Synthesis and Structure of Polysilabridged and Doubly Bridged Allenes

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Abstract: Polysilacycloalka-1,2-dienes **1, 2**, and **3** are synthesized by reactions of the Ph_2C_3 dianion with corresponding dichloropolysilanes. X-ray crystallographic analyses of the tetrasilacyclohepta-1,2-diene **1** and the trisilacyclohexa-1,2-diene **3** show allenic sp carbons to be bent by 6° and 19°, respectively, and the torsional angles around the allenic moieties are 85.3° and 52.2°, respectively. Photoirradiation (254 nm) of **1** gives a 1,3-bridged cyclopropene (**11**) via photoinduced rearrangement. Synthesis and X-ray-determined structure of the doubly bridged allene octasila[4.4]-betweenallene **4** are also reported. The betweenallene **4** is synthesized by the reaction of dichlorooctamethyltetrasilane with hexachloropropene in the presence of magnesium. The optimized structures of their smaller ring systems are also reported by semiempirical PM3 calculations.

Introduction

Recent interests have focused on attempts to synthesize and study the properties of highly strained unsaturated cyclic compounds.[1] Medium-ring cycloalkynes[2] and *trans*-cycloalkenes[3] are the most widely investigated of such compounds. Recently, we reported the synthesis of strained polysilacycloalkynes I[4,5] and *trans*-polysilacycloalkene II.[6] and it was found that the long silicon–silicon bonds release the ring strains. On the other hand,
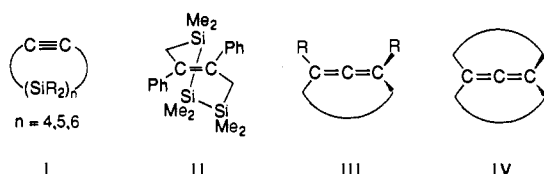
one of the cyclic allenes III is the subject of considerable interest as a strained unsaturated cyclic compound.[7] *tert*-Butyl-substituted cycloocta-1,2-diene is known as the smallest isolable cyclic allene.[8] Seven- and six-membered cyclic allenes are also well known as important intermediates in organic synthesis, and many synthetic methods have been documented.[9,10] However, no example of their isolation has been reported so far, probably

because of the instabilities caused by the ring strains. Our continued interest in the strained cyclopolysilanes prompted us to synthesize the strained cyclic allenes containing silicon atoms. We will report here the synthesis and stereochemistry of medium-ring polysilacyclic allenes. Doubly bridged cyclic allenes IV, namely betweenallene or screw[2]ene, had also been subjects of interest for their molecular chirality.[11] However, no example of the isolation of such compounds had been reported until 1981, when the synthesis of [8.10]betweenallene was reported for the first time by Nakazaki et al.[12] Furthermore, few examples of the synthesis of heterocyclic betweenallene have been reported.[13] We have accomplished the syntheses of polysilabetweenallenes. In this paper, we report the optimized structures of their smaller ring systems calculated by semiempirical PM3 method.

Results and Discussion

Synthesis of Polysilacyclic and Bicyclic Allenes. Ph_2C_3 dianion prepared from 1,3-diphenylpropyne and 2 equiv of *n*-butyllithium easily reacted with 1,4-dichlorooctamethyltetrasilane in THF/hexane to give 1,3-diphenyl-4,4,5,5,6,6,7,7-octamethyl-4,5,6,7-tetrasilacyclohepta-1,2-diene (**1**) in 72% yield after purification by GPC (Scheme I). Tetrahydrofuran was an indispensable solvent in promoting this reaction. The similar reaction of Ph_2C_3 dianion with 1,6-dichlorododecamethylhexasilane also gave a corresponding cyclic allene (**2**) in 24% yield. The decrease of the yield can be attributed to the unfavorable conformation during ring closure. The reaction of Ph_2C_3 dianion with 1,3-dichlorohex-

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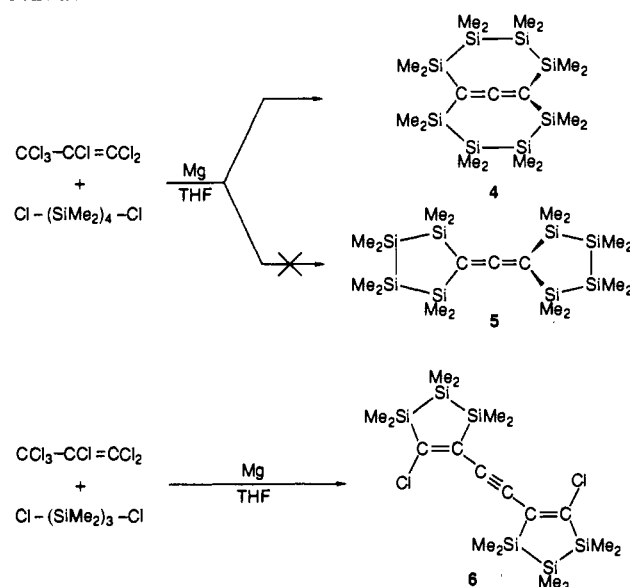
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Scheme I

$PhCH_2C \equiv CPh \xrightarrow[\text{hexane}]{\text{n-BuLi}} Ph_2C_3Li_2$

1

2

3

Scheme II

4

5

6
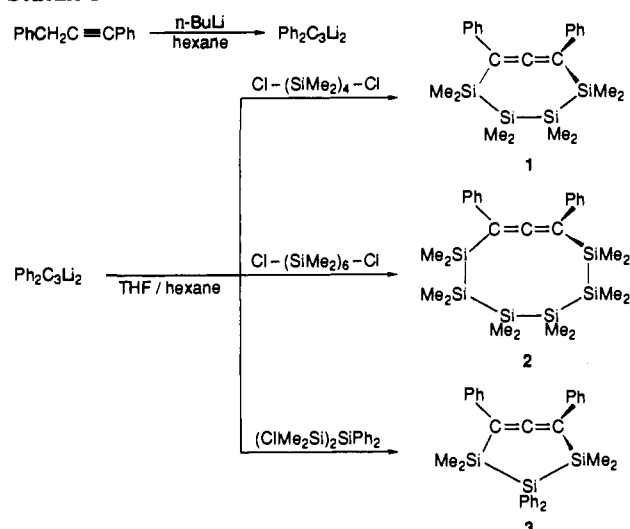
amethyltrisilane was also carried out under similar conditions. However, no 1:1 cycloadduct could be detected. The six-membered cyclic allene **3** was obtained from reaction of 1,3-dichloro-2,2-diphenyltetramethyltrisilane with Ph_2C_3 dianion, though in only 11% yield. The difference of the reactivities of the two types of dichlorotrisilanes might be explained on the basis of steric effects of two phenyl groups on a silicon atom which prevent intermolecular reaction. Fourteen, eighteen, and twelve-membered dimeric compounds could not be obtained in each reaction. The structures of cyclic allenes **1**, **2**, and **3** were determined by spectroscopic analysis. The ^1H and ^{13}C NMR spectra of **1**, **2**, and **3** show four, six, and two types of methyl groups, respectively. The ^{13}C NMR spectra of **1**, **2**, and **3** show the characteristic allenic sp carbons at 209.1, 210.5, and 207.4 ppm and the sp² carbons at 95.4, 95.5, and 96.2 ppm, respectively.

A reaction of hexachloropropene with 1,4-dichlorooctamethyltetrasilane in the presence of magnesium gave octasila[4.4]-betweenallene **4** in 34% yield (Scheme II). ^1H and ^{13}C NMR spectra of **4** show the four unequivalent methyl groups and the characteristic allenic sp and sp² carbons at 207.8 and 122.9 ppm, respectively. In this reaction, another isomer (**5**), expected to be formed, could not be obtained. Similarly, a reaction of hexachloropropene with 1,3-dichlorohexamethyltrisilane was examined. However, the corresponding [3.3]betweenallene could not be obtained, and the unexpected 2:2 adduct **6** was isolated as the
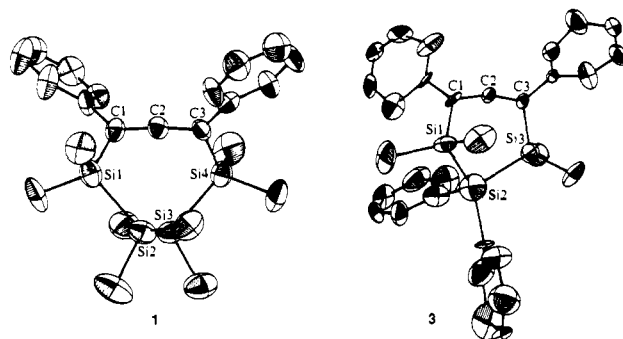
Figure 1. X-ray-determined structures of **1** and **3** with hydrogen atoms removed for clarity.
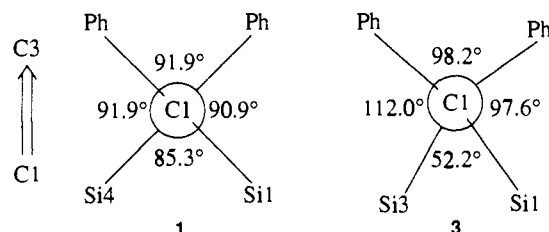
Figure 2. X-ray-determined dihedral geometries around allenic moieties of **1** and **3**.

Table I. X-ray-Determined Selected Bond Lengths (Å) and Bond Angles (deg) in Seven- and Six-Membered Cyclic Allenes **1** and **3**[a]

	1	3		1	3
C1–C2	1.30(2)	1.30(1)	C1–C2–C3	174(1)	161(1)
C2–C3	1.31(2)	1.27(2)	C2–C1–Si1	114.5(8)	110.3(8)
C1–Si1	1.91(1)	1.92(1)	C2–C3–Si3		111.2(8)
C3–Si3		1.96(1)	C2–C3–Si4	111.4(8)	
C3–Si4	1.91(1)		C1–Si1–Si2	104.5(4)	110.8(6)
Si1–Si2	2.350(5)	2.354(6)	C3–Si3–Si2		101.8(4)
Si2–Si3	2.344(5)	2.410(7)	C3–Si4–Si3	105.7(4)	
Si3–Si4	2.334(6)		Si1–Si2–Si3	105.5(2)	104.6(2)
			Si2–Si3–Si4	106.9(2)	

[a] esd's are in parentheses.

volatile product in 16% yield. The reaction of the 1,3-dichloro-2,2-diphenyltetramethyltrisilane and hexachloropropene with magnesium likewise did not afford the hexasila[3.3]betweenallene.

Structure of Polysilacyclic and Bicyclic Allenes. The stereochemistries of tetrasilacyclohepta-1,2-diene **1** and trisilacyclohexa-1,2-diene **3** were established by X-ray crystallographic analysis. The X-ray structures of **1** and **3** are shown in Figure 1, and the dihedral geometries around the allenic moieties are shown in Figure 2. The selected bond lengths and angles are summarized in Table I. The slightly longer bond lengths of skeletal C–Si and Si–Si bonds of **3** (1.94 and 2.38 Å as the averages, respectively) in comparison with those of **1** (1.91 and 2.34 Å) release the strain caused by the allenic moiety to a greater extent. The most interesting point of the structures of **1** and **3** is the relationship of the allenic moiety. The bond angle on the sp carbon, C1–C2–C3, of **3** is found to be highly strained (19°) from linear geometry, while that of **1** is almost strain free (6°). The bond angle on the sp carbon of **3** (161°) corresponds to that of carbon skeletal eight-membered cyclic allene, which was estimated from MNDO calculation by Angus et al.[14] Other semiempirical and ab initio molecular orbital calculations indicate that the bending potential is remarkably soft for the first 20°.[15] However, it has been reported that the all carbon skeleton eight-membered cyclic allene dimerized ([2 + 2] cycloaddition) even

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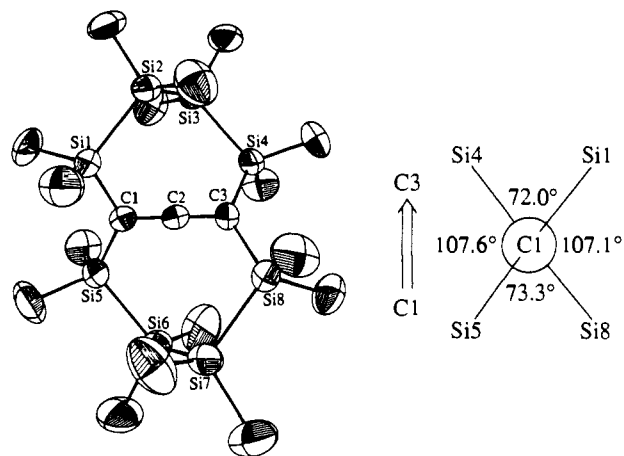
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Figure 3. X-ray-determined structure of **4** with the dihedral geometry around the allenic moiety.

Table II. X-ray-Determined Selected Bond Lengths (Å) and Bond Angles (deg) in Octasila[4.4]betweenallene **4**[a]

C1–C2	1.32(1)	C1–C2–C3	179.2(5)
C2–C3	1.30(1)	C2–C1–Si1	115.2(4)
C1–Si1	1.867(6)	C2–C1–Si5	114.5(4)
C1–Si5	1.879(5)	C2–C3–Si4	115.2(6)
C3–Si4	1.874(8)	C2–C3–Si8	114.5(6)
C3–Si8	1.870(8)	C1–Si1–Si2	106.9(2)
Si1–Si2	2.349(3)	C1–Si5–Si6	107.2(2)
Si2–Si3	2.343(3)	C3–Si4–Si3	107.0(2)
Si3–Si4	2.351(3)	C3–Si8–Si7	107.2(2)
Si5–Si6	2.347(3)	Si1–Si2–Si3	109.57(9)
Si6–Si7	2.347(3)	Si2–Si3–Si4	109.6(1)
Si7–Si8	2.345(3)	Si5–Si6–Si7	108.2(1)
		Si6–Si7–Si8	108.2(1)

[a] esd's are in parentheses.

at 0 °C.[9c] Therefore, we anticipate that the successful synthesis of **3** is due to the steric effect of phenyl groups on carbon atoms and methyl substituents. The dihedral geometries around the allenic structures of **1** and **3** are also influenced by the ring strains. The dihedral angle, Si1–C1–C3–Si3, of **3** is strongly contracted (52.2°) from normal vertical geometry, while that of **1** is nearly a right angle (85.3°).

The structure of octasila[4.4]betweenallene **4** was also determined by the X-ray crystallographic analysis. The X-ray structure of **4** is shown in Figure 3 along with the dihedral geometry around the allenic structure. Selected bond distances and angles are listed in Table II. The Ortep plot of **4** shows a symmetrical conformation. The bond lengths and angles are almost normal. The torsional angles, Si1–C1–C3–Si4 and Si5–C1–C3–Si8, are 72.0° and 73.3°, respectively. This deformation from the vertical geometry of the allene is increased as compared with that of **1**, which has the same-membered monocyclic system. The allenic sp carbon of **4** is almost linear, though in the case of **1** it is slightly bent. Therefore, the strain as indicated by the dihedral angles of **4** can be explained on the basis of the linear geometry of the allenic sp carbon.

Semiempirical PM3 calculations[16] for the smaller ring systems of polysilacyclic allenes and polysilabetweenallenes were carried out. The optimized bond angles, bond distances, and dihedral angles are summarized in Table III. Although carbon–silicon bonds around the allenic structures of seven- and six-membered cyclic allenes **7** and **8** are estimated to be shorter than those of the X-ray structures, the bond angles around the allenic moieties show good correspondence with those of the X-ray structures. The estimated bond angles of allenic sp carbons are 178° and 164° for **7** and **8**, and these values are slightly larger than those

(16) MOPAC Version 6.01: Stewart, J. J. P., Frank J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado Springs, CO 80840. Unix version by Teijin Systems Technology Ltd.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in Polysilacyclic Allenes and Polysilabetweenallenes Estimated by PM3 Calculations

	7	8	9		7	8	9
C1–C2	1.30	1.30	1.31	C1–C2–C3	178	164	147
C2–C3	1.30	1.30	1.31	C2–C1–Si1	118	112	102
C1–Si1	1.81	1.82	1.86	C2–C3–Si2	118	110	103
C3–Si2	1.81	1.83	1.85	C1–Si1–Si	108	100	88
Si–Si (av)	2.41	2.44	2.50	C3–Si2–Si	107	103	87
Si1–C1–C3–Si2	75.3	54.0	29.9	Si–Si–Si (av)	113	104	

	4	10		4	10
C1–C2	1.30	1.30	C1–C2–C3	179	180
C2–C3	1.30	1.30	C2–C1–Si1	116	110
C1–Si1	1.81	1.81	C2–C1–Si5	115	110
C1–Si5	1.81	1.82	C2–C3–Si4	116	111
C3–Si4	1.81	1.81	C2–C3–Si8	117	111
C3–Si8	1.81	1.81	C1–Si1–Si	104	99
Si–Si (av)	2.45	2.49	C1–Si5–Si	107	96
			C3–Si4–Si	102	100
Si1–C1–C3–Si4	71.2	39.5	C3–Si8–Si	104	101
Si5–C1–C3–Si8	75.9	37.5	Si–Si–Si (av)	111	107
Si1–C1–C3–Si8	107.7	140.6			
Si5–C1–C3–Si4	105.2	142.5			
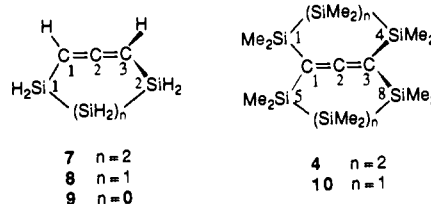
(174° and 161° (X-ray)) of the similar ring systems **1** and **3**, respectively. The estimated torsional angle (54.0°) of **8** shows a good agreement with that (52.2°) of **3** determined by X-ray analysis. The bond angle at the sp carbon of the smaller ring system **9** is estimated to be 147°, and its value falls between those of the seven- and six-membered carbocyclic systems estimated by MNDO method.[14] The bond length of the C=C double bonds of **9** was calculated to be 1.31 Å, which is slightly longer than those of **7** and **8**. This estimation of the bond lengths is explained on the basis of distortion of the π orbitals. The bond lengths of C–Si and Si–Si bonds of **9** are also longer than those of the larger ring systems **7** and **8**. The torsional angle (29.9°) of **9** indicates it to be strongly contracted, and the isolation of disilacyclopenta-1,2-diene seems to be difficult under ambient conditions. The optimized structures of betweenallenes **4** and **10** were estimated as methyl-substituted systems because steric repulsion is expected between geminal SiMe₂ substituents on sp² carbons. The torsional angles of **4** also show a good relationship with those of the X-ray structure. Comparison of the bond angles and torsional angles of **4** and **10** gives interesting features. The differences of the bond angles on the sp² carbons of **4** and **10** are not large (5.6° as an average); however, the torsional angles of **10** are highly distorted. The torsional angles of **10** are twisted between 50.5° and 52.5° from the vertical geometry of nonstrained allene, while those of **4** are 17.4° (X-ray) and 16.5° (PM3) as an average. The deformation of the structure of **10** should be caused by the tension of the silicon chains. On the basis of the torsional angle (52.2°) of **3**, which has the same-membered monocyclic system, the large deformation of the torsional angles of **10** is considered to be caused by the fundamentally linear relationship of the sp carbon to the doubly bridged system.

Photochemical Reaction of 1. The photochemical behavior of **1** was examined as a preliminary study of reactivities of the polysilacyclic allenes. Photoirradiation of a hexane solution of **1** with a low-pressure mercury lamp gave a rearranged bicyclic product (**11**) in 2.5% yield along with a majority of polymeric compounds (Scheme III). The structure of **11** was determined

Table IV. Crystallographic Data for **1**, **3**, and **4**

	1	**3**	**4**
molecular formula	$C_{23}H_{34}Si_4$	$C_{31}H_{32}Si_3$	$C_{19}H_{48}Si_8$
formula weight	422.87	488.86	501.28
crystal system	monoclinic	monoclinic	triclinic
space group	$C2$ (No. 5)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
a, Å	20.370(5)	10.354(3)	10.880(3)
b, Å	8.466(1)	9.908(1)	10.882(3)
c, Å	23.794(6)	27.945(7)	16.230(9)
α, deg			103.25(4)
β, deg	104.17(1)	100.50(1)	103.34(4)
γ, deg			108.28(2)
V, Å^3	3978.3	2818.7	1678.0
Z	6	4	2
t, °C	23	23	23
$F(000)$	1368	1040	548
ρ(calcd), g/cm^3	1.06	1.15	0.99
crystal dimens, mm	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.2
radiation	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)
μ, cm^{-1}	2.2	1.8	3.2
scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
2θ range, deg	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 50$
total no. of reflcns	2435	5393	3948
no. of unique obsd reflcns	1952 ($I > 3\sigma(I)$)	1818 ($I > 3\sigma(I)$)	3484 ($I > 3\sigma(I)$)
no. of least-squares params	288	409	339
R	0.068	0.048	0.081
R_w	0.072	0.052	0.089

Scheme III
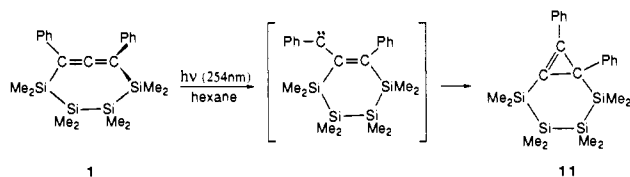
by the spectroscopic analysis of the mixture of **1** and **11** because the product **11** could not be separated from unreacted **1**. Compound **11** is also an interesting material as one of the 1,3-bridged cyclopropenes, and **11** is stable at room temperature although carbon skeletal bicyclo[4.1.0]hept-1(7)-ene dimerizes below ca. –90 °C via an ene reaction.[17] This type of rearrangement has been reported by Stierman et al. on irradiation of 1-methyl-cyclonona-1,2-diene.[18] According to the mechanism, this reaction may proceed via a vinylcarbene intermediate.

Experimental Section

Melting points were determined with a Büchi 535 apparatus and are uncorrected. Infrared and UV spectra were recorded with Jasco FT/IR-5000 and Jasco Ubest-50 instruments, respectively. Proton, carbon, and silicon magnetic resonance spectra were obtained with JEOL JNM-EX90, Bruker AC-400, and Bruker AM-500 spectrometers. Mass spectral data were obtained on Shimadzu QP-2000A (70 eV) and JEOL JMS-SX102A (30 eV) spectrometers. Liquid chromatography (GPC) was performed with Japan Analytical Industry LC-08 and LC-908 instruments. All solvents were predried by standard methods, and all the reactions were carried out under an inert atmosphere.

1,3-Diphenyl-4,4,5,5,6,6,7,7-octamethyl-4,5,6,7-tetrasilacyclohepta-1,2-diene (1). The dilithiated allene $Ph_2C_3Li_2$[19] was prepared in hexane (10 mL) from 1,3-diphenylpropyne (316 mg, 1.65 mmol) and *n*-butyllithium (1.52 N, 2.2 mL) at room temperature. The hexane suspension of $Ph_2C_3Li_2$ was added to a hexane (100 mL) solution of 1,4-dichlorooctamethyltetrasilane (450 mg, 1.50 mmol). After the mixture was stirred for few minutes, THF (20 mL) was added by syringe. During the addition of THF, the pale orange color of the solution quickly changed to deep red. After a few minutes, the red color disappeared. Stirring was continued overnight. After removal of the solvent, hexane (50 mL) was added to the residue. The precipitated inorganic salts were filtered,

and the filtrate was concentrated. A 455-mg yield (72%) of **1** was obtained after purification by GPC. Colorless prisms suitable for X-ray diffraction were obtained by recrystallization from hexane: mp 89–91 °C; ^1H NMR (90 MHz, C_6D_6) δ 0.17 (s, 6 H), 0.23 (s, 6 H), 0.33 (s, 6 H), 0.47 (s, 6 H), 7.0–7.5 (m, 10 H); ^{13}C NMR (22.5 MHz, C_6D_6) δ –6.1 (q), –5.0 (q), –1.4 (q), 0.3 (q), 95.4 (s), 126.6 (d), 128.4 (d) 129.1 (d), 137.7 (s), 209.1 (s); ^{29}Si NMR (17.6 MHz, C_6D_6) δ –41.1, –16.9; UV (hexane, nm (ϵ)) 265 (sh, 9.40 × 10^3); IR (KBr, cm^{-1}) 1891, 1597, 1491, 1245; LRMS (70 eV) m/z 422 (M$^+$), 407, 349; HRMS (30 eV) m/z calcd for $C_{23}H_{34}$-Si_4 422.1738, found 422.1761.

1,3-Diphenyl-4,4,5,5,6,6,7,7,8,8,9,9-dodecamethyl-4,5,6,7,8,9-hexa-silacyclonona-1,2-diene (2). Similar reaction of $Ph_2C_3Li_2$ with 1,6-dichlorododecamethylhexasilane gave the corresponding nine-membered cyclic allene **2** in 24% yield: mp 102–103 °C; ^1H NMR (400 MHz, C_6D_6) δ 0.25 (s, 12 H), 0.30 (s, 6 H), 0.40 (s, 6 H), 0.46 (s, 6 H), 0.48 (s, 6 H), 7.1–7.6 (m, 10 H); ^{13}C NMR (22.5 MHz, C_6D_6) δ –4.4 (q), –4.3 (q), –4.1 (q), –3.9 (q), –0.8 (q), –0.7 (q), 95.5 (s), 127.0 (d), 128.5 (d), 129.3 (d), 138.2 (s), 210.5 (s); ^{29}Si NMR (17.6 MHz, C_6D_6) δ –43.2, –40.7, –17.1; UV (hexane, nm (ϵ)) 241 (2.73 × 10^4), 264 (2.78 × 10^4); IR (KBr, cm^{-1}) 1887, 1596, 1493, 1246; LRMS (70 eV) m/z 538 (M$^+$), 465, 349, 246; HRMS (30 eV) m/z calcd for $C_{27}H_{46}Si_6$ 538.2215, found 538.2224.

1,3,5,5-Tetraphenyl-4,4,6,6-tetramethyl-4,5,6-trisilacyclohexa-1,2-diene (3). The six-membered trisilacyclic allene **3** was obtained by the reaction of $Ph_2C_3Li_2$ with 1,3-dichloro-2,2-diphenyltetramethyltrisilane in yield of 11%. Colorless prisms suitable for X-ray diffraction were obtained by recrystallization from hexane: mp 131–132 °C; ^1H NMR (500 MHz, C_6D_6) δ 0.44 (s, 6 H), 0.53 (s, 6 H), 6.9–7.6 (m, 20 H); ^{13}C NMR (125 MHz, C_6D_6) δ 0.2 (q), 1.3 (q), 96.2 (s), 127.1 (d), 128.7 (d), 129.1 (d), 129.2 (d), 129.3 (d), 135.9 (s), 136.8 (s), 137.0 (d), 207.4 (s); ^{29}Si NMR (17.6 MHz, C_6D_6) δ –32.2, –7.9; UV (hexane, nm (ϵ)) 252 (4.05 × 10^4), 320 (sh, 2.00 × 10^3); IR (KBr, cm^{-1}) 1856, 1491, 1427; LRMS (70 eV) m/z 488 (M$^+$), 473, 411; HRMS (30 eV) m/z calcd for $C_{31}H_{32}Si_3$ 488.1812, found 488.1802.

Hexadecamethyl-2,3,4,5,6,7,8,9,10-octasilabicyclo[4.4.1]undeca-1-(11),6(11)-diene (4). To a magnesium powder (972 mg, 40.0 mmol) in THF (10 mL) was added dropwise for 1 h a THF (15 mL) solution of hexachloropropene (498 mg, 2.00 mmol) and 1,4-dichlorooctamethyltetrasilane (1.51 g, 5.00 mmol). Exothermic reaction occurred, and the solution darkened. The THF solution was heated at 50 °C for 4 h after addition was completed. After the solvent was removed, hexane (30 mL) was added to the residue. The excess magnesium and the precipitate were filtered, and the filtrate was concentrated. A 344 mg (34%) yield of **4** was separated from the reaction mixture by GPC. Colorless prisms suitable for X-ray diffraction were obtained by recrystallization from hexane: mp 146.5–147.5 °C; ^1H NMR (500 MHz, C_6D_6) δ 0.31 (s, 12 H), 0.37 (s, 12 H), 0.42 (s, 12 H), 0.45 (s, 12 H); ^{13}C NMR (125 MHz, C_6D_6) δ –6.4 (q), –4.4 (q), –0.5 (q), 0.2 (q), 122.9

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(s), 207.8 (s); ^{29}Si NMR (17.6 MHz, C_6D_6) δ -39.9, -16.6; UV (cyclohexane, nm (ϵ)) 285 (sh, 8.36 × 10^2), 233 (sh, 1.74 × 10^4); IR (KBr, cm^{-1}) 2960 m, 1865 s, 1245 m, 900 m; LRMS (70 eV) m/z 500 (M$^+$), 485, 427 (base), 412; HRMS (30 eV) m/z calcd for $C_{19}H_{48}Si_8$ 500.1910, found 500.1934.

Reaction of 1,3-Dichlorotrisilane with Hexachloropropene in the Presence of Magnesium. Similar reaction of 1,3-dichlorohexamethyltrisilane with hexachloropropene in the presence of magnesium gave the bicyclic product **6** (16%) after purification by GPC: mp 157.5–158.5 °C; ^{1}H NMR (500 MHz, C_6D_6) δ 0.17 (s, 12 H), 0.38 (s, 12 H), 0.42 (s, 12 H); ^{13}C NMR (125 MHz, C_6D_6) δ -7.5 (q), -2.8 (q), -2.3 (q), 120.2 (s), 156.4 (s), 173.1 (s); ^{29}Si NMR (17.6 MHz, C_6D_6) δ -54.7, -35.1, -20.5; UV (cyclohexane, nm (ϵ)) 308 (8.32 × 10^3), 258 (2.63 × 10^4), 218 (1.64 × 10^4); IR (KBr, cm^{-1}) 2960, 2900, 1545, 1405, 1250; LRMS (70 eV) m/z 490 (M$^+$), 475 (base), 397, 367, 289; HRMS (30 eV) m/z calcd for $C_{17}H_{33}Si_6Cl_2$ (M$^+$ – Me) 475.0575, found 475.0554.

Photochemical Reaction of 1. A hexane (300 mL) solution of **1** (300 mg, 0.70 mmol) was irradiated for 32 h with a low-pressure mercury lamp through a quartz tube. The solvent was removed in vacuo, and the reaction mixture was separated by preparative TLC (silica gel, hexane) and GPC. The product **11** could not be separated from unreacted starting material **1** (total 15 mg). Spectroscopic analysis of the mixture **1** and **11** gave following spectral data for **11**, and the yield (2.5%) was determined by the integral ratio of the ^{1}H NMR measurement: ^{1}H NMR (400 MHz, C_6D_6) δ 0.10 (s, 3 H), 0.27 (s, 3 H), 0.30 (s, 3 H), 0.31 (s, 3 H), 0.36 (s, 3 H), 0.38 (s, 3 H), 0.48 (s, 3 H), 0.58 (s, 3 H), 7.0–7.8 (m, 10 H); ^{13}C NMR (100 MHz, C_6D_6) δ -6.0 (q), -5.9 (q), -5.6 (q), -5.5 (q), -2.2 (q), -1.9 (q), -0.9 (q), -0.8 (q), 24.9 (s), 119.1 (s), 125.5 (d), 126.8 (d), 128.5 (d), 128.7 (d), 129.4 (d), 129.8 (d), 131.2 (s), 136.3 (s), 149.8 (s); ^{29}Si NMR (17.6 MHz, C_6D_6) δ -46.5, -44.9, -26.6, -11.1; LRMS (70 eV, capillary GC) m/z 422 (M$^+$), 407, 349.

X-ray Analysis. Crystals of **1**, **2**, and **4** were mounted on a glass fiber and subjected to a detailed photographic examination followed by intensity data collection on an Enraf–Nonius CAD4 diffractometer. The unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters and results of the analyses are summarized in Table IV. All data processing was performed on a Micro VAX 3100 computer using the SDP structure-solving program obtained from Enraf–Nonius Corp., Delft, the Netherlands. Neutral-atom scattering factors were calculated by the standard procedures.[20] Full-matrix least-squares refinements minimized the function $\sum\omega(|F_o| - |F_c|)^2$, $\omega = 1$.

Compounds **1** and **3** crystallized in the monoclinic crystal systems, and **4** crystallized in the triclinic crystal system. The space groups of **1**, **3**, and **4** were determined to be $C2$, $P2_1$, and $P\bar{1}$, respectively. It was found that a 1:2 enantiomixture was packed in the unit cell of crystal **1** a 1:1 enantiomixture was packed in each unit cell of the crystals **3** and **4**.

Supplementary Material Available: Detailed information of the X-ray crystal analysis of **1**, **3**, and **4** including structure diagrams, details of data collection and reduction and structure solution and refinement, tables of positional and thermal parameters, general temperature factor expressions, root-mean-square amplitudes of thermal vibration, and bond distances and angles (24 pages); list of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

(20) *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1975; Vol. IV.