Transition Metal-Catalyzed Reactions of π–Electron System-Substituted Disilanes

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Hiroshima University

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Preface

The studies presented in this thesis have been carried out under the direction of Professor Mitsuo Ishikawa at the Department of Applied Chemistry of Hiroshima University during 1990-1994. The thesis is concerned with the interaction between π-electron system-substituted disilanes and transition metal-complexes. The author wishes to express his sincerest gratitude to professor Mitsuo Ishikawa for his constant guidance, helpful suggestions and hearty encouragement throughout this work. The author also appreciates to Dr. Atsutaka Kunai and Dr. Joji Ohshita for their continuing advice and stimulating discussion during the course of his studies. The author also acknowledges Dr. Hiromu Sakamoto and Mr. Eiji Toyoda for their warm encouragement. He also thanks to Mr. Shougo Okazaki, Mr. Masayoshi Kikuchi, Mr. Masaki Hayashi, Mr. Kazushige Morita, Mr. Takanori Hiraoka, Mr. Shouhei Matsui, Mr. Taiichi Okada, and Mr. Toshiyuki Mihara for their collaborations.

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Akinobu Naka

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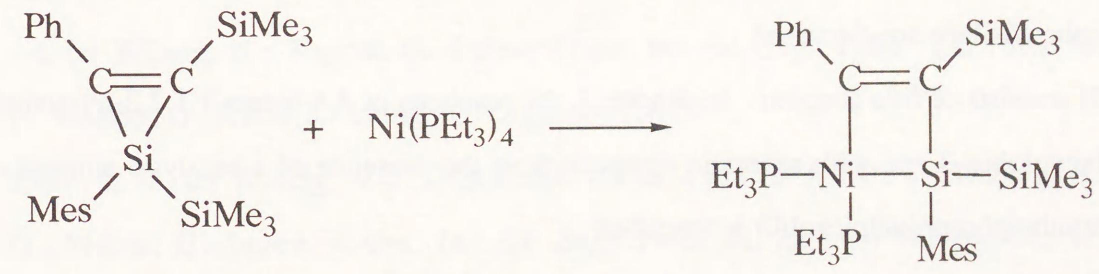
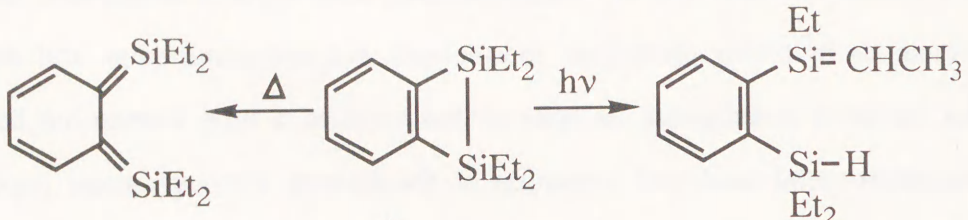
General Introduction

Silicon-carbon unsaturated compounds, silenes are kinetically labile and show interesting chemical behavior.[1-4] In 1967, the first evidence for the production of the silene was presented by Flowers and Gusel'nikov, who were able to trap transient 1,1-dimethylsilene formed from the pyrolysis of 1,1-dimethylsilacyclobutene.[2] Since that time, many types of silenes have been prepared by the methods involving photolysis, thermolysis, and salt elimination, and their chemical behavior has been investigated. In spite of these studies, a little interest has been shown in the transition-metal-catalyzed formation of the silenes, although some papers concerning the formation of the silene- and disilene-transition-metal complexes have been published to date.[5]

In 1984, Ishikawa and his coworkers have found that a silene-nickel complex is produced as a reactive intermediate in the reaction of phenylethynylpolysilanes with phenyl(trimethylsilyl)acetylene in the presence of tetrakis(triethylphosphine)nickel(0).[6] They also found that the reaction of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacycloprop-2-ene with 1 equiv of tetrakis(triethylphosphine)nickel(0) affords 2-mesityl-4-phenyl-1,1-bis(triethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobut-3-ene which isomerizes thermally to give a transient silene-nickel complex.[7]



On the other hand, it has been reported that 3,4-benzo-1,2-disilacyclobut-3-enes show unique chemical behavior. For examples, heating 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene at 60°C or treatment with a catalytic amount of aluminum chloride gives poly[*o*-(tetramethyldisilanylene)phenylene] with high molecular weight.[8] Heating 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) at 250°C, however, affords an *o*-quinodisilane, while the photolysis of this compound produces another intermediate, 1-ethyl-1-[*o*-(diethylsilyl)phenyl]-1-silapropene, arising from homolytic scission of a silicon-silicon bond, followed by intramolecular disproportionation of the resulting radical.[9,10]



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The studies presented in this thesis are concerned mainly with the transition-metal-catalyzed reactions of disilanyl-substituted enynes and 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with various reagents.

Part I consists of two chapters. In Chapter 1, the reactions of disilanyl-substituted enynes with diphenylacetylene in the presence of a nickel catalyst are reported. These reactions involve the formation of a silapropadiene-nickel complex as a reactive intermediate, and the silapropadiene thus formed reacts with diphenylacetylene.

In chapter 2, the nickel-catalyzed reactions of disilanyl-substituted enynes with methyldiphenylsilane are discussed.

Part II consists of five chapters. In chapter 3, the reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with aromatic compounds in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) is described.

Chapter 4 deals with the nickel-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with carbonyl compounds.

Chapter 5 describes the nickel-catalyzed reactions of disilacyclobutene with alkenes and dienes. In these nickel-catalyzed reactions, we proposed the formation of an *o*-quinodisilane-nickel complex.

In chapter 6, the results of the palladium-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene are reported.

Finally, the reactions of disilacyclobutene with benzene, olefins, acetylenes, and carbonyl compounds in the presence of (η2-ethylene)bis(triphenylphosphine)platinum is described in chapter 7.

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Part I Nickel-Catalyzed Reactions of Disilanyl-Substituted Enynes

Chapter 1

Nickel-Catalyzed Reactions of Disilanyl-Substituted Enynes with Diphenylacetylene

Introduction

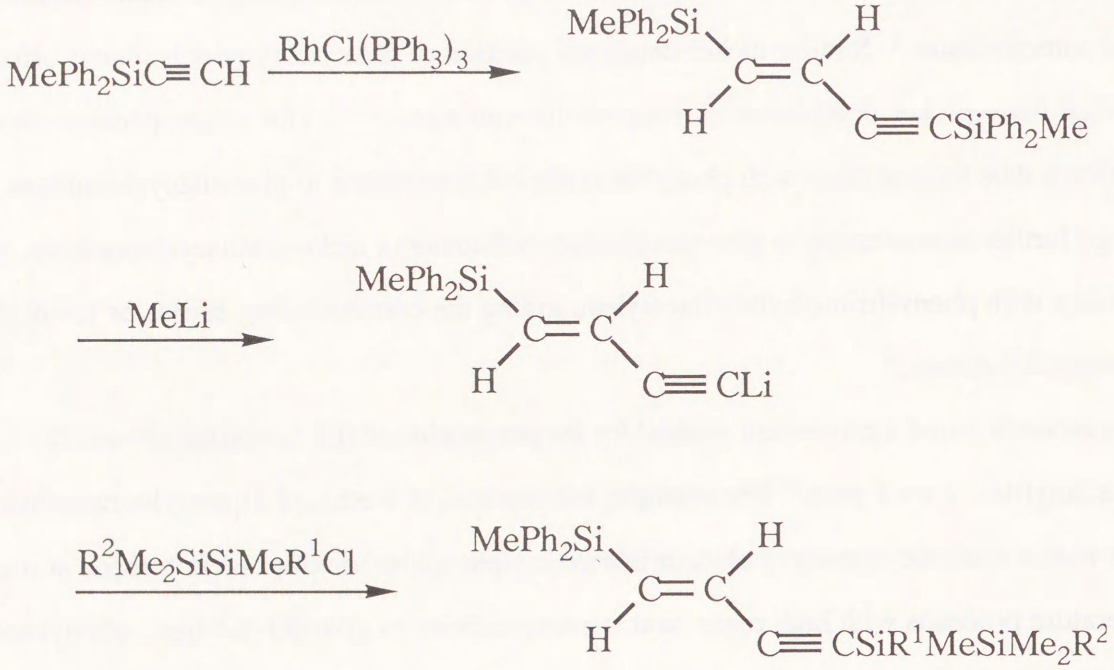
The nickel-catalyzed reaction of vinyldisilanes gives novel dimerization products via silene-nickel intermediates.[1] Similar nickel-catalyzed reaction of phenylethynylpolysilanes affords silapropadiene-nickel complexes as reactive intermediates.[2-5] The silapropadiene-nickel complexes thus formed react with phenyl(trimethylsilyl)acetylene to give silacyclobutenes, or undergo further isomerization to give nickelasilacyclobutenes or nickeladisilacyclopentenes, and then react with phenyl(trimethylsilyl)acetylene giving the corresponding siloles or 1,4-disilacyclohexa-2,5-dienes.[5]

We recently found a convenient method for the preparation of (E)-1,4-bis(silyl)- and (E)-1,4-bis(disilanyl)but-1-en-3-ynes.[6] For example, the reaction of 1-ethynyl-1-phenyltetramethyldisilane with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) in toluene at room temperature proceeds with high regio- and stereospecificity to give (E)-1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne in high yield. It is of interest to us to investigate the nickel-catalyzed reaction of the bis(disilanyl)enynes with acetylene, because this type of compounds involves two different reactive centers towards a nickel species, a disilanylethenyl and disilanylethynyl unit in the molecule. In this chapter we report the reaction of (E)-4-disilanyl-1-silyl-, (E)-1,4-bis(disilanyl)-, and (E)-1-disilanyl-4-silyl-but-1-en-3-ynes with diphenylacetylene in the presence of dichlorobis(triethylphosphine)nickel(II) in a sealed tube.

Results and Discussion

Synthesis. The starting compounds, (E)-1-methyldiphenylsilyl-4-(pentamethyldisilanyl)but-1-en-3-yne (**1a**), (E)-1-methyldiphenylsilyl-4-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**2**), and (E)-1-methyldiphenylsilyl-4-(2-phenyltetramethyldisilanyl)but-1-en-3-yne (**3**) were prepared by the rhodium-catalyzed head-to-head dimerization of ethynylmethyldiphenylsilane, followed by the reaction of the resulting dimer with 1 equiv of methyllithium, and then treatment of the lithio compound with the corresponding chlorodisilanes (Scheme I).

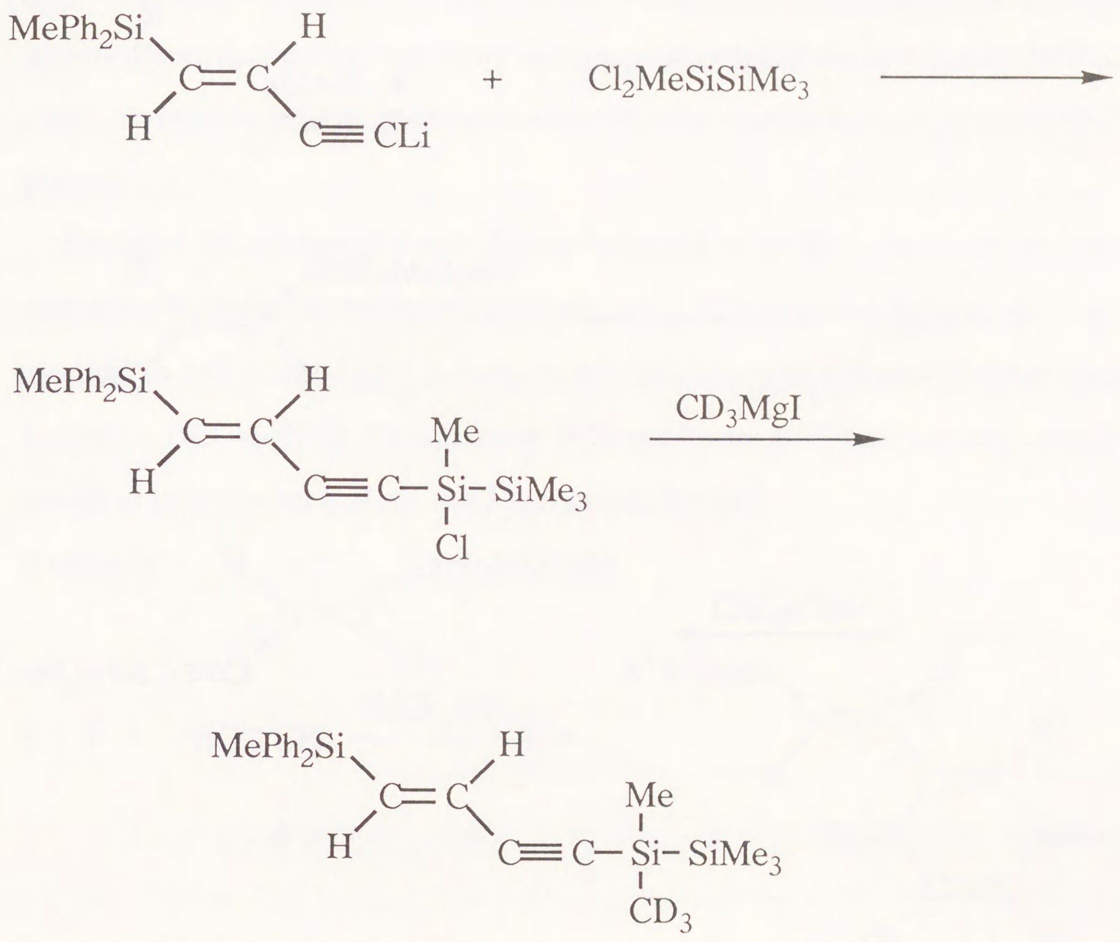
Scheme I



1a, $R^1=R^2=$Me
2, $R^1=$Ph, $R^2=$Me
3, $R^1=$Me, $R^2=$Ph

4-[1-(Deuteriomethyl)tetramethyldisilanyl]-1-(methyldiphenylsilyl)but-1-en-3-yne (**1b**) was prepared by the reaction of lithio compound prepared from 1,4-bis(methyldiphenylsilyl)but-1-en-3-yne and methyllithium, with 1 equiv of 1,1-dichlorotetramethyldisilane, followed by treatment with deuteriomethylmagnesium iodide (Scheme II).

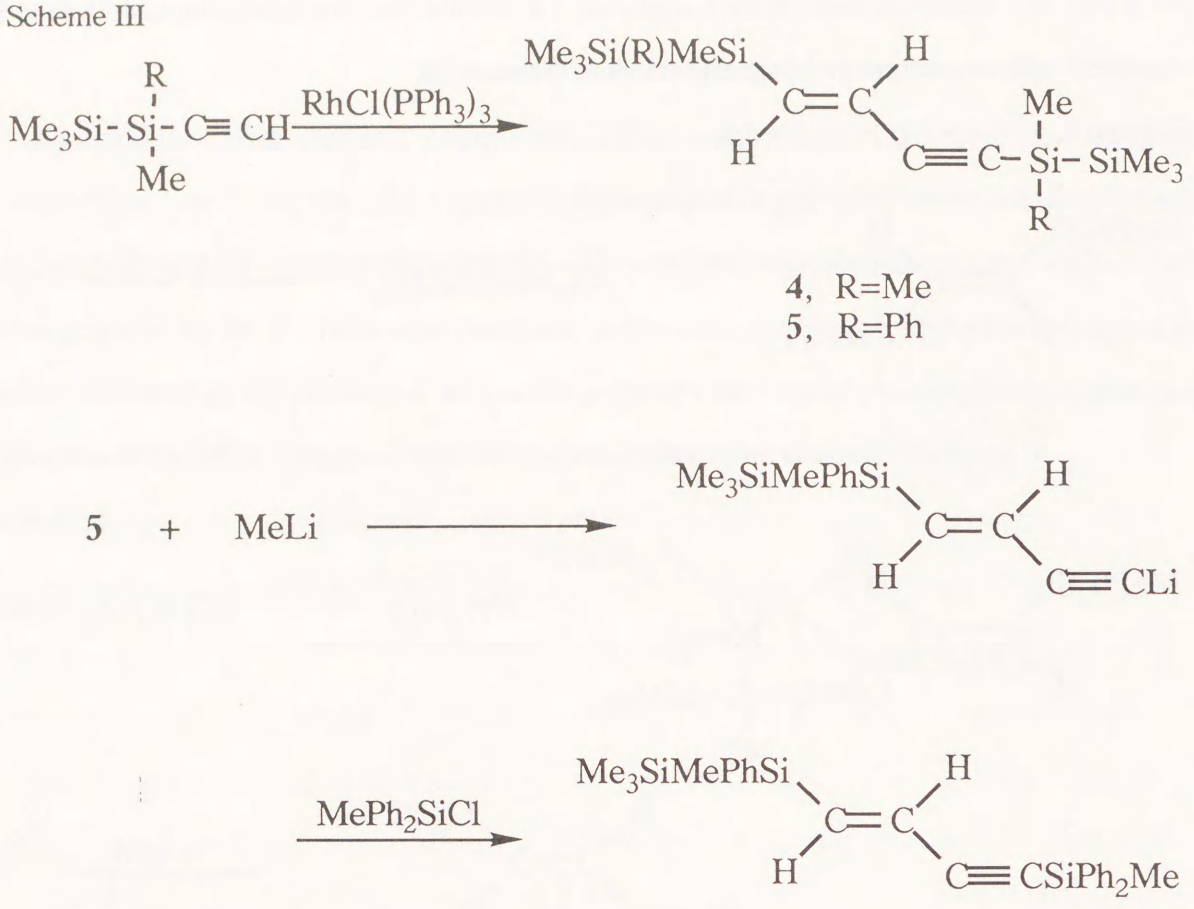
Scheme II



1b

1,4-Bis(pentamethyldisilanyl)- and 1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**4** and **5**) were synthesized by the rhodium-catalyzed head-to-head dimerization of ethynylpentamethyldisilanes and 1-ethynyl-1-phenyltetramethyldisilane, as the method reported in the literature.[6] (E)-4-Methyldiphenylsilyl-1-(l-phenyltetramethyldisilanyl)but-1-en-3-yne (**6**) was prepared by the reaction of **5** with 1 equiv of methyllithium, followed by treatment of the resulting lithio compound with chloromethyldiphenylsilane (Scheme III).

Scheme III



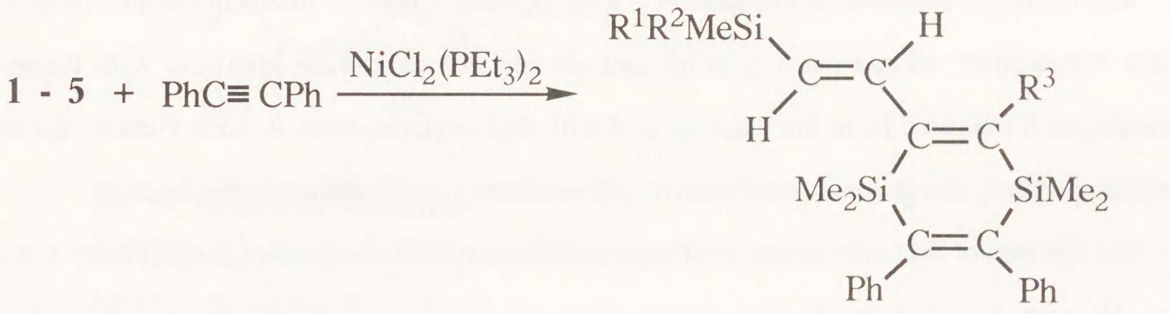
4, R=Me
5, R=Ph

6

Nickel-catalyzed reaction. Treatment of **1a** with a catalytic amount of dichlorobis-(triethylphosphine)nickel(II) in the absence of a trapping agent in a degassed sealed tube at 200°C for 20 h afforded polymeric substances. No volatile products were detected by either GLC or GPC analysis. Therefore, we carried out the reaction in the presence of phenyl(trimethylsilyl)acetylene, which we always used as a trapping agent in the nickel-catalyzed reactions of phenylethynylpolysilanes.[2-5] Unfortunately, heating **1a** in the presence of a slight excess of phenyl(trimethylsilyl)acetylene under the same conditions afforded a complicated mixture composed of various products. GLC-Mass spectrometric analysis of the mixure showed the presence of two isomers, corresponding to the molecular weight of the adduct, $C_{33}H_{44}Si_4$. When diphenylacetylene was used as the trapping agent, however, the reaction proceeded cleanly to give the adduct. In fact, treatment of **1a** with diphenylacetylene at 200°C for 20 h gave 1,1,4,4,5-pentamethyl-6-[trans-(methyldiphenylsilyl)ethenyl]-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**7a**) (Scheme IV). The product **7a** could be readily separated from the reaction mixture by medium pressure liquid chromatography (MPLC) in 53% yield. No other volatile products were detected in the reaction mixture by either GLC or GPC analysis.

Similarly, the reaction of **2** with diphenylacetylene under the same conditions gave 1,1,4,4-tetramethyl-6-[trans-(methyldiphenylsilyl)ethenyl]-2,3,5-triphenyl-1,4-disilacyclohexa-2,5-diene (**8**) in 43% yield. Again, no other volatile products were detected by either spectrometric analysis or GLC analysis. The structures of **7a** and **8** were confirmed by spectroscopic analysis as well as by elemental analysis (see Experimental Section).

Scheme IV



7a, $R^1=R^2=Ph$, $R^3=Me$
8, $R^1=R^2=R^3=Ph$
9, $R^1=SiMe_3$, $R^2=R^3=Me$
10, $R^1=SiMe_3$, $R^2=R^3=Ph$

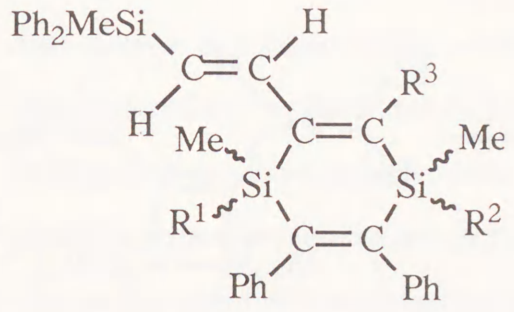
The location of the substituents on the 1,4-disilacyclohexa-2,5-diene ring for compound **7a** was verified by NOE-FID difference experiments at 270 MHz. Thus, saturation of dimethylsilyl protons of the disilacyclohexadienyl ring at -0.02 ppm caused a strong enhancement of an olefinic proton and phenyl ring protons, while saturation of the dimethylsilyl protons at 0.29 ppm resulted in a positive NOE of methyl protons on the sp^2 ring carbon and also phenyl ring protons. Irradiation of methylsilyl protons at 0.69 ppm caused the enhancement of two olefinic protons, as well as phenyl ring protons. These results are consistent with the structure proposed for compound **7a**.

In marked contrast to the structure of **7a** in which a methyl group is attached to the sp^2 carbon atom of the 1,4-disilacyclohexa-2,5-diene ring, the product **8** involves no methyl group on the sp^2 ring carbon, but a phenyl group on this carbon. In the NOE-FID difference experiments for compound **8**, irradiation of dimethylsilyl protons at -0.22 ppm led to the enhancement of phenyl ring protons, while saturation of dimethylsilyl protons at 0.07 ppm resulted in a positive NOE of phenyl ring protons and a proton on the sp^2 carbon atom attached to a methyldiphenylsilyl group. Irradiation of methyl protons of a methyldiphenylsilyl group led to the enhancement of two olefinic protons, as well as phenyl protons on this silicon atom.

Interestingly, treatment of compound **3** with diphenylacetylene under the same conditions gave the product whose melting point and all spectral data were identical with those of compound **8** obtained from the reaction of **2** with diphenylacetylene, in 15% yield as the sole volatile product. Large amounts of nonvolatile products were produced in this reaction.

The reaction of 4-[1-(deuteriomethyl)tetramethyldisilanyl]-1-(methydiphenylsilyl)but-1-en-3-yne **1b** with diphenylacetylene under the same conditions, a 1,4-disilacyclohexa-2,5-diene derivative was obtained. To our surprise, ^{1}H and ^{2}H NMR spectra for this product show that a deuteriomethyl group is distributed on the sp^2 ring carbon and also two ring silicon atoms. Thus, the ^{1}H NMR spectrum of the product reveals methyl resonances at δ -0.01, 0.30, 0.71, and 2.20 ppm, due to Me_2Si, Me_2Si, $MePh_2Si$, and MeC=, respectively. However, integral ratio of these resonances is determined to be 4.8:4.7:3.0:2.5, indicating that a deuteriomethyl group exists on the sp^2 ring carbon atom and two ring silicon atoms. The ^{2}H NMR spectrum also reveals the presence of a deuteriomethyl group on the sp^2 ring carbon and two different ring silicon atoms. Thus, the spectrum of the product shows the resonances at δ 0.00, 0.31 and

0.36, and 2.20 ppm with integral ratio of 2.9:3.4:1.0, attributable to the deuteriomethyl group on two different ring silicon atoms and on the sp^2 ring carbon. Two resonances at 0.31 and 0.36 ppm are probably due to an axial and equatorial deuteriomethyl group on the ring silicon atom. The resonance at 0.00 ppm seems to be the overlapping resonances of axial and equatorial deuteriomethyl groups. Indeed, the ^{13}C NMR spectrum of this product shows two sets of resonances at δ -0.09 and -0.84, and -0.59 and -0.54 ppm, respectively, due to the axial and equatorial methyl carbons of two different dimethylsilyl groups in the six-membered cyclic system. These results clearly indicate that the reaction of **1b** with diphenylacetylene in the presence of the nickel catalyst affords the mixture composed of the following compounds **7b**, **7c**, and **7d**.



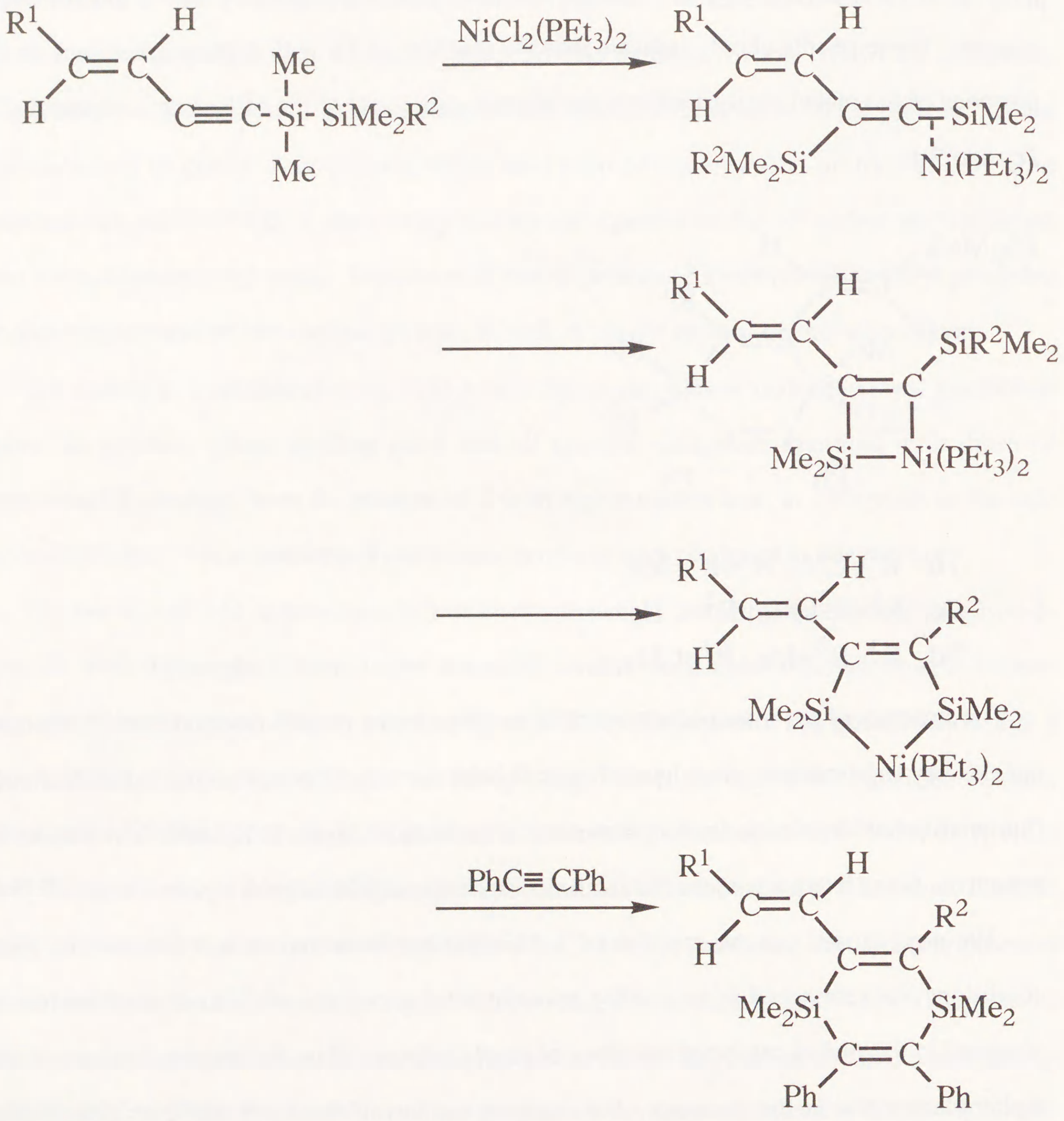
7b, $R^1=CD_3$, $R^2=R^3=Me$
7c, $R^1=R^3=Me$, $R^2=CD_3$
7d, $R^1=R^2=Me$, $R^3=CD_3$

The structure of the intermediate which is involved in the present reaction is still unknown, but the key intermediate must have fluxional behavior. As the intermediate that has such fluxional behavior, a nickelasilacyclobutene intermediate shown in Scheme V seems to be attractive. Some examples of the fluxional silicon compounds have been reported to date.[7-10]

We next carried out the reaction of 1,4-bis(disilanyl)butenyne **4** and **5** under the same conditions to learn whether or not the trimethylsilyl group migrates to ethenyl carbon as observed in the nickel-catalyzed reactions of vinyldisilanes. Thus, heating a mixture of **4** and diphenylacetylene in the presence of a catalytic amount of dichlorobis(triethylphosphine)-

nickel(II) in a sealed tube at 200°C for 20 h afforded 6-[trans-(pentamethyldisilanyl)ethenyl]-1,1,4,4,5-pentamethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**9**) in 52% yield, while compound **5** gave 1,1,4,4-tetramethyl-6-[trans-(1-phenyltetramethyldisilanyl)ethenyl]-2,3,5,-triphenyl-1,4-disilacyclohexa-2,5-diene (**10**) in 40% yield. The structures of **9** and **10** were verified by spectroscopic analysis involving NOE-FID difference experiments at 270 MHz, as well as by elemental analysis. In the reaction of **4** and **5**, the disilanylethenyl unit remained unchanged, and only disilanylethynyl group interact with a nickel catalyst to form the 1,4-disilacyclohexa-2,5-diene structure.

Scheme V



Scheme V illustrates a possible mechanistic interpretation of the observed reaction course. The mechanism involves the formation of silapropadiene-nickel complexes, followed by isomerization to the nickeladisilacyclopentene intermediates, via nickelasilacyclobutene derivatives. Finally, the reaction of the intermedates with diphenylacetylene gives the 1,4-disilacyclohexa-2,5-dienes. The intermediary formation of the silapropadiene-nickel complexes, nickelasilacyclobutenes, and nickeladisilacyclopentenes has been proposed previously.$^{2-5}$ It has also been found that the nickel-catalyzed reaction of phenylethynylpolysilanes with phenyl(trimethylsilyl)acetylene produces 1,4-disilacyclohexa-2,5-dienes.^{4,5}

Treatment of (E)-4-methyldiphenylsilyl-1-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**6**) that involves no disilanyl group on ethynyl carbon with the nickel catalyst in the absence of diphenylacetylene at 200°C for 20 h resulted in the formation of nonvolatile products. The structure of the nonvolatile products is still unknown, but the ^{13}C NMR spectrum of the products shows no resonances due to ethynyl carbons, but revealed the presence of the resonances with low intensities attributed to vinylic carbons. The ^{1}H NMR spectrum also reveals very weak signals due to vinylic protons, in addition to multiplet resonances in the methylsilyl region and also in the phenyl region. The reaction of **6** with diphenylacetylene under the same conditions again afforded nonvolatile products.

Recently, we have found that the thermolysis of 2-mesityl-2-phenylethynylhexamethyltrisilane at 280°C undergoes isomerization to give 1-mesityl-3,3-dimethyl-4-phenyl-5-trimethylsilyl-1,3-disilacyclopent-4-ene and 1-mesityl-1,3-bis(trimethylsilyl)-1-silaindene via a silapropadiene intermediate.^{11} The present reactions, however, produced no products in the absence of the nickel catalyst at 200°C. For example, heating a mixture of compound **4** with diphenylacetylene at 200°C for 20 h in a sealed glass tube afforded no product, but the starting compound **4** was recovered unchanged.

In conclusion, the nickel-catalyzed reaction of the disilanyl-substituted but-1-en-3-ynes with diphenylacetylene affords the 6-ethenyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-dienes, which are derived from the activation of ethynyldisilanyl unit by the nickel species, as the sole volatile product. No volatile products arising from the activation of ethenyldisilanyl unit are produced.

Experimental Section

General Procedure. All reactions for the synthesis of the starting compounds **1-6** were carried out under a purified argon atmosphere. The nickel-catalyzed reactions of compounds **1-5** were carried out in a degassed sealed glass tube (1.0 cm x 20 cm). NMR spectra were determined with a JEOL Model EX-270 spectrometer. Mass spectra were measured on a Shimadzu Model GC-MS-QP 1000. Infrared spectra were recorded on a Perkin-Elmer 1600-FT-IR spectrophotometer.

Materials. 1,4-Bis(methyldiphenylsilyl)but-1-en-3-yne, 1,4-bis(pentamethyldisilanyl)but-1-en-3-yne (**4**), and 1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**5**) were prepared as the method reported in the literature.[6]

1-(Methyldiphenylsilyl)-4-(pentamethyldisilanyl)but-1-en-3-yne (1a). In a 25-mL two-necked flask fitted with a condenser and dropping funnel was placed 2.2983 g (5.18 mmol) of 1,4-bis(methyldiphenylsilyl)but-1-en-3-yne in 15 mL of dry ethyl ether. To this was added 4.1 mL (6.15 mmol) of a methyllithium-ether solution at -78°C for 2 min. The mixture was allowed to warm to 0°C, and then 1.2 g (7.21 mmol) of chloropentamethyldisilane in 5 mL of ether was added to the mixture. After the mixture was stirred for 5 h, at room temperature, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvent ether was evaporated, and the residue was chromatographed on silica gel eluting with hexane, to give 1.2814 g (66% yield) of **1a**: MS *m/z* 378 (M^+); IR $\nu_{C\equiv C}$ 2147 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.13 (s, 9H, Me_3Si), 0.22 (s, 6H, Me_2Si), 0.64 (s, 3H, MeSi), 6.02 (d, 1H, HC=C, J = 19 Hz), 6.74 (d, 1H, HC=C, J = 19 Hz), 7.34-7.54 (m, 10H, ring protons); ^{13}C NMR $\delta(CDCl_3)$ -4.04 (MeSi), -3.07 (Me_2Si), -2.52 (Me_3Si), 95.37 and 107.18 ($C\equiv C$), 127.33 (HC=),127.92, 129.50, 134.86, 135.35 (phenyl ring carbons), 141.41 (HC=). Anal. Calcd for $C_{22}H_{30}Si_3$: C, 69.77; H, 7.98. Found: C, 69.70; H, 7.90.

4-[1-(Deuteriomethyl)tetramethyldisilanyl]-1-(methyldiphenylsilyl)but-1-en-3-yne (1b). To a solution of 1.8041 g (4.06 mmol) of 1,4-bis(methyldiphenylsilyl)but-1-en-3-yne in 20 mL of diethyl ether was added 3.2 mL (4.8 mmol) of a methyllithium-ether solution at -78°C. The mixture was stirred for 20 h at room temperature. The solution of the resulting lithio compound was added to 0.8050 g (4.30 mmol) of 1,1-dichlorotetramethyldisilane at room temperature. The mixture was stirred for 5 h, and then a solution of deuteriomethylmagnesium iodide prepared from 0.7733 g (5.5 mmol) of deuteriomethyl iodide and 0.1290 g (5.31 mmol) of magnesium in 5 mL of ether was added to the chlorodisilane derivative. The reaction mixture was heated to reflux for 5 h, and hydrolyzed with water to give 0.5367 g (35% yield) of **1b**. Pure **1b** was separated by MPLC: MS *m/z* 381 (M^+); IR ν_{C-D} 2120, $\nu_{C\equiv C}$ 2147 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.13 (s, 9H, Me_3Si), 0.21 (s, 3H, MeSi), 0.64 (s, 3H, MeSi), 6.02 (d, 1H, HC=C, J = 19 Hz), 6.74 (d, 1H, HC=C, J = 19 Hz), 7.34-7.54 (m, 10H, phenyl ring protons); ^{13}C NNR $\delta(CDCl_3)$ -4.04 (MeSi), -3.16 (MeSi), -3.11 (CD_3Si, J = 17 Hz),[12] -2.53 (Me_3Si), 95.33, 107.17 ($C\equiv C$), 127.31, 141.42 (olefinic acarbons), 127.92, 129.54, 134.88, 135.29 (phenyl ring carbons).

1-Methyldiphenylsilyl-4-(1-phenyltetramethyldi-silanyl)but-1-en-3-yne (2). In a 25-mL flask was placed 2.0787 g (4.68 mmol) of 1,4-bis(methyldiphenylsilyl)but-1-en-3-yne in 15 mL of ether, and the flask was cooled at -78°C. To this was added 3.8 mL (mmol) of a methyllithium-ether solution. The mixture was stirred at room temperature for 20 h, and then, 1.6 g (7.00 mmol) of 1-chloro-1-phenyltetramethyldisilane in 5 mL of ether was added to the lithio compound with ice cooling. The mixture was stirred at room temperature for 5 h and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. After evaporation of the solvent, the residue was chromatographed on silica gel eluting with hexane. Evaporation of the hexane gave 1.370 g (67% yield) of pure **2**: MS *m/z* 440 (M^+); IR $\nu_{C\equiv C}$ 2148 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.19 (s, 9H, Me_3Si), 0.51 (s, 3H, MeSi), 0.67 (s, 3H, MeSi), 5.92 (d, 1H, HC=C, J = 19 Hz), 6.68 (d, 1H, HC=C, J = 19 Hz), 6.95-7.42 (m, 15H, ring protons); ^{13}C NMR $\delta(CDCl_3)$ -4.20 (MeSi), -4.04 (MeSi), -2.36 (Me_3Si), 92.93 and 108.75 (C≡C), 127.22 (HC=), 127.92, 128.84, 129.06, 129.55, 134.10, 134.91, 135.29, 135.78 (Phenyl ring carbons), 142.01 (HC=). Anal. Calcd for $C_{27}H_{32}Si_3$: C, 73.57; H, 7.32. Found: C, 73.50; H, 7.30.

1-Methyldiphenylsilyl-4-(2-phenyltetramethyldisilanyl)but-1-en-3-yne (3). To a solution of 1.7244 g (3.88 mmol) of 1,4-bis(methyldiphenylsilyl)but-1-en-3-yne in 15 mL of diethyl ether was added 3.4 mL (5.1 mmol) of a methyllithium-ether solution at -78°C. The reaction mixture was stirred at room temperature for 20 h, and 1.1 g (4.81 mmol) of 1-chloro-2-phenyltetramethyldisilane was added to the resulting lithio compound with ice cooling. The mixture was stirred at room temperature for 10 h and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvent was evaporated and the residue was chromatographed on silica gel eluting with hexane to give 1.4283 g (84% yield) of **3**: Mass *m/z* 440 (M^+); IR $\nu_{C\equiv C}$ 2147 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.19 (s, 6H, Me_2Si), 0.41 (s, 6H, Me_2Si), 0.63 (s, 3H, MeSi), 6.00 (d, 1H, HC=C, J = 19 Hz), 6.73 (d, 1H, HC=C, J = 19 Hz), 7.30-7.53 (m, 15H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ -4.08 (Me_2Si and MeSi), -2.96 (Me_2Si), 94.97, 107.62 (C≡C), 127.17 (HC=), 127.75, 127.92, 128.63, 129.54, 133.91, 134.86, 135.26, 138.24 (phenyl ring carbons), 141.71 (HC=). Anal. Calcd for $C_{27}H_{32}Si_3$: C, 73.57; H, 7.32. Found: C,73.45; H, 7.18.

4-Methyldiphenylsilyl-1-(1-phenyltetramethyldislanyl)but-1-en-3-yne (6). To a solution of 1.1252 g (2.58 mmol) of **5** in 10 mL of diethyl ether was added 2.4 mL (3.6

mmol) of a diethyl ether solution of methyllithium at -78°C. The mixture was stirred at room temperature for 20 h. To this was added 0.8 g (3.44 mmol) of chloromethyldiphenylsilane in 3 mL of diethyl ether. The mixture was stirred at room temperature for 10 h, and hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The organic layer and extracts were combined, and washed with water, and then dried over calcium chloride. The solvent ether was evaporated, and the residue was chromatographed on silica gel eluting with hexane to give 0.9577 g (84% yield) of **6**: MS *m/z* 440 (M^+); IR $\nu_{C\equiv C}$ 2154 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.12 (s, 9H, Me_3Si), 0.42 (s, 3H, MeSi), 0.70 (s, 3H, MeSi), 6.06 (d, 1H, HC=C, J = 19 Hz), 6.79 (d, 1H, HC=C, J = 19 Hz), 7.32-7.65 (m, 15H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$, -6.02 (MeSi), -2.05 (MeSi), -1.96 (Me_3Si), 90.96, 108.32 (C≡C), 124.56 (HC=), 127.92 (two carbons), 128.86, 129.65, 134.39, 134.52, 135.20, 136.17 (phenyl ring carbons), 145.00 (HC=). Anal. Calcd for $C_{27}H_{32}Si_3$: C, 73.57; H, 7.32. Found: C, 73.49; H, 7.32.

Nickel-catalized reaction of 1a with diphenylacetylene. A mixture of 0.3377 g (0.89 mmol) of **1a**, 0.2390 g (1.34 mmol) of diphenylacetylene, and 0.0250 g (0.09 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The mixture was chromatographed using a short silica gel column and eluting with hexane to remove nickel species from the reaction mixture. The product **7a** (0.2624 g, 53% yield) was separated by MPLC (silica gel 40-63 mm) as colorless crystals: mp 155-157°C (after recrystallization from ethanol); MS *m/z* 556 (M^+); ^1H NMR $\delta(CDCl_3)$ -0.02 (s, 6H, Me_2Si), 0.29 (s, 6H, Me_2Si), 0.69 (s, 3H, MeSi), 2.19 (s, 3H, MeC), 6.32 (1d, 1H, HC=C, J=18 Hz), 6.73 (d, 1H, HC=C, J=18 Hz), 6.79-7.57 (m, 20H, ring protons); ^{13}C NMR $\delta(CDCl_3)$, -3.65 (MeSi), -0.84 (Me_2Si), -0.54 (Me_2Si), 21.82 (MeC=), 124.96, 125.01 (phenyl ring protons), 126.52 (HC=), 127.49 (two carbons), 127.67 (two carbons), 127.92, 129.42, 134.95, 136.06 (phenyl ring carbons), 142.61 (HC=), 142.66, 143.09 (phenyl ring carbons), 152.33, 157.74, 160.52, 160.93 (olefinic ring carbons). Anal. Calcd for $C_{36}H_{40}Si_3$: C, 77.63; H, 7.24. Found: C, 77.62; H, 7.17.

Nickel-catalyzed reaction of 1b with diphenylacetylene. A mixture of 0.3090 g (0.81 mmol) of **1b**, 0.1761 g (0.988 mmol) of diphenylacetylene, and 0.0224 g (0.0801 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The mixture was chromatographed on silica gel eluting with hexane to remove any nickel complexes, and the product (0.5367 g, 35% yield) was separated by MPLC: MS *m/z* 559 (M^+); ^{1}H NMR δ($CDCl_3$)-0.02 (s, 4.8H, Me_3Si), 0.29 (s, 4.7H, Me_2Si), 0.70 (s, 3H, MeSi), 2.20 (s, 2.5H, MeC), 6.32 (d, 1H, HC=C, J = 18 Hz), 6.73 (d, 1H, HC=C, J = 18 Hz), 6.80-7.58 (m, 20H, ring protons); ^{13}C NMR^{13} δ($CDCl_3$) -3.63 (MeSi), -0.90 (MeSi), -0.84 (MeSi), -0.59 (MeSi), -0.54 (MeSi), 21.82 (MeC), 126.52 and 152.35 (HC=CH), 124.98, 125.01, 127.49, 127.53, 127.67 (two carbons), 127.92, 129.42, 134.95, 136.05, 142.66, and 143.09 (phenyl ring carbons), 142.61, 157.72, 160.50, and 160.93 (C=C), ^{2}H NMR δ($CDCl_3$) 0.00 (CD_3Si), 0.31 (CD_3Si), 0.36 (CD_3Si), 2.22 (CD_3C).

Nickel-catalyzed reaction of 2 with diphenylacetylene. A mixture of 0.3515 g (0.80 mmol) of **2**, 0.1708 g (0.96 mmol) of diphenylacetylene, and 0.022 g (0.08 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The mixture was chromatographed on silica gel eluting with hexane to remove any nickel complexes, and then the mixture was separated by MPLC to give 0.2144 g (43% yield) of **8**: mp 174-177°C (after recrystallization from ethanol); MS *m/z* 618 (M^+); ^{1}H NMR δ($CDCl_3$) -0.22 (s, 6H, Me_2Si), 0.07 (s, 6H, Me_2Si), 0.61 (s, 3H, MeSi), 5.82 (d, 1H, HC=C, J = 18 Hz), 6.92 (d, 1H, HC=C, J = 18 Hz), 6.74-7.50 (m, 25H, ring protons); ^{13}C NMR δ($CDCl_3$), -3.66 (MeSi), -0.75 (Me_2Si), -0.47 (Me_2Si), 124.94, 125.00, 126.99, 127.44, 127.51 (two carbons), 127.69 (two carbons), 127.89, 129.09, 129.36 (phenyl ring carbons), 131.45 (HC=), 134.91, 136.03 (HC=), 142.53, 142.59, 142.64, 145.86 (phenyl ring carbons), 152.08, 160.04, 161.55, 163,90 (olefinic ring carbons). Anal. Calcd for $C_{41}H_{42}Si_3$: C, 79.55; H, 6.84. Found: C, 79.33; H, 6.74.

Nickel-catalyzed reaction of 3 with diphenylacetylene. A mixture of 0.3882 g (0.88 mmol) of **3**, 0.2038 g (1.14 mmol) of diphenylacetylene, and 0.0264 g (0.094 mmol) of

dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The product (0.0814 g, 15% yield) was isolated by MPLC: mp 174-177°C. All spectral data for the product were identical with those of **8**.

Nickel-catalyzed reaction of 4 with diphenylacetylene. A mixture of 0.3121 g (1.00 mmol) of **4**, 0.2670 g (1.49 mmol) of diphenylacetylene, and 0.0280 g (0.1 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The mixture was separated by MPLC to give 0.2530 g (52% yield) of **9**: mp 113-114°C (after recrystallization from ethanol); MS *m/z* 490 (M^+); ^{1}H NMR δ($CDCl_3$), 0.08 (s, 9H, Me_3Si), 0.17 (s, 6H, Me_2Si), 0.29 (s, 6H, Me_2Si), 0.30 (s, 6H, Me_2Si), 2.14 (s, 3H, MeC), 6.09 (d, 1H, HC=C, J = 18 Hz), 6.80 (d, 1H, HC=C, J = 18 Hz), 6.86-7.09 (m, 10H, phenyl ring protons); ^{13}C NMR δ($CDCl_3$) -4.27 (Me_2Si), -2.26 (Me_3Si), -0.73 (Me_2Si), -0.11 (Me_2Si), 21.85 (MeC), 125.00 (HC=), 127.53 (two carbons), 127.73 (two carbons), 130.28 (two carbons), 140.05 (two carbons) (phenyl ring carbons), 142.73 (olefinic ring carbon), 148.46 (HC=), 158.22, 160.77, 160.84 (olefinic ring carbons). Anal. Calcd for $C_{28}H_{42}Si_4$: C, 68.50; H, 8.62. Found : C, 68.42; H, 8.50.

Nickel-catalyzed reaction of 5 with diphenylacetylene. A mixture of 0.2080 g (0.48 mmol) of **5**, 0.1303 g (0.73 mmol) of diphenylacetylene, and 0.013 g (0.05 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The product **10** (0.1178 g, 40% yield) was separated by MPLC: mp 158-159°C (after recrystallization from ethanol); MS *m/z* 614 (M^+); ^{1}H NMR δ($CDCl_3$) -0.23 (s, 6H, Me_2Si), 0.08 (s, 9H, Me_3Si), 0.28 (s, 3H, MeSi), 0.39 (s, 3H, MeSi), 5.70 (d, HC=C, J = 18 Hz), 6.98 (d, 1H, HC=C, J = 18 Hz), 6.75-7.43 (m, 20H, ring protons); ^{13}C NMR δ($CDCl_3$) -5.61 (MeSi), -1.85 (Me_3Si), -0.70 (Me_2Si), -0.25 (Me_2Si), 124.92, 125.01, 126.92, 127.30, 127.44, 127.53, 127.60, 127.67, 127.75, 127.87 (phenyl ring carbons), 128.68 (olefinic ring carbon), 129.09 (phenyl ring carbon), 133.33 (HC=), 134.54, 142.62, 142.71, 142.77, 143.74 (phenyl ring carbons), 149.60 (HC=), 160.00, 161.67, 164.28 (olefinic ring carbons). Anal. Calcd for $C_{38}H_{46}Si_4$: C, 74.20; H, 7.54. Found: C, 74.21, H, 7.47.

Nickel-catalyzed reaction of 6 with diphenylacetylene. A mixture of 0.2099 g (0.48 mmol) of **6**, 0.1168 g (0.66 mmol) of diphenylacetylene, and 0.0158 g (0.06 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. By GLC and GPC analysis of the reaction mixture, no volatile product was detected.

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12. Resonances due to a trideuteriomethyl group showed the overlapping resonances with methylsilyl carbons, and therefore, chemical shift of the center of septet was calculated on the basis of that of the four signals observed.

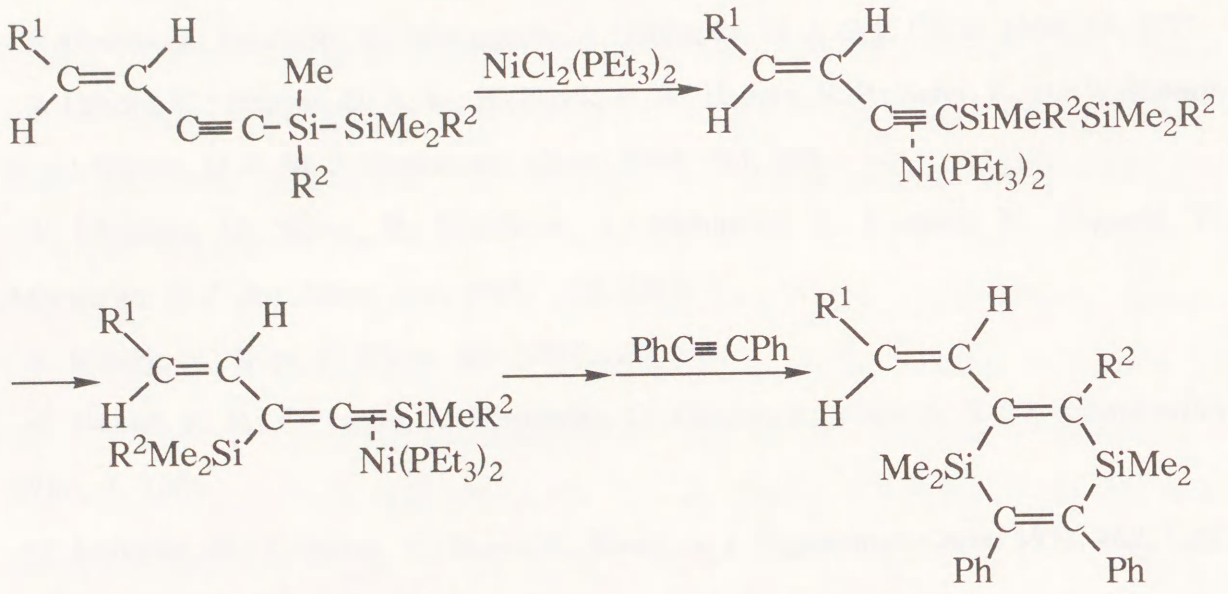
13. Splitting resonances at δ -0.90 and -0.84, and at -0.59 and -0.54 are presumably due to the axial and equatorial carbons. Resonances due to deuteriomethyl groups could not be assigned because of the overlapping resonances with other resonances of different environment of the deuteriomethyl groups and also methylsilyl carbons.

Chapter 2

Nickel-Catalyzed Reactions of Disilanyl-Substituted Enynes with Methyldiphenylsilane

Introduction

The nickel-catalyzed reactions of phenylethynylpolysilanes afford silapropadiene-nickel complexes,[1,2] while similar reactions of vinyldisilanes produce silene-nickel complexes as reactive intermediates.[3] As shown in chapter 1, disilanyl-substituted enynes which can be readily obtained by the rhodium-catalyzed reaction of ethynyldisilanes,[4] (E)-1,4-bis(disilanyl)-but-1-en-3-ynes and (E)-4-(disilanyl)-1-(silyl)but-1-en-3-ynes react with diphenylacetylene in the presence of a catalytic amount of dichlorobis(triethylphospine)nickel(II) to give 1,4-disilacyclohexa-2,5-diene derivatives.[5] In these reactions, the nickel catalyst adds to a triple bond in the enyne molecules to produce the 1,4-disilacyclohexa-2,5-dienes. For the mechanism of these reactions, we proposed the initial formation of the silapropadiene-nickel complex as a key intermediate.

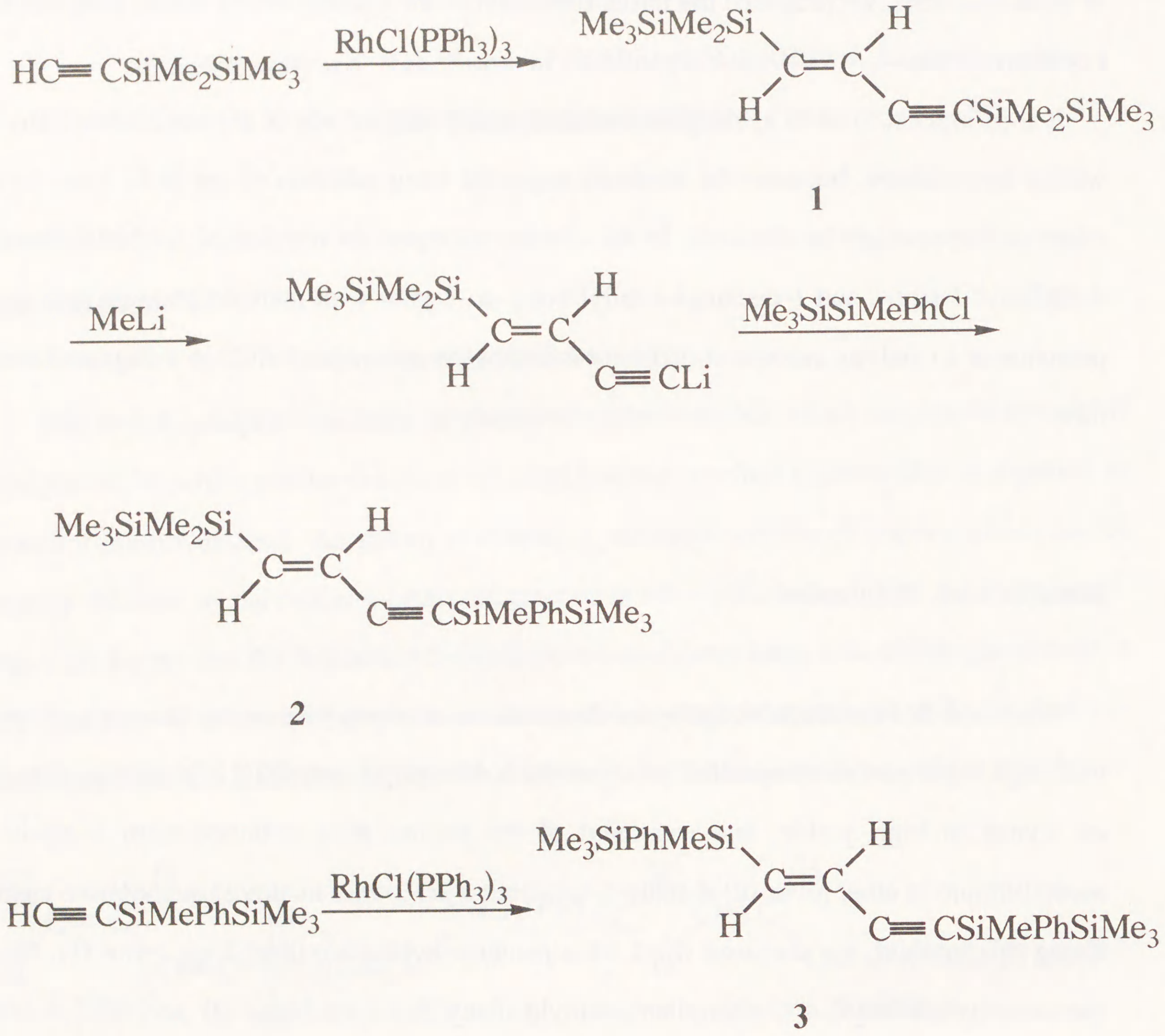


It is of interest to us to investigate the nickel-catalyzed reaction of the bis(disilanyl)enynes with a hydrosilane, because the products expected from addition of an Si-H bond to the silapropadienes might be obtained. In this chapter we report the reaction of 1,4-bis(disilanyl)-, 4-disilanyl-1-silyl-, and 1-disilanyl-4-(silyl)but-1-en-3-ynes with methyldiphenylsilane in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) in a degassed sealed tube.

Results and Discussion

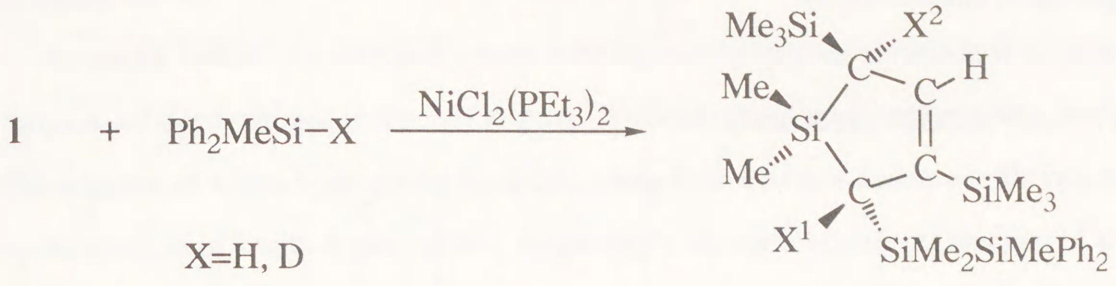
We found that the rhodium-catalyzed dimerization of ethynylsilanes and disilanes proceeds with high regio- and stereospecificity to give (E)-1,4-bis(silyl)- and (E)-1,4-bis(disilanyl)but-1-en-3-ynes in high yields, and treatment of the enynes thus obtained with 1 equiv of methyllithium in ether gives (E)-4-lithio-1-(silyl)but-1-en-3-ynes in almost quantitative yields.[4] Using this method, we prepared (E)-1,4-bis(pentamethyldisilanyl)but-1-en-3-yne (**1**), (E)-1-(pentamethyldisilanyl)-4-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**2**), and (E)-1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**3**) used as starting compounds (Scheme I).

Scheme I



When a mixture of 1,4-bis(pentamethyldisilanyl)but-1-en-3-yne (**1**) and a slight excess of methyldiphenylsilane in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) in a degassed glass tube was heated at 200°C for 20 h, an adduct was obtained in 63% yield, as the sole product (Scheme II). No other products were detected by either spectrometric analysis or GLC analysis. The adduct was readily isolated by preparative GLC and identified as *trans*-1,1-dimethyl-2-(2,2-diphenyltrimethyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (**4a**) by spectroscopic analysis, as well as by elemental analysis. Thus, the ^{1}H NMR spectrum of **4a** shows the presence of two kinds of trimethylsilyl protons, five nonequivalent methylsilyl protons, two methine protons, and one olefinic proton, as well as aromatic ring protons. The ^{13}C NMR spectrum of **4a** reveals resonances due to two kinds of trimethylsilyl carbons, five nonequivalent methylsilyl carbons, two different methine carbons, two olefinic carbons, and four phenyl ring carbons, respectively. Its ^{29}Si NMR spectrum indicates the presence of five nonequivalent silicon atoms. Furthermore, the long-range ^{13}C-^{1}H COSY spectrum shows that protons at 1.05 (X^1 = H) and 1.40 ppm (X^2 = H) couple with the C-2 and C-5 atom in the ring, respectively, while hydrogen on an olefinic carbon atom at 6.07 ppm couples with the C-4 atom.

Scheme II

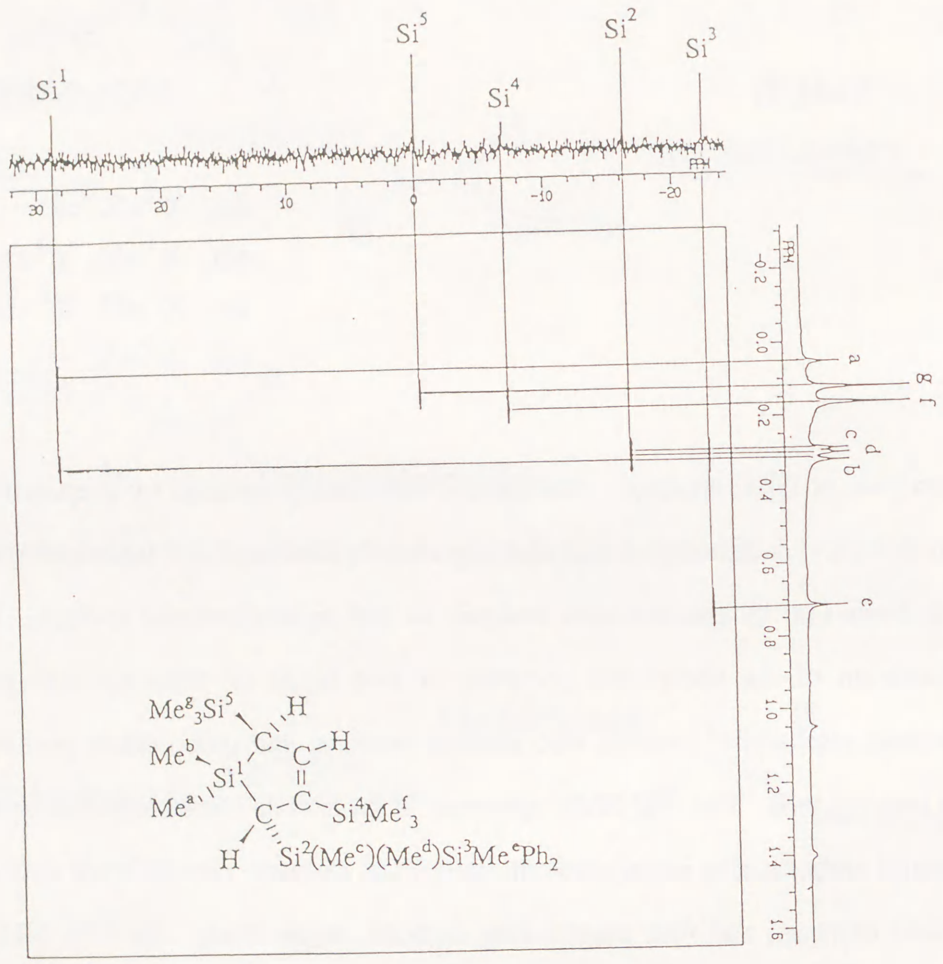


4a, $X^1=X^2=H$
4b, $X^1=D$, $X^2=H$
4c, $X^1=H$, $X^2=D$
4d, $X^1=X^2=D$

The ^{1}H-^{29}Si COSY NMR spectrum shown in Figure 1 reveals that methyl protons at 0.06 (Me^a) and 0.32 ppm (Me^b) couple with a ring silicon atom, while the protons at 0.72 and 0.17

ppm couple with Si^3 and Si^4, respectively. Similarly, two methyl protons at 0.29 (Me^c) and 0.30 ppm (Me^d) couple with Si^2.

Figure 1. ^1H-^{29}Si COSY spectrum of **4a**



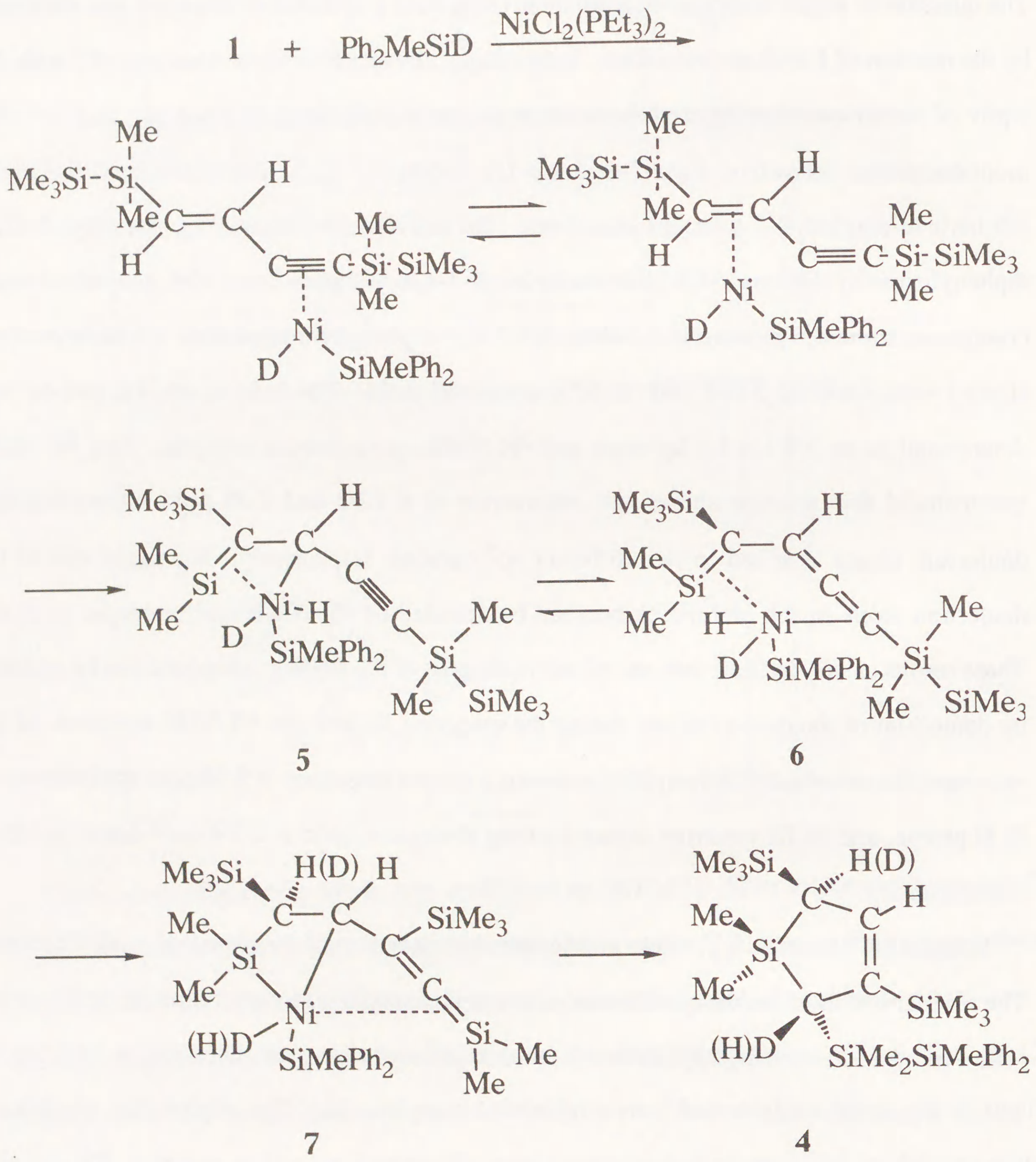
The *trans*-configuration for **4a** was confirmed by NOE-FID difference experiments at 270 MHz. Thus, saturation of trimethylsilyl protons (Me^g) on the C-5 atom in the five-membered ring of **4a** resulted in a strong enhancement of protons at C-2 and C-5 positions and protons of one methyl group (Me^b) on the ring silicon atom. Irradiation of hydrogen (X^2 = H) at the C-5 position led to the enhancement of trimethylsilyl protons (Me^g) on this carbon and all methyl protons on a disilanyl group, as well as protons of one methyl group (Me^a) on the ring silicon

atom and a proton on the C-4 atom. These results are wholly consistent with the structure proposed for **4a**.

As can be seen in the ^1H NMR spectrum of **4a**, two hydrogens are attached to different sp^3 carbons and one hydrogen is attached to the sp^2 carbon in the silacyclopentene ring, respectively. The question of which hydrogen of these three came from a hydrosilane molecule was answered by the reaction of **1** with deuteriosilane. Interestingly, the nickel-catalyzed reaction of **1** with 2.1 equiv of deuteriomethyldiphenylsilane under the same conditions afforded two isomers of a monodeuterated derivative, *trans*-2-deuterio-1,1-dimethyl-2-(2,2-diphenyltrimethyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (**4b**) and *trans*-5-deuterio-1,1-dimethyl-2-(2,2-diphenyltrimethyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (**4c**), and dideuterated compound, *trans*-2,5-dideuterio-1,1-dimethyl-2-(2,2-diphenyltrimethylsilyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (**4d**) in 57% combined yield. The ratio of **4b**, **4c**, and **4d** was determined to be 1.0:1.4:3.5 by mass and ^2H NMR spectrometric analysis. The ^2H NMR spectrum of this mixture shows two resonances at δ 1.02 and 1.38 ppm, indicating that deuterium atoms attached to two different sp^3 carbons, respectively. No signal due to the deuterium atom on the olefinic carbon can be detected by ^2H NMR spectroscopic analysis. These results clearly indicate that one of two hydrogens of the starting compound can be replaced by deuterium of the deuteriosilane during the reaction. In fact, the ^1H NMR spectrum of the recovered deuteriomethyldiphenylsilane reveals a quartet resonance at 5.18 ppm attributed to an Si-H proton, and its IR spectrum shows a strong absorption band at 2114 cm^{-1} due to the Si-H stretching.

Scheme III illustrates a possible mechanistic interpretation of the observed reaction course. The mechanism involves the coordination of the nickel species to a carbon-carbon double bond, followed by a 1,2-trimethylsilyl shift to a terminal sp^2 carbon to give silene-nickel complex (**5**) which would be transformed into silyl-nickel complex (**6**). The silyl-nickel complex **6** undergoes intramolecular isomerization giving silapropadiene-nickel complex (**7**). Finally, hydrosilylation of a silicon-carbon double bond and then the formation of the five-membered ring, accompanying by the reductive elimination of the nickel species produces product **4**. The similar nickel-catalyzed reactions of 1,4-bis(disilanyl)but-1-en-3-ynes with diphenylacetylene proceed with the coordination of the nickel species to a carbon-carbon triple bond, giving 2-

Scheme III



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disilanyl-1,4-disilacyclohexa-2,5-dienes.[4] In the present reactions, it seems likely that the nickel species coordinates to a carbon-carbon triple bond at the first step. The nickel complex thus formed would be transformed into a kinetically favored complex, a disilanyl-substituted olefin-nickel complex, which would undergo isomerization to give the silene-nickel complex **5**, although evidence for the coordination to the double bond has not yet been obtained.

The presence of deuterium atoms on sp^3 carbons in the silacyclopentenyl ring and of methyldiphenylsilane in the recovered deuteriomethyldiphenylsilane can be understood by hydrogen-deuterium exchange between an Ni-D and C-H bond in the nickel complexes **5**-**7**, and by exchange between coordinated methyldiphenylsilane ($MePh_2Si$-Ni-H) and free deuteriomethyldiphenylsilane.

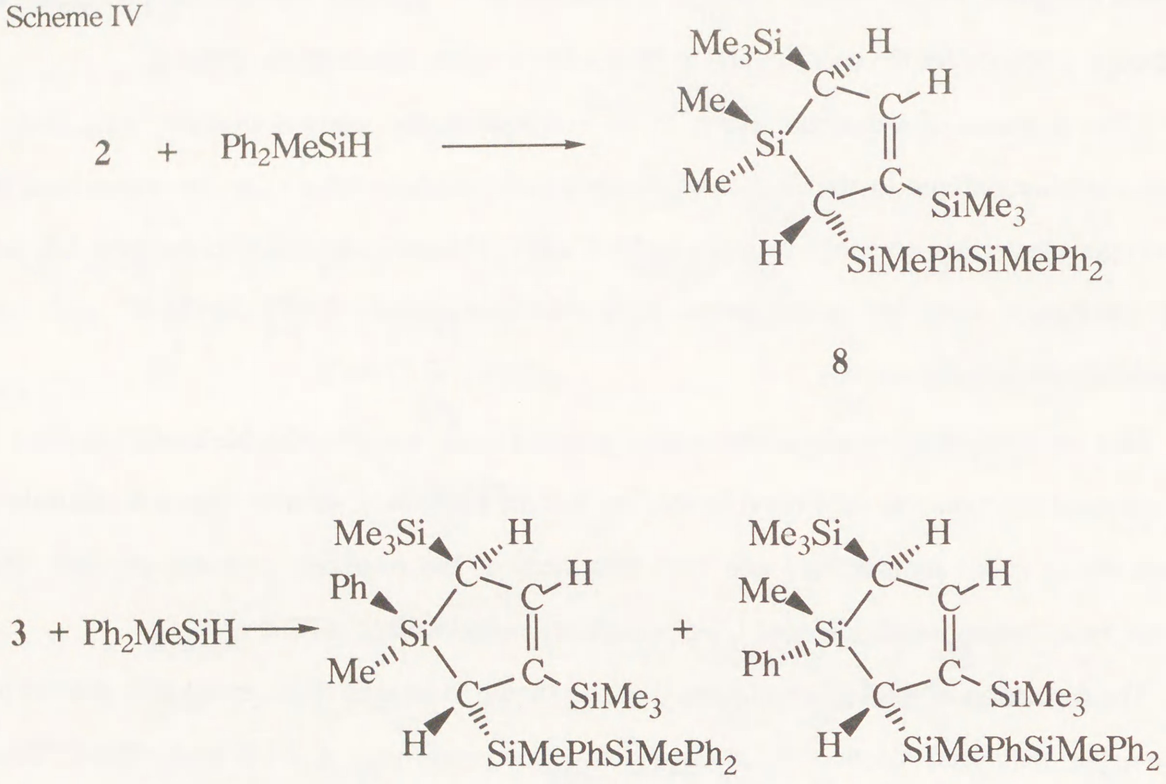
That the addition of a methyldiphenylsilyl group to a silicon-carbon double bond took place in the present reaction was confirmed by the fact that the reaction of **4a** with hydrogen chloride in benzene at room temperature and then treatment of the resulting cleavage product with methylmagnesium iodide afforded 1,1-diphenyltetramethyldisilane in 21% yield.

The formation of the 1-silacyclopent-3-ene as shown in scheme III is remarkably general for the nickel-catalyzed reaction of 1,4-bis(disilanyl)but-1-en-3-ynes with the hydrosilane. Thus, treatment of compound **2** with methyldiphenylsilane in the presence of a nickel catalyst under the same conditions gave trans-1,1-dimethyl-2-(1,2-dimethyltriphenyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (**8**) in 66% yield, as the sole product (Scheme IV).

The structure of **8** was confirmed by spectrometric analysis, as well as by elemental analysis. Similar treatment of compound **3** with methyldiphenylsilane, however, afforded two isomers of a 1-silacyclopent-3-ene derivative in 65% combined yield. The ratio of the isomers was calculated to be approximately 1:1 by the ^1H NMR spectromeric analysis. All attempts to separate one isomer from the other were unsuccessful. In all cases, a mixture of two isomers was obtained, but the isolated mixtures showed different ratios of the isomers. Therefore, we could identify two isomers tentatively as t-2-(1,2-dimethyl-1,2,2-triphenyldisilanyl)-1-methyl-r-

1-phenyl-3,c-5-bis(trimethylsilyl)silacyclopent-3-ene (**9a**) and c-2-(1,2-dimethyl-1,2,2-triphenyldisilanyl)-1-methyl-r-1-phenyl-3,t-5-bis(trimethylsilyl)silacyclopent-3-ene (**9b**).

Scheme IV



8

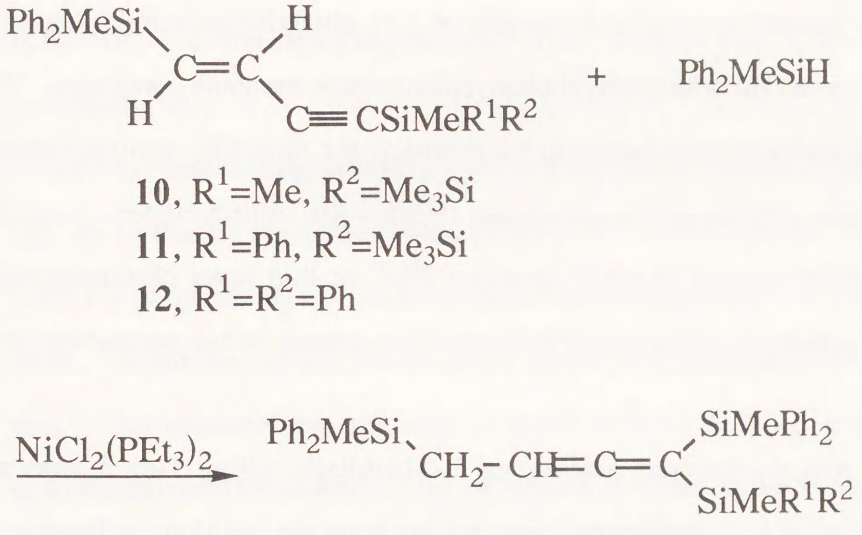
9a **9b**

In the ^{1}H NMR spectrum of **9a**, the trimethylsilyl protons at the C-5 position in the five-membered ring showed an upfield shift, due to the phenyl ring current. For this reason, we thought that the phenyl group on the ring silicon atom of **9a** should be *cis* to this trimethylsilyl group, while the phenyl group of isomer **9b** should be located at the *trans* position.

Next we turned our attention to 1-monosilyl-4-(disilanyl)but-1-en-3-ynes to obtain more information about the nickel-catalyzed reaction of silyl-substituted enynes with the hydrosilane. (E)-1-methyldiphenylsilyl-4-(pentamethyldisilanyl)but-1-en-3-yne (**10**), (E)-1-methyldiphenylsilyl-4-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**11**), and (E)-1,4-bis(methyldiphenylsilyl)but-1-en-3-yne (**12**) were prepared by the similar method to that shown in Scheme I.

The reaction of **10** with methyldiphenylsilane in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) at 200°C for 20 h produced 1,4-bis(methyldiphenylsilyl)-1-(pentamethyldisilanyl)buta-1,2-diene (**13**) in 73% yield, as the sole product. The structure of **13** was confirmed by spectroscopic analysis and the chemical reaction, as well as by elemental analysis. Thus, the IR spectrum of product **13** shows a strong absorption band at 1908 cm^{-1} due to stretching frequencies of an allenic bond. Treatment of **13** with hydrogen chloride in diethyl ether at room temperature afforded chloropentamethyldisilane and chloromethyldiphenylsilane in 31 and 50% yields, respectively. No 1-chloro-2,2-diphenyltrimethyldisilane was detected in the reaction mixture. These results clearly indicate that this reaction does not involve addition of methyldiphenylsilane to a 1-silapropadiene intermediate arising from a 1,3-trimethylsilyl shift in compound **10**, but involves 1,4-addition of the hydrosilane to the starting compound **10**. Presumably, the rate of the hydrosilylation is faster than that of a 1,3-silyl shift giving the silapropadiene under the conditions used. Similar reaction

Scheme V



10, R^1=Me, R^2=Me_3Si
11, R^1=Ph, R^2=Me_3Si
12, R^1=R^2=Ph

13, R^1=Me, R^2=Me_3Si
14, R^1=Ph, R^2=Me_3Si
15, R^1=R^2=Ph

of **11** with methyldiphenylsilane gave 1,4-bis(methyldiphenylsilyl)-1-(1-phenyltetramethyldisilanyl)buta-1,2-diene (**14**) in 50% yield, while compound **12** yielded 1,1,4-tris(methyldiphenylsilyl)buta-1,2-diene(**15**) in 49% yield. In these reactions, no other products were detected either by spectrometric analysis or GLC analysis (Scheme V).

In all cases, hydrosilylation products arising from 1,4-addition of methyldiphenylsilane in which a methyldiphenylsilyl group added to the sp carbon atom bearing a silyl or disilanyl group were produced. No products derived from addition of the silyl group to sp^2 carbon were detected either by spectrometric analysis or GLC analysis. In contrast to the similar reaction of **1-3**, the nickel species probably coordinates on a carbon-carbon triple bond in the enynes at the initial step. It has been reported that the hydrosilylation to an acetylenic bond in the enynes takes place much faster than that of the olefinic bond. In fact, the reaction of vinylacetylene with hydrosilanes in the presence of a platinum catalyst gives 1-(silyl)buta-1,3-dienes.[6,7] It has been also found that the hydrosilylation of 2-triethylsilyl-1,4-bis(trimethylsilyl)but-1-en-3-yne with triethylsilane in the presence of a platinum catalyst produced 1,3-bis(triethylsilyl)-1,4-bis(trimethylsilyl)buta-1,2-diene derived from 1,4-addition of the hydrosilane.[8]

We also carried out the nickel-catalyzed reaction of 1-(1-phenyltetramethyldisilanyl)-4-(trimethylsilyl)but-1-en-3-yne (**16**) with methyldiphenylsilane under the same conditions. Thus, when **16** was heated with methyldiphenylsilane in the presence of a nickel(II) catalyst under the same conditions, nonvolatile substances were produced. Neither the 1-silacyclopent-3-ene derivative nor the allene derivative was detected by either GLC or thin layer chromatographic analysis. The ^{1}H NMR spectrum of the nonvolatile products reveals broad resonances in the methylsilyl region.

In conclusion, the nickel-catalyzed reaction of 1,4-bis(disilanyl)but-1-en-3-ynes with methyldiphenylsilane afforded 1-silacyclopent-3-enes arising from the addition-cyclization of a hydrosilane to a silapropadiene-nickel complex. Similar reaction of 4-disilanyl-1-(silyl)but-1-en-3-ynes gave products derived from 1,4-hydrosilylation of the silane to the enynes, while the reaction of the 1-disilanyl-4-(monosilyl)but-1-en-3-yne produced nonvolatile substances.

Experimental Section

General procedure. All reactions for the synthesis of the starting compound **1-3**, **10-12** were carried out under a purified argon atmosphere. The nickel-catalyzed reactions of compounds **1-3**, **10-12**, **16** were carried out in a degassed sealed glass tube (1.0 cm x 20 cm). Gas chromatographic separations were carried out by using a column packed with 30% SE-30 Silicone on Chromosorb P. NMR spectra were determined with a JEOL MODEL EX-270 spectrometer. Mass spectra were measured on a Shimadzu Model GC-MS-QP 1000. Infrared spectra were recorded on a Perkin-Elmer 1600-FT-IR spectrophotometer. Gel-permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.). Yields of the products were calculated by analytical GLC with the use of an internal standard.

Materials. (E)-1,4-bis(pentamethyldisilanyl)but-1-en-3-yne (**1**), (E)-1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**3**), 1-(pentamethyldisilanyl)-4-(methyldiphenylsilyl)-but-1-en-3-yne (**10**), 1-(1-phenyltetramethyldisilanyl)-4-(methyldiphenylsilyl)but-1-en-3-yne (**11**), (E)-1,4-bis(methyldiphenylsilyl)but-1-en-3-yne (**12**) were prepared as reported previously.[4,5]

(E)-1-Pentamethyldisilanyl-4-(1-phenyltetramethydisilanyl)but-1-en-3-yne (2). In a 30-mL two-necked flask fitted with a condenser and a dropping funnel was placed 1.4151 g (4.54 mmol) of 1,4-bis(pentamethyldisilanyl)but-1-en-3-yne (**1**) in 15 mL of dry ethyl ether. To this was added 3.7 mL (5.55 mmol) of a methyllithium-ether solution at -78°C for 2 min. The mixture was allowed to warm to 0°C, and 1.3 g (5.69 mmol) of 1-chloro-1-phenyltetramethyldisilane in 5 mL of ether was added to the mixture. The mixture was stirred for 5 h at room temperature and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvent ether was evaporated, and the residue was chromatographed on silica gel eluting with hexane, to give 0.6579 g (39% yield) of

2: MS *m/z* 374 (M^+); IR $\nu_{C\equiv C}$ 2148 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.08 (s, 9H, Me_3Si), 0.14 (br s, 6H, Me_2Si, 9H, Me_3Si), 0.48 (s, 3H, MeSi) 5.99 (d, 1H, HC=C, J = 19 Hz), 6.75 (d, 1H, HC=C, J = 19 Hz), 7.33-7.37 (m, 3H, ring protons), 7.55-7.59 (m, 2H, ring protons); ^{13}C NMR $\delta(CDCl_3)$ -4.62 (Me_3Si), -4.15 (MeSi), -2.37 (Me_3Si), -2.32 (Me_3Si), 90.80, 109.24 (C≡C), 123.37 (C=C), 127.85, 128.81, 134.12, 136.01 (ring carbons), 146.34 (C=C). Anal. Calcd for $C_{19}H_{34}Si_4$: C, 60.89; H, 9.14. Found: C, 60.82, H, 9.04.

***trans*-1,1-Dimethyl-2-(2,2-diphenyltrimethyldisilanyl)-3,5-bis(trimethylsilyl)silacyclopent-3-ene (4a).** A mixture of 0.2598 g (0.83 mmol) of **1**, 0.2473 g (1.25 mmol) of methyldiphenylsilane, and 0.0230 g (0.082 mmol) of dichlorobis(triethylphosphine)-nickel(II) was heated at 200°C for 20 h. The mixture was chromatographed on a short florisil column eluting with hexane, to remove nickel species from the reaction mixture. The product **4a** (63% yield) was isolated by preparative GLC: MS *m/z* 510 (M^+); ^1H NMR $\delta(C_6D_6)$ 0.06 (s, 3H, MeSi), 0.12 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.29 (s, 3H, MeSi), 0.30 (s, 3H, MeSi), 0.32 (s, 3H, MeSi), 0.72 (s, 3H, MeSi), 1.05 (br s, 1H, HC), 1.40 (br d, 1H, HC, J = 1.5 Hz), 6.07 (br d, 1H, HC=C, J = 1.5 Hz), 7.22-7.68 (m, 10H, ring protons); ^{13}C NMR δ (C_6D_6) -4.22 (MeSi), -3.26 (MeSi), -2.10 (MeSi), -0.86 (MeSi), 0.28 (Me_3Si), 0.46 (MeSi), 0.51 (Me_3Si), 20.35 and 26.35 (HC), 129.08 (phenyl ring carbon), 129.11.(olefinic ring carbon), 135.22, 135.30 (phenyl ring carbons), 140.76 (olefinic ring carbon), 147.17 (phenyl ring carbon); ^{29}Si NMR δ (C_6D_6) -22.59, -16.31, -6.89, -0.12, 28.63. Anal. Calcd for $C_{27}H_{46}Si_5$: C, 63.45; H, 9.07. Found: C, 63.39, H, 9.07.

Reaction of 4a with hydrogen chloride.. In a 30 mL flask fitted with a condenser and an inlet capillary tube for hydrogen chloride was placed 0.0960 g (0.19 mmol) of **4a** in 1 mL of benzene. Into this was introduced hydrogen chloride for 3 h. After the solvent benzene and excess of hydrogen chloride were removed under reduced pressure, 0.5 mL (0.69 mmol) of a methylmagnesium iodide-ether solution was added to the resulting mixture. The mixture was stirred for 5 h at room temperature and then hydrolyzed with water. The organic layer was analyzed as being 1,1-diphenyltetramethyldisilane (21% yield). The retention time on GLC and mass fragmentation pattern for 1,1-diphenyltetramethyldisilane were identical with those of an authentic sample.

***trans*-2-Deuterio-1,1-dimethyl-2-(2,2-diphenyltrimethyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (4b), *trans*-5-deuterio-1,1-dimethyl-2-(2,2-diphenyltrimethyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (4c), and *trans*-2,5-dideuterio-1,1-dimethyl-2-(2,2-diphenyltrimethylsilyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (4d).** A mixture of 0.1962 g (0.63 mmol) of **1**, 0.2677 g (1.35 mmol) of deuteriomethyldiphenylsilane, and 0.0177 g (0.063 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The mixture was treated with a short florisil column to remove nickel species from the reaction mixture. A mixture of **4b-4d** (57% yield) was isolated by preparative GLC: MS *m/z* 511 (M^+) for **4b** and **4c**, 512 (M^+) for **4d**; ^1H NMR $\delta(C_6D_6)$ 0.05 (s, 3H, MeSi), 0.12 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.29 (s, 3H, MeSi), 0.30 (s, 3H, MeSi), 0.32 (s, 3H, MeSi), 0.72 (s, 3H, MeSi), 1.05 (br s, 0.24H, HC), 1.40 (br d, 0.17H, HC, J = 1.5 Hz), 6.07 (br d, 1H, HC=C, J = 1.5 Hz), 7.24-7.73 (m, 10H, ring protons); ^{13}C NMR $\delta(C_6D_6)$ -4.22 (MeSi), -3.26 (MeSi), -2.10 (MeSi), -0.86 (MeSi), 0.28 (Me_3Si), 0.46 (MeSi), 0.51 (Me_3Si), 20.35 and 26.35 (HC), 129.08 (phenyl ring carbon), 129.11 (olefinic ring carbon), 135.22, 135.30 (phenyl ring carbons), 140.76 (olefinic ring carbon), 147.17 (phenyl ring carbon); ^2H NMR $\delta(C_6D_6)$ 1.02, 1.38.

***trans*-1,1-Dimethyl-2-(1,2-dimethyltriphenyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (8).** A mixture of 0.2473g (0.66 mmol) of **2**, 0.1742 g (0.88 mmol) of methyldiphenylsilane, and 0.0188 g (0.067 mmol) of dichlorobis(triethylphosphine)-nickel(II) was heated at 200°C for 20 h. The mixture was treated with a short florisil column to remove nickel species from the reaction mixture. The product **8** (66% yield) was isolated by preparative GLC: MS *m/z* 572 (M^+); ^1H NMR $\delta(C_6D_6)$ -0.08 (s, 9H, Me_3Si), 0.19 (s, 3H, MeSi), 0.22 (s, 9H, Me_3Si), 0.35 (s, 3H, MeSi), 0.36 (s, 3H, MeSi), 0.71 (s, 3H, MeSi), 1.22 (br s, 1H, HC), 2.03 (br d, 1H, HC, J = 2.0 Hz), 6.21 (br d, 1H, HC=C, J = 2.0 Hz), 7.24-7.68 (m, 15H, ring protons); ^{13}C NMR δ(C_6D_6) -4.31 (MeSi), -3.30 (MeSi), -2.62 (MeSi), -1.76 (MeSi), 0.37 (Me_3Si), 17.17 and 27.05 (HC), 129.10, 129.13 (phenyl ring carbons), 129.80 (olefinic ring carbon), 135.04, 135.22, 135.28, 135.33, 138.17 (phenyl ring carbons), 140.54 (olefnic ring carbon), 147.14 (phenyl ring carbon). Anal. Calcd for $C_{32}H_{48}Si_5$: C, 67.06; H, 8.44. Found : C 66.91; H, 8.37.

t-2-(1,2-Dimethyl-1,2,2-triphenyldisilanyl)-1-methyl-r-1-phenyl-3,c-5-bis(trimethylsilyl)silacyclopent-3-ene (9a) and c-2-(1,2-dimethyl-1,2,2-triphenyl-disilanyl)-1-methyl-r-1-phenyl-3,t-5-bis(trimethylsilyl)-silacyclopent-3-ene (9b). A mixture of 0.3618 g (0.83 mmol) of **3**, 0.1973 g (1.00 mmol) of methyldiphenylsilane, and 0.0251 g (0.090 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The mixture was treated with a short florisil column to remove nickel species from the reaction mixture. A mixture of **9a** and **9b** (65% combined yield) was isolated by preparative MPLC: MS *m/z* 572 (M^+); ^{1}H NMR δ(C_6D_6) -0.12 (s, 9H, Me_3Si), -0.09 (s, 9H, Me_3Si), 0.06 (s, 3H, MeSi), 0.16 (s, 9H, Me_3Si), 0.16 (s, 3H, MeSi), 0.19 (s, 9H, Me_3Si), 0.40 (s, 3H, MeSi), 0.58 (s, 3H, MeSi), 0.67 (s, 3H, MeSi), 0.69 (s, 3H, MeSi), 1.14 (br s, 1H, HC), 1.17 (br s, 1H, HC), 2.23 (br d, 1H, HC, J = 1.7 Hz), 2.34 (br d, 1H, HC, J = 1.7 Hz), 6.40 (br d, 1H, HC=C, J = 1.7 Hz), 6.46 (br d, 1H, HC=C, J = 1.7 Hz), 6.90-7.61 (m, 40H, ring protons); ^{13}C NMR δ(C_6D_6) -5.37 (MeSi), -4.02 (MeSi), -3.84 (MeSi), -3.71 (MeSi), -2.85 (MeSi), -2.55 (MeSi), 0.33 (Me_3Si), 0.47 (Me_3Si), 0.51 (Me_3Si), 0.82 (Me_3Si), 18.33, 18.89, 26.98, 27,21 (HC), 127.84, 128.25, 128.90, 129.17 (2C), 129.24, 129.51, 129.80, 134.69, 134.94, 135.12, 135.17, 135.43, 135.46, 135.53 (2C), 137.11, 137.20, 137.33, 137.56, 137.94 (2C), 138.05, 138.33, 141.19, 141,57, 146.78 (2C) (phenyl ring carbons and olefinic carbons). Anal. Calcd for $C_{37}H_{50}Si_5$: C, 69.96; H, 7.93. Found : C 69.85; H, 7.84.

1,4-Bis(methyldiphenylsilyl)-1-(pentamethyl-disianyl)buta-1,2-diene (13). A mixture of 0.3224 g (0.85 mmol) of **10**, 0.2001 g (1.01 mmol) of methyldiphenylsilane, and 0.0240 g (0.086 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h.

The mixture was treated with a short florisil column to remove nickel species from the reaction mixture. The product **13** (73% yield) was isolated by preparative GLC: MS *m/z* 576 (M^+); IR $\nu_{C=C=C}$ 1908 cm^{-1}; ^{1}H NMR δ(C_6D_6) 0.14, (s, 9H, Me_3Si), 0.16 (s, 3H, MeSi), 0.22 (s, 3H, MeSi), 0.44 (s, 3H, MeSi), 0.67 (s, 3H, MeSi), 1.97 (d, 2H, HC, J = 8.0 Hz), 4.52 (t, 1H, HC=C, J = 8.0 Hz), 7.22-7.26 (m, 10H, ring protons), 7.46-7.51 (m, 5H, ring protons), 7.66-7.70, (m, 5H, ring protons); ^{13}C NMR δ(C_6D_6) -4.47 (MeSi), -1.97 (MeSi), -1.58 (Me_3Si, MeSi), -1.31 (MeSi), 13.91 (CH_2), 72.58, (HC=), 84.39, (C=), 129.46 (2C), 134.85, 134.88, 135.26, 135.44, 136.81, 137.38 (phenyl ring carbons), 215.15 (=C=). Anal. Calcd for $C_{35}H_{44}Si_4$: C, 72.85; H, 7.68. Found : C 72.90; H, 7.76.

Reaction of 13 with hydrogen chloride. Into a solution of 0.003 g (0.0052 mmol) of **13** in 3 mL of ether was introduced hydrogen chloride for 1 h with ice-cooling. The mixture was analyzed by GLC as being chloropentamethyldisilane (31% yield) and chloromethyldiphenylsilane (50% yield). The retention time on GLC and mass fragmentation pattern obtained for chloropentamethyldisilane and chloromethyldiphenylsilane were identical with those of the authentic samples.

1,4-Bis(methyldiphenylsilyl)-1-(1-phenyltetramethyl-disianyl)buta-1,2-diene (14). A mixture of 0.3156 g (0.72 mmol) of **11**, 0.1645 g (0.83 mmol) of methyldiphenylsilane, and 0.0201 g (0.072 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The mixture was treated with a short florisil column to remove nickel species from the reaction mixture. The product **14** (50% yield) was isolated by preparative MPLC: MS *m/z* 638 (M^+); IR $\nu_{C=C=C}$ 1908 cm^{-1}; ^{1}H NMR δ(C_6D_6) 0.15, (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.30 (s, 3H, MeSi), 0.32 (s, 3H, MeSi), 0.34 (s, 3H, MeSi), 0.36 (s, 3H, MeSi), 0.42 (s, 3H, MeSi), 0.48 (s, 3H, MeSi), 2.01 (d, 2H, HC, J = 8.0 Hz), 4.55 (t, 1H, HC=C, J = 8.0 Hz), 7.14-7.56 (m, 25H, ring protons); ^{13}C NMR δ(C_6D_6) -4.56 (MeSi), -3.77 (MeSi), -1.54 (Me_3Si), -1.41 (MeSi), 13.75, 14.02 (HC), 72.73, 72.80 (HC=), 83.08 (C=), 128.81, 128.88, 129.40, 129.51, 134.65, 134.79, 134.85, 134.94, 135.21, 135.44, 136.49, 137.53

(phenyl ring carbons), 216.64 (=C=). Anal. Calcd for $C_{40}H_{46}Si_4$: C, 75.17; H, 7.25. Found : C 75.32; H, 7.32.

1,1,4-Tris(methyldiphenylsilyl)buta-1,2-diene (15). A mixture of 0.4391 g (0.99 mmol) of **12**, 0.2077 g (1.05 mmol) of methyldiphenylsilane, and 0.0291g (0.10 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200°C for 20 h. The mixture was treated with a short florisil column to remove nickel species from the reaction mixture and the product **15** (49% yield) was isolated by preparative MPLC: mp 84-86°C (after recrystallization from hexane); MS *m/z* 642 (M^+); IR $\nu_{C=C=C}$ 1911 cm^{-1}; ^1H NMR $\delta(C_6D_6)$ 0.29 (s, 3H, MeSi), 0.54 (s, 6H, MeSi), 1.83 (d, 2H, HC, J = 8.0 Hz), 4.49 (t, 1H, HC=C, J = 8.0 Hz), 7.11-7.62 (m, 30H, ring protons); ^{13}C NMR $\delta(C_6D_6)$ -4.72 (MeSi), -1.72 (MeSi), 13.21 (HC), 73.75 (HC=), 83.35 (C=), 127.93, 128.13, 129.42, 134.86, 135.44, 136.81, 137.18, 137.22 (phenyl ring carbons), 218.06 (=C=). Anal. Calcd for $C_{43}H_{42}Si_3$: C, 80.31; H, 6.58. Found : C 80.22; H, 6.51.

(*E*)-1-(1-Phenyltetramethyldisilanyl)-4-(trimethylsilyl)but-1-en-3-yne (16). In a 30 mL two-necked flask fitted with a condenser and a dropping funnel was placed 1.1872 g (2.72 mmol) of 1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**3**) in 15 mL of dry ethyl ether. To this was added 2.4 mL (3.60 mmol) of a methyllithium-ether solution at -78°C for 2 min. The mixture was allowed to warm at 0°C and 0.50 g (4.61 mmol) of chlorotrimethylsilane in 5 mL of ether. After the mixture was stirred for 5 h at room temperature, the mixture was hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvent ether was evaporated and the residue was chromatographed on silica gel eluting with hexane, to give 0.6599 g (77% yield) of **16**: MS *m/z* 316 (M^+); IR $\nu_{C\equiv C}$ 2154 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.15 (s, 9H, Me_3Si), 0.24 (s, 9H, Me_3Si), 0.42 (s, 3H, MeSi), 5.85 (d, 1H, HC=C, J = 19 Hz), 6.60 (d, 1H, HC=C, J = 19 Hz), 7.08-7.45 (m, 5H, ring protons); ^{13}C NMR $\delta(CDCl_3)$ -5.88 (MeSi), -1.93 (Me_3Si), -0.09 (Me_3Si), 94.99 and 105.38 (C≡C), 124.94 (C=C), 127.92, 128.84, 134.42, 136.38 (ring carbons), 143.69 (C=C). Anal. Calcd for $C_{17}H_{28}Si_3$: C, 64.48; H, 9.14. Found: C, 64.44, H, 8.86.

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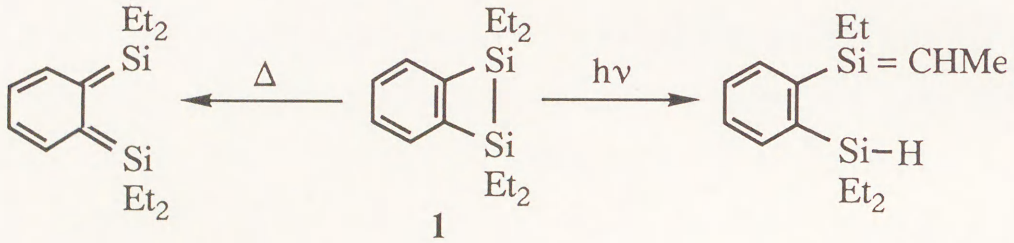
Part II Transition Metal-Catalyzed Reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene

Chapter 3

Nickel-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene with Aromatic Compounds

Introduction

3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) shows interesting chemical behavior. Thermolysis of this compound affords an *o*-quinodisilane which reacts with acetylenes to give [4 + 2] cycloadducts.[1] The photolysis of **1**, however, gives a different reactive intermediate from the *o*-quinodisilane, 1-ethyl-1-(*o*-diethylsilyl)phenyl-1-silapropene.[2]



1

It is of interesting to us to investigate the chemical behavior of **1** towards a transition-metal complex. We have now initiated systematic investigation concerning the transition-metal-catalyzed reaction of **1** and found that treatment of **1** with a catalytic amount of tetrakis-(triethylphosphine)nickel(0) in benzene gives a benzene adduct derived from the C-H bond activation of a benzene molecule. In this chapter we report the reaction of **1** with aromatic compounds in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0).

Results and Discussion

In order to learn more about the chemical behavior of 3,4-benzodisilacyclobutene towards a nickel complex, we treated **1** with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in hexane in a degassed sealed tube at 150°C for 24 h. GLC analysis of the reaction mixture showed no appreciable amount of volatile products. GPC analysis of the mixture, however, indicated the presence of polymeric substances whose molecular weight was determined to be Mw = 2900, relative to the polystyrene standards. The ^{1}H NMR spectrum of the polymeric substances reveals broad resonances due to ethylsilyl protons, hydrosilyl protons and phenylene ring protons. Its IR spectrum shows a strong absorption due to stretching frequencies of an Si-H group. To our surprise, similar reaction of **1** in refluxing benzene afforded a benzene adduct as the sole volatile product. Thus, the reaction of **1** with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in refluxing benzene for 17 h gave 1-diethylphenylsilyl-2-(diethylsilyl)benzene (**4a**) in 97% yield. The structure of **4a** was confirmed by spectrometric analysis, as well as by elemental analysis. The IR spectrum of **4a** shows a strong absorption band at 2139 cm^{-1}, due to Si-H stretching frequencies. Its ^{13}C NMR spectrum reveals ten resonances in the aryl region, attributed to phenyl and phenylene carbons. The ^{29}Si NMR spectrum shows two resonances at δ -9.78 and -3.32 ppm, due to two nonequivalent silicon atoms. These results are wholly consistent with the structure proposed for **4a**.

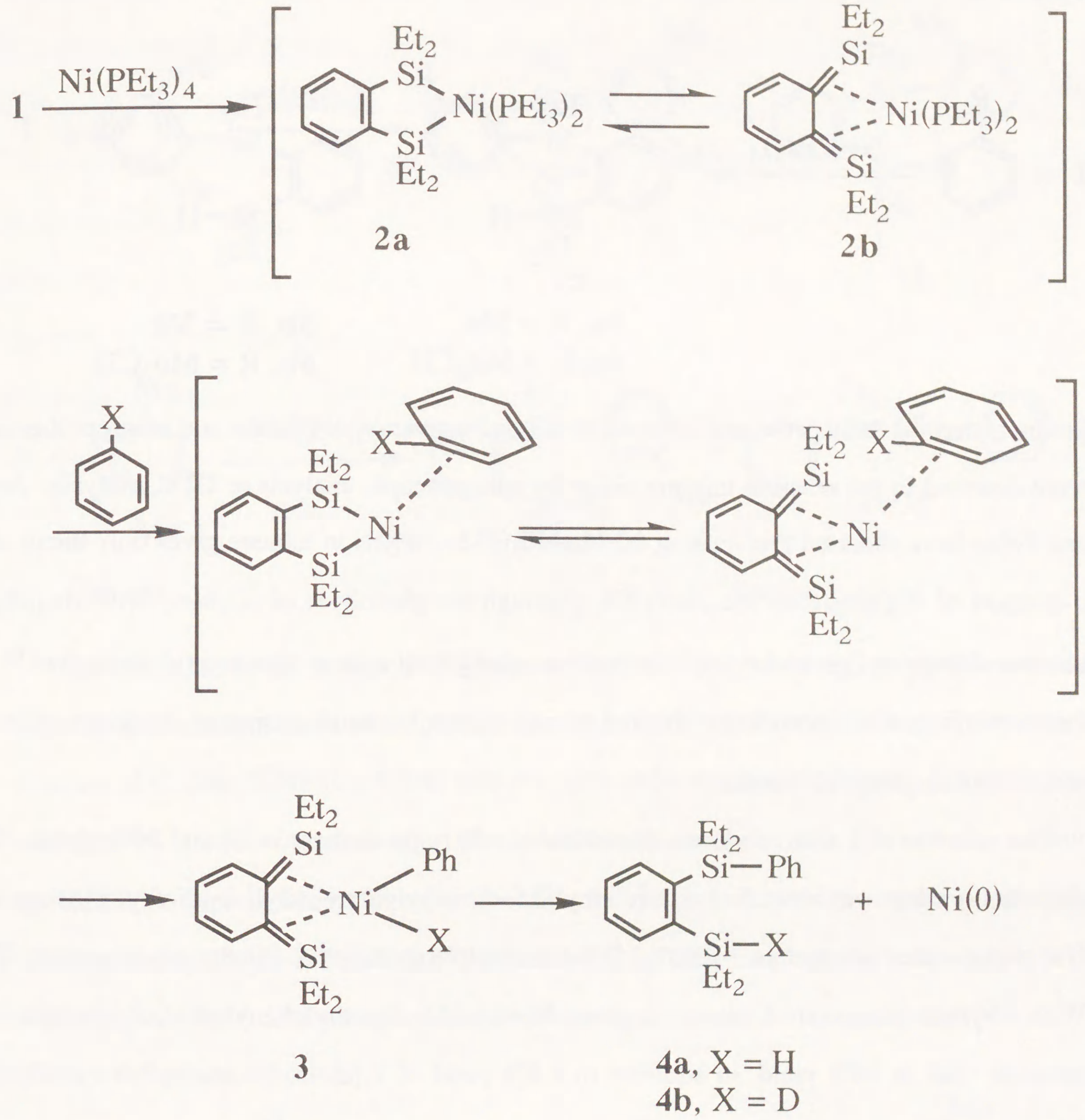
In order to confirm whether or not the hydrogen attached to a silicon atom in compound **4a** was originated from the benzene molecule, we carried out the reaction of **1** with deuteriobenzene. In this reaction, 2-deuteriodiethylsilyl-1-[diethyl(pentadeuteriophenyl)silyl]benzene (**4b**) in 59% yield, in addition to 12% of the starting compound **1**. The mass spectrum of **4b** indicates a fragment (M$^+$-Et) at *m/e* 303, and ^{2}H NMR spectrum reveals broad signals at 4.3 and 7.2 ppm, due to a D-Si bond and a pentadeuteriophenyl group. These results clearly indicate that the hydrogen on the silicon atom comes from the benzene molecule.

The formation of **4** may be best explained in terms of C-H bond activation of benzene by a nickel complex. The C-H bond activation of arenes by transition metal complexes have been extensively investigated and many types of the complexes involving Zr, Rh, Ta, and Re metals have been used as catalysts.[3-13] However, the nickel-catalyzed C-H bond activation is rather rare, and is limited only to silicon compounds. It has been found in our laboratory that sp-hybridized C-H bond of ethynylsilanes[14] can be activated by a nickel(0) catalyst giving dienynes and that the thermolysis of 2-mesityl-4-phenyl-1,1-bis(trimethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobut-3-ene affords two isomers of a 5,6-benzo-1,3-disla-cyclohexene derivative arising from intramolecular C-H bond activation of a mesityl methyl group.[15,16] Similar intramolecular C-H bond activation of a tolyl methyl group in the reaction of 2-(*o*-tolyl)-2-(phenylethynyl)hexamethyltrisilane with a catalytic amount of tetrakis(triethylphosphine)nickel(0) has also been reported from this laboratory.[17]

Scheme I illustrates a possible mechanistic interpretation of the observed reaction course. We suggest that *o*-quinodisilane-nickel complex (**2b**), which would be produced from 3,4-benzo-2,2,5,5-tetraethyl-1-nickela-2,5-disilacyclopent-3-ene (**2a**) is involved as a key intermediate in C-H bond activation of benzene. Benzene would coordinate to the nickel atom in **2a** or **2b** in an η^2 fashion, and then the oxidative addition of a C-H bond of the coordinated benzene to the nickel atom takes place to give complex (**3**). Finally reductive elimination of nickel(0) species from complex **3** gives the observed product **4**.

The formation of 3,4-benzo-1-metala-2,5-disilacyclopent-3-enes, analogous to **2a**, from the reaction of 1,2-bis(dimetylsilyl)benzene with transition metal complexes has been reported.[18-22] Evidence for the production of **2b** has not yet been obtained so far. The coordination of arenes to the metal in an η^2-fashion is well known and evidence for the intermediacy of the η^2-arene complex has been reported by Jones and Feher.[6c,d]

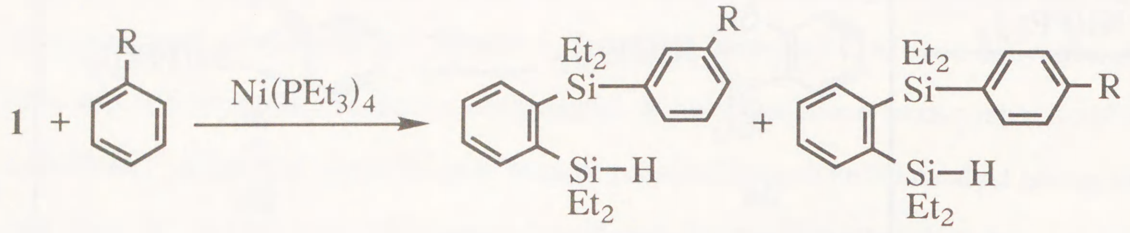
Scheme I



Toluene also reacted with **1** in the presence of the nickel(0) catalyst, to give two isomers of the adduct, which could be identified as 1-[diethyl(3-methylphenyl)silyl]-2-(diethylsilyl)benzene (**5a**) and 1-[diethyl(4-methylphenyl)silyl]-2-(diethylsilyl)benzene (**5b**) in 69% and 14% yields, respectively. Similar reaction of **1** with isopropylbenzene again produced two isomers of the adduct, 1-[diethyl(3-isopropylphenyl)silyl]-2-(diethylsilyl)benzene (**6a**) and 1-[diethyl(4-isopropylphenyl)silyl]-2-(diethylsilyl)benzene (**6b**) in 55 and 19% yields, respectively (Scheme II).

In both cases, *m*-substituted isomers, **5a** and **6a** were produced as abundant isomers, and no products derived from ortho and benzylic C-H bond activation of toluene and isopropylbenzene were detected in the reaction mixture either by spectroscopic analysis or GLC analysis. Jones and Feher have reported that heating $(C_5Me_5)Rh(PMe_3)(Ph)H$ in toluene gives only the *m*- and *p*-isomers of $(C_5Me_5)Rh(PMe_3)(tolyl)H$, although the photolysis of $(C_5Me_5)Rh(PMe_3)H_2$ in toluene affords *m*-, *p*-, and *o*-tolyl derivatives, along with a trace of a benzyl derivative.[6a] In these reactions, it has been found that the *m*-tolyl isomer is abundant species, as observed in the present nickel-catalyzed reaction.

Scheme II

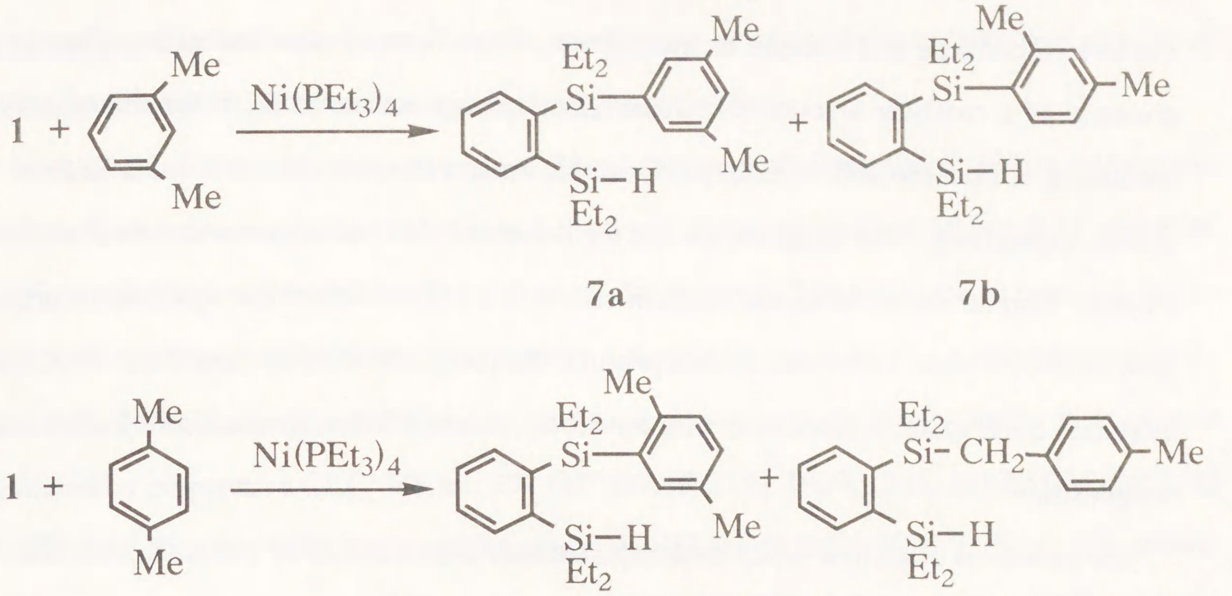


5a, R = Me
6a, R = Me_2CH

5b, R = Me
6b, R = Me_2CH

The reaction of **1** with *m*-xylene also afforded two regio isomers in 58 and 24% yields. The abundant product was identified as 1-[diethyl(3,5-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**7a**) and a minor product as 1-[diethyl(2,4-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**7b**). With *p*-xylene, compound **1** reacted to give 1-[diethyl(2,5-dimethylphenyl)silyl]-2-(diethylsilyl)-benzene (**8a**) in 40% yield, in addition to a 6% yield of 1-[diethyl(4-methylbenzyl)silyl]-2-(diethylsilyl)benzene (**8b**) (Scheme III).

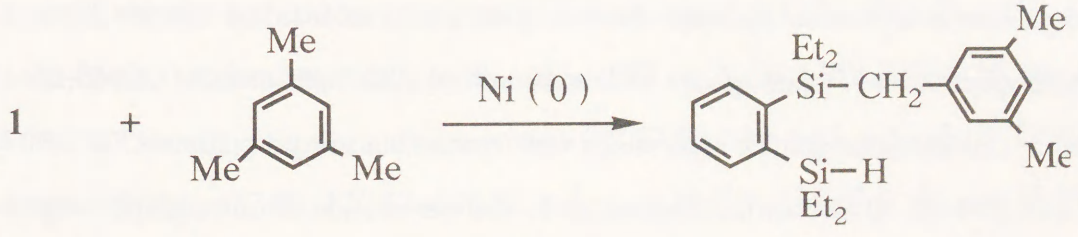
Scheme III



7a **7b**

8a **8b**

The formation of **8b**, in which C-H bond activation of a xylyl methyl group is involved, is of considerable interest, because no product arising from the benzylic C-H bond is detected in the reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with *p*-xylene under thermal conditions. We carried out the reaction of **1** with mesitylene. Thus, the reaction of **1** with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in refluxing mesitylene for 30 h gave 1-[diethyl(3,5-dimethylbenzyl)silyl]-2-(diethylsilyl)benzene (**9**) in 28% yield, as the sole volatile product, indicating that the C-H bond activation on sp^3 carbon occurs in the present system.[23]



9

In order to learn more about the selectivity of the present reaction for arene C-H bond activation, we carried out the competition experiments, which involve the reaction of **1** with a 1:1 mixture of benzene and toluene or mesitylene. Thus, when **1** was heated to reflux in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in the mixed solvent consisting of benzene and toluene, products, **4a**, **5a** and **5b** were obtained in 56, 22, and 9% yields, respectively. The result shows that the benzene C-H bond is more reactive than that of toluene. Similar nickel-catalyzed reaction of **1** with a 1:1 mixture of benzene and mesitylene gave **4a** in 69% yield as the sole volatile product. No product **9** could be detected in the reaction mixture. Such trend is consistent with the result obtained from the reaction of other metal complexes.[6d]

The structures of all new compounds reported here were verified by mass, IR, and, ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis (see Experimental Section).

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry argon. Yields were determined by GLC using an internal standard. NMR spectra were recorded on a JEOL Model EX-270 spectrometer using a deuteriochloroform 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 instrument. Gas chromatographic separations were carried out using a column (3 m x 10 mm) packed with 30% SE-30 silicone on Chromosorb P. Gel-permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.). Tetrakis(triethylphosphine)nickel(0) was prepared by the method reported in the literature.[25]

Materials. 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disila-cyclobutene (**1**) was prepared as reported previously.[1] Benzene and hexane used as solvents were dried over lithium aluminum hydride and distilled before use. Toluene, *m*-xylene, *p*-xylene and mesitylene were dried over sodium and distilled just before use under an argon atmosphere.

Reaction of 1 with Benzene. In a 30-ml two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.5616 g (2.26 mmol) of **1** and 59 mg (0.11 mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry benzene. The mixture was heated to reflux for 17 h. GLC analysis of the reaction mixture indicated the presence of 1-diethylphenylsilyl-2-(diethylsilyl)benzene (**4a**) (97% yield) and the starting compound **1** (1% yield). Pure **4a** was isolated by preparative GLC: MS *m/z* 297 (M^+-Et); IR 2139, 1429, 1225, 1112, 1004 cm^{-1}; ^{1}H NMR 0.51-1.24 (m, 20H, EtSi), 4.22 (quint, 1H, HSi, J = 3.3 Hz), 7.27-7.67 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR 4.26, 5.01, 7.51, 8.19 (EtSi), 127.48, 127.80, 127.92, 128.59, 134.90, 134.99, 136.10, 138.47, 143.07, 143.67 (phenyl and phenylene ring carbons); ^{29}Si NMR -9.78, -3.32. Anal. Calcd for $C_{20}H_{30}Si_2$: C, 73.55; H, 9.26. Found: C, 73.50; H, 9.20.

Reaction of 1 with Benzene-d$_6$. In a 15-mL glass tube fitted with a stirrer and reflux condenser was placed 0.4593 g (1.85 mmol) of **1** and 46 mg (8.62 x 10^{-2} mmol) of tetrakis-(triethylphosphine)nickel(0) in 1 mL of dry benzene-d$_6$. The mixture was heated to reflux for 15 h. GLC analysis of the resulting mixture showed the presence of 2-(deuteriodiethylsilyl)-1-[diethyl(pentadeuteriophenyl)silyl]benzene (**4b**) (59% yield) and 12% of the starting compound **1**. Pure **4b** was isolated by preparative GLC: MS *m/z* 303 (M^+-Et); IR 2270, 1567, 1556, 1462, 1455, 1416, 1260, 1233, 1118, 1056, 1007 cm^{-1}; ^{1}H NMR 0.51-1.26 (m, 20H, EtSi), 7.33-7.67 (m, 4H, phenylene ring protons); ^{13}C NMR 4.19, 5.03, 7.53, 8.18 (EtSi), 126.97 (t, $J_{C\text{-}D}$ = 23 Hz), 127.80, 127.92, 128.55 (t, $J_{C\text{-}D}$ = 23 Hz), 134.47 (t, $J_{C\text{-}D}$ = 23 Hz), 135.00, 136.10, 138.20, 143.11, 143.67 (deuteriophenyl and phenylene ring carbons); ^{2}H NMR (d, in $(CD_3)_2CO$) 4.3 (broad s, DSi), 7.2 (broad s, C_6D_5).

Reaction of 1 with Toluene. In a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed 0.4707 g (1.89 mmol) of **1** and 52 mg (9.79×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry toluene. The mixture was heated to reflux for 4 h. The reaction mixture was analyzed by GLC as being 1-[diethyl(3-methylphenyl)silyl]-2-(diethylsilyl)benzene (**5a**) (69% yield) and 1-[diethyl(4-methylphenyl)silyl]-2-(diethylsilyl)-benzene (**5b**) (14% yield). Pure **5a** and **5b** were isolated by preparative GLC. For **5a**: MS *m*/*z* 311 (M^+-Et); IR 3043, 2954, 2873, 2155, 1458, 1414, 1232, 1117, 1008, 971, 813, 738, 714 cm^{-1}; ^1H NMR 0.49-1.21 (m, 20H, EtSi), 2.28 (s, 3H, Me), 4.19 (quint, 1H, HSi, J = 3.3 Hz), 7.11-7.64 (m, 8H, tolyl and phenylene ring protons); ^{13}C NMR 4.28, 5.07, 7.57, 8.20 (EtSi), 21.48 (Me), 127.39, 127.76, 127.87, 129.36, 131.91, 134.97, 135.54, 136.12, 136.66, 138.24, 143.20, 143.68 (tolyl and phenylene ring carbons); ^{29}Si NMR -9.78, -3.34. Anal. Calcd for $C_{21}H_{32}Si_2$: C, 74.04; H, 9.47. Found: C, 74.01; H, 9.33. For **5b**: MS *m*/*z* 311 (M^+-Et); IR 3037, 2954, 2873, 2156, 1458, 1414, 1232, 1117, 1007, 972, 806, 708 cm^{-1}; ^1H NMR 0.45-1.25 (m, 20H, EtSi), 2.33 (s, 3H, Me), 4.21 (quint, 1H, HSi, J = 3.3 Hz), 7.10-7.65 (m, 8H, tolyl and phenylene ring protons); ^{13}C NMR 4.32, 5.16, 7.57, 8.20 (EtSi), 21.46 (Me), 127.76, 127.84, 128.32, 131.91, 134.95, 135.54, 136.12, 138.35, 143.32, 143.68 (tolyl and phenylene ring carbons); ^{29}Si NMR -9.83, -3.39. Anal. Calcd for $C_{21}H_{32}Si_2$: C, 74.04; H, 9.47. Found: C, 73.95; H, 9.36.

Reaction of 1 with Isopropylbenzene. A mixture of 0.3577 g (1.44 mmol) of **1** and 38 mg (7.15×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry isopropylbenzene was heated to reflux for 7 h. GLC analysis of the reaction mixture showed the presence of 1-[diethyl(3-isopropylphenyl)silyl]-2-(diethylsilyl)benzene (**6a**) (55% yield), 1-[diethyl(4-isopropylphenyl)silyl]-2-(diethylsilyl)-benzene (**6b**) (19% yield) and 2% of the starting compound **1**. Pure **6a** and **6b** were isolated by preparative GLC. For **6a**: MS *m*/*z* 368 (M^+); IR 2952, 2857, 2139, 1459, 1411, 1232, 1112, 1010, 807, 735, 708 cm^{-1}; ^1H NMR 0.46-1.17 (m, 20H, EtSi), 1.20 (d, 6H, Me_2CH-, J = 6.9 Hz), 2.83 (sep, 1H, -$HCMe_2$, J = 6.9 Hz), 4.24 (quint, 1H, HSi, J = 3.3 Hz), 7.16-7.65 (m, 8H, cumyl and phenylene ring protons); ^{13}C NMR 4.21, 5.10, 7.60, 8.21 (EtSi), 24.04 (Me), 34.20 (-$CHMe_2$), 126.47, 127.46, 127.74, 127.85, 132.50, 133.39, 134.98, 136.08, 138.09, 143.41, 143.65, 147.56 (cumyl and phenylene ring carbons); ^{29}Si NMR -9.73, -3.43. Anal. Calcd for $C_{23}H_{36}Si_2$: C, 74.92; H, 9.84. Found: C, 74.87; H, 9.75. For **6b**: MS *m*/*z* 368 (M^+); IR 2957, 2873, 2156, 1600, 1462, 1415, 1260, 1232, 1117, 1008, 972, 820, 741, 711, 681 cm^{-1}; ^1H NMR 0.45-1.18 (m, 20H, EtSi), 1.23 (d, 6H, Me_2CH-, J = 6.9 Hz), 2.86 (sep, 1H, -$HCMe_2$, J = 6.9 Hz), 4.19 (quint, 1H, HSi, J = 3.3 Hz), 7.13-7.65 (m, 8H, cumyl and phenylene ring protons); ^{13}C NMR 4.30, 5.07, 7.60, 8.25 (EtSi), 23.94 (Me), 34.09 (-$CHMe_2$), 125.68, 127.74 (two carbons), 127.85, 134.95, 135.07, 136.03, 143.57, 143.74, 149.38 (cumyl and phenylene ring carbons); ^{29}Si NMR -9.58, -3.66. Anal. Calcd for $C_{23}H_{36}Si_2$: C, 74.92; H, 9.84. Found: C, 74.86; H, 9.83.

Reaction of 1 with *m*-Xylene. A solution of 0.4845 g (1.95 mmol) of **1** and 51 mg (9.60×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry *m*-xylene was heated to reflux for 27 h. The reaction mixture was analyzed by GLC as being 1-[diethyl(3,5-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**7a**) (58% yield), 1-[diethyl(2,4-dimethylphenyl)-silyl]-2-(diethylsilyl)benzene (**7b**) (24% yield), and 9% of the starting compound **1**. Pure **7a** and **7b** were isolated by preparative GLC. For **7a**: MS *m*/*z* 354 (M^+); IR 2954, 2873, 2154, 1594, 1459, 1414, 1231, 1139, 1117, 1008, 971, 813, 739, 715, 621 cm^{-1}; ^1H NMR 0.51-1.20 (m, 20H, EtSi), 2.25 (s, 6H, two Me), 4.19 (quint, 1H, HSi, J = 3.3 Hz), 6.95, 7.01 (broad s, 3H, *m*-xylyl ring protons), 7.31-7.64 (m, 4H, phenylene ring protons); ^{13}C NMR 4.35, 5.18, 7.64, 8.25 (EtSi), 21.37 (Me), 127.78, 127.85, 130.35, 132.61, 134.95, 136.15, 136.58, 138.08, 143.34, 143.72 (*m*-xylyl and phenylene ring carbons); ^{29}Si NMR -9.78, -3.39. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.41; H, 9.65. For **7b**: MS *m*/*z* 354 (M^+); IR 2954, 2872, 2154, 1604, 1458, 1413, 1229, 1116, 1007, 971, 812, 738, 708, 679 cm^{-1}; ^1H NMR 0.43-1.28 (m, 20H, EtSi), 2.03 (s, 3H, Me), 2.29 (s, 3H, Me), 4.19 (quint, 1H, HSi, J = 3.3 Hz), 6.88, 6.95, 6.98 (broad s, 3H, *m*-xylyl ring protons), 7.29-7.65 (m, 4H, phenylene ring protons); ^{13}C NMR 4.21, 4.92, 7.64, 8.10 (EtSi), 21.28, 22.93 (Me), 125.53, 127.58, 127.90, 130.51, 132.59, 134.86, 135.47, 136.22, 138.72, 142.96, 143.84, 144.87 (*m*-xylyl and phenylene ring carbons); ^{29}Si NMR -9.85, -3.78. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.41; H, 9.60.

Reaction of 1 with *p*-Xylene. A mixture of 0.2408 g (0.969 mmol) of **1** and 25 mg (4.71×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry *p*-xylene was heated to reflux for 33 h. The reaction mixture was analyzed by GLC as being 1-[diethyl(2,5-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**8a**) (40% yield) and 1-[diethyl(4-methylbenzyl)-silyl]-2-(diethylsilyl)benzene (**8b**) (6% yield) and 10% of unchanged **1**. Pure **8a** was isolated by preparative GLC: MS *m*/*z* 354 (M^{+}); IR 2954, 2872, 2156, 1458, 1415, 1378, 1232, 1117, 1007, 971, 810, 740, 706, 619 cm^{-1}; ^{1}H NMR 0.42-1.27 (m, 20H, EtSi), 2.03 (s, 3H, Me), 2.28 (s, 3H, Me), 4.19 (quint, 1H, HSi, J = 3.3 Hz), 6.92-7.65 (m, 7H, *p*-xylyl and phenylene ring protons); ^{13}C NMR 4.17, 4.98, 7.66, 8.12 (EtSi), 21.11, 22.53 (Me), 127.60, 127.92, 129.52, 129.67, 133.58, 134.86, 135.51, 136.21, 136.80, 140.68, 142.99, 144.78 (*p*-xylyl and phenylene ring carbons); ^{29}Si NMR -9.73, -3.62. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.60; H, 9.54. Pure **8b** was isolated by preparative Recycling HPLC: MS *m*/*z* 325 (M^{+}-Et); IR 3049, 2954, 2872, 2146, 1508, 1418, 1233, 1156, 1117, 1009, 972, 817, 745, 706 cm^{-1}; ^{1}H NMR 0.69-1.02 (m, 20H, EtSi), 2.25 (s, 3H, Me), 2.43 (s, 2H, CH_2), 4.63 (quint, 1H, HSi, J = 3.3 Hz), 6.82-6.96 (m, 4H, *p*-xylyl ring protons), 7.14-7.56 (m, 4H, phenylene ring protons); ^{13}C NMR 4.65, 4.69, 7.51, 8.41 (EtSi), 20.90 (Me), 22.82 (CH_2), 127.73, 127.87, 128.34, 128.77, 133.26, 135.06, 135.63, 136.87, 142.77, 143.68 (*p*-xylyl and phenylene ring carbons); ^{29}Si NMR -9.69, 0.96. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.50; H, 9.60.

Reaction of 1 with Mesitylene. A mixture of 0.2859 g (1.15 mmol) of **1** and 29 mg (5.46×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry mesitylene was heated to reflux for 30 h. The reaction mixture was analyzed by GLC as being 1-[diethyl(3,5-dimethylbenzyl)silyl]-2-(diethylsilyl)benzene (**9**) (28% yield) and unchanged **1** (3% yield). Pure **9** was isolated by preparative GLC: MS *m*/*z* 368 (M^{+}); IR 2955, 2874, 2146, 1602, 1457,

1417, 1117, 1016, 809 cm^{-1}; ^{1}H NMR 0.81-1.05 (m, 20H, EtSi), 2.18 (s, 6H, two Me), 2.40 (s, 2H, CH_2), 4.65 (quint, 1H, HSi, J = 3.3 Hz), 6.56 (broad s, 2H, mesityl ring protons), 6.67 (broad s, 1H, mesityl ring proton), 7.25-7.57 (m, 4H, phenylene ring protons); ^{13}C NMR 4.69 (two carbons), 7.51, 8.41 (EtSi), 21.26 (Me), 23.18 (CH_2), 125.64, 126.41, 127.69, 127.81, 135.04, 135.67, 137.30, 139.94, 142.71, 143.75 (mesityl and phenylene ring carbons); ^{29}Si NMR -9.69, 1.00. Anal. Calcd for $C_{23}H_{36}Si_2$: C, 74.92; H, 9.84. Found: C, 74.91; H, 9.81.

Reaction of 1 with Hexane. A mixture of 0.4229 g (1.70 mmol) of **1** and 46 mg (8.66×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 0.6 mL of dry hexane was heated in a degassed sealed tube at 150°C for 24 h. GLC analysis of the mixture showed the presence of 8% of the starting compound **1** and a small amount of an unidentified product (less than 4% yield). Nonvolatile products were isolated by precipitation of the mixture from methanol-chloroform: IR 3050, 2954, 2153 (H-Si), 1462, 1455, 1416, 1378, 1348, 1233, 1138, 1010, 972, 800, 704 cm^{-1}; ^{1}H NMR 0.45-1.12 (m, EtSi), 4.21 (broad s, HSi), 7.31-7.72 (m, phenylene ring protons).

Reaction of 1 with a 1:1 Mixture of Benzene and Toluene. A mixture of 0.6829 g (2.75 mmol) of **1** and 74 mg (1.39×10^{-1} mmol) of tetrakis(triethylphosphine)nickel(0) in the mixed solvent consisting of 5.63 g (72 mmol) of benzene and 6.63 g (72 mmol) of toluene was heated to reflux for 5 h. The mixture was analyzed by GLC as being **4a** (56% yield), **5a** (22% yield), and **5b** (9% yield). All spectral data obtained for **4a**, **5a**, and **5b** were identical with those of authentic samples.

Reaction of 1 with a 1:1 Mixture of Benzene and Mesitylene. A mixture of 0.5310 g (2.14 mmol) of **1** and 55 mg (1.04×10^{-1} mmol) of the nickel catalyst in the mixed solvent consisting of 5.80 g (74 mmol) of benzene and 8.85 g (74 mmol) of mesitylene was heated to reflux for 5 h. GLC analysis of the reaction mixture showed the presence of **4a** (69% yield) as the sole product. All spectral data for **4a** were identical with those of an authentic sample.

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Chapter 4

Nickel-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene with Carbonyl Compounds

Introduction

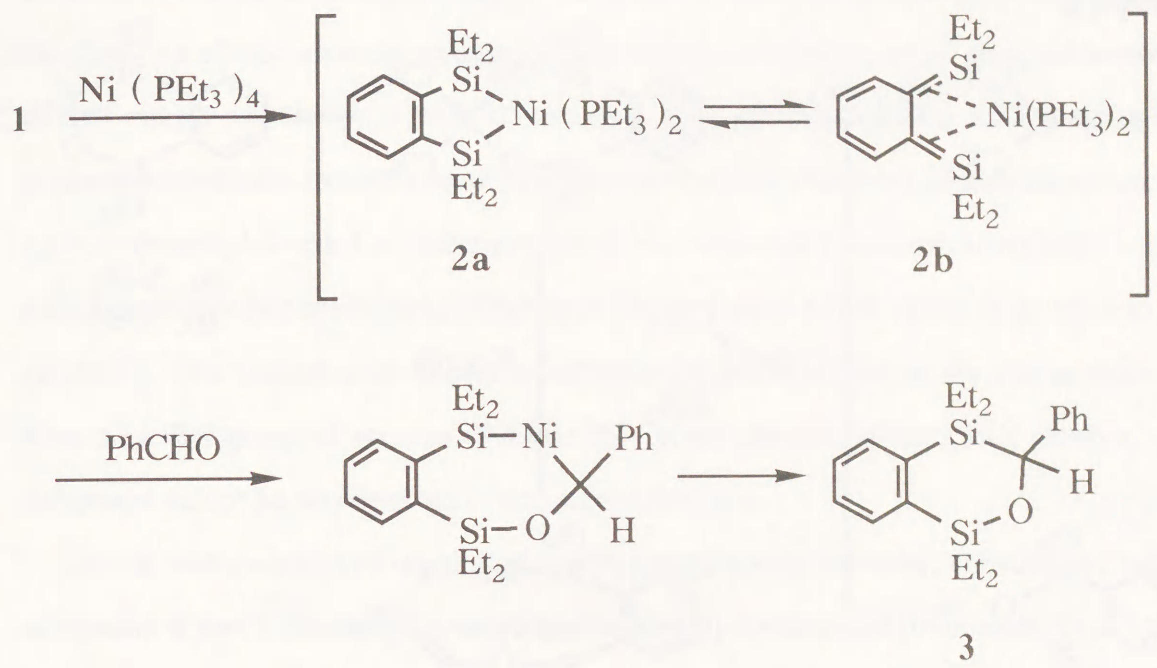
3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) shows interesting chemical behavior. The reaction of **1** with arenes such as benzene, toluene, and xylene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) produces 1-arenyldiethylsilyl-2-(diethylsilyl)-benzenes arising from C-H bond activation of arenes as discussed in Chapter 3.[1] In these reactions, we proposed the formation of the reactive intermediates, 3,4-benzo-1,1-bis-(triethylphosphine)-2,2,5,5-tetraethyl-1-nickela-2,5-disilacyclopent-3-ene and an *o*-quinodisilane-nickel complex, in which an arene molecule can coordinate to the nickel atom. In order to get more information about the chemical behavior of the nickel complex, we initiated systematic investigation concerning the nickel-catalyzed reaction of **1** with various unsaturated compounds. In this chapter we report the reaction of **1** with carbonyl compounds in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0).

Results and Discussion

When a mixture of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) and benzaldehyde in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) was heated in a sealed glass tube at 150°C for 24 h, 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene (**3**) was obtained in 75% yield as the sole product. All spectral data

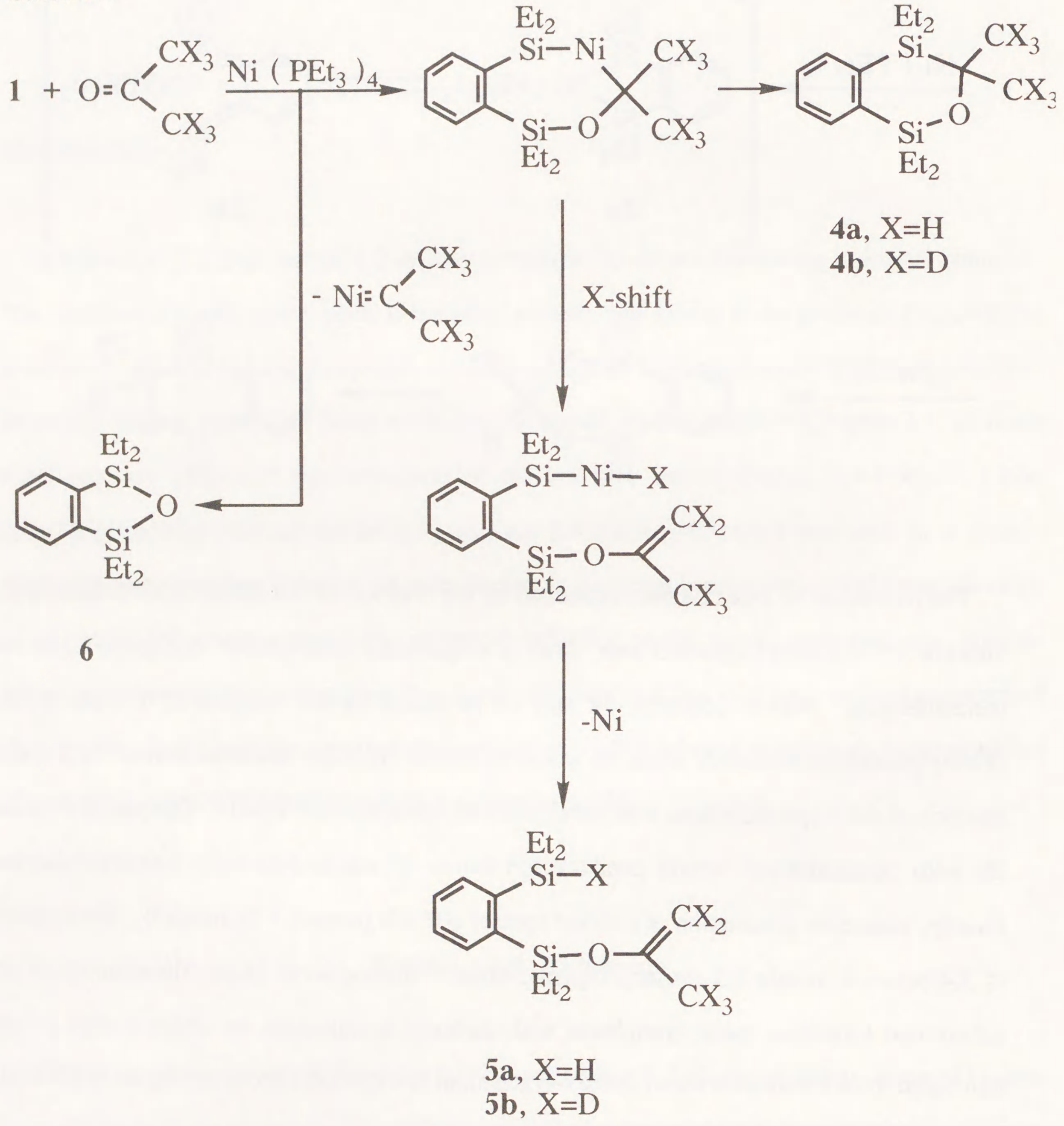
obtained from **3** were identical with those of the authentic sample prepared from the thermal reaction of **1** with benzaldehyde.[2]

Scheme I



The formation of **3** can be best explained by the reaction of 3,4-benzo-2,2,5,5-tetraethyl-1-nickela-2,5-disilacyclopent-3-ene (**2a**) or *o*-quinodisilane-nickel complex (**2b**) with benzaldehyde. Nickel complex **2a** may be produced by the reaction of **1** with tetrakis-(triethylphosphine)nickel(0), while **2b** would be formed by either isomerization of **2a** or a direct reaction of the *o*-quinodisilane with tetrakis(triethylphosphine)nickel(0). The reaction of **2a** or **2b** with benzaldehyde would produce 5,6-benzo-4,7-disila-1-nickela-3-oxacycloheptene. Finally, reductive elimination of a nickel species afffords product **3** (Scheme I). The formation of 3,4-benzo-1-metala-2,5-disilacyclopent-3-enes,[3-7] analogous to **2a** and the reaction of silyl-substituted transition metal complexes with carbonyl compounds, in which a silyl group is transfered from a transition metal to the oxygen atom of a carbonyl group giving an α-siloxyalkyl complex[3,8,9] have been reported to date.

Scheme II

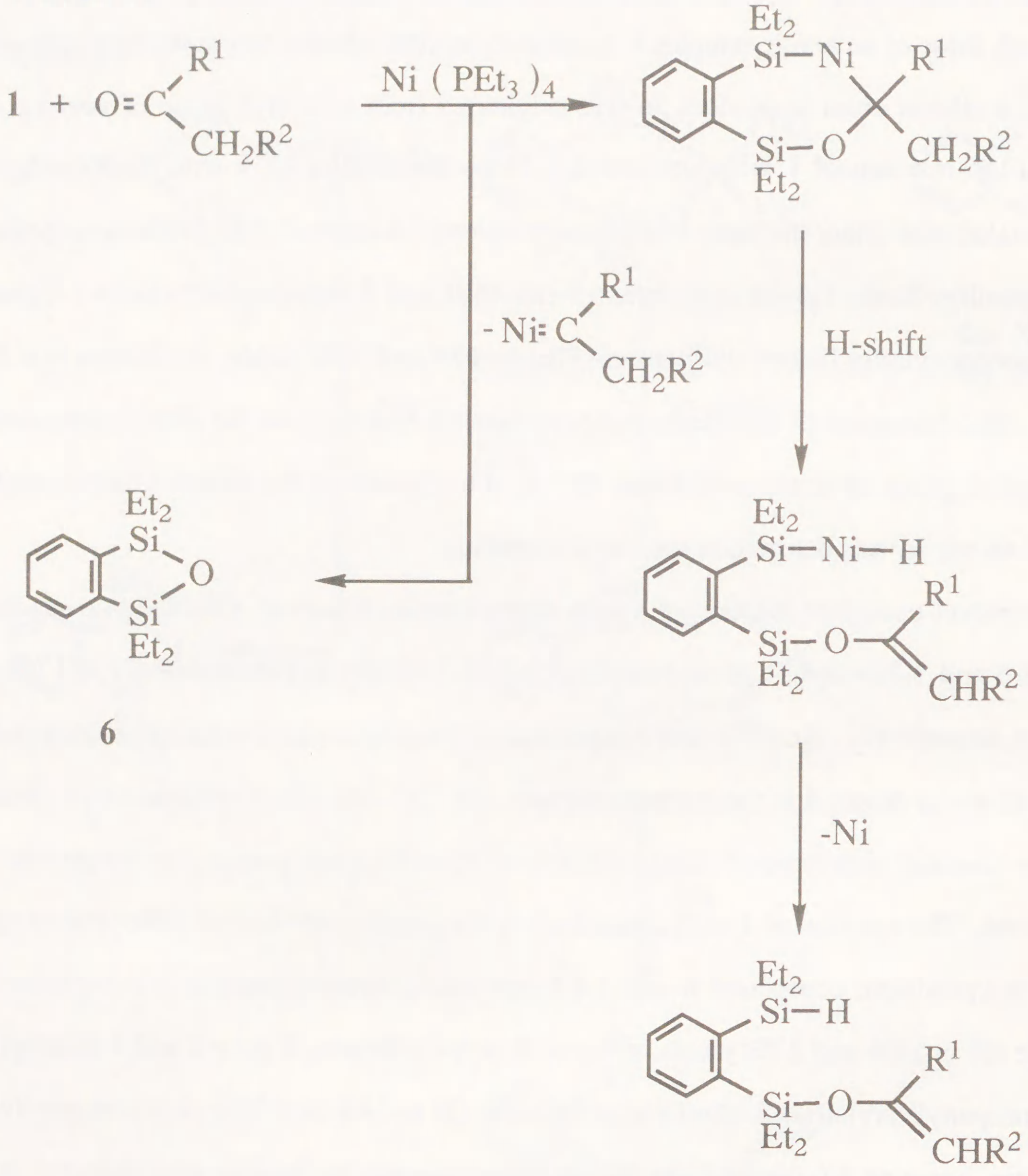


The reaction of **1** with acetone in the presence of the nickel catalyst at 150°C gave three products, 5,6-benzo-1,1,4,4-tetraethyl-3,3-dimethyl-2-oxa-1,4-disilacyclohex-5-ene (**4a**), 1-[diethyl(isopropenyloxy)silyl]-2-(diethylsilyl)benzene (**5a**), and 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene (**6**) in 26%, 31%, and 24% yields, respectively. The products, **4a**, **5a** and **6** could readily be isolated by preparative GLC. All spectral data for **5** and **6** were identical with those of authentic samples.[2] In order to confirm whether or not the hydrogen atom attached to a silicon atom in product **5a** was originated from a methyl group of acetone, we carried out the reaction of **1** with acetone-d_6. Thus, the reaction of **1** with acetone-d_6 in a degassed sealed tube under the same conditions produced 5,6-benzo-3,3-bis(trideuteriomethyl)-1,1,4,4-tetraethyl-2-oxa-1,4-disilacyclohex-5-ene (**4b**) and 2-deuteriodiethylsilyl-1-[(pentadeuterioisopropenyloxy)diethylsilyl]benzene (**5b**) in 44% and 20% yields, in addition to a 13% yield of **6**. The formation of **5b** clearly indicates that the hydrogen on the silicon atom comes from a methyl group of acetone (Scheme II). In the absence of the nickel catalyst, neither compound **4a** nor **5a** was detected in the reaction mixture.

Similar nickel-catalyzed reaction of **1** with acetophenone, however, afforded two products, compound **6** and 1-[diethyl[(1-phenylvinyl)oxy]silyl]-2-(diethylsilyl)benzene (**7**) in 17% and 59% yields, respectively. No C-O insertion product, 5,6-benzo-2-oxa-1,4-disilacyclohex-5-ene, analogous to **4** was detected in the reaction mixture. ^{1}H, ^{13}C, and ^{29}Si NMR spectra for product **7** were also identical with those of compound isolated from the photolysis of **1** in the presence of acetophenone. The reaction of **1** with pinacolone in the presence of the nickel(0) catalyst again afforded two products, compound **6** and 1-[(1-tert-butylvinyloxy)diethylsilyl]-2-(diethylsilyl)benzene (**8**) in 18% and 27% yields, while with propiophenone, **1** gave **6** and 1-[diethyl[(1-phenyl-1-propenyl)oxy]silyl]-2-(diethylsilyl)benzene (**9**) in 24% and 70% yields, respectively. In both cases, again no 5,6-benzo-2-oxa-1,4-disilacyclohexene derivatives were detected in the reaction mixture. Presumably, the presence of bulky substituents on the carbonyl carbon prevents the formation of the 5,6-benzo-2-oxa-1,4-disilacyclohexene (Scheme III).

In marked contrast to the enolizable ketones, nonenolizable ketones produce quite different products. Thus, treatment of **1** with benzophenone in the presence of the nickel catalyst at 150°C afforded 4,5-benzo-1,1,3,3-tetraethyl-2,2-diphenyl-1,3-disilacyclopent-4-ene (**10**) in 20% yield, in addition to a 57% yield of compound **6**. In this reaction, again no C-O insertion product, 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3,3-diphenyl-1,4-disilacyclohex-5-ene was detected in the reaction mixture. Similarly, the reaction of **1** with 4,4'-dimethylbenzophenone gave 4,5-benzo-1,1,3,3-tetraethyl-2,2-di(*p*-tolyl)-1,3-disilacyclopent-4-ene (**11**) in 16% yield, along with a 37% yield of **6**. The structures of **10** and **11** were verified by mass, IR, and ^1H, ^{13}C, and ^{29}Si NMR spectra. The mass spectrum of **10** shows a parent ion at *m/z* 414, corresponding to the calculated molecular weight of $C_{27}H_{34}Si_2$. The ^{13}C NMR spectrum of **10** reveals two resonances at 6.33 and 8.45 ppm, attributed to ethylsilyl carbons, and a single resonance at 41.30 ppm, due to diphenyl-substituted carbon, as well as seven resonances attributable to phenylene and phenyl ring carbons. The ^{29}Si spectrum shows a single resonance due to two equivalent silicon atoms. The mass spectrum of **11** reveals a parent ion at *m/z* 442. Its ^{13}C NMR spectrum shows resonances at δ 6.27 and 8.47 ppm attributed to ethyl carbons and at 20.88 and 39.97 ppm due to methyl carbons and a di(*p*-tolyl)-substituted carbon, as well as seven resonances attributable to tolyl and phenylene ring carbons. The ^{29}Si NMR spectrum exhibits a single resonance at d 12.71 ppm. These results are wholly consistent with the structures proposed for **10** and **11**.

Scheme III



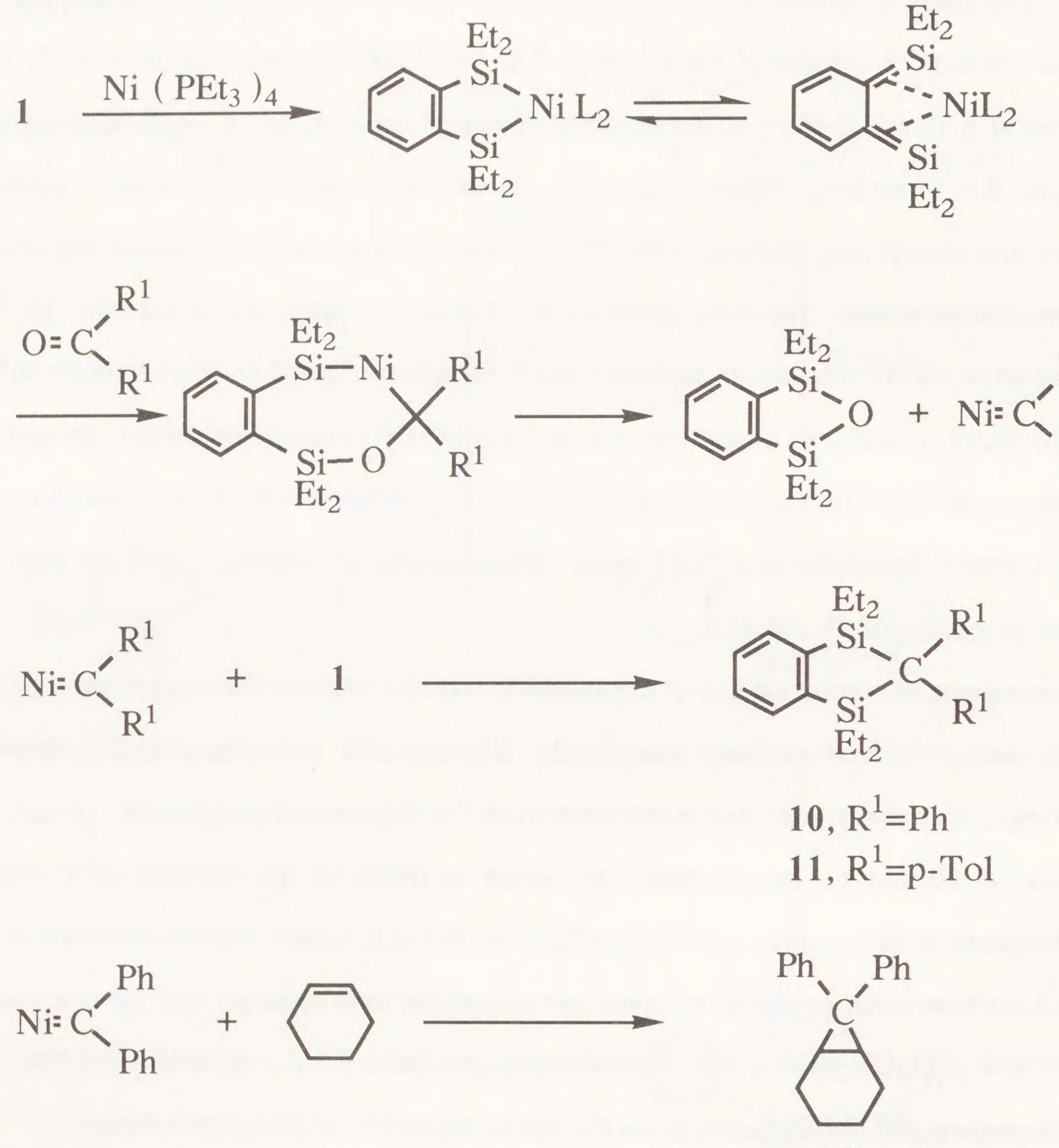
6

7, R^1=Ph, R^2=H
8, R^1=t-Bu, R^2=H
9, R^1=Ph, R^2=CH_3

The formation of compound **6** is of considerable interest, because the oxygen atom in this molecule must come from carbonyl compounds. Consequently, carbenes, probably carbene-nickel complexes must be extruded in the reaction of **2** with carbonyl compounds. In fact, the formation of **10** and **11** can be best understood in terms of the reaction of **1** with a diphenylcarbene-nickel complex and di(*p*-tolyl)carbene-nickel complex. For the formation of the carbene-transition metal complex, Gladysz and coworkers have reported that the reaction of $(CO)_4FeSiMe_2CH_2CH_2SiMe_2$ with benzaldehyde produces 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane and iron carbene species that can be trapped by triphenylphosphine.[9]

In an attempt to trap the carbene species, we carried out the nickel-catalyzed reaction of **1** with benzophenone in cyclohexene. Thus, when a mixture of **1** and benzophenone was heated to reflux in the presence of the nickel(0) catalyst in cyclohexene for 48 h, 7,7-diphenylnorcarane (**12**) was obtained in 39% yield, in addition to **6** (57% yield) and **10** (2% yield). The formation of **12** clearly indicates that the carbene species is produced in the present reaction as shown in Scheme IV.

Scheme IV



10, R^1=Ph
11, R^1=p-Tol

12

Since compound **1** reacts with the enolizable ketones in the presence of the nickel(0) catalyst to give mainly adducts such as 1-alkenyloxydiethylsilyl-2-(diethylsilyl)benzenes, the production of carbene species would be a minor pathway, as indicated by the fact that compound **6** is produced only in low yields, while with nonenolizable ketones **1** affords no 1-alkenyloxydiethylsilyl derivatives, and therefore, the formation of the carbene species would be a main route.

Experimental Section

General procedure. All nickel-catalyzed reactions of compound **1** with carbonyl compounds were carried out in a degassed sealed glass tube (1.0 cm x 10 cm) with one exception of a carbene trapping experiment. Gas chromatographic separations were carried out by using a column packed with 30% SE-30 Silicone on Chromosorb P. NMR spectra were determined with a JEOL MODEL EX-270 spectrometer. Mass spectra were measured on a Shimadzu Model GC-MS-QP 1000. Infrared spectra were recorded on a Perkin-Elmer 1600-FT-IR spectrophotometer. Tetrakis(triethylphosphine)nickel(0) was prepared by the method reported in the literature. Yields of the products were calculated by analytical GLC with the use of tridecane as an internal standard.

Materials. The starting compound, 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) was prepared as reported in the literature.[2]

Reaction of 1 with Benzaldehyde. A mixture of 0.2366 g (0.95 mmol) of **1**, 0.1845 g (1.74 mmol) of benzaldehyde, and 0.0200 g (0.038 mmol) of tetrakis(triethylphosphine)-nickel(0) was heated at 150°C for 24 h. GLC analysis of the reaction mixture indicated the presence of **3** (75% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. The product **3** was isolated by preparative GLC. All spectral data for **3** were identical with those of an authentic sample.[2]

Reaction of 1 with Acetone. A mixture of 0.2811 g (1.13 mmol) of **1**, 0.1222 g (2.10 mmol) of acetone, and 0.0310 g (0.058 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150°C for 24 h. The mixture was analyzed by GLC as being **4a** (26% yield), **5a** (31% yield), **6** (24% yield) and the starting compound **1** (1% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Products **4a**, **5a**, and **6**

were isolated by preparative GLC. All spectral data for **5a** and **6** were identical with those of authentic samples.[1,3] For **4a**: MS *m/z* 264 (M^+-CMe_2); IR 3046, 2954, 2875, 1462, 1416, 1235, 1120, 1015, 742, 716, 613 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.68-1.04 (m, 20H, EtSi), 1.33 (s, 6H, 2Me), 7.32-7.55 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 2.55, 7.05, 7.77, 8.05 (EtSi), 28.77 (Me), 67.03 (CO), 128.0, 128.1, 132.7, 134.6 , 141.7, 143.7 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ -6.62, 1.80. Anal. Calcd for $C_{17}H_{30}OSi_2$: C, 66,60; H, 9.86. Found: C, 66.53; H, 9.73.

Reaction of 1 with Acetone-d_6. A mixture of 0.4204 g (1.69 mmol) of **1**, 0.4435 g (6.93 mmol) of acetone-d_6, and 0.0395 g (0.074 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150°C for 24 h. GLC analysis of the reaction mixture indicated the presence of **4b** (44% yield), **5b**, (20% yield), and **6** (13% yield). Products **4b**, **5b**, and **6** were isolated by preparative GLC. For **4b**: MS *m/z* 312 (M^+); IR 2956, 2912, 2876, 2208, 1461, 1414, 1236, 1120, 1087, 1035, 1009, 935, 773, 743, 718 cm^{-1}; ^1H NMR $\delta(C_6D_6)$ 0.75-1.16 (m, 20H, EtSi), 7.26-7.54 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(C_6D_6)$ 2.94, 7.37, 7.97, 8.54 (EtSi), 28.29 (CD_3), 66.71 ($C(CD_3)$), 128.49, 128.54, 133.2, 135.0, 141.8, 144.2 (phenylene ring carbons); ^2H NMR $\delta(C_6D_6)$ 1.32(CD_3). For **5b**: MS *m/z* 283 (M^+-Et); IR 2956, 2876, 2227, 1602, 1560, 1459, 1415, 1233, 1119, 1007, 738, 719 cm^{-1}; ^1H NMR $\delta(C_6D_6)$ 0.80-1.29 (m, 20H, EtSi), 7.24-7.87 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(C_6D_6)$ 4.75, 7.14, 7.36, 8.56 (EtSi), 128.7, 129.1, 132.0, 135.3, 135.5, 143.2 (phenylene ring carbons), 156.0 ($C=CD_2$); ^2H NMR $\delta(C_6D_6)$ 1.85 (CD_3), 4.18 (CD_2), 4.82 (SiD).

All spectral data for **6** were identical with those of the authentic sample.[2]

Reaction of 1 with Acetophenone. A mixture of 0.2409 g (0.97 mmol) of **1**, 0.1981 g (1.65 mmol) of acetophenone, and 0.0200 g (0.038 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150°C for 24 h. Products **6** (17% yield) and **7** (59% yield) were isolated by preparative GLC. For **7**: MS *m/z* 368 (M^+); IR 3060, 2955, 2874, 2146, 1618, 1458, 1317, 1118, 917, 812, 698 cm^{-1}; ^1H NMR $\delta(C_6D_6)$ 0.79-1.32 (m, 20H, EtSi), 4.44 (d, 1H, $CH_2=C$, J = 2.0 Hz), 4.80 (quintet, 1H, HSi, J = 3.3 Hz), 4.90 (d, 1H, $CH_2=C$, J = 2.0 Hz), 7.10-7.95 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 4.47, 6.65, 6.95, 8.28 (EtSi), 90.53 ($CH_2=C$), 125.3, 128.0, 128.1, 128.4, 131.6, 134.9, 135.2, 137.7, 142.4, 142.9(phenyl and phenylene ring carbons), 155.5 ($C=CH_2$); ^{29}Si NMR $\delta(CDCl_3)$ -8.26, 9.53. Anal. Calcd for $C_{22}H_{32}OSi_2$: C, 71.68; H, 8.75. Found: C, 71.48; H, 8.71.

All spectral data for **6** were identical with those of the authentic sample.[2]

Reaction of 1 with Pinacolone. A mixture of 0.3155 g (1.25 mmol) of **1**, 0.2104 g (2.10 mmol) of pinacolone, and 0.0340 g (0.064 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150°C for 24 h. GLC analysis of the reaction mixture indicated the presence of **6** (18% yield), **8** (27% yield), and the starting compound **1** (1% yield). Products **6** and **8** were isolated by preparative GLC. For **8**: MS *m/z* 319 (M^+-Et); IR 3044, 2956, 2146, 1618, 1459, 1415, 1296, 1221, 1184, 1118, 1008, 816, 775, 742, 709, 613 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.76-1.09 (m, 20H, EtSi), 1.15 (s, 9H, Me), 3.75 (d, 1H, $CH_2=C$, J = 1.6 Hz), 4.02 (d, 1H, $CH_2=C$, J = 1.6 Hz), 4.48 (quintet, 1H, HSi, J = 3.3 Hz), 7.32-7.76 (m, 9H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 4.53, 7.03 (2C), 8.30 (EtSi), 28.34 (Me), 36.77 (CMe_3), 85.75 ($CH_2=C$), 128.0, 128.1, 134.7, 135.2, 142.1, 143.6 (phenylene ring carbons), 166.6 ($C=CH_2$); ^{29}Si NMR $\delta(CDCl_3)$ -9.26, 6.30. Anal. Calcd for $C_{20}H_{36}OSi_2$: C, 68.89; H, 10.41. Found: C, 68.69; H, 10.37.

All spectral data for **6** were identical with those of the authentic sample.[2]

Reaction of 1 with Propiophenone. A mixture of 0.4852 g (1.95 mmol) of **1**, 0.3832 g (2.86 mmol) of propiophenone, and 0.0530 g (0.100 mmol) of tetrakis(triethylphosphine)-nickel(0) was heated at 150°C for 24 h. GLC analysis of the reaction mixture indicated the presence of **6** (20% yield) and **9** (70% yield, E:Z = 1:4.8). Products **6** and **9** were isolated by preparative GLC. For **9**: MS *m/z* 382 (M^+); IR 3047, 2955, 2875, 2145, 1651, 1456, 1415, 1322, 1233, 1119, 1059, 1007, 969, 917, 807, 738, 720, 698 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.66-1.25 (m, 20H, EtSi), 1.63 (d, 3H, Me (Z), J = 6.9 Hz), 4.52 (quintet, 1H, HSi (E), J = 3.3 Hz), 4.61 (quintet, 1H, HSi (Z), J = 3.3 Hz), 4.99 (q, 1H, HMeC=C (E), J = 7.3 Hz), 5.25 (q, 1H, HMeC=C (Z), J = 6.9 Hz), 7.17-7.79 (m, 9H, phenyl and phenylene ring protons); ^{13}C

NMR δ(CDCl$_3$) 4.38, 6.94, 7.37, 8.34 (EtSi), 12.09 (Me), 104.9 (CHMe=C), 125.5, 127.2, 127.8, 127.9, 128.2, 134.9, 135.1, 139.4, 142.3, 143.6 (phenyl and phenylene ring carbons), 150.3 (C=CHMe); ^{29}Si NMR δ(CDCl$_3$) -8.62 (E), -8.23 (Z), 8.85 (E+Z). Anal. Calcd for $C_{23}H_{34}OSi_2$: C, 72.19; H, 8.95. Found: C, 72.17; H, 8.93.

All spectral data for **6** were identical with those of the authentic sample.[2]

Reaction of 1 with Benzophenone. A mixture of 0.3898 g (1.57 mmol) of **1**, 0.4282 g (2.35 mmol) of benzophenone, and 0.0408 g (0.077 mmol) of tetrakis(triethylphosphine)-nickel(0) was heated at 150°C for 24 h. The mixture was analyzed by GLC as being **6** (58% yield) and **10** (24% yield). Products **6** and **10** were isolated by MPLC. For **10**: mp 127-129°C; MS *m/z* 414 (M$^+$); IR 2948, 1595, 1486, 1002, 850, 809, 710 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.73-0.98 (m, 20H, EtSi), 6.93-7.70 (m, 14H, phenyl and phenylene ring protons); ^{13}C NMR δ(CDCl$_3$) 6.33, 8.45 (EtSi), 41.30 (CPh$_2$), 124.2, 128.0, 128.2, 130.5, 133.5, 145.4, 148.7(phenyl and phenylene ring carbons); ^{29}Si NMR δ(CDCl$_3$) 13.12. Anal. Calcd for $C_{27}H_{34}Si_2$: C, 78.19; H, 8.26. Found: C, 78.20; H, 8.29.

All spectral data for **6** were identical with those of the authentic sample.[2]

Reaction of 1 with 4,4'-Dimethylbenzophenone. A mixture of 0.5618 g (2.26 mmol) of **1**, 0.6260 g (2.98 mmol) of 4,4'-dimethylbenzophenone, and 0.0670 g (0.126 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150°C for 24 h. Products **6** (37% yield) and **11** (16% yield) were isolated by preparative MPLC. For **11**: mp 104-105°C; MS *m/z* 442 (M$^+$); IR 3022, 2955, 2873, 1509, 1459, 1115, 839, 723, 703 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.68-0.94 (m, 20H, EtSi), 2.26 (s, 6H, 2Me), 6.77-7.66 (m, 12H, *p*-tolyl and phenylene ring protons); ^{13}C NMR δ(CDCl$_3$) 6.27, 8.47 (EtSi), 20.78 (CH$_3$), 39.97 (C(*p*-tol$_2$)), 128.1, 128.7, 130.3, 133.39, 133.42, 142.3, 148.9 (*p*-tolyl and phenylene ring carbons); ^{29}Si NMR δ(CDCl$_3$) 12.71. Anal. Calcd for $C_{29}H_{38}Si_2$: C, 78.66; H, 8.65. Found: C, 78.63; H, 8.58.

All spectral data for **6** were identical with those of the authentic sample.[2]

Reaction of 1 with Benzophenone in Refluxing Cyclohexene. In a 30-mL two-necked flask fitted with a condenser was placed 0.3732 g (1.50 mmol) of **1**, 0.3948 g (2.17 mmol) of benzophenone, and 0.0364 g (0.069 mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of cyclohexene. The mixture was heated to reflux for 48 h. GLC analysis of the reaction mixture indicated the presence of **6** (57% yield), **10** (2% yield) and **12** (39% yield). Cyclohexene was evaporated, and the residue was treated with a short silica gel column to remove nickel species from the reaction mixture. Product **12** was isolated by preparative GLC: MS *m/z* 248 (M$^+$); IR 3023, 2930, 1598, 1488, 1447, 1075, 702 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.58-1.98 (m, 10H, HC), 6.93-7.32 (m, 10H, phenyl ring protons); ^{13}C NMR δ(CDCl$_3$) 21.21, 21.24 (CH$_2$), 24.19 (CH), 35.71 (CPh$_2$), 125.0, 126.2, 126.8, 128.0, 128.5, 132.0, 139.8, 149.7 (phenyl ring carbons). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.73; H, 8.12.

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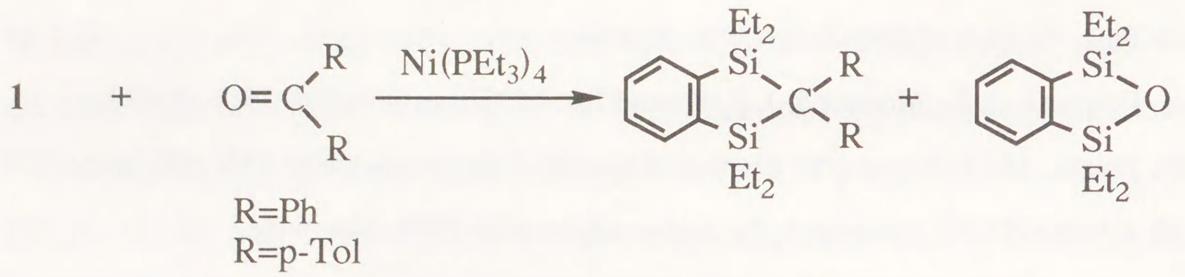
Chapter 5

Nickel-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with Alkenes and Dienes

Introduction

We described the reaction of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in refluxing benzene affords 1-(diethylphenylsilyl)-2-diethylsilylbenzene arising from C-H bond activation of a phenyl ring in chapter 3.[1] Recently, we have found that the similar nickel-catalyzed reaction of **1** with enolizable ketones such as acetone and acetophenone affords 1-[diethyl(isopropenyloxy)silyl]-2-(diethylsilyl)benzene and 1-[diethyl[(1-phenylvinyl)oxy]silyl]-2-(diethylsilyl)benzene, in addition to 4,5-benzo-1,1,3,3-tetraethyl-1,3-disila-2-oxacyclopent-4-ene. The reaction of **1** with benzophenone and 4,4'-dimethylbenzophenone, however, gives products arising from insertion of diphenylcarbene and di(*p*-tolyl)carbene into a silicon-silicon bond of **1** and 4,5-benzo-1,1,3,3-tetraethyl-1,3-disila-2-oxacyclopent-4-ene, respectively.[2]



In order to obtain more information about the reactive species in the nickel-catalyzed reaction, we investigated the reaction of **1** with alkenes and dienes in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0). We also carried out MO calculations for 1-nickela-2,5-disilacyclopent-3-ene as a model of 3,4-benzo-2,2,5,5-tetraethyl-1-nickela-2,5-disilacyclopent-3-ene.

Results and Discussion

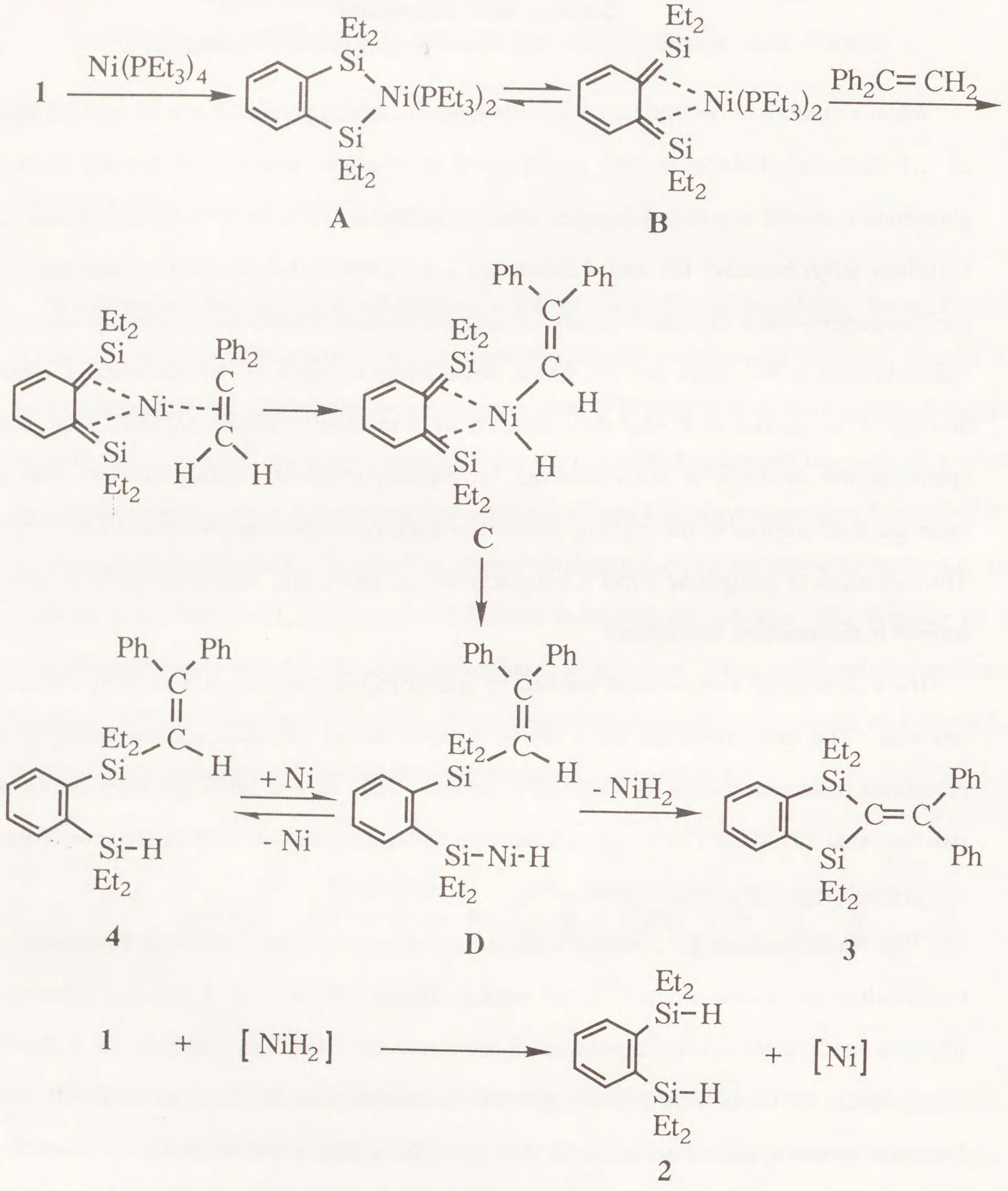
When a mixture of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) and 1.5 equiv of 1,1-diphenylethylene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in a sealed degassed tube was heated at 150°C for 24 h, three products, 1,2-bis(diethylsilyl)benzene (**2**) and 4,5-benzo-1,1,3,3-tetraethyl-2-(diphenylmethylene)-1,3-disilacyclopent-4-ene (**3**), and 1-[diethyl(2,2-diphenylethenyl)silyl]-2-diethylsilylbenzene (**4**) were obtained in 4%, 55%, and 7% yields, respectively (Scheme I). In this reaction, a trace amount of an isomer of **4** was also detected by mass spectrometric analysis. GC-Mass spectrometric analysis of the recovered 1,1-diphenylethylene fraction showed that the hydrogenated product of the starting olefin, 1,1-diphenylethane was produced in 28% yield. The formation of compound **2** and 1,1-diphenylethane shows that nickel dihydride species is formed in this reaction (see below).

The structures of **3** and **4** were verified by spectrometric analysis, as well as by elemental analysis. The mass spectrum for **3** shows a parent ion at m/z 426, corresponding to the calculated molecular weight for $C_{28}H_{34}Si_2$ (adduct - 2H). Its ^{13}C NMR spectrum shows two resonances at 137.4 and 170.1 ppm, attributed to olefinic carbons, as well as seven resonances due to phenylene and phenyl carbons.

The ^{29}Si NMR spectrum for **3** reveals a single resonance at -2.82 ppm, showing the presence of two equivalent silicon atoms. These results clearly indicate that **3** has a 4,5-benzo-2-(diphenylmethylene)-1,3-disilacyclopent-3-ene structure. The mass spectrum for **4** shows a fragment ion at m/z 428, corresponding to the calculated value for $C_{28}H_{36}Si_2$. Its ^1H NMR spectrum shows a quintet resonance at 4.57 ppm and a singlet at 6.45 ppm, due to an Si-H proton and a vinylic proton, respectively. The IR spectrum for **4** shows Si-H stretching frequencies at 2147 cm^{-1}. These results are wholly consistent with the structure proposed for **4**.

All spectral data obtained for **2** were identical with those of an authentic sample reported previously.

Scheme I

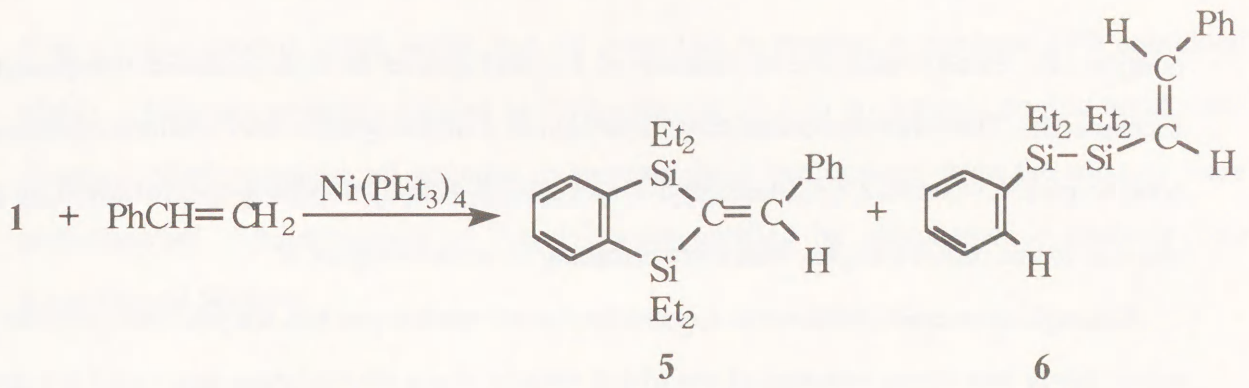


In the nickel-catalyzed reactions of **1** with arenes and carbonyl compounds[2] with alkenes and alkynes, we suggested the formation of 3,4-benzo-1-nickela-2,5-disilacyclopent-3-enes (**A**) and *o*-quinodisilane-nickel complexes (**B**) as key reactive species. The production of **3** and **4** in the present reaction may be best explained in terms of the reaction of *o*-quinodisilane-nickel complex **B**, which would be formed from isomerization of 3,4-benzo-1-nickela-2,5-disilacyclopent-3-ene **A** arising from insertion of a nickel species into an Si-Si bond of **1**, with 1,1-diphenylethylene. Oxidative addition of an olefinic C-H bond of 1,1-diphenylethylene to the nickel atom in complex **B** would produce nickel complex **C**. The shift of a diphenylethenyl group from the nickel atom to one of two silicon atoms in the complex **C** would yield complex **D**. Reductive elimination of nickel dihydride from **D** leads to the formation of **3**, while elimination of nickel species from **D** results in the production of **4** (Scheme I).

Interestingly, addition of a hydrosilane to the nickel-catalyzed reaction of **1** with 1,1-diphenylethylene results in acceleration of the reaction rate, and also affects the product distribution. Thus, the reaction of **1** with 1,1-diphenylethylene in the presence of 5 mol% of the nickel(0) catalyst and 89 mol% of dimethylphenylsilane in refluxing hexane for 20 h gave compound **4** in 70% yield, in addition to a trace amount of **3**. The selective formation of **4** is probably due to rapid nickel transfer from complex **D** to dimethylphenylsilane. The reaction of **4** isolated in a pure form with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in a sealed tube at 150°C for 24 h gave **3** in 76% yield. These results strongly suggest that the initial step of the reaction involves oxidative addition of an sp^2 C-H bond of 1,1-diphenylethylene to *o*-quinodisilane-nickel complex **B** giving complex **C**,[3] which undergoes further reaction to form complex **D**, as shown in Scheme I. That the product **2** was produced by the reaction of **1** with nickel dihydride which would be eliminated from **D** was confirmed by the fact that the reaction of **1** with hydrogen in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in an autoclave at 150°C for 24 h produced **2** in quantitative yield. Furthermore, treatment of **4** with the nickel(0) catalyst in the presence of 1 equiv of **1** at 150°C for 24 h produced **2** and **3** in 47% and 84% yields, together with 15% of the unchanged compound **1**. Similar treatment of **4** in the presence of 3.4 equiv of 1,1-diphenylethylene at 150°C for 24 h gave **3** and 1,1-diphenylethane in 70% and 43% yields. These results can best be understood by elimination of nickel dihydride species from nickel complex **D** arising from insertion of a nickel catalyst into an Si-H bond in compound **4**. The resulting nickel dihydride reacts with **1** or 1,1-diphenylethylene to give the observed products.

The nickel-catalyzed reaction of **1** with styrene under the same conditions afforded two products, which were identified as 4,5-benzo-1,1,3,3-tetraethyl-2-phenylmethylene-1,3-disilacyclopent-4-ene (**5**) and (E)-1-tetraethyl(2-phenyl)disilanyl-2-phenylethene (**6**) in 12% and 47% yields, in addition to a trace amount of compound **2**. In this reaction, no 1-[diethyl(2-phenylethenyl)silyl]-2-diethylsilylbenzene, analogous to **4** was detected in the reaction mixture by spectrometric analysis. Pure **5** and **6** could readily be isolated by preparative HPLC.

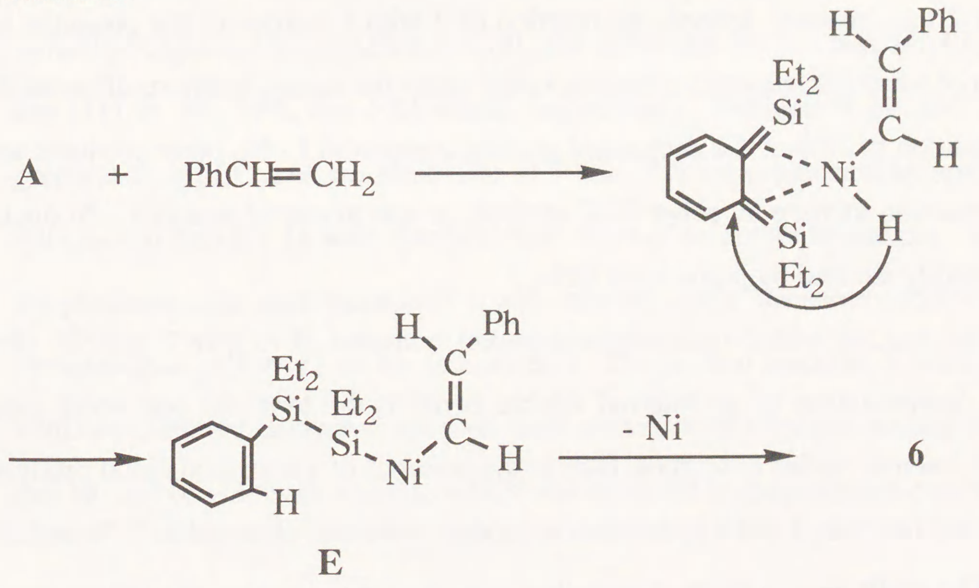
The mass spectrum of **5** reveals a molecular ion at m/z 350, corresponding to the calculated value for $C_{22}H_{30}Si_2$ (adduct - 2H). The ^1H NMR spectrum of **5** shows a singlet resonance at δ 7.89 ppm, attributed to an olefinic proton, along with resonances at 0.71-0.99 and 7.30-7.63 ppm, due to ethyl protons, and phenyl and phenylene protons, respectively. The ^{13}C NMR spectrum indicates two resonances at δ 139.0 and 155.5 ppm attributable to olefinic carbons, while its ^{29}Si NMR spectrum reveals two resonances at 6.46 and 0.50 ppm due to two nonequivalent silicon atoms. These results are wholly consistent with the structure proposed for **5**. The mass spectrum of **6**, however, shows a parent peak at m/z 352, and its ^1H NMR spectrum reveals two doublets at 6.44 and 6.79 ppm due to two olefinic protons. The ^{13}C NMR spectrum also reveals two olefinic carbons at 126.3 and 144.5 ppm, together with eight resonances for phenyl carbons, while the ^{29}Si NMR spectrum reveals two resonances at -14.81 and -17.90 ppm. On the basis of the coupling constant (J = 19.1 Hz) of the olefinic protons, compound **6** must have the trans configuration.



The formation of compound **5** may be explained by a series of the reaction involving activation of a terminal sp^2 C-H bond,[3] which is similar to the mechanism proposed for the formation of compound **3**. The production of **6** is of considerable interest, because scission of a silicon-phenylene bond is involved. In the nickel-catalyzed reactions of **1** with aromatic compounds and carbonyl compounds reported previously,[1,2] no compounds derived from scission of the silicon-phenylene bond were detected at all.

Two possible mechanism may be considered for the formation of **6**. One involves isomerization of a nickel complex, analogous to **C**, which would be formed from oxidative addition of an sp^2 C-H bond of styrene to *o*-quinodisilane **B**. Hydrogen on the nickel atom in this complex migrates to the silene carbon, and a silicon-silicon bond is produced to give nickel

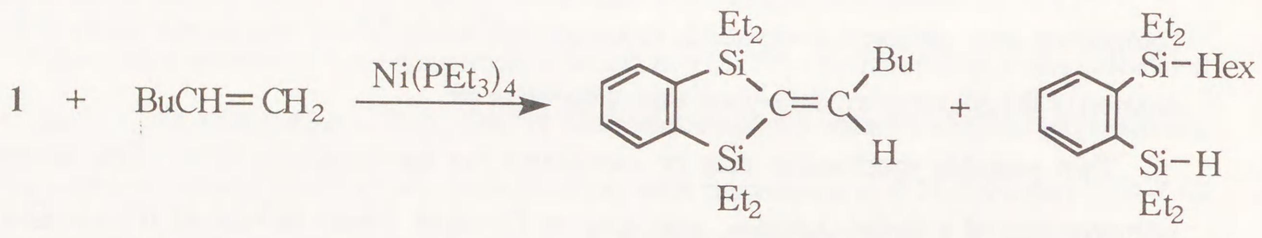
Scheme II



complex **E**. Finally reductive elimination of a nickel species from **E** produces compound **6** (Scheme II). The other comprises direct insertion of a nickel species into a silicon-phenylene bond to give 4,5-benzo-2,2,3,3-tetraethyl-1-nickela-2,3-disilacyclopent-4-ene, followed by the reaction of this nickel complex with styrene leading to nickel complex **E**.

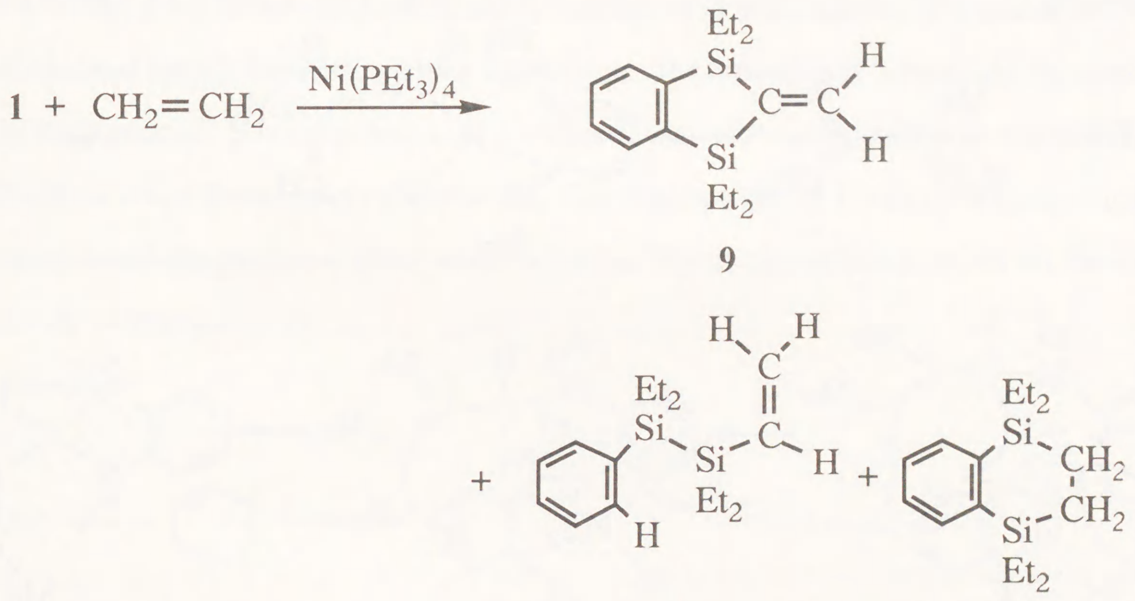
Although, at present, evidence to support the former mechanism has not yet been obtained, it seems likely that direct insertion of the nickel species into a silicon-phenylene bond is highly unfavorable because of the steric reasons.

Similarly, 1-hexene reacted with **1** under the same conditions to give 4,5-benzo-1,1,3,3-tetraethyl-2-(n-pentylidene)-1,3-disilacyclopent-4-ene (**7**) and 1-[diethyl(n-hexyl)silyl]-2-(diethylsilyl)benzene (**8**) in 52% and 44% yields. Compound **7** is probably produced from the reaction which is similar to that of **3** and **5**. Compound **8**, however, would be produced from hydrosilation of **2** to 1-hexene. Indeed, the reaction of **2** with 1-hexene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) under the same conditions afforded **8** in 58% yield, in addition to 28% of the unchanged starting compound **1**. No other products were detected in the reaction mixture by either GLC analysis or spectrometric analysis. Products **7** and **8** could be readily isolated by preparative HPLC.



7 **8**

2-Hexene also reacted with *o*-quinodisilane-nickel complex **B** to give **7** in 56% yield, indicating that isomerization of an internal double bond to the terminal one takes place. Isomerization of internal olefins to terminal ones in the presence of a transition metal catalyst is well known. In this reaction, **2** and a hydrosilation product were also obtained in 11% and 20% yields. ^{1}H and ^{13}C NMR spectra for the hydrosilation product show the presence of compound **8** as a major product (16% yield), but the other two hydrosilation products (4% combined yield), which are probably formed by hydrosilation of **2** to an internal double bond were detected. Unfortunately, all attempts to separate these two isomers from the mixture were unsuccessful. The structures of **7** and **8** were verified by spectrometric analysis (see Experimental Section).



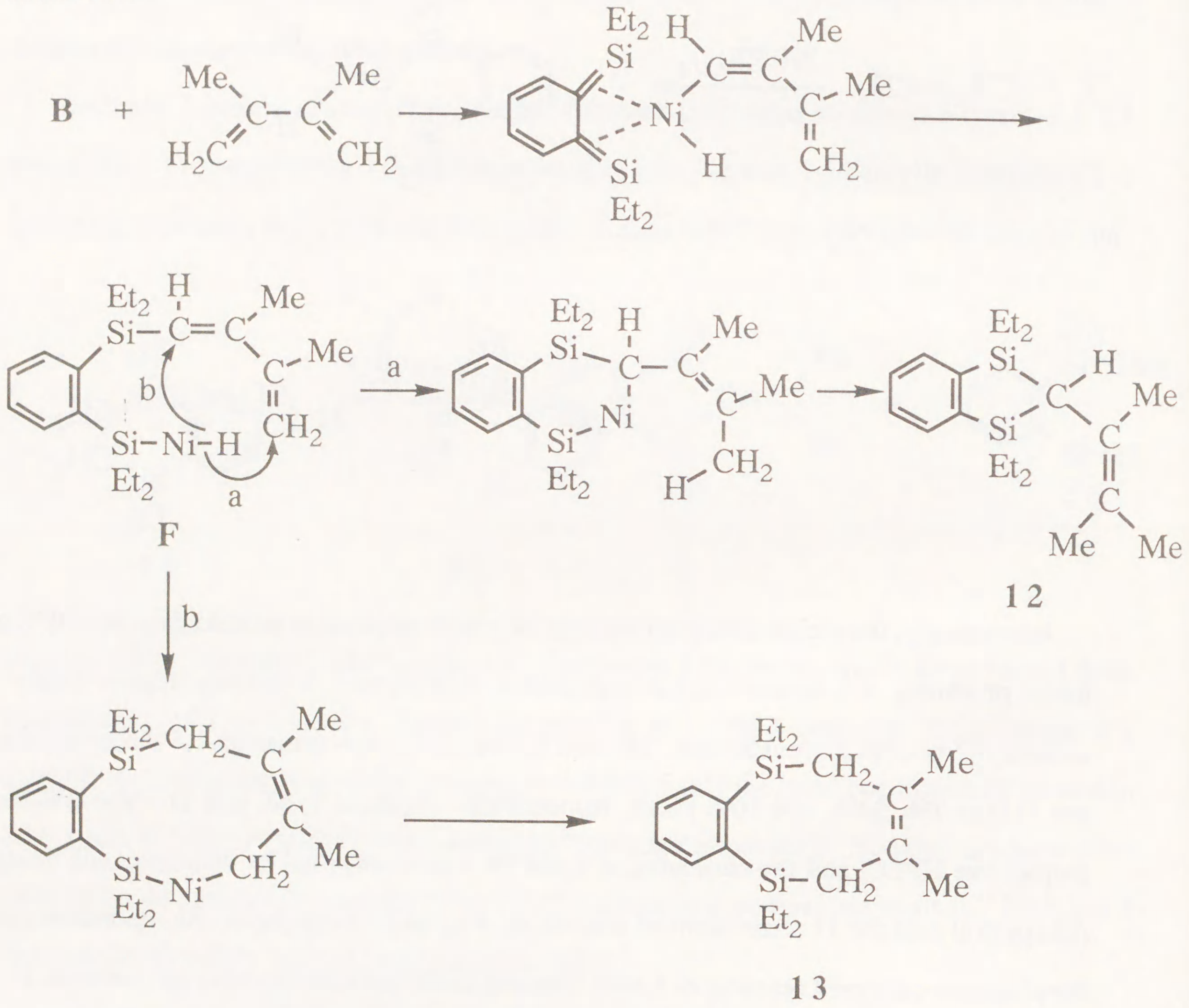
9

10 **11**

Interestingly, the nickel-catalyzed reaction of **1** with ethylene in an autoclave at 150°C gave three products, 4,5-benzo-1,1,3,3-tetraethyl-2-methylene-1,3-disilacyclopent-4-ene (**9**), tetraethyl-1-phenyl-2-vinyldisilane (**10**), and 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-2-ene (**11**) in 7%, 34%, and 10% yields, respectively. Products **9**, **10**, and **11** were isolated by preparative HPLC, and the structures of **9** and **10** were confirmed by spectroscopic analysis. All spectral data for **11** were identical with those of an authentic sample. As reported recently, the platinum-catalyzed reaction of **1** with ethylene under the same conditions proceeds [4 + 2] cycloaddition to give **11** as the sole product. The present reaction, however, seems to proceed with two different pathways, sp^2 C-H bond activation of ethylene leading to the formation of **9** and **10**, and [4 + 2] cycloaddition which was observed in the platinum-catalyzed reactions.

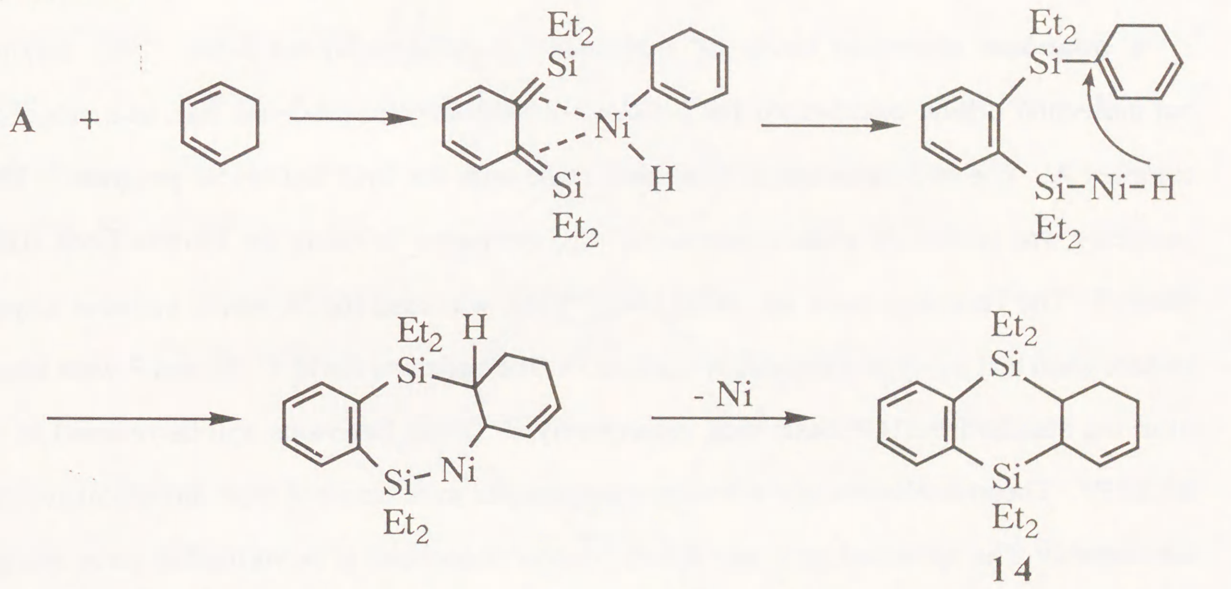
The nickel-catalyzed reaction of **1** with dienes gives the products whose formation can be explained in terms of activation of an sp^2 C-H bond of dienes. Thus, the reaction of **1** with 2,3-dimethylbutadiene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) at 150°C for 20 h produced two products, 4,5-benzo-1,1,3,3-tetraethyl-2-(1,2,2-trimethylethenyl)-1,3-disilacyclopent-4-ene (**12**) and 2,3-benzo-1,1,4,4-tetraethyl-6,7-dimethyl-1,4-disilacycloocta-2,6-diene (**13**) in 33% and 30% yields, respectively. The migration of a diene group in the nickel complex formed from oxidative addition of an sp^2 C-H bond of 2,3-dimethylbutadiene to a nickel atom of *o*-quinodisilane-nickel complex **B** to one of two silicon atoms gives complex **F**. Intramolecular addition of the Ni-H bond across the terminal carbon-carbon double bond affords **12**, while addition of this Ni-H bond to an internal carbon-carbon double bond produces **13** (Scheme III).

Scheme III



Similar nickel-catalyzed reaction of **1** with 1,3-cyclohexadiene gave 5,5,10,10-tetraethyl-8,9,13,14-tetrahydrosilanthrene (**14**) in 80% yield. With 1,4-cyclohexadiene, **1** also afforded **14** in 80% yield as the sole product, indicating that rapid isomerization of a double bond to the conjugated system takes place during the reaction. The formation of **14** may also be understood in terms of sp^2 C-H bond activation of cyclohexadiene, followed by intramolecular addition of a Ni-H bond to a diene moiety (Scheme IV). Since the reaction of **1** with cyclohexene under the same conditions gave no volatile products, formal [4 + 2] cycloaddition would not be involved for the production of **14**.

Scheme IV



In an effort to learn more about the reactive species in the present reaction, we carried out the stoichiometric reaction of **1** with tetrakis(triethylphosphine)nickel(0) in benzene-d_6. The reactions of **1** with a stoichiometric amount of (η^2-ethylene)bis(triphenylphosphine)platinum(0)[4] in toluene-d_8 and tetrakis(triphenylphosphine)palladium(0) in benzene-d_6 at room temperature proceed cleanly to give the reactive 3,4-benzo-2,2,5,5-tetraethyl-1-metala-2,5-disilacyclopent-3-enes in almost quantitative yields. However, similar reaction of **1** with tetrakis-

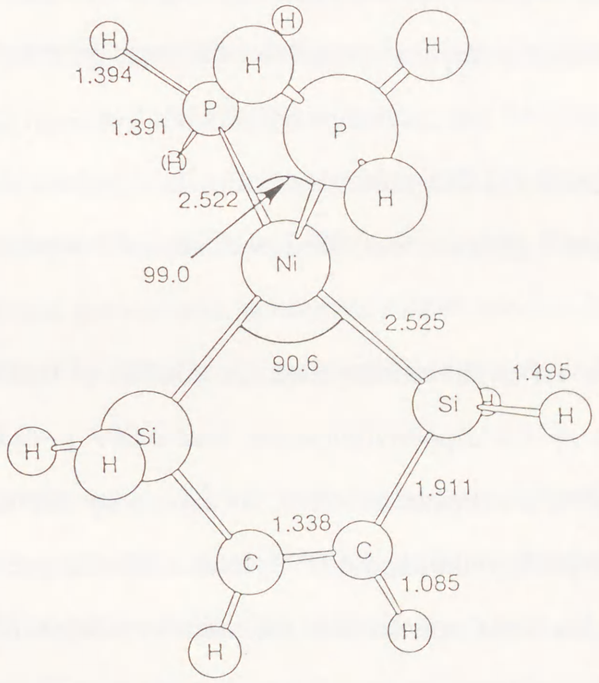
(triethylphosphine)nickel(0) produces no 3,4-benzo-1-nickela-2,5-disilacyclopent-3-ene **A**. Thus, when compound **1** was added to a benzene-d_6 solution containing 1 equiv of tetrakis(triethylphosphine)nickel(0) at room temperature, the light yellow solution changed to a dark red color. However, the ^{1}H NMR spectrum of this solution showed only resonances attributed to **1** and tetrakis(triethylphosphine)nickel(0). Furthermore, the ^{29}Si NMR spectrum of the solution reveals a single resonance whose chemical shift is identical with that of **1**. When the solution was stirred for 36 h at room temperature, no change was observed in its ^{1}H and ^{29}Si NMR spectra. Heating the solution at 80°C for 12 h gave an oligomer whose ^{1}H NMR spectrum showed broad signals in the region of ethyl protons and also phenylene protons. The molecular weight of the oligomer was determined to be 700, relative to polystyrene standards. Unfortunately, all attempts to detect 3,4-benzo-1-nickela-2,5-disilacyclopent-3-ene **A** in the present system were unsuccessful.

A quantum chemical study of 1-nickela-2,5-disilacyclopent-3-ene. We carried out molecular orbital calculations for 1-nickela-2,5-disilacyclopent-3-ene (**G**), as a model of complex **A**. The MO calculations were performed with the GAUSSIAN 92 program.[5] The geometry was optimized under constraint of C_{2v} symmetry by using the Hartree-Fock (HF) theory.[6] The Huzinaga basis set, (43321/4211*/31), was used for Ni which includes a split valence shell and a p-type polarization function.[7a] The basis sets for H, C, Si, and P were taken from the standard 6-31G* basis sets, respectively.[7b] These basis sets will be referred to as HUZSP*. Theoretical harmonic vibrational frequencies were obtained from analytical second derivatives.[6] The optimized geometry has all positive frequencies to be verified as a true energy minimum.

The HF/HUZSP* geometry of complex **G** is displayed in Fig. 1. The Ni-P bond length of 2.522Å, which is comparable with the Ni-Si bond length of 2.525Å, is somewhat larger than the experimental value of 2.15Å in $Ni(PPh_3)_2(C_2H_4)$ and $Ni(PCy_3)_2(\eta\text{-}CO_2)$.[8,9] This may indicate that the Ni-Si and Ni-P bond in **1** are relatively weak, because the HOMO is the σ-orbital of Ni-Si, while the LUMO the σ* of Ni-Si and Ni-P. The SiC bond of 1.911Å may be compared to the single bond in methylsilane of 1.888Å ,[7] while the C-C bond of 1.338Å may be compared to the double bond in cyclobutene of 1.322Å.[7] In addition, HOMO-1 is mainly composed of p orbitals on C atoms, which correspond to the π-orbital. Therefore, it is concluded that the Si-C and C-C bonds in complex **G** have the single and double bond character, respectively.

In order to clarify the role of 3,4-benzo-1-nickela-2,5-disilacyclopent-3-ene **A** and its another isomer, *o*-quinodisilane-nickel complex **B** in catalytic reactions, further study by using higher level of theory including electron correlation effect is now in progress.

Figure 1. HF/HUZSP* optimized structure for 1-nickela-2,5-disilacyclopent-3-ene (**G**). Bond lengths are in angstroms and bond angles in degrees.



Experimental Section

General Procedure. All nickel-catalyzed reactions of compound **1** with olefinic compounds were carried out in a degassed sealed glass tube (1.0 cm x 10 cm) with one exception of an experiment to reflux hexane. Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard. NMR spectra were recorded on a JEOL Model EX-270 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. Gas chromatographic separations were carried out using a column (3 m x 10 mm) packed with 30% SE-30 silicone on Chromosorb P. Gel-permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.). Tetrakis(triethylphosphine)nickel(0) was prepared by the method reported in the literature.

Materials. 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene **1** was prepared as reported in the literature.[10] Hexane was dried over lithium aluminum hydride and distilled before use.

Reaction of 1 with 1,1-diphenylethylene. A mixture of 0.110 g (0.443 mmol) of **1**, 0.118 g (0.655 mmol) of 1,1-diphenylethylene, and 0.009 g (0.017 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **2** (4% yield), **3** (55% yield), and **4** (7% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **2** was isolated by preparative GLC. The product **3** was obtained from recrystallization of the mixture from ethanol. Compound **4** was isolated by preparative HPLC. For **3**: mp 102°C-103°C; MS *m/e* 426 (M$^+$); IR 2961, 2862, 1563, 1456, 1120, 966, 818, 748, 701, 668 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.28-0.39 (m, 2H, CH$_2$), 0.56-0.67 (m, 2H, CH$_2$), 0.76-0.82 (m, 6H, CH$_3$), 7.23-7.52 (m, 14H, phenyl and phenylene ring protons); ^{13}C NMR δ(CDCl$_3$) 7.51, 7.91 (EtSi), 126.9, 127.0, 127.9, 128.2, 132.5, 146.7, 148.2 (phenyl and phenylene ring carbons), 137.4, 170.1 (olefinic carbons); ^{29}Si NMR δ(CDCl$_3$) -2.82. Anal. Calcd for C$_{28}$H$_{34}$Si$_2$: C, 78.81; H, 8.03. Found: C, 78.62; H, 8.02. For **4**: MS *m/e* 428 (M$^+$); IR 3059, 2954, 2873, 2147, 1564, 1489, 1416, 1232, 1116, 1009, 972, 896, 793, 692, 604 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.51-0.94 (m, 20H, EtSi), 4.57 (quint, 1H, HSi, J = 3.3 Hz), 6.45 (s, 1H, HC=C), 6.91-7.52 (m, 14H, phenyl and phenylene ring protons); ^{13}C NMR δ(CDCl$_3$) 4.56, 5.28, 7.60, 8.34 (EtSi), 127.2, 127.3, 127.5, 127.8 (two carbons), 127.9 (two carbons), 128.1, 129.5, 134.7, 135.0, 142.2, 142.5, 143.8, 146.1, 157.4 (phenyl and phenylene ring and olefinic carbons); ^{29}Si NMR δ(CDCl$_3$) -8.44 (two silicons). Anal. Calcd for C$_{28}$H$_{36}$Si$_2$: C, 78.44; H, 8.46. Found: C, 78.44; H, 8.49. All spectral data for **2** were identical with those of the authentic sample.

Reaction of 1 with 1,1-Diphenylethylene in the presence of hydrosilane in Hexane. A mixture of 0.309 g (1.24 mmol) of **1**, 0.396 g (2.20 mmol) of 1,1-diphenylethylene, 0.149 g (1.10 mmol) of dimethylphenylsilane, and 0.033 g (0.062 mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of hexane was heated to reflux for 20 h. The mixture was analyzed by GLC as being **4** (70% yield) and 4% of the starting compound **1**. The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **4** was isolated by HPLC. All spectral data for **4** were identical with those of the authentic sample.

Reaction of 4 in the presence of nickel catalyst. A mixture of 0.100 g (0.233 mmol) of **4**, and 0.017 g (0.032 mmol) of tetrakis(triethylphosphine)nickel(0) in 1 mL of hexane was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **3** (76% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **3** was isolated by preparative HPLC. All spectral data for **3** were identical with those of the authentic sample.

Reaction of 1 with Hydrogen. Into a 50-mL autoclave was placed 0.300 g (1.21 mmol) of **1** and 0.031 g (0.058 mmol) of tetrakis(triethylphosphine)nickel(0), and then hydrogen gas (60 kg/cm^2) was compressed into the autoclave. The autoclave was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **2** (98% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **2** was isolated by preparative GLC. All spectral data for **2** were identical with those of the authentic sample.

Reaction of 1 and 4 in the presence of nickel catalyst. A mixture of 0.335 g (1.35 mmol) of **1**, 0.557 g (1.23 mmol) of **4** and 0.053 g (0.100 mmol) of tetrakis-(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **2** (47% yield), **3** (84% yield), and 15% of the compound **1**. The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **2** was isolated by preparative GLC. Compound **3** was isolated by preparative HPLC. All spectral data for **2** and **3** were identical with those of authentic samples.

Reaction of 4 and 1,1-Diphenylethylene in the presence of nickel catalyst. A mixture of 0.063 g (0.147 mmol) of **4**, 0.089 g (0.494 mmol) of 1,1-diphenylethylene, and 0.007 g (0.013 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **3** (70% yield) and 1,1-diphenylethane (43% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **3** and 1,1-diphenylethane were isolated by preparative HPLC. All spectral data for **3** and 1,1-diphenylethane were identical with those of authentic samples.

Reaction of 1 with Styrene. A mixture of 0.374 g (1.51 mmol) of **1**, 0.255 g (2.45 mmol) of styrene, and 0.040 g (0.075 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **5** (12% yield) and **6** (47% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compounds **5** and **6** were isolated by preparative HPLC. For **5**: MS *m/e* 350 (M$^+$); IR 3045, 2954, 2908 , 2872, 1585, 1490, 1458, 1412, 1376, 1257, 1231, 1119, 1053, 1003, 960, 886, 752, 695 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.71-0.99 (m, 20H, EtSi), 7.30-7.63 (m, 9H, phenyl and phenylene ring protons), 7.89 (s, 1H, olefinic carbons); ^{13}C NMR δ(CDCl$_3$)

6.31, 7.35, 7.67, 7.82 (EtSi), 127.7, 128.0, 128.2, 128.3, 128.6, 132.5, 132.8, 141.5, 147.4, 149.0 (phenyl and phenylene ring carbons), 139.0, 155.5 (olefinic carbons); ^{29}Si NMR δ(CDCl$_3$) 0.50, 6.46. Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.38; H, 8.63. For **6**: MS *m/e* 352 (M$^+$); IR 3065, 2953, 2906 , 2872, 1596, 1493, 1458, 1460, 1376, 1330, 1231, 1196, 1069, 1006, 987, 910, 826, 775, 699 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.75-1.07 (m, 20H, EtSi), 6.44 (d, 1H, HC=CHPh, J = 19.1 Hz), 6.79 (d, 1H, HPhC=CH, J = 19.1Hz), 7.22-7.47 (m, 10H, phenyl and phenylene ring protons); ^{13}C NMR δ(CDCl$_3$) 3.92, 3.99, 8.25, 8.30 (EtSi), 127.7, 127.8, 128.3, 128.5, 134.5, 137.6, 138.7 (two carbons), (phenyl and phenylene ring carbons), 126.3, 144.5 (olefinic carbons); ^{29}Si NMR δ(CDCl$_3$) -17.90, -14.81. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.85; H, 9.12.

Reaction of 1 with 1-Hexene. A mixture of 0.449 g (1.81 mmol) of **1**, 0.272 g (3.23 mmol) of 1-hexene, and 0.048 g (0.090 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **7** (52% yield) and **8** (44% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compounds **7** and **8** were isolated by preparative HPLC. For **7**: MS *m/e* 330 (M$^+$); IR 3045, 2955, 2873, 1595, 1462, 1413, 1376, 1254, 1231, 1118, 1052, 1017, 960, 860, 788, 712, 618 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.71-0.99 (m, 23H, EtSi, CH$_3$), 1.33-1.50 (m, 4H, CH$_2$), 2.30 (q, 2H, CH$_2$, J = 7.3 Hz), 6.91 (t, 1H, HC=C, J = 6.9 Hz), 7.34-7.59 (m, 4H, phenylene ring protons); ^{13}C NMR δ(CDCl$_3$) 6.40, 7.08, 7.68, 7.93 (EtSi), 14.11 (Me), 22.57 (CH$_2$), 31.57 (CH$_2$), 38.92 (CH$_2$), 128.2, 128.3, 132.6, 132.7, 148.5, 148.7 (phenylene ring carbons), 133.8, 159.6 (olefinic carbons); ^{29}Si NMR δ(CDCl$_3$) 0.36, 1.66. Anal. Calcd for $C_{20}H_{34}Si_2$: C, 72.65; H, 10.36. Found: C, 72.57; H, 10.34. For **8**: MS *m/e* 334 (M$^+$); IR 2955, 2918, 2873, 2148, 1260, 1235, 1168, 1117, 1015, 972, 811, 743, 715, 698 cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 0.78-1.26 (m,33H, EtSi, n-Hex), 4.53 (quint 1H, HSi, J = 3.3 Hz), 7.29-7.55 (m, 4H, phenylene ring protons); ^{13}C NMR δ(CDCl$_3$) 4.69, 5.25, 7.66, 8.37 (EtSi), 13.99, 14.12, 22.64, 23.94, 31.54, 33.57 (n-Hex), 127.5, 127.8, 134.8, 135.4, 142.8, 144.6 (phenylene ring carbons), 133.8, 159.6 (olefinic carbons); ^{29}Si NMR δ(CDCl$_3$)

-9.69, 2.00. Anal. Calcd for $C_{20}H_{38}Si_2$: C, 71.77; H, 11.44. Found: C, 71.59; H, 11.52.

Reaction of 1 with 2-Hexene. A mixture of 0.389 g (1.57 mmol) of **1**, 0.249 g (2.96 mmol) of 2-hexene, and 0.040 g (0.075 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **2** (11% yield), **7** (56% yield), and **8** (20% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **2** was isolated by preparative GLC. Compounds **7** and **8** were isolated by preparative HPLC. All spectral data for **2**, **7**, and **8** were identical with those of authentic samples.

Reaction of 1 with Ethylene. Into a 50-mL autoclave was placed 0.195 g (0.785 mmol) of **1** and 0.022 g (0.041 mmol) of tetrakis(triethylphosphine)nickel(0), and then ethylene gas (60 kg/cm^2) was compressed into the autoclave. The autoclave was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **9** (7% yield), **10** (34% yield), and **11** (10% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compounds **9**, **10**, and **11** were isolated by preparative HPLC. For **9**: MS *m/e* 274 (M^+); IR 2954, 2872, 1508, 1458, 1120, 1032, 697 cm^{-1}; ^{1}H NMR $\delta(CDCl_3)$ 0.72-1.26 (m, 20H, EtSi), 6.62 (s, 2H, H_2C=C), 7.28-7.59 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 5.88, 7.55 (EtSi), 128.4, 133.0, 141.4, 148.3, 148.6 (phenylene ring and olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ 0.89. Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.00; H, 9.55. Found: C, 69.74; H, 9.47. For **10**: MS *m/e* 276 (M^+); IR 3047, 2954, 2873, 1462, 1008, 699 cm^{-1}; ^{1}H NMR $\delta(CDCl_3)$ 0.65-1.02 (m, 20H, EtSi), 5.61 (dd, 1H, olefinic proton, J_{trans} = 19.8 Hz, J_{gem} = 4.3 Hz), 5.97 (dd, 1H, olefinic protons, J_{cis} = 14.5 Hz, J_{gem} = 4.3 Hz), 6.13 (dd, 1H, olefinic protons, J_{trans} = 19.8 Hz, J_{cis} = 14.5 Hz), 7.28-7.53 (m, 5H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ 3.65, 3.92, 8.12, 8.27 (EtSi), 127.7, 128.3, 132.7, 134.5, 136.6, 136.8 (phenyl ring and olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ -18.58, -15.24. Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.43; H, 10.20. All spectral data for **11** were identical with those of the authentic sample.

Reaction of 1 with 2,3-dimethyl-1,3-butadiene. A mixture of 0.134 g (0.541 mmol) of **1**, 0.081 g (0.981 mmol) of 2,3-dimethyl-1,3-butadiene, and 0.013 g (0.025 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **12** (33% yield) and **13** (29% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **12** and **13** were isolated by preparative HPLC. For **12**: MS *m/e* 330 (M^+); IR 3044, 2954, 2874, 1458, 1414, 1375, 1230, 1156, 1113, 1008, 766, 731, 608 cm^{-1}; ^{1}H NMR $\delta(CDCl_3)$ 0.71-1.10 (m, 20H, EtSi), 1.59-1.69 (three broad peaks, 9H, Me), 2.00-2.01 (br s, 1H, CH), 7.24-7.58 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 5.82, 6.52, 7.46, 7.64 (EtSi), 19.01 (CH), 20.77, 21.06, 21.24 (Me), 128.2, 132.8, 149.0 (phenylene ring carbons), 119.2, 125.6 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ 10.89. Anal. Calcd for $C_{20}H_{34}Si_2$: C, 72.65; H, 10.36. Found: C, 72.65; H, 10.36. For **13**: MS *m/e* 330 (M^+); IR 3045, 2954, 2872, 1457, 1417, 1379, 1273, 1233, 1182, 1116, 1007, 773, 716 cm^{-1}; ^{1}H NMR $\delta(CDCl_3)$ 0.80-1.04 (m, 20H, EtSi), 1.68 (s, 6H, Me), 1.78 (s, 4H, CH_2), 7.24-7.60 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 6.24, 7.51 (EtSi), 21.10 (Me), 21.76 (CH_2), 127.4, 135.9, 143.6 (phenylene ring carbons), 122.7 (olefinic carbon); ^{29}Si NMR $\delta(CDCl_3)$ 5.53. Anal. Calcd for $C_{20}H_{34}Si_2$: C, 72.65; H, 10.36. Found: C, 72.64; H, 10.31.

Reaction of 1 with 1,3-cyclohexadiene. A mixture of 0.238 g (0.958 mmol) of **1**, 0.139 g (1.67 mmol) of 1,3-cyclohexadiene, and 0.024 g (0.045 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **14** (80% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **14** was isolated by preparative GLC: MS *m/e* 328 (M^+); IR 3011, 2952, 2873, 1462, 1414, 1234, 1146, 1117, 1008, 794, 742, 708 cm^{-1}; ^{1}H NMR $\delta(CDCl_3)$ 0.63-1.09 (m, 20H, EtSi), 1.50-1.58 (m, 2H, CH, CH_2 (axial)), 1.79-1.84 (m, 1H, CH_2 (equatorial)), 1.98-2.14 (m, 3H, CH, CH_2), 5.60-5.66 (m, 1H, CH=CH), 5.92-5.98 (m, 1H, CH=CH), 7.21-7.52 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 2.28, 5.45, 6.24, 6.61, 7.57, 7.62, 7.73, 7.89 (EtSi), 19.12 (CH), 22.98 (CH_2), 24.47 (CH), 25.82 (CH_2), 127.8 (two carbons), 134.2, 134.3, 143.3, 143.4 (phenylene ring carbons), 124.1, 130.5 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ -4.28, -6.66. Anal. Calcd for $C_{20}H_{32}Si_2$: C, 73.09; H, 9.81. Found: C, 73.19; H, 9.68.

Reaction of 1 with 1,4-cyclohexadiene. A mixture of 0.212 g (0.854 mmol) of **1**, 0.134 g (1.67 mmol) of 1,4-cyclohexadiene, and 0.015 g (0.028 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **14** (80% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Compound **14** was isolated by preparative GLC. All spectral data for **14** were identical with those of the authentic sample.

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Chapter 6

Palladium-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene

Introduction

The chemical behavior of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) toward transition-metal complexes is quite unique.[1-4] As discussed in chapter 3, the nickel-catalyzed reaction of **1** with aromatic compounds gives 1-aryldiethylsilyl-2-diethylsilylbenzenes arising from oxidative addition of an sp^2 C-H bond of the aromatic ring to an *o*-quinodisilane-nickel complex.[1] The similar nickel-catalyzed reactions of **1** with non-enolizable ketones proceeds with deoxygenation of the ketones to give nickel-carbene complexes and 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene,[2] while with olefins, **1** produces adducts derived from addition of a terminal sp^2 C-H bond to the *o*-quinodisilane-nickel complex.[3]

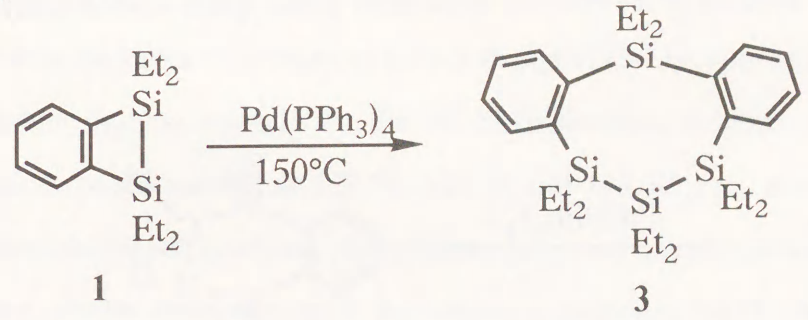
In order to get more information concerning the chemical behavior of **1** toward the transition-metal complex, we have investigated the palladium-catalyzed reactions of **1** in the presence or absence of a trapping agent.

Results and Discussion

Since the C-H bond activation of benzene in the nickel-catalyzed reaction of **1** occurred at 80°C, and the platinum-catalyzed isomerization of **1** also took place at reflux temperature of benzene, we first carried out the reaction of **1** with a catalytic amount of a palladium(0) complex in benzene to confirm whether or not C-H bond activation of benzene or isomerization of **1** occurs. When **1** was heated to reflux in the presence of 5 mol% of tetrakis(triphenylphosphine)-palladium(0) in benzene for 24 h, neither the product arising from C-H bond activation nor the isomerization product was formed. The starting compound **1** was recovered unchanged. Interestingly, when the same mixture was heated in a degassed sealed tube at 150°C for 24 h, a dimer was obtained in 79% yield as the sole volatile product, in addition to 5% of the starting compound **1**. Again, no product arising from C-H bond activation of benzene was detected in the reaction mixture by either spectrometric analysis or GLC analysis. The mass spectrum of the dimer shows the parent ion at m/z 496, corresponding to the calculated molecular weight for $C_{28}H_{48}Si_4$.

Thus, the ^{13}C NMR spectrum reveals six resonances at δ 2.48, 4.69, 7.30, 7.93, 8.38, and 10.19 ppm, attributed to three kinds of the ethyl groups, as well as six resonances due to phenylene ring carbons. Its ^{29}Si NMR spectrum shows three resonances at -35.18, -11.19, and -3.50 ppm, indicating the presence of three non-equivalent silicons. These results are wholly consistent with the structure proposed for 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (**3**) (Scheme I).

Scheme I



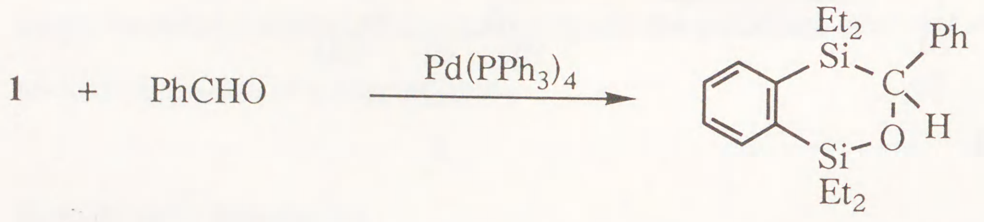
1　　**3**

$$\mathbf{3} \xrightarrow{\text{HCl-AlCl}_3} Et_2SiCl_2 + ClEt_2SiSiEt_2SiEt_2Cl$$

In order to get more information on the structure of **3**, we carried out the cleavage reaction of this compound by hydrogen chloride. Thus, the reaction of **3** with hydrogen chloride gas in the presence of a catalytic amount of aluminum chloride in dry benzene at room temperature for 1.5 h proceeded cleanly to give degradation products. GC-Mass spectrometric analysis of the reaction mixture indicated that dichlorodiethylsilane and 1,3-dichlorohexaethyltrisilane were produced in

34% and 58% yields, respectively. The retention time of dichlorodiethylsilane on GLC was identical with that of an authentic sample. 1,3-Dichlorohexaethyltrisilane was converted to a 1,3-dimethyltrisilane derivative, and the structure of the resulting hexaethyl-1,3-dimethyltrisilane was verified by spectrometric analysis, as well as by elemental analysis. All spectral data obtained for **3** and also the results of degradation reactions are wholly consistent with the structure proposed for **3**.

Next, we carried out the palladium-catalyzed reaction of **1** with carbonyl compounds, alkynes, and alkenes. As described in chapter 4, the nickel-catalyzed reaction of **1** with benzaldehyde in benzene gave an addition product derived from insertion of a carbonyl group into a silicon-silicon bond of **1** as the sole product.[2] The palladium-catalyzed reaction of **1** with benzaldehyde in refluxing benzene for 80 h led to the same result as that of the nickel-catalyzed reaction. 5,6-Benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene (**4**) whose spectral data were identical with those of an authentic sample was obtained in 90% yield. No other products were detected in the reaction mixture by either spectrometric analysis or GLC analysis.

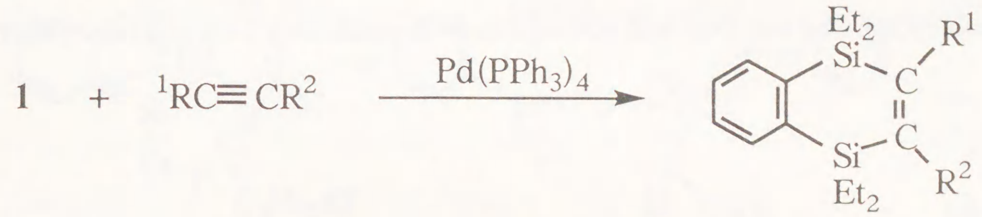


4

In contrast to the nickel-catalyzed reaction of **1** with acetone, in which two different types of acetone adducts and 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene were formed,[2] the palladium-catalyzed reaction with acetone in a degassed sealed tube at 150°C afforded no acetone adduct, but dimer **3** was obtained in 48 % yield, along with 25% of the unreacted starting compound **1**.

The reaction of **1** with alkynes in the presence of the palladium catalyst proceeded readily at room temperature, giving 5,6-benzo-1,4-disilacyclohexa-2,5-dienes arising from insertion of a carbon-carbon triple bond into a silicon-silicon bond of the starting compound **1**. Thus, the reaction of **1** with bubbling acetylene gas in the presence of a tetrakis(triphenylphosphine)-palladium(0) catalyst in benzene at room temperature for 30 min afforded 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene (**5**) in 70% yield as the sole product (Scheme II). The ^{1}H NMR spectrum of **5** reveals a single resonance at δ 7.14 ppm due to olefinic protons, together with multiplet resonances at 0.73-0.95 and 7.33-7.54 ppm attributed to ethyl protons and phenylene protons, respectively. Its ^{13}C NMR spectrum shows two resonances at 6.08 and 7.62 ppm, three resonances at 127.78, 133.48 and 143.29 ppm, and a single resonance at 149.40 ppm, due to ethyl carbons, phenylene carbons, and olefinic carbons, respectively. These results are wholly consistent with the structure proposed for **5**. The reaction of **1** with phenylacetylene in benzene at room temperature for 30 min produced 5,6-benzo-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (**6**) in 87% yield. Although diphenylacetylene reacted with **1** in benzene at room temperature to give a similar insertion product, 5,6-benzo-1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**7**), the rate of the reaction was quite slow. In refluxing benzene, however, diphenylacetylene readily reacted with **1** to give product **7** in 69% yield. Compound **6** was isolated by column chromatography, while **7** was obtained by recrystallization from ethanol. All spectral data obtained for **6** and **7** were identical with those of the authentic samples.[4]

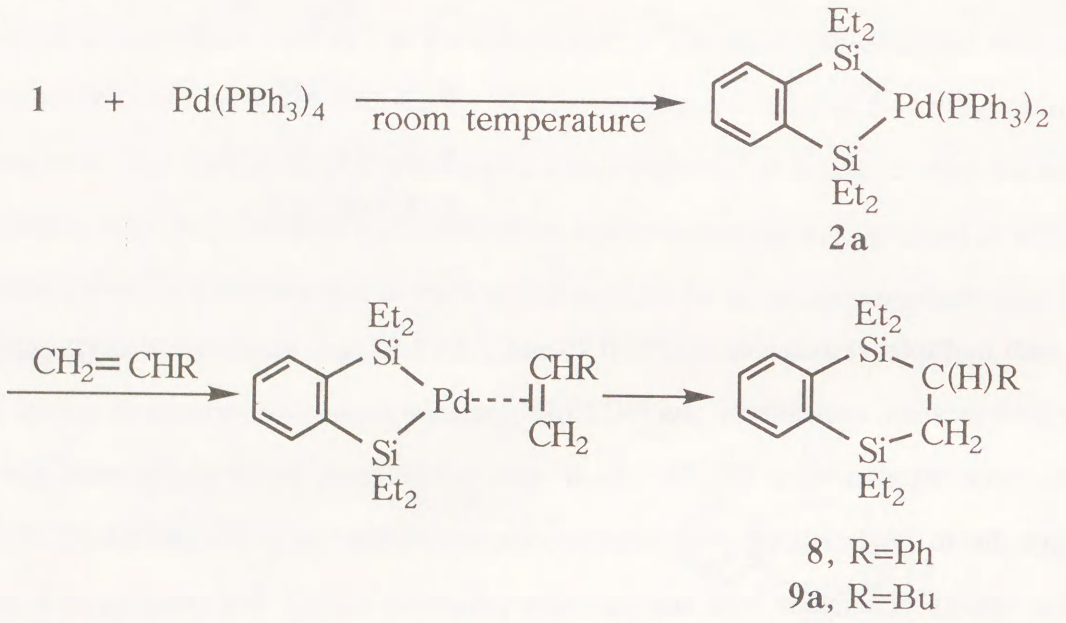
Scheme II



5, $R^1=R^2=H$
6, $R^1=H$, $R^2=Ph$
7, $R^1=R^2=Ph$

The nickel-catalyzed reaction of **1** with styrene and 1-hexene gives the products derived from sp^2 C-H bond activation,[3] however, the palladium-catalyzed reaction with these olefins proceeds with a different fashion. Thus, treatment of **1** with styrene in the presence of the palladium catalyst in benzene at room temperature for 10 h afforded 5,6-benzo-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-5-ene (**8**) in 84% yield. The reaction of **1** with 1-hexene at room temperature for 6 h afforded no product. In refluxing benzene, however, 2,3-benzo-5-butyl-1,1,4,4-tetraethyl-1,4-disilacyclohex-2-ene (**9a**) was obtained in 94% yield, after 14 h reaction (Scheme III).

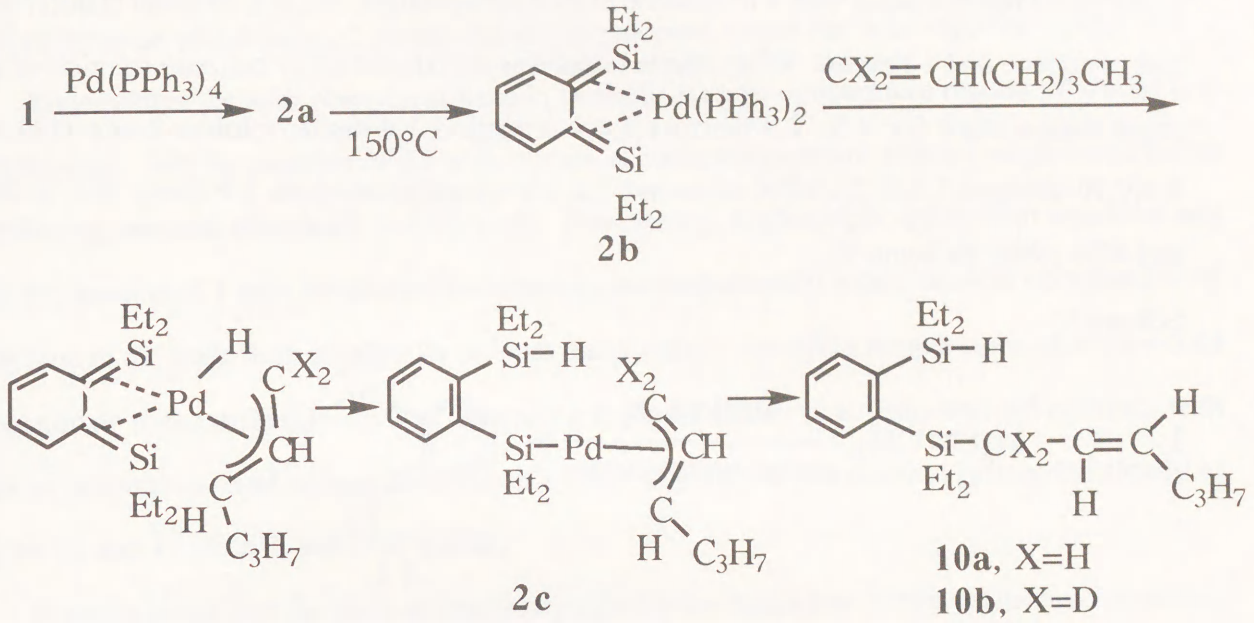
Scheme III



Interestingly enough, when the reaction of **1** with 1-hexene was carried out in a sealed tube at 150°C, two products, compound **9a** and (E)-1-[diethyl(2-hexenyl)silyl]-2-(diethylsilyl)benzene (**10a**) were obtained in 39% and 41% yields, respectively (Scheme IV).

The structures of **8**, **9a**, and **10a** were verified by spectroscopic and elemental analysis. Proton decoupling experiment of a 2-hexenyl group in compound **10a** shows double doublets with J = 15.4 Hz, indicating that **10a** must have a trans cofiguration.

Scheme IV

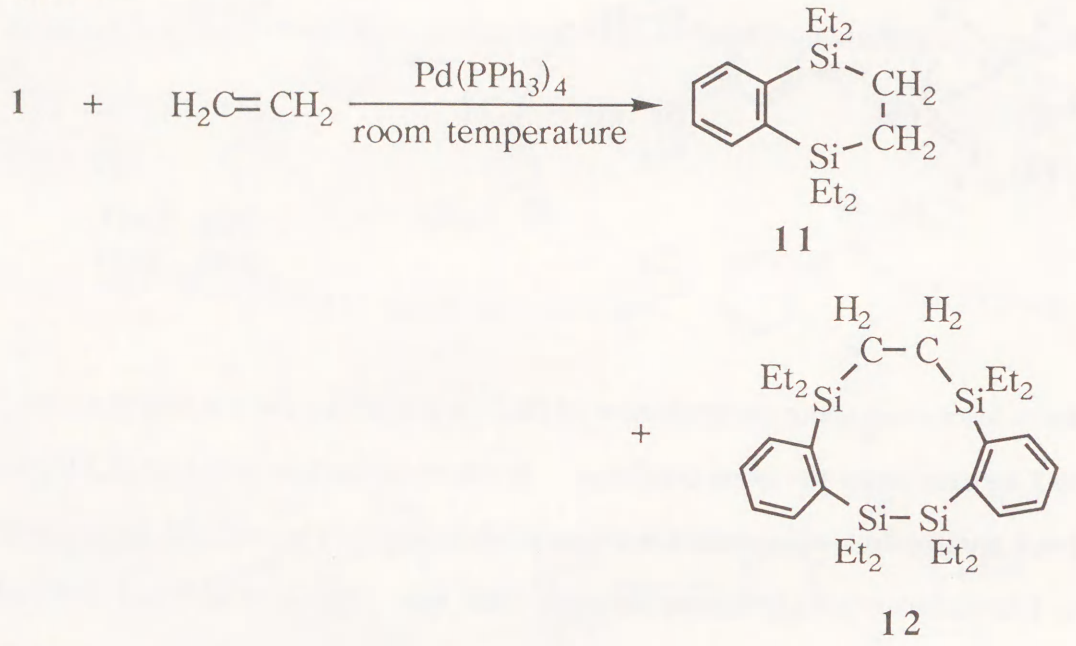


In order to learn more about the production of **10a**, we carried out the reaction of **1** with 1,1-dideuterio-1-hexene under the same conditions. In this reaction, two products, 2,3-benzo-5-butyl-1,1,4,4-tetrethyl-6,6-dideuterio-1,4-disilacyclohex-2-ene (**9b**) and (E)-1-[diethyl(1,1-dideuterio-2-hexenyl)silyl]-2-(diethylsilyl)benzene (**10b**) were obtained in 43% and 35% yields. The ^1H NMR spectrum for **10b** shows a quintet resonance at 4.55 ppm attributed to an Si-H proton, while the ^2H NMR spectrum reveals a single resonance at 1.84 ppm due to CD_2(Si). In marked contrast to the nickel-catalyzed reactions of **1** with olefins, in which the products derived from terminal sp^2 C-H bond activation are obtained, the present reaction with 1-hexene at 150°C affords no product rising from terminal sp^2 C-H bond activation, but gives the product formed from allylic C-H bond activation.

Similar reaction of **1** with styrene at 150°C afforded product **8** in 93% yield, but not the product arising from C-H bond activation.[6] The reaction of **1** with an internal olefin, 2-hexene at 150°C gave no adduct, but produced dimer **3** in 72% yield as the sole product. This result indicates that no olefin isomerization occurs in this system.

Ethylene reacts readily with **1** in benzene at room temperature, but in a different fashion from that of styrene and 1-hexene. When ethylene gas was introduced into a benzene solution of **1** at room temperature for 4 h, 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-2-ene (**11**) and 3,4,9,10-dibenzo-1,1,2,2,5,5,8,8-octaethyl-1,2,5,8-tetrasilacyclodeca-3,9-diene (**12**) in 28% and 40% yields (Scheme V).

Scheme V

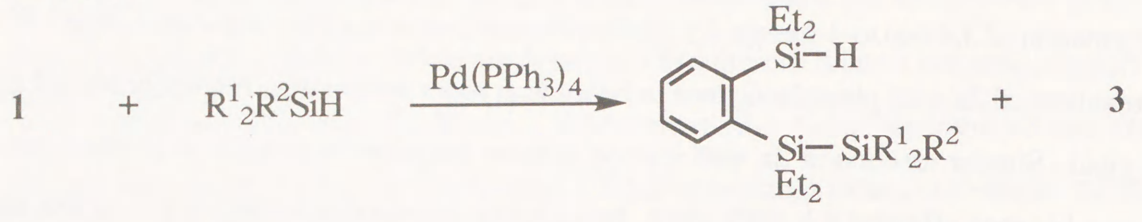


In order to learn more about the reactive species in the present system, we carried out the stoichiometric reaction of **1** with tetrakis(triphenylphosphine)palladium(0) in deuteriobenzene at room temperature, and analyzed the mixture by ^{13}C NMR spectrometry. The ^{13}C NMR spectrum of the mixture obtained after 30 min reaction showed that the starting compound **1** was completely transformed into a new product whose spectrum reveals resonances at 11.31 and 12.88 ppm due to ethyl carbons, in lower magnetic field than those of ethyl carbons of **1**. Its ^{29}Si NMR spectrum shows a singlet resonance at 44.28 ppm, again in lower field than that of the starting compound **1**. Unfortunately, all attempts to isolate this compound were unsuccessful. However, on the basis of ^{1}H, ^{13}C and ^{29}Si NMR data, we assigned this compound as 3,4-benzo-2,2,5,5-tetraethyl-1,1-bis(triphenylphosphine)-1-pallada-2,5-disilacyclopent-3-ene (**2a**). The formation of 3,4-benzo-1-metala-2,5-disilacyclopent-3-enes has been reported to date.[7-12]

Treatment of **2a** with phenylacetylene in benzene at room temperature readily produced **6** in 86% yield. Similar reaction of **2a** with styrene at room temperature yielded no product, but in refluxing benzene afforded **8** in 89% yield. Presumably, triphenylphosphine that was liberated in the reaction of **1** with tetrakis(triphenylphosphine)palladium(0) would prevent coordination of styrene to the palladium atom of **2a** at room temperature. At reflux temperature, styrene would coordinate to the palladium atom of **2a** leading to the formation of **8**. Ethylene did not react with **2a** in benzene at room temperature, but at reflux temperature, the reaction proceeded slowly to give **11** and **12** in 45% and 44% yields.

It seems likely that **2a** plays an important role for the formation of benzodisilacyclohexenes and benzodisilacyclohexanes. At the initial step, unsaturated compound would coordinate to the palladium atom of **2a**, and an unsaturated bond of the coordinated molecule inserts into a silicon-palladium bond to give seven-membered ring system. Finally, the palladium species eliminates reductively from the seven-membered ring system yielding the insertion product (see Scheme III). At higher temperature, a different reactive species from 3,4-benzo-1-pallada-2,5-disilacyclopent-3-ene **2a**, presumably *o*-quiodisilane-palladium complex (**2b**) would be produced as a key intermediate. In an effort to obtain some information concerning the formation of **2b**, we carried out the reaction of **1** with hydrosilanes in the presence of the palladium catalyst. Treatment of **1** with triethylsilane in the presence of the palladium catalyst in refluxing benzene for 16 h afforded no product. The starting compound **1** and triethylsilane were recovered unchanged. However, when the same mixture was heated in a sealed tube at 150°C for 24 h, 2-diethylsilyl-1-(pentaethyldisilanyl)benzene (**13a**) and dimer **3** were obtained in 31% and 41% yields, in addition to 11% of the starting compound **1** (Scheme VI). No other volatile products were detected by GLC analysis. Similar treatment of **1** with dimethylphenylsilane under the same conditions afforded 1-(1,1-diethyl-2,2-dimethyl-2-phenyldisilanyl)-2-(diethyl-

Scheme VI

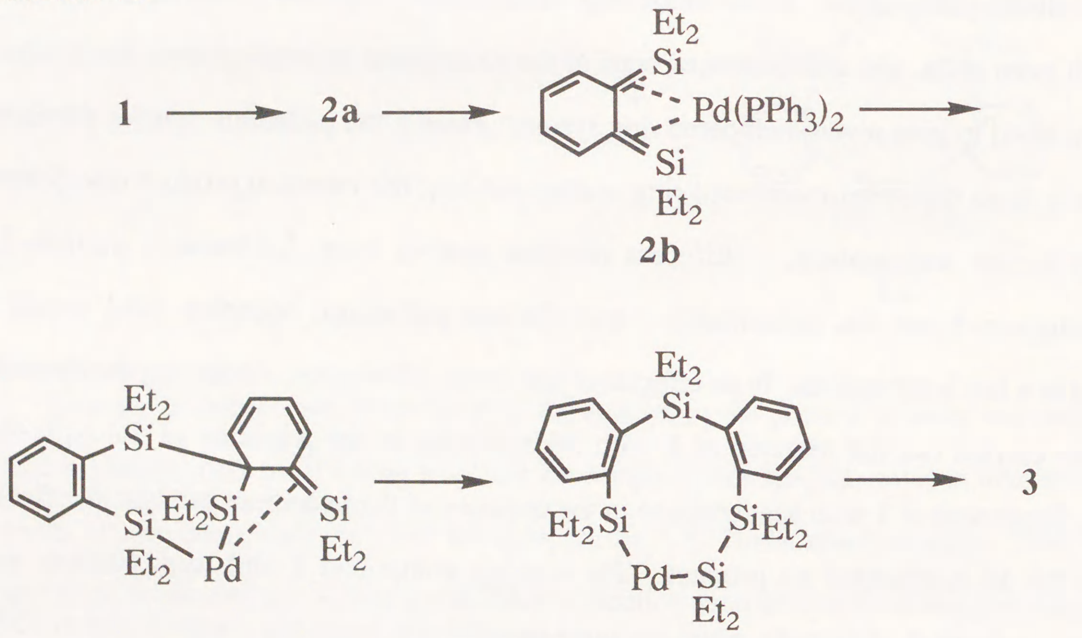


13a, $R^1 = R^2 = Et$

13b, $R^1 = Me$, $R^2 = Ph$

silyl)benzene (**13b**) in 52% yield, along with 24% of **1**. The formation of **13a** and **13b** may be explained in terms of 1,4-addition of hydrosilanes to *o*-quinodisilane-palladium complex **2b**. Compounds **3** and **10** would also be produced from *o*-quinodisilane-palladium complex **2b** arising from isomerization of **2a**. A possible mechanism for the formation of **3** would involve addition of **1** to *o*-quinodisilane-palladium complex **2b** formed from the reaction of **1** with tetrakis(triphenylphosphine)palladium(0), followed by cycloaddition, and then ring enlargement to eight-membered cyclic system as shown in Scheme VII.

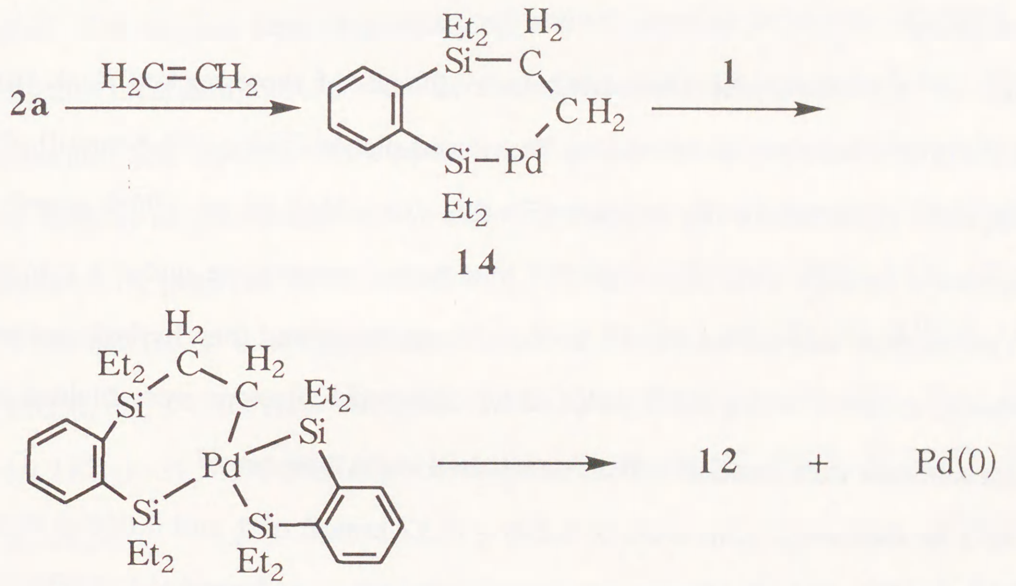
Scheme VII



The formation of **10** may be understood in terms of oxidative addition of an allylic C-H bond in hexene to *o*-quinodisilane-palladium complex (**2b**), and then a hydrogen shift on the palladium atom to one of two silicon atoms giving π-allylpalladium complex (**2c**). Reductive elimination of the palladium species from **2c** would produce product **10**. An alternative mechanism involving the π-coordination of 1-hexene to complex **2a**, followed by migration of the allylic hydrogen onto a silicon atom leading to **2c** can not be excluded at present.

That compound **12** is probably produced from the reaction of 3,4-benzo-2,2,5,5-tetraethyl-1-pallada-2,5-disilacyclohept-3-ene (**14**) arising from insertion of ethylene to a palladium-silicon bond in **2a** with compound **1** as shown in Scheme VIII.

Scheme VIII



Experimental Section

General Procedure. NMR spectra were recorded on a JEOL Model EX-270 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Low resolution mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument.

High resolution mass spectra were measured on a Hitachi M-80B mass spectrometer. Gas chromatographic separations were carried out using a column (3 m x 10 mm) packed with 30% SE-30 silicone on Chromosorb P with one exception of isolation of the products obtained from the thermolysis of **1**. The products from the thermolysis were isolated by using a column packed with silicon OV-17 on Uniport HP. Gel-permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.). Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard.

Materials. 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) was prepared as reported in the literature.[5] Benzene used as a solvent was dried over lithium aluminum hydride and distilled before use.

Preparation of 1,1-dideuterio-1-hexene. In a 100-mL of three-necked flask fitted with a magnetic stirrer, condenser, and dropping funnel was placed 7.53 g (90.8 mmol) of 1-deuterio-1-hexyne[13] in 10 mL of dry toluene. To this was added 90 mL (90.9 mmol) of di(isobutyl)aluminum hydride over a period of 1 h at room temperature under a nitrogen atmosphere. The mixture was stirred for 4 h at room temperature and then hydrolyzed with D_2O. After workup as usual, 4.93 g (63% yield) of 1,1-dideuterio-1-hexene was obtained: bp. 64-67°C. All spectral data were identical with those reported in the literature.[13]

Reaction of 1 in Benzene. A mixture of 0.290 g (1.17 mmol) of **1** and 0.057 g (0.049 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene in a degassed sealed tube was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **3** (79% yield) and 5% of the starting compound **1**. The mixture was treated with a short silica gel column to remove any palladium species from the reaction mixture. Compound **3** was isolated by MPLC: MS *m/z* 496 (M^+); IR 2950, 2872, 1460, 1109, 1004, 735, 696 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.54-1.13 (m, 40H, EtSi), 7.28-7.34 (m, 4H, phenylene ring protons), 7.50-7.53 (m, 2H, phenylene ring protons), 7.70-7.73 (m, 2H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 2.48, 4.69, 7.30, 7.93, 8.38, 10.19 (EtSi), 126.9, 127.5, 135.0, 136.1, 144.8, 145.2 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ -35.18, -11.19, -3.50. Anal. Calcd for $C_{28}H_{48}Si_4$: C, 67.66; H, 9.73. Found: C, 67.56; H, 9.68.

Reaction of 3 with Hydrogen Chloride. In a 50-mL two-necked flask fitted with a condenser and inlet tube for hydrogen chloride gas was placed 0.190 g (0.383 mmol) of **3** and 0.008 g (0.060 mmol) of anhydrous aluminum chloride in 3 mL of dry benzene. To this was introduced dry hydrogen chloride gas at room temperature for 1.5 h. The mixture was analyzed by GC-mass spectrometry as being 1,3-dichlorohexaethyltrisilane (58% yield, m/z 328) and dichlorodiethylsilane (34% yield, m/z 242). The solvent benzene was evaporated, and then 3.8 mL (3.8 mmol) of a methylmagnesium bromide-ether solution was added to the residue. The mixture was stirred for 5 h at room temperature and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and then dried over calcium chloride. The solvents were evaporated off, and the residue was distilled under reduced pressure (1 mmHg) to give hexaethyl-1,3-dimethyltrisilane. Pure hexaethyl-1,3-dimethyltrisilane was isolated by preparative GLC: MS *m/z* 288 (M^+); IR 2950, 2873, 1458, 1016, 789 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.06 (s, 6H, MeSi), 0.59-0.80 (m, 12H, CH_2Si), 0.96 (t, 12H, J = 7.9 Hz), 1.02 (t, 6H, J = 7.9 Hz); ^{13}C NMR $\delta(CDCl_3)$ -5.03, 2.97, 6.36, 8.23, 10.41 (EtSi); ^{29}Si NMR $\delta(CDCl_3)$ -37.50, -9.55. Anal. Calcd for $C_{14}H_{36}Si_3$: C, 58.25; H, 12.57. Found: C, 58.44; H, 12.51.

Reaction of 1 with Benzaldehyde. In a 30-mL two-necked flask fitted with a condenser was placed 0.129 g (0.520 mmol) of **1**, 0.066 g (0.622 mmol) of benzaldehyde, and 0.029 g (0.025 mmol) of $Pd(PPh_3)_4$ in 2 mL of benzene. The mixture was heated to reflux for 80 h. GLC analysis of the resulting mixture showed the presence of **4** (90% yield). Compound **4** was isolated by MPLC. All spectral data for product **4** were identical with those of an authentic sample.[2]

Reaction of 1 with Acetone. A mixture of 0.121 g (0.49 mmol) of **1**, 0.120 g (2.07 mmol) of acetone, and 0.026 g (0.023 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **3** (48% yield) and 25% of the starting compound **1**.

Reaction of 1 with Acetylene. In a 30-mL two-necked flask fitted with a condenser and inlet tube for acetylene gas was placed 0.098 g (0.40 mmol) of **1** and 0.021 g (0.018 mmol) of $Pd(PPh_3)_4$ in 4 mL of dry benzene. To this was introduced acetylene gas at room temperature for 0.5 h. The mixture was analyzed by GLC as being **5** (70% yield). After treatment of the mixture with a short silica gel column, compound **5** was isolated by MPLC: MS *m/z* 274 (M^+); IR 2953, 2873, 1458, 1413, 1120, 1003, 720 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.73-0.95 (m, 20H, EtSi), 7.14 (s, 2H, olefinic protons), 7.33-7.54 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 6.08, 7.62 (EtSi), 127.78, 133.48, 143.29 (phenylene carbons), 149.40 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ -16.47. Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.00; H, 9.54. Found: C, 69.84; H, 9.54.

Reaction of 1 with Phenylacetylene. In a 30-mL two-necked flask fitted with a condenser was placed 0.043 g (0.17 mmol) of **1**, 0.025 g (0.25 mmol) of phenylacetylene, and 0.012 g (0.010 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene. The mixture was stirred at room temperature for 0.5 h, and the resulting mixture was analyzed by GLC as being **6** (87% yield). Compound **6** was isolated by column chromatography. All spectral data for **6** were identical with those of an authentic sample.[4]

Reaction of 1 with Diphenylacetylene. In a 30-mL two-necked flask fitted with a condenser was placed 0.062 g (0.250 mmol) of **1**, 0.072 g (0.404 mmol) of diphenylacetylene, and 0.013 g (0.011 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene. The mixture was heated to reflux for 12.5 h, and the resulting mixture was analyzed by GLC as being **7** (69% yield). Compound **7** was isolated by recrystallization from ethanol. All spectral data for **7** were identical with those of an authentic sample.[4]

Reaction of 1 with Styrene at Room Temperature. In a 30-mL two-necked flask fitted with a condenser was placed 0.128 g (0.516 mmol) of **1**, 0.102 g (0.979 mmol) of styrene, and 0.025 g (0.022 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene. The mixture was stirred at room temperture for 10 h, and then analyzed by GLC as being **8** (84% yield). After treatment of the mixture with a short silica gel column, compound **8** was isolated by MPLC: MS *m/z* 352 (M^+); IR 2952, 2872, 1493, 1413, 1233, 1117, 1016, 755, 699 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.70-1.02 (m, 20H, EtSi), 1.25 (dd, 1H, CH, J = 2.6 Hz, 11.5 Hz), 1.59 (dd, 1H, CHPh, J = 11.5 Hz, 15.2 Hz), 2.74 (dd, 1H, CH, J = 2.6Hz, 15.2 Hz), 7.22-7.55 (m, 9H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 2.56, 3.12, 5.04, 5.98, 7.40, 7.60, 7.72, 7.92 (EtSi), 11.62 (CH_2), 26.36 (CH), 124.54, 127.04, 127.92, 127.95, 128.19, 134.01, 134.42, 143.26, 144.18, 146.93 (phenylene and phenyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ -1.46, -1.39. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.90; H, 9.10.

Reaction of 1 with Styrene at 150°C. A mixture of 0.239 g (0.964 mmol) of **1**, 0.151 g (1.45 mmol) of styrene, and 0.051 g (0.044 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **8** (93% yield) and 4% of the starting compound **1**. After treatment of the mixture with a short silica gel column, compound **8** was isolated by MPLC. All spectral data for **8** were identical with those of a compound obtained from the same reaction at room temperature.

Reaction of 1 with 1-Hexene in Refluxing Benzene. A mixture of 0.082 g (0.331 mmol) of **1**, 0.056 g (0.67 mmol) of 1-hexene, and 0.017 g (0.015 mmol) of $Pd(PPh_3)_4$ in 2 mL of benzene was heated to reflux for 14 h. The mixture was analyzed by GLC as being **9a** (94% yield). After treatment of the mixture with a short silica gel column, compound **9a** was isolated by MPLC: MS *m/z* 332 (M^+); IR 2954, 2873, 1458, 1413, 1232, 1118, 1014, 740, 702 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.65-1.65 (m, 32H, EtSi, CH_2Si, CHSi, n-Bu), 7.25-7.51 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 3.38, 3.78, 5.25, 6.20, 7.50, 7.53, 7.82, 8.09 (EtSi), 10.25 (CH_2Si), 14.16, 16.57, 22.66, 30.24, 33.21 (CHSi, n-Bu), 127.62 (2C), 133.69, 133.94, 144.08, 144.60 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ -2.71, -1.57. Anal. Calcd for $C_{20}H_{36}Si_2$: C, 72.21; H, 10.91. Found: C, 72.15; H, 10.80.

Reaction of 1 with 1-Hexene at 150°C. A mixture of 0.169 g (0.68 mmol) of **1**, 0.085 g (1.00 mmol) of 1-hexene, and 0.035 g (0.030 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **9a** (39% yield) and **10a** (41% yield). After treatment of the mixture with a short silica gel column, compounds **9a** and **10a** were isolated by MPLC. All spectral data for **9a** were identical with those of a compound obtained from the same reaction at 80°C. For **10a**: MS *m*/*z* 332 (M^+); IR 2955, 2893, 2146 (SiH), 1458, 1418, 1232, 1117, 1016, 814, 744, 708 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.67-1.02 (m, 23H, EtSi, CH_3), 1.31 (sext, 2H, CH_2), 1.83-1.99 (m, 4H, CH_2), 4.56 (quint, 1H, SiH, J = 3.3 Hz), 5.24-5.42 (m, 2H, CH=CH, J = 15.4 Hz[14]), 7.27-7.56 (m, 4H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 4.64, 5.09, 7.51, 8.36 (EtSi), 13.61 (CH_3), 19.10, 23.02, 34.95 (CH_2), 127.58, 127.78, 134.86, 135.47, 142.75, 143.94 (phenylene ring carbons), 125.97, 129.49 (olefinic carbons); ^{29}Si NMR δ($CDCl_3$) -9.69, 0.46. Anal. Calcd for $C_{20}H_{36}Si_2$: C, 72.21; H, 10.91. Found: C, 72.03; H, 10.96.

Reaction of 1 with 1,1-Dideuterio-1-hexene at 150°C. A mixture of 0.255 g (1.03 mmol) of **1**, 0.197 g (2.29 mmol) of 1,1-dideuterio-1-hexene, and 0.060 g (0.052 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150°C for 24 h. The mixture was analyzed by GLC as **9b** (43% yield) and **10b** (35% yield). After treatment of the mixture with a short silica gel column, compound **9b** and **10b** were isolated by MPLC. For **9b**: MS *m*/*z* 334 (M^+); ^1H NMR δ($CDCl_3$) 0.67-1.64 (m, 30H, EtSi, CHSi, n-Bu), 7.26-7.51 (m, 4H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 3.43, 3.83, 5.30, 6.22, 7.51, 7.53, 7.82, 8.09 (EtSi), 9.51 (CD_2Si, J = 16Hz), 14.14, 16.43, 22.70, 30.30, 33.21 (CHSi, n-Bu), 127.66 (2C), 133.71, 134.94, 144.08, 144.56 (phenylene ring carbons); ^2H NMR δ($CDCl_3$) 0.80, 1.28. For **10b**: MS *m*/*z* 334 (M^+); ^1H NMR δ($CDCl_3$) 0.69-1.02 (m, 23H, EtSi, CH_3), 1.31 (sext, 2H, CH_2), 1.87-1.99 (m, 2H, CH_2), 4.55 (quint, 1H, SiH, J = 3.3 Hz), 5.24-5.40 (m, 2H, CH=CH), 7.26-7.54 (m, 4H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 4.64, 5.07, 7.50, 8.34 (EtSi), 13.61 (CH_3), 18.40 (CD_2Si, J = 21Hz), 23.02, 34.95 (CH_2), 127.58, 127.78, 134.84, 135.47, 142.75, 143.94 (phenylene ring carbons), 125.89, 129.47 (olefinic carbons); ^2H NMR δ($CDCl_3$) 1.84.

Reaction of 1 with 2-Hexene. A mixture of 0.134 g (0.539 mmol) of **1**, 0.096 g (1.14 mmol) of 2-hexene, and 0.068 g (0.059 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150°C for 24 h. The mixture was analyzed by GLC as being **3** (72% yield). Product **3** was isolated by MPLC. All spectral data were identical with those of an authentic sample.

Reaction of 1 with Triethylsilane. A mixture of 0.046 g (0.186 mmol) of **1**, 0.106 g (0.914 mmol) of triethylsilane, and 0.012 g (0.010 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a degassed sealed tube at 150°C for 24 h. The mixture was analyzed by GLC as being **13a** (31% yield) and **3** (41% yield), along with 11% of unreacted starting compound **1**. Products **3** and **13a** were isolated by MPLC. For **13a**: MS *m*/*z* 335 (M^+-Et); IR 2955, 2873, 2148 (Si-H), 1456, 1003, 799, 690 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.76-1.27 (m, 35H, Et_2Si, Et_3Si), 4.77 (quint, 1H, HSi, J = 3.3 Hz), 7.24-7.27 (m, 2H, phenylene ring protons), 7.47-7.50 (m, 1H, phenylene ring proton), 7.65-7.68 (m, 1H, phenylene ring proton); ^{13}C NMR δ($CDCl_3$) 4.05, 4.60, 5.57, 8.16, 8.25, 8.36 (Et_2Si, Et_3Si), 126.90, 127.91, 134.93, 135.54, 142.91, 145.27 (phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) -12.71, -9.87, -9.48. Anal. Calcd for $C_{20}H_{40}Si_3$: C, 65.85; H, 11.05. Found: C, 65.92; H, 10.84. All spectrum data for **3** were identical with those of an authentic sample.

Reaction of 1 with Dimethylphenylsilane. A mixture of 0.250 g (1.01 mmol) of **1**, 0.533 g (3.92 mmol) of dimethylphenylsilane, and 0.052 g (0.045 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a degassed sealed tube at 150°C for 24 h. GLC analysis showed the presence of **13b** in 52% yield, in addition to 24% of **1**. Product **13b** was isolated by MPLC: MS *m*/*z* 355 (M^+-Et); IR 2953, 2872, 2142 (Si-H), 1459, 1426, 1242, 1009, 808, 698 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.37 (s, 6H, MeSi), 0.70-1.03 (m, 20H, EtSi), 4.43 (quint, 1H, HSi, J = 3.1 Hz), 7.23-7.50 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR δ($CDCl_3$) -1.97 (MeSi), 4.41, 5.21, 8.16, 8.29 (EtSi), 127.13, 127.51, 127.91, 128.10, 133.94, 135.00, 135.76, 140.12, 143.18, 144.00 (phenyl and phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) -21.56, -12.94, -9.80. Anal. Calcd for $C_{22}H_{36}Si_3$: C, 68.67; H, 9.43. Found: C, 68.68; H, 9.46.

Reaction of 1 with Ethylene. In a 30-mL two-necked flask fitted with a condenser and inlet tube for ethylene gas was placed 0.200 g (0.805 mmol) of **1** and 0.047 g (0.041 mmol) of Pd$(PPh_3)_4$ in 5 mL of dry benzene. To this was introduced ethylene gas at room temperature for 4 h. The mixture was analyzed by GLC as being **11** (28% yield) and **12** (40% yield). After treatment of the mixture with a short silica gel column, compounds **11** and **12** were isolated by MPLC. All spectrum data for **11** were identical with those of an authentic sample.[4] For **12**: mp 103-107°C; MS *m/z* 495 (M^+-Et); IR 2953, 2873, 1458, 1413, 1261, 1128, 1055, 1004, 694 cm^{-1}; ^{1}H NMR δ($CDCl_3$) 0.55-1.03 (m, 44H, EtSi, CH_2), 7.22-7.73 (m, 8H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 4.93, 5.16, 6.35, 7.84, 8.16 (EtSi, CH_2), 127.01, 127.17, 136.59, 136.75, 143.70, 144.03 (phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) -12.17, 4.30. Anal. Calcd for $C_{30}H_{52}Si_4$: C, 68.62; H, 9.98. Found: C, 68.45; H, 9.95.

Stoichiometric Reaction of 1 with tetrakis(triphenylphosphine)palladium(0). In a 30-mL two-necked flask fitted with a condenser was placed 0.023 g (0.093 mmol) of **1** and 0.105 g (0.091 mmol) of Pd$(PPh_3)_4$ in 1 mL of benzene-d_6. The mixture was stirred at room temperature for 0.5 h to give **2a**: ^{1}H NMR δ($CDCl_3$) 0.76-0.81 (m, 2H, CH_2Si), 1.04-1.14 (m, 2H, CH_2Si), 1.27 (t, 6H, CH_3, J = 7.7Hz), 7.00-7.80 (m, 64H, phenylene and phenyl ring protons); ^{13}C NMR δ($CDCl_3$) 11.31, 12.88 (EtSi), 127.60, 131.86, 157.07 (phenylene ring carbons) 128.41 ($^3J_{c\text{-}p}$ = 7.7 Hz), 129.10, 134.44 ($^2J_{c\text{-}p}$ = 16.8 Hz), 137.28 ($^1J_{c\text{-}p}$ = 5.8 Hz) (phenyl ring carbons); ^{29}Si NMR δ($CDCl_3$) 44.28; ^{31}P NMR δ($CDCl_3$) 1.17.

Reaction of 2a with Phenylacetylene. In a 30-mL two-necked flask fitted with a condenser was placed a benzene solution of **2a** prepared from 0.020 g (0.081 mmol) of **1** and 0.093 g (0.081 mmol) of Pd$(PPh_3)_4$ in 3 mL of benzene. To this was added 0.051 g (0.499 mmol) of phenylacetylene, and the mixture was stirred at room temperature for 1 h. The resulting mixture was analyzed by GLC as being **6** (86% yield). Compound **6** was isolated by column chromatography. All spectral data for **6** were identical with those of an authentic sample.[4]

Reaction of 2a with Styrene. In a 30-mL two-necked flask fitted with a condenser was placed a benzene solution of **2a** prepared from 0.048 g (0.193 mmol) of **1** and 0.223 g (0.193 mmol) of Pd$(PPh_3)_4$ in 3 mL of benzene. To this was added 0.081 g (0.778 mmol) of styrene, and the mixture was heated to reflux for 1 h. The resulting mixture was analyzed by GLC as being **8** (86% yield). Compound **8** was isolated by column chromatography. All spectral data for **8** were identical with those of a compound obtained from the catalytic reaction described above.

Reaction of 2a with Ethylene. In a 30-mL two-necked flask fitted with a condenser and inlet tube for ethylene gas was placed a benzene solution of **2a** prepared from 0.083 g (0.334 mmol) of **1** and 0.410 g (0.355 mmol) of Pd$(PPh_3)_4$ in 5 mL of dry benzene. To this was introduced ethylene gas at 80°C for 5 h. The resulting mixture was analyzed by GLC as being **11** (45% yield) and **12** (44% yield). All spectral data for **11** and **12** were identical with those of compounds obtained from the catalytic reaction of **1** with ethylene.

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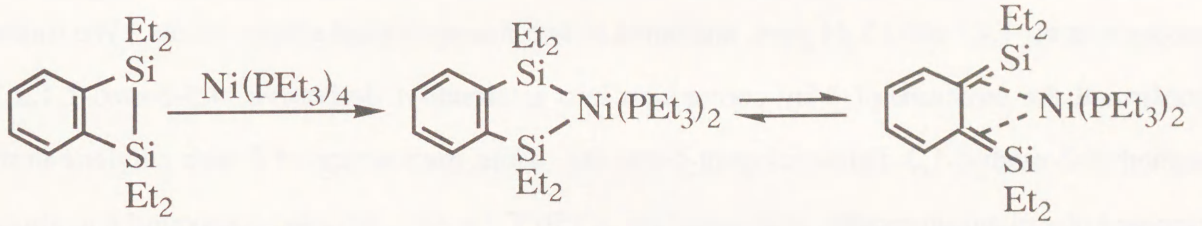
14. Since olefinic protons for **10** showed multiplet resonances, measurement of its coupling constant was carried out by proton decoupling technique. Decoupling of olefinic protons with hydrogens on C_1 and C_3 in a 2-hexenyl group resulted in two doublets with J = 15.4 Hz for the olefinic protons.

Chapter 7

Platinum-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene

Introduction

In the nickel-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) with aromatic compounds, carbonyl compounds, alkenes, we proposed the formation of an *o*-quinodisilane-nickel complex as a reactive intermediate.[1-3]



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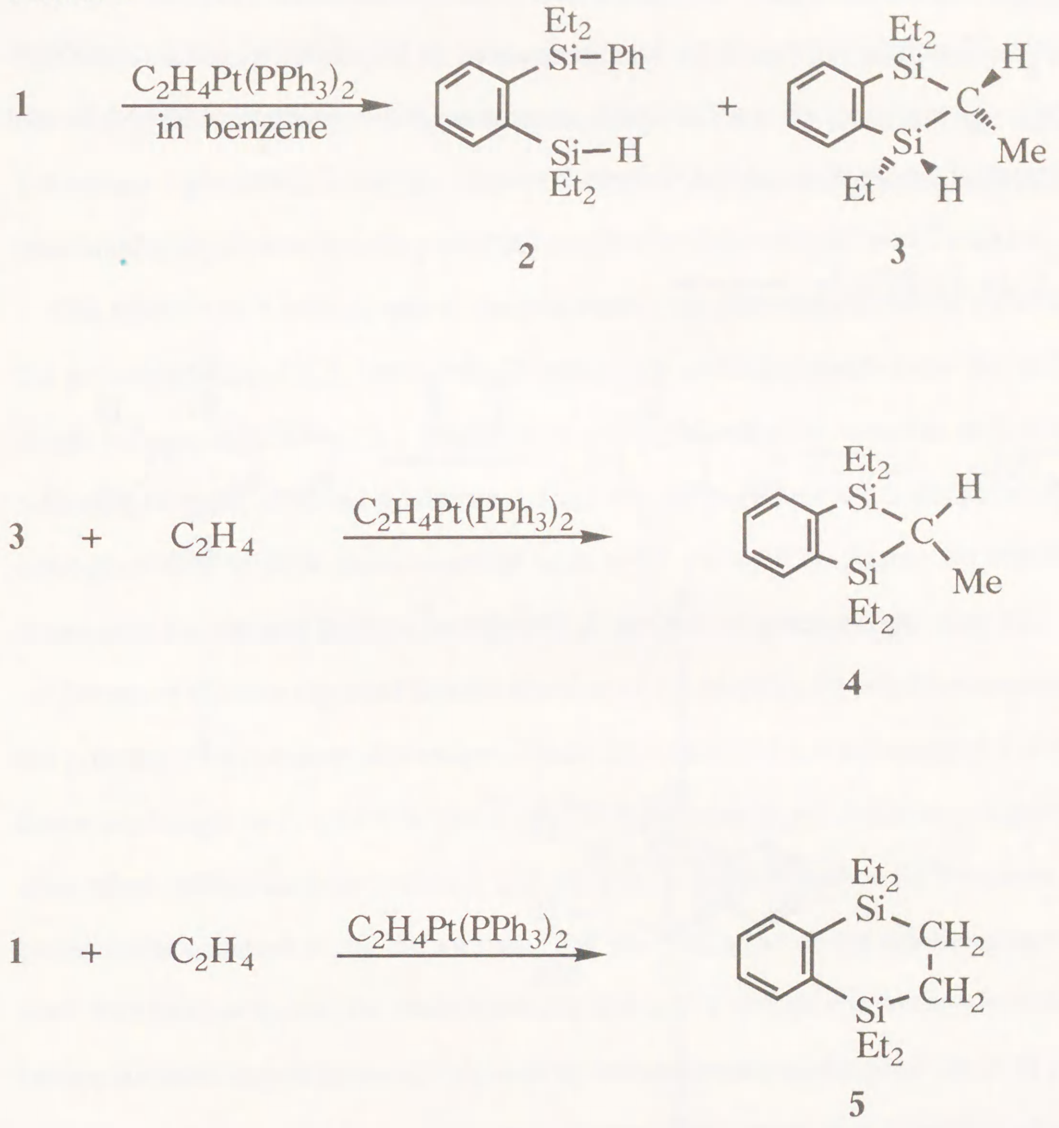
In order to clarify the similarity and dissimilarity between nickel catalyst and other transition metal catalysts in the reaction of **1** and to get more information about the reactive intermediates which are involved in these system, we investigated the reaction of **1** with benzene, olefins, acetylenes, and carbonyl compounds in the presence of (η^2-ethylene)bis(triphenylphosphine)-platinum.

Results and Discussion

First, we treated 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) with a catalytic amount of a platinum complex in benzene to confirm whether or not C-H bond activation of benzene occurs as observed in the nickel-catalyzed reaction.[1,2] When compound **1** was heated to reflux in the presence of 5 mol% of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in benzene for 56 h, 1-diethylphenylsilyl-2-(diethylsilyl)benzene (**2**) arising from C-H bond activation of benzene was obtained in 10% yield.[4] To our surprise, an isomerization product, cis-4,5-benzo-1,1,3-triethyl-2-methyl-1,3-disilacyclopent-4-ene (**3**) was obtained in 67% yield, as a single isomer, along with 6% of the unchanged starting compound **1** (Scheme I). No other isomers were detected in the reaction mixture either by spectrometric analysis or GLC analysis.

IR and ^{1}H, ^{13}C, and ^{29}Si NMR spectra obtained for compound **2** were identical with those of an authentic sample reported previously.[1] The structure of **3** was verified by spectrometric analysis, as well as by chemical reaction. The ^{13}C NMR spectrum of product **3** shows resonances at δ -2.28, 4.14, 4.52, 5.74, 7.72, 7.86, 8.58, and 8.74 ppm, due to three nonequivalent ethyl carbons and MeC(H) carbons. Its ^{29}Si NMR spectrum reveals two resonances at -1.07 and 15.44 ppm, attributed to two nonequivalent silicon atoms. We further confirmed the structure of **3** by conversion into a tetraethyl derivative, 4,5-benzo-1,1,3,3-tetraethyl-2-methyl-1,3-disilacyclopent-4-ene (**4**). Thus, the reaction of **3** with ethylene in the presence of a platinum catalyst in an autoclave at 150°C for 24 h, afforded compound **4** in almost quantitative yield. As expected, the ^{13}C NMR spectrum of **4** reveals four resonances at 4.32, 4.66, 5.54, and 7.55 ppm attributed to two non-equivalent Et carbons, and two resonances at -1.83 and 8.65 ppm due to MeC carbons, as well as three phenylene carbons at 128.19, 132.85, and 148.72 ppm. Its ^{29}Si NMR spectrum exhibits a single resonance at 13.60 ppm, in accord with down field shift for 4,5-benzo-1,3-disilacyclopent-4-ene derivatives. In fact, ^{29}Si chemical shifts of diethyl-substituted silicon atoms in the 2-alkyl-4,5-benzo-1,3-disilacyclopent-4-ene rings appear in the region of 12-16 ppm, but those of the diethylsilyl groups in 5,6-benzo-1,4-disilacyclohex-5-enes and 1,4-disilacyclohex-2,5-dienes appear in the region of -3--18 ppm, higher than the chemical shift of tetramethylsilane. Furthermore, the platinum-catalyzed reaction of **1** with ethylene in benzene at 100 °C in an autoclave gave an isomer of **4**, 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-2-ene (**5**) and compound **2** arising from C-H bond activation of benzene in 62% and 5% yields, respectively, in addition to a 11% yield of an unidentified

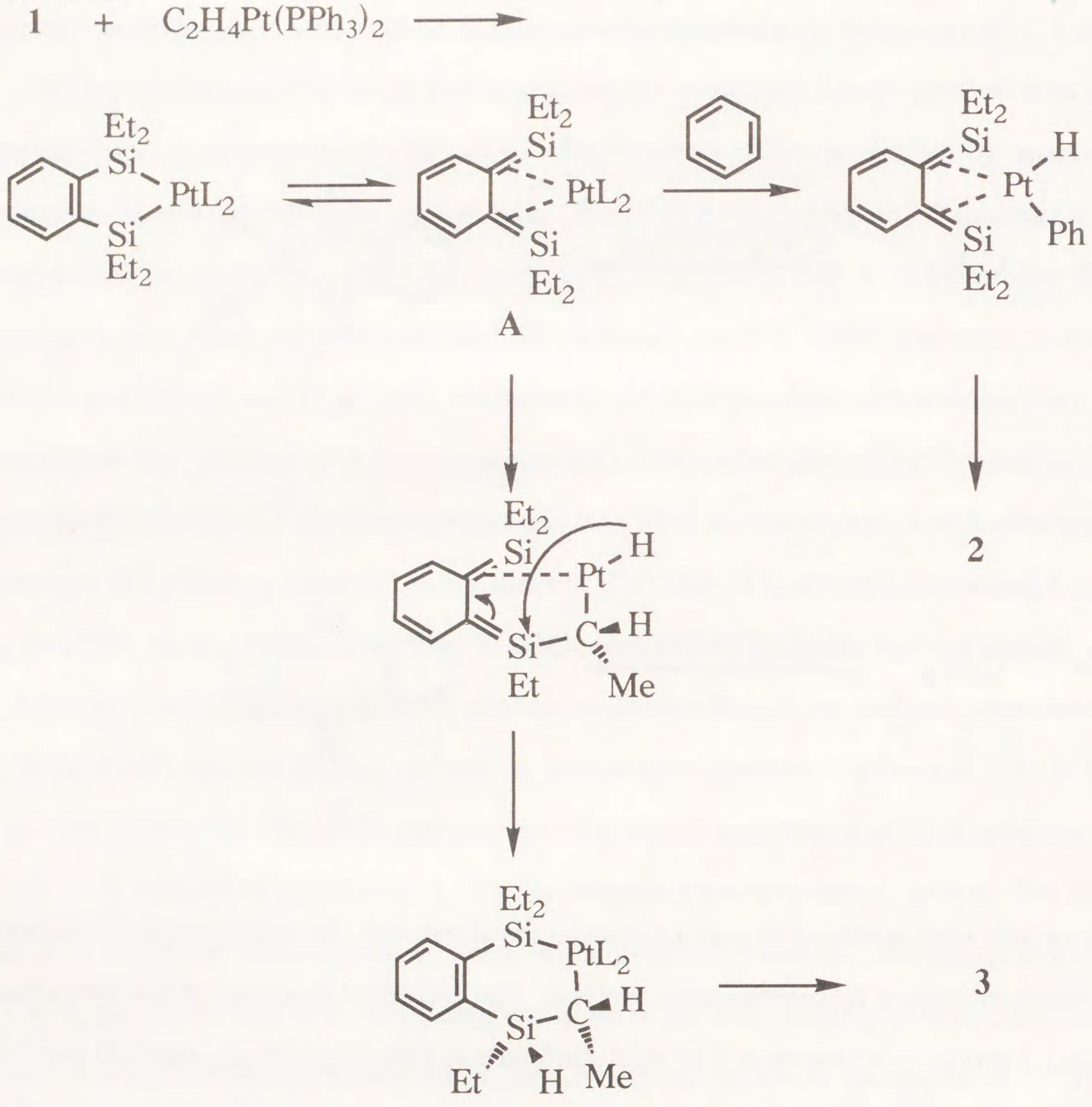
Scheme I



product whose mass spectrum reveals a molecular ion at m/z 486. No compound **4** was detected in the reaction mixture by spectrometric analysis. The ^{13}C NMR spectrum of **5** shows simple resonance patterns, a resonance at 3.35 ppm, attributed to CH_2CH_2 carbons, and 5.29 and 7.62 ppm, due to Et carbons, as well as three phenylene ring carbons at 127.67, 133.82, and 144.46 ppm. The ^{29}Si NMR spectrum reveals a single resonance at -3.48 ppm, which is consistent with the chemical shift observed for 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-2-ene derivatives. These results clearly indicate that compound **3** must have a 4,5-benzo-2-methyl-

1,3-disilacyclopent-4-ene structure. Unfortunately, NOE-FID difference experiments at 270 MHz did not give any clear-cut results for configuration of **3**. However, we assigned product 3 as a cis-isomer on the basis of the ^{1}H NMR spectrum of the product obtained from its hydrosilylation with α-methylstyrene (see below).

Scheme II

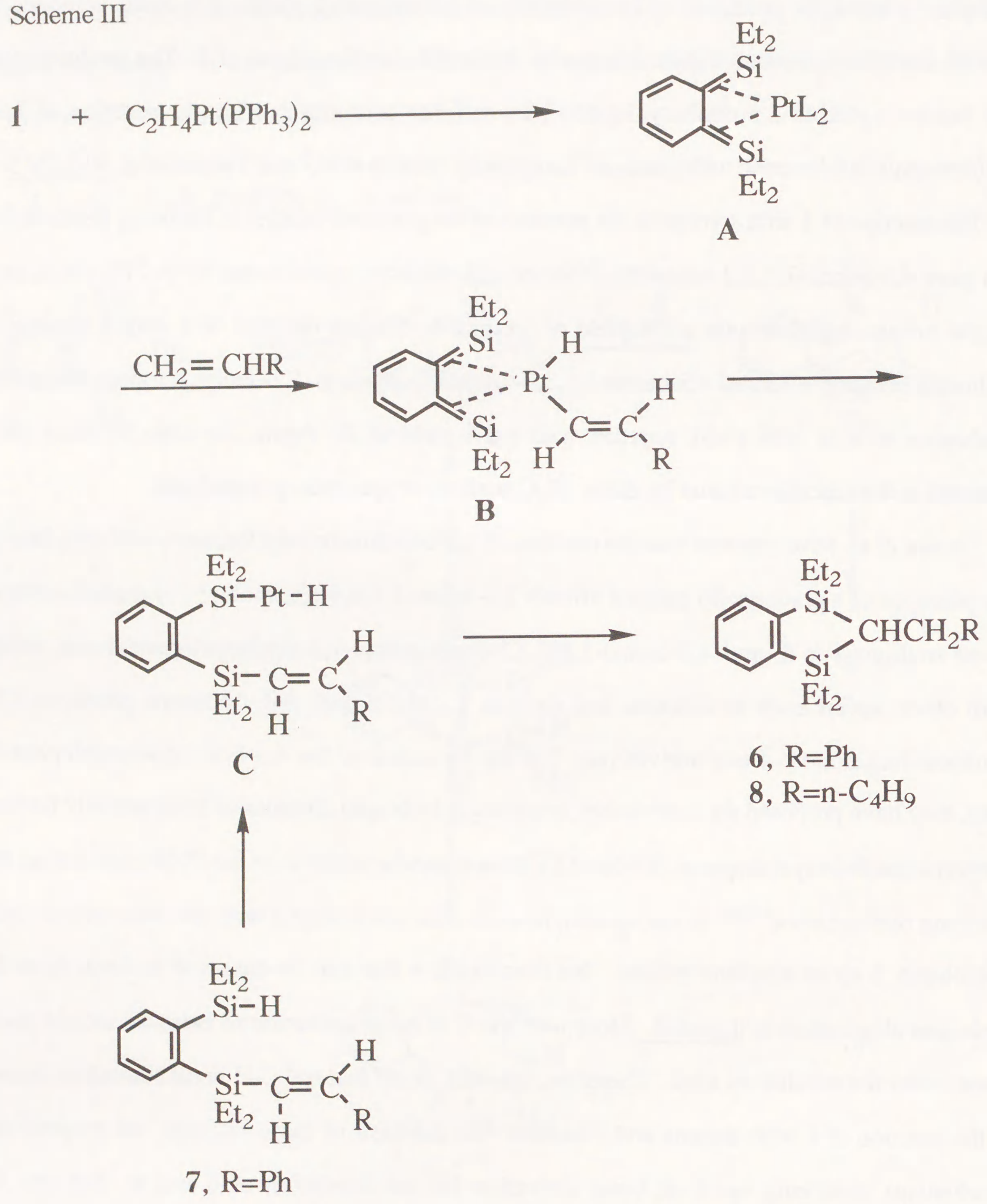


In the nickel-catalyzed reactions of **1** with arenes and carbonyl compounds, we suggested the formation of an *o*-quinodisilane-nickel complex as a reactive intermediate. The formation of **2** and **3** in the present reaction may also be explained in terms of the intermediacy of an *o*-quinodisilane-platinum complex (**A**) as shown in Scheme II. The *o*-quinodisilane-platinum complex **A** would be produced by isomerization of a 3,4-benzo-1-platina-2,5-disilacyclopent-3-ene arising from insertion of platinum species into a silicon-silicon bond of **1**. The production of 3,4-benzo-1-platina-2,5-disilacyclopent-3-ene[4-11] has been observed in the reaction of 1,2-bis(dimethylsilyl)benzene with platinum complex by Eaborn et al.[5] and Tanaka et al.[4,6,7,10,11]

The reaction of **1** with styrene in the presence of the platinum catalyst in refluxing benzene for 3 h gave 4,5-benzo-1,1,3,3-tetraethyl-2-benzyl-1,3-disilacyclopent-4-ene (**6**) in 77% yield, as a single isomer, together with a 8% yield of product **2**. Similar reaction of **1** with 1-hexene in refluxing benzene afforded 4,5-benzo-1,1,3,3-tetraethyl-2-pentyl-1,3-disilacyclopent-4-ene (**8**), analogous to **6** in 86% yield, together with a 2% yield of **2**. Again, no other isomers were detected in the reaction mixture by either GLC analysis or spectroscopic analysis.

Tanaka et al. have reported that the reaction of 1,2-bis(dimethylsilyl)benzene with ethylene in the presence of a platinum(0) catalyst affords 2,3-benzo-1,1,4,4-tetramethyl-1,4-disilacyclohex-2-ene analogous to **5**, and 4,5-benzo-1,1,2,3,3-pentamethyl-1,3-disilacyclopent-4-ene, while with other olefins such as 1-octene and styrene, 1,2-bis(dimethylsilyl)benzene produces 4,5-benzodisilacyclopent-4-ene derivatives. For the formation of the 4,5-benzodisilacyclopent-4-enes, they have proposed the mechanism involving β-hydrogen elimination from initially formed benzoplatinadisilacycloheptene, followed by intramolecular addition of the Pt-H bond across the resulting olefinic bond.[6,10] In our system, however, the reaction of **1** with ethylene affords only compound **5** as an ethylene adduct. No compound **4** that can be expected to form from β-hydrogen elimination is detected. Moreover, the C-H bond activation of benzene indeed takes place under the conditions used. Therefore, it seems likely that sp^2 C-H bond activation occurs in the reaction of **1** with styrene and 1-hexene. On the basis of these findings, we propose the mechanism involving sp^2 C-H bond activation for the formation of **6** and **8**. Scheme III illustrates a possible machanistic interpretation of the observed reaction course. The reaction of *o*-quinodisilane-platinum complex **A** with styrene produces platinum-hydride complex (**B**), and then complex **B** is transformed into complex (**C**). Intramolecular hydrosilylation gives product

Scheme III

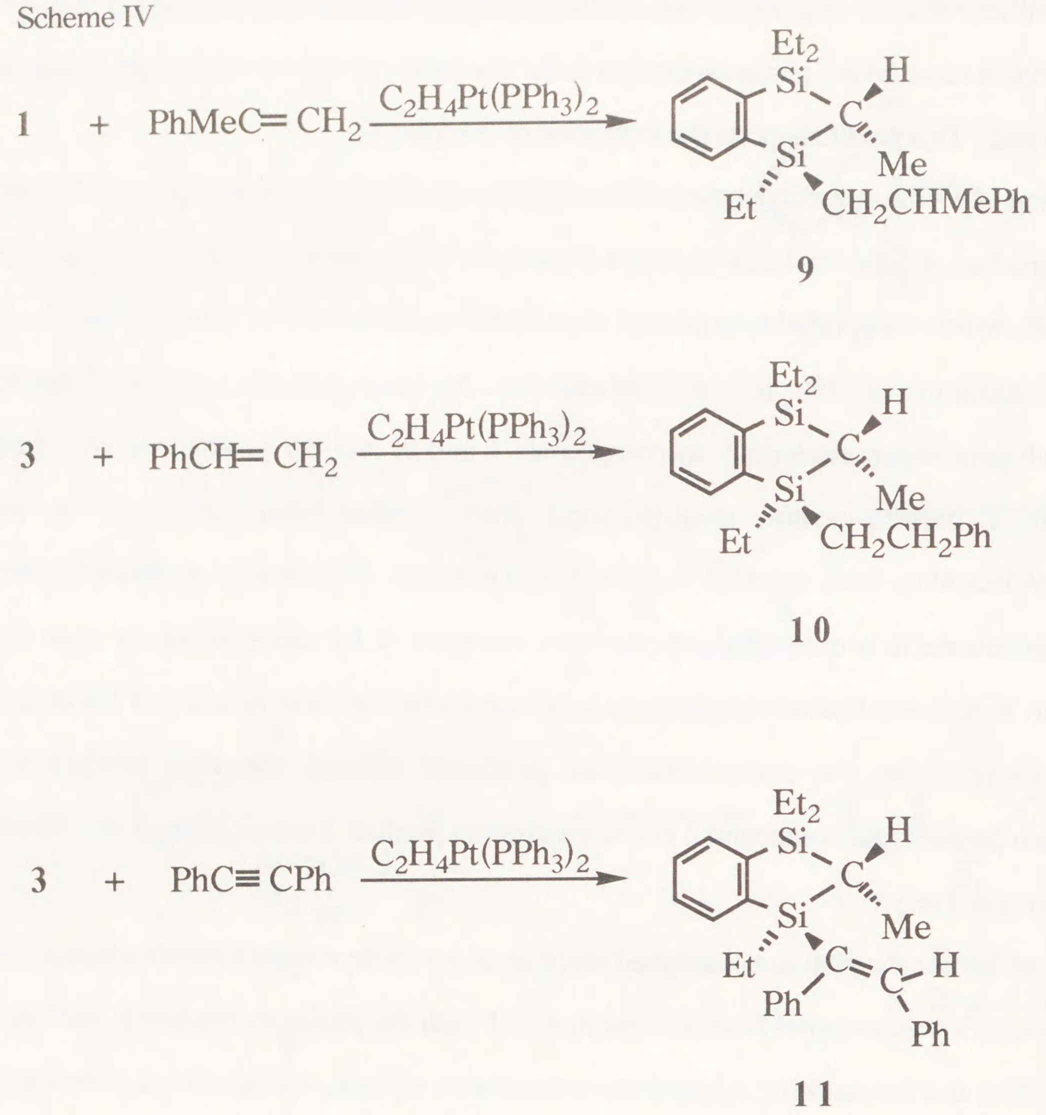


6 and **8**. Treatment of trans-1-diethyl(2-phenylethenyl)silyl-2-(diethylsilyl)benzene (**7**) prepared by an independent route with a platinum catalyst under the same conditions produced **6** in almost quantitative yield. This result supports the formation of complex **C**.

The reaction of **1** with α-methylstyrene under the same conditions, however, gave a different type of the product, 4,5-benzo-1,3,3-triethyl-t-2-methyl-r-1-(2-phenylpropyl)-1,3-disilacyclopent-4-ene (**9**), which was probably produced from hydrosilylation of **3** to α-methylstyrene, in 67% yield, in addition to a 11% yield of **2** (Scheme IV). No other products, such as 4,5-benzo-1,3-disilacyclopent-4-ene analogous to compounds **6** and **8**, and the product derived from insertion of a carbon-carbon double bond into a silicon-silicon bond in the benzodisilacyclobutene, were detected in the reaction mixture. Presumably, α-methylstyrene would not coordinate to *o*-quinodisilane-platinum complex **A** for steric reason or even if it coordinates to **A**, the coordinated complex would be nonproductive. The reaction of **1** with 1,1-diphenylethylene under the same conditions produced neither insertion product nor hydrosilylation product, but compound **2** and isomerization product **3** were obtained in 11% and 63% yields, respectively.

We also carried out the platinum-catalyzed reaction of **3** with styrene and diphenylacetylene. When compound **3** was prepared from the reaction of **1** with the platinum catalyst in refluxing benzene for 57 h, and the resulting mixture was treated with styrene, 4,5-benzo-1,3,3-triethyl-t-2-methyl-r-1-(2-phenylethyl)-1,3-disilacyclopent-4-ene (**10**) was obtained in almost quantitative yield.[12] The structure of **10** was confirmed by the ^{13}C DEPT (Distortionless enhancement by polarization transfer) spectrum. Its ^{13}C DEPT spectrum shows two negative signals at 15.80 and 30.50 ppm attributed to two nonequivalent methylene carbons, as well as three negative signals due to methylene carbons of three nonequivalent ethyl groups. This result is wholly consistent with the structure proposed for **10**. Similar treatment of **3** with diphenylacetylene yielded 4,5-benzo-1,3,3-triethyl-t-2-methyl-r-1-(1,2-diphenylethenyl)-1,3-disilacyclopent-4-ene (**11**) (Scheme IV). The structures of **10** and **11** were confirmed by spectrometric analysis, as well as by elemental analysis.

Scheme IV



9

10

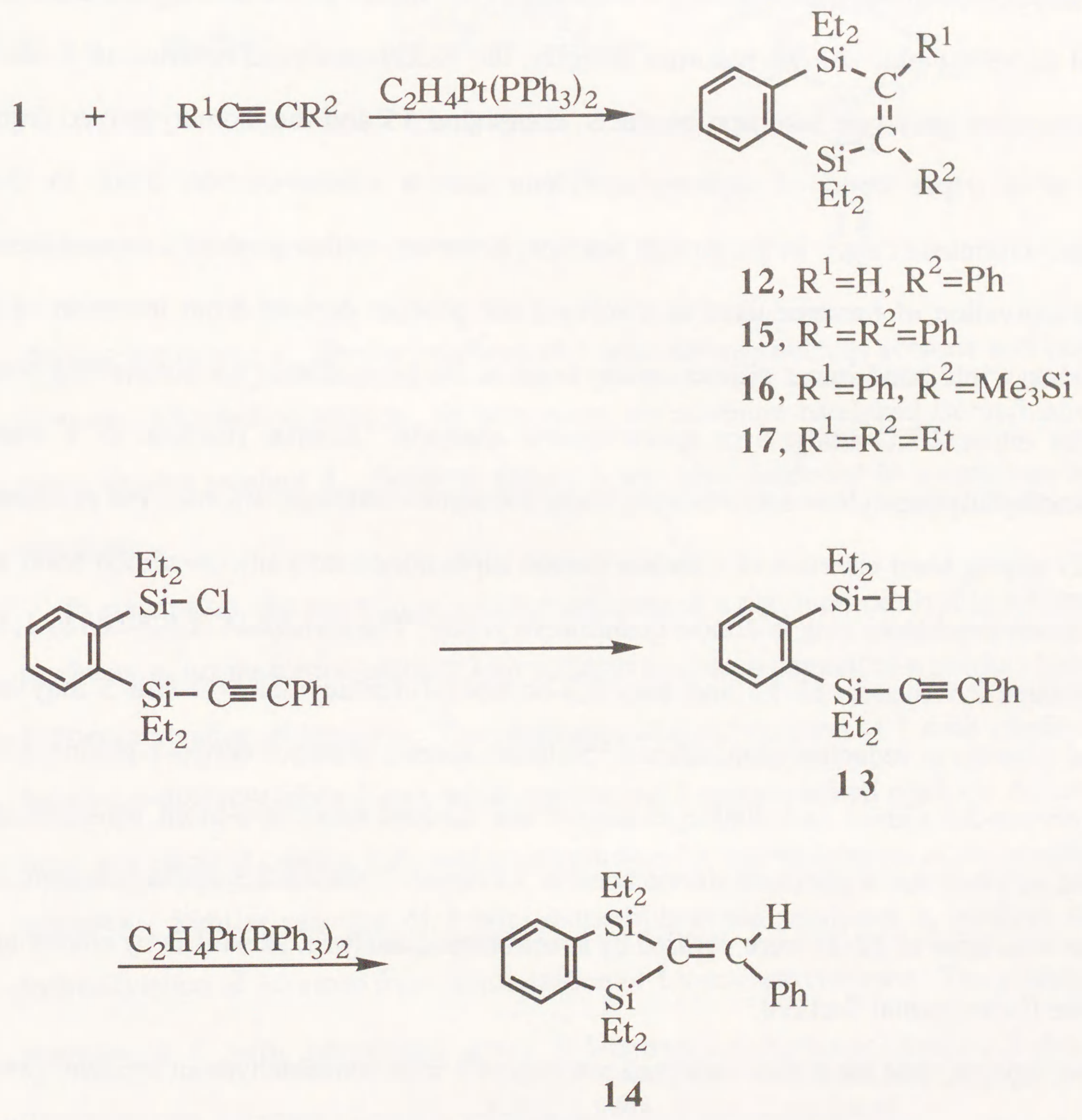
11

That substituents introduced on the Si-1 atom in the 1,3-disilacyclopentene ring for compounds **9-11** must be located in a cis fashion toward hydrogen on the C-2 position was verified by the fact that the resonance attributed to this reference hydrogen of product **9** appears at extremely high field. Examination of molecular models clealy indicates that this high field shift of the proton may be due to the ring current of a 2-phenylpropyl group on the silicon atom, which is located at the cis-position to this proton. In fact, saturation of the resonance of this proton on the C-2 position of the 1,3-disilacyclopentene ring in an NOE-FID difference experiment at 270 MHz produced a positive nuclear overhauser effect of phenyl protons, as well

as methyl protons on the C-2 position. On the basis of this result, configuration of product **3** must be a cis form and therefore, hydrosilylation products derived from **3** must be trans.

In contrast to the platinum-catalyzed isomerization of **1**, in which prolonged heating is necessary for completion of the reaction, the reaction of **1** with phenylacetylene in benzene proceeds readily to give an insertion product. Thus, treatment of **1** with phenylacetylene in the presence of the platinum catalyst in refluxing benzene for 5 min afforded 5,6-benzo-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (**12**) arising from insertion of a triple bond

Scheme V



12, R^1=H, R^2=Ph
15, R^1=R^2=Ph
16, R^1=Ph, R^2=Me_3Si
17, R^1=R^2=Et

13

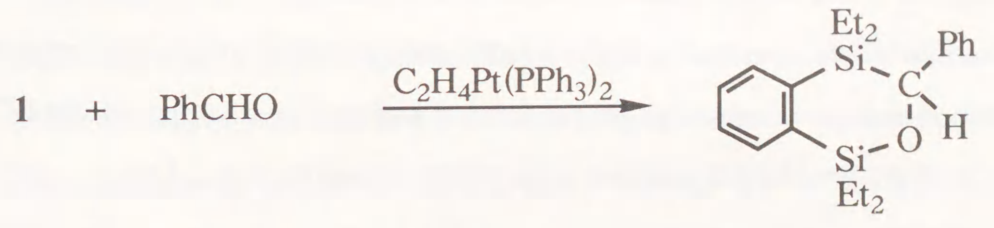
14

into a silicon-silicon bond in 98% yield. Interestingly, when 1-diethyl(phenylethynyl)silyl-2-(diethylsilyl)benzene (**13**) prepared from the reaction of 1,2-bis(chlorodiethylsilyl)benzene with phenylethynyl lithium, followed by reduction of the resulting 1-chlorodiethylsilyl-2-phenylethynylsilyl derivative was treated with a platinum catalyst under the same conditions yielded 4,5-benzo-1,1,3,3-tetraethyl-2-phenylmethylene-1,4-disilacyclopent-4-ene (**14**) in 99% yield (Scheme V). No compound **12** was detected in the reaction mixture. The result indicates that the reaction of **1** with phenylacetylene involves no C-H bond activation.

The platinum-catalyzed reaction of **1** with diphenylacetylene again gave a benzodisilacyclohexadiene, 5,6-benzo-1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**15**) in 98% yield. As we reported recently, the nickel-catalyzed reaction of **1** with diphenylacetylene gave two insertion products, compound **15** and the isomer derived from insertion of a triple bond of diphenylacetylene into a silicon-carbon bond in the benzodisilacyclobutene ring.[2] In the present reaction, however, neither product **2** formed from C-H bond activation of benzene used as a solvent nor product derived from insertion of a carbon-carbon triple bond into a silicon-carbon bond in the benzodisilacyclobutene ring was detected by either GLC analysis or spectrometric analysis. Similar reaction of **1** with phenyl(trimethylsilyl)acetylene and 3-hexyne under the same conditions afforded the products (**16** and **17**) arising from insertion of a carbon-carbon triple bond into a silicon-silicon bond in the benzodisilacyclobutene ring in almost quantitative yields. The formation of 5,6-benzo-1,4-disilacyclohexa-2,5-dienes **12**-**17** and also 2,3-benzo-1,4-disilacyclohex-2-ene **5** may be understood in terms of reductive elimination of platinum species from 5,6-benzo-1-platina-4,7-disilacyclohepta-2,5-dienes and disilacyclohept-5-ene derived from two-atom insertion of alkynes and ethylene into a platinum-silicon bond in 3,4-benzo-1-platina-2,5-disilacyclopent-3-ene.[11] The structures of **12**-**17** were verified by spectrometric analysis, as well as by elemental analysis (see Experimental Section).

We have reported that the nickel-catalyzed reaction of **1** with benzaldehyde in benzene gave 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene as the sole product, while

with acetone, **1** afforded 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene, 1-[diethyl(isopropenyloxy)silyl]-2-(diethylsilyl)benzene and 5,6-benzo-1,1,4,4-tetraethyl-3,3-dimethyl-2-oxa-1,4-disilacyclohex-5-ene.[3] Similar nickel-catalyzed reaction of **1** with benzophenone produced 4,5-benzo-1,1,3,3-tetraethyl-2,2-diphenyl-1,3-disilacyclopent-4-ene. The platinum-catalyzed reaction with benzaldehyde led to the same result as that of the nickel-catalyzed reaction. 5,6-Benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene (**18**) was obtained in 73% yield, in addition to a 3% yield of compound **2** and 8% of the unreacted starting compound **1**. Similar reactions of **1** with ketones such as acetone and benzophenone, however, afforded no adducts. In both cases, the platinum-catalyzed isomerization of **1** took place to give product **3**. Benzene adduct **2** was also produced in a small amount in these reactions.



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In conclusion, the reaction of **1** in the presence of a platinum catalyst in refluxing benzene produces an isomerization product **3**, in addition to a small amount of a product formed from C-H bond activation of benzene. The platinum-catalyzed reaction of **1** with ethylene gives 2,3-benzo-1,4-disilacyclohex-2-ene, while styrene and 1-hexene afford products derived from C-H bond activation of olefins, followed by intramolecular hydrosilylation of the resulting platinum complex. Similar reaction of **1** with α-methylstyrene produces a product arising from hydrosilylation of **3** formed from isomerization of **1** to α-methylstyrene. The platinum-catalyzed reaction of **1** with acetylenes gives 5,6-benzo-1,4-disilacyclohexa-2,5-dienes. With benzaldehyde, 5,6-benzo-2-oxa-1,4-disilacyclohex-5-ene is produced.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry argon. Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard. NMR spectra were recorded on a JEOL Model EX-270 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Low-resolution mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. High-resolution mass spectra were measured on a Hitachi M-80B mass spectrometer. Gas chromatographic separations were carried out using a column (3 m x 10 mm) packed with 30% SE-30 silicone on Chromosorb P. Gel-permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.). (η^2-Ethylene)bis(triphenylphosphine)platinum(0) was prepared by the method reported in the literature.[14]

Materials. 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene **1** was prepared as reported in the literature.[15] Benzene used as a solvent was dried over lithium aluminum hydride and distilled before use.

Reaction of 1 in Benzene. In a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.2658 g (1.07 mmol) of **1** and 40 mg (5.37 x 10^{-2} mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in 10 mL of dry benzene. The mixture was heated to reflux for 56 h. GLC analysis of the reaction mixture indicated the presence of **3** (67% yield), **2** (10% yield), and 6% of the unchanged starting compound **1**. Products **2** and **3** were isolated by preparative GLC. For **3**: MS *m/z* 248 (M^+); IR 3096, 3025, 2943, 2097 (Si-H), 1472, 1032, 673 cm^{-1}; ^{1}H NMR $\delta(C_6D_6)$ 0.59-1.16 (m, 20H, EtSi, MeC, HC), 4.84 (q, 1H, HSi, J = 3.6 Hz), 7.18-7.72 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(C_6D_6)$ -2.28, 4.14, 4.52, 5.74, 7.72, 7.86, 8.58, 8.74 (EtSi, MeC, CH), 128.97, 129.06, 133.30, 133.88, 146.72, 148.59 (phenylene ring carbons); ^{29}Si NMR $\delta(C_6D_6)$ -1.07, 15.44. Exact MS Calcd for $C_{14}H_{24}Si_2$: 248.1417. Found: 248.1431.[16] All spectral data for product **2** were identical with those of an authentic sample.

Reaction of 3 with ethylene. In a 30-mL two necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.2420 g (0.974 mmol) of **1** and 36 mg (4.83 x 10^{-2} mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in 10 mL of dry benzene. The mixture was heated to reflux for 57 h. GLC analysis of the resulting mixture showed the presence of **3** in 66% yield, along with a 10% yield of **2**. All contents of the flask were transferred into a 50-mL autoclave under an argon atmosphere, and then ethylene gas (60kg/cm^2) was compressed into the autoclave. The autoclave was heated at 150°C for 24 h. GLC analysis of the reaction mixture indicated that **3** was transformed into **4** in almost quantitative yield. Pure **4** was isolated by preparative HPLC. For **4**: MS *m/z* 276 (M^+); IR 3045, 2953, 2873, 1459, 1414, 1115, 1009, 750, 716 cm^{-1}; ^{1}H NMR $\delta(CDCl_3)$ 0.42 (q, 1H, HC, J = 7.6 Hz), 0.63-1.03 (m, 20H, EtSi), 1.21 (d, 3H, MeC, J = 7.6 Hz), 7.31-7.34 (m, 2H, phenylene ring protons), 7.51-7.55 (m, 2H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ -1.83 (CH), 4.32, 4.66, 5.54, 7.55 (EtSi), 8.65 (MeC), 128.19, 132.85, 148.72 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ 13.60. Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.26; H, 10.28.

Reaction of 1 with ethylene. In a 50-mL autoclave was placed 0.2331 g (0.94 mmol) of **1**, 35 mg (4.70 x 10^{-2} mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in 10 mL of dry benzene, and then ethylene gas (60kg/cm^2) was compressed into autoclave. The autoclave was heated at 100°C for 24 h. GLC analysis of the resulting mixture showed the presence of **2** (5% yield) and **5** (62% yield), in addition to a 11% yield of an unidentified product. Products **2** and **5** were isolated by MPLC. For **5**: MS *m/z* 276 (M^+); IR 3037, 2943, 2861, 1461, 1408, 1114, 1008, 714 cm^{-1}; ^{1}H NMR $\delta(CDCl_3)$ 0.71-1.03 (m, 24H, EtSi, CH_2Si), 7.29-7.35 (m, 2H, phenylene ring protons), 7.46-7.56 (m, 2H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 3.35 (CH_2Si), 5.29, 7.62 (EtSi), 127.67, 133.82, 144.46 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ -3.48. Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.42; H, 10.20.

Reaction of 1 with styrene. A solution of 0.2145 g (0.863 mmol) of **1**, 0.1349 g (1.30 mmol) of styrene, and 33 mg (4.36 x 10^{-2} mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 3 h. The mixture was analyzed by GLC as being **6** (77% yield) and **2** (10% yield). Product **6** was isolated by MPLC: MS *m/z* 323 (M^+-Et); IR 3026, 2956, 2862, 1455, 1232, 1109, 1009, 744 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.52-0.98 (m, 21H, EtSi, HC), 2.92 (d, 2H, H_2C), 7.16-7.52 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 5.20, 5.41, 7.35, 7.71 (EtSi) 8.63 (CH), 30.91 (CH_2), 125.71, 128.09, 128.19, 128.23, 132.83, 144.94, 148.21 (phenyl and phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) 12.80. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.83; H, 9.21.

***trans*-1-Diethyl(2-phenylethenyl)silyl-2-(diethylsilyl)benzene (7).** In a 30-mL two-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed a solution of 0.1020 g (0.291 mmol) of 1-diethyl(phenylethynyl)silyl-2-(diethylsilyl)benzene (**13**) in 5 mL of dry benzene. To this was added 0.20 mL (0.300 mmol) of a diisobutylaluminum hydride-toluene solution at room temperature. The mixture was heated to reflux for 18 h. GLC analysis of the resulting mixture showed the presence of **7** in 9% yield. Product **7** was isolated by preparative HPLC. For **7**: MS *m/z* 352 (M^+); IR 3046, 2954, 2873, 2146 (Si-H), 1560, 1458, 1260, 695 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.70-1.25 (m, 20H, EtSi), 4.53 (quint, 1H, HSi, J = 3.3 Hz), 6.64 (d, 1H, HC=C, J = 19 Hz), 6.87 (d, 1H, HC=C, J = 19 Hz), 7.17-7.64 (m, 9H, phenyl and phenylene ring protones); ^{13}C NMR δ($CDCl_3$) 4.50, 5.54, 7.66, 8.34 (EtSi), 126.36, 126.88, 127.76, 127.85, 127.91, 128.48, 128.59, 134.93, 135.76, 138.54 (phenyl and phenylene ring carbons), 132.42, 145.30 (olefinic carbons); Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.88; H, 9.04.

1-Diethyl(phenylethynyl)silyl-2-(diethylsilyl)benzene (13). In a 50-mL two-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed a solution of 0.6111 g (2.19 mmol) of 1,2-bis(chlorodiethylsilyl)benzene in 5 mL of dry hexane. To this solution was added dropwise phenylethynyllithium prepared from phenylacetylene (2.54 mmol) and an n-butyllithium-hexane solution (2.56 mmol) in 5 mL of hexane. The mixture was heated to reflux for 10 h. To this was added 3.50 mL (5.25 mmol) of a diisobutylaluminum hydride-toluene solution at room temperature. After the mixture was stirred for 18 h at room temperature, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined and dried over calcium chloride. GLC analysis of the resulting mixture showed the presence of **13** in 49% yield. Pure **13** was isolated by MPLC: MS *m/z* 350 (M^+); IR 2955, 2873, 2157 (Si-H), 1488, 1231, 1008, 830, 756, 689 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.83-1.15 (m, 20H, EtSi), 4.70 (quint, 1H, HSi, J = 3.3 Hz), 7.31-7.97 (m, 9H, phenyl and phenylene ring protones); ^{13}C NMR δ($CDCl_3$) 4.50, 7.30, 7.87, 8.32 (EtSi), 92.22, 108.11 (sp carbons), 123.49, 128.05, 128.20, 128.21, 128.45, 131.95, 134.83, 136.17, 141.83, 142.66 (phenyl and phenylene ring carbons); Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.12; H, 8.57.

Platinum-catalyzed reaction of 7. In a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed a solution of 0.0070 g (0.020 mmol) of **7** and 1 mg (1.34 x 10^{-3} mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in 5 mL of dry benzene. The mixture was heated to reflux for 3 h. GLC analysis of the resulting mixture showed the presence of **6** in 99% yield. All spectral data for **6** were identical with an authentic sample.

Reaction of 1 with 1-hexene. A solution of 0.2182 g (0.880 mmol) of **1**, 0.0887 g (1.05 mmol) of 1-hexene, and 33 mg (4.36 x 10^{-2} mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 3 h. The mixture was analyzed by GLC as being **8** (86% yield) and **2** (2% yield). Product **8** was isolated by MPLC: MS *m/z* 332 (M^+); IR 3044, 2953, 2873, 1462, 1116, 1016, 708 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.53 (t, 1H, $HC(Si)_2$, J = 8 Hz), 0.66-1.69 (m, 31H, EtSi, H_2C, H_3C), 7.34-7.41 (m, 2H, phenylene ring protons), 7.56-7.61 (m, 2H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 5.05, 6.04, 7.62, 7.77 (EtSi), 6.40 (CSi_2), 14.14 (CH_3), 22.63, 25.27, 32.13, 34.36 (CH_2), 128.14, 132.74, 148.66 (phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) 13.01. Anal. Calcd for $C_{20}H_{36}Si_2$: C, 72.21; H, 10.91. Found: C, 71.93; H, 11.03.

Reaction of 1 with α-methylstyrene. A mixture of 0.2605 g (1.05 mmol) of **1**, 0.1589 g (1.35 mmol) of α-methylstyrene, and 40 mg (5.37 x 10^{-2} mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 19 h. GLC analysis of the reaction mixture showed the presence of **9** (67% yield), **2** (11% yield), and 2% of the starting compound **1**. Product **9** was isolated by MPLC: MS *m/z* 337 (M^+-Et); IR 3014, 2956, 2876, 1447, 1119, 1009, 698 cm^{-1}; ^1H NMR δ($CDCl_3$) -0.31--0.17 (six signals[17], 1H, $HC(Si)_2$), 0.41-1.25 (m, 20H, EtSi, H_2C, MeC), 1.45 (d, 3H, MeC, J = 6.6 Hz), 2.99 (six signals, 1H, HC(Me)(Ph), J = 6.6 Hz), 7.16-7.55 (m, 9H, phenyl and phenylene ring protones); ^{13}C NMR δ($CDCl_3$) 4.51 ($CH(Si)_2$), 5.61, 5.72, 6.53, 7.05, 7.77, 7.80, 8.00 (EtSi, MeC), 15.82 (CH_2), 28.29 (MeC), 37.88 (CH), 126.02, 126.79, 128.05, 128.09, 128.21, 132.67, 132.72, 147.83, 148.25, 149.99 (phenyl and phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) 12.03, 12.08. Anal. Calcd for $C_{23}H_{34}Si_2$: C, 75.34; H, 9.35. Found: C, 75.28; H, 9.43.

Reaction of 3 with styrene. A mixture of 0.3308 g (1.33 mmol) of **1** and 51 mg (6.83 x 10^{-2} mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 57 h. GLC analysis of the resulting mixture showed that **3** was produced in 68% yield, along with 8% yield of **2**. To this was added 0.1605 g (1.54 mmol) of styrene, and the mixture was heated to reflux for 3 h. GLC analysis of the reaction mixture indicated the presence of **10** (67% yield), **2** (8% yield), and 1% of the starting compounds **1**. Pure **10** was isolated by MPLC. For **10**: MS *m/z* 323 (M^+-Et); IR 3042, 2949, 2868, 1451, 1107, 1003, 747 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.43 (q, 1H, HC, J = 7.6 Hz), 0.64-1.13 (m, 15H, EtSi), 1.12 (d, 3H, MeC, J = 7.6 Hz and m, 2H, H_2C), 2.63-2.71 (m, 2H, H_2C), 7.13-7.55 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR δ($CDCl_3$) -1.44 (CH), 4.30, 4.66, 5.50, 7.59, 7.64 (2C), 8.57 (EtSi, MeC), 15.80 (CH_2), 30.05 (CH_2), 125.52, 127.32 (2C), 128.28, 128.32, 132.87, 132.92, 145.12, 148.32, 148.70 (phenyl and phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) 12.33, 13.69. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.91; H, 9.22.

Reaction of 3 with Diphenylacetylene. To a solution of **3** prepared from 0.3767 g (1.52 mmol) of **1** and 47 mg (6.35 x 10^{-2} mmol) of the platinum catalyst in 10 mL of dry benzene was added 0.2706 g (1.52 mmol) of diphenylacetylene. The mixture was heated to reflux for 2 h. GLC analysis of the reaction mixture showed the presence of **11** (64% yield), **4** (7% yield), and **2** (4% yield). Product **11** was isolated by preparative HPLC: MS *m/z* 426 (M^+); IR 3026, 2943, 1596, 1490, 1455, 1108, 1008, 908, 732, 697 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.55 (q, 1H, HC, J = 7.6 Hz), 0.71-1.05 (m, 15H, EtSi), 1.14 (d, 3H, MeC, J = 7.6 Hz), 6.89 (s, 1H, HC=C), 6.93-7.60 (m, 14H, phenyl and phenylene ring protons); ^{13}C NMR δ($CDCl_3$) -1.13 (HC), 4.08, 4.21, 5.50, 7.39, 7.64, 8.61, 9.40 (EtSi, MeC), 125.68, 127.06, 127.58, 127.85, 128.27, 128.45, 128.59, 129.56, 132.92, 133.98, 137.30, 139.35, 142.53, 144.69, 146.76, 149.20.(phenyl and phenylene ring carbons and olefinic carbons); ^{29}Si NMR δ($CDCl_3$) 7.48, 14.15. Anal. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03. Found: C, 78.79; H, 8.03.

Reaction of 1 with phenylacetylene. In a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed 0.3001 g (1.21 mmol) of **1**, 44 mg (5.90 x 10^{-2} mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0), and 0.1963 g (1.92 mmol) of phenylacetylene in 10 mL of dry benzene. The mixture was heated to reflux for 5 min. GLC analysis of the resulting mixture showed the presence of **12** (98% yield). Compound **12** was isolated by MPLC: MS *m/z* 350 (M^+); IR 3056, 2953, 2872, 1458, 1414, 1120, 1002, 795, 739, 699 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.76-1.04 (m, 20H, EtSi), 6.89 (s, 1H, HC=C), 7.22-7.58 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 6.26, 6.35, 7.53, 7.75 (EtSi), 126.24, 126.45, 127.84, 128.07, 128.23, 133.23, 133.42, 142.93, 142.98, 147.92 (phenyl and phenylene ring carbons), 145.62, 161.17 (olefinic carbons); ^{29}Si NMR δ($CDCl_3$) -14.51, -12.53. Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.12; H, 8.82.

Platinum-catalyzed reaction of 13. In a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed a solution of 0.0621 g (0.177 mmol) of **13** and 6.6 mg (8.84 x 10^{-3} mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in 5 mL of dry benzene. The mixture was heated to reflux for 1 h. GLC analysis of the resulting mixture showed the presence of **14** in 98% yield. For **14**: MS *m/z* 350 (M^+); IR 3045, 2954, 2872, 1585, 1560, 1458, 1119, 1003, 886, 752, 695 cm^{-1}; ^1H NMR δ($CDCl_3$) 0.71-0.99 (m, 20H, EtSi), 7.30-7.63 (m, 9H, phenyl and phenylene ring protons), 7.89 (s, 1H, HC=C); ^{13}C NMR δ($CDCl_3$) 6.29, 7.33, 7.66, 7.80 (EtSi), 127.66, 128.00, 128.19, 128.27, 128.55, 132.52, 132.74, 141.46, 147.46, 149.02 (phenyl and phenylene ring carbons), 138.94, 155.44 (olefinic carbons); ^{29}Si NMR δ($CDCl_3$) 6.46, 0.50. Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.38; H, 8.63.

Reaction of 1 with Diphenylacetylene. In a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed 0.1658 g (0.667 mmol) of **1**, 24 mg (3.21×10^{-2} mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0), and 0.1429 g (0.803 mmol) of diphenylacetylene in 10 mL of dry benzene. The mixture was heated to reflux for 1 h. GLC analysis of the resulting mixture showed the presence of **15** (98% yield). Compound **15** was isolated by MPLC: mp. 116-117 °C. MS *m/z* 426 (M^+); IR 2953, 1485, 1002, 909, 850, 790, 734 cm^{-1}; ^{1}H NMR δ($CDCl_3$) 0.70-0.95 (m, 20H, EtSi), 6.79-7.62 (m, 14H, phenyl and phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 5.25, 7.68 (EtSi), 125.01, 127.37, 127.98, 128.03, 133.37, 142.61, 143.45 (phenyl and phenylene ring carbons), 157.32 (olefinic carbons) ; ^{29}Si NMR δ($CDCl_3$) -13.33. Anal. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03. Found: C, 78.80; H, 7.96.

Reaction of 1 with Phenyl(trimethylsilyl)acetylene. A mixture of 0.1423 g (0.573 mmol) of **1**, 0.1231 g (0.707 mmol) of phenyl(trimethylsilyl)acetylene, and 21 mg (2.85×10^{-2} mmol) of a platinum catalyst in 10 mL of dry benzene was heated to reflux for 4 h. The mixture was analyzed by GLC as being **16** (98% yield). Compound **16** was isolated by MPLC: mp. 96-99 °C. MS *m/z* 422 (M^+); IR 2947, 2869, 1477, 1414, 1113, 1074, 838, 772, 671 cm^{-1}; ^{1}H NMR δ($CDCl_3$) -0.13 (s, 9H, Me_3Si), 0.53-0.97, (m, 20H, EtSi), 6.98-7.57 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 2.93 (Me_3Si) 5.21, 7.62, 7.66, 8.05 (EtSi), 125.97, 127.44, 127.55, 127.64, 127.98, 132.74, 132.87, 141.98, 144.74, 147.04 (phenyl and phenylene ring carbons), 159.26 (PhC=C), 176.77 (Me_3SiC=C); ^{29}Si NMR δ($CDCl_3$) -18.17, -12.24, -9.17. Anal. Calcd for $C_{25}H_{38}Si_3$: C, 71.01; H, 9.06. Found: C, 71.00; H, 9.04.

Reaction of 1 with 3-Hexyne. A mixture of 0.1961 g (0.789 mmol) of **1**, 0.1060 g (1.29 mmol) of 3-hexyne, and 30 mg (3.96×10^{-2} mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 1 h. GLC analysis of the reaction mixture showed the presence of **17** (98% yield). Product **17** was isolated by MPLC: MS *m/z* 330 (M^+); IR 3055, 2956, 2877, 1458, 1413, 1377, 1230, 1123, 1002, 963, 725, 672, 512 cm^{-1}; ^{1}H NMR δ($CDCl_3$) 0.79 (br s, 20H, EtSi), 1.08 (t, 6H, $C\underline{H}_3CH_2$-, J = 7.6 Hz), 2.37 (q, 4H, -$C\underline{H}_2CH_3$, J = 7.6 Hz), 7.24-7.51 (m, 4H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 6.11, 7.80 (EtSi), 14.85 ($\underline{C}H_3CH_2$-), 24.08 (-$\underline{C}H_2CH_3$), 127.67, 132.79, 143.58 (phenylene ring carbons), 153.73 (olefinic carbon); ^{29}Si NMR δ($CDCl_3$) -13.28. Anal. Calcd for $C_{20}H_{34}Si_2$: C, 72.65; H, 10.36. Found: C, 72.63; H, 10.29.

Reaction of 1 with Benzaldehyde. A solution of 0.2281 (0.918 mmol) of **1**, 0.1261 g (1.19 mmol) of benzaldehyde, and 34 mg (4.58×10^{-2} mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 12 h. The reaction mixture was analyzed by GLC as being **18** (73% yield), **2** (3% yield), and 8% of the starting compound **1**. All spectral data for product **18** were identical with those of an authentic sample.

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16. Compound **3** is stable in an inert atmosphere but unstable in air.

17. Six lines are presumably produced by overlapping of two quartets, due to the presence of two chiral centers in the 4,5-benzo-1,3-disilacyclopent-4-ene ring.

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