3)	-0.2790(6)	0.3165(3)	0.046(4)
C34	0.3000(3)	-0.3263(6)	0.3093(4)	0.058(4)
C35	0.4090(3)	-0.3584(6)	0.3731(4)	0.057(4)
C36	0.3661(3)	-0.2875(6)	0.2314(4)	0.061(4)

Table 1-1c. Bond lengths [\AA] and angles [deg] for 3

INTRAMOLECULAR BOND LENGTHS (H omitted)

Bond length limits based on covalent radii			
Si(1)-Si(2)	2.138(3)	Si(1)-Si(3)	2.364(3)
Si(1)-Si(4)	2.371(3)	Si(2)-Si(3)	2.352(3)
Si(2)-Si(5)	2.367(3)	Si(3)-Si(6)	2.401(3)
Si(3)-Si(7)	2.403(3)	Si(4)-C(1)	1.876(8)
Si(4)-C(2)	1.915(7)	Si(4)-C(6)	1.908(7)
Si(5)-C(10)	1.887(8)	Si(5)-C(11)	1.910(7)
Si(5)-C(15)	1.908(7)	Si(6)-C(19)	1.888(7)
Si(6)-C(20)	1.913(7)	Si(6)-C(24)	1.924(7)
Si(7)-C(28)	1.889(7)	Si(7)-C(29)	1.938(6)
Si(7)-C(33)	1.914(7)	C(2)-C(3)	1.53(2)
C(2)-C(4)	1.52(1)	C(2)-C(5)	1.54(1)
C(6)-C(7)	1.55(2)	C(6)-C(8)	1.52(2)
C(6)-C(9)	1.54(1)	C(11)-C(12)	1.52(2)
C(11)-C(13)	1.55(1)	C(11)-C(14)	1.53(2)
C(15)-C(16)	1.533(9)	C(15)-C(17)	1.54(1)
C(15)-C(18)	1.54(1)	C(20)-C(21)	1.51(2)
C(20)-C(22)	1.54(1)	C(20)-C(23)	1.55(2)
C(24)-C(25)	1.53(1)	C(24)-C(26)	1.53(1)
C(24)-C(27)	1.54(1)	C(29)-C(30)	1.55(1)
C(29)-C(31)	1.52(1)	C(29)-C(32)	1.53(1)
C(33)-C(34)	1.56(1)	C(33)-C(35)	1.53(1)
C(33)-C(36)	1.547(9)		

INTRAMOLECULAR BOND ANGLES (H omitted)

Bond length limits based on covalent radii			
Si(2)-Si(1)-Si(3)	62.8(1)	Si(2)-Si(1)-Si(4)	146.4(2)
Si(3)-Si(1)-Si(4)	148.3(1)	Si(1)-Si(2)-Si(3)	63.3(1)
Si(1)-Si(2)-Si(5)	146.3(2)	Si(3)-Si(2)-Si(5)	148.5(2)
Si(1)-Si(3)-Si(2)	53.9(1)	Si(1)-Si(3)-Si(6)	111.3(1)
Si(1)-Si(3)-Si(7)	119.4(1)	Si(2)-Si(3)-Si(6)	112.9(1)
Si(2)-Si(3)-Si(7)	118.7(1)	Si(6)-Si(3)-Si(7)	122.0(1)
Si(1)-Si(4)-C(1)	106.8(3)	Si(1)-Si(4)-C(2)	107.3(3)
Si(1)-Si(4)-C(6)	110.1(3)	C(1)-Si(4)-C(2)	109.1(4)
C(1)-Si(4)-C(6)	108.2(4)	C(2)-Si(4)-C(6)	115.0(3)
Si(2)-Si(5)-C(10)	107.7(3)	Si(2)-Si(5)-C(11)	108.6(3)
Si(2)-Si(5)-C(15)	106.6(2)	C(10)-Si(5)-C(11)	108.2(3)
C(10)-Si(5)-C(15)	108.6(3)	C(11)-Si(5)-C(15)	116.7(3)
Si(3)-Si(6)-C(19)	104.0(3)	Si(3)-Si(6)-C(20)	112.6(2)
Si(3)-Si(6)-C(24)	113.2(3)	C(19)-Si(6)-C(20)	105.4(4)
C(19)-Si(6)-C(24)	105.5(3)	C(20)-Si(6)-C(24)	114.9(3)
Si(3)-Si(7)-C(28)	109.5(3)	Si(3)-Si(7)-C(29)	110.6(3)
Si(3)-Si(7)-C(33)	110.0(2)	C(28)-Si(7)-C(29)	105.7(3)
C(28)-Si(7)-C(33)	105.7(3)	C(29)-Si(7)-C(33)	115.0(3)
Si(4)-C(2)-C(3)	107.7(5)	Si(4)-C(2)-C(4)	111.3(5)
Si(4)-C(2)-C(5)	112.1(5)	C(3)-C(2)-C(4)	109.0(6)
C(3)-C(2)-C(5)	107.7(6)	C(4)-C(2)-C(5)	108.9(6)
Si(4)-C(6)-C(7)	107.7(6)	Si(4)-C(6)-C(8)	113.2(5)
Si(4)-C(6)-C(9)	111.0(5)	C(7)-C(6)-C(8)	108.0(6)
C(7)-C(6)-C(9)	107.3(6)	C(8)-C(6)-C(9)	109.4(6)
Si(5)-C(11)-C(12)	109.3(5)	Si(5)-C(11)-C(13)	110.1(5)
Si(5)-C(11)-C(14)	112.6(5)	C(12)-C(11)-C(13)	107.7(6)
C(12)-C(11)-C(14)	108.9(6)	C(13)-C(11)-C(14)	108.0(6)
Si(5)-C(15)-C(16)	108.5(5)	Si(5)-C(15)-C(17)	113.1(5)
Si(5)-C(15)-C(18)	110.6(5)	C(16)-C(15)-C(17)	107.9(6)
C(16)-C(15)-C(18)	107.7(6)	C(17)-C(15)-C(18)	108.8(6)
Si(6)-C(20)-C(21)	109.9(6)	Si(6)-C(20)-C(22)	112.5(5)
Si(6)-C(20)-C(23)	112.4(5)	C(21)-C(20)-C(22)	108.3(6)
C(21)-C(20)-C(23)	108.6(6)	C(22)-C(20)-C(23)	104.8(6)
Si(6)-C(24)-C(25)	114.1(5)	Si(6)-C(24)-C(26)	107.4(5)
Si(6)-C(24)-C(27)	111.5(5)	C(25)-C(24)-C(26)	107.1(6)
C(25)-C(24)-C(27)	108.4(6)	C(26)-C(24)-C(27)	108.2(5)
Si(7)-C(29)-C(30)	107.4(5)	Si(7)-C(29)-C(31)	112.4(5)
Si(7)-C(29)-C(32)	112.6(5)	C(30)-C(29)-C(31)	107.9(6)
C(30)-C(29)-C(32)	108.2(6)	C(31)-C(29)-C(32)	108.2(6)
Si(7)-C(33)-C(34)	112.8(5)	Si(7)-C(33)-C(35)	112.6(5)
Si(7)-C(33)-C(36)	108.4(5)	C(34)-C(33)-C(35)	107.9(6)
C(34)-C(33)-C(36)	106.4(5)	C(35)-C(33)-C(36)	108.5(6)

Table 1-1d. Torsional angles [deg] for 3

INTRAMOLECULAR TORSION ANGLES (H omitted)			
Bond length limits based on covalent radii			
Si(2)-Si(1)-Si(3)-Si(2)	0.0(1)	Si(3)-Si(1)-Si(2)-Si(3)	0.0(1)
Si(3)-Si(1)-Si(2)-Si(5)	165.3(3)	Si(2)-Si(1)-Si(3)-Si(6)	103.5(2)
Si(2)-Si(1)-Si(3)-Si(7)	-105.7(2)	Si(4)-Si(1)-Si(2)-Si(3)	162.8(3)
Si(4)-Si(1)-Si(2)-Si(5)	-31.9(2)	Si(2)-Si(1)-Si(4)-C(1)	-154.8(4)
Si(2)-Si(1)-Si(4)-C(2)	-37.8(3)	Si(2)-Si(1)-Si(4)-C(6)	87.9(3)
Si(4)-Si(1)-Si(3)-Si(2)	-161.8(3)	Si(4)-Si(1)-Si(3)-Si(6)	-58.4(2)
Si(4)-Si(1)-Si(3)-Si(7)	92.5(2)	Si(3)-Si(1)-Si(4)-C(1)	-4.9(3)
Si(3)-Si(1)-Si(4)-C(2)	112.1(3)	Si(3)-Si(1)-Si(4)-C(6)	-122.1(3)
Si(1)-Si(2)-Si(3)-Si(1)	0.0(1)	Si(1)-Si(2)-Si(3)-Si(6)	-100.4(2)
Si(1)-Si(2)-Si(3)-Si(7)	107.1(2)	Si(1)-Si(2)-Si(5)-C(10)	-143.3(3)
Si(1)-Si(2)-Si(5)-C(11)	99.7(3)	Si(1)-Si(2)-Si(5)-C(15)	-26.9(3)
Si(5)-Si(2)-Si(3)-Si(1)	-164.4(3)	Si(5)-Si(2)-Si(3)-Si(6)	95.2(2)
Si(5)-Si(2)-Si(3)-Si(7)	-57.3(2)	Si(3)-Si(2)-Si(5)-C(10)	11.0(3)
Si(3)-Si(2)-Si(5)-C(11)	-106.0(3)	Si(3)-Si(2)-Si(5)-C(15)	127.5(3)
Si(1)-Si(3)-Si(6)-C(19)	-24.6(3)	Si(1)-Si(3)-Si(6)-C(20)	89.0(3)
Si(1)-Si(3)-Si(6)-C(24)	-138.6(3)	Si(1)-Si(3)-Si(7)-C(28)	-143.8(3)
Si(1)-Si(3)-Si(7)-C(29)	-27.6(3)	Si(1)-Si(3)-Si(7)-C(33)	100.5(3)
Si(2)-Si(3)-Si(6)-C(19)	34.0(3)	Si(2)-Si(3)-Si(6)-C(20)	147.6(3)
Si(2)-Si(3)-Si(6)-C(24)	-80.0(3)	Si(2)-Si(3)-Si(7)-C(28)	153.8(3)
Si(2)-Si(3)-Si(7)-C(29)	-90.1(3)	Si(2)-Si(3)-Si(7)-C(33)	38.0(3)
Si(7)-Si(3)-Si(6)-C(19)	-174.6(3)	Si(7)-Si(3)-Si(6)-C(20)	-60.9(3)
Si(7)-Si(3)-Si(6)-C(24)	71.4(3)	Si(6)-Si(3)-Si(7)-C(28)	3.9(3)
Si(6)-Si(3)-Si(7)-C(29)	120.0(3)	Si(6)-Si(3)-Si(7)-C(33)	-111.9(3)
Si(1)-Si(4)-C(2)-C(3)	-69.7(5)	Si(1)-Si(4)-C(2)-C(4)	170.9(5)
Si(1)-Si(4)-C(2)-C(5)	48.6(5)	Si(1)-Si(4)-C(6)-C(7)	45.4(5)
Si(1)-Si(4)-C(6)-C(8)	-73.9(5)	Si(1)-Si(4)-C(6)-C(9)	162.6(6)
C(1)-Si(4)-C(2)-C(3)	45.7(5)	C(1)-Si(4)-C(2)-C(4)	-73.7(5)
C(1)-Si(4)-C(2)-C(5)	164.1(6)	C(1)-Si(4)-C(6)-C(7)	-71.0(6)
C(1)-Si(4)-C(6)-C(8)	169.6(6)	C(1)-Si(4)-C(6)-C(9)	46.2(5)
C(6)-Si(4)-C(2)-C(3)	167.5(6)	C(6)-Si(4)-C(2)-C(4)	48.1(5)
C(6)-Si(4)-C(2)-C(5)	-74.1(5)	C(2)-Si(4)-C(6)-C(7)	166.7(6)
C(2)-Si(4)-C(6)-C(8)	47.3(5)	C(2)-Si(4)-C(6)-C(9)	-76.2(5)
Si(2)-Si(5)-C(11)-C(12)	48.6(5)	Si(2)-Si(5)-C(11)-C(13)	166.8(5)
Si(2)-Si(5)-C(11)-C(14)	-72.6(5)	Si(2)-Si(5)-C(15)-C(16)	-64.4(4)
Si(2)-Si(5)-C(15)-C(17)	55.3(5)	Si(2)-Si(5)-C(15)-C(18)	177.7(5)
C(10)-Si(5)-C(11)-C(12)	-68.1(5)	C(10)-Si(5)-C(11)-C(13)	50.1(5)
C(10)-Si(5)-C(11)-C(14)	170.7(6)	C(10)-Si(5)-C(15)-C(16)	51.5(5)
C(10)-Si(5)-C(15)-C(17)	171.1(6)	C(10)-Si(5)-C(15)-C(18)	-66.5(5)
C(15)-Si(5)-C(11)-C(12)	169.0(6)	C(15)-Si(5)-C(11)-C(13)	-72.8(5)
C(15)-Si(5)-C(11)-C(14)	47.9(5)	C(11)-Si(5)-C(15)-C(16)	174.1(6)
C(11)-Si(5)-C(15)-C(17)	-66.2(5)	C(11)-Si(5)-C(15)-C(18)	56.2(5)
Si(3)-Si(6)-C(20)-C(21)	-30.9(5)	Si(3)-Si(6)-C(20)-C(22)	-151.7(6)

Table 1-1d (continued). Torsional angles [deg] for 3

Si(3)-Si(6)-C(20)-C(23)	90.2(5)	Si(3)-Si(6)-C(24)-C(25)	-61.5(5)
Si(3)-Si(6)-C(24)-C(26)	57.1(4)	Si(3)-Si(6)-C(24)-C(27)	175.4(5)
C(19)-Si(6)-C(20)-C(21)	81.8(6)	C(19)-Si(6)-C(20)-C(22)	-38.9(5)
C(19)-Si(6)-C(20)-C(23)	-157.0(6)	C(19)-Si(6)-C(24)-C(25)	-174.6(6)
C(19)-Si(6)-C(24)-C(26)	-56.0(5)	C(19)-Si(6)-C(24)-C(27)	62.3(5)
C(24)-Si(6)-C(20)-C(21)	-162.4(7)	C(24)-Si(6)-C(20)-C(22)	76.8(5)
C(24)-Si(6)-C(20)-C(23)	-41.3(5)	C(20)-Si(6)-C(24)-C(25)	69.8(5)
C(20)-Si(6)-C(24)-C(26)	-171.7(6)	C(20)-Si(6)-C(24)-C(27)	-53.4(5)
Si(3)-Si(7)-C(29)-C(30)	-48.0(4)	Si(3)-Si(7)-C(29)-C(31)	-166.4(6)
Si(3)-Si(7)-C(29)-C(32)	71.0(5)	Si(3)-Si(7)-C(33)-C(34)	-68.7(5)
Si(3)-Si(7)-C(33)-C(35)	168.8(5)	Si(3)-Si(7)-C(33)-C(36)	48.8(4)
C(28)-Si(7)-C(29)-C(30)	70.5(5)	C(28)-Si(7)-C(29)-C(31)	-48.0(5)
C(28)-Si(7)-C(29)-C(32)	-170.5(6)	C(28)-Si(7)-C(33)-C(34)	173.1(6)
C(28)-Si(7)-C(33)-C(35)	50.7(5)	C(28)-Si(7)-C(33)-C(36)	-69.3(5)
C(33)-Si(7)-C(29)-C(30)	-173.3(6)	C(33)-Si(7)-C(29)-C(31)	68.3(5)
C(33)-Si(7)-C(29)-C(32)	-54.3(5)	C(29)-Si(7)-C(33)-C(34)	56.8(5)
C(29)-Si(7)-C(33)-C(35)	-65.6(5)	C(29)-Si(7)-C(33)-C(36)	174.4(6)

Synthesis of *trans*-1,2-dichoro-1,2,3,3-tetrakis[di-*tert*-butyl(methyl)silyl]-cyclotrisilane (**4a**)

An excess of dry CCl_4 (1.0 mL) was added through a vacuum transfer to a cyclotrisilene **3** (50 mg, 0.070 mmol). Reaction immediately took place after melting of CCl_4 at low temperature, and the color of the reaction mixture was changed from red to yellow. The resulting 1,2-dichlorocyclotrisilane **4a** was isolated after evaporation of CCl_4 as yellow crystals in 91% (50 mg) yield, mp 222 °C (dec.). ^1H NMR (C_6D_6 , δ) 0.42 (s, 6 H), 0.46 (s, 6 H), 1.27 (s, 18 H), 1.29 (s, 18 H), 1.30 (s, 18 H), 1.35 (s, 18 H); ^{13}C NMR (C_6D_6 , δ) -3.3, 3.0, 22.8, 23.1, 23.3, 23.6, 30.2, 30.4, 31.0, 31.6; ^{29}Si NMR (C_6D_6 , δ) -127.1, -37.2, 21.9, 27.0; Anal. Calcd. for $\text{C}_{36}\text{H}_{84}\text{Cl}_2\text{Si}_7$: C, 55.11; H, 10.79. Found: C, 54.92; H, 10.90.

Synthesis of *trans*-1,2-dibromo-1,2,3,3-tetrakis[di-*tert*-butyl(methyl)silyl]-cyclotrisilane (**4b**)

An excess of dry 1,2-dibromoethane (1.0 mL) was added through a vacuum transfer to a toluene solution (1.0 mL) of cyclotrisilene **3** (37 mg, 0.052 mmol). Reaction immediately took place at low temperature, and the color of the reaction mixture was changed from red to yellow. The resulting 1,2-dibromocyclotrisilane **4b** was isolated after evaporation of 1,2-dibromoethane as yellow crystals in 88% (40 mg) yield, mp 207 °C (dec.). ^1H NMR (C_7D_8 , δ) 0.42 (s, 6 H), 0.51 (s, 6 H), 1.24 (s, 18 H), 1.287 (s, 18 H), 1.294 (s, 18 H), 1.35 (s, 18 H); ^{13}C NMR (C_7D_8 , δ) -2.4, 4.5, 22.9, 23.7, 23.8, 23.9, 30.5, 30.6, 31.2, 31.9; ^{29}Si NMR (C_7D_8 , δ) -125.9, -53.2, 21.0, 27.8; Anal. Calcd. for $\text{C}_{36}\text{H}_{84}\text{Br}_2\text{Si}_7$: C, 49.50; H, 9.69. Found: C, 49.88; H, 9.92.

X-ray Crystal Structure Determination of 4a

A single crystal of **4a** for X-ray diffraction was grown from a hexane solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement are summarized in Table 1-2a. The final atomic parameters, the bond length, and the bond angles of **4a** are listed in Table 1-2b and Table 1-2c, respectively.

Table 1-2a. Crystal data and structure refinement for 4a

Empirical formula	C ₃₆ H ₈₄ Cl ₂ Si ₇
Formula weight	784.56
Temperature	150 K
Wavelength	0.71070 Å
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 22.9370(8) Å alpha = 90 deg. b = 13.0280(3) Å beta = 114.888(2) deg. c = 18.0070(6) Å gamma = 90 deg.
Volume	4881.2(3) Å ³
Z, Calculated density	4, 1.068 Mg/m ³
Absorption coefficient	0.327 mm ⁻¹
F(000)	1728
Crystal size	0.25 x 0.1 x 0.1 mm
Theta range for data collection	2.44 to 27.94 deg.
Limiting indices	0<=h<=30, 0<=k<=17, -23<=l<=21
Reflections collected / unique	6076 / 5821 [R(int) = 0.0000]
Completeness to theta = 27.94	99.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5821 / 0 / 205
Goodness-of-fit on F ²	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1488
R indices (all data)	R1 = 0.0617, wR2 = 0.1575
Extinction coefficient	0.0106(8)
Largest diff. peak and hole	0.630 and -0.476 e.Å ⁻³

Table 1-2b.

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	5291(1)	-358(1)	1221(1)	33(1)
Si(1)	5000	1619(1)	2500	19(1)
Si(2)	5494(1)	-9(1)	2454(1)	20(1)
Si(3)	4533(1)	2442(1)	1154(1)	25(1)
Si(4)	6502(1)	-887(1)	3215(1)	27(1)
C(1)	4101(1)	1388(2)	416(1)	38(1)
C(2)	5136(1)	3026(2)	769(1)	32(1)
C(3)	4821(2)	2998(2)	-176(2)	44(1)
C(4)	5745(1)	2376(2)	1070(2)	51(1)
C(5)	5334(2)	4149(2)	1013(2)	50(1)
C(6)	3872(1)	3379(2)	1114(2)	46(1)
C(7)	3537(2)	3895(3)	272(2)	61(1)
C(8)	3369(2)	2759(4)	1277(3)	82(1)
C(9)	4128(2)	4213(3)	1757(2)	79(1)
C(10)	6901(1)	-451(2)	4311(2)	47(1)
C(11)	6324(1)	-2326(2)	3244(2)	34(1)
C(12)	6954(1)	-2949(2)	3599(2)	48(1)
C(13)	5886(2)	-2760(2)	2403(2)	53(1)
C(14)	6000(2)	-2472(2)	3833(2)	52(1)
C(15)	7083(1)	-552(2)	2725(2)	47(1)
C(16)	7780(1)	-787(3)	3325(3)	68(1)
C(17)	6949(2)	-1139(3)	1936(2)	71(1)
C(18)	7037(2)	603(3)	2541(3)	82(1)

Table 1-2c. Bond lengths [Å] and angles [deg] for **4a**

Cl(1)-Si(2)	2.1171(7)	Si(1)-Si(2')	2.4223(8)	Si(1)-Si(2)	2.4223(8)
Si(1)-Si(3)	2.4464(6)	Si(1)-Si(3')	2.4464(6)	Si(2)-Si(2')	2.3388(10)
Si(2)-Si(4)	2.4216(7)	Si(3)-C(1)	1.877(2)	Si(3)-C(6)	1.924(3)
Si(3)-C(2)	1.943(2)	Si(4)-C(10)	1.880(3)	Si(4)-C(11)	1.925(2)
Si(4)-C(15)	1.932(3)	C(2)-C(4)	1.526(4)	C(2)-C(5)	1.540(3)
C(2)-C(3)	1.545(3)	C(6)-C(9)	1.514(5)	C(6)-C(7)	1.536(4)
C(6)-C(8)	1.537(5)	C(11)-C(13)	1.531(4)	C(11)-C(12)	1.542(3)
C(11)-C(14)	1.540(4)	C(15)-C(17)	1.527(5)	C(15)-C(18)	1.534(5)
C(15)-C(16)	1.538(4)				
Si(2)#1-Si(1)-Si(2)	57.73(3)			Si(2)#1-Si(1)-Si(3)	113.66(2)
Si(2)-Si(1)-Si(3)	111.46(2)			Si(2)#1-Si(1)-Si(3)#1	111.46(2)
Si(2)-Si(1)-Si(3)#1	113.67(2)			Si(3)-Si(1)-Si(3)#1	128.04(4)
Cl(1)-Si(2)-Si(2)#1	106.38(3)			Cl(1)-Si(2)-Si(4)	103.17(3)
Si(2)#1-Si(2)-Si(4)	133.06(3)			Cl(1)-Si(2)-Si(1)	108.89(3)
Si(2)#1-Si(2)-Si(1)	61.132(14)			Si(4)-Si(2)-Si(1)	137.99(3)
C(1)-Si(3)-C(6)	105.33(13)			C(1)-Si(3)-C(2)	106.07(11)
C(6)-Si(3)-C(2)	113.90(12)			C(1)-Si(3)-Si(1)	105.17(8)
C(6)-Si(3)-Si(1)	108.95(8)			C(2)-Si(3)-Si(1)	116.40(7)
C(10)-Si(4)-C(11)	106.27(12)			C(10)-Si(4)-C(15)	106.61(14)
C(11)-Si(4)-C(15)	115.30(12)			C(10)-Si(4)-Si(2)	112.26(8)
C(11)-Si(4)-Si(2)	108.23(8)			C(15)-Si(4)-Si(2)	108.25(8)
C(4)-C(2)-C(5)	108.0(2)			C(4)-C(2)-C(3)	108.2(2)
C(5)-C(2)-C(3)	106.3(2)			C(4)-C(2)-Si(3)	109.79(15)
C(5)-C(2)-Si(3)	116.10(18)			C(3)-C(2)-Si(3)	108.10(16)
C(9)-C(6)-C(7)	108.2(3)			C(9)-C(6)-C(8)	108.1(3)
C(7)-C(6)-C(8)	108.3(3)			C(9)-C(6)-Si(3)	112.4(2)
C(7)-C(6)-Si(3)	112.04(19)			C(8)-C(6)-Si(3)	107.6(2)
C(13)-C(11)-C(12)	109.1(2)			C(13)-C(11)-C(14)	109.2(3)
C(12)-C(11)-C(14)	106.8(2)			C(13)-C(11)-Si(4)	113.03(17)
C(12)-C(11)-Si(4)	110.61(18)			C(14)-C(11)-Si(4)	107.93(17)
C(17)-C(15)-C(18)	108.8(3)			C(17)-C(15)-C(16)	107.2(3)
C(18)-C(15)-C(16)	107.7(3)			C(17)-C(15)-Si(4)	113.9(2)
C(18)-C(15)-Si(4)	108.8(2)			C(16)-C(15)-Si(4)	110.3(2)

Synthesis of 4,7-diphenyl-1,2,2,5-tetrakis[di-*tert*-butyl(methyl)silyl]-1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene (**5a**)

The red-orange crystals of **3** (36 mg, 0.05 mmol) were placed in a reaction vessel with a magnetic stirrer. Degassed phenylacetylene (0.15 mL, 1.59 mmol) was introduced by vacuum transfer, and the mixture was stirred for 15 h at room temperature. The solvent and excess phenylacetylene were removed in vacuo, the resulting residue being separated by a gel permeation chromatography to give **5a** (30 mg, 65%) as colorless crystals; mp 168 °C (dec); MS (EI, 70 eV) m/z (%) 916 (M⁺, 0.5), 859 (1.1), 759 (25), 158 (11), 73 (100); ¹H NMR (C₆D₆, δ) 0.15 (s, 3 H), 0.31 (s, 3 H), 0.50 (s, 3 H), 0.67 (s, 3 H), 0.89 (s, 9 H), 0.96 (s, 9 H), 1.05 (s, 9 H), 1.13 (s, 9 H), 1.14 (s, 9 H), 1.278 (s, 9 H), 1.282 (s, 9 H), 1.38 (s, 9 H), 7.02—7.08 (m, 2 H), 7.22—7.24 (m, 4 H), 7.42 (s, 1 H), 7.51—7.54 (m, 2 H), 7.72—7.75 (m, 2 H), 7.98 (s, 1 H); ¹³C NMR (C₆D₆, δ) –3.5, –1.7, –1.2, –0.6, 21.7, 22.1, 22.4, 22.6, 22.7, 23.6, 23.71, 23.74, 30.0 (2 C), 30.4, 31.3, 31.7 (2 C), 31.86, 31.94, 126.4, 126.9, 127.8, 128.1, 128.5, 128.7, 142.2, 150.4, 153.2, 155.7, 162.4, 167.4; ²⁹Si NMR (C₆D₆, δ) –54.8, –23.9, –21.1, 9.6, 16.4, 19.7, 21.7; Anal. Calcd for C₅₂H₉₆Si₇: C, 68.04; H, 10.54. Found: C, 68.34; H, 10.21.

X-ray Crystal Structure Determination of **5a**

A single crystal of **5a** for X-ray diffraction was grown from a hexane solution. Diffraction data were collected at 150 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71070 \text{ \AA}$). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement are summarized in Table 1-3a. The final atomic parameters, the bond length, and the bond angles of **5a** are listed in Table 1-3b and Table 1-3c, respectively.

Table 1-3a. Crystal data and structure refinement for **5a**

Empirical formula	$C_{52}H_{96}Si_7$		
Formula weight	917.92		
Temperature	150 K		
Wavelength	0.71070 Å		
Crystal system, space group	Triclinic, P -1		
Unit cell dimensions	$a = 13.7380(8)$ Å	$b = 14.6250(9)$ Å	$c = 15.751(1)$ Å
			alpha = 99.765(3) deg. beta = 114.847(3) deg. gamma = 92.241(3) deg.
Volume	2808.5(3) Å ³		
Z, Calculated density	2, 1.085 Mg/m ³		
Absorption coefficient	0.201 mm ⁻¹		
F(000)	1012		
Crystal size	0.5 x 0.3 x 0.2 mm		
Theta range for data collection	2.12 to 27.95 deg.		
Limiting indices	0<=h<=18, -19<=k<=19, -20<=l<=18		
Reflections collected / unique	26823 / 12169 [R(int) = 0.0240]		
Completeness to theta = 27.94	90.2 %		
Absorption correction	None		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	12169 / 0 / 533		
Goodness-of-fit on F ²	1.014		
Final R indices [I>2sigma(I)]	R1 = 0.0705, wR2 = 0.1851		
R indices (all data)	R1 = 0.0843, wR2 = 0.2051		
Extinction coefficient	0.0211(19)		
Largest diff. peak and hole	3.578 and -1.310 e.Å ⁻³		

Table 1-3b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si(1)	6998(1)	1960(1)	3441(1)	25(1)
Si(2)	6670(1)	3216(1)	2514(1)	23(1)
Si(3)	7824(1)	2677(1)	1800(1)	23(1)
Si(4)	5476(1)	708(1)	2727(1)	29(1)
Si(5)	8213(1)	2425(1)	5176(1)	38(1)
Si(6)	6644(1)	4893(1)	2988(1)	28(1)
Si(7)	9183(1)	3493(1)	1501(1)	28(1)
C(1)	8188(2)	1553(2)	2262(2)	25(1)
C(2)	7883(2)	1353(2)	2928(2)	29(1)
C(3)	5732(2)	2699(2)	1176(2)	25(1)
C(4)	6414(2)	2423(2)	789(2)	26(1)
C(5)	8778(2)	874(2)	1900(2)	28(1)
C(6)	8419(3)	526(2)	923(2)	33(1)
C(7)	8987(3)	-93(2)	587(3)	42(1)
C(8)	9921(3)	-373(2)	1227(3)	48(1)
C(9)	10279(3)	-47(3)	2200(3)	49(1)
C(10)	9708(3)	560(2)	2533(3)	40(1)
C(11)	4538(2)	2632(2)	625(2)	26(1)
C(12)	3954(2)	3275(2)	908(2)	32(1)
C(13)	2836(3)	3234(2)	396(3)	39(1)
C(14)	2285(3)	2527(3)	-401(2)	40(1)
C(15)	2843(3)	1874(2)	-693(2)	37(1)
C(16)	3958(2)	1926(2)	-197(2)	30(1)
C(17)	5276(3)	430(2)	1446(2)	34(1)
C(18)	4144(3)	1117(2)	2714(2)	36(1)
C(19)	4215(3)	2184(2)	2820(2)	35(1)
C(20)	3190(3)	689(3)	1737(3)	53(1)
C(21)	3846(4)	874(3)	3495(3)	53(1)
C(22)	5763(3)	-471(2)	3149(3)	41(1)
C(23)	4766(4)	-1198(2)	2548(3)	55(1)
C(24)	6053(5)	-393(3)	4215(3)	64(1)
C(25)	6700(3)	-851(2)	2980(3)	47(1)
C(26)	8866(3)	3651(2)	5310(3)	46(1)
C(27)	7470(3)	2465(2)	5997(2)	36(1)
C(28)	6274(4)	2526(5)	5435(4)	79(2)
C(29)	7905(6)	3357(3)	6763(4)	82(2)
C(30)	7552(4)	1656(3)	6498(3)	55(1)
C(31)	9459(3)	1756(3)	5597(3)	44(1)
C(32)	10173(3)	2107(3)	6678(3)	58(1)
C(33)	9157(3)	696(3)	5399(3)	54(1)
C(34)	10151(3)	1973(3)	5076(3)	45(1)
C(35)	8117(3)	5315(2)	3780(2)	39(1)
C(36)	5878(3)	5227(3)	3750(2)	42(1)
C(37)	6370(4)	4788(4)	4633(3)	62(1)
C(38)	4663(3)	4881(3)	3246(3)	49(1)
C(39)	6046(4)	6296(3)	4121(3)	56(1)
C(40)	6212(3)	5537(2)	1921(2)	33(1)
C(41)	5068(3)	5830(2)	1565(3)	43(1)
C(42)	7005(4)	6441(2)	2241(3)	47(1)
C(43)	6283(3)	4932(2)	1055(2)	36(1)
C(44)	9291(3)	4792(2)	1930(3)	44(1)
C(45)	8749(3)	3290(2)	143(2)	35(1)
C(46)	7787(4)	3843(3)	-302(3)	51(1)
C(47)	9675(4)	3649(3)	-68(3)	52(1)
C(48)	8387(3)	2256(2)	-358(2)	41(1)
C(49)	10608(3)	3181(2)	2245(3)	38(1)
C(50)	11497(3)	3959(3)	2411(3)	53(1)
C(51)	10858(3)	2266(2)	1783(3)	42(1)
C(52)	10683(3)	3099(3)	3232(3)	46(1)

Table 1-3c. Bond lengths [Å] and angles [deg] for **5a**

Si(1)-C(2)	1.893(3)	Si(1)-Si(4)	2.4525(11)	Si(1)-Si(2)	2.4767(10)
Si(1)-Si(5)	2.4819(12)	Si(2)-C(3)	1.943(3)	Si(2)-Si(3)	2.3877(10)
Si(2)-Si(6)	2.4454(10)	Si(3)-C(4)	1.892(3)	Si(3)-C(1)	1.909(3)
Si(3)-Si(7)	2.4257(10)	Si(4)-C(17)	1.887(3)	Si(4)-C(18)	1.940(3)
Si(4)-C(22)	1.947(3)	Si(5)-C(26)	1.911(3)	Si(5)-C(31)	1.931(4)
Si(5)-C(27)	1.951(3)	Si(6)-C(35)	1.884(4)	Si(6)-C(36)	1.921(4)
Si(6)-C(40)	1.951(3)	Si(7)-C(44)	1.883(3)	Si(7)-C(45)	1.928(3)
Si(7)-C(49)	1.932(3)	C(1)-C(2)	1.351(4)	C(1)-C(5)	1.493(4)
C(3)-C(4)	1.356(4)	C(3)-C(11)	1.488(4)	C(5)-C(6)	1.396(4)
C(5)-C(10)	1.403(4)	C(6)-C(7)	1.396(5)	C(7)-C(8)	1.387(6)
C(8)-C(9)	1.385(6)	C(9)-C(10)	1.385(5)	C(11)-C(12)	1.393(4)
C(11)-C(16)	1.412(4)	C(12)-C(13)	1.396(4)	C(13)-C(14)	1.385(5)
C(14)-C(15)	1.384(5)	C(15)-C(16)	1.389(4)	C(18)-C(19)	1.534(4)
C(18)-C(20)	1.546(5)	C(18)-C(21)	1.540(5)	C(22)-C(23)	1.535(5)
C(22)-C(24)	1.537(5)	C(22)-C(25)	1.528(5)	C(27)-C(30)	1.513(5)
C(27)-C(28)	1.519(6)	C(27)-C(29)	1.522(6)	C(31)-C(33)	1.533(5)
C(31)-C(32)	1.545(5)	C(31)-C(34)	1.547(5)	C(36)-C(38)	1.536(6)
C(36)-C(37)	1.533(5)	C(36)-C(39)	1.545(5)	C(40)-C(41)	1.537(5)
C(40)-C(43)	1.536(4)	C(40)-C(42)	1.545(5)	C(45)-C(47)	1.538(5)
C(45)-C(48)	1.539(5)	C(45)-C(46)	1.545(5)	C(49)-C(51)	1.535(5)
C(49)-C(52)	1.541(5)	C(49)-C(50)	1.541(5)		
C(2)-Si(1)-Si(4)	96.85(9)	C(2)-Si(1)-Si(2)	95.83(9)	Si(4)-Si(1)-Si(2)	111.83(4)
C(2)-Si(1)-Si(5)	103.31(10)	Si(4)-Si(1)-Si(5)	124.71(4)	Si(2)-Si(1)-Si(5)	116.46(4)
C(3)-Si(2)-Si(3)	73.72(9)	C(3)-Si(2)-Si(6)	113.75(8)	Si(3)-Si(2)-Si(6)	120.08(4)
C(3)-Si(2)-Si(1)	109.77(8)	Si(3)-Si(2)-Si(1)	92.57(3)	Si(6)-Si(2)-Si(1)	131.02(4)
C(4)-Si(3)-C(1)	107.81(12)	C(4)-Si(3)-Si(2)	75.04(9)	C(1)-Si(3)-Si(2)	101.67(9)
C(4)-Si(3)-Si(7)	116.33(9)	C(1)-Si(3)-Si(7)	115.92(9)	Si(2)-Si(3)-Si(7)	132.27(4)
C(17)-Si(4)-C(18)	107.02(15)	C(17)-Si(4)-C(22)	104.05(14)	C(18)-Si(4)-C(22)	112.75(15)
C(17)-Si(4)-Si(1)	101.56(10)	C(18)-Si(4)-Si(1)	113.51(10)	C(22)-Si(4)-Si(1)	116.33(12)
C(26)-Si(5)-C(31)	101.45(17)	C(26)-Si(5)-C(27)	109.80(17)	C(31)-Si(5)-C(27)	112.28(15)
C(26)-Si(5)-Si(1)	103.67(12)	C(31)-Si(5)-Si(1)	114.23(13)	C(27)-Si(5)-Si(1)	114.16(11)
C(35)-Si(6)-C(36)	106.70(16)	C(35)-Si(6)-C(40)	106.79(15)	C(36)-Si(6)-C(40)	111.60(14)
C(35)-Si(6)-Si(2)	102.11(11)	C(36)-Si(6)-Si(2)	115.41(12)	C(40)-Si(6)-Si(2)	113.18(9)
C(44)-Si(7)-C(45)	106.38(16)	C(44)-Si(7)-C(49)	103.99(16)	C(45)-Si(7)-C(49)	115.09(15)
C(44)-Si(7)-Si(3)	110.42(12)	C(45)-Si(7)-Si(3)	109.46(11)	C(49)-Si(7)-Si(3)	111.22(10)
C(2)-C(1)-C(5)	118.6(2)	C(2)-C(1)-Si(3)	119.0(2)	C(5)-C(1)-Si(3)	122.45(19)
C(1)-C(2)-Si(1)	130.5(2)	C(4)-C(3)-C(11)	124.3(3)	C(4)-C(3)-Si(2)	104.7(2)
C(11)-C(3)-Si(2)	130.9(2)	C(3)-C(4)-Si(3)	106.5(2)	C(6)-C(5)-C(10)	117.9(3)
C(6)-C(5)-C(1)	121.1(3)	C(10)-C(5)-C(1)	121.0(3)	C(7)-C(6)-C(5)	120.9(3)
C(8)-C(7)-C(6)	120.0(3)	C(9)-C(8)-C(7)	119.8(3)	C(8)-C(9)-C(10)	120.1(3)
C(9)-C(10)-C(5)	121.2(3)	C(12)-C(11)-C(16)	117.7(3)	C(12)-C(11)-C(3)	120.6(3)
C(16)-C(11)-C(3)	121.7(3)	C(11)-C(12)-C(13)	121.7(3)	C(14)-C(13)-C(12)	119.5(3)
C(13)-C(14)-C(15)	120.1(3)	C(14)-C(15)-C(16)	120.4(3)	C(15)-C(16)-C(11)	120.6(3)
C(19)-C(18)-C(20)	107.2(3)	C(19)-C(18)-C(21)	107.3(3)	C(20)-C(18)-C(21)	107.4(3)
C(19)-C(18)-Si(4)	109.2(2)	C(20)-C(18)-Si(4)	109.5(2)	C(21)-C(18)-Si(4)	116.0(3)
C(23)-C(22)-C(24)	109.5(3)	C(23)-C(22)-C(25)	106.7(3)	C(24)-C(22)-C(25)	107.2(3)
C(23)-C(22)-Si(4)	109.0(3)	C(24)-C(22)-Si(4)	113.4(3)	C(25)-C(22)-Si(4)	110.8(2)
C(30)-C(27)-C(28)	107.0(4)	C(30)-C(27)-C(29)	107.4(3)	C(28)-C(27)-C(29)	105.5(4)
C(30)-C(27)-Si(5)	116.5(3)	C(28)-C(27)-Si(5)	110.7(2)	C(29)-C(27)-Si(5)	109.1(3)
C(33)-C(31)-C(32)	108.8(3)	C(33)-C(31)-C(34)	109.4(3)	C(32)-C(31)-C(34)	106.9(3)
C(33)-C(31)-Si(5)	112.9(3)	C(32)-C(31)-Si(5)	110.3(3)	C(34)-C(31)-Si(5)	108.4(2)
C(38)-C(36)-C(37)	107.3(3)	C(38)-C(36)-C(39)	109.3(3)	C(37)-C(36)-C(39)	106.6(3)
C(38)-C(36)-Si(6)	114.6(2)	C(37)-C(36)-Si(6)	107.7(2)	C(39)-C(36)-Si(6)	110.8(3)
C(41)-C(40)-C(43)	106.9(3)	C(41)-C(40)-C(42)	106.8(3)	C(43)-C(40)-C(42)	108.0(3)
C(41)-C(40)-Si(6)	115.8(2)	C(43)-C(40)-Si(6)	110.93(19)	C(42)-C(40)-Si(6)	108.0(2)
C(47)-C(45)-C(48)	108.2(3)	C(47)-C(45)-C(46)	108.1(3)	C(48)-C(45)-C(46)	107.9(3)
C(47)-C(45)-Si(7)	110.9(3)	C(48)-C(45)-Si(7)	113.0(2)	C(46)-C(45)-Si(7)	108.6(2)
C(51)-C(49)-C(52)	109.3(3)	C(51)-C(49)-C(50)	107.5(3)	C(52)-C(49)-C(50)	107.3(3)
C(51)-C(49)-Si(7)	113.4(2)	C(52)-C(49)-Si(7)	107.7(2)	C(50)-C(49)-Si(7)	111.5(2)

Synthesis of 2,3-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]trisilagermetene **9**

The crystals of **3** (50 mg, 0.07 mmol) and GeCl₂ dioxane (16 mg, 0.07 mmol) were placed in a sealed tube with a magnetic stirrer. After degassing the tube, dry, oxygen-free THF (2.0 mL) was introduced by vacuum transfer and stirred at room temperature to give a yellow solution of **9** within 1 h. After the solvent was removed in vacuo, the reaction mixture was cooled to afford yellow crystals of **9** (58 mg, 97%). ¹H NMR (C₆D₆, δ) 0.35 (s, 3 H), 0.36 (s, 3 H), 0.48 (s, 3 H), 0.54 (s, 3 H), 1.14 (s, 9 H), 1.16 (s, 9 H), 1.17 (s, 9 H), 1.19 (s, 9 H), 1.30 (s, 9 H), 1.31 (s, 9 H), 1.36 (s, 18 H, 2 'Bu); ¹³C NMR (C₆D₆, δ) -5.5, -5.4, -4.1, -3.4, 21.5, 21.8, 22.2, 22.3 (3 C), 22.4, 29.66, 29.74, 29.9, 30.0, 20.4 (2 C), 30.59, 30.62; ²⁹Si NMR (C₆D₆, δ) 0.1, 4.8, 17.0, 17.9, 26.1, 37.4, 149.4.

Reaction of **9** with Phenylacetylene

The crystals of **9** (240 mg, 0.280 mmol) was placed in a sealed tube with a magnetic stirrer. After degassing the tube, dry oxygen-free hexane (5.0 mL) and phenylacetylene (0.5 ml, 0.308 mmol) were introduced by vacuum transfer and stirred at room temperature for 4 days. After the solvent and phenylacetylene were removed in vacuo, degassed hexane was introduced by vacuum transfer. The reaction mixture was cooled to afford pale-yellow crystals of **3** (234 mg, 87%). mp 254 °C (dec.); ¹H NMR (C₆D₆, δ) 0.15 (s, 3 H), 0.39 (s, 3 H), 0.57 (s, 6 H), 0.68 (s, 3 H), 1.03 (s, 9 H), 1.12 (s, 9 H), 1.18 (s, 9 H), 1.19 (s, 18 H, 2'Bu), 1.26 (s, 3 H), 1.28 (s, 3 H), 1.29 (s, 3 H), 7.04 (t, *J* = 7.3 Hz, 1 H), 7.18 (t, *J* = 7.3 Hz, 2 H), 7.36 (s, 1 H), 7.67 (d, *J* = 7.3 Hz, 2 H); ¹³C NMR (C₆D₆, δ) -5.2, -3.82, -3.77, -3.3, 20.8, 22.0, 22.2, 22.4, 22.7, 23.1, 23.2, 30.0, 30.6, 30.7, 30.8,

30.9, 127.4, 127.9, 128.1, 144.2, 145.8, 168.2; ^{29}Si NMR (C_6D_6 , δ) -26.5, 11.8, 14.7, 17.5, 20.3, 21.8, 27.7; Anal. Calcd for $\text{C}_{44}\text{H}_{90}\text{Cl}_2\text{GeSi}_7$: C, 55.09; H, 9.46%. Found: C, 54.60; H, 9.55%.

X-ray Crystal Structure Determination of **10**

A single crystal of **10** for X-ray diffraction was grown from a hexane solution. Diffraction data were collected at 150 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 1-4a. The final atomic parameters, the bond length, and the bond angles of **5a** are listed in Table 1-4b and Table 1-4c, respectively.

Table 1-4a. Crystal data and structure refinement for 10

Empirical formula	$C_{44}H_{90}Cl_2GeSi_7$		
Formula weight	959.28		
Temperature	120 K		
Wavelength	0.71070 Å		
Crystal system, space group	Monoclinic, $P\bar{2}_1/n$		
Unit cell dimensions	$a = 12.2730(3)$ Å	$b = 19.8420(8)$ Å	$c = 22.8490(7)$ Å
			alpha = 90 deg. beta = 90.752(2) deg. gamma = 90 deg.
Volume	5563.7(3) Å ³		
Z, Calculated density	4, 1.145 Mg/m ³		
Absorption coefficient	0.824 mm ⁻¹		
F(000)	2072		
Crystal size	0.2 x 0.2 x 0.2 mm		
Theta range for data collection	2.05 to 27.94 deg.		
Limiting indices	0<=h<=16, 0<=k<=26, -30<=l<=30		
Reflections collected / unique	13072 / 57836 [R(int) = 0.1010]		
Completeness to theta = 27.94	97.9 %		
Absorption correction	None		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	13072 / 0 / 488		
Goodness-of-fit on F ²	1.062		
Final R indices [I>2sigma(I)]	R1 = 0.0678, wR2 = 0.1777		
R indices (all data)	R1 = 0.0972, wR2 = 0.1960		
Extinction coefficient	0.0060(6)		
Largest diff. peak and hole	1.476 and -1.085 e.Å ⁻³		

Table 1-4b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ge(1)	7105(1)	2097(1)	2141(1)	26(1)
Cl(1)	3081(1)	2062(1)	2169(1)	69(1)
Cl(2)	6319(1)	430(1)	2731(1)	39(1)
Si(1)	5681(1)	2381(1)	1424(1)	27(1)
Si(2)	4508(1)	1584(1)	1869(1)	34(1)
Si(3)	5750(1)	1448(1)	2689(1)	30(1)
Si(4)	8749(1)	2700(1)	2437(1)	42(1)
Si(5)	4920(1)	3339(1)	936(1)	37(1)
Si(6)	3953(1)	601(1)	1334(1)	63(1)
Si(7)	5020(1)	1642(1)	3658(1)	41(1)
C(1)	7314(3)	1523(2)	1418(2)	36(1)
C(2)	6562(3)	1768(2)	1032(2)	37(1)
C(3)	8312(6)	3475(4)	2857(3)	88(3)
C(4)	9595(5)	2122(5)	2937(3)	102(3)
C(5)	9861(12)	1488(4)	2674(8)	294(14)
C(6)	8874(6)	2076(11)	3506(5)	299(14)
C(7)	10632(5)	2468(5)	3154(3)	83(2)
C(8)	9484(3)	3007(2)	1753(2)	40(1)
C(9)	10415(7)	3475(5)	1897(3)	117(4)
C(10)	9942(10)	2458(4)	1401(4)	158(6)
C(11)	8693(6)	3404(6)	1397(5)	166(6)
C(12)	3487(4)	3099(3)	709(2)	51(1)
C(13)	5686(5)	3527(4)	230(2)	69(2)
C(14)	6742(9)	3908(11)	359(4)	288(13)
C(15)	5928(11)	2907(5)	-89(3)	169(6)
C(16)	5002(8)	3988(3)	-160(2)	90(2)
C(17)	4823(5)	4074(3)	1477(3)	59(1)
C(18)	5889(8)	4280(6)	1734(7)	212(8)
C(19)	4185(6)	4663(3)	1233(3)	79(2)
C(20)	4141(11)	3820(4)	1982(3)	153(5)
C(21)	5226(6)	106(3)	1192(3)	79(2)
C(22)	3307(5)	854(3)	596(3)	72(2)
C(23)	4179(6)	1214(3)	232(3)	76(2)
C(24)	2329(5)	1334(4)	655(3)	86(2)
C(25)	2916(8)	227(4)	251(3)	111(3)
C(26)	3035(6)	58(3)	1818(4)	98(3)
C(27)	1873(6)	339(6)	1842(6)	194(7)
C(28)	3014(11)	-679(4)	1594(5)	182(7)
C(29)	3516(6)	28(4)	2428(3)	87(2)
C(30)	3511(4)	1411(4)	3625(3)	74(2)
C(31)	5680(4)	1051(2)	4233(2)	47(1)
C(32)	5357(5)	1282(3)	4854(2)	64(2)
C(33)	6915(4)	1033(3)	4213(2)	55(1)
C(34)	5239(5)	330(3)	4152(2)	60(1)
C(35)	5089(6)	2577(3)	3835(2)	60(2)
C(36)	4243(8)	2793(4)	4299(3)	107(3)
C(37)	6227(7)	2790(3)	4051(3)	86(2)
C(38)	4850(7)	2971(3)	3271(2)	77(2)
C(39)	8107(3)	979(2)	1273(2)	37(1)
C(40)	8309(4)	446(3)	1646(2)	53(1)
C(41)	9007(4)	-84(3)	1482(2)	56(1)
C(42)	9506(4)	-56(3)	953(2)	46(1)
C(43)	9336(4)	493(2)	578(2)	45(1)
C(44)	8620(4)	1003(2)	733(2)	40(1)

Table 1-4c. Bond lengths [Å] and angles [deg] for 10

Ge(1)-C(1)	2.024(4)	Ge(1)-Si(4)	2.4347(12)	Ge(1)-Si(1)	2.4447(11)
Ge(1)-Si(3)	2.4595(11)	Cl(1)-Si(2)	2.1146(17)	Cl(2)-Si(3)	2.1399(16)
Si(1)-C(2)	1.866(4)	Si(1)-Si(2)	2.3765(15)	Si(1)-Si(5)	2.3873(15)
Si(2)-Si(6)	2.3954(19)	Si(2)-Si(3)	2.4147(15)	Si(3)-Si(7)	2.4297(15)
Si(4)-C(3)	1.895(7)	Si(4)-C(8)	1.914(4)	Si(4)-C(4)	1.915(7)
Si(5)-C(12)	1.888(5)	Si(5)-C(17)	1.916(5)	Si(5)-C(13)	1.915(5)
Si(6)-C(21)	1.877(7)	Si(6)-C(26)	1.921(7)	Si(6)-C(22)	1.920(6)
Si(7)-C(35)	1.900(6)	Si(7)-C(30)	1.909(6)	Si(7)-C(31)	1.931(5)
C(1)-C(2)	1.359(6)	C(1)-C(39)	1.493(6)	C(4)-C(5)	1.434(16)
C(4)-C(7)	1.523(8)	C(4)-C(6)	1.584(13)	C(8)-C(10)	1.470(8)
C(8)-C(11)	1.484(8)	C(8)-C(9)	1.507(7)	C(13)-C(15)	1.462(11)
C(13)-C(16)	1.523(9)	C(13)-C(14)	1.526(11)	C(17)-C(18)	1.485(10)
C(17)-C(19)	1.510(7)	C(17)-C(20)	1.520(10)	C(22)-C(24)	1.539(10)
C(22)-C(25)	1.546(8)	C(22)-C(23)	1.541(9)	C(26)-C(29)	1.506(10)
C(26)-C(27)	1.532(12)	C(26)-C(28)	1.550(12)	C(31)-C(33)	1.517(7)
C(31)-C(34)	1.539(7)	C(31)-C(32)	1.549(6)	C(35)-C(38)	1.532(7)
C(35)-C(37)	1.535(10)	C(35)-C(36)	1.553(7)	C(39)-C(40)	1.380(7)
C(39)-C(44)	1.392(6)	C(40)-C(41)	1.409(7)	C(41)-C(42)	1.364(7)
C(42)-C(43)	1.399(7)	C(43)-C(44)	1.390(6)		
C(1)-Ge(1)-Si(4)	112.94(12)	C(1)-Ge(1)-Si(1)	71.43(12)	Si(4)-Ge(1)-Si(1)	130.94(4)
C(1)-Ge(1)-Si(3)	102.41(13)	Si(4)-Ge(1)-Si(3)	132.77(4)	Si(1)-Ge(1)-Si(3)	88.84(4)
C(2)-Si(1)-Si(2)	97.40(14)	C(2)-Si(1)-Si(5)	121.37(14)	Si(2)-Si(1)-Si(5)	119.64(6)
C(2)-Si(1)-Ge(1)	75.94(13)	Si(2)-Si(1)-Ge(1)	89.51(4)	Si(5)-Si(1)-Ge(1)	140.22(6)
Cl(1)-Si(2)-Si(1)	110.41(7)	Cl(1)-Si(2)-Si(6)	107.43(8)	Si(1)-Si(2)-Si(6)	119.55(7)
Cl(1)-Si(2)-Si(3)	108.39(7)	Si(1)-Si(2)-Si(3)	91.52(5)	Si(6)-Si(2)-Si(3)	118.55(6)
Cl(2)-Si(3)-Si(2)	110.01(6)	Cl(2)-Si(3)-Si(7)	103.45(6)	Si(2)-Si(3)-Si(7)	116.96(6)
Cl(2)-Si(3)-Ge(1)	107.12(5)	Si(2)-Si(3)-Ge(1)	88.29(4)	Si(7)-Si(3)-Ge(1)	129.90(6)
C(3)-Si(4)-C(8)	107.1(3)	C(3)-Si(4)-C(4)	109.8(4)	C(8)-Si(4)-C(4)	114.9(3)
C(3)-Si(4)-Ge(1)	107.5(2)	C(8)-Si(4)-Ge(1)	109.06(14)	C(4)-Si(4)-Ge(1)	108.2(2)
C(12)-Si(5)-C(17)	107.6(3)	C(12)-Si(5)-C(13)	106.5(2)	C(17)-Si(5)-C(13)	115.5(3)
C(12)-Si(5)-Si(1)	106.57(17)	C(17)-Si(5)-Si(1)	109.36(17)	C(13)-Si(5)-Si(1)	110.8(2)
C(21)-Si(6)-C(26)	107.6(3)	C(21)-Si(6)-C(22)	108.7(3)	C(26)-Si(6)-C(22)	114.4(3)
C(21)-Si(6)-Si(2)	106.44(18)	C(26)-Si(6)-Si(2)	109.1(3)	C(22)-Si(6)-Si(2)	110.34(19)
C(35)-Si(7)-C(30)	106.4(3)	C(35)-Si(7)-C(31)	115.6(2)	C(30)-Si(7)-C(31)	106.3(3)
C(35)-Si(7)-Si(3)	109.41(15)	C(30)-Si(7)-Si(3)	107.1(2)	C(31)-Si(7)-Si(3)	111.55(15)
C(2)-C(1)-C(39)	123.5(4)	C(2)-C(1)-Ge(1)	103.7(3)	C(39)-C(1)-Ge(1)	132.7(3)
C(1)-C(2)-Si(1)	108.3(3)	C(5)-C(4)-C(7)	109.8(8)	C(5)-C(4)-C(6)	115.2(11)
C(7)-C(4)-C(6)	103.5(8)	C(5)-C(4)-Si(4)	113.5(6)	C(7)-C(4)-Si(4)	111.6(6)
C(6)-C(4)-Si(4)	102.7(6)	C(10)-C(8)-C(11)	110.3(8)	C(10)-C(8)-C(9)	106.4(6)
C(11)-C(8)-C(9)	106.3(7)	C(10)-C(8)-Si(4)	113.5(4)	C(11)-C(8)-Si(4)	107.8(4)
C(9)-C(8)-Si(4)	112.4(4)	C(15)-C(13)-C(16)	109.1(6)	C(15)-C(13)-C(14)	109.6(10)
C(16)-C(13)-C(14)	106.0(8)	C(15)-C(13)-Si(5)	111.2(5)	C(16)-C(13)-Si(5)	109.7(5)
C(14)-C(13)-Si(5)	111.1(5)	C(18)-C(17)-C(19)	112.4(7)	C(18)-C(17)-C(20)	106.4(9)
C(19)-C(17)-C(20)	104.5(6)	C(18)-C(17)-Si(5)	113.8(5)	C(19)-C(17)-Si(5)	112.8(4)
C(20)-C(17)-Si(5)	106.1(4)	C(24)-C(22)-C(25)	107.8(6)	C(24)-C(22)-C(23)	108.0(5)
C(25)-C(22)-C(23)	108.1(6)	C(24)-C(22)-Si(6)	113.5(5)	C(25)-C(22)-Si(6)	111.1(4)
C(23)-C(22)-Si(6)	108.3(4)	C(29)-C(26)-C(27)	109.6(9)	C(29)-C(26)-C(28)	105.8(6)
C(27)-C(26)-C(28)	110.1(8)	C(29)-C(26)-Si(6)	109.2(4)	C(27)-C(26)-Si(6)	111.7(4)
C(28)-C(26)-Si(6)	110.2(7)	C(33)-C(31)-C(34)	109.0(4)	C(33)-C(31)-C(32)	107.6(4)
C(34)-C(31)-C(32)	106.9(4)	C(33)-C(31)-Si(7)	113.8(3)	C(34)-C(31)-Si(7)	109.8(4)
C(32)-C(31)-Si(7)	109.4(4)	C(38)-C(35)-C(37)	107.1(5)	C(38)-C(35)-C(36)	108.1(5)
C(37)-C(35)-C(36)	108.5(6)	C(38)-C(35)-Si(7)	108.2(4)	C(37)-C(35)-Si(7)	112.1(4)
C(36)-C(35)-Si(7)	112.7(4)	C(40)-C(39)-C(44)	119.6(4)	C(40)-C(39)-C(1)	121.9(4)
C(44)-C(39)-C(1)	118.5(4)	C(39)-C(40)-C(41)	120.8(4)	C(42)-C(41)-C(40)	119.2(5)
C(41)-C(42)-C(43)	120.6(4)	C(44)-C(43)-C(42)	120.1(4)	C(43)-C(44)-C(39)	119.7(4)

Reference and Notes

- [1] For reviews of $R_2M=MR_2$ ($M = Si, Ge, Sn$), see a) R. West, *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 1201; b) J. Barrau, J. Escudie, and J. Satge, *Chem. Rev.*, **1990**, *90*, 283; c) T. Tsumuraya, S. A. Batcheller, and S. Masamune, *Angew. Chem. Int. Ed. Engl.*, **1991**, *30*, 902; d) R. Okazaki, and R. West, *Adv. Organomet. Chem.*, **1996**, *39*, 231; e) G. Raabe and J. Michl in *The Chemistry of Organic Silicon Compounds*, Part 2 (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, chap. 17; f) H. Sakurai in *The Chemistry of Organic Silicon Compounds*, Vol. 2, Part 1 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, chap. 15.
- [2] R. West, M. J. Fink, and J. Michl, *Science*, **1981**, *214*, 1343.
- [3] A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, and R. K. Kallury, *J. Chem. Soc. Chem. Commun.*, **1981**, 191.
- [4] a) M. Kira, T. Iwamoto, and C. Kabuto, *J. Am. Chem. Soc.*, **1996**, *118*, 10303; b) T. Iwamoto, and M. Kira, *Chem. Lett.*, **1998**, 277.
- [5] N. Wiberg, H. Auer, H. Noth, J. Knizek, and K. Polborn, *Angew. Chem. Int. Ed.*, **1998**, *37*, 2869.
- [6] A. Sekiguchi, H. Yamazaki, C. Kabuto, H. Sakurai, and S. Nagase, *J. Am. Chem. Soc.*, **1995**, *117*, 8025.
- [7] a) A. Sekiguchi, M. Tsukamoto, and M. Ichinohe, *Science* **1997**, *275*, 60; b) A. Sekiguchi, M. Tsukamoto, M. Ichinohe, and N. Fukaya, *Phosphorus Sulfur Silicon Relat. Elem.*, **1997**, *124/125*, 323; c) M. Ichinohe, N. Fukaya, and A. Sekiguchi, *Chem. Lett.* **1998**, 1045.
- [8] a) A. Sekiguchi, N. Fukaya, M. Ichinohe, N. Takagi, and S. Nagase, *J. Am. Chem. Soc.*, **1999**, *121*, 11587; b) A. Sekiguchi, Y. Ishida, N. Fukaya, M. Ichinohe, N. Takagi, and S. Nagase, *J. Am. Chem. Soc.*, **2002**, *124*, 1158.
- [9] N. Wiberg, H.-W. Lerner, S.-K. Vasisht, S. Wagner, K. Karaghiosoff, H. Nöth,

and W. Ponikwar, *Eur. J. Inorg. Chem.* **1999**, 1211.

- [10] a) T. Iwamoto, C. Kabuto, and M. Kira, *J. Am. Chem. Soc.* **1999**, *121*, 886; b) T. Iwamoto, M. Tamura, C. Kabuto, and M. Kira, *Organometallics*, **2003**, *22*, 2342.
- [11] T. Iwamoto, M. Tamura, C. Kabuto, and M. Kira, *Science*, **2000**, *290*, 504.
- [12] a) S. Nagase, *Pure Appl. Chem.*, **1993**, *65*, 675; b) A. Sekiguchi, S. Nagase in *The Chemistry of Organic Silicon Compounds*, Vol. 2, Part 1 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, chap. 3.
- [13] A single crystal (0.50*0.35*0.15 mm) of **3** was sealed in a capillary glass tube, and diffraction data collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized MoKa radiation ($\lambda = 0.71073 \text{ \AA}$). The final R factor was 0.071 (Rw = 0.136) for 4291 reflections with $I > 3s(I)$. Crystal data: $C_{36}H_{84}Si_7$, MW = 713.67, monoclinic, space group $P2_1/c$, $a = 24.063(4)$, $b = 11.629(2)$, $c = 17.715(3) \text{ \AA}$, $\beta = 110.435(1)^\circ$, $V = 4645(2) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd}} = 1.018 \text{ g}\cdot\text{cm}^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118470. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [14] V. Ya. Lee, M. Ichinohe, A. Sekiguchi, N. Takagi, and S. Nagase, *J. Am. Chem. Soc.*, **2000**, *122*, 9034.
- [15] a) N. Fukaya, M. Ichinohe, and A. Sekiguchi, *Angew. Chem. Int. Ed.*, **2000**, *39*, 3881; b) V. Ya. Lee, M. Ichinohe, and A. Sekiguchi, *J. Am. Chem. Soc.*, **2000**, *122*, 12604.

- [16] Kira et al. reported the reaction of (*t*BuMe₂Si)₂Si=Si(*t*BuMe₂Si)₂ with haloalkanes produced corresponding 1,2-dihaloderivatives (in the case of CCl₄ and CBr₄). The reaction is explained by a radical mechanism.
T. Iwamoto, H. Sakurai, and M. Kira, *Bull. Chem. Soc. Jpn.*, **1998**, *71*, 2741.
- [17] M. Kaftory, M. Kapon, and M. Botoshansky, in *The Chemistry of Organic Silicon Compounds*, Vol. 2, Part 1 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, chap. 5.
- [18] a) D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, **1971**, *94*, 5837; b) H. Sakurai, T. Kobayashi, and Y. Nakadaira, *J. Organomet. Chem.*, **1978**, *162*, C43; c) M. J. Fink, D. J. DeYoung, and R. West, *J. Am. Chem. Soc.*, **1983**, *105*, 1070.
- [19] V. Ya. Lee, K. Takanashi, M. Ichinohe, and A. Sekiguchi, *J. Am. Chem. Soc.*, **2003**, *125*, 6012.
- [20] K. M. Baines, C. E. Dixon, J. M. Langridge, A. W. Liu, and F. Zhang, *Organometallics*, **1999**, *18*, 2209.
- [21] M. Weidenbruch, In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, **2001**; Vol. 3, Chapter 5.
- [22] M. P. Doyle and C. T. West, *J. Am. Chem. Soc.*, **1975**, *97*, 3777.
- [23] N. Wiberg and C.-K. Kim, *Chem. Ber.*, **1986**, *119*, 2980.
- [24] E. M. Dexheimer and L. Spialter, *J. Organomet. Chem.*, **1975**, *102*, 21.
- [25] S. Schuette, C. Freire-Erdbruegger, U. Klingebiel, and G. M. Sheldrick, *Phosphorus Sulfur Silicon Relat. Elem.*, **1993**, *78*, 75.
- [26] a) M. V. George, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **1960**, *82*, 403; b) H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **1951**, *73*, 5077.
- [27] A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **1954**, *76*, 278.