Organometallics 1989, *8*, 2050–2054

Silicon–Carbon Unsaturated Compounds. 24. Some Reactions of a Nickelasilacyclobutene

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Received March 31, 1989

The chemical behavior of 2-mesityl-4-phenyl-1,1-bis(triethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobut-3-ene (**3**) has been examined. When **3** was heated at 140 °C in xylene, 5,6-benzo-1,3-disilacyclohexene derivatives **4a** and **4b** were obtained. Irradiation of **3** with a high-pressure mercury lamp also produced **4a** and **4b**. Compound **3** reacted with methanol to give (*E*)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-1-phenyl-2-(trimethylsilyl)ethene and (*E*)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-2-phenyl-1-(trimethylsilyl)ethene. Treatment of **3** with hydrogen chloride in benzene followed by sodium methoxide gave (*Z*)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-2-phenyl-2-(trimethylsilyl)ethene. With hydrogen, **3** afforded (*E*)-1-(1-hydro-1-mesityltrimethyldisilanyl)-2-phenyl-1-(trimethylsilyl)ethene. In all reactions of **3** with bromine, methyl iodide, and benzyl bromide, reductive elimination of nickel species took place to give silacyclopropene **2**. When **3** was treated with 1 equiv of (diphenylphosphino)ethane, compound **3** was transformed into silacyclopropene **2**, quantitatively. The reaction of **3** with 1-hexyne afforded (*Z*)-1-(1-hexynyl-1-mesityltrimethyldisilanyl)-2-phenyl-2-(trimethylsilyl)ethene.

Introduction

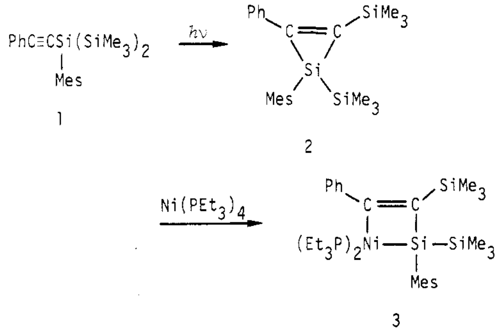
There has been a considerable interest in the chemistry of strained silicon-containing small ring compounds. Particularly, the reactions of silacyclopropenes with an acetylene in the presence of a transition metal catalyst have been extensively investigated.[1-3] In these reactions, metalasilacyclobutenes have been proposed to be formed as reactive intermediates. However, no evidence for the existence of these intermediates has been obtained until recently, when we demonstrated that the reaction of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene with 1 equiv of tetrakis(triethylphosphine)nickel(0) in a hydrocarbon solution such as benzene or xylene at room temperature gives 2-mesityl-4-phenyl-1,1-bis(triethylphosphin)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobut-3-ene in almost quantitative yield.[4]

All attempts to isolate the nickelasilacyclobutene were unsuccessful, but it was found that this compound is stable in solutions and can be stored without decomposition for several months in an inert atmosphere. In this paper, we report the unique chemical behavior of the nickelasilacyclobutene.

Results and Discussion

Preparation of Nickelasilacyclobutene. Irradiation of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane (**1**) with a low-pressure mercury lamp in a hexane solution followed by distillation under reduced pressure gave 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene (**2**) in 84% yield. The silacyclopropene **2** thus obtained was less sensitive to oxygen than the usual silacyclopropenes reported to date, but it still had to be handled under an inert atmosphere.

Scheme I



Treatment of **2** with 1 equiv of tetrakis(triethylphosphine)nickel(0) in benzene at room temperature afforded 2-mesityl-4-phenyl-1,1-bis(triethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobut-3-ene (**3**) quantitatively (Scheme I). In fact, monitoring this reaction in deuteriobenzene by ^{1}H NMR spectroscopy, resonances at δ 0.23, 0.36, 2.12, and 2.66 ppm, due to two nonequivalent trimethylsilyl protons, and para and ortho mesityl methyl protons of **2** were cleanly transformed into those at 0.20, 0.52, 2.15, 2.83, and 2.96 ppm, attributed to two trimethylsilyl protons and three nonequivalent mesityl methyl protons of **3** within 1 h. In this reaction, no signals due to the other product were observed.[4] Similar treatment of **2** with tetrakis(triethylphosphine)nickel(0) in xylene at room temperature again afforded **3** in quantitative yield.

That the nickel species inserts into the C(Ph)–Si bond in the silacyclopropene ring but not into the C($SiMe_3$)–Si bond could be verified by the ^{13}C NMR spectrum. The resonance at 143.3 ppm assigned to the phenyl-substituted carbon shows a doublet, due to the coupling only with one phosphine ligand which locates presumably at the trans position to this carbon. However, the resonance at 151.9 ppm due to the trimethylsilyl-substituted carbon shows a singlet, although the resonance is slightly broadened by the long-range coupling with the phosphine ligand (Figure 1). The coupling constant of the phenyl-substituted carbon with the cis phosphine ligand would be close to 0 Hz.

The ^{29}Si NMR spectrum of **3** shows a singlet at 3.1 ppm attributed to the silicon atom attached to the ring carbon. If compound **3** had a Ni–C–$SiMe_3$ structure, the resonance for the silicon atom on the carbon attached to nickel should

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[1] (a) Seyferth, D.; Duncan, D. P.; Vick, C. S. *J. Organomet. Chem.* **1977**, *125*, C5. (b) Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *J. Organomet. Chem.* **1977**, *135*, C7. (c) Seyferth, D.; Annalelli, D. C.; Vick, S. C. *J. Organomet. Chem.* **1984**, *272*, 123. (d) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57.

[2] (a) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1977**, 352. (b) Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43. (c) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, K. *Organometallics* **1982**, *1*, 1473. (d) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040.

[3] Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

[4] Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417.

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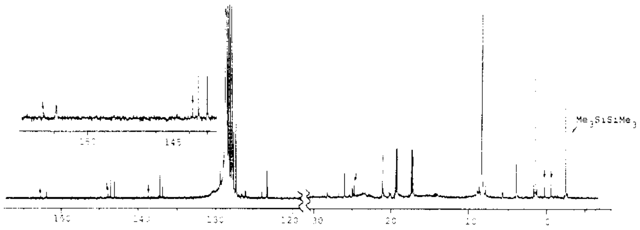
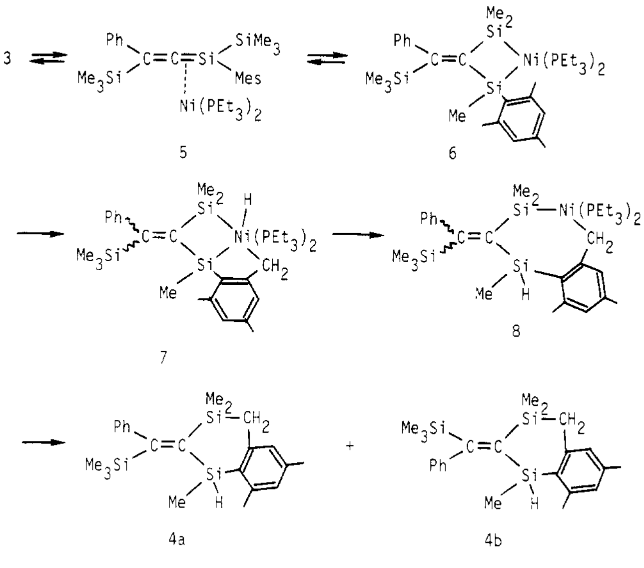


Figure 1. Proton-decoupled ^{13}C NMR spectra of nickelasilacyclobutene **3**. Arrows indicate silacyclopropene **2**.

Scheme II



be a doublet of doublets or a triplet, owing to the coupling with the phosphine ligands on the nickel atom. However, this is not the case. These results strongly suggest that **3** must have a Ni–C–Ph structure.

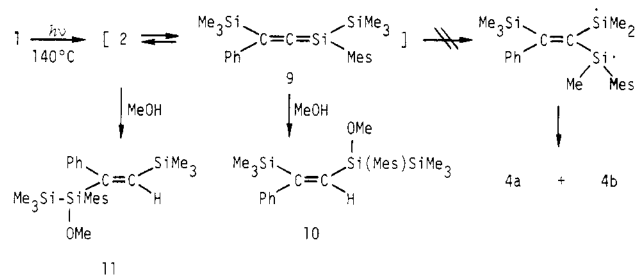
In order to isolate **3** as a pure form, we evaporated the solvent from the reaction mixture under reduced pressure at room temperature. However, product **3** could not be isolated, but complicated decomposition products were obtained. Therefore, we used the solution for further reactions to examine the chemical behavior of **3**.

Thermolysis of 3 in Xylene. When a xylene solution of **3** was heated to reflux for 2 h, two isomers, 5,6-benzo-1,3-disilacyclohexene derivatives **4a** and **4b** whose spectral data were identical with those of the compounds produced from the reaction of **1** with a nickel catalyst,[5] were obtained in 47 and 41% yields, respectively.

Scheme II illustrates a possible mechanistic interpretation. The formation of **4a** and **4b** requires isomerization of **3** to the silapropadiene–nickel complex **5** which would be transformed into nickeladisilacyclobutane **6**, as previously reported.[2d,5] The carbon–hydrogen bond activation of an ortho mesityl methyl group of **6** leading to intermediate **7**, followed by the ring expansion to the nickel-containing seven-membered ring compound **8**, and finally reductive elimination of nickel species from **8** would also be involved in a series of the reaction.

An alternate pathway involving thermolysis of a free silapropadiene might be considred for the formation of **4a** and **4b** under the conditions used. In an effort to learn whether or not the thermal isomerization of 1-mesityl-3-phenyl-1,3-bis(trimethylsilyl)-1-silapropadiene (**9**) is involved in the formation of **4a** and **4b**, we carried out the photolysis of **1** in refluxing xylene. Irradiation of **1** in the presence of methanol at 140 °C gave (*Z*)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-2-phenyl-2-(trimethylsilyl)ethene (**10**) in 21% yield, in addition to 37% of (*E*)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-1-phenyl-2-(trimethylsilyl)ethene (**11**) (Scheme III).

Scheme III



The *Z* geometry of the methanol adduct **10** was established from its NOE–FID difference spectra. Thus, saturation of the resonance of methoxy methyl protons at δ 3.54 produced a positive NOE of two different kinds of trimethylsilyl protons, while irradiation of trimethylsilyl protons on a carbon atom caused a positive NOE of both phenyl and methoxy protons, indicating that **10** must have the *Z* geometry. For compound **11**, all spectral data were consistent with the proposed structure (see Experimental Section).

The formation of **10** clearly indicates that 1-mesityl-3-phenyl-1,3-bis(trimethylsilyl)-1-silapropadiene was produced in the photolysis of **1** at 140 °C. Since the silacyclopropene **2** does not react with methanol in dark, even in refluxing xylene, compound **11** must be produced from the reaction of photoexcited **2** with methanol. Indeed, irradiation of **2** in the presence of a large excess of methanol in benzene at room temperature gave **10** and **11** in 29 and 26% yields, respectively. The photochemical isomerization of silacyclopropenes to silapropadienes has been reported previously.[6]

Next, we carried out the photolysis of **1** in the absence of methanol under the same condition. Irradiation of **1** in refluxing xylene, however, gave no isomerization products but produced **2** in 49% yield, as the sole volatile product. These results indicates that **4a** and **4b** must be produced via the silapropadiene–nickel complex **5**, but not from the silapropadiene **9**, and the nickel atom plays an important role for the C–H activation of the ortho mesityl methyl group of **5**.

Photolysis of 3 in Xylene. We found that the photochemical reaction of **3** also involves isomerization to the silapropadiene–nickel complex **5** which results in the formation of **4a** and **4b**. The ratio of **4a** and **4b** in the photolysis mixture, however, is different from that obtained from the thermal reaction. Thus, when the xylene solution of **3** in a Pyrex reaction vessel was photolyzed by irradiating externally with a high-pressure mercury lamp with ice cooling, two products, **4a** and **4b**, were produced in 54 and 29% yields, respectively.

$$\mathbf{3} \xrightarrow{h\nu} \mathbf{5} \rightarrow \mathbf{4a} + \mathbf{4b}$$

Reaction of 3 with Methanol. When **3** was treated with a 5-fold excess of methanol in xylene at room temperature, ring opened products **11** and its isomer which was identified as (*E*)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-1-(trimethylsilyl)-2-phenylethene (**12**) by mass, IR,

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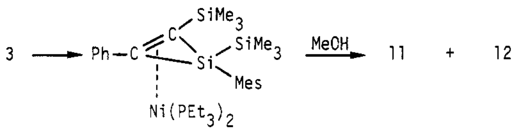
(5) Ishikawa, M.; Ohshita, J.; Ito, Y. *Organometallics* **1986**, *5*, 1518.

(6) Ishikawa, M.; Nishimura, K.; Sjugisawa, H.; Kumada, M. *J. Organomet. Chem.* **1980**, *194*, 147.

Scheme IV



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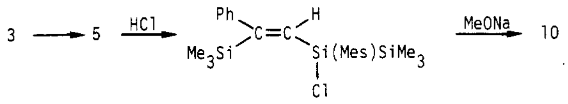
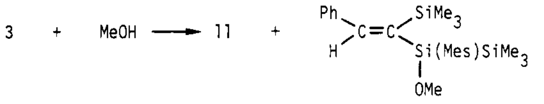
Scheme V



^{1}H NMR, and ^{13}C NMR spectrometric analysis were obtained in 33 and 29% yields, respectively.



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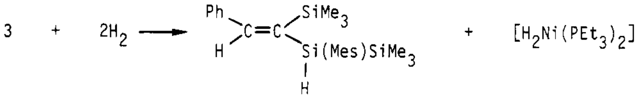
Since the silacyclopropene **2** does not react with methanol even in refluxing xylene, it seems unlikely that **11** and **12** were produced by the reaction of the silacyclopropene **2** arising from reductive elimination of nickel species from **3**, with methanol. Therefore, the formation of **11** and **12** can be best understood by assuming a π-complex, the silacyclopropene–nickel complex **13**, as an intermediate, which would be produced by nucleophilic attack of methanol on the silicon atom in the nickelasilacyclobutene ring, followed by isomerization. In the π-complex **13**, both silicon–carbon bonds in the silacyclopropene ring probably would be weakened by coordination of the nickel species to the carbon–carbon double bond and would be readily cleaved by methanol giving **11** and **12**, as shown in Scheme IV.

Reaction with Hydrogen Chloride. The reaction of a benzene solution of **3** with 1 equiv of hydrogen chloride dissolved in dry benzene with ice cooling, followed by treatment of the resulting product with sodium methoxide in methanol, gave compound **10** in 39% yield, along with 7% of the unidentified product. All spectral data obtained for **10** were identical with those of the authentic sample.

A reasonable pathway for the formation of **10** presumably involves isomerization of **3** to the silapropadiene–nickel complex **5**, followed by addition of hydrogen chloride to a silicon–carbon double bond of **5** (Scheme V).

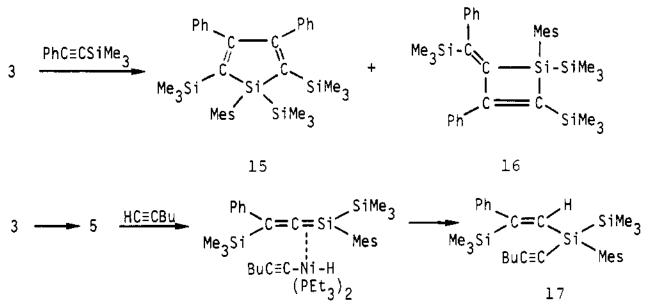
Reaction with Hydrogen. Compound **3** reacts readily with hydrogen to give a ring-opened product. Thus, the reaction of **3** in xylene with hydrogen gas under the pressure of 50 kg/cm^2 in an autoclave at room temperature afforded (*E*)-1-(1-hydro-1-mesityltrimethyldisilanyl)-2-phenyl-1-(trimethylsilyl)ethene (**14**) in 81% yield, as the sole product. In this reaction, both a nickel–silicon and a nickel–carbon bond in the nickelasilacyclobutene ring are cleaved by hydrogen.



14

The structure of **14** was verified by spectroscopic analysis as well as by elemental analysis. The IR spectrum of **14** shows a strong band at 2100 cm^{-1}, due to the stretching frequency of a Si–H bond. The chemical shift at δ 8.19 ppm in its ^{1}H NMR spectrum clearly indicates that compound **14** must have a PhC(H)=C structure, but not a $Me_3SiC(H)=C$ structure.[7]

Scheme VI



15 16

17

Reductive Elimination of a Nickel Species. When the nickelasilacyclobutene **3** was treated with bromine or alkyl halides, the reductive elimination occurred to give the silacyclopropene **2**. Treatment of **3** with 1 equiv of bromine in xylene with ice cooling gave **2** in quantitative yield. No other volatile product was detected by either VPC or spectroscopic analysis.

In sharp contrast to the reaction of nickelacycloalkanes with alkyl halides, in which coupling products are produced,[9] the nickelasilacyclobutene reacts with alkyl halides to give the reductive elimination product **2**. Thus, the reaction of **3** with methyl iodide in xylene at room temperature afforded **2** quantitatively. Similar reaction with benzyl bromide again gave **2** in quantitative yield. In this reaction, bibenzyl was isolated in 86% yield.

$$3 \quad + \quad Br_2 \longrightarrow 2 \quad + \quad (Et_3P)_2NiBr_2$$

$$3 \quad + \quad C_6H_5CH_2Br \longrightarrow 2 \quad + \quad C_6H_5CH_2CH_2C_6H_5 \quad + \quad (Et_3P)_2NiBr_2$$

We attempted exchange of phosphine ligands on the nickel atom of **3**. Treatment of **3** with 1 equiv of (diphenylphosphino)ethane in xylene at room temperature afforded the silacyclopropene **2** quantitatively. No other products were detected by the ^{1}H NMR spectroscopic study.

Reaction with Acetylenes. Compound **3** reacts with phenyl(trimethylsilyl)acetylene at 140 °C to give 1-mesityl-3,4-diphenyl-1,2,5-tris(trimethylsilyl)silole (**15**) and 1-mesityl-3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,2-bis(trimethylsilyl)-1-silacyclobut-2-ene (**16**) in 32 and 6% yields.[4] The formation of the silole **15** involves the direct reaction of **3** with phenyl(trimethylsilyl)acetylene, while the minor product **16** comprises cycloaddition of the silapropadiene–nickel complex **5** produced from isomerization of **3** with the acetylene.

With a monosubstituted acetylene, however, the reaction proceeds with a different mode to give a ring-opened product. Treatment of **3** with 1-hexyne in xylene at room temperature afforded (*Z*)-1-(1-hexynyl-1-mesityltrimethyldisilanyl)-2-phenyl-2-(trimethylsilyl)ethene (**17**) and an unidentified product whose parent peak in its mass spectrum is identical with those of **17**, in 18 and 3% yields, respectively (Scheme VI). In this reaction, appreciable amounts of polymeric substances were produced.

The structure of **17** was confirmed by IR, mass, and ^{1}H and ^{13}C NMR spectroscopic analysis. The fact that satu-

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[7] Chemical shift of the vinylic proton in a $(Me_3Si)C(H)=C$ structure appears at 6.4–6.6 ppm, while the proton of a PhC(H)=C structure appears at 7.7–8.2 ppm (see ref 8).

[8] Ishikawa, M.; Sugisawa, H.; Fuchikami, T.; Kumada, M.; Yamabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 2872.

[9] (a) Takahashi, S.; Suzuki, Y.;; Hagihara, N. *Chem. Lett.*, **1974**, 1363. (b) Takahashi, S.; Suzuki, Y.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1976**, 839.

ration of the orthomethyl protons of a mesityl group in the NOE–FID difference experiment produced a positive NOE of two different types of trimethylsilyl protons an olefinic proton, in addition to mesityl ring protons, but had no effect on the phenyl ring protons indicates that compound **17** must have *Z* geometry.

The formation of **17** can be explained by the reaction of oxidative addition of an ethynyl C–H bond to the nickel atom of **5**, followed by the addition of this bond to the silicon–carbon double bond, but not the carbon–carbon double bond. The C–H bond activation of the monosubstituted acetylene by the nickel complex has been reported recently.[10]

In conclusion, it seems likely that the reagents that have a strong affinity for a nickel atom such as (diphenylphosphino)ethane or alkyl halides accelerate the reductive elimination of the nickel species from **3**, and sterically bulky reagents such as alkynes or hydrogen chloride in benzene may cause isomerization to the silapropadiene–nickel complexes. Small reagents like hydrogen react directly with **3** to give the alkenylhydrosilane.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified argon. ^1H NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing cyclohexane as an internal standard. ^{13}C NMR spectra were measured on a JEOL Model JNM-GX-400 spectrometer in deuteriochloroform as a solvent. Mass spectra were measured on a JEOL Model JMS-D300 equipped with a JMA-2000 data processing system. Ionizing voltage was 70 eV for all compounds.

Materials. 2,2-Dichlorohexamethyltrisilane[11] and tetrakis(triethylphosphine)nickel(0)[12] were prepared as reported in the literature. Diethyl ether and tetrahydrofuran used as solvents were dried over butylmagnesium bromide and distilled just before use. Benzene and hexane were dried over lithium aluminum hydride and distilled before use. Xylene was dried over sodium and distilled before use.

Preparation of 2-Mesityl-2-(phenylethynyl)hexamethyltrisilane (1). In a 300-mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed 10 g (40.8 mmol) of 2,2-dichlorohexamethyltrisilane in 60 mL of ether. To this was added 70 mL of an ether solution involving 44.9 mmol of mesityllithium over a period of 30 min at room temperature. The mixture was heated to reflux for 1 h, and then a solution of 49.0 mmol of (phenylethynyl)lithium prepared from phenylacetylene and butyllithium in a mixed solvent of hexane (70 mL) and THF (30 mL) was added to the mixture. The reaction mixture was then heated to reflux for 2 h and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined and washed with water and then dried over anhydrous potassium carbonate. The solvents were evaporated, and the residue was distilled by using a short column under reduced pressure to give 6.1 g (38% yield) of **1**: bp 167 °C (2 mm); ^1H NMR (100 MHz) δ 0.23 (s, 18 H, Me_3Si), 2.23 (s, 3 H, *p*-Me), 2.51 (s, 6 H, *o*-Me), 6.69 (br s, 2 H, mesityl ring protons), 7.12–7.46 (m, 5 H, phenyl ring protons); MS *m/e* 394 (M^+). Anal. Calcd for $C_{23}H_{34}Si_3$: C, 69.98; H, 8.68. Found: C, 70.11; H, 8.96.

Preparation of 1-Mesityl-3-phenyl-1,2-bis(trimethylsilyl)silacyclopropene (2). In a 25-mL reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed a mixture of 0.2280 g (0.577 mmol) of **1** and 0.241 mmol of eicosane as an internal standard in 25 mL of dry benzene. The mixture was irradiated for 30 min with a slow stream of nitrogen bubbling through the mixture. VPC analysis of the mixture showed the presence of **2** (84% yield) and the starting **1** (11%). The solvent was evaporated, and the residue was distilled under reduced pressure (2 mm) to give **2**: ^1H NMR (100 MHz, C_6H_6) δ 0.23 (s, 9 H, Me_3Si), 0.36 (s, 9 H, Me_3Si), 2.12 (s, 3 H, *p*-Me), 2.66 (s, 6 H, *o*-Me); ^1H NMR (100 MHz, CCl_4) δ 0.15 (s, 9 H, Me_3Si), 0.29 (s, 9 H, Me_3Si), 2.20 (s, 3 H, *p*-Me), 2.25 (s, 6 H, *o*-Me), 6.65 (br s, 2 H, mesityl ring protons), 7.05–7.52 (m, 5 H, phenyl ring protons); ^{13}C NMR (30% C_6D_6 and 70% C_6H_6) δ –0.4 (Me_3Si), 0.4 (Me_3Si), 21.2 (*p*-Me), 25.0 (*o*-Me), 127.9–128.1, 129.3, 138.6, 143.8 (phenyl and mesityl ring carbons and carbons for solvents), 152.6 (=CPh), 171.0 (=$CSiMe_3$); ^{29}Si NMR (30% C_6D_6 and 70% C_6H_6, hexamethyldisilane as an internal standard) δ –109.5 (Si–$SiMe_3$), 3.7 (Me_3Si–C), 8.4 (Me_3Si–Si). Exact Mass Calcd for $C_{23}H_{34}Si_3$: 394.1968. Found: 394.1991.

Preparation of 2-Mesityl-4-phenyl-1,1-bis(triethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobutene (3). In a 150-mL reaction vessel fitted with a low-pressure mercury lamp was placed a mixture of 2.0 g (5.1 mmol) of **1** and 0.2119 g (0.75 mmol) of eicosane in 120 mL of hexane. The mixture was irradiated for 2 h with a slow stream of nitrogen through the mixture. The VPC analysis of the photolysis mixture showed that 95% of the starting **1** was photolyzed and the product **2** was produced in 75% yield. The solvent was evaporated, and the resulting **2** was distilled under reduced pressure into a 20-mL two-necked flask. The distillate was diluted with 10 mL of dry xylene. To this was added 2.2 g (4.1 mmol) of tetrakis(triethylphosphine)nickel(0), and the mixture was stirred for 6 h at room temperature. The ^1H NMR spectrum showed that compound **2** was transformed into **3**: ^1H NMR (C_6H_6) δ 0.20 (s, 9 H, Me_3Si), 0.52 (s, 9 H, Me_3Si), 2.15 (s, 3 H, *p*-Me), 2.83 (s, 3 H, *o*-Me), 2.96 (s, 3 H, *o*-Me); ^{13}C NMR (30% C_6D_6 in C_6H_6) 0.16 (Me_3Si), 4.1 (Me_3Si), 8.8 (CH_3CH_2P), 8.9 (CH_3CH_2P), 17.5 (CH_2P, dd, $^1J_{C-P}$ = 16.5, $^3J_{C-P}$ = 3.1 Hz), 19.5 (CH_2P, dd, $^1J_{C-P}$ = 16.2, $^3J_{C-P}$ = 4.0 Hz), 21.3, 25.2, 26.3 (*o*- and *p*-Me), 123.3, 127.3, 127.5–129.3, 136.8, 137.1 (mesityl and phenyl ring carbons and solvent carbons), 143.3 (=C(Ph)Ni, d, $^2J_{C-P}$ = 51.9 Hz), 151.9 (=C($SiMe_3$)); ^{29}Si NMR (30% C_6D_6 in C_6H_6, hexamethyldisilane as an internal standard) δ –105.4 (Si–$SiMe_3$, t, $^2J_{Si-P}$ = 2.8 Hz), 3.1 (Me_3Si–C), 12.8 (Me_3Si–Si, dd, $^3J_{Si-P}$ = 4.3, 1.0 Hz); ^{31}P NMR (30% C_6D_6 in C_6H_6, 85% phosphoric acid as an external standard) δ 9.7 (d, *J* = 36.6 Hz), 12.4 (d, *J* = 36.6 Hz). The solution was transferred into an ampule under an argon atmosphere. The ampule was sealed and stored in refrigerator until use.

Thermolysis of 3 in Xylene. In a 50-mL flask was placed a solution of 0.354 mmol of **3** and 0.233 mmol of eicosane as an internal standard in 20 mL of xylene. The flask was heated to reflux for 2 h. VPC analysis of the reaction mixture showed the presence of two isomers of 5,6-benzo-1,3-disilacyclo-hexene, **4a** (47%) and **4b** (41%). Both compounds were isolated by preparative VPC. All data obtained for **4a** and **4b** were identical with those of authentic samples.

Photolysis of 1 in the Presence of Methanol. A mixture of 0.327 g (1.53 mmol) of **1** and /.17 mL (44.2 mmol) of methanol in 25 mL of hexane was irradiated with a low-pressure mercury lamp for 4 h at 140 °C. VPC analysis of the mixture showed the presence of (*Z*)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-2-phenyl-2h(trimethylsilyl)ethene (**10**) and (*E*)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-1-phenyl-2-(trimethylsilyl)ethene (**11**). Compounds **10** and **11** were isolated by medium-pressure liquid chromatography in 21 and 37% yields. For **10**: ^1H NMR δ –0.07 (s, 9 H, Me_3Si), 0.13 (s, 9 H, Me_3Si), 2.24 (s, 3 H, *p*-Me), 2.39 (s, 6 H, *o*-Me), 3.54 (s, 3 H, MeO), 6.59 (s, 1 H, olefinic proton), 6.69 (br s, 2 H, mesityl protons), 6.81–7.41 (m, 5 H, phenyl ring protons); ^{13}C NMR δ –0.52 (Me_3Si), 0.11 (Me_3Si), 21.08 (*p*-Me), 25.17 (*o*-Me), 51.60 (MeO), 125.61, 126.20, 127.90, 128.98, 131.46, 138.63, 143.94, 145.06, 150.92, 163.84 (olefinic and aryl ring carbons); IR ν_{Si-OMe} 1077 cm^{-1}; MS *m/e* 426 (M^+). Anal. Calcd for $C_{24}H_{38}OSi_3$: C, 67.54; H, 8.97. Found: C, 67.26; H, 8.90. For **11**: ^1H NMR δ –0.13 (s, 9 H, Me_3Si), –0.04 (s, 9 H, Me_3Si), 2.27 (s, 3 H, *p*-Me), 2.34 (s, 6 H, *o*-Me), 3.47 (s, 3 H, MeO), 6.36 (s, 1 H, olefinic proton), 6.70 (br s, 2 H, mesityl ring protons), 6.83–7.30 (m, 5 H, phenyl ring protons); ^{13}C NMR –0.71 (Me_3Si), 0.07 (Me_3Si), 21.03 (*p*-Me), 21.90 (*o*-Me), 51.40 (MeO), 126.15, 127.66, 128.93, 130.24, 138.68, 144.77, 145.21, 147.36, 155.60, 161.93 (olefinic and aryl ring carbons); IR ν_{Si-OMe} 1078 cm^{-1}; MS *m/e* 426 (M^+). Anal. Calcd for $C_{24}H_{38}OSi_3$: C, 67.54; H, 8.97. Found: C, 67.41, H, 8.92.

Photolysis of 1 in Refluxing Xylene. A mixture of 0.260 g (0.512 mmol) of **1** and 0.139 mmol of eicosane was irradiated

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with a low-pressure mercury lamp for 3.5 h at 140 °C. The mixture was analyzed by VPC as being **2** (48%). All spectral data for **2** were identical with those of an authentic sample.[5]

Photolysis of 3 in Xylene. A solution of 0.182 mmol of **3** and 0.032 mmol of eicosane as an internal standard in 5 mL of xylene was irradiated externally with a high-pressure mercury lamp for 1.5 h with ice cooling. The reaction mixture was analyzed by VPC as being **4a** (54%) and **4b** (29%). Compounds **4a** and **4b** were isolated by preparative VPC. All spectral data for **4a** and **4b** were identical with those of authentic samples.[5]

Reaction of 3 with Methanol. To a solution of 0.79 mmol of **3** in 1.5 mL of xylene was added 0.1272 g (3.97 mmol) of methanol at room temperature. The reaction mixture was stirred for 12 h at room temperature. Nonvolatile products were removed from the mixture by flash column chromatography using silica gel, and the volatile products were chromatographed at medium pressure over silica gel to give 0.111 g (33% yield) of **11** and 0.099 g (29% yield) of (*E*)-(1-mesityl-1-methoxytrimethyldisilanyl)-2-phenyl-1-(trimethylsilyl)ethene (**12**). All spectral data obtained for **11** were identical with those of an authentic sample. For **12**: ^{1}H NMR δ −0.16 (s, 9 H, Me_3Si), 0.21 (s, 9 H, Me_3Si), 2.23 (s, 3 H, *p*-Me), 2.41 (s, 6 H, *o*-Me), 3.45 (s, 3 H, MeO), 6.62 (br s, 2 H, mesityl ring protons), 7.16 (br s, 5 H, phenyl ring protons), 8.01 (s, 1 H, olefinic proton); ^{13}C NMR δ 0.26 (Me_3Si), 1.38 (Me_3Si), 21.03 (*p*-Me), 24.20 (*o*-Me), 50.30 (MeO), 127.37, 127.76, 127.85, 129.02, 131.75, 138.48, 142.24, 144.04, 147.21, 157.94 (olefinic and aryl ring carbons); IR ν_{Si-OMe} 1080 cm^{-1}; MS *m/e* 426 (M$^+$). Anal. Calcd for $C_{24}H_{38}OSi_3$: C, 67.54; H, 8.97. Found: C, 67.54; H, 8.92.

Reaction of 3 with Hydrogen Chloride. To a mixture of 0.32 mmol of **3** and 0.069 mmol of eicosane as an internal standard in 1 mL of xylene was added 3.5 mL of 0.1 M hydrogen chloride–benzene solution at 0 °C. The mixture was stirred overnight at room temperature. To this was added 0.4 mmol of sodium methoxide in 1 mL of methanol at room temperature. The mixture was stirred overnight at room temperature, and then it was analyzed by VPC as being **10** (39% yield) and an unidentified product (7% yield). Product **10** was isolated by medium-pressure liquid chromatography. All spectral data for **10** were identical with those of an authentic sample.

Reaction of 3 with Hydrogen. In a 20-mL autoclave was placed a mixture of 0.363 mmol of **3** and 0.064 mmol of eicosane in 1 mL of xylene. The mixture was treated with hydrogen gas under the pressure of 50 kg/cm^2 for 20 h at room temperature. VPC analysis of the mixture indicated the presence of (*E*)-(1-hydro-1-mesityltrimethyldisilanyl)-1-(trimethylsilyl)-2-phenylethene (**14**) in 81% yield. Compound **14** was isolated by medium-pressure liquid chromatography: ^{1}H NMR δ 0.08 (s, 9 H, Me_3Si), 0.32 (s, 9 H, Me_3Si), 2.15 (s, 3 H, *p*-Me), 2.58 (s, 6 H, *o*-Me), 5.24 (s, 1 H, HSi), 6.73 (br s, 2 H, mesityl ring protons), 6.87–7.29 (m, phenyl ring protons), 8.19 (s, 1 H, olefinic proton); ^{13}C NMR δ 0.02 (Me_3Si), 1.48 (Me_3Si), 21.13 (*p*-Me), 25.12 (*o*-Me), 127.61, 128.00, 128.15, 129.07, 130.15, 138.68, 142.68, 143.70, 144.48, 158.08 (olefinic and aryl carbons); IR ν_{Si-H} 2100 cm^{-1}; MS *m/e* 322 (M$^+$ − Me_3SiH). Anal. Calcd for $C_{23}H_{36}Si_3$: C, 69.62; H, 9.14. Found: C, 69.37; H, 9.07.

Reaction of 3 with Bromine. To a mixture of 0.363 mmol of **3** and 0.063 mmol of eicosane in 2 mL of xylene was added 0.363 mmol of bromine in 2 mL of xylene with ice cooling. The mixture was stirred for 30 min, and then it was analyzed by VPC as being **2** (100%). Retention time on VPC, mass, and ^{1}H NMR data of **2** were identical with those of an authentic sample.

Reaction with Methyl Iodide. To a solution of 0.1 mmol of **3** in 1 mL of benzene was added 0.1 mL of methyl iodide at room temperature. A precipitate immediately developed. The supernatant solution was analyzed by ^{1}H NMR spectroscopy as being **2** (100%).

Reaction with Benzyl Bromide. To a solution of 0.726 mmol of **3** and 0.123 mmol of eicosane as an internal standard in 5 mL of xylene was added 0.2480 g (1.45 mmol) of benzyl bromide with ice cooling. The reaction mixture was stirred for 12 h at room temperature. The mixture was analyzed by VPC as being **2** (100%) and bibenzyl (86% yield). Products were isolated by medium-pressure liquid chromatography. All spectral data for **2** and bibenzyl were identical with those of authentic samples.

Reaction of 3 with Phenyl(trimethylsilyl)acetylene. To a solution containing 0.338 mmol of **3** in 5 mL of xylene was added 0.5 mL of phenyl(trimethylsilyl)acetylene at room temperature. The mixture was heated to reflux for 21 h. Nonvolatile substances in the mixture was removed by flash chromatography using silica gel. Treatment of the mixture with the medium-pressure liquid chromatography gave 91 mg (32% yield) of **15** and 11 mg (6%) of **16**. For **15**: mp 180.6 °C; ^{1}H NMR δ −0.28 (s, 18 H, Me_3Si), 0.36 (s, 9 H, Me_3Si), 2.26 (s, 6 H, *o*-Me), 2.68 (s, 3 H, *p*-Me), 6.65–7.05 (m, 12 H, Mes and Ph ring protons); ^{13}C NMR δ 0.9, 1.7 (Me_3Si), 19.7, 21.1, 26.2 (*o*- and *p*-Me), 126.0, 126.8, 128.3, 128.7, 128.9 (br), 129.3, 138.8, 143.0, 143.9, 146.6 (Mes and Ph ring carbons), 150.5, 168.3 (olefinic carbons); MS *m/e* 568. Anal. Calcd for $C_{34}H_{48}Si_4$: C, 71.76; H, 8.50. Found: C, 71.26; H, 8.50. All spectral data obtained for **16** were identical with those of authentic sample.[5]

Reaction of 3 with *n*-Hexyne. A mixture of 0.363 mmol of **3**, 0.0356 g (0.434 mmol) of *n*-hexyne, and 0.0644 mmol of eicosane as an internal standard in 3 mL of xylene was stirred at room temperature for 2 days. The mixture was warmed at 50 °C for 5 h. VPC analysis of the mixture showed the presence of **17** and its isomer (MS *m/e* 476). Compound **17** was isolated by medium-pressure liquid chromatography: ^{1}H NMR δ 0.03 (s, 9 H, Me_3Si), 0.24 (s, 9 H, Me_3Si), 0.76–1.62 (m, 9 H, C_4H_9), 2.24 (s, 3 H, *p*-Me), 2.46 (s, 6 H, *o*-Me), 6.51 (s, 1 H, olefinic proton), 6.64 (s, 2 H, mesityl ring protons), 6.92–7.42 (m, 5 H, phenyl ring protons); ^{13}C NMR δ −1.28 (Me_3Si), −0.03 (Me_3Si), 14.00, 25.81, 32.04, 42.76 (C_4H_9), 20.98 (*p*-Me), 22.72 (*o*-Me), 94.82, 109.45 (ethynyl carbons), 124.29, 127.76, 128.19, 128.90, 129.39, 131.45, 136.97, 138.43, 144.34, 162.92 (olefinic and aryl ring carbons); IR $\nu_{C\equiv C}$ 2150 cm^{-1}; MS *m/e* 476 (M$^+$). Anal. Calcd for $C_{29}H_{44}Si_3$: C, 73.03; H, 9.30. Found: C, 73.03; H, 9.47.

Acknowledgment. The cost of this research was defrayed by a Grant-in-Aid for Scientific Research by the Ministry of Education. We also express our appreciation to Shin-etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., and Dow Corning Japan Ltd. for financial support.