Organometallics **1993,** *12,* 3474–3479

Silicon–Carbon Unsaturated Compounds. 47. Dimerization of Silenes Generated from 1,4-Bis(pentamethyldisilanyl)benzene and 1-(Pentamethyldisilanyl)-4-(trimethylsilyl)benzene and Molecular Structure of a Dimer

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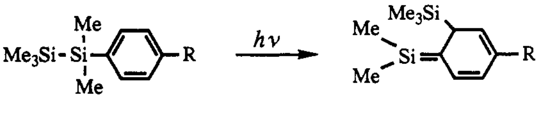
The photolysis of 1,4-bis(pentamethyldisilanyl)benzene in hexane or cyclohexane gave two isomeric dimers, 7,7,8,8-tetramethyl-3,12-bis(pentamethyldisilanyl)-13,14-bis(trimethylsilyl)-7,8-disilatricyclo$[7.3.1.1^{2,6}]$tetradeca-3,5,9,11-tetraene (**4**) and 7,7,8,8-tetramethyl-3,12-bis(pentamethyldisilanyl)-10,14-bis(trimethylsilyl)-7,8-disilatricyclo$[7.3.1.1^{2,6}]$tetradeca-3,5,9(13),11-tetraene (**5**), in a ratio of 1:1. Similar photolysis of 1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene afforded the two isomeric dimers **7** and **8**, analogous to **4** and **5**, in a ratio of 3:2. Heating **4** at 200 °C for 2 h produced 2-[4-(pentamethyldisilanyl)-6-(trimethylsilyl)cyclohexa-1,3-dienyl]-1-[4-(pentamethyldisilanyl)-2-(trimethylsilyl)phenyl]tetramethyldisilane (**3**) in 85% yield. Treatment of **7** at 200 °C for 2 h afforded 1-[2,4-bis(trimethylsilyl)phenyl]-2-[4,6-bis(trimethylsilyl)cyclohexa-1,3-dienyl]tetramethyldisilane (**6**) in 95% yield. Compound **8** also afforded **6** under the same conditions in 90% yield. The structure of **8** was verified by an X-ray crystallographic study. Compound **8** crystallizes in the space group *Cc* with cell dimensions of $a = 13.158(6)$ Å, $b = 18.04(1)$ Å, $c = 15.88(1)$ Å, $\beta = 104.77(4)°$, and $V = 3645(4)$ Å^3 ($Z = 4$).

Introduction

In 1975, we found that the photolysis of pentamethylphenyldisilane and pentamethyl(*p*-tolyl)disilane affords silenes, 1-(dimethylsilylene)-2-(trimethylsilyl)cyclohexa-3,5-diene and 4-methyl-1-(dimethylsilylene)-2-(trimethylsilyl)cyclohexa-3,5-diene arising from a 1,3-trimethylsilyl shift to the ortho position of the aryl ring:[2]



R = H or CH_3

The silylenecyclohexadienes thus formed react with various trapping agents, such as alcohols,[3] carbonyl compounds,[4] alkenes,[5] and alkynes,[6] to give addition products. In the absence of the trapping agent, the silylenecyclohexadienes undergo polymerization to give nonvolatile products. The photolysis of benzenoid aromatic disilanes such as pentamethyl-*o*-tolyl- and pentamethyl-*m*-tolyldisilane[7] and 2-(trimethylsilyl)- and 3-(trimethylsilyl)-1-(pentamethyldisilanyl)benzene[8] shows behavior similar to that of phenyl- and *p*-tolyl-substituted pentamethyldisilane. All of the silylenecyclohexadienes generated from these aryldisilanes afford nonvolatile products in the absence of a trapping agent.

Recently, we have reported that the photolysis of 1,2-, 1,3-, and 1,4-bis(pentamethyldisilanyl)benzene in the presence of isobutene in a benzene solution gives adducts produced by the reaction of the silylenecyclohexadiene arising from a 1,3-trimethylsilyl shift from one of two pentamethyldisilanyl groups with isobutene in high yield.[9] In the absence of isobutene in benzene, again the silylenecyclohexadienes thus formed undergo polymerization to give mainly nonvolatile substances. We have now found that the silylenecyclohexadiene generated photochemically from 1,4-bis(pentamethyldisilanyl)benzene in a hexane or cyclohexane solution undergoes dimerization to give two isomers of a tricyclic dimer in good yields. In this paper we report a novel dimerization reaction of the silylenecyclohexadiene produced from the photolysis of 1,4-bis(pentamethyldisilanyl)benzene and 1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene.[10] We also report an X-ray crystallographic study of the dimer obtained from 1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1993.

[1] (a) Hiroshima University. (b) Nara Women's University. (c) Tokushima University. (d) Otsuka Pharmaceutical Co., Ltd.

[2] Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923.

[3] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 155.

[4] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1977**, *133*, 19.

[5] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 139; **1978**, *162*, 223.

[6] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1977**, *127*, 261.

[7] Ishikawa, M.; Sakamoto, H. *J. Organomet. Chem.* **1991**, *414*, 1.

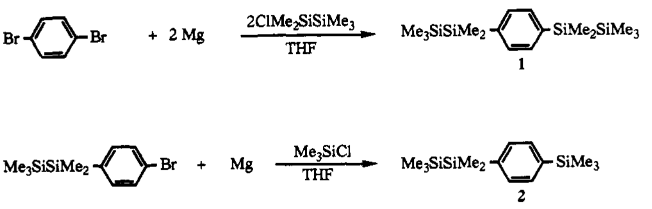
[8] The photolysis of these compounds in the absence of a trapping agent afforded no volatile products.

[9] Ishikawa, M.; Sakamoto, H.; Kanetani, F.; Minato, A. *Organometallics* **1989**, *8*, 2767.

[10] Ishikawa, M.; Kikuchi, M.; Watanabe, K.; Sakamoto, H.; Kunai, A. *J. Organomet. Chem.* **1993**, *443*, C3.

0276-7333/93/2312-3474\$04.00/0

Scheme I



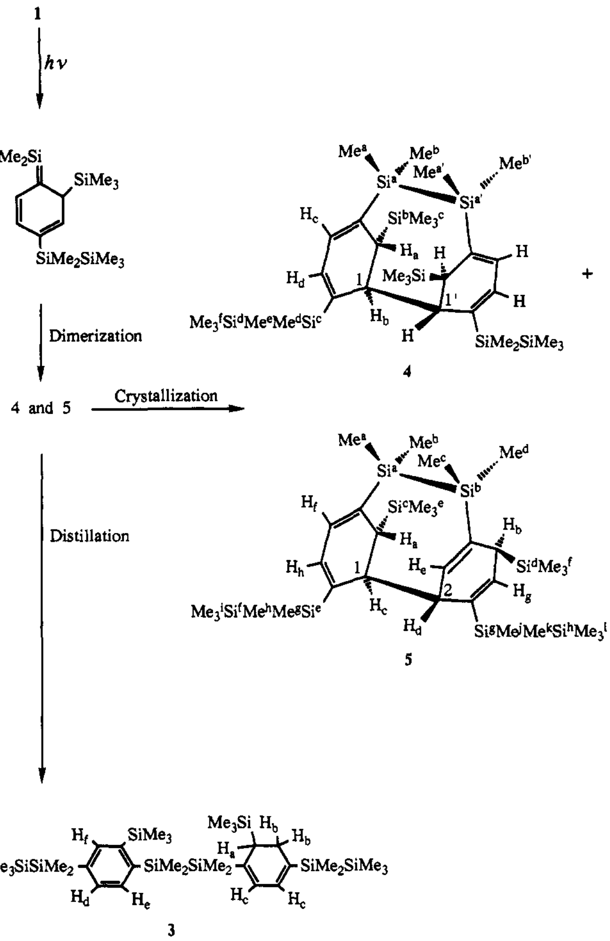
Results and Discussion

1,4-Bis(pentamethyldisilanyl)benzene (1) and 1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene (2), used as starting compounds, were synthesized by the reaction of the di-Grignard reagent prepared from *p*-dibromobenzene with chloropentamethyldisilane in THF and the reaction of the Grignard reagent of (4-bromophenyl)pentamethyldisilane with chlorotrimethylsilane in THF, respectively (Scheme I).

Photolysis. First, we reinvestigated the photolysis of compound 1 in benzene. Irradiation of a benzene solution of compound 1 with a low-pressure mercury lamp bearing a Vycor filter (254 nm) in the absence of a trapping agent afforded a trace of a product, 1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene, which was produced by extrusion of dimethylsilylene from the starting compound 1 as reported previously.[11] Careful analysis of the photolysis mixture by GC–mass spectrometry showed that the product with a molecular weight of 676, corresponding to the dimer of 1, was produced in 3% yield, although the main products were nonvolatile substances whose molecular weight was determined to be 2000, relative to polystyrene standards. The ^{13}C NMR spectrum of the polymeric substances shows multiple resonances at δ −3.5 to +3.5 and 134–142 ppm, due to methylsilyl carbons and phenylsilyl carbons, as well as resonances at δ 24–31 ppm, attributed to methylene carbons.

Interestingly, when a similar photolysis of 1 was carried out in a hexane solution, the dimer of 1 was produced in 46% yield, along with a trace of 1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene, when 89% of the starting compound 1 was photolyzed (Scheme II). We attempted to isolate the dimer by distillation. Thus, the photolysis mixture was distilled under reduced pressure to give the dimer. GC–mass spectrometric analysis of the distillate showed the presence of the dimer and small amounts of four products (less than 5% combined yields). The retention time of one of the four products was identical with that of 1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene, but other products could not be detected in the photolysis mixture before distillation. Molecular weights of these three were measured to be 280, 396, and 544, respectively. The retention times of the first two compounds were identical with those of [3-(trimethylsilyl)phenyl]pentamethyldisilane and 1-(pentamethyldisilanyl)-4-(1,1,2,2-tetramethyldisilanyl)-3-(trimethylsilyl)benzene, respectively. The molecular weight of the latter corresponds to the product which would be formed by elimination of pentamethyldisilane from the dimer. The dimer was isolated by preparative GLC and identified as 2-[4-(pentamethyldisilanyl)-6-(trimethylsilyl)cyclohexa-1,3-dienyl]-1-[4-(pentamethyldisilanyl)-2-(trimethylsilyl)phenyl]tetramethyldisilane (3) by spectrometric analysis.

Scheme II



The ^{13}C NMR spectrum of 3 reveals 4 resonances at −4.10, −4.04, 0.47, and 0.52 ppm and 4 resonances at −2.19, −1.87, 0.04, 2.12 ppm, attributed to Me$_2$Si carbons and Me$_3$Si carbons, respectively, in addition to 2 sp^3 ring carbons and 10 sp^2 ring carbons, in accord with the structure proposed for 3.

Surprisingly, when we attempted to isolate the photolysis products by fractional recrystallization without heating, two isomers were obtained as white crystals. These products were identified as 7,7,8,8-tetramethyl-3,12-bis(pentamethyldisilanyl)-13,14-bis(trimethylsilyl)-7,8-disilatricyclo[7.3.1.1^{2,6}]tetradeca-3,5,9,11-tetraene (4) and 7,7,8,8-tetramethyl-3,12-bis(pentamethyldisilanyl)-10,14-bis(trimethylsilyl)-7,8-disilatricyclo[7.3.1.1^{2,6}]tetradeca-3,5,9(13),11-tetraene (5) by spectroscopic analysis, as well as by elemental analysis. The photolysis of 1 in cyclohexane led to the same result as that in hexane. Dimerization products were obtained in 45% combined yield. In both cases, the ratio of two dimeric isomers thus formed is determined to be 1:1 by ^{1}H NMR spectroscopic analysis of the reaction mixture.

^{1}H, ^{13}C, and ^{29}Si NMR spectra of 4 show that the molecule has a C_2 symmetry axis passing through the center of an Si^a–$Si^{a'}$ bond and C_1–$C_1{}'$ bond (see the structure of 4 in Scheme II). In fact, the ^{29}Si NMR spectrum of 4 reveals only four resonances at δ 1.84, −18.26, −18.49, and −18.65 ppm. Furthermore, the location of the substituents on the six-membered rings was determined by NOE-FID difference experiments at 270 MHz. Thus, irradiation of an H_a proton led to a strong enhancement of trimethysilyl protons ($Me_3{}^cSi^b$) and two methyl protons on the ring silicon atom (Me^aSi^a, $Me^{a'}Si^{a'}$), as well as a proton (H_b)

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(11) For mechanistic studies of photoexcited aryldisilanes, see: Slugget, G. W.; Leigh, W. J. *Organometallics* **1992**, *11*, 3731 and references cited therein.

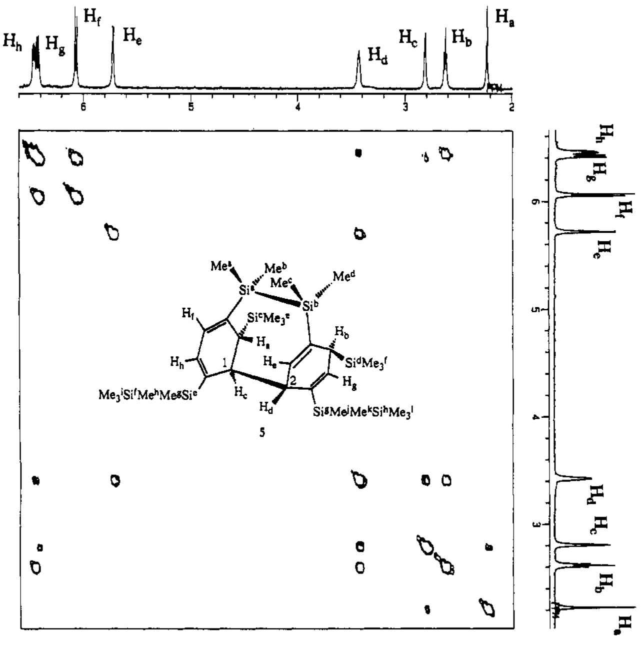
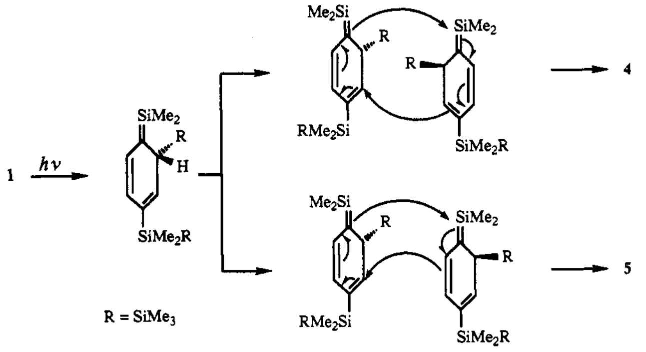


Figure 1. Two-dimensional ^{1}H COSY experiment for **5** in C_6D_6 at 270 MHz.

Scheme III

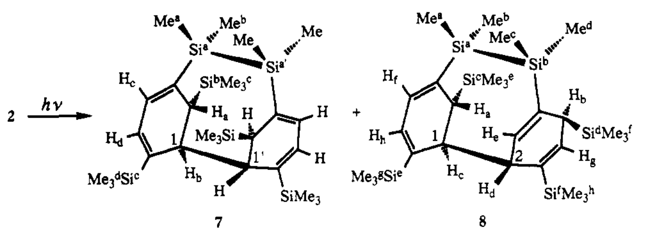


at 2.65 ppm. Saturation of the proton (H_b) resulted in a positive NOE of H_a, $Me_3{}^cSi^b$ protons, and two methyl protons on a pentamethyldisilanyl group ($Me^dMe^eSi^c$). These results are wholly consistent with the structure proposed for **4**.

In contrast to the case for **4**, compound **5** has no symmetry axis. Consequently, its ^{1}H and ^{13}C NMR spectra show complicated resonance patterns. The ^{29}Si NMR spectrum reveals eight resonances, indicating that all silicon atoms are nonequivalent (see Experimental Section). The structure of **5** was verified by ^{1}H, ^{13}C, and ^{29}Si NMR spectra in comparison with those of the unsymmetric dimer produced from the photolysis of **2**, whose structure was confirmed by an X-ray crystallographic analysis (see below). The 2D ^{1}H–^{1}H COSY spectrum of **5** is shown in Figure 1.

Compounds **4** and **5** are probably formed by head-to-head dimerization of the silylenecyclohexadiene arising from a 1,3-trimethylsilyl shift to the ortho position of the phenylene ring from one of two pentamethyldisilanyl groups as shown in Scheme III. Several examples of the head-to-head dimerization of photochemically generated silenes have been reported to date.[12]

Scheme IV



Since linear dimer **3** is obtained by distillation of the photolysis mixture, cyclic dimers **4** and **5** should be transformed thermally into **3**. In fact, heating **4** in a sealed tube at 200 °C for 2 h produced **3** in 85% yield, along with small amounts of decomposition products, whose GC–mass spectra show parent ions at *m/z* 280, 396, and 544, respectively.

It is worth noting that the photolysis of **1** in a saturated hydrocarbon such as hexane or cyclohexane produces dimers in good yields, but not in benzene. We carried out the photolysis of **1** with different concentrations in benzene and also in the mixed solvents consisting of hexane and benzene in different ratios. Interestingly, it was found that, in a benzene solution, the yield of the dimers highly depends on the concentration of the starting compound **1** used. The photolysis of a 3.0×10^{-2} M benzene solution of **1** gave dimers **4** and **5** only in 3% combined yield, while irradiation of a 6.0×10^{-2} M solution of **1** afforded **4** and **5** in 21% combined yield. The higher concentration of **1** led to the formation of dimers in higher yield. Thus, irradiation of a 1.5×10^{-1} M solution of **1** gave the dimers in 30% yield. Irradiation of a 3.0×10^{-2} M solution of **1** in a 1:1 mixture of benzene and hexane produced dimers in 12% yield. Irradiation of the same concentration of **1** in a 1:2 benzene–hexane solution afforded **4** and **5** in 15% yield, while the photolysis of a 1:5 benzene–hexane solution of **1** gave dimers in 24% yield. The reason for the decrease of dimers **4** and **5** in benzene or in the mixed solvent consisting of benzene and hexane is not yet clear at present.

The photolysis of **2** also afforded dimers in high yields. Thus, the photolysis of **2** in the absence of a trapping agent in hexane gave the dimers 7,7,8,8-tetramethyl-3,12,13,14-tetrakis(trimethylsilyl)-7,8-disilatricyclo[7.3.1.1^{2,6}]tetradeca-3,5,9,11-tetraene (**7**) and 7,7,8,8-tetramethyl-3,10,12,14-tetrakis(trimethylsilyl)-7,8-disilatricyclo[7.3.1.1^{2,6}]tetradeca-3,5,9(13),11-tetraene (**8**) in 61% yields, in addition to a 3% yield of 1,4-bis(trimethylsilyl)benzene, which would be produced by extrusion of dimethylsilylene from the starting compound **2** (Scheme IV). Interestingly, a similar photolysis of **2** in benzene afforded **7** and **8** in 63% combined yield. In this photolysis, no decrease of yields of dimers **7** and **8** was observed. The ratio of **7** and **8** was determined to be 3:2 by ^{1}H NMR spectrometric analysis of the photolysis mixture. Dimers **7** and **8** were isolated by MPLC and recrystallized from hexane. The structure of symmetric isomer **7** was confirmed by spectrometric analysis (see Experimental Section). The structure of **8** was verified by an X-ray crystallographic analysis (see below).

Like the dimers prepared from the photolysis of **1**, compounds **7** and **8** undergo thermal isomerization to give a ring-opened isomer. Thus when compound **7** was heated in a sealed glass tube at 200 °C for 2 h, 1-[2,4-bis(trimethylsilyl)phenyl]-2-[4,6-bis(trimethylsilyl)cyclohexa-1,3-dienyl]tetramethyldisilane (**6**) was obtained in almost quantitative yield (Scheme V). The formation of

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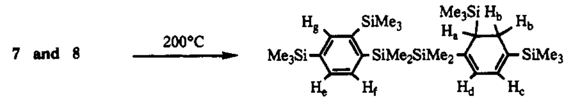
[12] Brook, A. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part II, Chapter 15.

Scheme V



6

Table I. Crystallographic Data for 8

chem formula	$C_{28}H_{56}Si_6$
fw	561.3
cryst syst	monoclinic
space group	*Cc*
a	13.16(1) Å
b	18.04(1) Å
c	15.88(1) Å
β	104.77(4)°
V	3645(4) Å^3
Z	4
T	296 K
D_{calcd}	1.023 g/cm^3
λ(Mo Kα)	0.710 69 Å
cryst dimens	0.4 × 0.4 × 0.4 mm
μ	2.37 cm^{-1}
scan mode	*θ*/2*θ*
2*θ*(min, max)	3.0, 45.0°
h range	0–14
k range	0–19
l range	–14 to +14
no. of measd rflns	2458
no. of unique rflns	2391
no. of obsd rflns ($I > 3\sigma(I)$)	1213
no. of params refined:	305
GOF	1.37
data/param ratio	3.98
transmissn coeff (max, min)	0.910, 0.875
R^a	0.043
$R_w{}^b$	0.047
F(000)	1232
residuals (max, min), e/Å^3	0.18, –0.18

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\{\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2\}]^{1/2}$, $w = 4F_o{}^2/\sigma(F_o{}^2)$.

6 may be best understood in terms of scission of a C_1–C_1' bond in compound 7, followed by a 1,3-H_a shift onto a C_1 atom. The thermolysis of 8 under the same conditions also produced 6, whose formation can be explained by scission of a C_1–C_2 bond in compound 8 and a 1,5-H_a shift, in quantitative yield. The structure of 6 was verified by mass, IR, and ^{1}H and ^{13}C NMR spectrometric analysis, as well as by elemental analysis.

X-ray Crystallographic Analysis of 8. Colorless crystals of 8 were obtained by recrystallization from ethanol. Detailed crystal data are shown in Table I. A crystal with dimensions of 0.4 × 0.4 × 0.4 mm was used for the X-ray study. The crystal belongs to the space group *Cc* with cell dimensions of $a = 13.158(6)$ Å, $b = 18.04(1)$ Å, and $c = 15.88(1)$ Å, $\alpha = \gamma = 90°$, $\beta = 104.77(4)°$, $V = 3645(4)$ Å^3, $Z = 4$, and $D_{calcd} = 1.02$ g/cm^3. Graphite-monochromatized Mo Kα radiation was used to collect intensity data for all the reflections in the range $2\theta < 50°$ in (*hkl*) and (–*hkl*). All the intensities were measured on a Rigaku AFC-5 four-circle diffractometer. The *θ*–2*θ* scan method was employed with *θ*-scanning width (1.78° + 0.30° tan *θ*). Three standard reflections monitored every 150 reflections showed no significant variation in intensity. The intensities were corrected for Lorentz and polarization factors, and an empirical absorption correction was applied by using the program DIFABS.[13] The structure was solved by direct methods using the program MITHRIL.[14] A total of 1213 observed reflections ($I > 3\sigma(I)$) were used in the least-squares refinement. Positional parameters and anisotropic temperature factors for all the non-hydrogen atoms were refined by full-matrix least-squares refinement. Atomic parameters of hydrogen atoms at calculated positions were not refined in the refinement procedure but included in the structure factor calculation. $\sum w(|F_o| - |F_c|)^2$ was minimized in the refinement with weight $w = 4F_o{}^2/\sigma^2(F_o{}^2)$, where F_o, F_c, and $F_o{}^2$ are an observed structure factor, a calculated factor, and an estimated standard deviation of $F_o{}^2$, respectively. Finally, *R*, R_w, and GOF values of 0.043, 0.047, and 1.37, respectively, were obtained. The maximum and minimum peaks of the final difference Fourier map were 0.18 and –0.18 e/Å^3, respectively. Atomic scattering factors taken from ref 15 were used in the structure factor calculation. The molecular structure with the atomic numbering system is shown in Figure 2. The final atomic coordinates and equivalent isotropic temperature factors are in Table II. Bond distances and angles are listed in Table III. The averaged temperature factor of 16 methyl carbon atoms is as high as 10 Å^2. There are no abnormal bond distances and angles and no close intermolecular contacts.

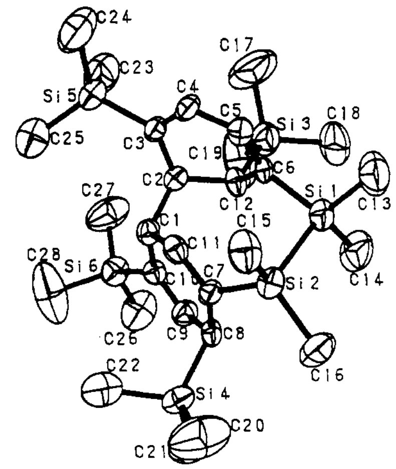


Figure 2. View of compound 8, showing the atomic numbering scheme.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry argon. Ultraviolet spectra were recorded on a Shimadzu UV–visible spectrophotometer. Infrared spectra were measured as thin liquid films for liquid samples and as KBr disks for crystal samples using a Perkin-Elmer 1600 FT-IR spectrometer. Gas chromatographic analysis was carried out using a Hitachi 263-30 gas chromatograph (2% OV-17 silicone on Uniport HP). Gas chromatographic separations of products were carried out by using a column packed with 30% SE-30 silicone on Chromosorb P. NMR spectra were determined with a JEOL Model JNM-EX 270 spectrometer. Mass spectra were determined on a Shimadzu Model GCMS-QP 1000.

Materials. 1,4-Bis(pentamethyldisilanyl)benzene was prepared as reported previously.[9] Benzene and hexane used as solvents were dried over lithium aluminum hydride and distilled just before use. Diethyl ether and tetrahydrofuran were dried over sodium–benzophenone ketyl and distilled just before use.

Preparation of 1-(Pentamethyldisilanyl)-4-(trimethylsilyl)benzene (2). In a 100-mL three-necked flask with a condenser, stirrer, and dropping funnel was placed 37.8 g (0.16

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(13) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

(14) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV (present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands).

Table II. Positional and Equivalent Isotropic Thermal Parameters with Their Esd's in Parentheses

atom	*x*	*y*	*z*	*B*(eq), Å^2
Si(1)	0.6372(4)	−0.0004(2)	0.2458(3)	4.5(2)
Si(2)	0.5256	−0.0123(2)	0.3377	4.1(2)
Si(3)	0.8650(4)	0.1560(3)	0.2662(4)	6.1(2)
Si(4)	0.3724(4)	0.1570(2)	0.4191(4)	5.0(2)
Si(5)	0.9931(4)	0.1318(3)	0.5796(4)	5.7(2)
Si(6)	0.6852(5)	0.3199(2)	0.4802(4)	5.0(2)
C(1)	0.708(1)	0.1577(7)	0.4721(8)	3.3(6)
C(2)	0.805(1)	0.1491(7)	0.4297(9)	3.5(6)
C(3)	0.891(1)	0.0981(8)	0.4835(8)	3.6(6)
C(4)	0.894(1)	0.0289(7)	0.455(1)	4.0(7)
C(5)	0.822(1)	−0.0006(7)	0.380(1)	4.1(6)
C(6)	0.757(1)	0.0432(8)	0.3212(8)	3.5(6)
C(7)	0.549(1)	0.0791(7)	0.3967(8)	3.4(7)
C(8)	0.484(1)	0.1472(7)	0.3670(8)	3.4(6)
C(9)	0.547(1)	0.2193(7)	0.3856(9)	3.9(7)
C(10)	0.643(1)	0.2247(7)	0.4381(9)	3.2(6)
C(11)	0.644(1)	0.0859(7)	0.4509(8)	3.3(6)
C(12)	0.771(1)	0.1256(7)	0.3328(8)	3.6(6)
C(13)	0.671(1)	−0.091(1)	0.204(1)	8(1)
C(14)	0.571(1)	0.059(1)	0.152(1)	8(1)
C(15)	0.570(1)	−0.0915(7)	0.412(1)	5.6(8)
C(16)	0.387(1)	−0.0284(8)	0.271(1)	6.7(9)
C(17)	0.999(1)	0.115(2)	0.307(1)	14(2)
C(18)	0.822(2)	0.125(1)	0.151(1)	9(1)
C(19)	0.870(2)	0.257(1)	0.269(1)	14(2)
C(20)	0.289(2)	0.074(1)	0.414(2)	12(1)
C(21)	0.288(2)	0.232(1)	0.369(1)	10(1)
C(22)	0.425(1)	0.179(1)	0.536(1)	11(1)
C(23)	1.072(2)	0.206(1)	0.545(1)	10(1)
C(24)	1.084(1)	0.056(1)	0.626(1)	10(1)
C(25)	0.939(1)	0.174(1)	0.665(1)	11(1)
C(26)	0.606(1)	0.3919(8)	0.411(1)	9(1)
C(27)	0.821(1)	0.346(1)	0.488(1)	10(1)
C(28)	0.665(2)	0.325(1)	0.592(1)	14(2)

mol) of *p*-dibromobenzene in 50 mL of THF. To this was added dropwise 90 mL of an *n*-butyllithium–hexane solution (0.16 mol) through the dropping funnel at −70 °C over a period of 1 h, and the mixture was then stirred at room temperature for 2 h. Chloropentamethyldisilane (26.7 g, 0.16 mol) was added at room temperature over a period of 1 h, and this mixture was heated to reflux for 1 h. The resulting lithium salt was filtered off and the solvents were evaporated. The residue was distilled under reduced pressure to give 29.8 g (63% yield) of (*p*-bromophenyl)pentamethyldisilane.

In a 200-mL three-necked flask with a condenser, stirrer, and dropping funnel were placed 2.5 g (0.10 mol) of magnesium and 12.4 g (0.11 mol) of trimethylchlorosilane in 30 mL of THF. To this was added a solution of 28.7 g (0.10 mol) of (*p*-bromophenyl)pentamethyldisilane in 30 mL of THF at room temperature over a period of 1 h. The mixture was heated to reflux for 1 h and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over magnesium sulfate. The solvents were evaporated, and the residue was distilled under reduced pressure to give 16.0 g (57% yield) of **2** as a colorless liquid: bp 131–132 °C/14 mmHg; MS *m/z* 280 (M$^+$); IR 3043, 2995, 2954, 2897, 1408, 1378, 1242, 1132, 834, 794, 752, 693, 659, 619 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.12 (s, 9H, $Me_3Si{-}Si$), 0.31 (s, 9H, $Me_3Si{-}C_6H_4$), 0.37 (s, 6H, Me_2Si), 7.51 (AB q, 4H, aromatic H, *J* = 14.19, 7.92 Hz); ^{13}C NMR (δ in CDCl$_3$) −4.00 ($Me_3Si{-}Si$), −2.19 (Me_2Si), −1.15 ($Me_3Si{-}C_6H_4$), 132.58, 133.10, 140.20, 140.29 (aromatic ring carbons). Anal. Calcd for $C_{14}H_{28}Si_3$: C, 59.92; H, 10.06. Found: C, 59.80; H, 10.23.

Photolysis of 1. A solution of 0.2568 g (0.76 mmol) of **1** and 0.0147 g (0.074 mmol) of tetradecane as an internal standard in 25 mL of hexane was placed in a 30-mL reaction vessel fitted with a low-pressure mercury lamp bearing a Vycor filter. The mixture was irradiated at room temperature for 20 min with a slow stream of argon bubbling through the mixture. The reaction mixture was analyzed by GLC as being **4** and **5** (46% combined yield) and 11% of the starting compound **1**. After the solvent was evaporated off, the mixture of **4** and **5** was isolated by preparative MPLC. Pure **4** and **5** were separated by fractional recrystallization from ethanol as colorless crystals. Data for **4**: mp 118.0–120.0 °C; MS *m/z* 545 (M$^+$ − Si_2Me_5); IR 3053, 2990, 2953, 2895, 1340, 1245, 1121, 1078, 1042, 947, 862, 835, 789, 757, 731 cm^{-1}; ^{1}H NMR (δ in C_6D_6) 0.14 (s, 18H, $Me_3{}^cSi^b$), 0.27 (s, 18H, $Me_3{}^fSi^d$), 0.26 (s, 6H, Me^bSi^a), 0.28 (s, 6H, Me^aSi^a), 0.48 (s, 6H, Me^dSi^c), 0.53 (s, 6H, Me^eSi^c), 2.50 (s, 2H, H_a), 2.65 (s, 2H, H_b), 6.08 (d, 2H, H_c, *J* = 4.95 Hz), 6.68 (d, 2H, H_d, *J* = 4.95 Hz); ^{13}C NMR (δ in C_6D_6) −6.55 (Me^bSi^a), −4.74 (Me^aSi^a), −2.15 (Me^dSi^c), 0.37 (Me^eSi^c), −1.38 ($Me_3{}^cSi^b$), 0.02 ($Me_3{}^fSi^d$), 28.79 (C–H_a), 40.63 (C–H_b), 129.62 (C–H_c), 136.00 (C–Si), 138.84 (C–H_d), 144.24 (C–Si); ^{29}Si NMR (δ in C_6D_6) −18.65, −18.49, −18.26, 1.84. Anal. Calcd for $C_{32}H_{68}Si_8$: C, 56.80; H, 10.06. Found: C, 56.80; H, 10.02. Data for **5**: mp 127.5–130.0 °C; MS *m/z* 545 (M$^+$ − Si_2Me_5); IR 2942, 2898, 1921, 1744, 1626, 1599, 1563, 1529, 1463, 1340, 1247, 1194, 1128, 1084, 970, 833 cm^{-1}; ^{1}H NMR (δ in C_6D_6) 0.13 (s, 9H, $Me_3{}^fSi^d$), 0.19 (s, 3H, Me^bSi^a), 0.21 (s, 9H, $Me_3{}^lSi^h$), 0.25 (s, 9H, $Me_3{}^eSi^c$), 0.27 (s, 3H, Me^cSi^b), 0.28 (s, 3H, Me^dSi^b), 0.29 (s, 9H, $Me_3{}^iSi^f$), 0.33 (s, 3H, Me^aSi^a), 0.44 (s, 3H, Me^jSi^g), 0.47 (s, 3H, Me^gSi^e), 0.48 (s, 3H, Me^kSi^g), 0.52 (s, 3H, Me^hSi^e), 2.24 (br s, 1H, H_a), 2.63 (t, 1H, H_b, *J* = 3.90 Hz), 2.82 (dd, 1H, H_c, *J* = 1.10, 1.00 Hz), 3.44 (m, 1H, H_d), 5.73 (d, 1H, H_e, *J* = 2.60 Hz), 6.07 (d, 1H, H_f, *J* = 5.00 Hz), 6.43 (dd, 1H, H_g, *J* = 3.90, 1.10 Hz), 6.46 (dd, 1H, H_h, *J* = 5.00, 1.10 Hz); ^{13}C NMR (δ in C_6D_6), −6.12 (Me^bSi^a), −5.92 (Me^aSi^a), −4.74 (Me^dSi^b), −3.16 (Me^cSi^b), −2.35 ($Me_3{}^fSi^d$), −1.79 (Me^gSi^e), −1.59 ($Me_3{}^eSi^c$), −1.02 ($Me_3{}^iSi^f$), −0.48 (Me^kSi^g), −0.35 (Me^hSi^e), 0.19 ($Me_3{}^lSi^h$), 27.95 (C–H_a), 37.27 (C–H_b), 42.72 (C–H_c), 48.65 (C–H_d), 129.74 (C–H_f), 129.98, 133.28 (C–Si), 134.69 (C–H_e), 137.70 (C–H_g), 140.31 (C–Si), 142.25 (C–H_h), 144.82 (C–Si); ^{29}Si NMR (δ in C_6D_6) −21.33, −20.17, −19.42, −18.81, −16.56, −13.10, 1.32, 2.73. Anal. Calcd for $C_{32}H_{68}Si_8$: C, 56.80; H, 10.06. Found: C, 56.78; H, 10.06.

Isolation of 3. A solution of 0.5015 g (1.50 mmol) of **1** and 0.0155 g (0.08 mmol) of tetradecane as an internal standard in 60 mL of hexane was placed in a 65-mL reaction vessel fitted with a low-pressure mercury lamp bearing a Vycor filter. The mixture was irradiated at room temperature for 45 min with a slow stream of argon bubbling through the mixture. After the solvent was evaporated off, the residue was fractionally distilled under reduced pressure. The reaction mixture was analyzed by GLC as being **3** (48% yield), 1-(pentamethyldisilanyl)-4-(trimethylsilyl)benzene (1% yield), and 17% of the starting compound **1**. Pure compound **3** was isolated by preparative GPC: MS *m/z* 676 (M$^+$); IR 2951, 2894, 2798, 1402, 1347, 1246, 1141, 1093, 1058, 989, 833, 794, 756, 688, 659, 620, 535 cm^{-1}; ^{1}H NMR (δ in C_6D_6) 0.15, 0.16, 0.20 (s, 9H, Me_3Si), 0.33, 0.36 (s, 3H, MeSi), 0.42 (s, 6H, Me_2Si), 0.43, 0.48 (s, 3H, MeSi), 0.49 (s, 9H, Me_3Si), 0.64_0, 0.64_1 (s, 3H, MeSi), 1.84 (dd, 1H, H_a, *J* = 7.76, 1.65 Hz), 2.43 (m, 2H, H_b), 6.21 (br s, 2H, H_c), 7.56 (dd, 1H, H_d, *J* = 7.59, 1.32 Hz), 7.89 (d, 1H, H_e, *J* = 7.59 Hz), 8.04 (br s, 1H, H_f); ^{13}C NMR (δ in C_6D_6) −4.10, −4.04 (Me_2Si), −2.19, −1.87, 0.04 (Me_3Si), 0.47, 0.52 (Me_2Si), 2.12 (Me_3Si), 26.88 (C–H_b), 27.57 (C–H_a), 132.63 (C–H_d), 133.06 (C–H_c), 134.75 (C–H_c), 135.72 (C–H_e), 137.84, 138.08 (C–Si), 140.49 (C–H_f), 140.97, 144.51, 145.41 (C–Si); ^{29}Si NMR (δ in C_6D_6), −23.56, −21.88, −21.77, −19.42, −18.99, −3.55, 2.32. Anal. Calcd for $C_{32}H_{68}Si_8$: C, 56.80; H, 10.06. Found: C, 56.75; H, 9.95.

Photolysis of 2. A solution of 0.2360 g (0.84 mmol) of **2** and 0.0297 g (0.19 mmol) of undecane as an internal standard in 25 mL of hexane was placed in a 30-mL reaction vessel. The mixture was irradiated at room temperature with a low-pressure mercury lamp for 30 min. The reaction mixture was analyzed by GLC as being a mixture of **7** and **8** in 61% combined yield in the ratio of 3:2, along with 16% of the starting compound **2**. Pure **7** and **8** were separated by fractional recrystallization from ethanol. Data for **7**: mp 125.0–126.5 °C, MS *m/z* 487 (M$^+$ − $SiMe_3$); IR 3014, 2951, 2909, 1401, 1243, 1138, 1080, 1048, 953, 834, 785, 748, 658, 664 cm^{-1}; ^{1}H NMR (δ in C_6D_6) 0.10 (s, 18H, $Me_3{}^cSi^b$), 0.28_7 (s, 6H, Me^bSi^a), 0.29 (s, 6H, Me^aSi^a), 0.34 (s, 18H, $Me_3{}^dSi^c$), 2.43 (s, 2H, H_a), 2.57 (s, 2H, H_b), 6.07 (d, 2H, H_c, *J* = 4.95 Hz), 6.49 (d, 2H, H_d, *J* = 4.95 Hz); ^{13}C NMR (δ in C_6D_6), −6.54 (Me^bSi^a),

Table III. Bond Lengths (Å) and Angles (deg) with Their Esd's in Parentheses

Bond Lengths							
Si(1)–Si(2)	2.328(5)	Si(1)–C(6)	1.89(1)	Si(5)–C(25)	1.85(2)	Si(6)–C(10)	1.88(1)
Si(1)–C(13)	1.87(2)	Si(1)–C(14)	1.86(2)	Si(6)–C(26)	1.84(2)	Si(6)–C(27)	1.82(2)
Si(2)–C(7)	1.88(1)	Si(2)–C(15)	1.85(1)	Si(6)–C(28)	1.87(2)	C(1)–C(2)	1.60(1)
Si(2)–C(16)	1.88(1)	Si(3)–C(12)	1.90(1)	C(1)–C(10)	1.50(2)	C(1)–C(11)	1.53(2)
Si(3)–C(17)	1.87(2)	Si(3)–C(18)	1.86(2)	C(2)–C(3)	1.54(2)	C(2)–C(12)	1.55(2)
Si(3)–C(19)	1.83(2)	Si(4)–C(8)	1.87(1)	C(3)–C(4)	1.33(2)	C(4)–C(5)	1.42(2)
Si(4)–C(20)	1.84(2)	Si(4)–C(21)	1.81(2)	C(5)–C(6)	1.35(2)	C(6)–C(12)	1.50(2)
Si(4)–C(22)	1.84(2)	Si(5)–C(3)	1.86(1)	C(7)–C(8)	1.50(2)	C(7)–C(11)	1.33(1)
Si(5)–C(23)	1.86(2)	Si(5)–C(24)	1.84(2)	C(8)–C(9)	1.53(2)	C(9)–C(10)	1.33(1)
Bond Angles							
Si(2)–Si(1)–C(6)	101.5(4)	Si(2)–Si(1)–C(13)	112.9(6)	C(10)–Si(6)–C(28)	106.2(7)	C(26)–Si(6)–C(27)	104.7(9)
Si(2)–Si(1)–C(14)	108.0(6)	C(6)–Si(1)–C(13)	110.7(7)	C(26)–Si(6)–C(28)	110(1)	C(27)–Si(6)–C(28)	107(1)
C(6)–Si(1)–C(14)	114.1(7)	C(13)–Si(1)–C(14)	109.5(8)	C(2)–C(1)–C(10)	112(1)	C(2)–C(1)–C(11)	106.2(9)
Si(1)–Si(2)–C(7)	100.5(4)	Si(1)–Si(2)–C(15)	109.1(5)	C(10)–C(1)–C(11)	112(1)	C(1)–C(2)–C(3)	112(1)
Si(1)–Si(2)–C(16)	109.6(6)	C(7)–Si(2)–C(15)	111.9(6)	C(1)–C(2)–C(12)	112.7(9)	C(3)–C(2)–C(12)	112(1)
C(7)–Si(2)–C(16)	115.3(6)	C(15)–Si(2)–C(16)	109.9(7)	Si(5)–C(3)–C(2)	122.4(9)	Si(5)–C(3)–C(4)	120(1)
C(12)–Si(3)–C(17)	112.5(8)	C(12)–Si(3)–C(18)	112.5(7)	C(2)–C(3)–C(4)	117(1)	C(3)–C(4)–C(5)	124(1)
C(12)–Si(3)–C(19)	107.4(8)	C(17)–Si(3)–C(19)	112(1)	C(4)–C(5)–C(6)	122(1)	Si(1)–C(6)–C(5)	118(1)
C(17)–Si(3)–C(18)	104(1)	C(18)–Si(3)–C(19)	108.5(9)	Si(1)–C(6)–C(12)	123(1)	C(5)–C(6)–C(12)	117(1)
C(8)–Si(4)–C(20)	115.4(8)	C(8)–Si(4)–C(21)	109.8(8)	Si(2)–C(7)–C(8)	123.6(9)	Si(2)–C(7)–C(11)	114(1)
C(8)–Si(4)–C(22)	109.2(6)	C(20)–Si(4)–C(21)	107(1)	C(8)–C(7)–C(11)	120(1)	Si(4)–C(8)–C(7)	112.8(9)
C(20)–Si(4)–C(22)	107(1)	C(21)–Si(4)–C(22)	108(1)	Si(4)–C(8)–C(9)	106.4(8)	C(7)–C(8)–C(9)	113.5(9)
C(3)–Si(5)–C(23)	109.4(7)	C(3)–Si(5)–C(24)	110.4(7)	C(8)–C(9)–C(10)	124(1)	Si(6)–C(10)–C(1)	121.3(9)
C(3)–Si(5)–C(25)	113.8(7)	C(23)–Si(5)–C(24)	107.0(9)	Si(6)–C(10)–C(9)	116(1)	C(1)–C(10)–C(9)	122(1)
C(23)–Si(5)–C(25)	106.0(9)	C(24)–Si(5)–C(25)	109.9(9)	C(7)–C(11)–C(1)	126(1)	Si(3)–C(12)–C(2)	114.1(8)
C(10)–Si(6)–C(26)	111.3(7)	C(10)–Si(6)–C(27)	117.4(7)	Si(3)–C(12)–C(6)	107.1(9)	C(2)–C(12)–C(6)	113(1)

−4.76 (Me^{a}Si^a), −0.34 (Me$_3^c$Si^b), 0.62 (Me$_3^d$Si^c), 28.77 (C–H$_a$), 39.92 (C–H$_b$), 129.85 (C–H$_c$), 136.28 (C–Si), 137.09 (C–H$_d$), 144.03 (C–Si). Anal. Calcd for $C_{28}H_{56}Si_6$: C, 60.00; H, 10.00. Found: C, 60.00; H, 9.92. Data for **8**: mp 111.0–114.0 °C, MS *m/z* 487 (M$^+$ − SiMe$_3$); IR 3007, 2953, 2897, 2861, 1566, 1400, 1246, 1246, 1118, 1078, 1046, 941, 832, 750 cm^{-1}; ^{1}H NMR (δ in C_6D_6) 0.10 (s, 9H, Me$_3^f$Si^d), 0.18 (s, 9H, Me$_3^e$Si^c), 0.20 (s, 3H, Me^{b}Si^a), 0.29 (s, 3H, Me^{c}Si^b), 0.30 (s, 3H, Me^{d}Si^b), 0.31 (s, 9H, Me$_3^h$Si^f), 0.33 (s, 9H, Me$_3^g$Si^e), 0.34 (s, 3H, Me^{a}Si^a), 2.24 (br s, 1H, H$_a$), 2.62 (t, 1H, H$_b$, J = 3.63 Hz), 2.70 (dd, 1H, H$_c$, J = 0.99, 0.66 Hz), 3.47 (m, 1H, H$_d$), 5.83 (d, 1H, H$_e$, J = 2.64 Hz), 6.09 (d, 1H, H$_f$, J = 4.95 Hz), 6.36 (dd, 1H, H$_g$, J = 3.63, 0.99 Hz), 6.41 (dd, 1H, H$_h$, J = 4.95, 0.99 Hz); ^{13}C NMR (δ in C_6D_6) −6.05 (Me^{b}Si^a), −5.94 (Me^{a}Si^a), −4.52 (Me^{d}Si^b), −3.14 (Me^{c}Si^b), −2.33 (Me$_3^f$Si^d), 0.02 (Me$_3^e$Si^c), 0.26 (Me$_3^g$Si^e), 0.71 (Me$_3^h$Si^f), 27.80 (C–H$_a$), 36.79 (C–H$_b$), 42.67 (C–H$_c$), 47.93 (C–H$_d$), 129.47 (C–Si), 129.60 (C–H$_f$), 133.37 (C–Si), 134.72 (C–H$_e$), 136.43 (C–H$_h$), 140.08 (C–Si), 140.67 (C–H$_g$), 145.81 (C–Si). Anal. Calcd for $C_{28}H_{56}Si_6$: C, 60.00; H, 10.00. Found: C, 60.00; H, 9.97.

Thermolysis of 7. Compound **7** (0.020 g, 0.036 mmol) was heated in a sealed tube at 200 °C for 2 h. The GLC analysis of the resulting product showed the presence of **6** in quantitative yield: MS *m/z* 560 (M$^+$); IR 2954, 2898, 2364, 1405, 1349, 1248, 1144, 1074, 989, 837, 790, 750, 688, 658, 624, 465 cm^{-1}; ^{1}H NMR (δ in C_6D_6) 0.14, 0.15, 0.30 (s, 9H, Me$_3$Si), 0.35, 0.38 (s, 6 H, Me$_2$Si), 0.47 (s, 9H, Me$_3$Si), 0.65, 0.66 (s, 6H, Me$_2$Si), 1.83 (dd, 1H, H$_a$, J = 7.26, 1.65 Hz), 2.37 (m, 2H, H$_b$), 6.19 (dd, 1H, H$_c$, J = 4.95, 2.64 Hz), 6.24 (d, 1H, H$_d$, J = 4.95 Hz), 7.54 (dd, 1H, H$_e$, J = 7.59, 1.32 Hz), 7.87 (d, 1H, H$_f$, J = 7.59 Hz), 8.07 (br s, 1H, H$_g$); ^{13}C NMR (δ in C_6D_6), −2.26 (Me$_2$Si), −1.90, −1.16, 0.15 (Me$_3$Si), 0.94 (Me$_2$Si), 2.23 (Me$_3$Si), 26.83 (C–H$_b$), 27.27 (C–H$_a$), 132.80 (C–H$_e$), 133.70 (C–H$_d$), 134.88 (C–H$_c$), 136.45 (C–H$_f$), 138.57, 138.87 (C–Si), 140.24 (C–H$_g$), 141.89, 144.96, 146.35 (C–Si). Anal. Calcd for $C_{28}H_{56}Si_6$: C, 60.00; H, 10.00. Found: C, 59.93; H, 10.00.

Thermolysis of 8. Compound **8** (0.025 g, 0.045 mmol) was heated in a sealed tube at 200 °C for 2 h. The GLC analysis of the resulting product showed the presence of **6** in 90% yield.

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Supplementary Material Available: Tables of anisotropic temperature factors for non-hydrogen atoms, calculated positional and isotropic thermal parameters for hydrogen atoms, and selected torsion angles and a stereoview of **8** (4 pages). Ordering information is given on any current masthead page.

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