highest occupied molecular orbital). Fp–arene (and by logical extension Fp–azine) complexes are expected[27] to adopt geometries having Fp–substituent orientations which maximize overlap between the a″ HOMO and the aromatic π*-acceptor orbitals. Indeed, this electronic preference would be expected to be stronger for the more strongly π-accepting[2,11] fluorinated aromatics than it is for the $C_6H_5$ group used in the calculations. In the case of σ-bonded aromatic ligands, these calculations predict a geometry in which the aromatic ring is coplanar with the mirror plane or pseudo mirror plane of the Fp fragment(s) (i.e. Figure 7a). Surprisingly, in these complexes (Figures 4–6) the aromatic rings are observed to have the opposite orientations in which the aromatic planes are perpendicular to the Fp mirror planes or pseudo mirror planes (i.e. Figure 7b). We do not believe that crystal-packing effects can account for this orientational preference, since no unusual intermolecular contacts are observed. In addition, this orientational preference is observed for a wide variety of different complexes and crystal environments.[38] This observation suggests that, at least in the solid state, the major π interaction involves the $Fp^+$ 2a′ orbitals donating to the aromatic LUMO's, since this is the only type of π-symmetry overlap available for the observed perpendicular orientations. Since the 2a′ orbital is of lower energy than a″ and is therefore presumably a poorer π donor, the explanation for the observed orientational preference shown in Figure 7b is unlikely to be electronic in nature.[39] Indeed, qualitative molecular modeling studies[40] indicate that adverse steric interactions between the ortho substituents on the aromatic rings and the other ligands on the iron atoms are much smaller at the crystallographically observed orientations than they are at the orientations predicted by molecular orbital theory.[41]

**Acknowledgment.** We gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada and the University of Alberta (R.C., A.D.H., and B.D.S.) and the National Science Foundation (S.G.B., J.L.A., and J.C.) for their financial support of this work. We also thank Dr. George B. Richter-Addo for his contributions to the electrochemical studies.

**Registry No.** **1**, 119945-86-7; **2**, 119970-49-9; **3**, 37366-22-6; $\mathbf{3}^+$, 137007-60-4; $\mathbf{3}^{2+}$, 137007-67-1; **4**, 37355-34-3; $\mathbf{4}^+$, 137007-61-5; $\mathbf{4}^{2+}$, 137007-66-0; **5**, 12126-73-7; **6**, 12176-60-2; $\mathbf{6}^+$, 137007-62-6; **7**, 31781-18-7; **8**, 33136-08-2; **9**, 33072-10-5; $\mathbf{9}^+$, 137007-63-7; **10**, 12129-49-6; $\mathbf{10}^+$, 137007-64-8; **11**, 134705-81-0; $\mathbf{11}^+$, 137038-76-7; **12**, 134705-82-1; $\mathbf{12}^+$, 137007-65-9; **13**, 134705-80-9; **14**, 134705-73-0; **15**, 134705-68-3; **16**, 134705-74-1; **17**, 134705-76-3; **18**, 134705-78-5; NaFp, 12152-20-4; 1,2,3,5-$C_6H_2F_4$, 2367-82-0; 1,4-$C_6H_4FBr$, 460-00-4; FpI, 12078-28-3; *n*-BuLi, 109-72-8; [*n*-$Bu_4N$]$PF_6$, 3109-63-5; Pt, 7440-06-4; $CH_2Cl_2$, 75-09-2; 1,3-$C_6H_2F_4$, 2367-82-0.

**Supplementary Material Available:** Complete descriptions of the X-ray crystal structure determinations and tables of atomic coordinates and anisotropic Gaussian parameters, bond lengths, bond angles, hydrogen atom coordinates and Gaussian parameters, least-squares planes, torsional angles, and root-mean-square amplitudes of vibration for 3, 6, and 10 (22 pages); listings of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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(38) Similar orientations are observed in numerous related arene and azine derivatives.[2,11c,35]

(39) The predictions of these and similar calculations have proven to be very reliable predictors of other metal–arene orientations in the past;[27,37] however, no similar *intra*molecular steric interactions are expected for these other systems.

(40) Using the program Chem 3D$^+$ from Cambridge Scientific Computing and the crystallographically derived internal coordinates for the molecules.

(41) The electronically preferred orientations result in unreasonably short intramolecular H(Cp)–F(aromatic) nonbonded contacts of ~2.0 Å.

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# Silicon–Carbon Unsaturated Compounds. 37. Thermal Behavior of 1-Mesityl-3-phenyl-1,2-bis(trimethylsilyl)silacyclopropene

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*Department of Biological Science and Technology, Faculty of Engineering, Tokushima University,*
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*Received June 12, 1991*

The thermolysis of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)silacycloprop-2-ene (**1**) at 250 °C afforded 1-mesityl-3,3-dimethyl-4-phenyl-5-(trimethylsilyl)-1,3-disilacyclopent-4-ene (**2**) and 1-mesityl-1,3-bis(trimethylsilyl)-1-silaindene (**3**). Similar thermolysis of **1** in the presence of phenyl(trimethylsilyl)acetylene produced *cis*- and *trans*-7a-mesityl-1-phenyl-2,2a,7-tris(trimethylsilyl)cyclobutenosilaindan (**7** and **8**), together with **2** and **3**. When compound **1** was heated with methyldiphenylsilane under the same conditions, 2-mesityl-1,3,3,3-tetramethyl-1,1-diphenyltrisilane and (*E*)-1-(1-mesityl-2-methyl-2,2-diphenyldisilanyl)-1,2-bis(trimethylsilyl)-2-phenylethene were obtained, in addition to the products **2** and **3**. *cis*-Cyclobutenosilaindan **7**, $C_{34}H_{48}Si_4$ crystallizes in the space group $P1$ with cell dimensions $a = 11.186$ (1) Å, $b = 17.105$ (1) Å, $c = 10.208$ (1) Å, $\alpha = 107.37$ (1)°, $\beta = 87.92$ (1)°, $\gamma = 109.63$ (1)°, $V = 1751.3$ (3) Å$^3$, and $D_{calcd} = 1.02$ g/cm$^3$ ($Z = 2$).

## Introduction

The silapropadienes which are useful intermediates for the preparation of silicon-containing small-ring compounds can be readily synthesized by the photolysis of phenylethynylpolysilanes.[2-5] Recently, we have found that the reaction of phenylethynylpolysilanes and their photoi-

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(1) (a) Hiroshima University. (b) Tokushima University. (c) Osaka University.

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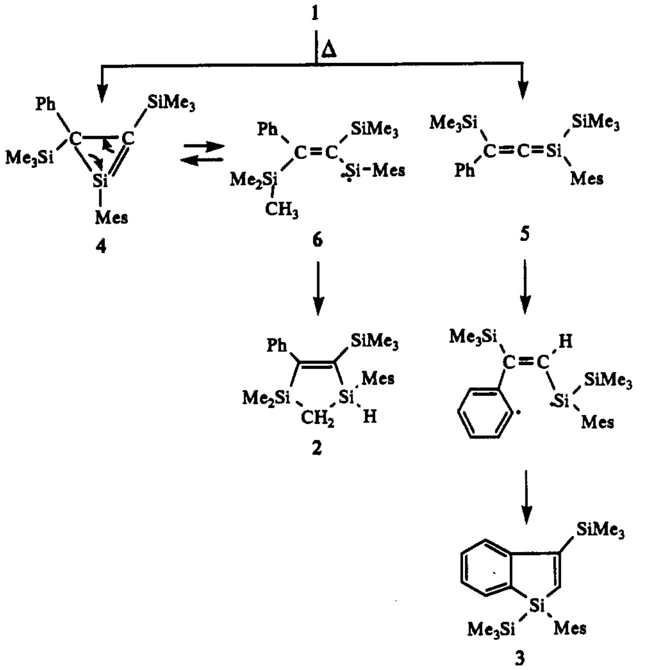
Scheme I

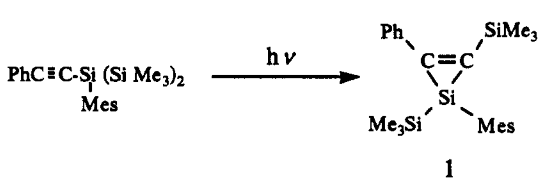


somers with a nickel complex affords silapropadiene derivatives as reactive intermediates. The silapropadienes prepared by the reaction of the phenylethynylpolysilanes with the nickel complex show quite different behavior from that of photochemically generated ones.[6-8] The silapropadiene–nickel complexes react with phenyl(trimethylsilyl)acetylene to give four-membered cyclic compounds or undergo further isomerization to give nickel-containing reactive species such as nickelasilacyclobutenes and nickeladisilacyclopentenes, which then add to the triple bond of the acetylene leading to cyclic compounds. More recently, we have demonstrated that the thermolysis of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane and its photoisomer, 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)silacycloprop-2-ene (1) affords two products which can best be understood by assuming the formation of the silapropadiene intermediate.[9] In order to get more information about the chemical behavior of compound 1 under thermal conditions, we investigated the thermolysis of 1 in the presence or absence of a trapping agent.

## Results and Discussion

The starting 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)silacycloprop-2-ene (1) was synthesized by the photolysis of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane as reported previously.[8]

First, we carried out the thermolysis of 1 in the absence of a trapping agent. The thermolysis of 1 in a degassed sealed tube at 280 °C for 6 h proceeded cleanly to give two isomers, 1-mesityl-3,3-dimethyl-4-phenyl-5-(trimethylsilyl)-1,3-disilacyclopent-4-ene (2) and 1-mesityl-1,3-bis(trimethylsilyl)-1-silaindene (3) in 49 and 29% yields, respectively (Scheme I).



As reported previously,[9] the formation of product 2 can best be understood by a series of the reaction shown in Scheme I. A 1,2-trimethylsilyl shift from the ring silicon atom to the sp$^2$ carbon at the C-3 position of the silacyclopropene 1 would produce 1-mesityl-3-phenyl-2,3-bis(trimethylsilyl)-1-silacyclopropene (4), which isomerizes to give silylene species 6. Insertion of the resulting silylene into a C–H bond of the trimethylsilyl group affords compound 2. Intramolecular insertion of the silylene into a C–H bond under thermal conditions has been reported by Barton et al.[10,11] The product 3, however, may be explained by isomerization of the silacyclopropene 1 to silapropadiene 5, followed by a hydrogen shift from the ortho position of the phenyl ring to the internal carbon of the silapropadiene and then coupling of the resulting diradical to form a silaindenyl ring. In fact, the photochemical and the nickel-catalyzed isomerization of silacyclopropenes to silapropadienes are known,[7,8,12] and ring closure of the silene has been reported by Eaborn et al.[13]

Next, we carried out the thermolysis of 1 in the presence of phenyl(trimethylsilyl)acetylene. Thus, heating 1 in the presence of a large excess of phenyl(trimethylsilyl)acetylene in a sealed tube at 280 °C for 6 h gave two isomers of a cyclobutenosilaindan derivatives, 7 and 8, in 20 and 26% yields, respectively, in addition to 2 (13% yield) and 3 (23% yield). Compounds 2, 3, 7, and 8 could be isolated by MPLC. The structure of 7 was verified by an X-ray crystallographic analysis, as well as by spectrometric analysis (see below). The regioisomer 8 was identified by spectrometric analysis. The location of the substituents on the silaindanyl ring for 8 was confirmed by NOE-FID difference experiments at 270 MHz. Thus, saturation of trimethylsilyl protons (-0.05 ppm) at the C-7 position of the silaindanyl ring caused a positive NOE of protons at the C-6 (7.39 ppm) and C-7 (1.90 ppm) positions, while saturation of trimethylsilyl protons (-0.39 ppm) at the C-2a position resulted in the strong enhancement of the proton at the C-7 position of the ring. Irradiation of the proton at the C-7 position led to the enhancement of one methyl proton (2.62 ppm) of the two *o*-methyl groups on the mesityl ring, as well as trimethylsilyl protons at the C-7 position. Irradiation of the *o*-methyl protons at 2.62 ppm resulted in the enhancement of the proton at the C-7 position, while saturation of the protons of the other *o*-methyl group (2.89 ppm) led to the enhancement of a phenyl ring proton (8.02 ppm). These results are wholly consistent with the structure proposed for compound 8.

Scheme II illustrates a possible mechanistic interpretation for the formation of products 7 and 8. The formation of 7 and 8 can be best understood in terms of [2 + 2] cycloaddition of the silene intermediate 4 with phe-

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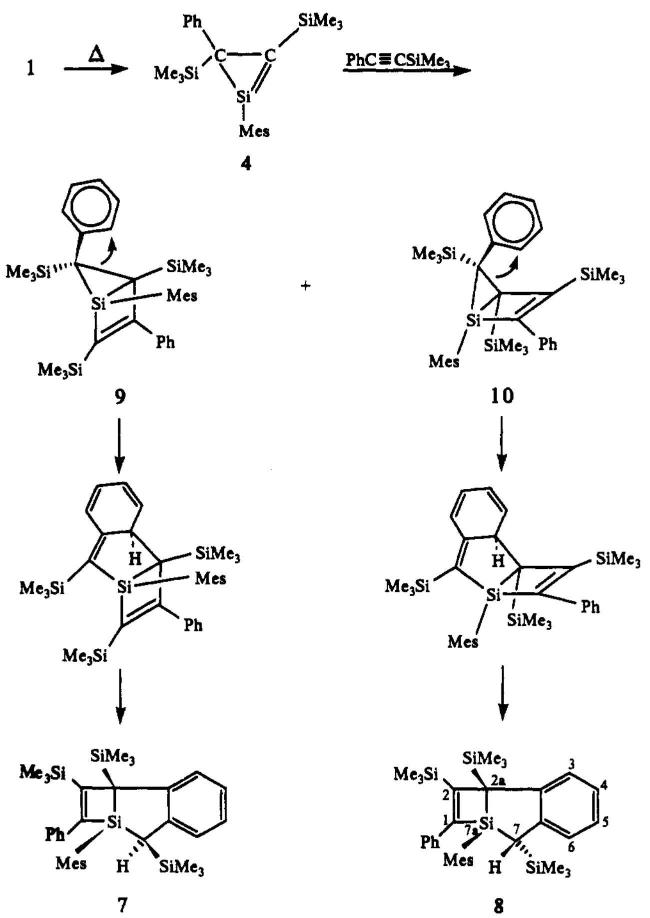
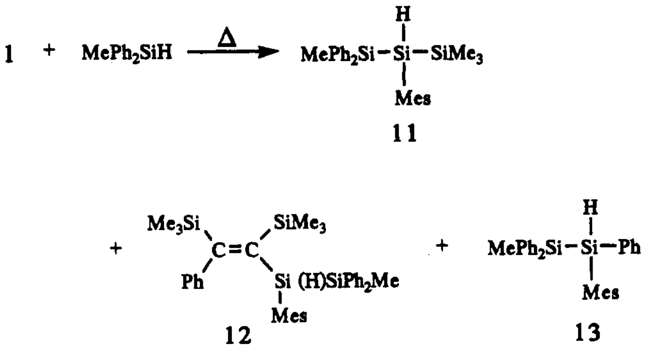
**Scheme II**



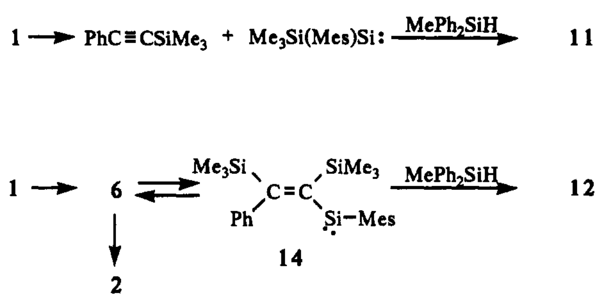
**Scheme III**



nyl(trimethylsilyl)acetylene. Thus, the [2 + 2] cycloaddition of 4 with phenyl(trimethylsilyl)acetylene gives two regioisomers, 9 and 10. Ring enlargement of the three-membered ring of 9 and 10 to the five-membered one, followed by a 1,3 shift of the allyl hydrogen to stabilize the ring by restoring the aromatic sextet, results in the formation of 7 and 8, respectively. The decrease in the yield of 2 in the presence of phenyl(trimethylsilyl)acetylene is also consistent with the formation of the intermediate 4.

When compound 1 was heated in the presence of methyldiphenylsilane under the same conditions, 2-mesityl-1,3,3,3-tetramethyl-1,1-diphenyltrisilane (11), (*E*)-1-(1-mesityl-2-methyl-2,2-diphenyldisilanyl)-2-phenyl-1,2-bis(trimethylsilyl)ethene (12), and 1-mesityl-2-methyl-1,2,2-triphenyldislane (13) were obtained in 4, 5, and 9% yields, respectively, in addition to a 30% yield of product 2 and a 27% yield of compound 3 (Scheme III). The formation of compound 11 indicates that mesityl(trimethylsilyl)silylene is probably produced in the present thermolysis. It

**Scheme IV**



is well-known that silacyclopropenes decompose to give silylene species and acetylene in the thermal reactions.[12,14] The production of compound 12 is of considerable interest, because this result clearly indicates that silylene (14), a stereoisomer of the silylene 6 must be produced. The silylene 6 inserts intramolecularly into a C–H bond of the trimethylsilyl group which is located on the same side as the silylene center with respect to a carbon–carbon double bond to give 2, but the isomer 14 in which no such C–H bond is available, inserts into an Si–H bond of methyldiphenylsilane to afford the insertion product 12 (Scheme IV).

The structure of 12 was verified by spectrometric analysis, and its *E* geometry was readily confirmed by NOE-FID difference experiments. Thus, saturation of the resonance of the trimethylsilyl protons at $\delta$ –0.44 ppm produced a positive NOE of trimethylsilyl protons at 0.02 ppm, while saturation of the trimethylsilyl protons at 0.02 ppm led to the strong enhancement of trimethylsilyl protons at –0.44 ppm and a proton on a mesityl-substituted silicon atom, as well as *o*-methyl protons of a mesityl group. These results are wholly consistent with the proposed structure.

The formation of 13 shows the intermediacy of mesitylphenylsilylene, but unfortunately, evidence for the production of this silylene has not yet been obtained at present.

**X-ray Analysis of Compound 7.** Colorless crystals of 7 were obtained by recrystallization from ethanol. The crystal with dimensions of 0.1 × 0.8 × 0.2 mm was used for the X-ray experiment. The crystal belongs to the group $P\bar{1}$ with cell dimensions of $a$ = 11.186 (1) Å, $b$ = 17.105 (1) Å, $c$ = 10.208 (1) Å, $\alpha$ = 107.37 (1)°, $\beta$ = 87.92 (1)°, $\gamma$ = 109.63 (1)°, $V$ = 1751.3 (3) Å$^3$, $Z$ = 2, and $D_{\text{calcd}}$ = 1.02 g/cm$^3$. Graphite-monochromatized Cu K$\alpha$ radiation was used to collect intensity data for all the reflections in the range $0 < 2\theta < 120°$ in $(hkl)$, $(h\bar{k}l)$, $(hk\bar{l})$, and $(h\bar{k}\bar{l})$. All intensities were measured on a Rigaku AFC-5 rotating-anode four-circle diffractometer. The $\theta$–$2\theta$ scan method was employed with $\theta$-scanning width (1.0 + 0.14 tan $\theta$)°. Three standard reflections monitored with every 100 reflections showed no significant variation in intensity. Out of 3151 unique reflections measured, 2775 intensities ($F > 3\delta_F$) were used in the least-squares refinement. The intensities were corrected only for Lorentz and polarization factors. The structure was solved by MULTAN.[15] Positional parameters and anisotropic thermal parameters for Si and C atoms were refined by block-diagonal least-squares refinement.[16] Atomic parameters of hydrogen atoms at calculated positions were not refined in the least-squares

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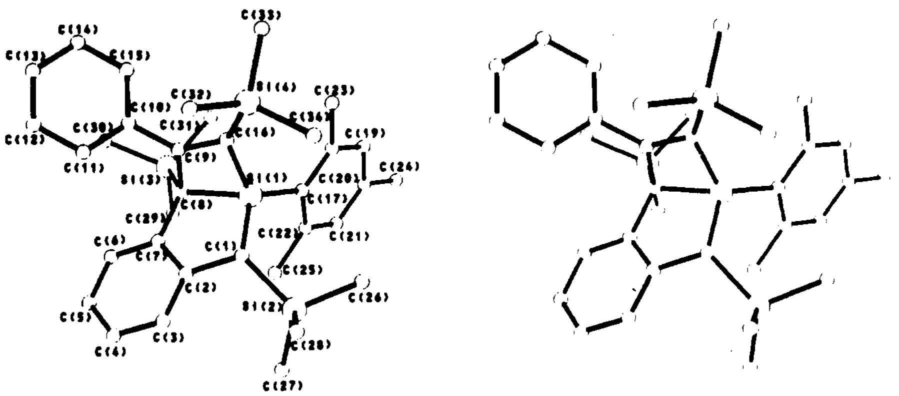

**Figure 1.** Stereoview of compound 7, showing the atom-numbering scheme.

refinement but included in the structure factor calculation of the refinement. $w\sum|F_o - F_c|^2$ was minimized in the refinement with weight $w = 1.0$ for $0 < F_o < 25$ and $w = [1.0 + 0.401(F_o - 25)]^{-1}$ for $F_o > 56$. Finally, $R$, $R_w$, and $S$ values of 0.068, 0.096, and 1.420, respectively, were obtained for all atoms. Atomic scattering factors from ref 17 were used for refinement.

A stereoview of the molecule with the atomic numbering system drawn by DCM-3[18] is represented in Figure 1. Out of four Si atoms, three Si atoms exhibit regular tetrahedral coordination, while one in the four-membered ring represents a distorted tetrahedral. The final atomic coordinates and equivalent isotropic temperature factors are given in Table I. Bond distances and angles are listed in Table II. There is no close intermolecular contact.[19]

## Experimental Section

**General Procedures.** All thermal reactions were carried out in a 10 cm × 0.8 cm degassed sealed glass tube at 280 °C. Yields were determined by GLC using docosane as an internal standard on the basis of the starting silacyclopropene.

$^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL Model JNM-EX 270 spectrometer. IR spectra were measured on a Perkin-Elmer 1600-FT infrared spectrometer.

**Materials.** Silacyclopropene 1 was prepared by the photolysis of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane in hexane.[8] Solvent hexane was dried over lithium aluminum hydride and distilled just before use.

**Thermolysis of 1.** A mixture of 1.317 g (3.34 mmol) of 1 and 0.702 g (2.26 mmol) of docosane as an internal standard was heated in a sealed tube at 280 °C for 6 h. The mixture was analyzed by GLC as being 2 (49% yield) and 3 (28.7% yield). Compounds 2 and 3 were isolated by medium-pressure liquid chromatography (spectral and analytical data for 2 and 3, see ref 9).

**Thermolysis of 1 in the Presence of Phenyl(trimethylsilyl)acetylene.** A mixture of 0.881 g (2.23 mmol) of 1, 2.630 g (15.1 mmol) of phenyl(trimethylsilyl)acetylene, and 0.693 g (2.23 mmol) of docosane as an internal standard was heated at 280 °C for 6 h. The reaction mixture was analyzed by GLC as being 2 (13% yield), 3 (23% yield), 7 (20% yield), and 8 (26% yield). The products, 2, 3, 7, and 8 were isolated by MPLC. Compound 2 was recrystallized from ethanol to remove a trace of impurity. All spectral data for 2 and 3 were identical with those of authentic samples. For 7: MS *m/e* 568 ($M^+$); IR 2950, 1605, 1536, 1441, 835 $cm^{-1}$; $^1H$ NMR $\delta$ ($CDCl_3$) -0.60 (s, 9 H, $Me_3Si$), -0.39 (s, 9 H, $Me_3Si$), -0.05 (s, 9 H, $Me_3Si$), 1.87 (s, 1 H, $HCSiMe_3$), 2.33 (s, 3 H, MeC), 2.62 (s, 3 H, MeC), 2.89 (s, 3 H, MeC), 6.88 (s, 1 H, mesityl ring proton), 6.94 (s, 1 H, mesityl ring proton), 7.06–8.03 (m, 9 H, phenyl ring protons); $^{13}C$ NMR $\delta$ ($CDCl_3$) 0.04 ($Me_3Si$), 1.51 ($Me_3Si$), 2.02 ($Me_3Si$), 21.17, 25.34, and 27.24 (*o*- and *p*-methyl carbons), 51.14 ($CH(Si)_2$), 56.80 ($C(Si)_2$), 124.22, 125.03, 126.42, 126.54, 127.40, 127.55, 127.89, 128.21, 128.46, 129.15, 129.88, 133.55, 139.84, 143.16, 145.14, 145.66, 145.71, 148.75 (phenyl and mesityl ring carbons), 157.77 and 183.79 (olefin carbons). Anal. Calcd for $C_{34}H_{48}Si_4$: C, 71.76; H, 8.50. Found: C, 71.90; H, 8.42. For 8: MS *m/e* 568 ($M^+$); IR 2953, 1605, 1536, 1484, 1249, 835 $cm^{-1}$; $^1H$ NMR $\delta$ ($CDCl_3$) -0.61 (s, 9 H, $Me_3Si$), -0.39 (s, 9 H, $Me_3Si$), -0.05 (s, 9 H, $Me_3Si$), 1.90 (s, 1 H, HC), 2.33 (s, 3 H, *p*-MeC), 2.62 (s, 3 H, *o*-MeC), and 2.89 (s, 3 H, *o*-MeC), 6.88 (s, 1 H, mesityl ring proton), 6.94 (s, 1 H, mesityl ring proton), 7.09–8.02 (m, 9 H, phenyl ring protons); $^{13}C$ NMR $\delta$ ($CDCl_3$) 0.04 ($Me_3Si$), 1.51 ($Me_3Si$), 2.02 ($Me_3Si$), 21.19, 25.36, and 27.26 (*o*- and *p*-methyl

**Table I. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å$^2$) with Esd's in Parentheses**

| atom | $x$ | $y$ | $z$ | $B_{eq}$[a] |
|---|---|---|---|---|
| Si(1) | 0.1497 (2) | 0.7930 (1) | 0.6045 (2) | 1.90 (4) |
| Si(2) | 0.2606 (2) | 1.0139 (1) | 0.7258 (2) | 2.73 (5) |
| Si(3) | -0.0466 (2) | 0.6441 (1) | 0.3428 (2) | 2.54 (4) |
| Si(4) | 0.4127 (2) | 0.7337 (1) | 0.6363 (2) | 2.81 (5) |
| C(1) | 0.2459 (6) | 0.9057 (4) | 0.5911 (6) | 2.5 (2) |
| C(2) | 0.2161 (6) | 0.8969 (4) | 0.4405 (6) | 2.3 (2) |
| C(3) | 0.2592 (7) | 0.9669 (4) | 0.3878 (7) | 3.2 (2) |
| C(4) | 0.2285 (8) | 0.9570 (5) | 0.2506 (7) | 3.5 (2) |
| C(5) | 0.1539 (8) | 0.8769 (5) | 0.1665 (7) | 3.3 (2) |
| C(6) | 0.1139 (7) | 0.8069 (4) | 0.2170 (7) | 3.0 (2) |
| C(7) | 0.1437 (6) | 0.8140 (4) | 0.3524 (6) | 2.2 (2) |
| C(8) | 0.1061 (5) | 0.7385 (4) | 0.4105 (6) | 2.0 (1) |
| C(9) | 0.2191 (6) | 0.7072 (4) | 0.4259 (6) | 2.2 (1) |
| C(10) | 0.2713 (6) | 0.6570 (4) | 0.3064 (6) | 2.7 (2) |
| C(11) | 0.3129 (7) | 0.6912 (5) | 0.1948 (7) | 3.7 (2) |
| C(12) | 0.3617 (8) | 0.6429 (6) | 0.0837 (9) | 4.9 (3) |
| C(13) | 0.3671 (9) | 0.5623 (7) | 0.0844 (10) | 5.9 (3) |
| C(14) | 0.3257 (9) | 0.5290 (6) | 0.1927 (10) | 5.4 (3) |
| C(15) | 0.2773 (7) | 0.5766 (4) | 0.3049 (8) | 3.8 (2) |
| C(16) | 0.2608 (6) | 0.7301 (4) | 0.5608 (6) | 2.2 (1) |
| C(17) | 0.0232 (6) | 0.7760 (4) | 0.7306 (6) | 2.0 (1) |
| C(18) | -0.0749 (6) | 0.8112 (4) | 0.7267 (6) | 2.4 (2) |
| C(19) | -0.1791 (6) | 0.7936 (4) | 0.8086 (7) | 2.9 (2) |
| C(20) | -0.1884 (6) | 0.7405 (4) | 0.8908 (6) | 2.8 (2) |
| C(21) | -0.0930 (6) | 0.7048 (4) | 0.8945 (6) | 2.7 (2) |
| C(22) | 0.0130 (7) | 0.7219 (4) | 0.8154 (6) | 2.5 (2) |
| C(23) | -0.0731 (7) | 0.8690 (5) | 0.6395 (8) | 3.2 (2) |
| C(24) | -0.3028 (7) | 0.7204 (5) | 0.9783 (8) | 4.0 (2) |
| C(25) | 0.1114 (7) | 0.6807 (5) | 0.8257 (8) | 3.3 (2) |
| C(26) | 0.2177 (9) | 0.9953 (5) | 0.8969 (7) | 4.6 (2) |
| C(27) | 0.1613 (8) | 1.0744 (5) | 0.6812 (9) | 4.0 (2) |
| C(28) | 0.4336 (8) | 1.0838 (5) | 0.7456 (9) | 4.7 (2) |
| C(29) | -0.1804 (8) | 0.6845 (6) | 0.3295 (11) | 5.1 (3) |
| C(30) | -0.0332 (8) | 0.5703 (5) | 0.1671 (7) | 4.0 (2) |
| C(31) | -0.0835 (8) | 0.5751 (5) | 0.4628 (8) | 4.3 (2) |
| C(32) | 0.4056 (8) | 0.6310 (5) | 0.6725 (10) | 4.5 (3) |
| C(33) | 0.5443 (7) | 0.7592 (7) | 0.5184 (9) | 5.0 (3) |
| C(34) | 0.4543 (8) | 0.8256 (6) | 0.8024 (9) | 4.7 (2) |

[a] $B_{eq} = (a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23})$.

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

(18) Takenaka, A. DCM-3. Program for drawing crystal and molecular structures. Tokyo Institute of Technology, Japan, 1977.

(19) All computations were performed on the HITAC 280D system at the Tottori University Computing Center and the FACOM M780/30 system at the Data Processing Center of Kyoto University.

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

| | | | | | |
|---|---|---|---|---|---|
| Si(1)–C(1) | 1.906 (6) | Si(1)–C(8) | 1.916 (6) | Si(1)–C(16) | 1.859 (6) |
| Si(1)–C(17) | 1.891 (6) | Si(2)–C(1) | 1.902 (7) | Si(2)–C(26) | 1.881 (10) |
| Si(2)–C(27) | 1.893 (9) | Si(2)–C(28) | 1.888 (9) | Si(3)–C(8) | 1.891 (6) |
| Si(3)–C(29) | 1.878 (10) | Si(3)–C(30) | 1.896 (8) | Si(3)–C(31) | 1.888 (9) |
| Si(4)–C(16) | 1.870 (6) | Si(4)–C(32) | 1.869 (9) | Si(4)–C(33) | 1.889 (11) |
| Si(4)–C(34) | 1.881 (9) | C(1)–C(2) | 1.540 (9) | C(2)–C(3) | 1.391 (10) |
| C(2)–C(7) | 1.410 (9) | C(3)–C(4) | 1.404 (11) | C(4)–C(5) | 1.372 (11) |
| C(5)–C(6) | 1.377 (11) | C(6)–C(7) | 1.395 (9) | C(7)–C(8) | 1.507 (9) |
| C(8)–C(9) | 1.564 (8) | C(9)–C(10) | 1.494 (9) | C(9)–C(16) | 1.360 (9) |
| C(10)–C(11) | 1.407 (10) | C(10)–C(15) | 1.378 (10) | C(11)–C(12) | 1.396 (13) |
| C(12)–C(13) | 1.377 (15) | C(13)–C(14) | 1.377 (14) | C(14)–C(15) | 1.383 (12) |
| C(17)–C(18) | 1.412 (9) | C(17)–C(22) | 1.419 (9) | C(18)–C(19) | 1.408 (10) |
| C(18)–C(23) | 1.522 (10) | C(19)–C(20) | 1.373 (10) | C(20)–C(21) | 1.393 (10) |
| C(20)–C(24) | 1.534 (11) | C(21)–C(22) | 1.405 (9) | C(22)–C(25) | 1.516 (11) |
| C(1)–Si(1)–C(8) | 95.9 (3) | C(1)–Si(1)–C(16) | 104.8 (3) | C(1)–Si(1)–C(17) | 122.0 (3) |
| C(8)–Si(1)–C(16) | 79.4 (3) | C(8)–Si(1)–C(17) | 119.9 (3) | C(16)–Si(1)–C(17) | 124.1 (3) |
| C(1)–Si(2)–C(26) | 109.5 (4) | C(1)–Si(2)–C(27) | 114.4 (3) | C(1)–Si(2)–C(28) | 106.9 (3) |
| C(26)–Si(2)–C(27) | 109.4 (4) | C(26)–Si(2)–C(28) | 107.3 (4) | C(27)–Si(2)–C(28) | 109.0 (4) |
| C(8)–Si(3)–C(29) | 110.4 (4) | C(8)–Si(3)–C(30) | 112.4 (3) | C(8)–Si(3)–C(31) | 108.6 (3) |
| C(29)–Si(3)–C(30) | 108.1 (4) | C(29)–Si(3)–C(31) | 110.2 (4) | C(30)–Si(3)–C(31) | 106.7 (4) |
| C(16)–Si(4)–C(32) | 114.9 (4) | C(16)–Si(4)–C(33) | 109.5 (4) | C(16)–Si(4)–C(34) | 106.7 (3) |
| C(32)–Si(4)–C(33) | 108.4 (5) | C(32)–Si(4)–C(34) | 108.7 (4) | C(33)–Si(4)–C(34) | 108.3 (4) |
| Si(1)–C(1)–Si(2) | 126.0 (4) | Si(1)–C(1)–C(2) | 102.8 (4) | Si(2)–C(1)–C(2) | 117.6 (4) |
| C(1)–C(2)–C(3) | 122.4 (6) | C(1)–C(2)–C(7) | 118.2 (5) | C(3)–C(2)–C(7) | 119.3 (6) |
| C(2)–C(3)–C(4) | 121.1 (7) | C(3)–C(4)–C(5) | 119.2 (7) | C(4)–C(5)–C(6) | 119.9 (7) |
| C(5)–C(6)–C(7) | 122.3 (7) | C(2)–C(7)–C(6) | 117.9 (6) | C(2)–C(7)–C(8) | 117.6 (5) |
| C(6)–C(7)–C(8) | 124.3 (6) | Si(1)–C(8)–Si(3) | 121.6 (3) | Si(1)–C(8)–C(7) | 103.8 (4) |
| Si(1)–C(8)–C(9) | 80.7 (3) | Si(3)–C(8)–C(7) | 119.6 (4) | Si(3)–C(8)–C(9) | 111.8 (4) |
| C(7)–C(8)–C(9) | 112.7 (5) | C(8)–C(9)–C(10) | 122.9 (5) | C(8)–C(9)–C(16) | 111.0 (5) |
| C(10)–C(9)–C(16) | 125.9 (6) | C(9)–C(10)–C(11) | 120.4 (6) | C(9)–C(10)–C(15) | 119.8 (6) |
| C(11)–C(10)–C(15) | 119.7 (7) | C(10)–C(11)–C(12) | 119.0 (8) | C(11)–C(12)–C(13) | 120.0 (9) |
| C(12)–C(13)–C(14) | 120.7 (10) | C(13)–C(14)–C(15) | 119.9 (9) | C(10)–C(15)–C(14) | 120.5 (8) |
| Si(1)–C(16)–Si(4) | 137.3 (4) | Si(1)–C(16)–C(9) | 88.2 (4) | Si(4)–C(16)–C(9) | 129.5 (5) |
| Si(1)–C(17)–C(18) | 117.3 (5) | Si(1)–C(17)–C(22) | 123.1 (5) | C(18)–C(17)–C(22) | 119.0 (6) |
| C(17)–C(18)–C(19) | 119.7 (6) | C(17)–C(18)–C(23) | 122.9 (6) | C(19)–C(18)–C(23) | 117.3 (6) |
| C(18)–C(19)–C(20) | 121.4 (6) | C(19)–C(20)–C(21) | 119.1 (6) | C(19)–C(20)–C(24) | 120.8 (7) |
| C(21)–C(20)–C(24) | 120.0 (6) | C(20)–C(21)–C(22) | 121.7 (6) | C(17)–C(22)–C(21) | 118.9 (6) |
| C(17)–C(22)–C(25) | 123.1 (6) | C(21)–C(22)–C(25) | 117.8 (6) | | |

carbons), 51.14 (CH(Si)$_2$), 56.80 (C(Si)$_2$), 124.22, 125.03, 126.42, 126.54, 127.40, 127.55, 127.89, 128.21, 128.46, 129.15, 129.88, 133.55, 139.84, 143.16, 145.14, 145.66, 145.71, 148.75 (phenyl and mesityl ring carbons), 157.77 and 183.79 (olefin carbons). Anal. Calcd for $C_{34}H_{48}Si_4$: C, 71.76; H, 8.50. Found: C, 71.75; H, 8.40.

**Thermolysis of 1 in the Presence of Methyldiphenylsilane.** A mixture of 0.537 g (1.36 mmol) of 1, 0.946 g (4.78 mmol) of methyldiphenylsilane and 0.315 g (1.01 mmol) of docosane as an internal standard was heated in a sealed tube at 280 °C for 6 h. The mixture was analyzed by GLC as being **2** (30% yield), **3** (27% yield), **11** (4% yield), **12** (5% yield), and **13** (9% yield). All compounds were isolated by MPLC. All spectral data for **2** and **3** were identical with those of authentic samples. For **11**: IR 2143 cm$^{-1}$; $^1$H NMR $\delta$ (CDCl$_3$) 0.05 (s, 9 H, Me$_3$Si), 0.71 (s, 3 H, MeSi), 2.22 (s, 3 H, *p*-Me), 2.24 (s, 6 H, *o*-Me), 4.30 (s, 1 H, HSi), 6.77 (s, 2 H, mesityl ring protons), 7.22–7.54 (m, 10 H, phenyl ring protons); $^{13}$C NMR $\delta$ (CDCl$_3$) −1.89 (MeSi), 0.81 (Me$_3$Si), 21.32 (*o*-Me), 25.77 (*p*-Me), 128.05, 128.16, 129.02, 129.15, 134.77, 135.20, 135.31, 137.95 (phenyl and mesityl ring carbons). Exact Mass Calcd for $C_{25}H_{34}Si_3$: 418.1969. Found: 418.1993. For **12**: IR 2132 cm$^{-1}$; $^1$H NMR $\delta$ (CDCl$_3$) −0.44 (s, 9 H, Me$_3$Si), 0.02 (s, 9 H, Me$_3$Si), 0.90 (s, 3 H, MeSi), 2.06 (s, 3 H, *p*-Me), 2.20 (s, 3 H, *o*-Me), 2.25 (s, 3 H, *o*-Me), 5.56 (s, 1 H, HSi), 6.75 (s, 2 H, mesityl ring protons), 7.27–7.69 (m, 15 H, phenyl ring protons); $^{13}$C NMR $\delta$ (CDCl$_3$) −1.97 (MeSi), 1.73 (Me$_3$Si), 2.91 (Me$_3$Si), 20.90 (*p*-Me), 21.17 (*o*-Me), 21.48 (*o*-Me), 127.80, 127.85, 127.91, 128.79, 129.02, 132.97, 133.12, 134.84, 135.38, 135.49, 135.83, 137.32, 137.63, 145.44 (phenyl and mesityl ring carbons), 152.49 and 184.98 (olefin carbons); $^{29}$Si NMR $\delta$ (CDCl$_3$) −9.71 (Me$_3$Si), −10.37 (Me$_3$Si), −22.42 (SiH), −37.05 (SiPh$_2$Me). Exact Mass Calcd for (M$^+$ - Me$_3$Si): 519.2361. Found: 519.2339. For **13**: IR 2116 cm$^{-1}$; $^1$H NMR $\delta$ (CDCl$_3$) 0.76 (s, 3 H, MeSi), 2.16 (s, 6 H, *o*-Me), 2.29 (s, 3 H, *p*-Me), 5.42 (s, 1 H, HSi), 6.82 (s, 2 H, mesityl ring protons), 7.21–7.57 (m, 15 H, phenyl ring protons); $^{13}$C NMR $\delta$ (CDCl$_3$) −3.12 (MeSi), 21.15 (*p*-Me), 25.05 (*o*-Me), 127.80, 127.87, 127.94, 128.45, 128.75, 128,95, 129.09, 134.95, 135.20, 135.63, 139.16, 145.18 (phenyl and mesityl ring carbons). Exact Mass Calcd for $C_{28}H_{30}Si_2$: 422.1887. Found: 422.1901.

**Acknowledgment.** This research was supported in part by a Grant-in-Aid for Scientific Research of Priority Area of Organic Unusual Valency, No. 03233105, from the Ministry of Education, Science, and Culture, to which our thanks are due. We also thank Shin-Etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., Dow Corning Japan Ltd., and Toshiba Silicone Co. Ltd. for financial support.

**Supplementary Material Available:** A table of anisotropic temperature factors of non-hydrogen atoms (1 page); a listing of observed structure factors (8 pages). Ordering information is given on any current masthead page.