Transition-Metal-Catalyzed Reactions of Organosilanes

Joji Ohshita

1991

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Preface

The studies presented in this thesis have been carried out under the direction of Professor Mitsuo Ishikawa during 1985-1987 at Kyoto University and 1987-1990 at Hiroshima University. In this thesis, the studies concerning the interaction between organosilicon compounds and transition-metal-complexes are described.

I, the author of this thesis, wish to express my sincerest gratitude to Professor Ishikawa for his constant guidance throughout this work. I also appreciate to Professor Yoshihiko Ito, Dr. Kohei Tamao Kyoto University, Dr. Tamio Hayashi Hokkaido University, and Dr. Atsutaka Kunai Hiroshima University for their continuing advice and stimulating and valuable discussions, during the course of my studies. I also acknowledge Dr. Reng-Fang Hong, Mr. Yudai Isomura, Mr. Takashi Yoshitomi, Mr. Tetsuya Mukai, Mr. Hiroshi Ohsaki, Mr. Daisuke Kanaya, Mr. Kenji Furumori, Mr. Akira Matsuguchi, Mr. Akinobu Naka, Mr. Yoshiteru Masaoka, Mr. Yasuo Nomura, Mr. Eizo Tozaki, and Mr. Toshihide Takahashi for their active collaborations.

I also express my appreciation to my parents, Mr. Takaaki Ohshita and Mrs. Kishiko Ohshita.

Finally, I wish to thank Miss Yoshiko Yokota for her constant encoura-gement.

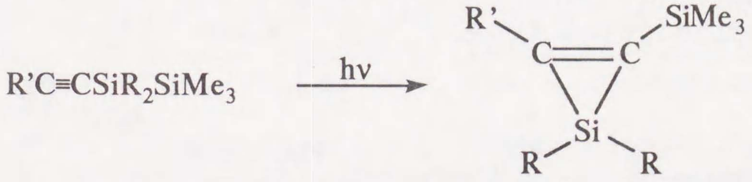
Joji Ohshita

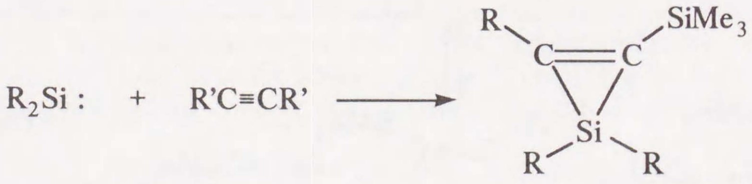
Contents

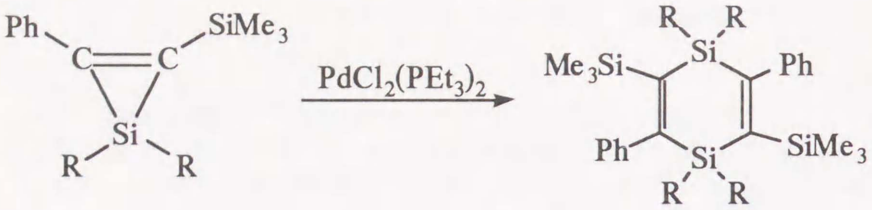
General Introduction

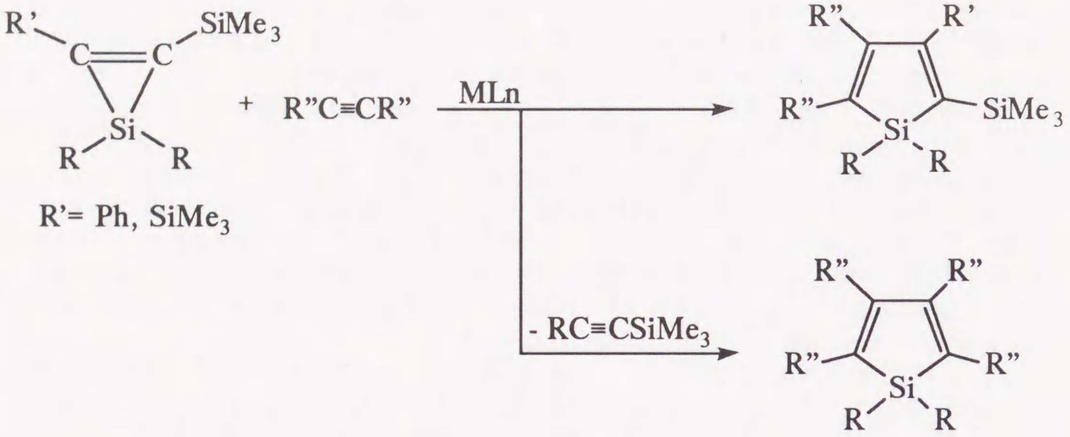
Since G. Wilkinson and his coworkers[1] reported the first synthesis of a silyl-substituted transition-metal complex, $Cp(CO)_2FeSiMe_3$, many papers dealing with the synthesis and properties of the silyl-substituted transition-metal complexes have been published. The transition-metal-catalyzed reactions of organosilicon compounds have been also widely investigated.[2] It is well known that the synthetically useful reactions such as hydrosilylation[3] and double silylation[2] of unsaturated carbon compounds involve the silyl-substituted transition-metal complex as a key intermediate. Recently, a considerable interest has been focused on the chemistry of silylene complexes and, silene- and disilene-complexes analogous to carbene- and olefine-complexes.[4]

On the other hand, the reaction of highly strained small ring compounds with the transition-metal complexes is of considerable interests. It has been reported that silacyclopropenes, which can readily be prepared from the photolysis of ethynylpolysilanes[5] or the reaction of acetylenes with silylene species[6] react with many reagents to give various interesting compounds. The reactions of silacyclopropenes in the presence of the transition-metal complexes, such as dimerization,[7e] the reactions with unsaturated carbon



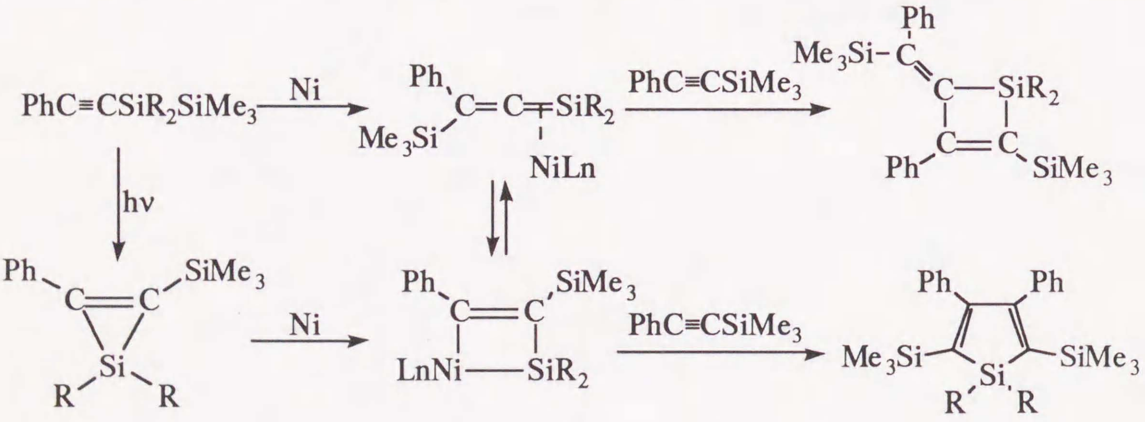






compounds[7a-d,8,9] and silylene abstraction reactions[8d] have been reported so far.

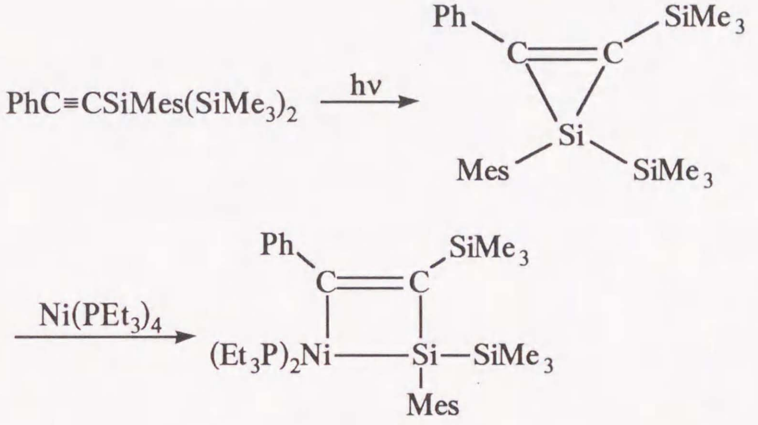
Recently, we have demonstrated that the nickel-catalyzed reactions of the silacyclopropene produce variety types of a novel reactive intermediate such as a nickelasilacyclobutene and a 1-silapropadiene-nickel complex. These intermediates can readily be trapped by using phenyl(trimethylsilyl)acetylene as a silole, methylenesilacyclobutene, and some other cyclic



compounds.[7d] In the same paper, it has been reported that (Phenylethynyl)polysilane also reacts with phenyl(trimethylsilyl)acetylene to give the same reaction intermediates.

The studies presented in this thesis were carried out for the purpose of obtaining more information about the interaction of transition-metal complexes with ethynylpolysilanes and silacyclopropenes.

Part I entitled "Reactions of (Phenylethynyl)-polysilanes and Silacyclopropenes with Transition-Metal-Complexes", consists of four chapters. In Chapter 1, the formation and characterization of a nickelasilacyclobutene is reported. Some reactions of the nickelasilacyclobutene is also described.



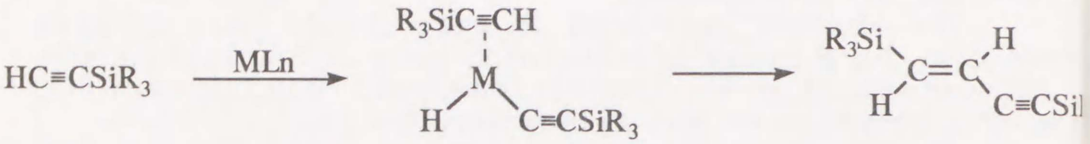
In Chapter 2, we report the nickel-catalyzed reaction of 2-aryl-substituted 2-(phenylethynyl)-trisilane, involving the novel isomerization reaction of a (phenylethynyl)trisilane via a silapropadiene-nickel complex.

Chapter 3 deals with platinum catalyzed reactions of (phenylethynyl)disilanes. In contrast to the nickel-catalyzed reactions which always proceed via a 1-silapropadiene-nickel complex, these reactions produced a platinasilacyclobutene intermediate.

Chapter 4 describes the tungsten-catalyzed silylene extrusion reaction from silacyclopropenes.

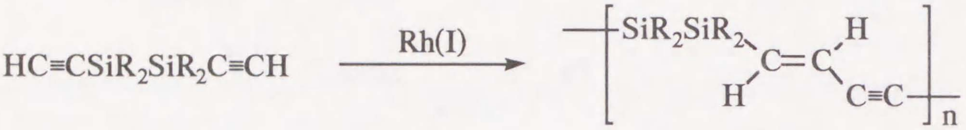
In Part II entitled "Transition-Metal-Catalyzed C-H Bond Activation of Ethynylsilanes", the transition-metal-catalyzed head-to-head coupling reactions of ethynylsilanes are described.

In Chapter 5, we describe the dimerization reaction of ethynylsilanes which offers a convenient route to enyne system.



In Chapter 6, we describe the nickel-catalyzed C-H bond activation reaction for the formation of dienyne systems.

Finally, the synthesis of the polymers which contain an alternating arrangement of a silyl unit and an enyne unit in the polymer backbone, utilizing the coupling reaction of 1,2-diethynyldisilanes is described in Chapter 7. Some properties of these polymers are also mentioned in this Chapter.



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Part I

Reactions of (Phenylethynyl)polysilanes and Silacyclopropenes with Thrasition-Metal-Complexes

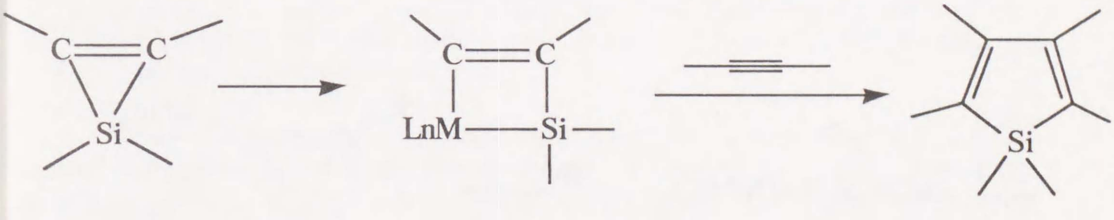
Chapter 1

Formation and Reactions of a Nickelasilacyclobutene

Introduction

There has been a considerable interest in the chemistry of silicon-containing small ring compounds in many aspects. Particularly, the transition-metal catalyzed reactions of silacyclopropenes with acetylenes has been extensively investigated.[1-3] In these reactions metalasilacyclobutene arising from insertion of transition-metal-center of the catalyst into an Si-C bond of a silacyclopropene, has been assumed as a key intermediate. The metalasilacyclobutene thus formed reacts with acetylenes to produce silacyclopentadienes (Scheme 1).

Scheme 1



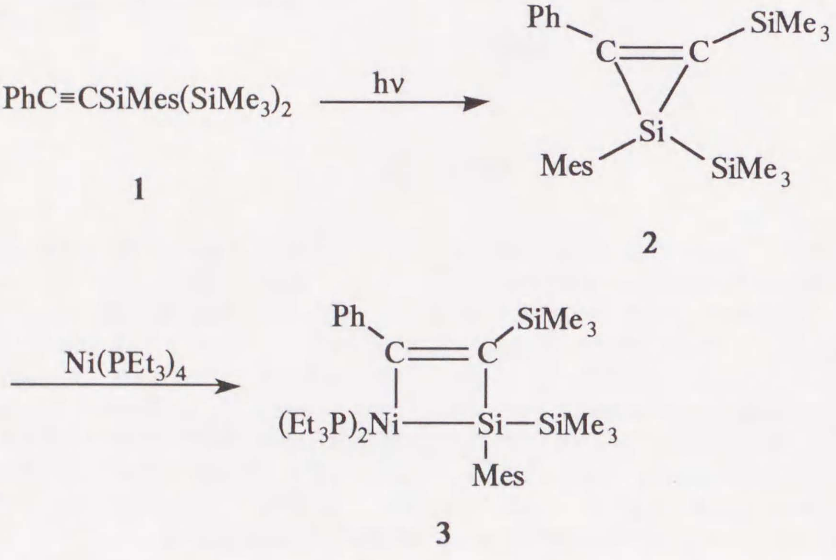
M=Ni, Pd

However, no direct evidence for the formation of metalasilacyclobutenes has been reported to date. In this Chapter, we describe the synthesis of 2-mesityl-4-phenyl-1,1-bis(triethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobut-3-ene from the stoichiometric reaction of 1-mesityl-1,2-bis(trimethylsilyl)-3-phenyl-1-silacyclopropene and tetrakis(triethylphosphine)nickel(0), and its characterization by NMR spectroscopic analysis. Some reactions of the nickelasilacyclobutene are also described.

Results and Discussion

Formation and Characterization of a Nickelasilacyclobutene. Irradiation of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane (**1**) with a low-pressure mercury lamp in hexane, followed by distillation under reduced pressure gave 1-mesityl-1,2-bis(trimethylsilyl)-3-phenyl-1-silacyclopropene (**2**) in 84% yield. Treatment of **2** with a small excess 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 2). 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 the starting silacyclopropene **2** cleanly transformed into those at 0.20, 0.50, 2.15, 2.83, and 2.96 ppm attributed to two nonequivalent trimethylsilyl protons and three mesityl methyl protons of **3** within 1 h.

Scheme 2



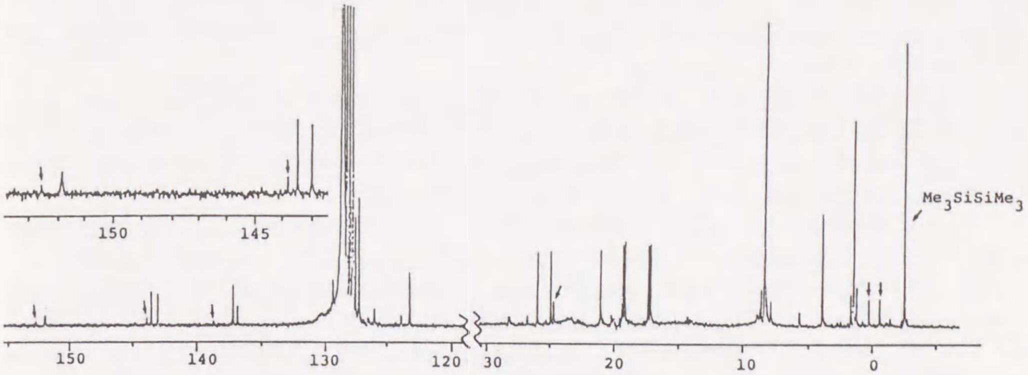


Figure 1. Proton-decoupled ^{13}C NMR spectra of nickelasilacyclobutene **3**. Arrows indicate silacyclopropene **2**.

That the nickel species inserts into the C(Ph)-Si bond in the silacyclopropene ring but not to 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 two phosphine ligands (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** showed three resonances at δ -105.4 ppm (t, $^2J_{Si-P}$=2.8 Hz), 3.1 ppm (s), and 12.8 ppm (dd, $^3J_{Si-P}$=4.3, 1.0 Hz), due to the ring silicon, a silicon on carbon, and a silicon of the trimethylsilyl on the ring silicon, respectively.

These are also consistent with the -NiC(Ph)=C($SiMe_3$)-Si($SiMe_3$)- structure. If compound 3 had a Ni-C-$SiMe_3$ structure, the resonance for the silicon atom on the carbon attached to the nickel atom should be a doublet of doublet or a triplet, owing to the coupling with two phosphine ligands on the nickel atom. However, this is not the case.

The ^{31}P NMR spectrum displays two doublets at 9.7 ppm (J=36.6 Hz) and 12.4 ppm (J=36.6 Hz), indicating the presence of two nonequivalent phosphines on the nickel atom in the four membered ring.

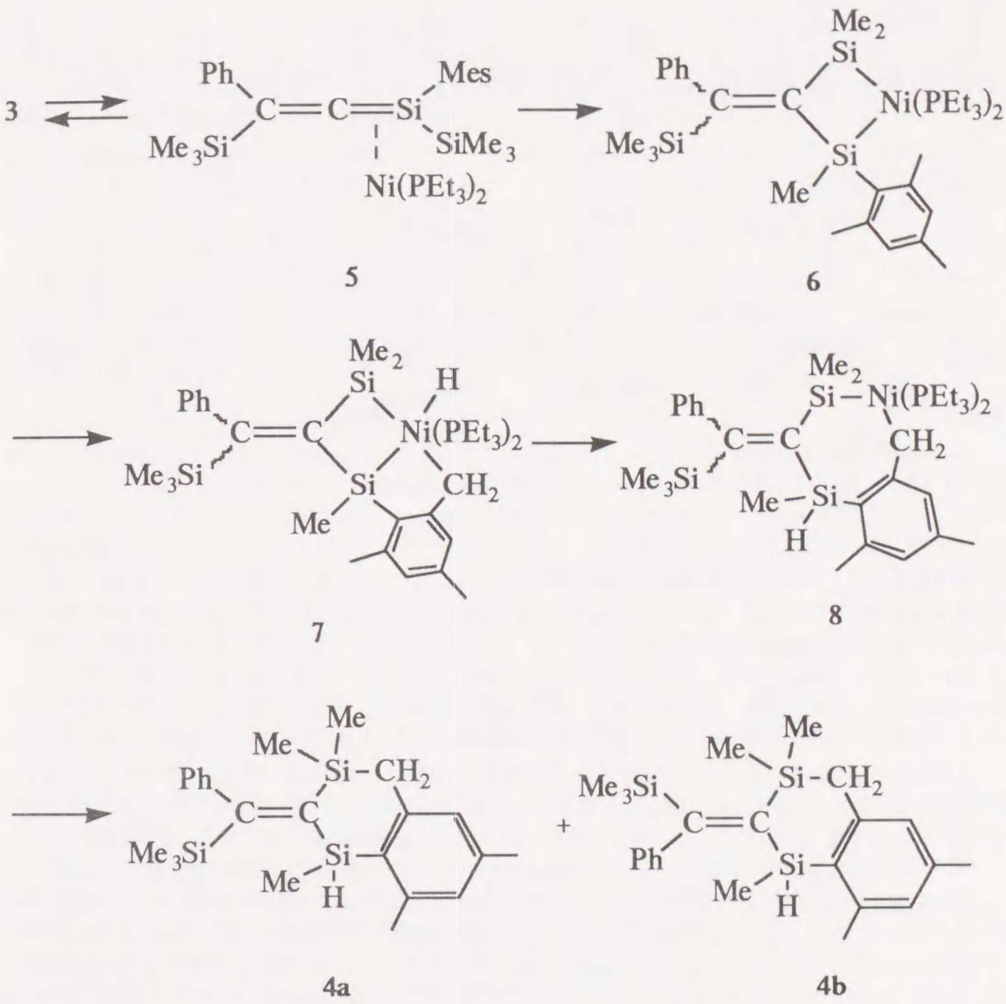
Although, all these NMR spectrometric analyses strongly support the formation of nickelasilacyclobutene in this solution, the compound 3 could not be isolated. In order to obtain 3 in a pure form, the solvent was evaporated under reduced pressure at room temperature. However, only complicated decomposition products were obtained. Therefore, to check the chemical properties of 3, the solution of 3 was used without further purification.

Thermolysis of 3 in Xylene. Nickelasilacyclobutene 3 could be also produced 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** were obtained in 47 and 41% yields, respectively.

The structure of **4a** and **4b** were verified by spectroscopic analysis as well as elemental analysis particularly by an NOE-FID difference experiment. Thus, saturation of the resonance of the trimethylsilyl protons of **4a** produced a positive NOE of the hydrogen (H-SiMe) and methyl protons (Me-SiH) and also the phenyl ring protons and one of two methyl protons on an aromatic ring. Irradiation of the trimethylsilyl protons of **4b**, however, caused a positive NOE of the dimethylsilyl protons in a disilacyclohexene ring and phenyl ring protons.

Scheme 3 illustrates a possible mechanistic interpretation. The formation of **4a** and **4b** requires isomerization of 3 to a silapropadiene-nickel complex (5) which would be transformed into a nickeladisilacyclobutane (6). The carbon-hydrogen bond activation of an ortho mesityl methyl group of 6 leading to a six-coodinated nickel complex intermediate

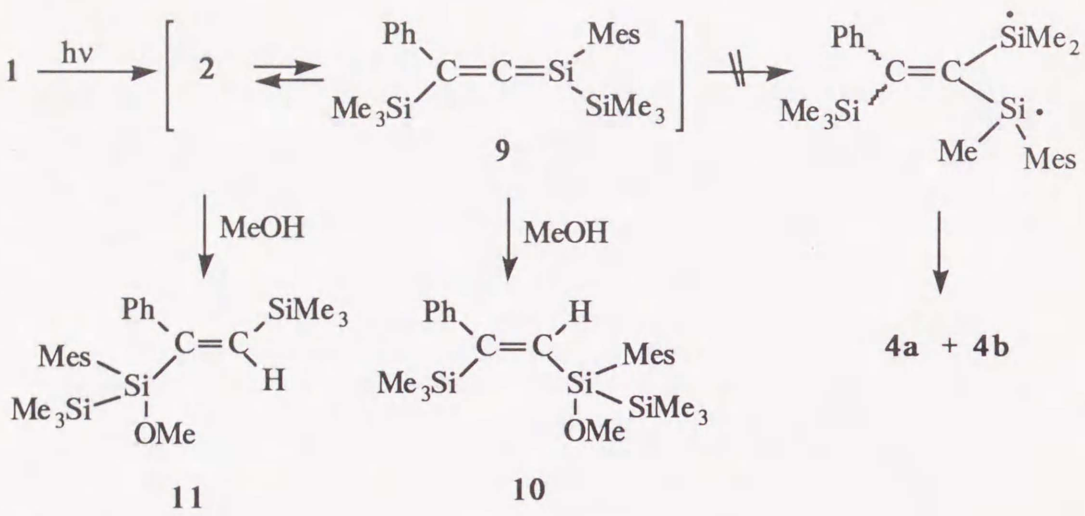
Scheme 3



(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 included in a series of the reaction. The isomerization of the silapropadiene-nickel complex to nickeladisilacyclobutane system has been already reported.[2d]

An alternate pathway involving thermolysis of a free silapropadiene might be considered for the formation of **4a** and **4b** under the condition used. In

Scheme 4



an effort to learn whether or not the thermal isomerization of 1-mesityl-3-phenyl-1,3-bis(trimethylsilyl)-1-silapropadiene (**9**) involved in the formation of **4a** and **4b**, we investigated the thermolysis of **9** generated in the absence of nickel. The photochemical isomerization of silacyclopropene to silapropadiene has been reported previously.[4] First, we checked whether or not this isomerization takes place in the case of **2** and **9**. Irradiation of **1** in the presence of methanol at 140 °C gave (Z)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-2-phenyl-2-(trimethylsilyl)ethene (**10**) and (E)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-1-phenyl-2-(trimethylsilyl)ethene (**11**) in 21 and 37% yields, respectively (Scheme 4). The Z geometry of **10** was established from its NOE-FID difference spectra. Thus, saturation of the resonance of methoxy methyl protons at 3.54 ppm 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 silapropadiene **9** 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 methanol in benzene at room temperature gave **10** and **11** in 29 and 26% yields, respectively.

Next, we carried out the photolysis of 1 in the absence of methanol under the same conditions. Irradiation of 1 in refluxing xylene gave no isomerization products **4a** and **4b**, and 2 was produced in 49% yield as the sole volatile product. These results clearly indicate that the nickel atom plays an important role for the isomerization of silapropadiene (9) to **4a** and **4b**.

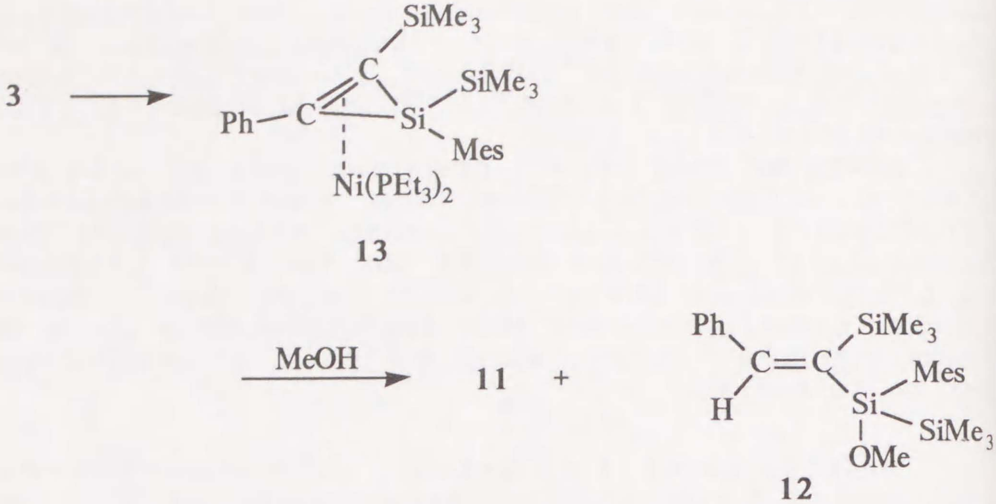
Photolysis of 3 in Xylene. The photochemical reaction of 3 also involves isomerization of 3 to the silapropadiene-nickel complex 5. Thus, irradiation of a xylene solution of 3 with a high-pressure mercury lamp afforded **4a** and **4b** in 54 and 29% yields, respectively.

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

Reactions of 3 with Methanol. When a xylene solution of 3 was treated with a 5-fold excess of methanol, ring opened product (**11**) and its isomer which was identified as (E)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-1-(trimethylsilyl)-2-phenylethene (**12**) by spectroscopic analysis, as well as by elemental analysis (see Experimental Section) were obtained in 33 and 29% yields, respectively.

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 by methanol on the nickel atom in the nickelasilacyclobutene ring. In the π-complex **13**, both silicon-carbon bonds would be weakened by

Scheme 5

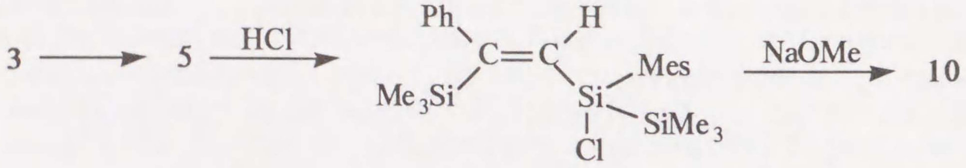


coodination of the nickel species to the carbon-carbon double bond and would be readily cleaved by methanol to give 11 and 12 (Scheme 5).

Reaction with Hydrogen Chloride. The reaction of a benzene solution of 3 with 1 equiv of hydrogen chloride dissolved in 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 an unidentified product. All spectral data obtained for 10 were identical with those of an authentic sample.

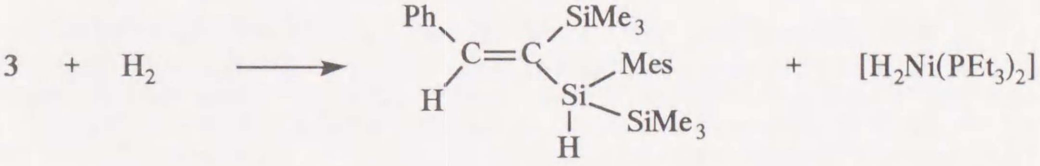
A reasonable pathway for 10 presumably involves isomerization of 3 to the silapropadiene-nickel complex 5, followed by addition of hydrogen chloride to a silicon-carbon double bond of 5 (Scheme 6).

Scheme 6



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 volatile product. In this reaction, both a nickel-silicon bond and a nickel-carbon bond in the nickelasilacyclobutene ring are cleaved by hydrogen.

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 an H-Si bond. ^{1}H NMR spectrum shows a singlet at 8.19 ppm due to an olefinic proton, indicating that **14** has a PhC(H)=C structure, but not a Me$_3$SiC(H)=C structure.[5]



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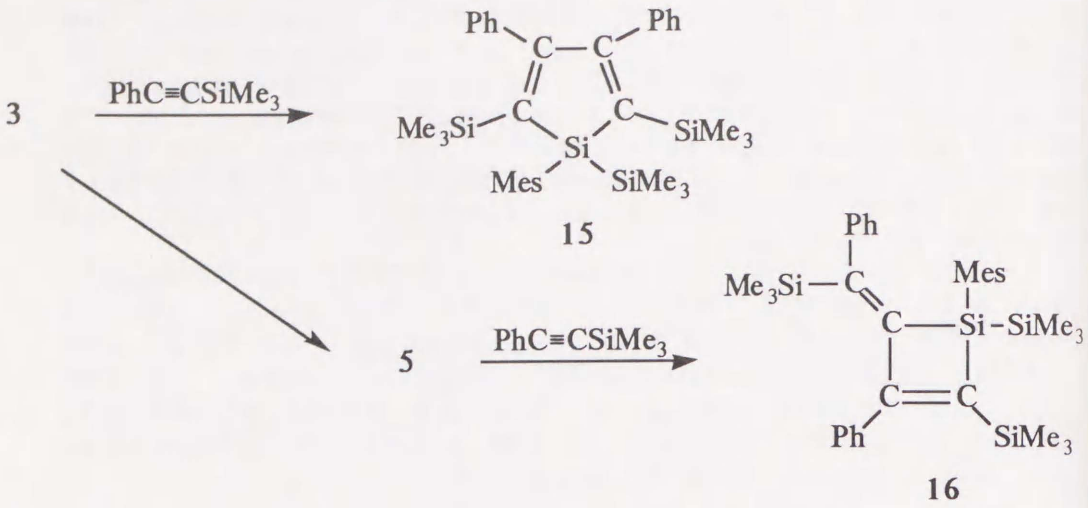
Reaction with Acetylenes. Compound **3** reacts with phenyl(trimethylsilyl)acetylene at 140°C to give 1-mesityl-3,4-phenyl-1,2,5-tris(trimethylsilyl)silole (**15**) and 1-mesityl-3-phenyl-4-[phenyl(trimethylsilyl)-methylene]-1,2-bis(trimethylsilyl)-1-silacyclobut-2-ene (**16**) in 32 and 6% yields, respectively. The structures of **15** and **16** were verified by spectroscopic analysis, as well as by elemental analysis (see Experimental Section).

The formation of silole **15** can be readily understood by the direct reaction of **3** with the acetylene, while **16** may be explained in terms of cycloaddition of the silapropadiene-nickel complex **5** arising from isomerization of **3** with acetylene (Scheme 7).

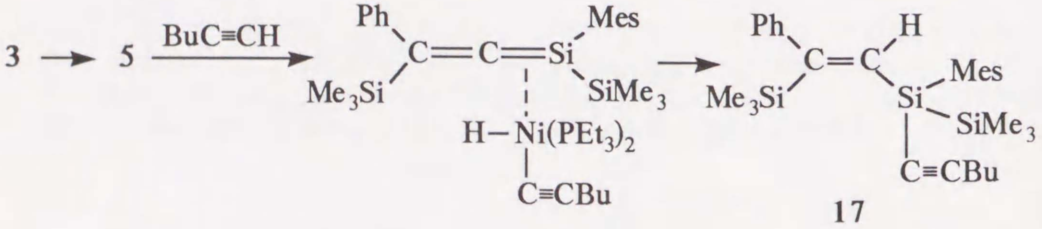
Scheme 7



The reaction of 3 with a terminal acetylene proceeded in a quite different manner to give a ring opened product. Thus, treatment of a xylene solution of 3 with 1-hexyne at room temperature afforded (Z)-1-(1-hexynyl-1-mesityltrimethyldisilanyl)-2-phenyl-2-(trimethylsilyl)ethene (17) and its unidentified isomer, in 18 and 3% yields, respectively, together with appreciable amounts of polymeric substances.

The structure of 17 was confirmed by IR, mass, and ^{1}H and ^{13}C NMR spectroscopic analysis, as well as by elemental analysis. The fact that saturation of the ortho methyl protons of a mesityl group in the NOE-FID difference experiment produced a positive NOE of two different kinds of trimethylsilyl protons and an

Scheme 8



olefinic proton, in addition to mesityl ring protons, but no effect on the phenyl ring protons indicates that compound 17 must have a Z geometry.

The formation of 17 can be explained by oxidative addition of an ethynyl C-H bond to the nickel atom of 5, followed by addition of this bond across the silicon-carbon double bond (Scheme 8). The C-H activation by the nickel complex is described in Chapter 6.

Reductive Elimination of a Nickel Species. When the nickelasilacyclobutene 3 was treated with bromine or alkyl halide, the reductive elimination occurred to reproduce the silacyclopropene 2. Treatment of 3 with 1 equiv of bromine in xylene with ice cooling gave 2 in quantitative yield. No other products were detected by either GLC or spectroscopic analysis.

In sharp contrast to the reaction of nickelacycloalkanes with alkylhalides, in which coupling products are produced,[6] the nickelasilacyclobutene reacts with 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.

$$\mathbf{3} + Br_2 \longrightarrow \mathbf{2} + (Et_3P)_2NiBr_2$$

$$\begin{aligned} \mathbf{3} + C_6H_5CH_2Br \longrightarrow \mathbf{2} &+ C_6H_5CH_2CH_2C_6H_5 \\ &+ (Et_3P)_2NiBr_2 \end{aligned}$$

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

Experimental

General. All reactions were carried out under an atmosphere of purified argon. NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer, a JEOL Model JNM-FX-90A spectrometer, and a JEOL model JNM-GX-400 spectrometer. IR spectra were measured on a Perkin-Elmer 1600-FT infrared spectrometer. Mass spectra were measured on a JEOL Model JMN-D300 spectrometer equipped with a JMA-2000 data processing system.

Materials. 2,2-Dichlorohexamethyltrisilane[8] and tetrakis(triethylphosphine)nickel(0)[9] were prepared as reported in the literature. Diethyl ether and THF were dried over butylmagnesium bromide and distilled just before use. Benzene and hexane were dried over lithium aluminum hydride and distilled just 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 the extracts were combined and washed with water and then dried over potassium carbonate. The solvent was 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 (2.0 mmHg); MS m/e 394 (M^+); 100 MHz ^1H NMR (δ in CCl_4) 0.23 (s, 18H, Me_3Si), 2.23 (s, 3H, p-Me), 2.51 (s, 6H, o-Me), 6.69 (br s, 2H, mesityl ring protons), 7.12-7.46 (m, 5H, phenyl ring protons); 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)-1-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 228.0 mg (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. GLC 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 mmHg) to give **2**: MS m/e 394 (M^+); 100 MHz ^1H NMR (δ in C_6H_6) 0.23 (s, 9H, Me_3Si), 0.36 (s, 9H, Me_3Si), 2.12 (s, 3H, p-Me), 2.26 (s, 6H, o-Me); 100 MHz ^1H NMR (δ in CCl_4) 0.15 (9s, 9H, Me_3Si), 0.29 (s, 9H, Me_3Si), 2.20 (s, 3H, p-Me), 2.25 (s, 6H, o-Me), 6.65 (br s, 2H, mesityl ring protons), 7.05-7.52 (m, 5H, phenyl ring protons); 100 MHz ^{13}C NMR (δ in 30% C_6D_6 and 70% C_6H_6) -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 solvent carbons), 152.6 (=CPh), 171.0 (=$CSiMe_3$); ^{29}Si NMR (δ in 30% C_6D_6 and 70% C_6H_6, hexamethyldisilane as an internal standard) -109.5 (ring silicon), 3.7 (Me_3Si-Si), 8.4 (Me_3Si-C). Exact MS 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-silacyclobut-2-ene (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 211.9 mg (0.73 mmol) of eicosane as an internal standard in 120 mL of hexane. The mixture was irradiated for 2 h with a slow stream of nitrogen through the mixture. The GLC 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

^{1}H NMR spectrum showed that compound **2** was transformed into **3**: 100 MHz ^{1}H NMR (δ in C_6H_6) 0.20 (s, 9H, Me_3Si), 0.52 (s, 9H, Me_3Si), 2.15 (s, 3H, p-Me), 2.83 (s, 3H, o-Me), 2.96 (s, 3H, o-Me); 100 MHz ^{13}C NMR (δ in 30% C_6D_6 and 70% 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 (δ in 30% C_6D_6 and 70% C_6H_6, hexamethyldisilane as an internal standard) -105.4 (ring silicon, 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 (δ in 30% C_6D_6 and 70% C_6H_6, phosphoric acid as an external standard) 9.7 (d, J=36.6 Hz), 12.4 (d, J=36.6 Hz). The solution was transfered into an ampule under an argon atmosphere. The ampul 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. GLC analysis of the resulting mixture showed the formation of two isomers of 5,6-benzo-1,3-disilacyclohexene, **4a** (47%) and **4b** (41%). Both compounds were isolated by preparative GLC. For **4a**: mp 96°C; MS m/e 394 (M^+); 400 MHz ^{1}H NMR (δ in $CDCl_3$) -0.34 (s, 3H, MeSi(Me)), -0.20 (s, 9H, Me_3Si), 0.09 (s, 3H, MeSi(Me)), 0.60 (d, 3H, MeSi(H), J=4.2 Hz), 2.00 (d, 1H, HC(H), J=4.5 Hz), 2.26 (s, 3H, Me(aryl)), 2.51 (s, 3H, Me(aryl)), 3.04 (d, 1H, HC(H), J=4.5 Hz), 5.11 (q, 1H, HSi(Me), J=4.2 Hz), 6.68-7.25 (m, 7H, phenyl and aryl ring protons); 100 MHz ^{13}C NMR (δ in $CDCl_3$) -3.9 (MeSi), -1.3 (MeSi), -1.1 (MeSi), 1.2 (MeSi), 21.2 (Me(aryl)), 24.4 (Me(aryl)), 27.4, (Me(aryl)), 125.7, 126.7, 127.3, 127.4, 127.5, 127.7, 127.8, 131.1, 139.3, 143.9, 146.9, 147.3 (phenyl and aryl ring carbons), 158.2, 175.3 (olefinic carbons). Exact Mass Calcd for $C_{23}H_{34}Si_3$: 394.1968. Found: 394.1952. Anal. Calcd for $C_{23}H_{34}Si_3$ (1:1 mixture of **4a** and **4b**): C, 69.98; H, 8.68. Found:

C, 69.96; H,8.86. For **4b**: mp 83.5; MS m/e 394 (M^+); 400 MHz ^1H NMR (δ in $CDCl_3$) -0.23 (s, 9H, Me_3Si), -0.05 (s, 3H, MeSi(Me)), 0.28 (d, 3H, MeSi(H), J=4.3 Hz), 0.33 (3H, s, MeSi(Me)), 2.01 (d, 1H, HC(H), J=4.4 Hz), 2.27 (d, 1H, HC(H), J=4.4 Hz), 2.41 (s, 3H, Me(aryl)), 2.87 (d, 1H HC(H), J=4.4 Hz), 4.82 (q, 1H, HSi(Me), J=4.3 Hz), 6.68-7.31 (m, 7H, phenyl and aryl ring protons); 100 MHz ^{13}C NMR (δ in $CDCl_3$) -4.7 (MeSi), -1.5 (MeSi), 1.6 (MeSi), 2.5 (Me_3Si), 21.3 (Me(aryl)), 23.6 (Me(aryl)), 29.5 (CH_2(aryl)), 126.1, 126.6, 127.1, 127.5, 127.6, 128.2, 129.0, 129.2, 139.7, 144.2, 147.6, 149.1 (phenyl and aryl ring carbons), 160.9, 174.8 (olefinic carbons). Exact Mass Calcd for $C_{23}H_{34}Si_3$: 394.1968. Found: 394.1981.

Photolysis of 1 in the Presence of Methanol. A mixture of 327 mg (1.53 mmol) of **1** and 0.17 mL (44.2 mmol) of methanol in 25 mL of xylene was irradiated with a low-pressure mercury lamp for 4 h at 140°C. GLC analysis of the mixture showed the presence of (Z)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-2-phenyl-2-(trimethylsilyl)ethene (**10**) and (E)-1-(1-mesityl-1-methoxytrimethyldisilanyl)-1-phenyl-2-(trimethylsilyl)ethene (**11**). Compounds **10** and **11** were isolated by MPLC in 21 and 37% yields, respectively. For **10**: MS m/e 426 (M^+); IR ν_{Si-O} 1077 cm^{-1}; ^1H NMR (δ in $CDCl_3$) -0.07 (s, 9H, Me_3Si), 0.13 (s, 9H, Me_3Si), 2.24 (s, 3H, p-Me), 2.39 (s, 6H, o-Me), 3.54 (s, 3H, MeO), 6.59 (s, 1H, olefinic proton), 6.69 (br s, 2H, mesityl ring protons), 6.81-7.41 (m, 5H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) -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). Anal. Calcd for $C_{24}H_{38}OSi_3$: C, 67.54; H, 8.97. Found: C, 67.26; H, 8.90. For **11**: MS m/e 426 (M^+); IR ν_{Si-O} 1078 cm^{-1}; ^1H NMR (δ in $CDCl_3$) -0.13 (s, 9H, Me_3Si), -0.04 (s, 9H, Me_3Si), 2.27 (s, 3H, p-Me), 2.34 (s, 6H, o-Me), 3.47 (s, 3H, MeO), 6.36 (s, 1H, olefinic proton), 6.70 (br s, 2H, mesityl ring protons), 6.83-7.30 (m, 5H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) -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). 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 260 mg (0.512 mmol) of **1** and 0.139 mmol of eicosane as an internal standard was irradiated with a low-pressure mercury lamp for 3.5 h at 140°C. The mixture was analyzed by GLC as being **2** (48%). All spectral data for **2** were identical with those of an authentic sample.

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 GLC as being **4a** (54%) and **4b** (29%). Compounds **4a** and **4b** were isolated by preparative GLC. All spectral data obtained for **4a** and **4b** were identical with those of authentic samples.

Reaction of 3 with Methanol. To a solution of 0.79 mmol of **3** in 1.5 mL of xylene was added 127.2 mg (3.97 mmol) of methanol at room temperature. The reaction mixture was stirred for 12 h at room temperature. Non volatile products were removed from the mixture by flash column chromatography using silica gel, and the volatile products were treated with MPLC to give 111 mg (33% yield) of **11** and 99 mg (29%) of (E)-1-(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**: MS m/e 426 (M^+); IR ν_{Si-O} 1080 cm^{-1}; ^1H NMR (δ in $CDCl_3$) -0.16 (s, 9H, Me_3Si), 0.21 (s, 9H, Me_3Si), 2.23 (s, 3H, p-Me), 2.41 (s, 6H, o-Me), 3.45 (s, 3H, MeO), 6.62 (br s, 2H, mesityl ring protons), 7.16 (br s, 5H, phenyl ring protons), 8.01 (s, 1H, olefinic proton; ^{13}C NMR (δ in $CDCl_3$) 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). 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 GLC as being **10** (39% yield) and unidentified product (7% yield). Product **10** was isolated by MPLC. All spectral data obtained 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 as an internal standard 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. GLC analysis of the resulting mixture showed the formation of **14** in 81% yield. Compound **14** was isolated by MPLC: MS m/e 396 (M^+); IR ν_{Si-H} 2100 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.08 (s, 9H, Me_3Si), 0.32 (s, 9H, Me_3Si), 2.15 (s, 3H, p-Me), 2.58 (s, 6H, o-Me), 5.24 (s, 1H, HSi), 6.73 (br s, 2H, mesityl ring protons), 6.87-7.29 (m, 5H, phenyl ring protons), 8.19 (s, 1H, olefinic proton); ^{13}C NMR (δ in $CDCl_3$) 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 ring carbons). 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 Phenyl(trimethylsilyl)acetylene. To a solution of 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 were removed by flash chromatography on silica gel eluting with hexane. Treatment of the mixture with MPLC gave 91 mg (32% yield) of **15** and 11 mg (6%) of **16**. For **15**: mp 180.6°C; MS m/e 568 (M^+); ^{1}H NMR (δ in CCl_4) -0.28 (s, 18H, Me_3Si), 0.36 (s, 9H, Me_3Si), 2.26 (s, 6H, o-Me), 2.68 (s, 3H, p-Me), 6.65-7.05 (m, 12H, mesityl and phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) 0.9, 1.7 (Me_3Si), 19.7, 21.1, 26.2 (mesityl methyl), 126.0, 126.8, 128.3, 128.7, 128.9 (br), 129.3, 138.8, 143.0, 143.9, 146.6 (mesityl and phenyl ring carbons), 150.5, 168.3 (olefinic carbons). Anal. Calcd for $C_{34}H_{48}Si_4$: C, 71.76; H, 8.50. Found: C, 71.26; H, 8.50. For **16**: mp 165-166 °C; MS m/e 568 (M^+); ^1H NMR (δ in CCl_4) -0.32 (s, 9H, Me_3Si), -0.15 (s, 9H, Me_3Si), 0.40 (s, 9H, Me_3Si), 2.36 (s, 3H, p-Me), 2.70 (s, 6H, o-Me), 6.64-7.04 (m, 12H, mesityl and phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) -1.0 (Me_3Si), 0.0 (Me_3Si), 1.1 (Me_3Si), 21.1 (o- and p-Me), 124.5, 125.3, 126.5, 126.8, 127.0, 128.1, 128.9 (two carbons), 131.4, 139.2, 142.2, 142.3 (mesityl and phenyl ring carbons), 144.9, 155.8, 162.6, 174.1 (olefinic carbons). Anal. Calcd for $C_{34}H_{48}Si_4$: C, 71.76; H, 8.50. Found: C, 71.75; H, 8.64.

Reaction of 3 with 1-Hexyne. A mixture of 0.363 mmol of **3**, 35.6 mg (0.434 mmol) of 1-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. GLC analysis of the mixture showed the presence of **17** (18%) and its isomer (3%, MS m/e 476). Compound **17** was isolated by MPLC: MS m/e 476 (M^+); IR $\nu_{C\equiv C}$ 2150 cm^{-1}; ^1H NMR (δ in CCl_4) 0.03 (s, 9H, Me_3Si), 0.24 (s, 9H, Me_3Si), 0.76-1.62 (m, 9H, Bu), 2.24 (s, 3H, p-Me), 2.46 (s, 6H, o-Me), 6.51 (s, 1H, olefinic proton), 6.64 (s, 2H, mesityl ring protons), 6.92-7.42 (m, 5H, Ph); ^{13}C NMR (δ in $CDCl_3$) -1.28 (Me_3Si), -0.03 (Me_3Si), 14.00, 25,81, 32.04, 42.76 (Bu), 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). Anal. Calcd for $C_{29}H_{44}Si_3$:C, 73.03; H, 9.30. Found: C, 73.03; H, 9.47.

Reaction of 3 with Bromine. To a 0.363 mmol of **3** and 0.063 mmol of eicosane as an internal standard in 2 mL of xylene was added 0.363 mmol of bromine in 2 mL of dry xylene with ice cooling. The mixture was stirred for 30 min, and then it was analyzed by GLC as being **2** (100%). Retention time on GLC, 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 248.0 mg (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 GLC as being 2 (100%) and bibenzyl (86%). Products were isolated by MPLC. All spectral data for **2** and bibenzyl were identical with those of authentic samples.

Reaction of 3 with Trimethylphosphine. To a solution of 0.395 mmol of **3** in 1.5 mL of xylene 52.2 mg (0.87 mmol) of trimethylphosphine was added at room temperature. The solution was stirred at room temperature for 1.5 h. The resulting mixture was analyzed by ^{1}H NMR spectroscopy as being **2** (100%).

Reaction of 3 with (Diphenylphosphino)-ethane. To a solution of 0.395 mmol of **3** in 1.5 mL of xylene was added 157.5 mg (0.395 mmol) of (diphenylphosphino)ethane at room temperature. The solution was stirred at room temperature for 1.5 h. The resulting mixture was analyzed by ^{1}H NMR spectroscopy as being **2** (100%).

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Chapter 2

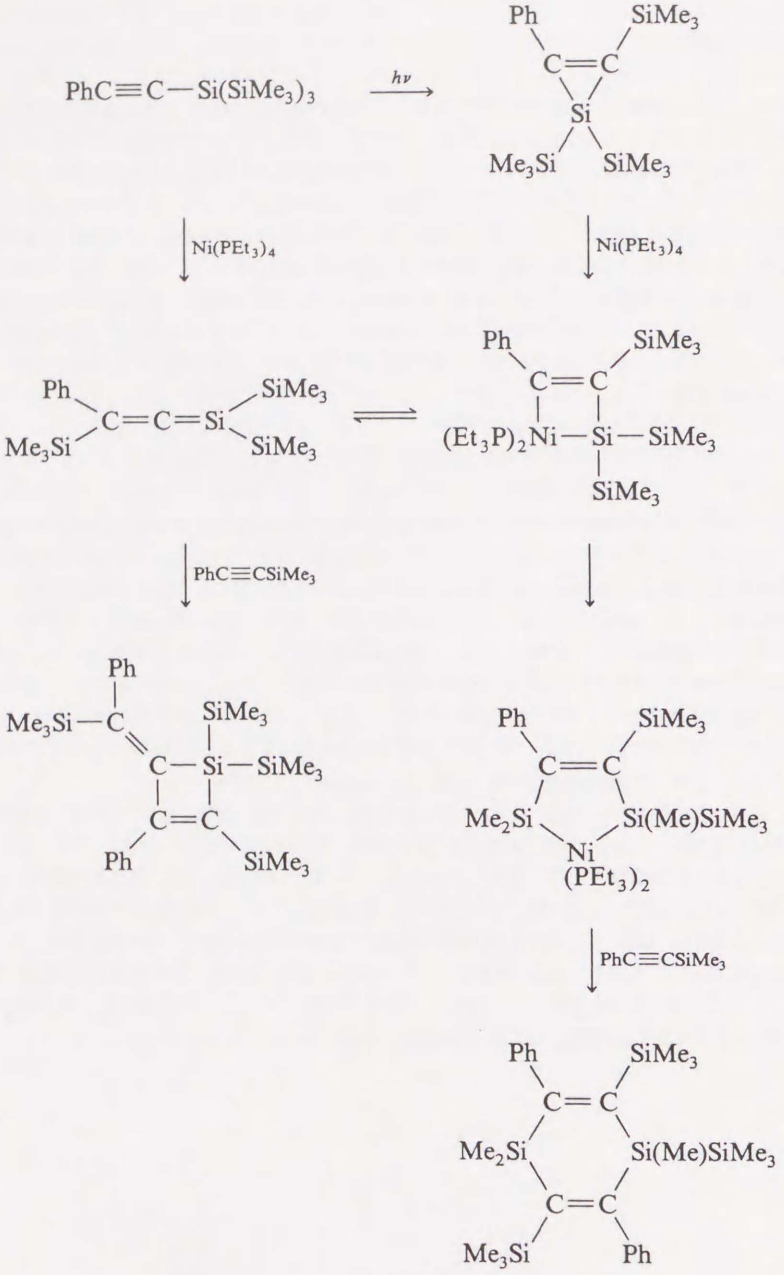
Isomerization of 2-Aryl-2-(phenylethnyl)hexamethyltrisilane in the Presence of Tetrakis(triethylphosphine)nickel(0)

Introduction

The transition-metal-catalyzed reactions of organosilicon compounds are of current interest, because they might have a large possibility to produce many types of a reactive intermediate. Recently, it has been reported that nickel-catalyzed reactions of (phenylethynyl)polysilanes proceed to give several interesting intermediates such as silapropadiene-nickel complexes and nickelasilacyclobutenes, which polymerize to give nonvolatile substances in the absence of a trapping agent. While, in the presence of phenyl(trimethylsilyl)acetylene as a trapping agent, these reactive intermediates undergo cycloaddition with the acetylene to give cyclic products such as silacyclobutene and silacyclopentadiene derivatives.[1-3] It has been also reported that the photoisomers of (phenylethynyl)polysilanes, silacyclopropenes also react with a nickel catalyst to produce the same intermediates. As an example, the reaction of (phenylethynyl)tris(trimethylsilyl)silane with phenyl(trimethylsilyl)acetylene in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) is presented in Scheme 1.[2d]

In an effort to learn much more about the reactive intermediates, we investigated the reaction of 2-aryl-2-(phenylethynyl)trisilane in the presence of a catalytic amount of a nickel complex, and found a novel isomerization of 1-silapropadiene-nickel complexes. In this Chapter, the nickel(0) catalyzed reactions of 2-mesityl-, 2-o-tolyl-, and 2-phenyl-2-(phenylethynyl)hexamethyltrisilane are described.

Scheme 1


PhC≡C—Si(SiMe3)3
hν
Ni(PEt3)4
PhC≡CSiMe3
Ph
SiMe3
Me3Si
Me2Si
Si(Me)SiMe3
(Et3P)2Ni
Ni
(PEt3)2

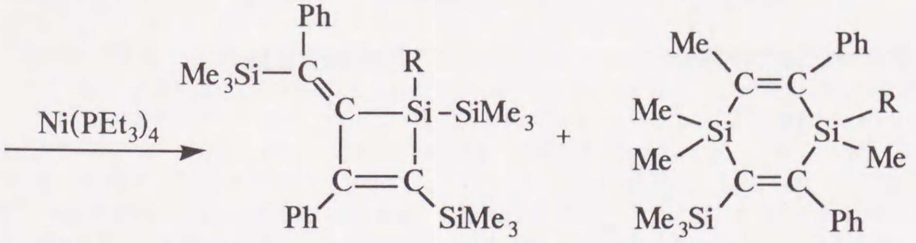
Results

Reactions of 2-Aryl-substituted 2-(phenylethynyl)hexamethyltrisilanes with Phenyl-(trimethylsilyl)acetylene. First, we investigated the reaction of 2-mesityl-2-(phenylethynyl)-hexamethyltrisilane (**1a**), 2-(phenylethynyl)-2-(o-tolyl)hexamethyltrisilane (**1b**), and 2-phenyl-2-(phenylethynyl)hexamethyltrisilane (**1c**) in the presence of a nickel(0) catalyst with phenyl-(trimethylsilyl)acetylene (**2**), which is often used as a trapping agent of silapropadiene-nickel complex and related complex intermediates[2]. Thus, when **1a** was heated to 195°C for 20 h with a small excess of **2** in the presence of a catalytic amount of tetrakis-(triethylphosphine)nickel(0), two products, 1-mesityl-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1-sila-cyclobut-3-ene (**3a**) and 2,6-diphenyl-1-mesityl-1,4,4-trimethyl-1,3-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**4a**) were obtained in 77 and 11% yields, respectively. The structure of **3a** and **4a** were confirmed by spectroscopic analysis (see Experimental Section).

$PhC{\equiv}CSiR(SiMe_3)_2$ + $PhC{\equiv}CSiMe_3$

1a R = Mes
1b R = o-Tol

2



3a R = Mes
3b R = o-Tol

4a R = Mes
4b R = o-Tol

Similarly, when **1b** was heated with a small excess of **2** in the presence of the nickel catalyst at 180°C for 20 h, two products, 3-phenyl-2-[phenyl(trimethyl-silyl)methylene]-1,4-bis(trimethylsilyl)-1-(o-tolyl)-1-silacyclobut-3-ene (**3b**) and 4,4,5-trimethyl-2,6-

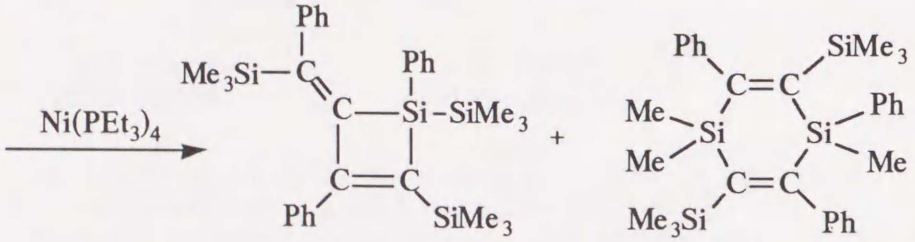
diphenyl-1,3-bis(trimethylsilyl)-1-(o-tolyl)-1,4-disilacycohexa-2,5-diene (**4b**) in 75 and 18% yields, respectively. The structures of the products **3b** and **4b** were verified by spectroscopic method and also by elemental analysis. Furthermore, the location of substituents of **3b** and **4b** was confirmed by NOE-FID difference experiments. Thus, saturation of a resonance of trimethylsilyl protons in **3b** at δ 0.43 ppm led to a positive NOE of the tolyl methyl protons and trimethylsilyl protons (-0.16 ppm), while irradiation of the trimethylsilyl protons at -0.28 ppm resulted in the enhancement of the phenyl protons.

For compound **4b**, irradiation of the trimethylsilyl protons (-0.13 ppm) on the ring silicon atom produced a positive NOE of the methyl protons (2.54 ppm) of the tolyl group and also phenyl protons. Irradiation of the tolyl methyl protons led to the enhancement of one of methyl protons of a dimethylsilyl group and the tolyl ring protons, and also phenyl protons. Irradiation of methyl protons (2.14 ppm) on sp^2 carbon caused the strong enhancement of dimethylsilyl protons, as well as protons of a phenyl group. These results are consistent with the proposed structure for **3b** and **4b**.

Treatment of **1c** with a small excess of **2** in the presence of the nickel catalyst at 180°C for 20 h resulted in the formation of 1,3-diphenyl-2-[phenyl(trimethylsilyl)methylene]-1,4-bis(trimethylsilyl)-1-silacyclobut-3-ene (**3c**) and 1,4,4-trimethyl-1,3,6-triphenyl-2,5-bis(trimethylsilyl)-1,4-disila-

$PhC{\equiv}CSiPh(SiMe_3)_2$ + $PhC{\equiv}CSiMe_3$

1c **2**

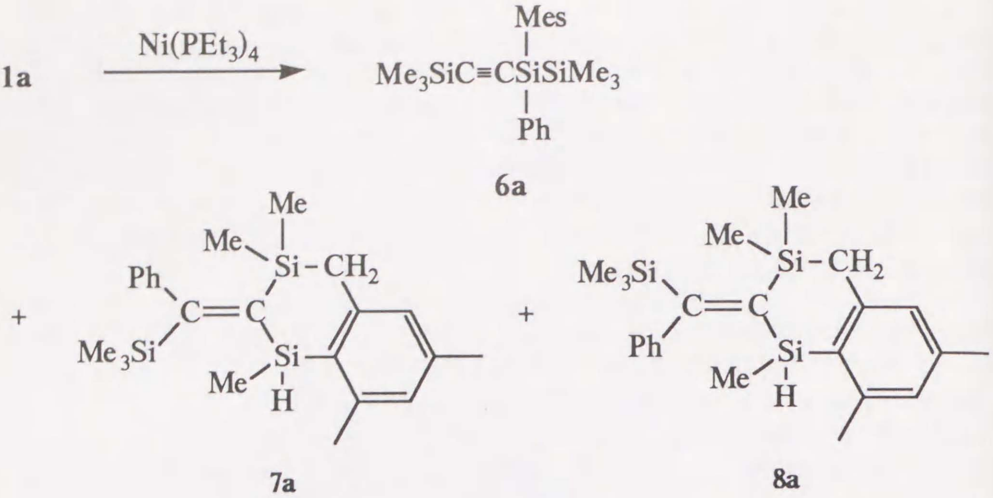


3c **5**

cyclohexa-2,5-diene (**5**) in 21 and 50% yields, respectively. The product **5** could be separated from **3c** in a pure form by MPLC, however, **3c** could not be separated by this method. A mixture consisting of **3c** and **5** in the ratio of 7:3 was obtained. Since **5** was obtained in the pure form, the structure of **3c** could be confirmed by eliminating the signals corresponding to **5** in ^{1}H and ^{13}C NMR spectrum of the mixture (see Experimental Section).

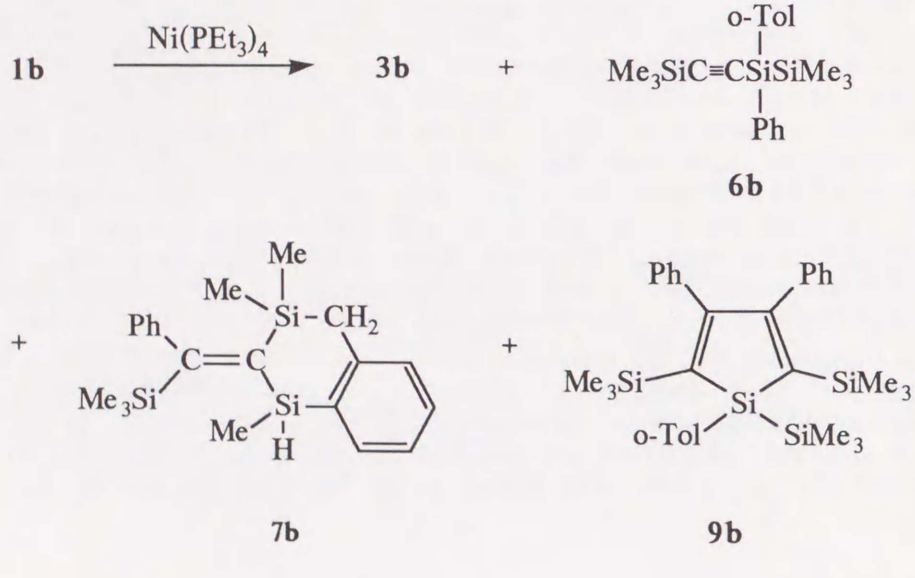
The location of the substituents of the disilacyclohexa-2,5-diene ring for **5** was established by NOE-FID difference experiments at 500 MHz. Thus, saturation of trimethylsilyl protons at δ -0.29 ppm caused a positive NOE of one of methyl protons (-0.15 ppm) of a dimethylsilyl group in the six-membered ring, while irradiation of methyl protons at δ -0.15 ppm resulted in the strong enhancement of trimethylsilyl protons (-0.29 ppm) and methyl protons (-0.09 ppm). Similar irradiation of a resonance of the trimethylsilyl protons at δ 0.21 ppm produced a positive NOE of methyl protons (0.50 ppm) of a methylphenylsilyl group. These results are wholly consistent with the proposed structure.

Reaction of 1a-c in the Absence of 2. Next, we investigated the reaction of **1a-c** in the absence of **2**. Thus, when **1a** was treated with Ni(PEt$_3$)$_4$ in the absence of **2** at 205°C for 20 h, three products, 1-mesityl-1-phenyl-1-(trimethylsilylethynyl)trimethyldisilane (**6a**) whose spectral data were identical with those of an authentic sample prepared independently, and two isomers of a 5,6-benzo-1,3-disilacyclohexene derivative (**7a** and **8a**) were obtained in 36, 36, and 22% yields, respectively. All spectral data obtained for **7a** and **8a** were also identical with those of the authentic samples formed from the thermal- and the photoreaction of 2-mesityl-4-phenyl-1,1-bis(triethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-1-silacyclobutene.[5] In contrast to the reaction of **1a**, the reaction of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene produced photochemically from **1a** with a catalytic amount of tetrakis(triethylphosphine)-nickel(0) at 135°C afforded only **7a** and **8a** in 45 and



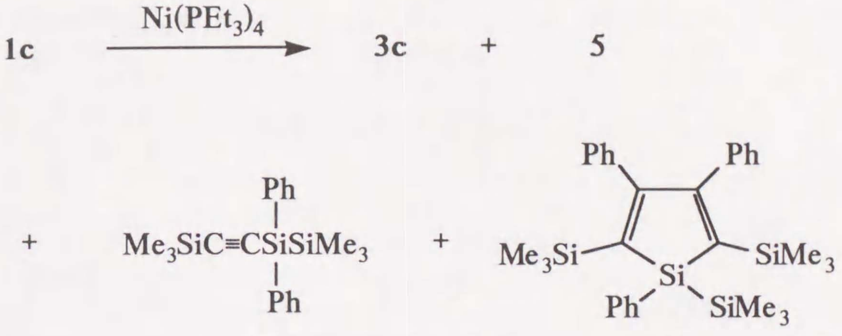
27% yields, respectively. No compound **6a** was detected by either GLC or spectroscopic analysis.

Heating **1b** with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in a sealed glass tube at 180 °C for 20 h gave compound **3b**, 1-phenyl-1-(o-tolyl)-1-(trimethylsilylethynyl)trimethyldisilane (**6b**), 4,5-benzo-3-hydro-1,1,3-trimethyl-2-[phenyl(trimethylsilyl)methylene]-1,3-disilacyclo-hexene (**7b**), and 3,4-diphenyl-1-(o-tolyl)-1,2,5-tris(trimethylsilyl)silole (**9b**), in 16, 16, 10 and 17% yields, in addition to 23% of the starting compound **1b**.



In marked contrast to the reaction of **1a** which afforded **7a** and **8a**, this reaction afforded only compound **7b**. No other isomer of **7b**, an analogue to **8a** was detected in the reaction mixture.

Similar reaction of **1c** with a catalytic amount of the nickel(0) complex afforded four compounds, **3c**, **5**, 1,1-diphenyl-1-(trimethylsilylethynyl)trimethyldisilane (**6c**) and 1,3,4-triphenyl-1,2,5-tris(trimethylsilyl)-silole (**9c**) in 10, 11, 15, and 29% yields, respectively.



$$\mathbf{1c} \xrightarrow{Ni(PEt_3)_4} \mathbf{3c} + \mathbf{5} + Me_3SiC{\equiv}C\overset{Ph}{\underset{Ph}{Si}}SiMe_3 + \mathbf{9c}$$

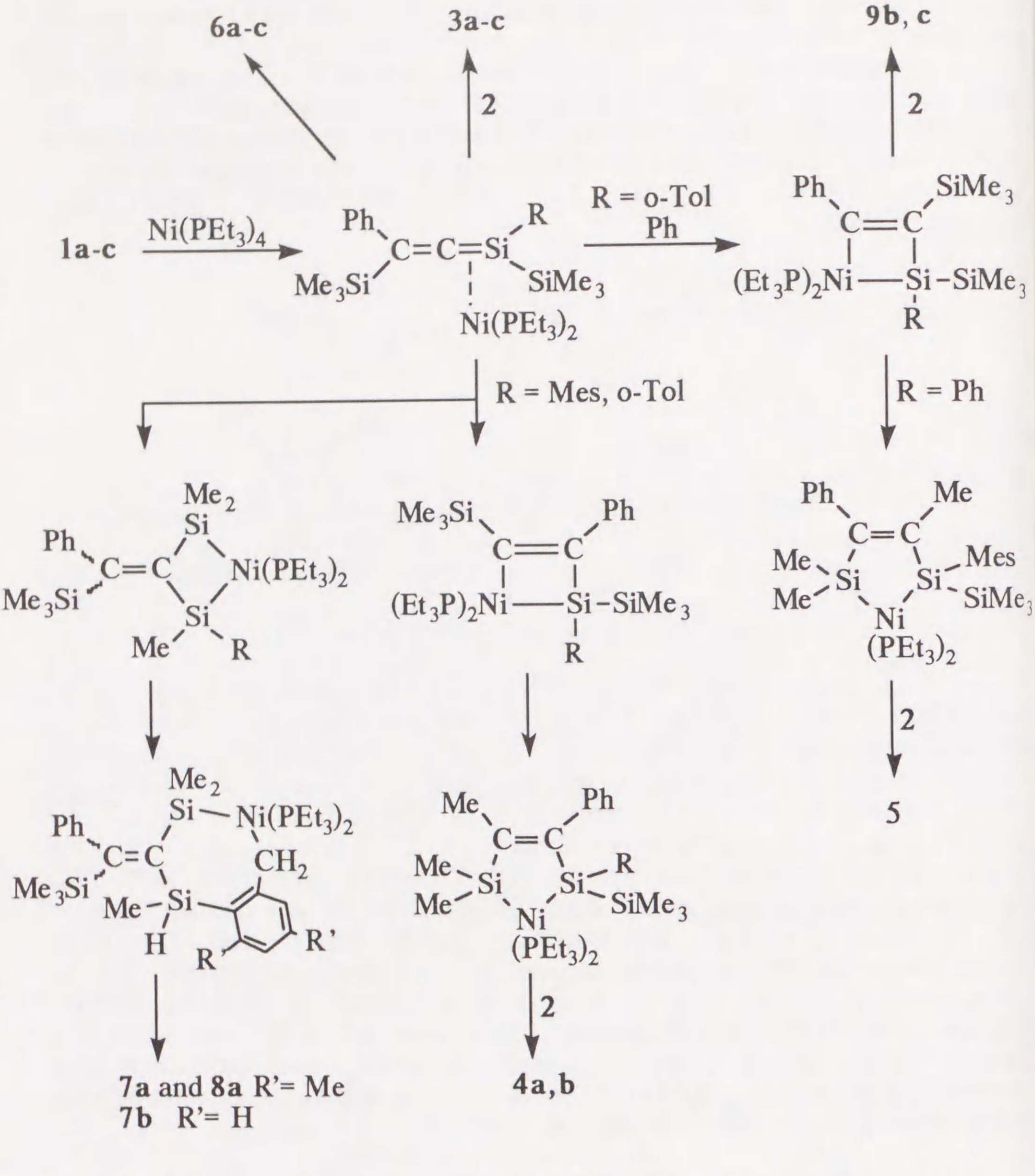
6c **9c**

All spectral data obtained for **6b** and **6c** were identical with those of authentic samples prepared from an independent synthesis. The structures of **9b** and **9c** could readily be confirmed by spectroscopic method, as well as by elemental analysis. The IR spectrum of **7b** shows a strong absorption band at 2121 cm^{-1}, due to the stretching vibration of an Si-H bond. In the NOE-FID difference experiments for **7b** at 500 MHz, irradiation of trimethylsilyl protons (-0.21 ppm) led to the enhancement of a resonance of methyl protons of a hydromethylsilyl group and a proton of a hydrosilane, while irradiation of methyl protons of a dimethylsilyl group produced a positive NOE of methylene protons and phenyl protons. These results are wholly consistent with the proposed structure for **7b**.

Discussion

Reaction Mechanism in the Presence of 2. Scheme 2 illustrates a possible mechanistic interpretation of the observed reaction course. The mechanism involves the formation of silapropadiene-

Scheme 2



nickel complexes. Compounds 3a-c may be explained by [2+2] cycloaddition of these silapropadiene-nickel complexes to phenyl(trimethylsilyl)acetylene giving the four-membered cyclic system. This type of the reaction has been found in the other systems.[2d,5] When R=Mes or o-Tol, the silapropadiene-nickel complex isomerizes to a nickelasilacyclobutene by a 1,2-phenyl shift. The nickelasilacyclobutene thus formed isomerizes to a nickeladisilacyclopentene. Finally, the resulting nickeladisilacyclobutene reacts with 2 resulting in the formation of compound **4a** and **4b**. The formation of the product 5 can be understood by isomerization of the silapropadiene-nickel complex (R=Ph) to a nickelasilacyclobutene involving a 1,2-trimethylsilyl shift and then to a nickeladisilacyclopentene, followed by the reaction with 2.

Reaction Mechanism in the Absence of 2. In the absence of 2, the formation of the products **6a-c** may be understood in terms of isomerization of the silapropadiene-nickel complex involving a 1,3-phenyl shift from sp^2 carbon onto a sp^2 silicon atom. The formation of benzodisilacyclohexene **7a,b** and **8a** can be explained by the similar manner to that of the thermal and photochemical reaction of 2-mesityl-4-phenyl-1,1-bis(triethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-1-silacyclobutene described previously.[5] Thus, the reaction requires isomerization of the silapropadiene-nickel complex to 3-[phenyl(trimethylsilyl)methylene]-1-nickela-2,4-disilacyclobutane and the carbon-hydrogen bond activation of tolyl or mesityl methyl group of the nickeladisilacyclobutane intermediate leading to a seven membered ring system, and finally reductive elimination of nickel species would be involved in this reaction.

The fact that compounds **3b** and **9b** for the reaction of **1b**, and **3c**, **6c**, **9c** for **1c** could be isolated, clearly indicates that a significant amount of 2 must be formed in these reactions. Presumably, 2 is produced by elimination of a nickel-silylene complexes from nickelasilacyclobutenes, although evidence for the formation of the nickel-silylene complex has not yet been obtained. The formation of the siloles **9b,c** apparently indicates the presence of the nickelasilacyclobutenes.

Experimental Section

General. All nickel-catalyzed reactions were carried out in a 10 cm x 1 cm degassed sealed glass tube. NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100, a JNM-FX-90A, and a JNM-GX-400 spectrometer. NOE-FID difference spectra were obtained on a JEOL Model JNM-GX-500 spectrometer. IR spectra were measured on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were determined with a Shimadzu Model QP-1000 spectrometer and a JEOL Model JMN-D300 spectrometer equipped with a JMA-2000 data processing system.

Materials. 2-mesityl-2-(phenylethynyl)hexamethyltrisilane (**1a**) and 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene were prepared as described in Chapter 1. Tetrakis(triethylphosphine)-nickel(0) was prepared as reported in the literature.[4]

Preparation of 2-(phenylethynyl)-2-(o-tolyl)hexamethyltrisilane (1b). To an ether solution of 3 g (12.2 mmol) of 2,2-dichlorohexamethyltrisilane was added 15 mL of an ether solution of o-tolyllithium (13.4 mmol) at room temperature, and the mixture was stirred overnight. To this was added 15 mL of a hexane solution containing 14 mmol of pheylethynyllithium. The mixture was hydrolyzed with water. The organic layer was separated and washed with water, and dried over anhydrous magnesium sulfate. The solvents were evaporated and the product **1b** (4.3 g, 95% yield) was isolated by MPLC: MS m/e 366; IR 2145 cm^{-1}; 90 MHz ^{1}H NMR (δ in $CDCl_3$) 0.31 (s, 18H, Me_3Si), 2.50 (s, 3H, CH_3), 6.89-7.74 (m, 9H, phenyl and tolyl ring protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -0.4 (Me_3Si), 24.1 (CH_3), 90.6, 111.6 (C≡C), 124.4, 125.2, 128.2, 128.3, 128.7, 129.4, 131.8, 133.0, 136.5, 143.2 (Ph). Anal. Calcd for $C_{21}H_{30}Si_3$: C, 68.77, H, 8.25. Found: C, 68.50, H, 8.23.

Preparation of 2-Phenyl-2-(phenylethynyl)-hexamethyltrisilane (1c). To a solution of phenylethynyllithium prepared from 4.085 g (40 mmol) of phenylacetylene in 100 mL of hexane and 25 mL (40 mmol) of a butyllithium-hexane solution, was slowly added 7.6 g (27 mmol) of 2-chloro-2-phenylhexamethyltrisilane in 50 mL of hexane. The mixture was stirred overnight and then hydrolyzed with water. Organic layer was separated and washed with water and then dried over potassium carbonate. The solvent was distilled off and the residue was fractionally distilled under reduced pressure to give 4.0 g (42% yield) of **1c**: bp 121°C (1 mm Hg); MS m/e 352; IR 2145.8 cm^{-1} ; 90 MHz ^1H NMR (δ in $CDCl_3$) 0.29 (s, 18H, Me_3Si), 7.03-7.48 (m, 10H, Ph). Anal. Calcd for $C_{20}H_{28}Si_3$: 68.11; H, 8.00. Found: 68.34; H, 8.19.

Preparation of 6a. In a 100 mL two necked flask fitted with a reflux condenser and a dropping funnel, was placed a solution of 13.6 g (50.5 mmol) of 1,1-dichloro-1-(trimethylsilylethynyl)trimethyldisilane in 20 mL of ether. To this was added an ether solution of 55.6 mmol of mesityllithium prepared from mesityl bromide and lithium, and then, the solution was refluxed for 24 h. To the resulting mixture, 10 mL THF solution of 66 mmol of phenyl magnesium chloride prepared from phenyl chloride and magnesium was added. The solution was again refluxed for 10 h, and hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water. After during over potassium carbonate, the solvent was evaporated under reduced pressure to give 4.1 g (21% yield) of **6a**. Recrystallization from methanol gave analytically pure sample: bp 180-190°C (1 mm Hg); mp 89-90°C; MS m/e 394 (M^+); 100 MHz ^1H NMR (δ in $CDCl_3$) 0.20 (s, 18H, Me_3Si), 2.26 (s, 3H, p-Me), 2.41 (s, 6H, o-Me), 6.82 (br s, 2H, mesityl ring protons), 7.20-7.61 (m, 5H, phenyl ring protons); 100 MHz ^{13}C NMR (δ in $CDCl_3$) -1.3, -2.0 (Me_3Si), 21.1, 25.3 (mesityl methyl), 111.4. 119.9 (C≡C), 127.8, 128.3, 128.4, 128.7, 134.3, 136.4, 139.4, 145.5 (mesityl and phenyl ring carbons). Anal. Calcd for $C_{23}H_{34}Si_3$: C, 69.98; H, 8.68. Found: C, 70.24; H, 8.77.

Preparation of 6b. A solution of o-tolyllithium prepared from 1.5 g (8.8 mmol) of o-bromotoluene and 0.223 g (32 mmol) of lithium in ca. 10 mL of ether was added to 2.0 g (8.0 mmol) of 1,1-dichloro-1-phenyltrimethyldisilane at room temperature. The mixture was stirred for 2 h at room temperature. To this was added a hexane solution of (trimethylsilyl)-ethynyllithium prepared from 0.868 g (8.8 mmol) of trimethylsilylacetylene and butyllithium. The mixture was stirred for 2 h and then hydrolyzed with water. Product **6b** (2.2 g, 75% yield) was isolated by MPLC: MS m/e 366; 90 MHz ^{1}H NMR (δ in $CDCl_3$) 0.28 (s, 9H, Me_3Si), 0.29 (s, 9H, Me_3Si), 2.38 (s, 3H, CH_3), 7.11-7.80 (m, 9H, phenyl and tolyl ring protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -1.5 (Me_3Si), -0.1 (Me_3Si), 23.5 (CH_3), 109.6, 120.3 (C≡C), 125.0, 128.0, 128.9, 129.9, 130.0, 132.6, 134.7, 134.9, 136.8, 144.8 (phenyl and tolyl ring carbons). Anal. Calcd for $C_{21}H_{30}Si_3$: C, 68.71; H, 8.23. Found: 68.77; H, 8.25.

Preparation of 6c. To a solution of 0.737 g (7.5 mmol) of trimethylsilylacetylene in 10 mL of THF was added 5 mL of a 1.6 M butyllithium-hexane solution with ice-cooling. The mixture was stirred for 20 min at room temperature. To this was added 2.4 g (8.3 mmol) of 1-chloro-1,1-diphenyltrimethyldisilane in 5 mL of THF. The mixture was stirred overnight and then hydrolyzed with water. The organic layer was separated and washed with water and dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave 2.3 g (88% yield) of **6c**: MS m/e 352; 90 MHz ^{1}H NMR (δ in $CDCl_3$) 0.23 (s, 9H, Me_3Si), 0.26 (s, 9H, Me_3Si), 7.31-7.71 (phenyl ring protons, m, 10H); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -2.04 (Me_3Si), -0.03 (Me_3Si), 108.53 (≡C-Si), 120.29 (≡C-C), 127.98, 129.17, 134.10, 135.08 (phenyl ring carbons). Anal. Calcd for $C_{20}H_{28}Si_3$: 68.11; H, 8.00. Found: C, 68.03; H, 7.96.

Reaction of 1a with 2 in the Presence of Ni(PEt$_3$)$_4$. A mixture of 143 mg (0.363 mmol) of **1a**, 112 mg (0.644 mmol) of **2**, and 25 mg (13 mol%) of tetrakis(triethylphosphine)nickel(0) was heated at 195 °C for 20 h in a sealed glass tube. The resulting mixture was analyzed by GLC using 26.2 mg (0.0844 mmol) of docosane as an internal standard, as being **3a** (77% yield) and **4a** (11% yield). A mixture of **3a** and **4a** was obtained by treating the reaction mixture with a silica gel column Compounds **3a** and **4a** were isolated by fractional recrystallization from ethanol. All spectral data obtained for **3a** were identical with those of an authentic sample.[5] For **4a**: mp 191-191.5°C; MS m/e 568 (M^+); 400 MHz ^{1}H NMR (δ in $CDCl_3$)

-0.36 (s, 9H Me_3Si), -0.12 (s, 9H, Me_3Si), 0.56 (s, 3H, MeSi), 0.57 (s, 3H, MeSi), 1.85 (s, 3H, MeC), 2.32 (s, 3H, mesityl methyl), 2.43 (s, 3H, mesityl methyl), 2.60 (s, 3H, mesityl methyl), 6.58-7.08 (m, 12H, phenyl and mesityl ring protons); 100 MHz ^{13}C NMR (δ in $CDCl_3$) 0.6 (Me_3Si), 1.5 (MeSi), 2.0 (Me_3Si), 2.6 (MeSi), 21.1, 25.1, 15.6 (mesityl methyl), 28.5 (MeC), 125.6, 126.9, 127.0, 127.2, 127.3, 127.7, 128.4, 128.8, 135.4, 138.4, 139.1, 143.7, 144.7, 147.2 (mesityl and phenyl ring carbons), 148.1, 160.0, 162.5, 179.3 (olefinic carbons). Exact MS Calcd for $C_{34}H_{48}Si_4$: 568.2833. Found: 568.2817.

Reaction of 1b with 2 in the Presence of $Ni(PEt_3)_4$. A mixture of 0.152 g (0.42 mmol) of **1b**, 0.199 g (1.1 mmol) of **2** and 9 mg (4.0 mol%) of $Ni(PEt_3)_4$ was heated at 180°C for 20 h. The products were chromatographed on silica gel to remove nickel complexes, eluting with hexane. The resulting hexane solution was concentrated and the residue was analyzed by GPC using nonadecane as an internal standard, as being **3b** (75% yield) and **4b** (18% yield). Products **3b** and **4b** were isolated by MPLC. For **3b**: MS m/e 540; 90 MHz ^1H NMR (δ in $CDCl_3$) -0.28 (s, 9H, Me_3Si), -0.16 (s, 9H, Me_3Si), 0.43 (s, 9H, Me_3Si), 2.62 (s, 3H, MeC), 6.51-7.74 (m, 14H, phenyl and tolyl protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -0.7 (Me_3Si), 0.0 (Me_3Si), 0.2 (Me_3Si), 21.6 (Me), 124.5, 125.0, 125.4, 126.6, 126.8, 127.0, 128.1, 129.9, 130.0, 136.2, 142.2, 142.5, 145.5 (phenyl and tolyl carbons), 146.0, 153.9, 162.8, 175.6 (olefinic carbons). Anal. Calcd for $C_{32}H_{44}Si_4$: C, 71.03; H, 8.20. Found: C, 70.97; H, 8.12. For **4b**: MS m/e 540; 500 MHz ^1H NMR (δ in $CDCl_3$) -0.44 (s, 9H, Me_3Si), -0.13 (s, 9H, Me_3Si), 0.51 (s, 3H, MeSi), 0.56 (s, 3H, MeSi), 2.41 (s, 3H, MeC), 2.54 (s, 3H, tol-Me), 6.40-7.43 (m, 14H, phenyl and tolyl protons); ^{13}C NMR (δ in $CDCl_3$) -0.9 (Me_3Si), 1.1 (MeSi), 1.7 (MeSi), 2.0 (Me_3Si), 23.5 (Me-C), 28.8 (Me-tol), 124.9, 125.6, 126.9, 127.1, 127.4, 127.6, 129.0, 129.8, 136.5, 136.8, 139.6, 143.5, 142.2 (phenyl and tolyl ring carbons), 147.9, 162.5, 164.2, 179.0 (olefinic carbons). Anal. Calcd for $C_{32}H_{44}Si_4$: C, 71.03; H, 8.20. Found: C, 71.02; H, 8.10.

Reaction of 1c with 2 in the Presence of $Ni(PEt_3)_4$. In a degassed sealed tube, a mixture of 0.418 g (1.19 mmol) of **1c**, 0.422 g (2.42 mmol) of **2** and 29 mg (4.6 mol%) of tetrakis(triethylphosphine)nickel(0) was heated at 180°C for 20 h. The resulting mixture was chromatographed on silica gel to remove any nickel complexes, eluting with hexane. The solution was concentrated and the residue was analyzed by GPC, using nonadecane as an internal standard, as being **3c** (21% yield) and **5** (50% yield). Product **5** was isolated in a pure form by MPLC. The product **3c** could not be obtained in a pure form, but the mixture consisting of **3c** and **5** in the ratio of 7:3 was isolated. For **3c**: MS m/e 526; 90 MHz ^1H NMR (δ in $CDCl_3$) -0.30 (s, 9H, Me_3Si), -0.15 (s, 9H, Me_3Si), 0.42 (s, 9H, Me_3Si), 6.69-7.75 (phenyl ring protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -0.47 (Me_3Si), 0.18 (two Me_3Si), 124.46, 125.32, 126.57, 126.73, 127.27, 127.87, 128.30, 129.50, 135.08 137.40, 142.33, 142.55 (phenyl ring carbons), 145.26, 152.90, 162.76, 178.63 (olefinic carbons). For **5**: mp 129°C; MS m/e 526; 500 MHz ^1H NMR ($CDCl_3$) -0.29 (s, 9H, Me_3Si), -0.21 (s, 9H, Me_3Si), -0.15 (s, 3H, Me-SiMe), -0.09 (s, 3H, Me-SiMe), 0.50 (s, 3H, Me-SiPh), 6.95-7.39 (m, 15H, phenyl ring protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -2.58 (Me-SiPh), 0.56 (Me_3Si), 1.59 (Me_3Si), 1.70 (MeSi), 2.35 (MeSi), 125.22, 125.65, 126.73, 126.89, 127.17, 127.44, 128.79, 134.64, 138.43, 146.07, 149.05 (phenyl ring carbons), 156.80, 163.95, 179.77, 180.42 (olefinic carbons). Anal. Calcd for $C_{31}H_{42}Si_4$: 70.65; H, 8.03. Found: C, 70.59; H, 7.90.

Reaction of 1a with a Catalytic Amount of $Ni(PEt_3)_4$. A mixture of 166 mg (0.313 mmol) of **1a** and 29.8 mg (18 mol%) of tetrakis(triethylphosphine)nickel(0) was heated at 205°C for 20 h in a sealed glass tube. The resulting mixture was analyzed by GLC using 32.5 mg (0.114 mmol) of eicosane as an internal standard, as being **6a** (36% yield), **7a** (36% yield), and **8a** (22% yield). Compound **6a** and a mixture of **7a** and **8a** were separated from the mixture by preparative TLC. **7a** and **8a** were isolated by preparative GLC. All spectral data obtained for **6a**, **7a**[5] and **8a**[5] were identical with those of authentic samples.

Reaction of 1-Mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene with a Catalytic Amount of $Ni(PEt_3)_4$. A mixture of 0.462 mmol of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene, 0.195 mmol of eicosane, and 28.7 mg (12 mol%) of tetrakis(triethylphosphine)nickel(0) was heated at 135°C for 20 h in a sealed glass tube. The resulting mixture was analyzed by GLC as being **7a** (45% yield) and **8a** (27% yield). **7a** and **8a** were isolated by preparative GLC. All spectral data obtained for **7a** and **8a** were identical with those of authentic samples.[5]

Reaction of 1b with a Catalytic Amount of $Ni(PEt_3)_4$. A mixture of 0.440 g (1.20 mmol) of **1b** and 30 mg (4.7 mol%) of tetrakis(triethylphosphine)-nickel(0) was heated at 180°C for 20 h. Nickel species was removed by a short silica gel column, eluting with hexane. The resulting hexane solution was concentrated and the residue was analyzed by GPC as being **3b** (16% yield), **6b** (16% yield), **7b** (10% yield) and **9b** (17% yield), in addition to 23% of **1b**. Products **3b**, **6b**, **7b** and **9b** were isolated by MPLC. All spectral data obtained for **3b** and **6b** were identical with those of authentic samples. For **7b**: mp 124.9-126.2°C; MS m/e 366; IR 2121 cm^{-1}; 500 MHz ^1H NMR (δ in $CDCl_3$) -0.37 (s, 3H, MeSi), -0.21 (s, 9H, Me_3Si), 0.05 (s, 3H, MeSi), 0.56 (d, 3H, J=4.0 Hz, MeSiH), 2.0 (d, 1H, J=14.4 Hz, HC), 2.9 (d, 1H, J=14.4 Hz, HC), 4.7 (q, 1H, J=4 Hz, HSi), 7.0-7.6 (m, 9H, phenyl and tolyl ring protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -3.77 (MeSi), -1.60 (MeSi), -1.06 (MeSi), 1.27 (Me_3Si), 27.76 (CH_2), 123.6, 125.8, 127.3, 127.5, 127.9, 130.1, 136.1, 136.8, 146.0, 147.2 (phenyl and tolyl ring carbons), 158.3, 175.2 (olefinic carbons). Anal. Calcd for $C_{21}H_{30}Si_3$: C, 68.77; H, 8.25. Found: C, 68.83; H, 8.25. For **9b**: MS m/e 540; 500 MHz ^1H NMR (δ in $CDCl_3$) -0.28 (s, 18H, Me_3Si), 0.41 (s, 9H, Me_3Si), 2.3 (s, 3H, MeC), 6.8-7.8 (m, 14H, phenyl and tolyl ring protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) 0.78 (Me_3SiSi), 1.1 (Me_3Si), 20.2 (Me), 125.2, 126.1, 126.8, 129.1, 129.5, 129.6, 134.5, 137.2, 142.9, 145.3 (phenyl and tolyl ring carbons), 147.6, 169.4 (olefinic carbons). Anal. Calcd for $C_{32}H_{44}Si_4$: C, 71.04; H, 8.20. Found: C, 71.10; H, 8.28.

Reaction of 1c with a Catalytic Amount of $Ni(PEt_3)_4$. A mixture of 0.433 g (1.23 mmol) of **1c** and 31 mg (4.7 mol%) of $Ni(PEt_3)_4$ was heated at 180°C for 20 h. The mixture was chromatographed on silica gel to remove nickel species, eluting with hexane. The mixture was analyzed by GPC as being **3c** (10% yield), **5** (11% yield), **6c** (15% yield) and **9c** (29% yield). Products **6c** and **9c** were isolated by MPLC. All spectral data for **3c**, **5** and **6c** were identical with those of authentic samples. For **9c**: mp 159°C; MS m/e 526; 90 MHz ^1H NMR (δ in $CDCl_3$) -0.32 (s, 18H, Me_3Si), 0.39 (s, 9H, Me_3Si), 7.01-7.37 (m, 15H, phenyl ring protons). Anal. Calcd for $C_{31}H_{42}Si_4$: C, 70.65; H, 8.03. Found: C, 70.46; H, 7.94.

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5) see Chapter 1

Chapter 3

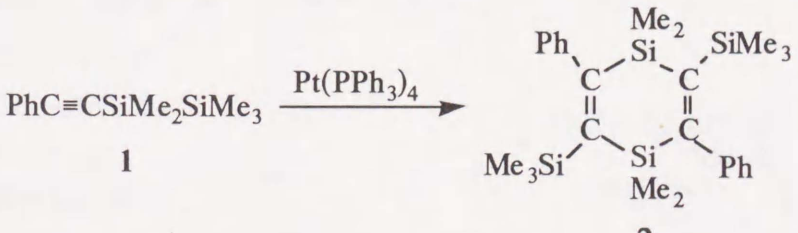
Platinum-Catalyzed Reactions of (Phenylethynyl)-disilanes

Introduction

Nickel-catalyzed reactions of phenylethynyl-substituted disilanes and trisilanes have been well studied, and many interesting reactions involving the formation of 1-silapropadiene-nickel complexes and nickelasilacyclobutenes have been reported.[1] However, no interest has been shown in the transition-metal-catalyzed reactions of (phenylethynyl)polysilanes other than nickel complexes. In this chapter, the platinum-catalyzed reactions of (phenylethynyl)disilanes are reported. These reactions proceed in a quite different fashion from that of the nickel catalyzed reactions, and involve a transient formation of a platinasilacyclobutene.

Results and Discussion

Heating pentamethyl(phenylethynyl)disilane (1) in the presence of a catalytic amount of tetrakis(triphenylphosphine)platinum(0) at 135°C for 20 h produced 1,1,4,4-tetramethyl-3,6-diphenyl-2,5-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (2)



1

2

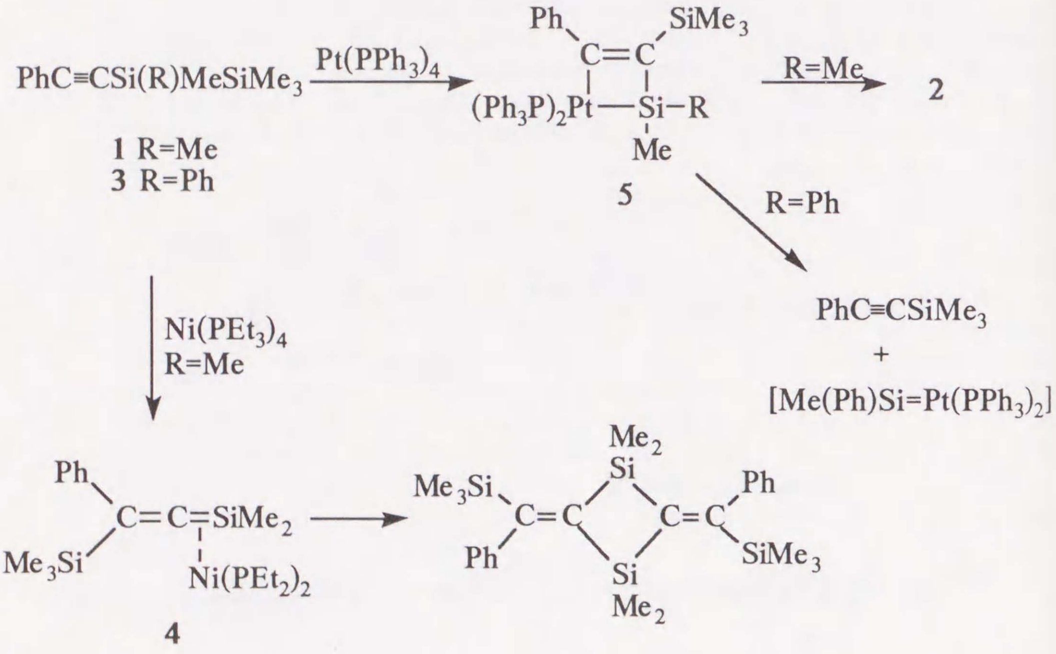
$$\mathrm{PhC{\equiv}CSi(Ph)MeSiMe_3} \xrightarrow{\mathrm{Pt(PPh_3)_4}} \mathrm{PhC{\equiv}CSiMe_3}$$

3

in 36% yield, in addition to a small amount of phenyl(trimethylsilyl)acetylene. All spectral data obtained for **2** were identical with those of an authentic sample prepared by the method reported in the literature.[2] Similar reaction of 1-pheny-1-(phenylethynyl)tetramethyldisilane (**3**) under the same conditions produced phenyl(trimethylsilyl)acetylene in 52% yield as the sole volatile product. No disilacyclohexadiene derivative analogous to **2** was detected in the reaction mixture.

In sharp contrast to nickel-catalyzed dimerization of (phenylethynyl)pentamethyldisilanes, which proceeds via silapropadiene intermediate (**4**) arising from 1,3-shift of a trimethylsilyl group from silicon to the ethynylic carbon atom,[3] this platinum-catalyzed reaction can be best understood by considering the formation of platinasilacyclobutene intermediate (**5**) which is presumably formed from a 1,2-trimethylsilyl shift of (phenylethynyl)disilane (Scheme 1).

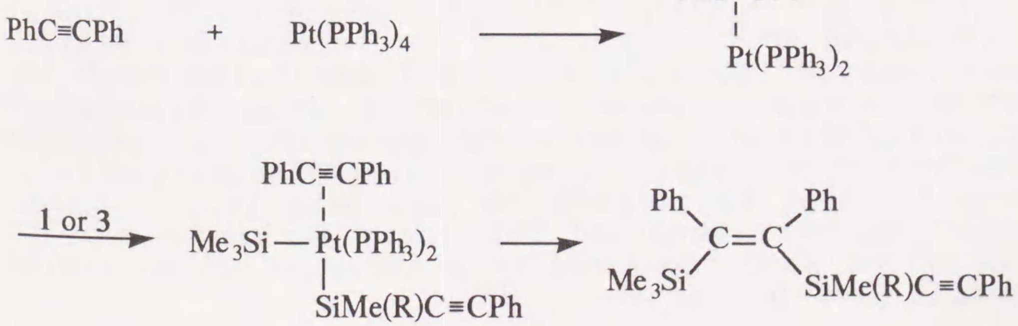
Scheme 1



When R is a methyl group, 5 dimerizes to afford 2, while in the case of a phenyl group, 5 presumably decomposes to phenyl(trimethylsilyl)acetylene and a silylene-platinum complex. However, at present no evidence for the formation of the silylene-platinum complex has been obtained. The difference of the reactivities of **1** and **3** may be understood in terms of the steric and electronic effect. The bulky substituent on the silicon atom would prevent the nucleophilic attack on this silicon atom, and a π-electron system attached to the silicon atom may support the formation of the silylene-platinum complex.

To learn much more about these reactions, we carried out the reactions in the presence of diphenylacetylene. Thus when **1** was heated at 135°C for 20 h with a slight excess of diphenylacetylene in the presence of the platinum catalyst, Z-1-[dimethyl(phenylethynyl)silyl]-2-trimethylsilyl-1,2-diphenylethene (**6**) was obtained in 96% yield. Treatment of **3** with diphenylacetylene under the same conditions gave Z-1-[methylphenyl(phenylethynylsilyl]-2-trimethylsilyl-1,2-diphenylethene (7) in 68% yield, in addition to 12% of an unidentified product. The mass spectrum of the unidentified product showed its parent peak at m/e 526 which is identical with that of 7. The formation of these double silylated products can be best understood in terms of the Si-Si bond activation by the platinum complex, followed by insertion of the acetylene to the resulting Si-Pt bond (Scheme 2). The palladium-catalyzed double silylation

Scheme 2



6 R=Me
7 R=Ph

of acetylenes and olefines is well established so far,[1-7] but no example for the platinum-catalyzed double silylation reaction has been reported.

Presumably in the absence of diphenylacetylene, this disilyl-platinum complex undergoes a 1,3-trimethylsilyl shift to produce the platinasilacyclobutene intermediate (**5**).

Experimental Section

General. All platinum-catalyzed reactions were carried out in degassed sealed glass tube. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL Model JNM-FX-90A and a JEOL Model JMN-PMX-60A spectrometer using deuteriochloroform and carbon tetrachloride solution containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 spectrometer.

Materials. (Phenylethynyl)disilanes **1** and **3** were prepared as reported in the literature.[9]

Reaction of 1 with a Catalytic Amount of $Pt(PPh_3)_4$. A mixture of 351.2 mg (1.51 mmol) of **1** and 34.5 mg (1.8 mol%) of Pt(PPh3)4 was heated at 135°C for 20 h in a sealed glass tube. The resulting mixture was treated with preparative TLC (silica gel) to give 128.0 mg (36% yield) of **3**. All spectral data obtained for **3** were identical with those of an authentic sample.

Reaction of 3 with a Catalytic Amount of $Pt(PPh_3)_4$. A mixture of 308.9 mg (1.05 mmol) of **3** was heated at 135°C for 20 h. The resulting mixture was analyzed by GLC using 18.0 mg (0.114 mmol) of undecane as an internal standard showing the presence of phenyl(trimethylsilyl)acetylene as the sole volatile product (52% yield). Phenyl(trimethylsilyl)acetylene was isolated by preparative TLC (silica gel). All spectral data obtained for phenyl(trimethylsilyl)acetylene were identical with those of an authentic sample (see Chapter 4).

Reaction of 1 with Diphenylacetylene in the Presence of Pt(PPh$_3$)$_4$. A mixture of 227.2 mg (0.979 mmol) of **1**, 176 mg (o.989 mmol) of diphenylacetylene, and 22.4 mg (1.8 mol%) of Pt(PPh$_3$)$_4$ was heated at 135°C for 20 h. The resulting mixture was analyzed by GLC using 29.9 mg (0.132 mmol) of hexadecane as an internal standard as being **6** (96% yield). The mixture was treated with preparative TLC (silica gel) to give a crude **6** as a white solid. The solid was recrystallized from ethanol to give pure **6**: mp 82.1°C; MS m/e 464 (M^+); IR $\nu_{C\equiv C}$ 2160 cm^{-1}; 60 MHz ^{1}H NMR (δ in CCl$_4$) -0.31 (s, 9H, Me$_3$Si), -0.21 (s, 6H, Me$_2$Si), 7.17 (br s, 15H, Ph); 22.5 MHz ^{13}C NMR (δ in CDCl$_3$) 1.3, 1.6 (MeSi), 94.6, 107.5 (C≡C), 123.3, 124.3, 124.7, 127.1, 127.2, 127.5, 128.1, 128.2, 128.6, 131.9, 145.2, 146.2 (Ph), 154.1, 160.8 (C=C). Anal. Calcd for $C_{27}H_{30}Si_2$: C, 78.96; H, 7.36. Found: C, 78.91; H, 7.36.

Reaction of 3 with Diphenylacetylene in the Presence of Pt(PPh$_3$)$_4$. A mixture of 242.5 mg (0.825 mmol) of **1**, 150 mg (0.843 mmol) of diphenylacetylene, and 18.4 mg (1.8 mol%) of Pt(PPh$_3$)$_4$ was heated at 135°C for 20 h. The resulting mixture was analyzed by GLC using 33.2 mg (0.131 mmol) of octadecane as an internal standard as being **7** (68% yield) and an unidentified product (12% yield). The mixture was treated with preparative TLC (silica gel) to give a crude **7** as a white solid. The crude solid was recrystallized from ethanol to give pure **7**: mp 88.3°C; MS m/e 526 (M^+); IR $\nu_{C\equiv C}$ 2160 cm^{-1}; 60 MHz ^{1}H NMR (δ in CCl$_4$) 0.07 (s, 9H, Me$_3$Si), 0.23 (s, 3H, MeSi), 6.60-7.83 (br s, 20H, Ph); 22.5 MHz ^{13}C NMR (δ in CDCl$_3$) 1.48 (MeSi and Me$_3$Si), 93.0, 108.7 (C≡C), 123.1, 124.5, 124.7, 127.1 (2 carbons), 127.5, 127.7, 128.2, 128.5, 128.7, 129.3, 131.9, 134.8, 136.7, 144.9, 146.1 (Ph), 151.8, 163.4 (C=C). Anal. Calcd for $C_{32}H_{32}Si_2$: C, 81.30; H, 6.82. Found: C, 81.25; H, 6.80.

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Chapter 4

Tungsten-Catalyzed Reactions of Silacyclopropenes.

Introduction

A considerable interest has been focused on the chemistry of silicon-containing small ring compounds.[1] To date, many papers dealing with the transition-metal-catalyzed reactions of silacyclopropenes have been reported.[2-7]

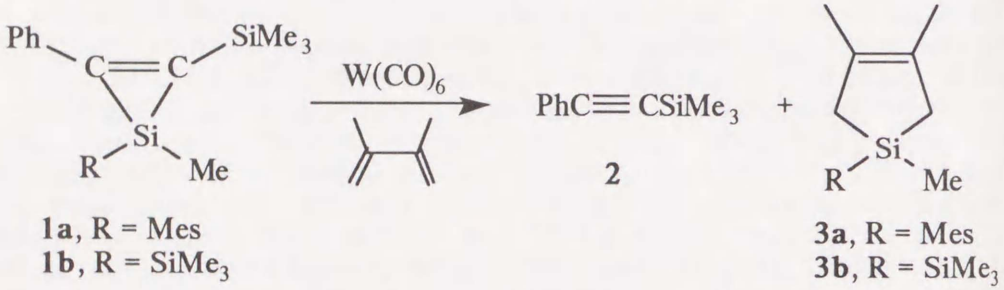
Recently, we have found that the nickel(0)-[4-6] and palladium(0)-catalyzed reactions[7] of silacyclopropenes produce the reactive intermediates such as metalasilacyclobutenes arising from insertion of metals into the Si-C bond in the silacyclopropene ring and silapropadiene-metal complexes formed from isomerization of the resulting metalasilacyclobutenes. In Chapter 1, we described the first synthesis of a nickelasilacyclobutene by the stoicheometric reaction of 1-mesityl-2-phenyl-1,3-bis(trimethylsilyl)-1-silacyclopropene and tetrakis(triethylphosphine)nickel(0). In an effort to learn much more about the chemical behavior of the silacyclopropenes toward the transition metal complexes, we have investigated the reaction of the silacyclopropene with the transition metal complex other than nickel and palladium complexes. In this Chapter, we wish to report the tungsten(0)-catalyzed reaction of silacyclopropenes which proceeds in a quite different fashion from the nickel- and palladium-catalyzed reactions. The reaction involves abstraction of a silylene from the silacyclopropene by the transition metal complex.

Results and Discussion

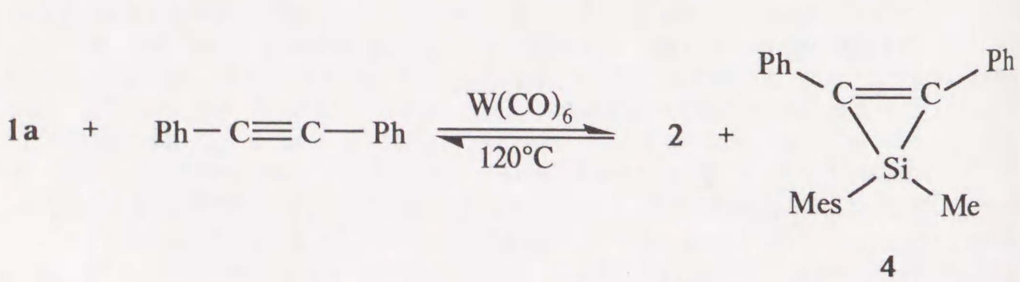
Tungstenhexacarbonyl-Catalyzed Generation of a Silylene from Silacyclopropenes. When a THF solution of 1-mesityl-1-methyl-3-phenyl-2-trimethylsilyl-1-silacyclopropene (**1a**) was heated to 120°C for 20 h in a sealed glass tube with slightly excess of 2,3-dimethyl-1,3-butadiene in the presence of a catalytic amount of $W(CO)_6$, phenyl(trimethylsilyl)acetylene (**2**) and 1-mesityl-1,3,4-trimethyl-1-silacyclopent-3-ene (**3a**) were obtained in 38 and 40%

yields, respectively, in addition to an unidentified product (less than 5% yield) whose mass spectrum showed a parent peak at 418, corresponding to a 1:1 adduct of **1a** and 2,3-dimethyl-1,3-butadiene. In the absence of the tungsten catalyst under the same conditions, the starting silacyclopropene **1a** was recovered unchanged. These results clearly show that the reaction involves the tungsten-catalyzed abstraction of mesitylmethylsilylene from the silacyclopropene **1a**. The silylene thus formed can be readily trapped by 2,3-dimethyl-1,3-butadiene, which is known as an efficient silylene trapping agent,[8] to give **3a**.

Similarly, the reaction of 1-methyl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene (**1b**) in the presence of 2,3-dimethyl-1,3-butadiene under the same conditions afforded **2** and 1,3,4-trimethyl-1-trimethylsilyl-1-silacyclopent-3-ene (**3b**) in 22 and 25% yields, respectively, indicating the formation of methyl(trimethylsilyl)silylene.

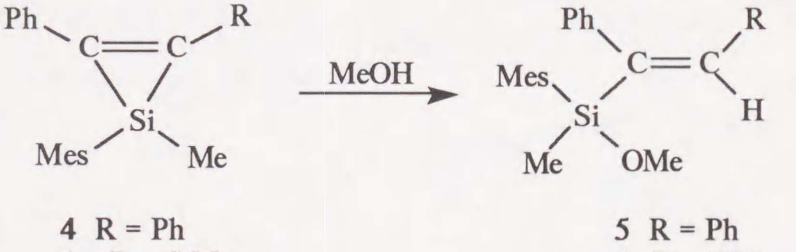


Mesitylmethylsilylene can also be trapped by diphenylacetylene. Thus, a mixture of **1a** and diphenylacetylene in a THF solution was heated to 120°C with a catalytic amount of $W(CO)_6$, and the progress of the reaction was monitored by GLC. After 32 h, GLC analysis of the reaction mixture showed the formation of **2** and 1-mesityl-1-methyl-2,3-diphenyl-1-silacyclo-



propene (**4**), together with the starting compound **1a**. The ratio of **4** to **1a** was determined to be 1:3. This ratio increased with increasing the reaction time, and after 220 h, it reached a constant value of 2:3. In sharp contrast to the nickel- and palladium-catalyzed reactions of silacyclopropenes in the presence of acetylenes, in which adducts arising from the reaction of silacyclopropenes with acetylenes are always produced,[2-7] the present reaction afforded no adduct derived from the reaction of diphenylacetylene and **1a**.

Compound **4** is extremely air-sensitive, and therefore, all attempts to isolate **4** were unsuccessful. However, its GC-MS spectrum shows a parent ion peak at m/e 340, corresponding to the calculated molecular weight of the product arising from the reaction of mesitylmethylsilylene with diphenylacetylene. Moreover, the structure of **4** could be verified by an indirect method. Thus, treatment of the reaction mixture with a large excess of methanol led to the formation of methanol adduct (**5**) in quantitative yield, along with methoxysilane (**6**) produced from the reaction of **1a** with methanol.



4 R = Ph
1a R = $SiMe_3$

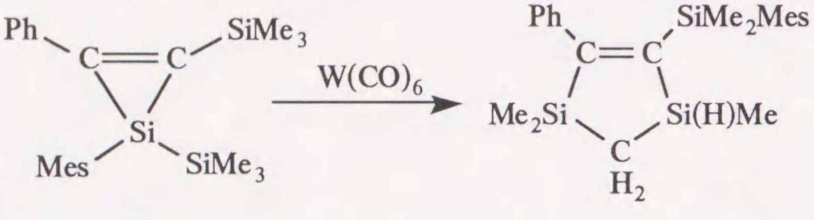
5 R = Ph
6 R = $SiMe_3$

Adducts **5** and **6** were identified as (E)-1-[mesityl(methoxy)methylsilyl]-1,2-diphenylethene and (E)-1-[mesityl(methoxy)methylsilyl]-2-phenyl-1-trimethylsilylethene, respectively, by spectroscopic analysis, as well as by elemental analysis (see Experimental Section).

Isomerization of Silacyclopropene 1c. Treatment of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene (**1c**) in the presence of the tungsten catalyst at 120°C gave no volatile product. The starting compound **4** was recovered unchanged. Similar treatment of **1c** at 190°C in the presence of

2,3-dimethyl-1,3-butadiene, however, gave 2 in quantitative yield. In this reaction, mesityl(trimethylsilyl)silylene should be formed, but no silylene adduct, analogous to **3a** and **3b**, was detected by either GLC or spectrometric analysis. The silacyclopentene was probably formed, but this product would undergo ring-opening polymerization to give nonvolatile substances.

To our surprise, when similar reaction was carried out in the absence of 2,3-dimethyl-1,3-butadiene at 190°C for 20 h in a sealed glass tube, an isomerization product, 4-(mesityldimethylsilyl)-2-phenyl-1,1,3-trimethyl-1,3-disilacyclopent-4-ene (7) was obtained in 33% yield, together with six minor products (ca. 5% each). Mass spectra of all minor products showed a parent peak at m/e 394 which is identical with that of 1c. In this reaction, no phenyl(trimethylsilyl)acetylene was detected, indicating that no silylene species was produced. The real catalyst produced in this system presumably differs from that formed in the presence of 2,3-dimethyl-1,3-butadiene.

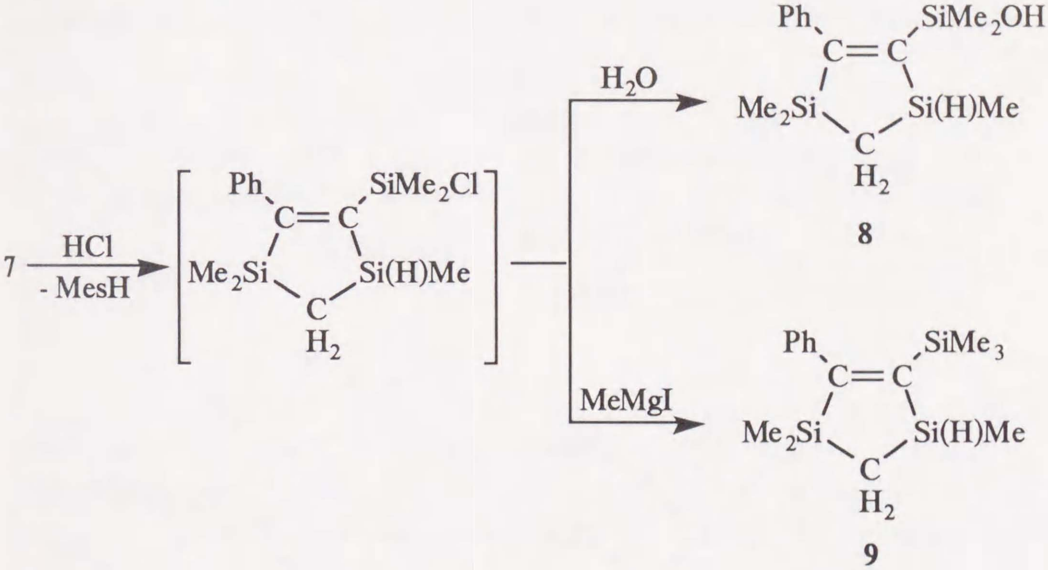


1c **7**

The structure of 7 was verified by spectrometric analysis, elemental analysis, and also by chemical reactions. The IR spectrum of 7 shows a strong absorption band at 2104 cm^{-1}, due to the stretching frequency of an Si-H bond. The ^{1}H NMR spectrum shows four singlets and one doublet signal at δ 0.11, 0.14, 0.41, and 0.47 ppm, and 0.30 ppm, due to four MeSi and one MeSi(H) protons, as well as maltiplet signal at δ 4.54 ppm attributed to hydrogen on the ring silicon. Two doublets of doublet at δ -2.84 and 0.09 ppm can be assigned as methylene protons in the silacyclopentene ring. The ^{13}C NMR spectrum shows six signals due to six different kinds of silyl-substituted sp^{3} carbons. The carbon atom appeared in the highest field may be assigned to the carbon having two silicon atoms. These results are wholly consistent with the proposed structure.

In order to get more information about the structure of 7, we investigated its chemical behavior (Scheme 1). Treatment of a benzene solution of 7 with dry hydrogen chloride gas, followed by hydrolysis of the resulting product afforded 4-(hydroxydimethylsilyl)-1,1,3-trimethyl-5-phenyl-1,3-disilacyclopent-4-ene (**8**) in 51% yield. All spectral data obtained for **8** reveal the absence of a mesityl group, but the presence of a hydroxy group.

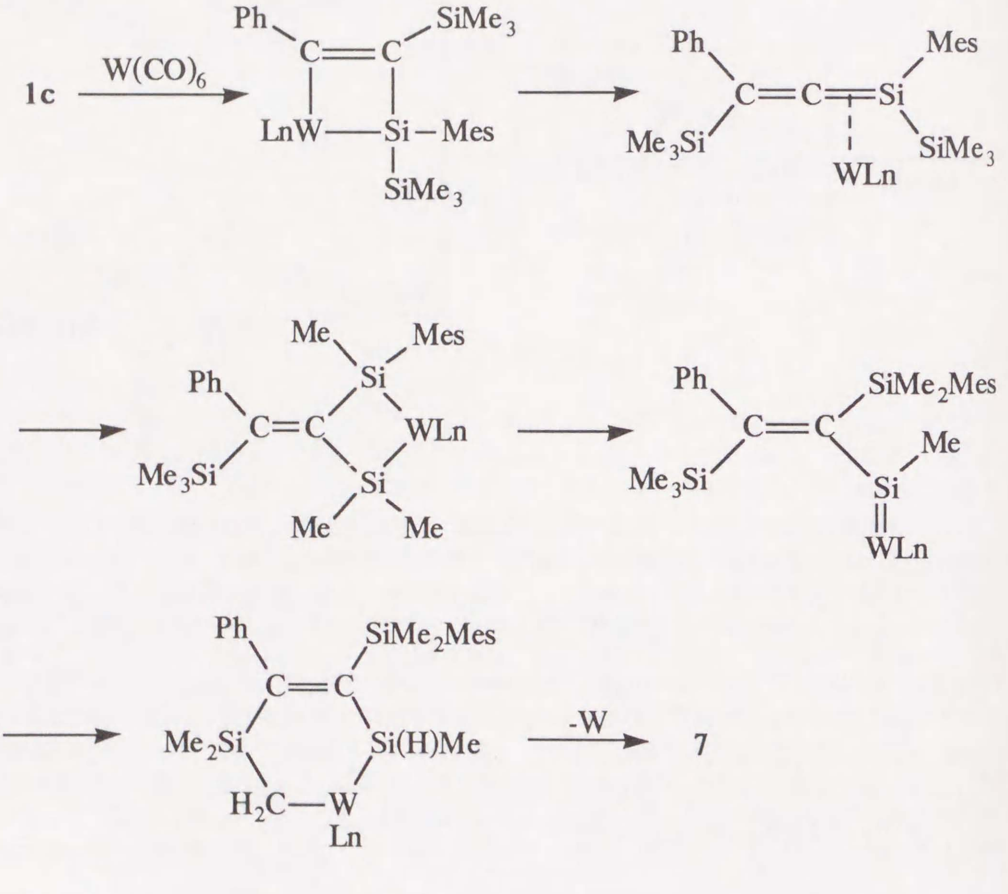
Scheme 1



Next, we carried out the methylation reaction of the product obtained from the reaction of 7 with hydrogen chloride gas. If the structure of 7 is correct, two non-equivalent methyl groups on the silicon atom bearing a mesityl group should be transformed into equivalent by replacing of this mesityl group with a methyl group. When 7 was treated with dry hydrogen chloride gas, followed by methylation of the resulting chlorosilane with methyl magnesium iodide, compound **9** was obtained in 89% yield. As expected, ^{1}H and ^{13}C NMR spectra of the product **9** show the presence of three non-equivalent silyl methyl groups and one trimethylsilyl group in the molecule.

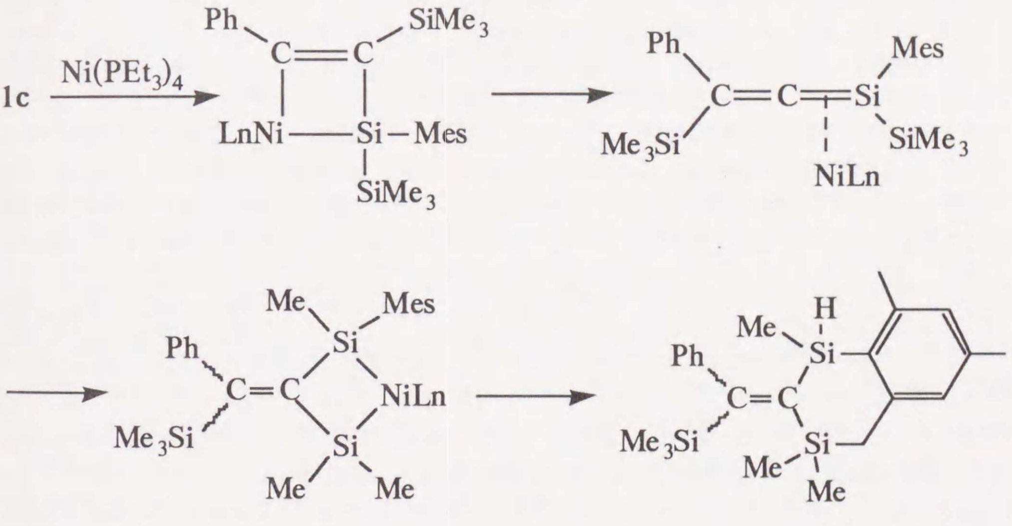
A possible mechanistic interpretation for the formation of **7** is presented in Scheme 2. Tungstenasilacyclobutene arising from insertion of a tungsten species into an Si-C bond of the starting compound **1c** rearranges to a silapropadiene-tungsten complex intermediate via a 1,2-shift of a trimethylsilyl group. The silapropadiene-tungsten complex thus formed isomerizes to a tungstenadisilacyclobutane, in which migration of a mesityl group or a methyl group on the ring silicon atom to another ring silicon is involved, to give a silylene-complex. Finally, the resulting silylene-complex undergoes intramolecularly insertion of the silylene center into a C-H bond of a methyl group of a

Scheme 2



trimethylsilyl moiety to afford the five-membered cyclic compound 7. As described in Chapter 2, the nickel-catalyzed reaction of **1c** produced disilacyclohexane derivatives (**10a**) and (**10b**). This reaction presumably proceeds with the transient formation of a silapropadiene-nickel complex which rearranges to a nickeladisilacyclobutane intermediate (Scheme 3). It seems likely that the present reaction proceeds with the similar manner to that of the nickel-catalyzed isomerization of 1c. In the case of the nickeladisilacyclobutane, however, activation of the C-H bond of a mesityl methyl group occurs, while the tungstenadisilacyclobutane would involve the formation of the silylene-complex.

Scheme 3



10a, b

Experimental Section

General. All reactions were carried out under an atmosphere of purified argon. ^1H and ^{13}C NMR spectra were determined with a JEOL Model JNM-GX-500 spectrometer, a JEOL Model JNM-FX-90A spectrometer, and a JEOL Model JMN-PMX-60A spectrometer using deuteriochloroform and carbon tetrachloride solution containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMN-QP 1000 and a JEOL Model JMS-D300 equipped with JMA-2000 data processing system.

Materials. All starting (phenylethynyl)polysilanes were prepared as reported in the literature.[4,7,9] Hexane and THF used as solvents were dried over lithium aluminum hydride and distilled just before use.

Synthesis of Silacyclopropenes (1a, 1b, and 1c). All silacyclopropenes **1a**[9], **1b**[4], and **1c**[7] were synthesized as reported in the literature. In a 25 mL reaction vessel fitted with a 6-W low pressure mercury lamp was placed a solution of (phenylethynyl)polysilane in 25 mL of hexane. The solution was irradiated until 90-95% of (phenylethynyl)polysilane was consumed. After evaporation of the solvent, the residue was distilled under reduced pressure to give silacyclopropene, **1a** (60-65% yield), **1b** (40-45% yield), and **1c** (75-80% yield). For **1a**: MS m/e 336 (M^+); 60 MHz ^1H NMR (δ in THF) 0.26 (s, 9H, Me_3Si), 0.49 (s, 3H, MeSi), 2.16 (s, 3H, p-Me), 2.58 (s, 6H, o-Me), 6.60 (br s, 2H, mesityl ring protons), 6.93-7.43 (m, 5H, Ph); 22.5 MHz ^{13}C NMR (δ in THF/C_6D_6=2/1) -2.4, 0.4, 21.0, 24.4, 127.8, 128.5, 128.1, 128.9, 132.9, 137.3, 139.1, 143.2, 160.9, 177.6. For **1b**: MS m/e 290 (M^+); ^1H NMR (δ in THF) 0.02 (s, 3H, MeSi), 0.15 (s, 9H, Me_3Si), 0.26 (s, 9H, Me_3Si), 7.00-7.47 (m, 5H, Ph). For **1c**: MS m/e 394 (M^+); ^1H NMR (δ in THF) 0.16 (s, 9H, Me_3Si), 0.29 (s, 9H, Me_3Si), 2.16 (s, 3H, p-Me), 2.53 (s, 6H, o-Me), 6.60 (br s, 2H, mesityl ring protons), 6.90-7.50 (m, 5H, Ph).

Reaction of 1a in the Presence of 2,3-Dimethyl-1,3-butadiene. A mixture of 0.700 mmol of **1a**, 0.5 mL of 2,3-dimethyl-1,3-butadiene, 18 mg (10 mol%) of $W(CO)_6$, and 0.0767 mmol of nonadecane as an internal standard in THF was heated at 120 °C for 20 h in a sealed glass tube. GLC analysis of the resulting mixture showed the presence of **2** (33%), **3a** (35%), and **1a** (13%). The solvent was distilled off and the residue was treated with MPLC (silica gel, elution with hexane) to give pure **2** and **3a**. All spectral data obtained for **2** were identical with those of the authentic sample prepared from the reaction of phenylethynyllithium and chlorotrimethylsilane:[10] MS m/e 174 (M^+); IR $\nu_{C\equiv C}$ 2159 cm^{-1}; 100 MHz ^1H NMR (δ in CCl_4) 0.27 (s, 9H, Me_3Si), 7.08-7.38 (m, 5H, Ph); 22.5 MHz ^{13}C NMR (δ in C_6D_6) -0.1, 94.2, 106.0, 123.9, 128.4, 128.9, 132.2. For **3a**: MS m/e 244 (M^+); 90 MHz ^1H NMR (δ in $CDCl_3$) 0.24 (s, 3H, MeSi), 1.60 (br s, 2H, silacyclopentene ring protons), 1.74 (br s, 6H, Me-C=C), 1.82 (br s, 2H, silacyclopentene ring protons), 2.26 (s, 3H, p-Me), 2.38 (s, 6H, o-Me), 6.83 (br s, 2H, mesityl ring protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -2.0, 21.0, 24.0, 27.0, 28.6, 128.3, 130.0, 132.7, 138.7, 143.9. Anal. Calcd for $C_{16}H_{24}Si$: C, 78.62; H, 9.90. Found: C, 78.58; H, 9.86.

Reaction of 1b in the Presence of 2,3-Dimethyl-1,3-butadiene. A mixture of 0.375 mmol of **1b**, 0.5 mL of 2,3-dimethyl-1,3-butadiene, 13 mg (10 mol%) of $W(CO)_6$, and 0.123 mmol of tetradecane as an internal standard in THF was heated at 120°C for 20 h in a sealed glass tube. The resulting mixture was analyzed by GLC as being **2** (22% yield) and **3b** (25% yield). At this stage ca. 90% of starting **1b** was consumed. Product **2** and **3b** were isolated by preparative GLC. All spectral data obtained for **2** were identical with those of the authentic sample. For **3b**: MS m/e 198 (M^+); 90 MHz ^1H NMR (δ in C_6D_6) 0.06 (s, 9H, Me_3Si), 0.11 (s, 3H, MeSi), 1.31 (br d, 2H, J=11.7 Hz, silacyclopentene ring protons), 1.48 (br d, 2H, J=11.7 Hz, silacyclopentene ring protons), 1.67 (br s, 6H, Me-C), 22.5 MHz ^{13}C NMR (δ in C_6D_6) -4.2, -1.9, 19.4, 24.5, 130.9. Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.52; H, 11.17. Found: C, 60.30; H, 11.04.

Reaction of 1a with Diphenylacetylene. A mixture of 0.382 mmol of **1a**, 68 mg (0.382 mmol) of diphenylacetylene, and 0.174 mmol of nonadecane in THF was heated to 120 °C for 20 h with 10 mol% of $W(CO)_6$ in a sealed glass tube. The reaction mixture was analyzed by GLC and GC-MS as being **1a** (32% yield), **2** (17% yield), and **4** (13% yield; MS m/e 340 (M^+)). The mixture was treated with 0.2 mL of methanol at room temperature. GLC analysis of the resulting mixture showed that compounds **4** and **1a** were completely converted to **5** and **6**. Compounds **5** and **6** were isolated by preparative GLC. For **5**: MS m/e 414 (M^+); IR ν_{Si-O} 1085 cm^{-1}; 60 MHz ^1H NMR (δ in CCl_4) 0.49 (s, 3H, MeSi), 2.22 (s, 3H, p-Me), 2.35 (s, 6H, o-Me), 3.40 (s, 3H, MeO), 6.26-7.20 (m, 12H, ring protons), 7.46 (s, 1H, olefinic proton); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -2.0, 21.0, 23.9, 50.4, 125.9, 127.2, 127.4, 127.9, 128.0, 128.2, 128.5, 128.8, 129.1, 129.7, 139.3, 139.6, 144.1, 145.2. Anal. Calcd for $C_{25}H_{28}OSi$: C, 80.59; H, 7.57. Found: C, 80.37; H, 7.47. For **6**: MS m/e 368 (M^+); IR ν_{Si-O} 1086 cm^{-1}; 60 MHz ^1H NMR (δ in CCl_4) 0.18 (s, 9H, Me_3Si), 0.42 (s, 3H, Me-Si), 2.21 (s, 3H, p-Me), 2.29 (s, 6H, o-Me), 3.40 (s, 3H, MeO), 6.35 (s, 1H, olefinic proton), 6.63 (br s, 2H, mesityl ring protons), 6.70-7.22 (m, 5H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -0.8, 20.9, 23.9, 50.3, 125.9, 127.6 (2 carbons), 127.8, 127.9, 129.0, 129.3, 139.1, 145.1, 146.6. Anal. Calcd for $C_{22}H_{32}OSi_2$: C, 71.68; H, 8.75. Found: C, 71.67; H, 8.71.

Reaction of 1c in the Presence of 2,3-Dimethyl-1,3-butadiene at 120°C. A mixture of 0.568 mmol of **1c**, 0.5 mL of 2,3-dimethyl-1,3-butadiene, 24 mg (10 mol%) of $W(CO)_6$, and 0.0719 mmol of eicosane as an internal standard in 1 mL of THF was heated at 120°C for 20 h in a sealed glass tube. GLC and the mass spectrometric analysis of the resulting mixture showed that all **1c** remained unchanged.

Reaction of 1c in the Presence of 2,3-Dimethyl-1,3-Butadiene at 190°C. A mixture of 0.577 mmol of **1c**, 0.5 mL of 2,3-dimethyl-1,3-butadiene, 14 mg (7 mol%) of $W(CO)_6$, and 0.259 mmol of eicosane as an internal standard in 1 mL of THF was heated at 190°C for 20 h in a sealed glass tube. The resulting mixture was analyzed by GLC as being **2** (100% yield). The retention time of GLC and the mass spectrum of **2** were identical with those of the authentic sample.

Isomerization of 1c. A mixture of 0.427 mmol of **1c**, 15 mg (10 mol%) of $W(CO)_6$, and 0.155 mmol of docosane as an internal standard was heated at 190°C in a sealed glass tube. Analysis of the resulting mixture by GLC showed the formation of **7** (33% yield) together with six unidentified products (each less than 5% yields). Pure **7** was separated from the mixture by MPLC (silica gel, elution with hexane): MS m/e 394 (M^+); IR ν_{Si-H} 2104 cm^{-1}; 500 MHz ^1H NMR (δ in C_6D_6) -2.84 (dd, 1H, J=14.3, 2.5 Hz, H_2CSi_2), 0.09 (dd, 1H, J=14.3, 2.5 Hz, H_2CSi_2), 0.11 (s, 3H, MeSi), 0.14 (s, 3H, MeSi), 0.30 (d, 3H, J=3.7 Hz, MeSiH), 0.41 (s, 3H, MeSi), 0.47 (s, 3H, MeSi), 2.16 (s, 3H, p-Me), 2.34 (s, 6H, o-Me), 4.54 (m, 1H, HSi), 6.70 (br s, 2H, mesityl ring protons), 6.80-7.02 (m, 5H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -5.7, -1.0, -0.5, 0.6, 4.0, 4.8, 20.9, 24.5, 125.1, 125.4, 127.3, 128.7, 133.4, 138.0, 143.8, 145.8, 163.3, 181.9. Anal. Calcd for $C_{23}H_{34}Si_3$: C, 69.98; H, 8.68. Found: C, 69.93; H, 8.67.

Reaction of 7 with Hydrogen Chloride, Followed by Hydrolysis. A solution of 61.3 mg (0.156 mmol) of **7** in 10 mL of benzene was placed in a 25 mL two-necked flask. Dry hydrogen chloride gas was bubbled into the solution for 30 min with the rate of 1-2 mL/sec. The resulting mixture was hydrolyzed with water and the organic layer was separated. The aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over potassium carbonate. The solvent was evaporated and then the residue was treated with preparative TLC (silica gel) to give pure **8** (23.2 mg, 51% yield): MS m/e 292 (M^+); IR ν_{O-H} 3264 cm^{-1}, ν_{Si-H} 2125 cm^{-1}, ν_{Si-O} 1070 cm^{-1}; 90 MHz ^1H NMR (δ in $CDCl_3$) -0.25 (dd, 1H, J=14.5, 2.2 Hz, H_2CSi_2), -0.01 (s, 3H, MeSi), 0.05 (s, 3H, MeSi), 0.10 (dd, 1H, J=14.5, 2.2 Hz, H_2CSi_2), 0.11 (s, 3H, MeSi), 0.16 (s, 3H, MeSi), 0.36 (d, 3H, J=3.5 Hz, MeSiH), 4.65 (m, 1H, HSi), 6.90-7.35 (m, 5H, Ph). Exact MS Calcd for $C_{14}H_{24}OSi_3$: 292.1134. Found: 292.1149. Anal Calcd: C, 57.47; H, 8.27. Found:C, 57.46; H, 8.24.

Reaction of 7 with Hydrogen Chloride, Followed by Methylation. A solution of 92.8 mg (0.236 mmol) of **7** in 10 mL of benzene was placed in a

25 mL two-necked flask. Dry hydrogen chloride gas was bubbled into the solution for 30 min with the rate of 1-2 mL/sec. After evaporation of hydrogen chloride and a half volume of benzene under the reduced pressure, 0.2 mL (0.3 mmol) of a 1.5 M ether solution of methyl magnesium iodide was added. After hydrolysis with water, the organic layer was separated. The aqueous layer was extracted with hexane. The organic layer and the extracts were combined and dried over potassium carbonate. The solvent was evaporated and then the residue was treated with MPLC (silica gel, elution with hexane) to give 62.5 mg (91% yield) of **9**. Analytically pure compound was obtained by preparative GLC: MS m/e 290 (M^+); IR ν_{Si-H} 2107 cm^{-1}; 90 MHz ^1H NMR (δ in $CDCl_3$) -0.41 (dd, 1H, J=16.0, 2.0 Hz, silacyclopentene ring proton), -0.27 (s, 9H, Me_3Si), -0.05 (s, 3H, MeSi), 0.02 (s, 3H, MeSi), 0.04 (dd, 1H, J=16.0, 3.7 Hz, silacyclopentene ring proton), 0.21 (d, 3H, MeSi(H)), 4.48-4.59 (m, 1H, HSi), 6.72-7.17 (m, 5H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -5.9, -0.8, -0.7, -0.5, -0.2, 0.9, 125.5, 126.0, 127.7, 128.4, 146.7, 162.4. Exact MS Calcd for $C_{15}H_{26}Si_3$: 290.1342. Found: 290.1347.

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Part II

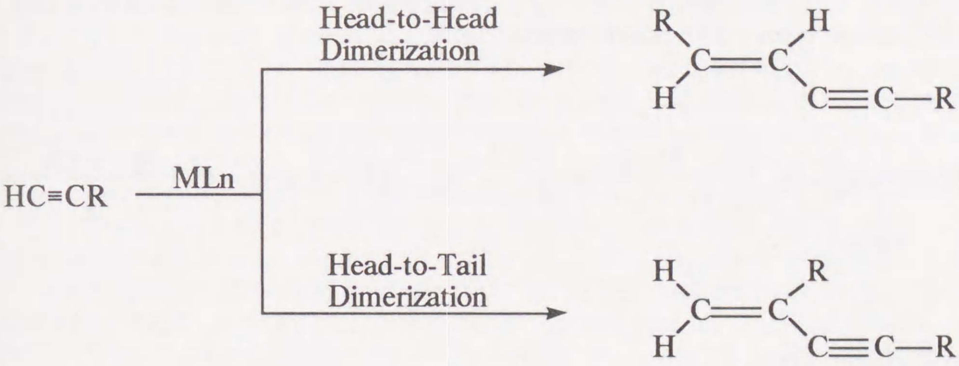
Transition-Metal-Catalyzed C-H Bond Activation of Ethynylsilanes

Chapter 5.

Synthesis and Reactions of (E)-1,4-Bis(silyl)-Substituted Enynes

Introduction

The C-H bond activation of 1-alkynes by a transition metal catalyst constitutes one of the most important methods of preparing enynes, which can be used in synthetic routes to many complex compounds including natural products. Many papers that deal with the transition-metal-catalyzed dimerization of 1-alkynes leading to enynes have been reported to date.[1-6] Most of the papers, however, are concerned with head-to-tail dimerization.



M = Ni, Cu, Rh, Pd, ...

The head-to-head couplings with high yields of the enynes were observed when 1-alkynes were heated in benzene in the presence of a catalytic amount of chlorotris(triphenylphosphine)rhodium(I).[2] These couplings, however, are restricted to the case of 1-alkynes bearing a 3-hydroxy group.

In the course of our studies concerning the investigation about the interaction between transition-metal complexes and ethynylsilanes,[7] we found that transition-metal-catalyzed dimerization of ethynylsilanes proceeds completely in a head-to-head coupling fashion to give (E)-1,4-bis(silyl)-substituted enynes in high yields.

Results and Discussion

Synthesis of (E)-1,4-Bis(silyl)-substituted Enynes. Reactions of ethynylsilanes (**1a-c**) and ethynyldisilanes (**1d,e**) with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) at 100°C in benzene or toluene solution gave corresponding head-to-head dimers, (E)-1,4-bis(silyl)-substituted enynes (**2a-e**) in moderate yields. Similar reactions of **1a**-e with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) at room temperature also proceeded to afford enynes **2a-2e**. The results of these reactions are summarized in Table 1. The structures of **2a-e** were verified by mass, IR, and ^{1}H and ^{13}C NMR spectroscopic analysis, as well as by elemental analysis (see Experimental Section). In the ^{1}H NMR spectrum, the coupling constants (J=19 Hz) of the olefinic protons clearly indicate that compounds 2a-e must have an (E)-configuration.

Scheme 1

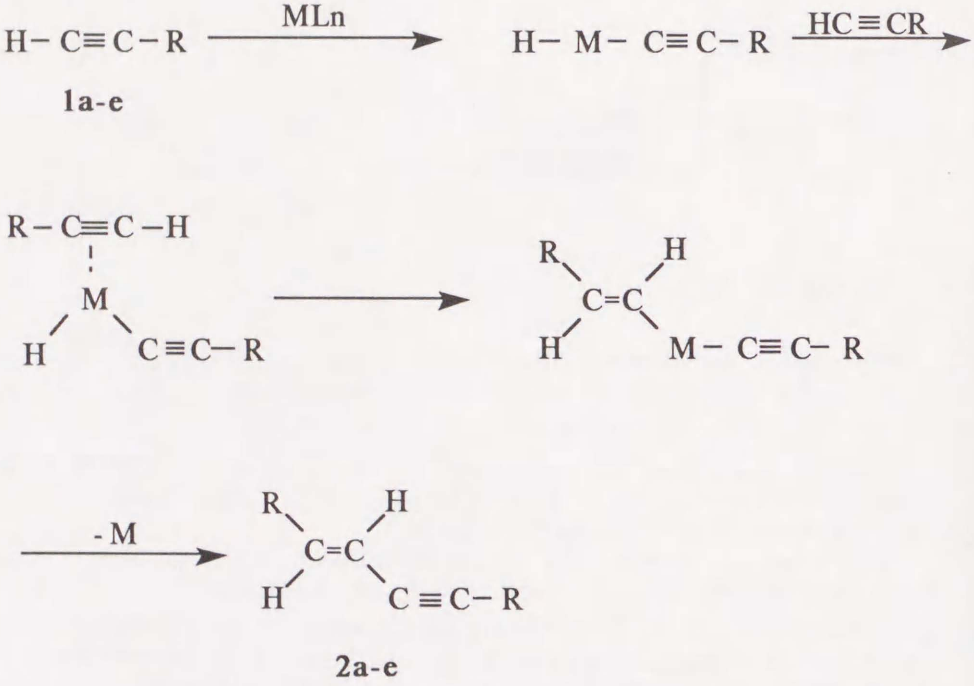


Table 1. Yields of enynes

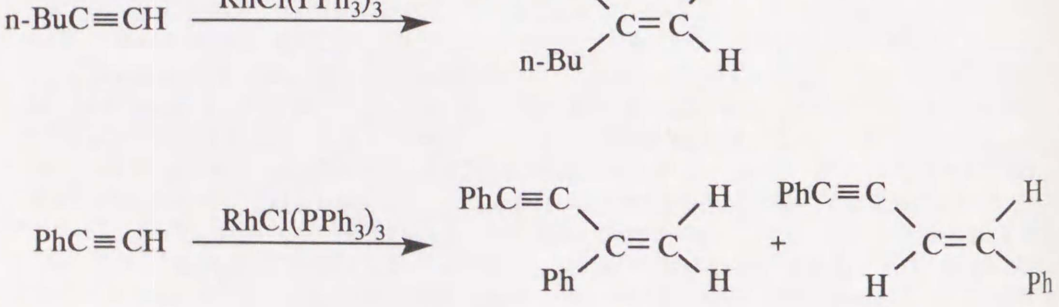
	MLn = $Pd(PPh_3)_4$	$RhCl(PPh_3)_3$
R = $SiMePh_2$ (**2a**)	62 %	94 %
$SiMe_2Ph$ (**2b**)	50 %	84 %
$SiMe_2{}^tBu$ (**2c**)	21 %	82 %
$SiMe_2SiMe_3$ (**2d**)	33 %	51 %
$SiPhMeSiMe_3$ (**2e**)	65 %	88 %

The rhodium-catalyzed dimerization proceeds readily at room temperature, while palladium(0) catalyst needs to heat at 100 °C to produce enynes. Ethynylsilanes **1a-e** did not react in the presence of the palladium(0) catalyst at room temperature, and the starting compounds were recovered unchanged. In the case of palladium(0) catalyzed reaction, introduction of at least one phenyl group onto a ethynyl silicon atom is necessary to get enynes in good yields.

These reactions proceed with remarkable regio- and stereochemical specificity. No other regio- and stereoisomers were detected in the reaction mixture by either GLC or spectrometric analysis. Although, as described in Chapters 2 and 3, an Si-Si bond of (phenylethynyl)disilane can be readily activated by transition-metal complexes to give silapropadiene-metal complex or metalasilacyclobutene intermediate, no products arising from the Si-Si bond activation were detected in the reaction mixture obtained from ethynyldisilane **1d** and **1e**.

Scheme 1 illustrates a possible mechanistic interpretation of the observed reaction course. The mechanism involves the insertion of a rhodium or palladium complex into an acetylenic C-H bond giving an ethynyl-metal complex, followed by regiospecific addition of the M-H across the triple bond of the coodinated ethynylsilane. Finally, reductive elimination of the rhodium or palladium species takes place to give the product. Head-to-head coupling may be ascribed to the steric requirement of a bulky silyl group. Examination of molecular models shows that the steric interaction between two bulky silyl groups in the head-to-tail coupling is much larger than that of the head-to-head coupling.

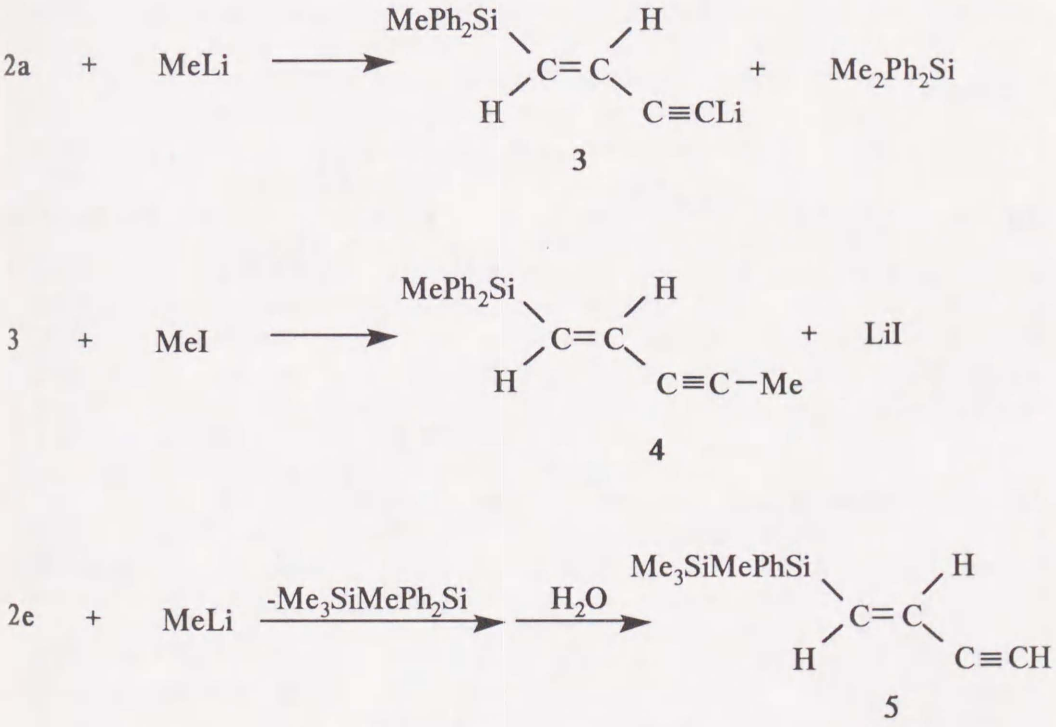
In order to check whether or not organic monosubstituted acetylenes give the head-to-head dimers in the presence of the rhodium complex, we carried out the reaction by using 1-hexyne and phenylacetylene as starting materials under the same conditions. Thus, treatment of 1-hexyne with a catalytic amount of chlorotris(triphenylphosphine)rhodium afforded a dimer in 64% yield. Proton chemical shifts of the product were identical with those of 2-butyloct-1-en-3-yne reported by Nakamura, et al.[4] Furthermore, the coupling constants (J=2.2 Hz) of two resonances at 5.07 and 5.11 ppm, determined by proton-decoupling were consistent with the structure of the head-to-tail dimer. In contrast to the rhodium-catalyzed reaction of 1-hexyne, phenylacetylene gave two isomers of the dimer, 2,4-diphenylbut-1-en-3-yne and 1,4-diphenylbut-1-en-3-yne in 14 and 20% yields, respectively. All attempts to isolate the pure 2,4-isomer by using preparative TLC or GLC were unsuccessful. This compound always decomposed to give nonvolatile products. The structure of the 2,4-isomer, however, could be verified by ^{1}H and ^{13}C NMR spectroscopic analysis of the mixture. The pure 1,4-isomer that was isolated by preparative TLC, followed by recrystallization from ethanol, was characterized by spectroscopic method as well as by elemental analysis. These results show that the only silyl-substituted acetylene proceeds regio- and stereospecifically head-to-head coupling.



Substitution Reactions of (E)-Bis(silyl)-Substituted Enynes. Next, we carried out the substitution reaction of a silyl group on an acetylenic carbon atom by using enynes **2a** and **2e**, in order to learn the chemical behavior of the present enynes. When 1 equiv of methyllithium was added to a THF solution of **2a** at -78°C, (E)-4-lithio-1-(methyl-diphenylsilyl)but-1-en-3-yne (**3**) was formed in almost quantitative yield, as indicated by the fact that treatment of the resulting solution with methyl iodide gave 1-(methyldiphenylsilyl)pent-1-en-3-yne (**4**) in 94% yield. Similarly, the reaction of **2e** with 1 equiv of methyllithium at -78°C in diethylether, followed by hydrolysis gave 1-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**5**) in 96% yield (Scheme 2).

The structure of **4** was verified by IR, mass, and ^1H and ^{13}C NMR spectrometric analysis. The ^1H NMR spectrum of **4** shows resonances at δ 0.57 and 1.90 ppm

Scheme 2

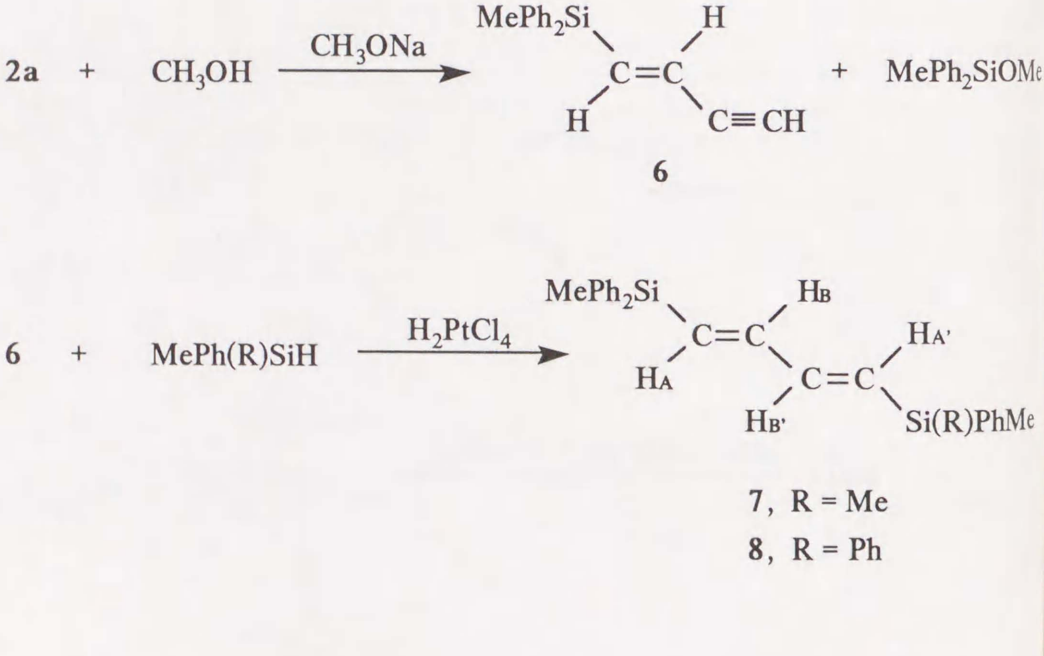


due to methylsilyl protons and methyl protons on acetylenic carbon, and resonances δ at 5.87, 6.59 and 7.13-7.66, attributed to two nonequivalent vinylic protons (J=19 Hz) and phenyl ring protons. The ^{13}C NMR spectrum of **4** reveals signals δ at 80.27, 88.02 and 127.90, 139.01, due to acetylenic and vinylic carbons, respectively. The structure of **5** was also verified by mass, ^{1}H, and ^{13}C NMR spectroscopic method (see Experimental Section).

Treatment of **2a** with methanol in the presence of a catalytic amount of sodium methoxide in diethyl ether at room temperature afforded (E)-1-(methyldiphenylsilyl)butenyne (**6**) in 92% yield (Scheme 3). The ^{1}H NMR spectrum of **6** shows a doublet signal δ at 2.65 ppm (J=2 Hz) due to acetylenic hydrogen, indicating that the only the silyl group on the acetylenic carbon is replaced by hydrogen.

Hydrosilylation of **6** readily produced (E,E)-1,4-bis(silyl)but-1,3-dienes in high yields. Thus, the reaction of **6** with dimethylphenylsilane and methyldiphenylsilane in the presence of a catalytic amount of chloroplatinic acid at room temperature gave

Scheme 3



(E,E)-1-(dimethylphenylsilyl)-4-(methyldiphenylsilyl)-but-1,3-diene (**7**) and (E,E)-1,4-bis(methyldiphenylsilyl)but-1,3-diene (**8**) in 67% and 65% yields, respectively (Scheme 3). No other isomers were detected by either GLC or spectroscopic analysis.

The coupling constants ($J_{H_A-H_B}$=18.2 Hz, $J_{H_A-H_{B'}}$=0.7 Hz, $J_{H_A-H_{A'}}$=0.6 Hz, $J_{H_B-H_{B'}}$=9.7 Hz) of protons δ at 6.21 (H_A,$H_{A'}$) and 6.69 ppm (H_B,$H_{B'}$) for compound **8** clearly show that **8** must have an (E,E)-configuration.

In conclusion, the rhodium and palladium catalyzed reactions of (silyl)- and (disilanyl)-substituted acetylenes gave head-to-head dimers stereospecifically. The reactions of the resulting (E)-1,4-bis(silyl)- and bis(disilanyl)but-1-en-3-yne with methyllithium afforded (E)-4-lithio-1-(silyl)- and (disilanyl)but-1-en-3-yne in solution. (E)-1-(silyl)but-1-en-3-yne reacted with hydrosilanes in the presence of a platinum catalyst to give (E,E)-1,4-bis(silyl)but-1,3-dienes.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified argon. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000. ^{1}H NMR (90 MHz) and ^{13}C NMR (22.5 MHz) spectra were determined on JEOL Model JNM-FX-90A spectrometer.

Materials. All ethynylsilanes used as the starting compounds were synthesized by the reaction of ethynyl magnesium bromide with the corresponding chlorosilanes and chlorodisilanes by the method reported in the literature.[8] Toluene and THF were dried over lithium aluminium hydride and distilled before use.

(E)-1,4-Bis(methyldiphenylsilyl)but-1-en-3-yne (2a). a) Rhodium(I)-Catalyzed Reaction: In a 200 mL-flask was placed a mixture of 5.00 g (22.5 mmol) of ethynylmethyldiphenylsilane (**1a**) and 1.05 g (1.14 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 125 mL of toluene. The mixture was stirred at room temperature for 30 h, and solvent toluene was evaporated under reduced pressure at room temperature. Then, the product was chromatographed on silica gel

(200-300 mesh, length 200 mm, i.d. 35 mm) eluting with hexane. Hexane was evaporated to give 4.7 g (94% yield) of **2a**: mp 96.0 °C; MS m/e 444 (M^+); IR $\nu_{C\equiv C}$ 2160 cm^{-1}; 60 MHz ^1H NMR (δ in CCl_4) 0.63 (s, 3H, MeSi), 0.69 (s, 3H, MeSi), 5.93 (d, 1H, J=19 Hz, HC=C), 6.75 (d, 1H, J=19 Hz, HC=C), 6.96-7.66 (m, 20H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -4.1, -2.1 (MeSi), 92.3, 108.0 (acetylenic carbons), 126.8 (olefinic carbon), 127.9 (2 carbons), 129.7 (2 carbons), 133.9, 134.5, 134.8, 135.1 (Phenyl ring carbons), 143.3 (olefinic carbon). Anal. Calcd for $C_{30}H_{28}Si_2$: C, 81.02; H, 6.35. Found: C, 81.02; H, 6.36.

b) Palladium(0)-Catalyzed Reaction: A solution of 320.7 mg (0.773 mmol) of **1a** and 100 mg (0.0897 mmol) of tetrakis(triphenylphosphine)-palladium(0) in 2 mL of benzene was heated at 100 °C for 20 h in a sealed glass tube. After evaporation of the solvent under reduced pressure at room temperature, the mixture was chromatographed on silica gel (200-300 mesh, length 200 mm, i.d. 35 mm) eluting with hexane. Hexane was evaporated to give 188 mg (62% yield) of **2a**. All spectral data obtained for **2a** were identical with those of an authentic sample.

Compounds **2b-e** were synthesized as the similar manner to that of **2a**

(E)-1,4-Bis(dimethylphenylsilyl)but-1-en-3-yne (2b): MS m/e 320 (M^+); IR $\nu_{C\equiv C}$ 2160 cm^{-1}; 60 MHz ^1H NMR (δ in CCl_4) 0.38 (s, 6H, Me_2Si), 0.43 (s, 6H, Me_2Si), 5.90 (d, 1H, J=19 Hz, HC=C), 6.59 (d, 1H, J=19 Hz, HC=C), 7.21-7.64 (m, 10H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -3.0, -0.9 (Me_2Si), 93.4, 106.7 (acetylenic carbons), 125.0 (olefinic carbon), 127.7, 129.7, 129.3, 129.4, 133.7, 133.9, 136.9, 137.1 (Phenyl ring carbons), 145.1 (olefinic carbon). Anal. Calcd for $C_{20}H_{24}Si_2$: C, 74.93; H, 7.55. Found: C, 74.92; H, 7.46.

(E)-1,4-Bis(tert-butyldimethylsilyl)but-1-en-3-yne (2c): sub. 80°C, mass m/e 227 (M^+-^tBu); IR

$\nu_{C\equiv C}$ 2155 cm^{-1}; ^{1}H NMR (δ in CCl_4) 0.06(s, 6H, MeSi), 0.12 (s, 6H, MeSi), 0.91 (s, 9H, ^{t}Bu), 0.96 (s, 6H, tBu), 6.03 (d, 1H, HC=C, J=19 Hz), 6.61 (d, 1H, HC=C, J=19 Hz); ^{13}C NMR (δ in $CDCl_3$) -6.2, -4.4 (MeSi), 16.8, 16.9 (CMe_3), 26.3, 26.6 (Me_3C), 93.0, 106.2 (acetylenic carbons), 125.0, 144.3 (olefinic carbons). Anal. Calcd for $C_{16}H_{32}Si_2$: C, 68.49; H, 11.49. Found: C, 68.33; H, 11.48.

(E)-1,4-Bis(pentamethyldisilanyl)but-1-en-3-yne (2d): Mass m/e 312 (M^+); IR $\nu_{C\equiv C}$ 2150 cm^{-1}; ^{1}H NMR (δ in CCl_4) 0.07 (s, 6H, Me_2Si), 0.12 (s 6H, Me_2Si), 0.12 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 5.90 (d, 1H, HC=C, J=19 Hz), 6.48 (d, 1H, HC=C, J=19 Hz); ^{13}C NMR (δ in $CDCl_3$) -4.4, -2.7, -2.3, -2.1 (MeSi), 93.3, 107.9 (acetylenic carbons), 123.7, 145.6 (olefinic carbons). Anal. Calcd for $C_{14}H_{32}Si_4$: C, 53.77; H, 10.31. Found: C, 53.53; H, 10.34.

(E)-1,4-Bis(1-phenyltetramethyldisilanyl)-but-1-en-3-yne (2e): MS m/e 436 (M^+); IR $n_{C\equiv C}$ 2150 cm^{-1}; 100 MHz ^{1}H NMR (δ in CCl_4) 0.11 (s, 18H, $2Me_3Si$), 0.31 (s, 3H, MeSi), 0.35 (s, 3H, MeSi), 6.02 (d, 1H, J=20 Hz, HC=C), 6.66 (d, 1H, J=20 Hz, HC=C), 7.17-7.68 (m, 10H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -5.9, -4.1, -2.3, -1.9 (MeSi), 91.7, 109.2 (acetylenic carbons), 125.1 (olefinic carbon), 128.0 (2 carbons), 128.8 (2 carbons), 134.1, 134.4, 135.9, 136.4 (phenyl ring carbons), 143.6 (olefinic carbon). Anal. Calcd for $C_{24}H_{36}Si_4$: C, 65.98; H, 8.31. Found: C, 65.73; H, 8.45.

2-Butyloct-1-en-3-yne.[4] A mixture of 283 mg (3.45 mmol) of 1-hexyne and 160 mg (0.173 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 5 mL of toluene was stirred at room temperature for 15 h. The mixture was treated with a silica gel column (200-300 mesh, length 200 mm, i.d. 35 mm) to remove any rhodium complexes and was concentrated under reduced pressure. The yield of the product (64% yield) was determined by GLC using tetradecane as an internal standard. Pure product was isolated by MPLC (silica gel, 40-63 mμ, length 310 mm, i.d. 25 mm, flow rate 10 mL/min, elution with hexane): Mass m/e 164(M^+); IR $\nu_{C\equiv C}$ 2220 cm^{-1}; ^1H NMR[4] (δ in $CDCl_3$) 0.86-1.10 (m, 6H, CH_3), 1.10-1.77 (m, 8H, CH_2CH_2), 2.13 (t, 2H, J=7 Hz, CH_2CH_2), 2.32 (t, 2H, J=7 Hz, $CH_2C\equiv C$), 5.12 (br d, 1H, J=2.2 Hz, $H_AC(H_B)=C$), 5.19 (br d, 1H, J=2.2 Hz, $H_BC(H_A)=C$); ^{13}C NMR (δ in $CDCl_3$) 13.5 (CH_3C), 13.8 (CH_3C), 18.9, 22.0, 22.1, 30.3, 30.9, 37.3 (CH_2), 81.1, 89.9 (acetylenic carbons), 119.1, 132.4 (olefinic carbons).

1,4-Diphenylbut-1-en-3-yne. A mixture of 70.3 mg (6.89 mmol) of phenylacetylene and 2 mol% of chlorotris(triphenylphosphine)rhodium(I) in 5 mL of toluene was stirred for 14 h at room temperature. To this was added 50.7 mg (0.275 mmol) of tridecane as an internal standard and the mixture was then analyzed as being 2,4-diphenylbut-1-en-3-yne (14%) and 1,4-diphenylbut-1-en-3-yne (20%). 1,4-Diphneylbut-1-en-3-yne was isolated by preparative TLC (silica gel) and recrystallized from ethanol: mp 93.8°C; mass m/e 204(M^+); ^1H NMR (δ in $CDCl_3$) 6.17 (d, 1H, J=16 Hz, $H_AC(H_B)=C$), 6.87 (d, 1H, J=16 Hz, $H_BC(H_A)=C$), 6.99-7.44 (m, 10H, phenyl ring protons); ^{13}C NMR 89.0, 91.8 (acetylenic carbons), 108.2, 123.4, 126.2, 128.1, 128.3, 128.5, 128.7, 131.4 (phenyl ring carbons), 136.3, 141.2 (olefinic carbons). Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.85; H, 5.85.

2,4-Diphenylbut-1-en-3-yne. A mixture of 1.10 g (10.8 mmol) of phenylacetylene and 1.3 mol% of chlorotris(triphenylphosphine)rhodium(I) in 5 mL of benzene was stirred for 14 h at room temperature. The resulting mixture was treated with a silica gel column (200-300 mesh, length 30 mm, i.d. 35 mm, elution with hexane) to remove any rhodium complexes. After evaporation of hexane, the residue was distilled under reduced pressure (1 torr) to give a mixture of 2,4-diphenylbut-1-en-3-yne and 1,4-diphenylbut-1-en-3-yne in a ratio of 2:3. For 2,4-diphenylbut-1-en-3-yne: mass m/e 204(M^+); ^1H NMR 5.79 (d, 1H, J=0.9 Hz, $H_AC(H_B)=C$), 6.00 (d, 1H, J=0.9 Hz, $H_BC(H_A)=C$), 7.28-7.82

(m, 10H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) 88.7, 90.8 (acetylenic carbons), 120.5, 123.0, 126.0, 128.2 (3 carbons), 128.6, 131.5 (phenyl ring carbons), 136.9, 137.1 (olefinic carbons).

(E)-1-(Methyldiphenylsilyl)pent-1-en-3-yne (4). In a 10 mL Schlenk tube was placed 0.2120 g (0.48 mmol) of **2a** dissolved in 2 mL of THF. The contents of the Schlenk tube were cooled down to -78°C. To this solution was added 0.4 mL of an ether solution of methyllithium (0.6 mmol) and the mixture was stirred at room temperature for 6 h. The mixture was again cooled down to -78 °C, and then 0.35 mL (0.60 mmol) of methyl iodide was added to the mixture. The reaction mixture was stirred overnight at room temperature. To this was added 10 mL of hexane, and the resulting precipitates were filtered off. Product **4** (0.1172 g, 94% yield) was isolated by MPLC (silica gel 40-63 mμ, length 300 mm, i.d. 25 mm, flow rate 10 mL/min, elution with hexane). Mass m/e 262(M^+); IR $\nu_{C\equiv C}$ 2215 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.57 (s, 3H, MeSi), 1.90 (d, 3H, MeC, J= 2 Hz), 5.87 (dq, 1H, HC=C, J= 19 Hz and 2 Hz), 6.59 (d, 1H, HC=C, J=19 Hz), 7.13-7.66 (m, 10H, ring protons); ^{13}C NMR (δ in $CDCl_3$) -3.98 (MeSi), 4.26 (Me-C), 80.27, 88.02 (acetylenic carbons), 127.90 (olefinic and ring carbon), 139.01 (olefinic carbon), 129.46, 134.87, 135.70 (phenyl ring carbons). Anal. Calcd for $C_{18}H_{18}Si$: C,82.38; H, 6.91. Found: C, 82.35; H, 6.87.

1-(1-Phenyltetramethyldisilanyl)but-1-en-3-yne (5). To a solution of 5.05 g (11.6 mmol) of **2e** in 20 mL of diethylether was added 19.2 mL (28.8 mmol) of a diethylether solution of methyllithium at -78°C. The mixture was stirred at room temperature for 14 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with diethylether. The organic layer and extracts were combined and washed with water, and then dried over potassium carbonate. The solvent ether was evaporated and the yield of the product was determined by GLC (96% yield). Product **5** was isolated by MPLC (silica gel 40-63 mμ, length 310 mm, i.d. 25 mm, elution with hexane). Mass m/e 244 (M^+); ^{1}H NMR (δ in CCl_4) 0.07

(s, 9H, Me_3Si), 0.35 (s, 3H, MeSi), 2.74 (d, 1H, acetylenic proton, J=1.8 Hz), 5.72 (dd, 1H, olefinic proton, J=18.3 Hz, 1.8 Hz), 6.54 (d, 1H, olefinic proton, J=18.3 Hz), 7.02-7.35 (m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) -6.05 (Me_3Si), -2.04 (MeSi), 77.70, 83.88 (acetylenic carbons), 123.75, 127.92, 128.84, 134.37 (phenyl ring carbons), 136.21, 144.83 (olefinic carbons). Exact mass Calcd for $C_{14}H_{20}Si_2$: 244.1101. Found: 244.1093.

(E)-4-(Methyldiphenylsilyl)but-1-en-3-yne (6). To a solution of 0.5056 g (1.14 mmol) of **2a** dissolved in 12.5 mL of ether was added 0.25 mL of 0.1N sodium methoxide-methanol solution. The mixture was stirred for 50 h at room temperature. The mixture was treated with a silica gel column (200-300 mμ, length 200 mm, i.d.35 mm, elution with hexane) and then the mixture was concentrated under reduced pressure. Product **6** (0.2591 g, 92% yield) was isolated by MPLC (silica gel, 40-63 mμ, length 310 mm, i.d. 25 mm, flow rate 10 mL/min, elution with hexane). Mass m/e 248 (M^+); IR $\nu_{C\equiv C}$ 2097 cm^{-1}, ^1H NMR (δ in $CDCl_3$) 0.62 (s,3H, MeSi), 2.65 (d, 1H, HC≡C), 5.90 (dd, 1H, HC=C, J=2 and 19 Hz), 6.82 (d, 1H, HC=C, J=19 Hz), 7.10-7.65 (m, 10H, ring protons); ^{13}C NMR (δ in $CDCl_3$) -4.08 (MeSi), 78.76, 83.58 (acetylenic carbons), 126.05, 128.00, 129.61, 134.87 (phenyl ring carbons), 135.07, 143.31 (olefinic carbons). Anal. Calcd for $C_{17}H_{16}Si$: C, 82.20; H, 6.49. Found: C, 82.10; H,6.38.

(E,E)-1-(dimethylphenylsilyl)-4-(methyldiphenylsilyl)but-1,3-diene (7). A solution of 0.2160 g (0.87 mmol) of **6** and 0.1365 g (1.0 mmol) of dimethylphenylsilane in the presence of chloroplatinic acid catalyst in 2 mL of hexane was stirred for 60 h at room temperature. The reaction mixture was treated with a silica gel column (200-300 mesh, length 200 mm, i.d. 35 mm), eluting with hexane to remove the platinum catalyst. Product **7** (0.2242 g, 67% yield) was isolated by MPLC under the same conditions as above. Mass m/e 307 (M^+-C_6H_5); ^1H NMR (δ in $CDCl_3$) 0.38 (s, 6H, Me_2Si), 0.66 (s, 3H, MeSi), 5.93-6.70 (m, 4H, HC=C), 7.30-7.61 (m, 15H, ring protons); ^{13}C NMR (δ in

$CDCl_3$) -3.74 (MeSi), -2.62 (Me_2Si), 129.02, 130.73, 147.84, 149.79 (olefinic carbons), 127.85 (2 carbons), 129.32, 133.85, 134.87 (2 carbons), 136,39, 138.34 (phenyl ring carbons). Anal. Calcd for $C_{25}H_{28}Si_2$: C, 78.06; H, 7.34. Found: C, 77.98; H, 7.30.

(E,E)-1,4-Bis(methyldiphenylsilyl)but-1,3-diene (8). A mixture of 10.00 g (22.5 mmol) of **2a** and 5 mL of 0.1 N sodium methoxide-methanol solution in 200 mL of ether was stirred for 2 days. The solvent was evaporated and the residue was directly chromatographed on silica gel (200-300 mesh, length 300 mm, i.d. 35 mm),eluting with hexane. The resulting solution was concentrated to give crude **6**. To the crude **6** dissolved in 40 mL of hexane was added 7.4736 g (22.6 mmol) of methyldiphenylsilane and two drops of a solution of chloroplatinic acid-isopropanol. The mixture was stirred for 2 days and the resulting crystals were filtered off. Recrystallization from ethanol gave 6.5273 g (65% yield) of **8**: mp 136 °C; mass m/e 446 (M^+); ^1H NMR (δ in $CDCl_3$) 0.63 (s, 6H, MeSi), 6.04-6.91 (m, 4H, HC=C), 7.29-7.70 (m, 20H, ring protons); ^{13}C NMR (δ in $CDCl_3$) -3.79 (MeSi), 127.85, 129.32, 134.83, 136.24 (phenyl ring carbons), 131.41, 149.55 (olefinic carbons). Anal. Calcd for $C_{30}H_{30}Si_2$: C, 80.66; H, 6.77. Found: C, 80.55; H, 6.70.

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Chapter 6.

Nickel-Catalyzed Reactions of Ethynylsilanes for the Formation of Dienyne Systems

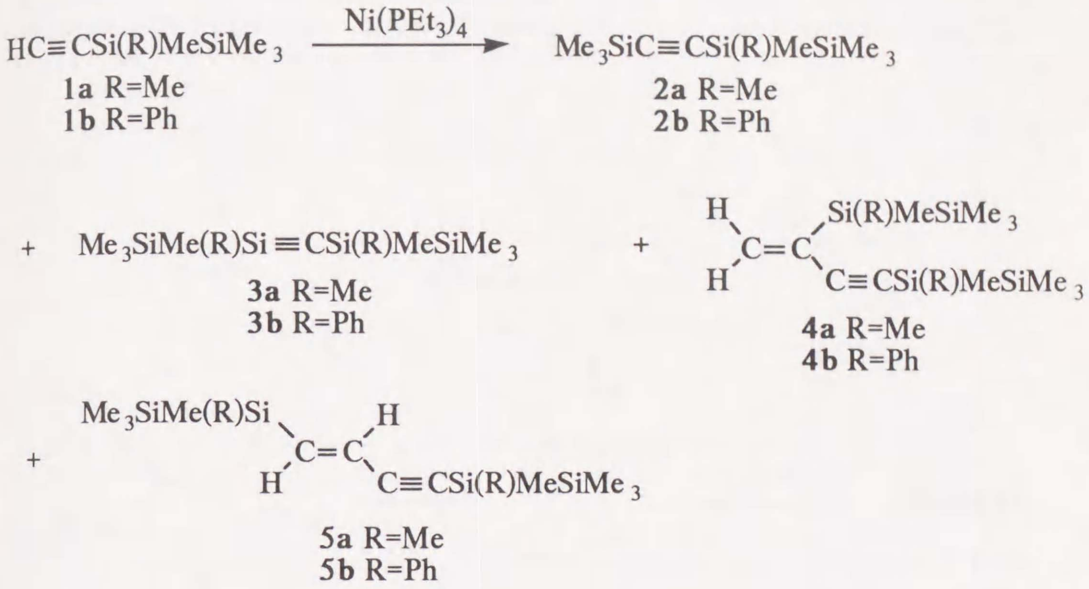
Introduction

As described in Chapter 5, we found that the palladium(0)- and rhodium(I)-catalyzed reaction of ethynylsilanes offers a convenient route to constitute enyne systems. In this Chapter, we will describe the nickel-catalyzed reactions of ethynylsilanes. The reactions of ethynylsilanes with diphenylacetylene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) proceed with remarkable regio- and stereospecificities to afford dienynes in good yields.

Results and Discussion

Nickel-Catalyzed Reactions of Ethynylsilanes. First, we investigated the reactions of ethynylsilanes in the absence of diphenylacetylene. Thus, when a benzene solution of a mixture of ethynylpentamethyldisilane (**1a**) and a catalytic amount of tetrakis(triethylphosphine)nickel(0) was heated in a degassed sealed glass tube at 100°C for 20 h, four products, (trimethylsilylethynyl)pentamethyldisilane (**2a**), bis(pentamethyldisilanyl)acetylene (**3a**), 1-(pentamethyldisilanyl)-1-[(pentamethyldisilanyl)ethynyl]ethene (**4a**), and (E)-1,4-bis(pentamethyldisilanyl)but-1-ene-3-yne (**5a**) in 14, 4, 28, and 48% yields, respectively. Similar reaction of 1-ethynyl-1-phenyltetramethyldisilane (**1b**) afforded 1-(trimethylsilylethynyl)-1-phenyltetramethyldisilane (**2b**), bis(1-phenyltetramethyldisilanyl)acetylene (**3b**), 1-(1-phenyltetramethyldisilanyl)-1-[(1-phenyltetramethyldisilanyl)ethynyl]ethene (**4b**), and (E)-1,4-bis(1-phenyltetramethyldisilanyl)but-1-ene-3-yne (**5b**), in 10, 2, 8, and 38% yields, respectively.

These products were isolated by preparative GLC. All spectral data obtained for **2a**,**b**, **3a**,**b**, and **5a**,**b** were identical with those of authentic samples. The structure of **4a**,**b** were confirmed by spectroscopic analysis (see Experimental Section). Compounds **2a**, **2b**, **3a**, and **3b** can be explained in terms of the redistribution reactions of ethynyldisilanes, while **4a** and **4b**, and **5a** and **5b** are head-to-tail[1] and head-to-head coupling products, respectively.[2-5]



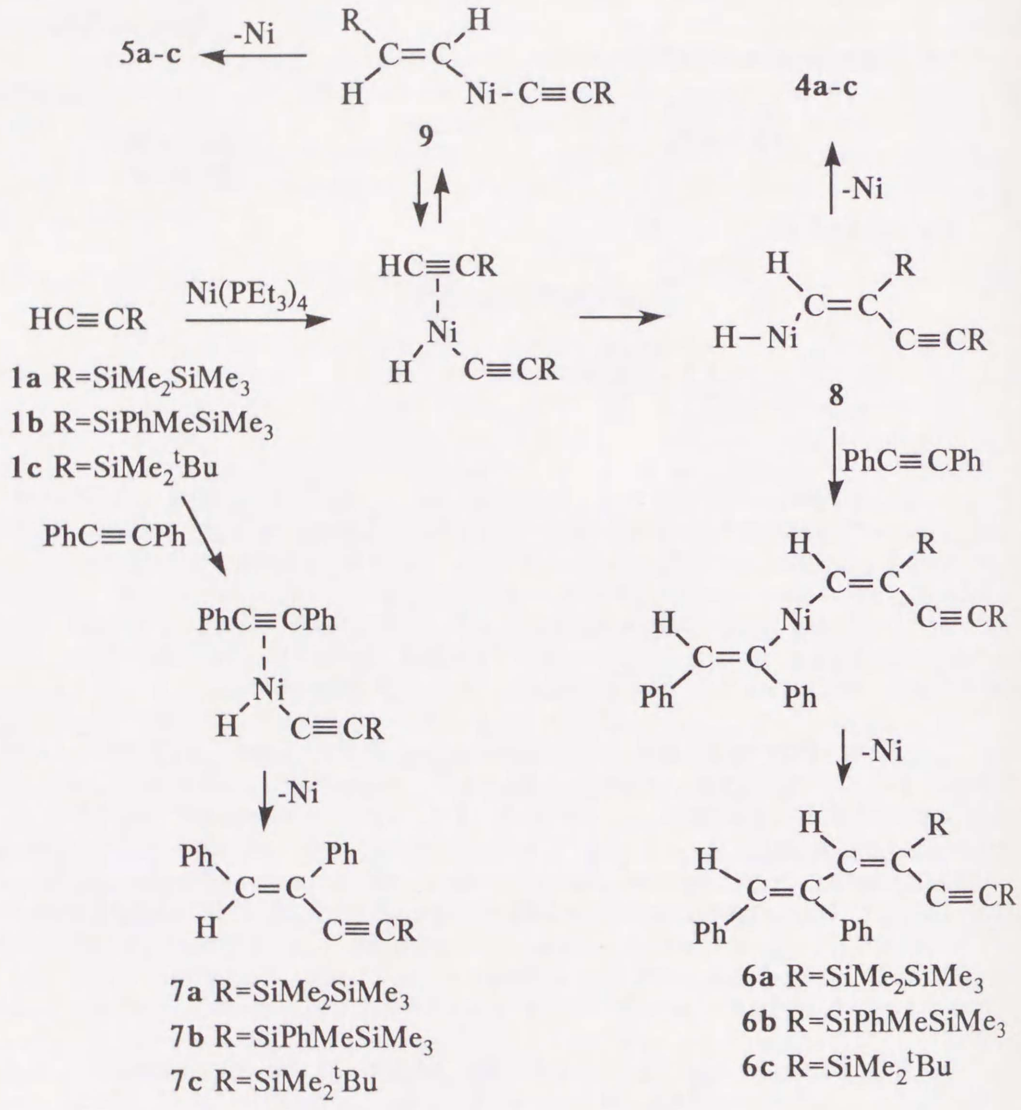
In sharp contrast to the palladium- and rhodium-catalyzed reactions of ethynyldisilanes which gave head to head dimer as the sole volatile product (Chapter 5), these nickel-catalyzed reactions proceeded with relative low regioselectivities to give mixtures of the head-to-tail and the head-to-head dimers in addition to a large amount of redistribution products.

The Formation of Dienyne Systems. Next, we carried out the reaction of ethynylsilanes with diphenylacetylene. When **1a** was treated with an equimolar amount of diphenylacetylene under the same conditions, a dienyne identified from its spectral data as (E,E)-bis(pentamethyldisilanyl)-5,6-diphenylhexa-3,5-dien-1-yne (**6a**) was obtained in 60% yield, in addition to a small amount of an enyne, (E)-1-(pentamethyldisilanyl)-3,4-diphenylbut-3-en-1-yne (**7a**) (9%).

Similar reaction of **1b** with diphenylacetylene readily proceeded to afford (E,E)-1,3-bis(1-phenyltetramethyldisilanyl)-5,6-diphenyl-3,5-dien-1-yne (**6b**) in 60% yield, in addition to 10% of homo-coupling product (**5b**) and 8% of cross-coupling product, (E)-(1-phenyltetramethyldisilanyl)-3,4-diphenylbut-3-en-1-yne (**7b**).

Ethynyl-substituted monosilanes also react with diphenylacetylene to give the dienyne system, analogous

Scheme 1



to the reactions of ethynyldisilanes. Thus, heating of a 1:1 mixture of ethynyl(tert-butyl)dimethylsilane (**1c**) and diphenylacetylene in the presence of the nickel catalyst afforded (E,E)-1,3-bis(tert-butyldimethylsilyl)-5,6-diphenylhexa-3,5-dien-1-yne (**6c**) in 49% yield, in addition to 15% of (E)-(tert-butyldimethylsilyl)-3,4-diphenylbut-3-en-1-yne (**7c**). All products were isolated by MPLC. In all cases, only a single regio- and stereoisomer is observed for dienyne system.

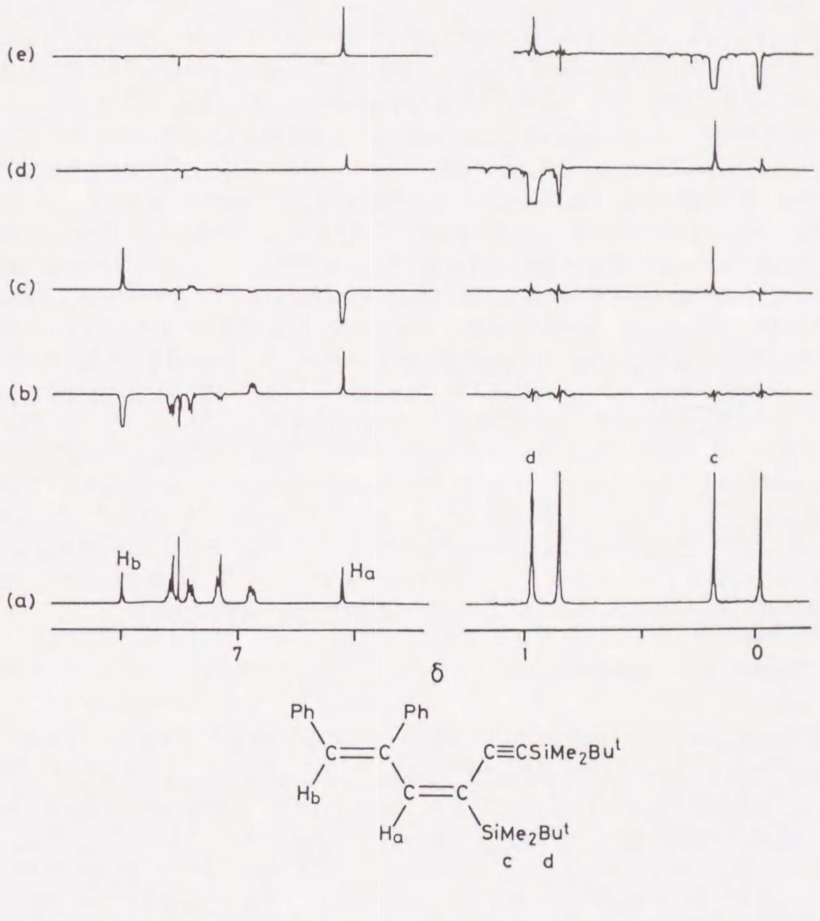


Figure 1. NOE-FID difference spectra of compound **7c**: (a) 400 MHz ^1H NMR spectrum of **7c** in $CDCl_3$; (b) irradiation of Hb proton; (c) irradiation of Ha proton; (d) irradiation of tert-butyl protons; (e) irradiation of dimethylsilyl protons.

The (E,E)-geometry of the products, **7a**, **7b**, and **7c** were easily established from their NOE-FID difference spectra. Figure 1 shows the results of NOE experiments for the product **7c** as a typical example. Thus, irradiation of an olefinic proton at the C_6 position (7.50 ppm) led to enhancement of the olefinic proton at the C_4 position (6.55 ppm), while irradiation of the olefinic proton at the C_4 position (6.55 ppm) resulted in a positive NOE of the olefinic proton at the C_6 position (7.50 ppm) as well as dimethylsilyl protons at the C_3 position (0.18 ppm). Similar irradiation of tert-butyl protons and dimethylsilyl protons of a tert-butyldimethylsilyl group at the C_3 position, respectively, led to enhancement of the olefinic proton at the C_4 position (6.55 ppm).

Scheme 1 illustrates a possible mechanistic interpretation. The formation of the dienyne system requires activation of a carbon-hydrogen bond, followed by two successive carbon-carbon bond formation. Insertion of a nickel species into a C-H bond of the ethynylsilane gave a hydrido-(ethynyl)-nickel species. Migration of the hydride ligand to the triple bond of another coodinated ethynylsilane affords an ethynyl-nickel complex (**8**), while migration of ethynyl ligand gives a hydrido-nickel complex (**9**). From the complexes **8** and **9**, elimination of the nickel species would take place to give the respective head-to-head and head-to-tail coupling products **4** and **5** in the absence of diphenylacetylene. In the presence of diphenylacetylene, however, **8** reacts with diphenylacetylene to afford dienyne systems.

Experimental Section

General. All nickel-catalyze reactions were carried out in degassed sealed glass tube. ^1H NMR spectra were determined at ambient temperature with a JEOL Model PMX-60, a JEOL Model JNM-FX-90, a JEOL Model JNM-MH-100, and a JEOL Model JNM-GX-400 spectrometer using carbon tetrachloride or deuteriochloroform solutions containing cyclohexane as an internal standard. ^{13}C NMR spectra were measured on a JEOL Model JNM-FX-90A spectrometer and a JEOL Model JNM-GX-400 spectrometer in deuteriochloroform as a solvent. Mass spectra were measured on a JEOL Model JMN-D300 spectrometer equipped with a JMA-2000 data processing system.

Materials. All ethynylsilanes used as the starting compounds were synthesized by the reaction of ethynylmagnesium bromide with the corresponding chlorosilanes and chlorodisilanes by the method reported in the literature.[6] Benzene, THF, and hexane were dried over lithium aluminum hydride and distilled just before use.

Preparation of 2a. To 2.9 g (17.4 mmol) of chloropentamethyldisilane was added dropwise with ice-cooling 21.6 mmol of (trimethylsilyl)ethynyllithium prepared from (trimethylsilyl)acetylene and n-butyllithium in a mixed solvent of 5 mL of THF and 10 mL of hexane. The mixture was stirred for 2 h at room temperature and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over potassium carbonate. The solvent was evaporated and the residue was distilled under reduced pressure to give 2.9 g (73% yield) of **2a**: bp 64°C (20 mmHg); MS m/e 228 (M^+); 90 MHz ^1H NMR (δ in $CDCl_3$) 0.10 (s, 9H, Me_3Si), 0.15 (s, 9H, Me_3Si), 0.17 (s, 6H, Me_2Si); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -3.1, -2.6, 0.1 (MeSi), 113.0, 116.3 (C≡C). Anal Calcd for $C_{10}H_{24}Si_3$: C, 52.55; H, 10.58. Found: C, 52.52; H, 10.43.

Preparation of 2b. To 4.0 g (17.5 mmol) of 1-chloro-1-phenyltetramethyldisilane was added dropwise with ice-cooling 21.6 mmol of (trimethylsilyl)-ethynyllithium prepared from (trimethylsilyl)acetylene and n-butyllithium in a mixed solvent of 5 mL of THF and 10 mL of hexane. The mixture was stirred for 2 h at room temperature and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over potassium carbonate. The solvent was evaporated and the residue was distilled under reduced pressure to give 3.8 g (75% yield) of **2b**: bp 60-62°C (1 mmHg); MS m/e 290 (M^+); 90 MHz ^1H NMR (δ in $CDCl_3$) 0.09 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 0.42 (s, 3H, MeSi), 7.20-7.65 (m, 5H, Ph); ^{13}C NMR (δ in $CDCl_3$) -4.3, -2.5, 0.0 (MeSi), 110.4, 118.5 (C≡C), 127.9, 128.8, 134.1, 135.7 (Ph). Anal Calcd for $C_{15}H_{26}Si_3$: C, 61.99; H, 9.02. Found: C, 61.91; H, 9.02.

Nickel-Catalyzed Reaction of 1a. A mixture of 168.3 mg (0.929 mmol) of **1a** and 82.2 mg (16.7 mol%) of tetrakis(triethylphosphine)nickel(0) in 2 mL of benzene was heated at 100°C in a sealed glass tube. The resulting mixture was treated with flash column chromatography on silica gel eluting with hexane to remove any nickel species and polymeric substances. 20.7 mg (0.145 mmol) of decane was added to the mixture as an internal standard, and the mixture was analyzed by GLC as being **2a** (14%), **3a** (4%), **4a** (28%), and **5a** (48%). The products were isolated by preparative GLC. All spectral data obtained for **2a**, **3a**,[6] and **5a**[7] were identical with those of authentic samples. For **4a**: MS m/e 312 (M^+); IR $\nu_{C\equiv C}$ 2120 cm^{-1}; 100 MHz ^1H NMR (δ in CCl_4) 0.08 (s, 6H, Me_2Si), 0.10 (s, 9H, Me_3Si), 0.18 (2s, 15H, Me_2Si and Me_3Si), 5.65 (d, 1H, J=4 Hz, olefinic proton), 6.14 (d, 1H, J=4 Hz, olefinic proton). Exact MS Calcd for $C_{14}H_{32}Si_4$: 312.1581. Found: 312.1605.

Nickel-Catalyzed Reaction of 1b. Reaction of **2b** was carried out as a similar manner to that of 1a. All spectral data obtained for **2b** and **5b**[7] were identical with those of authentic samples. For **3b**: MS m/e 410 (M^+); IR $\nu_{C\equiv C}$ 2100 cm^{-1}; 100 MHz ^1H NMR (δ in CCl_4) 0.12 (s, 18H, Me_3Si), 0.42 (s, 6H, Me_2Si), 7.20-7.66 (m, 10H, Ph). Anal. Calcd for $C_{22}H_{34}Si_4$: C, 64.31; H, 8.34. Found: C, 64.47; H, 8.51. For **4b**: MS m/e 436 (M^+); IR $\nu_{C\equiv C}$ 2120 cm^{-1}; 100 MHz ^1H NMR (δ in CCl_4) 0.06 (s, 9H, Me_3Si), 0.15 (s, 9H, Me_3Si), 0.42 (s, 3H, MeSi), 0.45 (s, 3H, MeSi), 5.73 (d, 1H, J=4 Hz, olefinic proton), 6.28 (d, 1H, J=4 Hz, olefinic proton), 7.19-7.65 (m, 10H, Ph). Exact MS Calcd for $C_{24}H_{36}Si_4$: 436.1894. Found: 436.1908.

Reaction of 1a with Diphenylacetylene. A mixture of 280.6 mg (1.80 mmol) of **1a**, 312.8 mg (1.76 mmol) of diphenylacetylene, and 37.4 mg (4 mol%) of tetrakis(triethylphosphine)nickel(0) in 2 mL of benzene was heated at 100°C for 20 h. The resulting mixture was treated with flash column chromatography on silica gel to remove any nickel species. The resulting mixture was analyzed by GLC using 19.4 mg (0.114 mmol) of dodecane as an internal standard as being **6a** (60%) and **7a** (9%). Compounds **6a** and **7a** were isolated by MPLC (silica gel, elution with hexane). For **6a**: MS m/e 490 (M^+); IR $\nu_{C\equiv C}$ 2100 cm^{-1}; 400 MHz ^1H NMR (δ in $CDCl_3$) 0.05 (s, 9H, Me_3Si), 0.07 (s, 6H, Me_2Si), 0.14 (s, 9H, Me_3Si), 0.25 (s, 6H, Me_2Si), 6.50 (br s, 1H, olefinic proton), 6.93-7.32 (m, 10H, Ph), 7.37 (br s, 1H, olefinic proton); 100 MHz ^{13}C NMR (δ in $CDCl_3$) -4.2, -2.6, -2.4, -1.8 (MeSi), 107.5, 107.9 (acetylenic carbons), 127.0, 127.3, 127.8, 128.5, 129.6, 129.7, 130.7, 132.3, 136.9, 140.1, 140.3, 147.1 (olefinic and phenyl ring carbons). Exact MS Calcd for $C_{28}H_{42}Si_4$: 490.2362. Found: 490.2345. For **7a**: MS m/e 334 (M^+); IR $\nu_{C\equiv C}$ 2130 cm^{-1}; 100 MHz ^1H NMR (δ in CCl_4) 0.15 (s, 9H, Me_3Si), 0.25 (s, 6H, Me_2Si), 6.33 (br s, 1H, olefinic proton), 6.84-7.37 (m, 10H, Ph). Exact MS Calcd for $C_{21}H_{26}Si_2$: 334.1572. Found: 334.1542.

Reaction of 1b with Diphenylacetylene. A mixture of 261.6 mg (1.47 mmol) of **1b**, 384.0 mg (1.76 mmol) of diphenylacetylene, and 31.0 mg (4 mol%) of tetrakis(triethylphosphine)nickel(0) in 2 mL of benzene was heated at 100°C for 20 h. The resulting mixture was treated flash column chromatography on silica gel to remove any nickel species. The resulting mixture was analyzed by GLC using 19.1 mg (0.122 mmol) of undecane as an internal standard as being **5b** (8%), **6b** (60%) and **7b** (10%). Compounds **5b**, **6b** and **7b** were isolated by MPLC (silica gel, elution with hexane). All spectral data obtained for **5b** were identical with those of an authentic sample. For **6b**: MS m/e 614 (M^+); IR $\nu_{C\equiv C}$ 2100 cm^{-1}; 100 MHz ^1H NMR (δ in CCl_4) -0.04 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 0.28 (s, 3H, MeSi), 0.53 (s, 3H, MeSi), 6.55 (br s, 1H, olefinic proton), 6.71-7.71 (m, 21H, olefinic and phenyl ring protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -5.2 , -3.9, -2.3, -1.3 (MeSi), 105.3, 108.7 (acetylenic carbons), 127.0, 129.9, 134.2, 134.8, 137.4, 140.7, 141.7, 147.3 (olefinic and phenyl ring carbons). Exact MS Calcd for $C_{38}H_{46}Si_4$: 614.2676. Found: 614.2722. For **7b**: IR $\nu_{C\equiv C}$ 2140 cm^{-1}; 60 MHz ^1H NMR (δ in CCl_4) 0.11 (s, 9H, Me_3Si), 0.47 (s, 3H, MeSi), 6.65-7.29 (m, 15H, Ph). Exact MS Calcd for $C_{26}H_{28}Si_2$: 396.1729. Found: 396.1739.

Reaction of 1c with Diphenylacetylene. A mixture of 276.5 mg (1.98 mmol) of **1c**, 331.0 mg (1.86 mmol) of diphenylacetylene, and 37.4 mg (4 mol%) of tetrakis(triethylphosphine)nickel(0) in 2 mL of benzene was heated at 100°C for 20 h in a sealed glass tube. The resulting mixture was analyzed by GLC using 19.6 mg (0.115 mmol) of dodecane as an internal standard as being **6c** (49%) and **7c** (15%). Compounds **6c** and **7c** were isolated by MPLC (silica gel, elution with hexane). For **6c**: MS m/e 458 (M^+); IR $\nu_{C\equiv C}$ 2100 cm^{-1}; 400 MHz ^1H NMR (δ in $CDCl_3$) -0.02 (s, 6H, Me_2Si), 0.18 (s, 6H, Me_2Si), 0.85 (s, 9H, ^tBu), 0.97 (s, 9H, ^tBu), 6.55 (d, 1H, J=0.85 Hz, olefinic proton), 6.93-7.31 (m, 10H, Ph), 7.50 (br s, 1H, olefinic proton); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -6.1, -4.3 (MeSi), 16.7, 17.9 (CMe_3), 26.3, 26.9 (Me_3C), 106.9, 107.1 (acetylenic carbons), 127.1, 127.4, 127.8, 128.5, 129.5, 129.8, 130.7, 132.7, 136.9, 138.5, 139.9, 149.6 (olefinic and phenyl ring carbons). Exact MS Calcd for $C_{30}H_{42}Si_2$: 458.2825. Found: 458.2840. For **7c**: MS m/e 318 (M^+); IR $\nu_{C\equiv C}$ 2130 cm^{-1}; 60 MHz ^1H NMR (δ in CCl_4) 0.16 (s, 6H, Me_2Si), 0.99 (s, 9H, ^tBu), 6.90-7.40 (m, 11H, olefinic and phenyl ring protons). Exact MS Calcd for $C_{22}H_{26}Si$: 318.1803. Found: 318.1818.

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7) see Chapter 5

Chapter 7.

Synthesis and Properties of Poly[(disilanylene)-butenyne-1,4-diyls] and Poly[(methylphenylsilylene)butenyne-1,4-diyl]

Introduction

The polymers that have silicon-silicon bonds in a main chain are of considerable interest, because they might be used as functional materials such as photoresists, semiconducting materials, and precursors of silicon carbide.[1] Recently, we have reported the synthesis and some properties of the polymers that have regular alternating arrangement of an Si-Si bond and a π-electron system such as phenylene,[2] ethenylene,[3] ethynylene,[4] diethynylene,[5] furylene,[6] and thienylene[7] in the polymer backbone. We have found that these polymers are highly photoactive, and become conducting when thin solid films of the polymers are treated with SbF_5 vapor. The method used for the synthesis of these polymers is limited to either the sodium condensation reactions of bis(chlorosilyl)-substituted compounds[2,3,6-10] or the reaction of dilithio compounds bearing a π-electron system with 1,2-dichlorodisilanes,[5,11] with one exception of ring-opening polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes catalyzed by alkyllithium.[4] Although the sodium condensation reaction of bis(chlorosilyl)-substituted compounds offers a convenient route to the polymer synthesis, there are some limitation for reproducibility of yields and molecular weights of the polymers. Moreover, this method cannot be used for the synthesis of the polymers bearing functional groups which are sensitive to alkali metals.

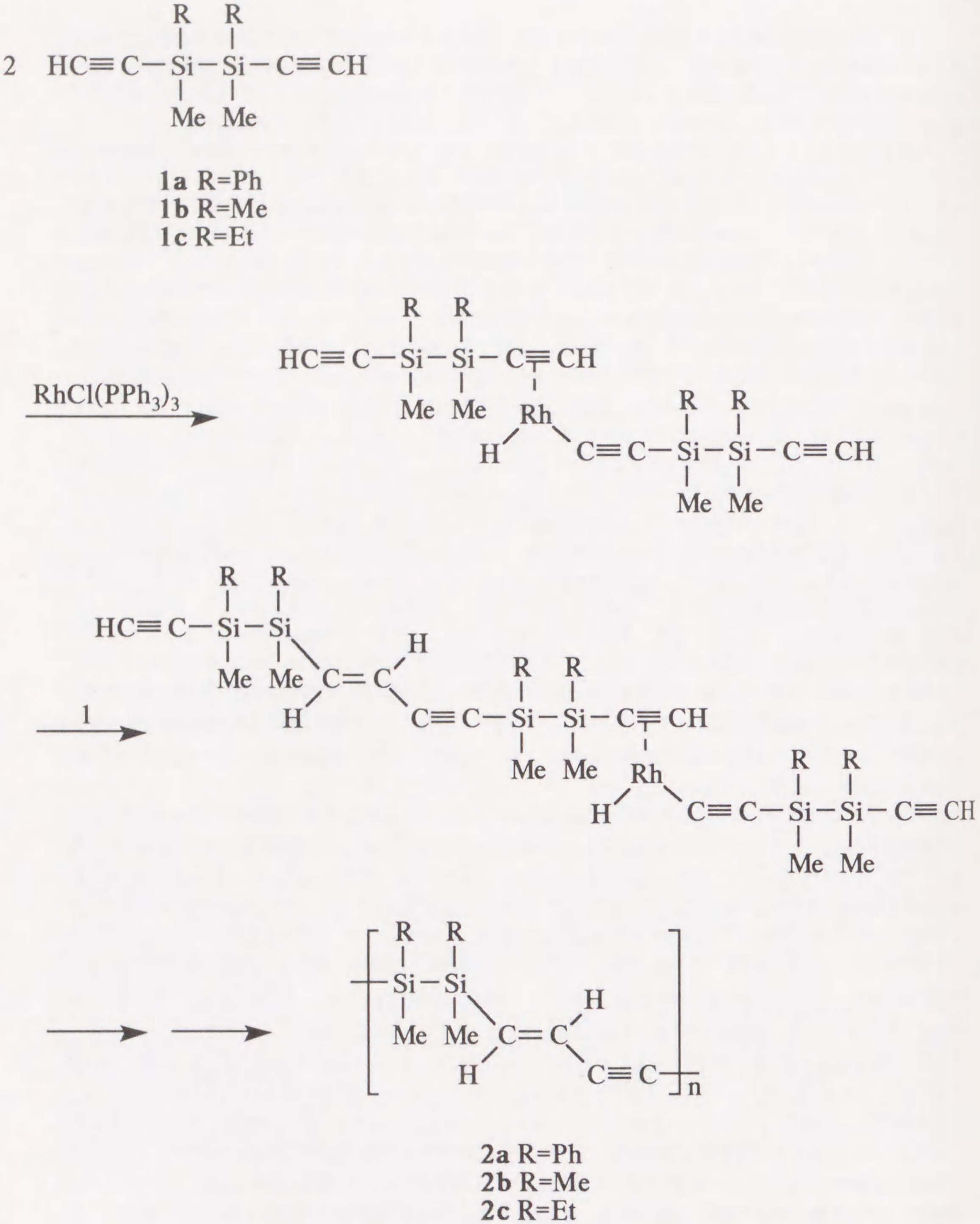
In Chapter 5, it is described that the rhodium(I)-catalyzed dimerization reaction of ethynylsilanes affords enynes in high yields.[10] In this Chapter the synthesis of poly[(disilanylene)butenyne-1,4-diyls] and poly[(silylene)butenyne-1,4-diyl] by the rhodium(I)-catalyzed reaction of 1,2-diethynyldisilanes and diethynylmonosilane is described. The photochemical and conducting properties of the resulting polymers are also described.

Results and Discussion

Synthesis of Poly[(disilanylene)butenyne-1,4-diyls] and Poly[(methylphenyllsilylene)-butenyne-1,4-diyl]. The reactions of 1,2-diethynyldisilanes with a catalytic amount of a rhodium(I) complex readily proceed to give poly[(disilanylene)butenyne-1,4-diyls] in good yields. Thus, when 1,2-diethynyl-1,2-dimethyldiphenyldisilane (**1a**) was treated with 1 mol% of chlorotris-(triphenylphosphine)rhodium(I) in toluene at room temperature for 2 days, poly[(1,2-dimethyldiphenyl-disilanylene)butenyne-1,4-diyl] (**2a**) was obtained as light yellow solids in 73% yield. Monitoring the progress of the reaction by using an IR spectrometer, the absorption bands at 3280 and 2040 cm^{-1} due to the stretching frequencies of an acetylenic C-H bond and a mono-substituted carbon-carbon triple bond of the starting monomer decrease with increasing reaction time. A new absorption band at 2146 cm^{-1} attributable to the stretching frequency of a disubstituted carbon-carbon triple bond appears during the reaction and this band increases with increasing reaction time. After 2 d-reaction, the IR spectrum of the reaction mixture showed that almost all starting **1a** was consumed as indicated by the disappearance of the absorption bands at 3280 and 2040 cm^{-1}. Only one absorption band at 2146 cm^{-1} was observed in the IR spectrum of the reaction mixture.

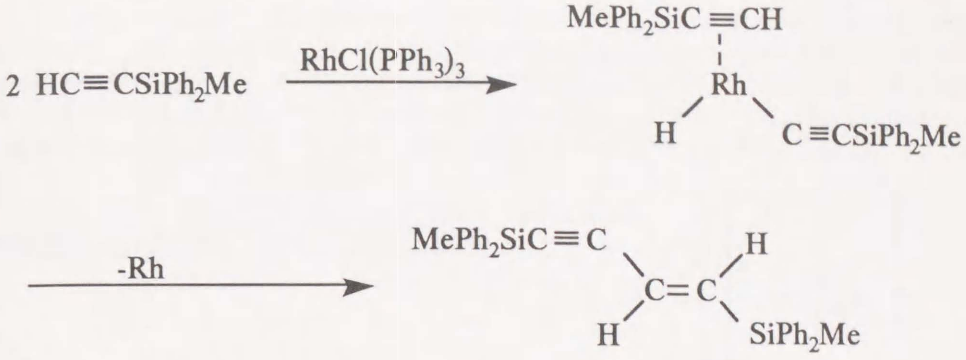
The structure of **2a** was verified by spectrometric analysis. The ^1H NMR spectrum of **2a** shows a singlet δ at 0.47 ppm and doublets at 5.93 and 6.66 ppm attributed to methylsilyl protons and olefinic protons, respectively. The coupling constant of the olefinic protons (19 Hz) clearly indicates that the polymer must have an (E)-configuration. Furthermore, the IR, and ^1H and ^{13}C NMR spectra of **2a** are similar to those of 1,4-bis(methyldiphenylsilyl)butenyne (**3**) prepared from the rhodium-catalyzed reaction of ethynylmethyldiphenyl-silane, as reported previously.[12] These results clearly indicate that the polymer backbone consists of the repeating unit of $-SiCH{=}CHC{\equiv}CSi-$. Although the ^{13}C NMR spectrum of **2a** is similar to that of **3** as shown in Figure 1, each of two singlets due to two kinds of

Scheme 1



1a R=Ph
1b R=Me
1c R=Et

2a R=Ph
2b R=Me
2c R=Et



3

methylsilyl carbons observed for **3** splits into two signals, with intensity ratio of 1:1 in the spectrum of **2a**. Each acetylenic carbon near at 91 and 110 ppm for **2a** also splits into four signals in the ratio of 1:1:1:1, but two of them are overlapping each other. Similar splitting is also observed for the olefinic carbons of **2a**. Thus, each of two signals observed in the spectrum of **3** splits into two signals with equal intensities. These splitting can be best explained by the existence of three kinds of the microstructure in the polymer backbone. The reaction presumably proceeds with activation of an acetylenic C-H bond, followed by addition of this bond across a triple bond of the molecule coordinating on the rhodium atom as shown in Scheme I. The C-H activation probably occurs both in the monomer and in the polymer with equal possibility, and therefore the polymer having three kinds of the microstructure **A**, **B**, and **C**, with a statistical ratio of 1:2:1 in the main chain would be produced.

-C≡CSiSiC≡C-	-CH=CHSiSiC≡C-	-CH=CHSiSiCH=CH-
A	B	C

Similar reactions of 1,2-diethynyltetramethyldisilane (**1b**) and 1,2-diethyl-1,2-diethynyldimethyldisilane (**1c**) in the presence of the rhodium(I) catalyst readily proceeded successfully to give poly[(tetramethyldisilanylene)butnyne-1,4-diyl] (**2b**) and poly[(1,2-diethyldimethyldisilanylene)butenyne-1,4-diyl] (**2c**) in 52% and 58% yields, respectively.

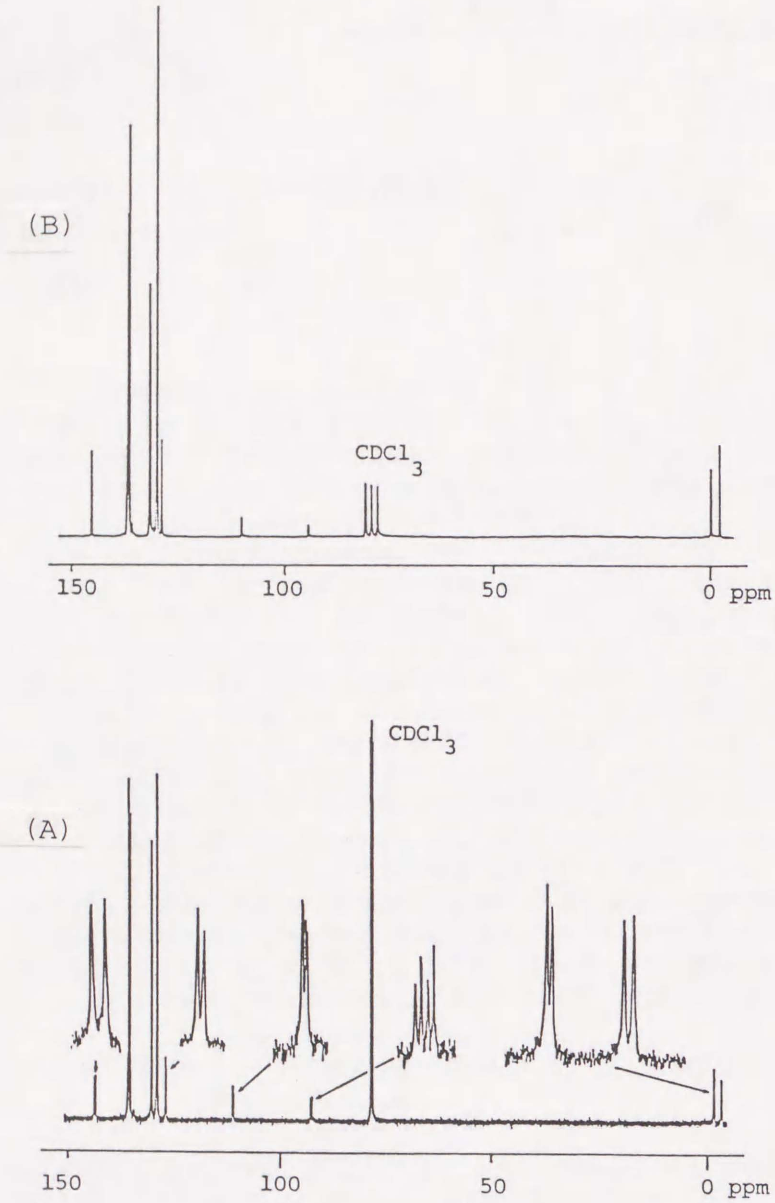
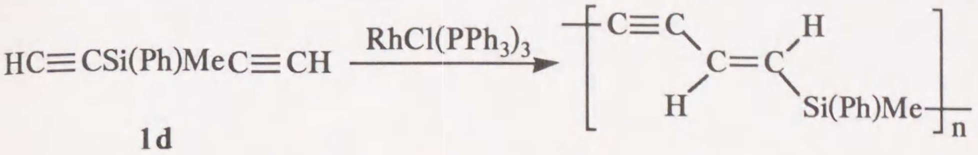


Figure 1. (A) 125 MHz $^{13}C\{^{1}H\}$ NMR spectra of **2a**; (B) 22.5 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **3**.

Diethynylmonosilane can also be used as a starting monomer. Thus, when diethynylmethylphenylsilane (**1d**) was treated with the rhodium catalyst in toluene under the same conditions, poly[(methylphenylsilylene)-butenyne-1,4-diyl] (**2d**) was obtained in 60% yield.



2d

The structures of these polymers **2b**-**d** were also confirmed by spectrometric analysis (see Experimental Section). The ^{13}C NMR spectra of the polymers **2b**-**d** indicate the presence of three different microstructures, **A**, **B**, and **C** with the ratio of 1:2:1.

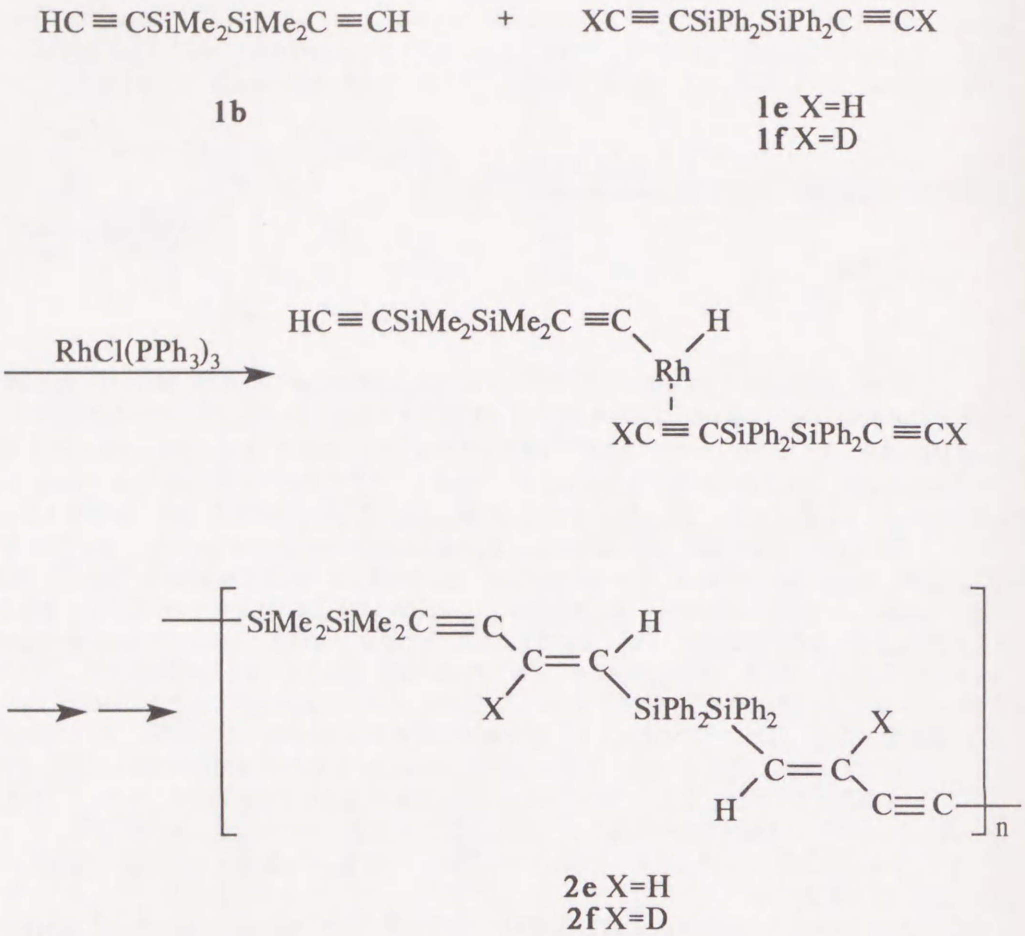
Polymers **2a**-**d** thus obtained are light yellow solids and soluble in common organic solvents, such as benzene, toluene, ethers, and chlorocarbons, but slightly soluble in hydrocarbons and insoluble in alcohols. The polymers **2a** and **2d** melt at 90-95°C and 114-122°C, respectively without decomposition, while, **2b** and **2c** don't melt even at above 300°C. The molecular weights of the polymers were determined by GPC, relative to polystyrene standards, to be Mw=117,000 (Mw/Mn=6.1), 28,000 (13.0), 22,000 (2.7), and 24,000 (3.5) for **2a**, **2b**, **2c**, and **2d**, respectively.

Although monomers **1a**-**d** could be transformed into polymers **2a**-**d** with high molecular weights, 1,2-diethynyltetraphenyldisilane (**1e**) and 1,3-diethynylhexamethyltrisilane did not afford corresponding polymers under the same conditions. The starting compounds were recovered unchanged.

When 1,4-diethynylbenzene was used as a starting monomer, insoluble substances were produced. No soluble polymers were obtained in this system. The presence of silylene or disilanylene units in the polymer chain seems to be necessary for obtaining soluble polymers.

Synthesis of Copolymer from Diethynyltetraphenyldisilane (1e) and 1b. As mentioned above diethynyltetraphenyldisilane (**1e**) afforded no

Scheme 2



polymer in the presence of the rhodium catalyst even at 50°C. However, when a 1:1 mixture of **1e** and **1b** was treated with the rhodium catalyst at room temperature, the reaction proceeded successfully to give alternating copolymer (**2e**) in 55% yield. The polymer **2e**, thus obtained is light yellow solids and melts at 84-98°C without decomposition. The molecular weight was measured to be 16,000 (Mw/Mn=2.6) by GPC relative to polystyrene standards. The IR spectrum shows an absorption band at 2146 cm^{-1} due to the stretching frequency of a disubstituted carbon-carbon triple bond. The ^1H NMR spectrum shows two doublets δ at 6.00 and 6.54 ppm (J=19 Hz) due to trans olefinic protons. The

^{13}C NMR spectrum of **2e** shows 4 signals δ at 89.1, 111.7 and 123.8, 146.3 ppm attributed to olefinic and acetylenic carbons, respectively. In contrast to the ^{13}C NMR spectra of **2a**-**d** in which each of four resonances due to the olefinic and acetylenic carbons splits into two, the spectrum for **2e** shows no such splitting, indicating the presence of only one microstructure in the polymer backbone.

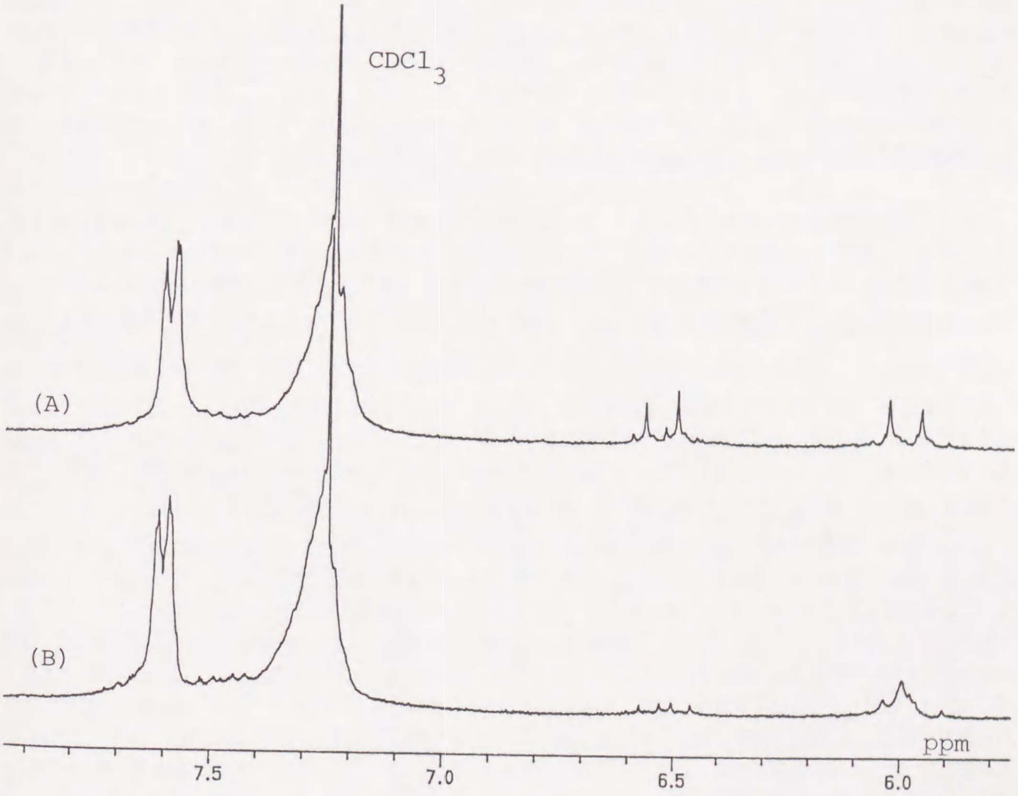


Figure 2. 270 MHz ^{1}H NMR spectra of (A) **2e** and (B) **2f**.

In order to get more information about the structure of **2e**, we carried out the copolymerization of 1,2-di(deuterioethynyl)tetraphenyldisilane (**1f**) with **1b** under the same conditions. As expected, copolymer (**2f**) was obtained in 49% yield. The ^{1}H NMR spectrum of the copolymer **2f** thus obtained shows no signals δ at 6.54 ppm, due to the olefinic protons, and the signal δ at 6.00 ppm observed as a doublet in the ^{1}H NMR spectrum of **2e** changes to a broad singlet, indicating that only the proton at the C_2 position in the enyne unit was replaced by a deuterium atom (Figure 2). These results can be best understood by assuming that the C-H bond activation by the rhodium(I)-catalyst occurs only in the acetylenic C-H bond of **1b**, but not the acetylenic C-H bond of **1e** and **1f**. The triple bonds of **1e** and **1f** can be coordinate to the rhodium species which insert into the C-H bond of **1b**. Addition of the activated C-H bond across the coordinated triple bond would produce the alternative polymer **2e** and **2f** as shown in Scheme 2.

Photochemical Properties of the Polymers 2a-e. UV spectra of disilanylene polymers **2a-c** and **2e** show absorption bands near at 290 nm which are remarkably red-shifted relative to that of **2d** (λ_{max} 220 nm), due to the delocarization of π-electrons through the Si-Si bonds and enyne units. Such red shifts are always observed in the polymers which involve a regular alternating arrangement of a disilanylene unit and a π-electron system.[1-11]

We investigated the photochemical behavior of the disilanylene polymers **2a-e**, by irradiating their thin solid films with a low-pressure mercury lamp in air. The progress of the reactions was followed by UV and IR spectroscopic method. Irradiation of the films of **2a-c** and **2e** resulted in rapid decrease of the absorption near at 290 nm in their UV spectra (Figure 3), and their IR spectra of the resulting films showed strong absorption bands at 3100 and 1050 cm^{-1} due to O-H and Si-O groups, respectively (Figure 4) . These results can be understood in terms of the homolytic scission of Si-Si bonds, followed by the reaction of the resulting silyl radicals with oxygen in air, analogous to the similar photolysis of poly[p-(disilanylene)phenylene] reported previously.[2]

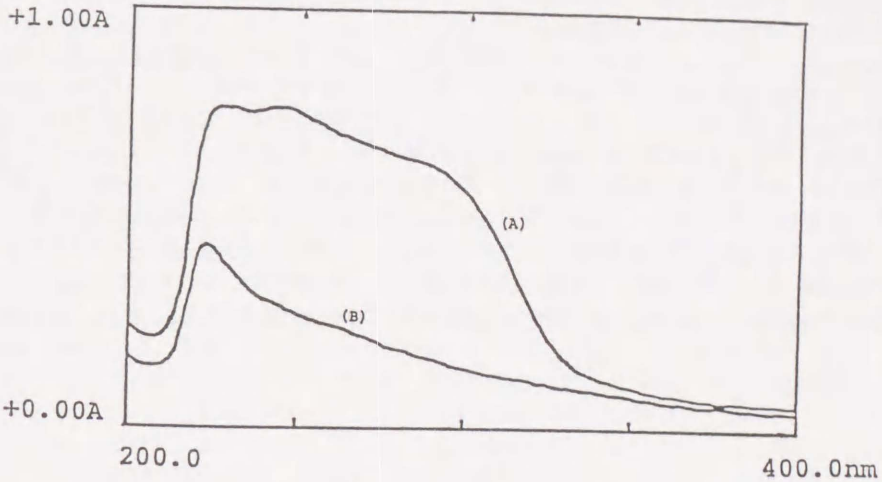


Figure 3. UV spectra of **2a** (A) before irradiation; (B) after 60 min irradiation

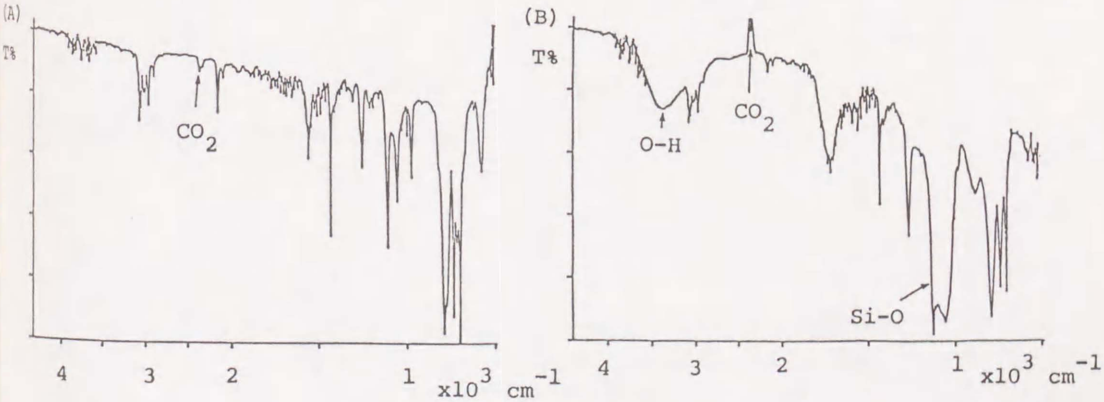


Figure 4. IR spectra of **2a** (A) before irradiation; (B) after 60 min irradiation

In order to learn much more about the photochemical properties of these polymers, we carried out the photolyses of the polymers **2a**-**e** in a benzene solution, and the molecular weights of photodegradation products were determined by GPC. As can be seen in Figure 5, the molecular weights of the photoproducts in the photolysis of **2a** and **2e** decreased in the early stages of the reaction, but increased gradually with increasing irradiation time. Finally, insoluble products were produced in the reaction mixtures. After 40 h-irradiation, the soluble products separated from the insoluble substances in the resulting mixtures were analyzed by ^{1}H and ^{13}C NMR spectrometric method. The ^{1}H NMR spectrum of both soluble products obtained from

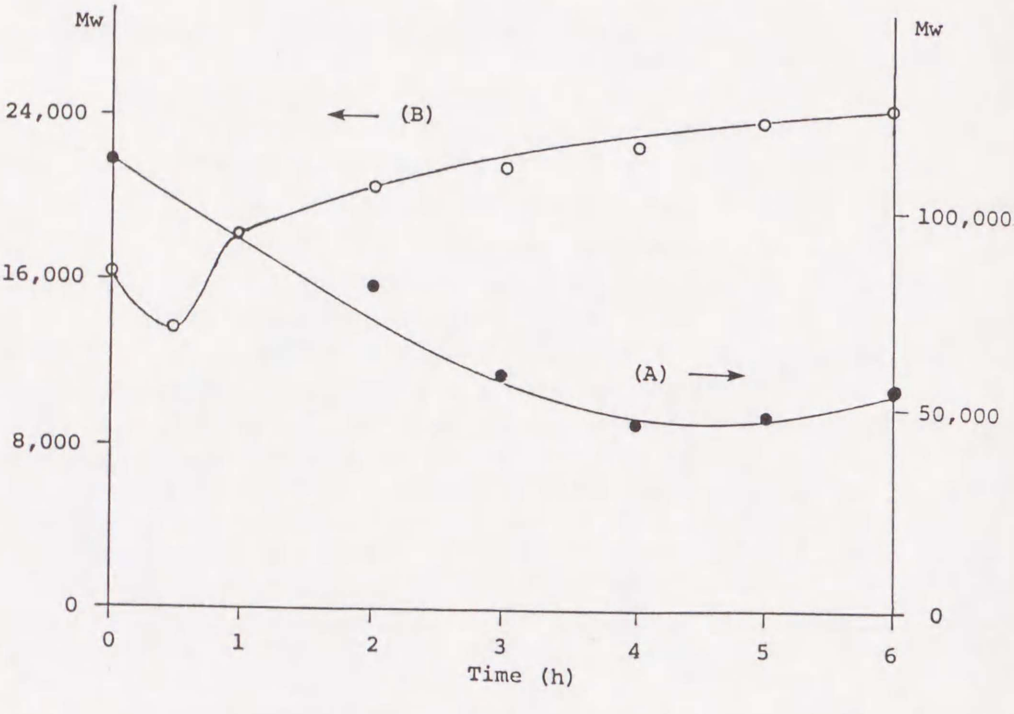


Figure 5. Plots of molecular wights of products vs. irradiation time for the photolysis of (A) **2a** and (B) **2e**.

the photolysis of **2a** and **2e** showed no signals in the region of olefinic protons (5-6.5 ppm). The ^{13}C NMR spectrum reveals no resonances attributed to the olefinic carbons and also acetylenic carbons (Figure 6). A possible mechanism for this photodegradation is shown in Scheme 3. The mechanism involves homolytic scission of Si-Si bonds in the polymer backbone to produce silyl radicals, which can add across the unsaturated bonds. At the early stages of the photolysis, the cleavage of the Si-Si bonds would result mainly in the decrease of molecular weights of the photoproducts, but with increasing reaction time, the reaction of carbon radicals arising from addition of the initially formed silyl radicals to unsaturated bonds would be responsible for the increase of the molecular weights of the photoproducts, although fate of the carbon radicals are still unknown.

Similar profile for the molecular weight changes has been observed in the photolysis of poly[p-(1,2-diethyldimethyldisilanylene)phenylene].[4] The presence of Si-Si bonds in the polymer backbone seems to be absolutely necessary for photoactive properties of these polymers. In fact, silylene polymer **2d** did not show such photochemical behavior. Irradiation of the thin solid film prepared from **2d** showed no changes both in the IR and UV spectrum. In the photolysis of **2d** in a benzene solution, again no change was observed for the molecular weight of the product.

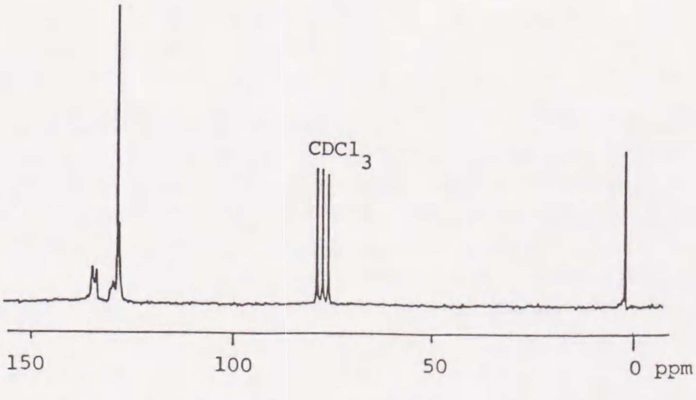
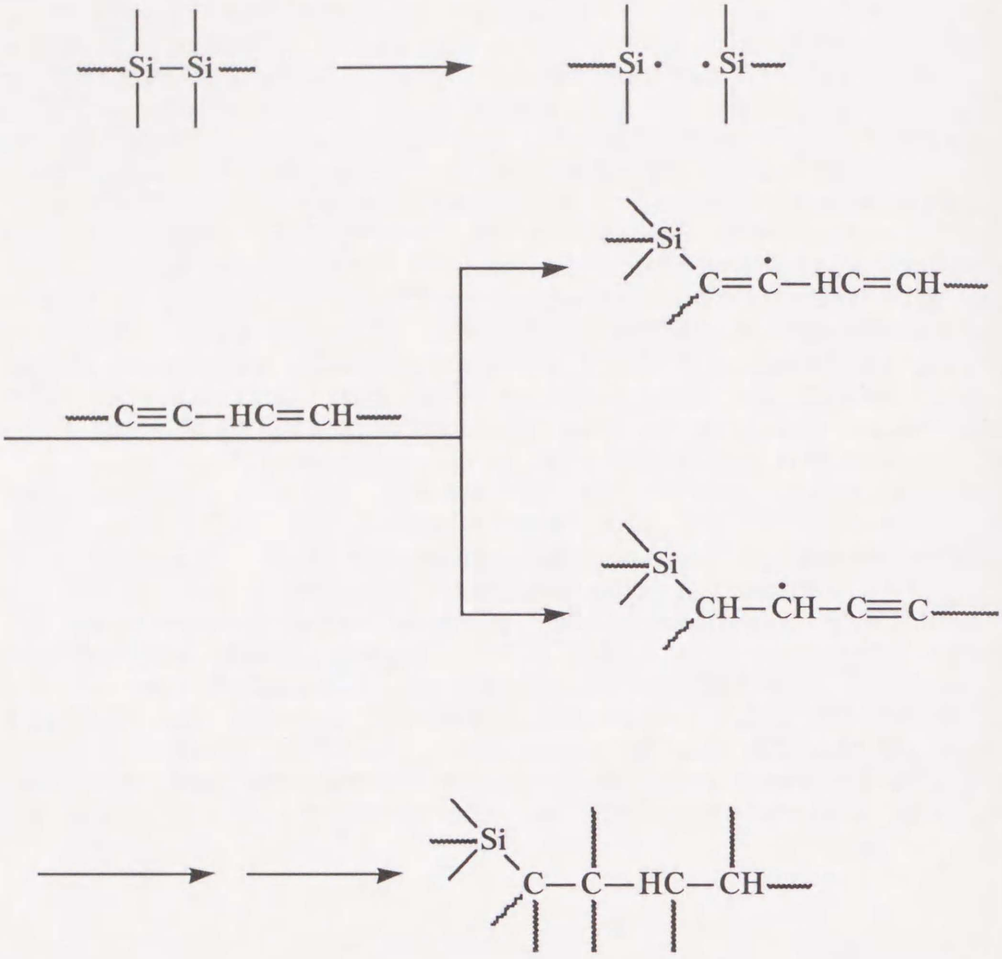


Figure 6. 22.5 MHz $^{13}C\{^1H\}$ NMR sprectrum of the soluble product from the photolysis of **2a** in benzene.

Scheme 3



Photolysis of the polymers **2b** and **2c** which have less hindered substituents on the silicon atom led to the formation of large amounts of insoluble substances even in the early stages of the photolysis. Presumably the rate of addition of the silyl radical across the unsaturated bonds is sufficiently fast. Lack of a radical stabilizing group on the silicon atom such as phenyl group may also accelerate the addition reaction.

Conducting Properties of 2a-e. The polymers **2a-e** can be cast to thin solid films with thickness of 3,000-10,000 Å by spin-coating. When these films were treated with SbF_5 vapor, each transparent film changed to dark green or blue black, and the films became conducting, whose conductivities were determined to be 0.0009-1.09 S/cm by the four-probe method (Table 1).

Polymer	Thickness of the film (Å)	Conductivity (S/cm)
2a	9,200	1.09
2b	4,600	0.022
2c	4,400	0.0009
2d	4,000	0.14
2e	3,400	0.038

Table 1. Thickness and conductivities of the SbF_5 doped films.

Experimental Section

General. All reactions were carried out under an atmosphere of purified argon. ^1H and ^{13}C NMR spectra were recorded on a JEOL Model JNM-GX-500 spectrometer, a JEOL Model JNM-GX-400 spectrometer, a JEOL Model JNM-EX-270 spectrometer, a JEOL Model JNM-FX-90A spectrometer, and a JEOL Model JNM-PMX-60 spectrometer, using deuteriochloroform or carbon tetrachloride containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 spectrometer.

Materials. 1,2-Dimethyldiphenyldisilane,[13] **1b**,[14] 1,1,2,2-tetraphenyldisilane,[13] 1,3-dichlorohexamethyltrisilane,[15] 1,4-diethynylbenzene,[16] and chlorotris(triphenylphosphine)rhodium(I)[17] were prepared as reported in the literatures. Ether, benzene, THF, and hexane used as solvents were dried over lithium aluminum hydride and distilled just before use.

Preparation of 1,2-Dichloro-1,2-dimethyldiphenyldisilane.[18] A solution of 71.7 g (0.296 mol) of 1,2-dimethyldiphenyldisilane and a catalytic amount of palladium dichloride in 500 mL of carbon tetrachloride was refluxed for 2 days. The solvent was evaporated, and the residue was distilled under reduced pressure (117°C/0.4 mmHg) to give 48.7 g of 1,2-dichloro-1,2-dimethyldiphenyldisilane (65% yield).

Preparation of 1,2-Diethynyl-1,2-dimethyldiphenyldisilane (1a). To a solution of ethynyl magnesium bromide prepared from 0.5 mol of ethyl magnesium bromide and acetylene in 300 mL of THF in a 1L three-necked flask, was added 48.7 g (0.19 mol) of 1,2-dichloro-1,2-dimethyldiphenyldisilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water, and dried over potassium carbonate. After the solvent was evaporated, the residue was distilled under reduced pressure to give **1a** as a 1:1 diastereomeric mixture. Recrystallization of the mixture from ethanol gave one isomer as a pure form (19% yield): bp 138-140°C (1.0 mmHg); mp 34-36°C; IR $\nu_{\equiv C\text{-}H}$ 3280 cm^{-1}, $\nu_{C\equiv C}$ 2040 cm^{-1}; ^{1}H NMR (δ in CCl_4) 0.48 (s, 3H, MeSi), 0.54 (s, 3H, MeSi), 2.56 (s, 2H, acetylenic protons), 7.2-7.8 (m, 10H, Ph). Anal. Calcd for $C_{18}H_{18}Si_2$: C, 74.42; H, 6.24. Found: C, 74.35; H, 6.10.

Preparation of 1,2-Diethyl-1,2-dimethyldiphenyldisilane. To a solution of 0.59 mol of ethylmethylphenylsilyl lithium prepared from 112 g (0.59 mol) of chloroethylmethylphenylsilane and 37 g (4.5 eq) of lithium in 500 mL of THF, was added an equimolar amount of chloroethylmethylphenylsilane (0.59 mol) with ice-cooling. The resulting mixture was allowed to stand at room temperature for 2 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water, and dried over potassium carbonate. After evaporation of the solvents, the residue was distilled under reduced pressure to give 114.9 g of 1,2-diethyl-1,2-dimethyldiphenyldisilane (66% yield): bp 100-120 °C (0.06 mmHg); MS m/e 298 (M^+); 60 MHz ^{1}H NMR (δ in CCl_4) 0.34 (s, 6H, MeSi), 0.91 (br s, 10H, Et), 6.73-6.99 (m, 10H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -6.37, -6.26 (MeSi), 5.44, 5.55, 7.93 (Et), 127.7, 128.3, 134.2 (Ph). Anal. Calcd for $C_{18}H_{26}Si_2$: C, 72.41; H, 8.78. Found: C, 72.31; H, 8.65.

Preparation of Dichlorodiethyldimethyldisilane. A mixture of 111.3 g (0.37 mol) of 1,2-diethyl-1,2-dimethyldiphenyldisilane and a catalytic amount of aluminum trichloride was dissolved in 100 mL of benzene. Dry hydrogen chloride gas was passed through the solution (ca. 1 ml/min) with stirring for 20 h at room temperature. After 5 mL of acetone was added to the solution, the solvent and hydrogen chloride was evaporated. The residue was distilled under reduced pressure to give 57.2 g of dichlorodiethyldimethyldisilane (73% yield): bp 90-93 °C (23 mmHg); MS m/e 214 (M^+); 60 MHz ^{1}H NMR (δ in $CDCL_3$) 0.57 (s, 6H, MeSi), 1.00-1.14 (m, 10H, Et); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -0.6, -0.4 (MeSi), 6.6, 10.0 (Et). Anal. Calcd for $C_6H_{16}Cl_2Si_2$: C, 33.48; H, 7.49. Found: C, 33.53; H, 7.39.

Preparation of 1,2-Diethyl-1,2-diethynyldimethyldisilane (1c). Ethynyl magnesium bromide was prepared from the reaction of 0.225 mol of ethyl magnesium bromide and acetylene in 300 mL of THF in a 1L three-necked flask. To this was added 15.47 g (0.072 mol) of 1,2-dichloro-1,2-diethyldimethyldisilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water. After the solvent was evaporated, the residue was distilled under reduced pressure to give 11.85 g of **1c** (84%

yield): bp 77-79°C (15 mmHg); MS m/e 194 (M^+); IR $\nu_{\equiv C-H}$ 3287 cm^{-1}, $\nu_{C\equiv C}$ 2028 cm^{-1}; 60 MHz ^1H NMR (δ in $CDCl_3$) 0.47 (s, 3H, MeSi), 0.6-1.47 (m, 5H, EtSi), 2.57 (s, 2H, acetylenic protons); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -5.1 (MeSi), 6.1, 8.0 (EtSi), 87.1, 96.1 (acetylenic carbons). Anal. Calcd for $C_{14}H_{18}Si_2$: C, 61.78; H, 9.33. Found: C, 61.59; H, 9.23.

Preparation of Diethynylmethylphenylsilane (1d). Ethynyl magnesium bromide was prepared from the reaction of 0.17 mol of ethyl magnesium bromide and acetylene in 300 mL of THF in a 1L three-necked flask. To this was added 10.0 g (0.052 mol) of dichloromethylphenylsilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water. After the solvent was evaporated, the residue was distilled under reduced pressure to give 3.8 g of **1d** (42% yield): bp 115-125°C (30 mmHg); MS m/e 170 (M^+); IR $\nu_{\equiv C-H}$ 3276 cm^{-1}, $\nu_{C\equiv C}$ 2040 cm^{-1}; 270 MHz ^1H NMR (δ in $CDCl_3$) 0.45 (s, 3H, MeSi), 2.42 (s, 2H, acetylenic protons), 7.19-7.61 (m, 5H, Ph); 67.8 MHz ^{13}C NMR (δ in $CDCl_3$) -0.7 (MeSi), 84.5, 96.0 (acetylenic carbons), 128.1, 130.3, 132.3, 133.9 (Ph). Exact MS Calcd for $C_{11}H_{10}Si$: 170.0552. Found: 170.0560.

Preparation of 1,2-Dichlorotetraphenyldisilane.[19] A solution of 18.33 g (0.05 mol) of 1,1,2,2-tetraphenyldisilane in 80 mL of CCl_4 was heated to reflux with a catalytic amount of palladium dichloride for 20 h. After the solvent was evaporated, the residue was recrystallized from hexane to give 20.7 g of 1,2-dichlorotetraphenyldisilane (95% yield) as a white crystal: mp 99.5-100.5°C; MS m/e 434 (M^+); 60 MHz ^1H NMR (δ in CCl_4) 7.25-7.93 (m, Ph).

Preparation of 1,2-Diethynyltetraphenyldisilane (1e). Ethynyl magnesium bromide was prepared from the reaction of 0.08 mol of ethyl magnesium bromide and acetylene in 300 mL of THF in a 1L three-necked flask. To this solution was added 8.71 g (0.02 mol) of 1,2-dichlorotetraphenyldisilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water. After the solvent was evaporated, the residue was recrystallized from ethanol to give 8.29 g of **1e** (64% yield); mp 151-151.5°C; MS m/e 414 (M^+); IR $\nu_{\equiv C-H}$ 3277 cm^{-1}, $\nu_{C\equiv C}$ 2030 cm^{-1}; 60 MHz ^1H NMR (δ in $CDCl_3$) 2.19 (s, 2H, acetylenic protons), 6.83-7.75 (m, 20H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) 84.4, 99.7 (acetylenic carbons), 128.0, 129.8, 131.8, 134.5, 135.5. Anal. Calcd. for $C_{28}H_{22}Si_2$: C, 81.11; H, 5.35. Found: C, 80.96; H, 5.35.

Preparation of 1,2-(Deuterioethynyl)tetraphenyldisilane (1f). To a solution of 2.0734 g (5.01 mmol) of **1e** in 12 mL of ether, 8 mL (12.0 mmol) of 1.5 M hexane solution of n-BuLi was added at room temperature. The resulting mixture was heated to reflux for 2 h, then 0.22 mL (11.0 mmol) of D_2O was added dropwise with ice-cooling. The resulting mixture was allowed to stand at room temperature for 10 h. The solvent was evaporated, and the residue was extracted with three potions of 10 mL of benzene. The extracts were combined and benzene was evaporated to give crude **1f**. The crude product was recrystallized from ethanol to give 1.1847 g of pure **1f** (56% yield): mp. 150.5-151.5°C; MS m/e 416 (M^+); IR $\nu_{C\equiv C}$ 2030 cm^{-1}; 60 MHz ^1H NMR (δ in $CDCl_3$) 6.83-7.75 (m, 20H, Ph).

Preparation of 1,3-Diethynylhexamethyltrisilane. Ethynyl magnesium bromide was prepared from the reaction of 0.112 mol of ethyl magnesium bromide and acetylene in 350 mL of THF in a 1L three-necked flask. To this was added 6.9 g (0.028 mol) of 1,3-dichlorohexamethyltrisilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water. After the solvent was evaporated, the residue was treated with a silica gel column chromatography using hexane as an eluent to give 1.98 g of 1,3-diethynylhexamethyltrisilane (32% yield): MS m/e 224 (M^+); ^{1}H NMR (δ in CCl_4) 0.22 (s, 6H, Me_2Si), 0.28 (s, 12H, Me_2Si), 2.31 (s, 2H, acetylenic protons); Anal. Calcd for $C_{10}H_{20}Si_3$: C, 53.49; H, 8.98. Found: C, 53.33; H, 8.95.

Preparation of Poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (2a). A solution of 2.05 g (7.1 mmol) of **1a** and 2 mol% of chlorotris(triphenylphosphine)rhodium in 2 mL of toluene was stirred for 2 days at room temperature. After removal of the solvent at room temperature, the residue was reprecipitated twice from isopropyl alcohol-chloroform to give 1.50 g (73% yield) of **2a**: mp 90-95°C; Mw=117,000; Mn=19,200; IR $\nu_{C\equiv C}$ 2146 cm^{-1}; 60 MHz ^{1}H NMR (δ in CCl_4) 0.47 (br s, 6H, MeSi), 5.93 (d, 1H, J=19 Hz, olefinic proton), 6.66 (d, 1H, J=19 Hz, olefinic proton), 6.87-7.91 (m, 10H, Ph); 100 MHz ^{13}C NMR (δ in $CDCl_3$) -5.7, -5.4, -3.9, -3.8 (MeSi), 91.2, 91.3, 91.5, 91.6, 109.81, 109.84, 109.9 (acetylenic carbons), 125.8, 125.9, 142.5, 142.8 (olefinic carbons), 127.86, 127.93, 127.97, 128.1, 129.3, 134.4, 134.5, 134.6, 134.7, 134.8, 134.9 (Ph); UV (film) λmax 294 nm.

Preparation of Poly[(tetramethyldisilanylene)butenyne-1,4-diyl] (2b). A solution of 0.9853 g (5.92 mmol) of **1b** and 0.102 g (2 mol%) of chlorotris(triphenylphosphine)rhodium in 2 mL of toluene was stirred for 2 days at room temperature. The solvent was evaporated under reduced pressure at room temperature. Then the residue was reprecipitated twice from isopropyl alcohol-benzene to give 0.516 g (52%) of **2b**: mp >300°C; Mw=28,000; Mn=2,200; IR $\nu_{C\equiv C}$ 2149 cm^{-1}; 90 MHz ^{1}H NMR (δ in $CDCl_3$) 0.13-0.29 (br, 12H, MeSi), 5.91 (d, 1H, J=19 Hz, olefinic proton), 6.56, 6.54 (2d, 1H, J=19 Hz, olefinic proton); 22.5 MHz

^{13}C NMR (δ in CDCl$_3$) -4.58, -4.47, -2.96, -2.85 (MeSi), 92.80, 93.04, 107.99 (acetylenic carbons), 123.92, 124.13, 144.72, 145.05 (olefinic carbons); UV (film) λ_{max} 293 nm.

Preparation of Poly[(1,2-diethyldimethyldisilanylene)butenyne-1,4-diyl] (2c). A solution of 2.1225 g (10.9 mmol) of **1c** and 0.1028 mg (1 mol%) of chlorotris(triphenylphosphine)rhodium in 10 mL of toluene was stirred at room temperature for 21 h. After evaporation of the solvent, the residue was repecipitated twice from isopropyl alcohol-chloroform to give 1.2264 g (58% yield) of **2c**: mp >300°C; Mw=22,000, Mn=8,300; IR $\nu_{C\equiv C}$ 2146 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.12, 0.19, 0.26, 0.27 (s, 6H, MeSi), 0.61-1.23 (m, 10H, EtSi), 5.91, 5.97 (2d, 1H, J=19 Hz, olefinic proton), 6.46, 6.50 (2d, 1H, J=19 Hz, olefinic proton); 22.5 MHz ^{13}C NMR (δ in CDCl$_3$) -6.59, -4.69 (MeSi), 5.38, 6.47, 8.04 (EtSi), 92.28, 103.98 (acetylenic carbons), 124.29, 124.51, 143.74, 143.96 (olefinic carbons); UV (film) λ_{max} 300 nm.

Preparation of Poly[(methylphenylsilylene)-butenyne-1,4-diyl] (2d). A solution of 1.23 g (7.22 mmol) of **1d** and 42.9 mg (6.4 mol%) of chlorotris(triphenylphosphine)rhodium in 2 mL of toluene was stirred at room temperature for 14 days. After removal of the solvent, the residue was reprecipitated from ethanol-chloroform to give 0.732 g (60% yield) of **2d**: Mw=24,000; Mn=6,700; IR $\nu_{C\equiv C}$ 2155 cm^{-1}; 90 MHz ^{1}H NMR (δ in CDCl$_3$) 0.47, 0.52, 0.58 (3s with an intensity ratio of 1:2:1, 3H, MeSi), 6.11, 6.21 (2d, 1H, J=18.9 Hz, olefinic proton), 6.66, 6.70 (2d, 1H, J=18.9 Hz, olefinic proton), 7.41-7.65 (Ph); 22.5 MHz ^{13}C NMR (δ in CDCl$_3$) -4.8, -2.7, -0.3 (MeSi), 91.1, 91.2, 106.9, 108.0 (acetylenic carbons), 126.4, 126.7, 142.1, 142.2 (olefinic carbons), 128.0,129.9, 133.7, 134.2, 134.5 (Ph); UV (film) λ_{max} 220 nm.

Rhodium(I) Catalyzed Reaction of 1,3-Diethynylhexamethyltrisilane. A mixture of 0.449 g (2.0 mmol) of 1,3-diethynylhexamethyltrisilane and 37.0

mg (2 mol%) of chlorotris(triphenylphosphine)rhodium in 2 mL of toluene was stirred at room temperature for 2 days. The GLC analysis and IR and ^{1}H NMR spectrometric analysis of the resulting mixture showed that all starting 1,3-diethynylhexamethyltrisilane was remained unchanged.

Rhodium(I) Catalyzed Reaction of 1,4-Diethynylbenzene. A solution of 383 mg (3.04 mg) of 1,4-diethynylbenzene and 5 mol% of chlorotris-(triphenylphosphine)rhodium in 5 mL of toluene was stirred at room temperature. After 24 h-reaction, a large amount of insoluble gel was formed. The solvent was evaporated to give a yellow solids (ca. 100% yield), which were insoluble in alcohol, benzene, chlorocarbons, ethers, and hydrocarbons.

Rhodium(I) Catalyzed Reaction of 1e. A mixture of 2.0733 g (5.0 mmol) of **1e** and 92.5 mg (2 mol%) of chlorotris(triphenylphosphine)rhodium in 2 mL of toluene was stirred at 50°C for 2 days. The solvent was evaporated under reduced pressure. The GLC analysis and IR and ^{1}H NMR spectrometric analysis of the resulting mixture showed that all starting **1e** was remained unchanged.

Preparation of Copolymer (2e). A mixture of 1.0367 g (25 mmol) of **1e**, 0.4159 g (25 mmol) of **1b**, and 92.5 mg (2 mol%) of chlorotris(triphenylphosphine)-rhodium in 2 mL of toluene was stirred at room temperature for 60 h. The solvent was evaporated under reduced pressure, and the residue was reprecipitated twice from isopropyl alcohol-chloroform to give 0.80 g of **2e** (55% yield): Mw=16,000; Mn=6,200; mp 84-98 °C; IR $\nu_{C\equiv C}$ 2146 cm^{-1}; 270 MHz ^{1}H NMR (δ in $CDCl_3$) 0.19 (s, 12H, Me_2Si), 6.00 (d, 2H, J=19 Hz, olefinic protons), 6.54 (d, 2H, J=19 Hz, olefinic protons), 7.19-7.62 (m, 20H, Ph); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) -4.4 (MeSi), 89.1, 111.7 (C≡C), 123.8, 146.3 (olefinic carbons), 127.9, 129.5, 132.9, 135.6 (Ph); UV (film) λ_{max} 293 nm.

Preparation of Copolymer (2f). A mixture of 0.6251 g (1.5 mmol) of **1f**, 0.2496 g (1.5 mmol) of **1b**, and 55.5 mg (2 mol%) of chlorotris(triphenylphosphine)-

rhodium in 0.8 mL of toluene was stirred at room temperature for 60 h. The solvent was evaporated, and the residue was reprecipitated twice from isopropyl alcohol-chloroform to give 0.424 g of **2f** (49% yield): mp 84-95°C; Mw=16,000, Mn=1,900; IR $\nu_{C\equiv C}$ 2146 cm^{-1}; 270 MHz ^{1}H NMR (δ in $CDCl_3$) 0.19 (s, 12H, Me_2Si), 6.00 (br s, 2H, olefinic protons), 7.19-7.62 (m, 20H, Ph).

Photolyses of the Polymers in Solid Films. A 10% chloroform solution of the polymer was coated on a quartz plate or an NaCl plate and dried under reduced pressure to give solid film with thickness of ca. 0.05-0.1 mm. The film was irradiated with low pressure mercury lamp bearing a Vicor filter in air. And the reaction was monitored by UV and IR spectra.

Photolysis of Polymers 2a-e in Benzene. In a 25 mL of reaction vessel bearing a Vycor filter fitted internally with a low pressure mercury lamp, was placed ca. 100 mg of polymer in 25 mL of benzene. The mixture was irradiated and the progress of the reaction was monitored by GPC. ^{13}C NMR spectrum of the soluble part of the photoproduct of **2a** is presented in Figure 6: (δ in $CDCl_3$) 1.0, 127.8 (br), 128.3, 129.2 (br), 133.3 (br), 134.4 (br).

Doping Experiment of Thin Solid Films of 2a-e. A ca.10% of methylene dichloride solution of the polymer was spin-coated on a quartz plate by spinner (3000 rpm), and baked at 70°C for 2 h under reduced pressure. The thickness of the resulting film was measured by the mechanical probe method (Dektak 3030). The film was treated with a stream of SbF_5 vapor diluted with nitrogen (0.2 ml SbF_5/min) for 2 h, and then, allowed to stand under reduced pressure (1 mmHg) for 30 m. The conductivities of the resulting films were measured by the four-probe method under a nitrogen atmosphere.

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