Silicon–Carbon Unsaturated Compounds. 38. Nickel-Catalyzed Reactions of Disilanyl-Substituted Enynes with Diphenylacetylene

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Received July 29, 1991

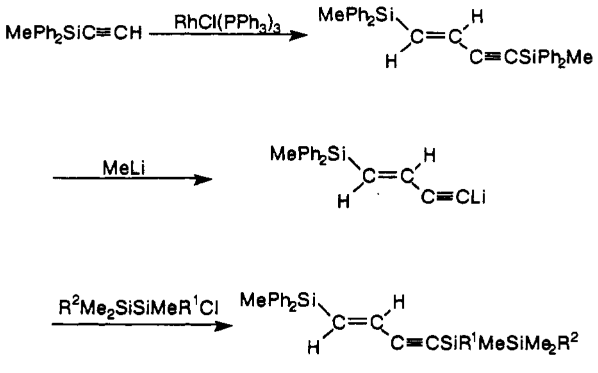
(*E*)-1-(Methyldiphenylsilyl)-4-pentamethyldisilanyl-, (*E*)-1-(methyldiphenylsilyl)-4-(1-phenyltetramethyldisilanyl)-, (*E*)-1-(methyldiphenylsilyl)-4-(2-phenyltetramethyldisilanyl)-, (*E*)-1,4-bis(pentamethyldisilanyl)-, (*E*)-1,4-bis(1-phenyltetramethyldisilanyl)-, and (*E*)-4-(methyldiphenylsilyl)-1-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (1–6) were prepared, and their nickel-catalyzed reactions with diphenylacetylene were investigated. The reaction of **1a** and **4** with diphenylacetylene in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) at 200 °C for 20 h in a sealed glass tube gave 6-[*trans*-(methyldiphenylsilyl)ethenyl]-1,1,4,4,5-pentamethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**7a**) and 1,1,4,4,5-pentamethyl-6-[*trans*-(pentamethyldisilanyl)ethenyl]-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**9**). The reaction of **2** and **5** under the same conditions afforded 1,1,4,4-tetramethyl-6-[*trans*-(methyldiphenylsilyl)ethenyl]-2,3,5-triphenyl-1,4-disilacyclohexa-2,5-diene (**8**) and 1,1,4,4-tetramethyl-2,3,5-triphenyl-6-[*trans*-(1-phenyltetramethyldisilanyl)ethenyl]-1,4-disilacyclohexa-2,5-diene. Compound **3** also reacted with diphenylacetylene under the same conditions, affording **8** as the sole volatile product. Treatment of (*E*)-4-[1-(deuteriomethyl)tetramethyldisilanyl]-1-(methyldiphenylsilyl)but-1-en-3-yne with diphenylacetylene in the presence of the nickel catalyst gave a mixture consisting of products in which a deuteriomethyl group was distributed onto a ring sp^2 carbon atom and two ring silicon atoms. The reaction of **6** with diphenylacetylene under the same conditions, however, afforded no volatile products.

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]

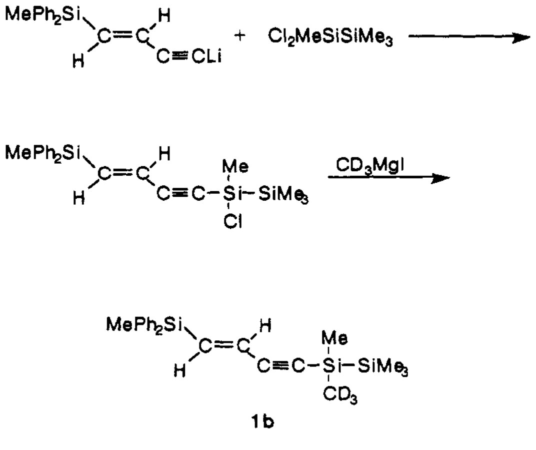
We recently found a convenient method for the preparation of (*E*)-1,4-bis(silyl)- and (*E*)-1,4-bis(disilanyl)but-1-en-3-ynes.[6] For example, the reaction of 1-ethynyl-1-phenyltetramethyldisilane with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) in toluene at room temperature proceeds 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 compound involves two different reactive centers toward a nickel species, a disilanylethenyl and disilanylethynyl unit in the molecule. In this paper we report the reaction of (*E*)-4-disilanyl-1-silyl-, (*E*)-1,4-bis(disilanyl)-, and (*E*)-1-disilanyl-4-silylbut-1-en-3-ynes with diphenylacetylene in the presence of dichlorobis(triethylphosphine)nickel(II) in a sealed tube.

Scheme I



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

Scheme II



1b

Results and Discussion

Synthesis. The starting compounds, (*E*)-1-(methyldiphenylsilyl)-4-(pentamethyldisilanyl)but-1-en-3-yne (**1a**),

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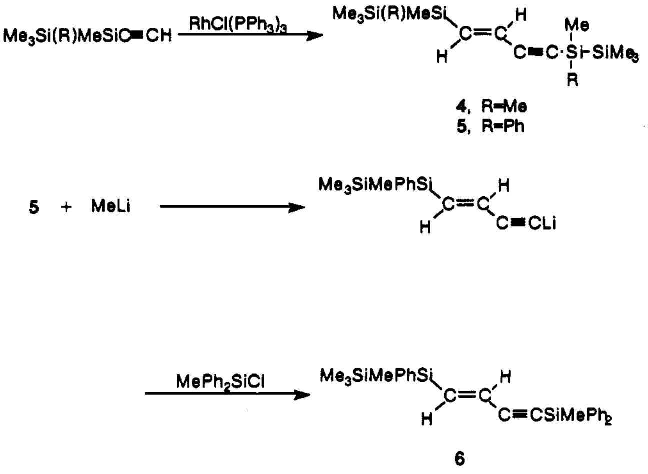
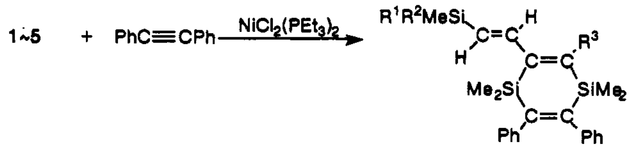
Scheme III



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, $R^1=SiMe_3, R^2=R^3=Ph$

(*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).

4-[1-(Deuteriomethyl)tetramethyldisilanyl]-1-(methyldiphenylsilyl)but-1-en-3-yne (**1b**) was prepared by the reaction of the 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).

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 reported previously.[6] (*E*)-4-(Methyldiphenylsilyl)-1-(1-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).

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] Unfortunatly, 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 mixture 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).

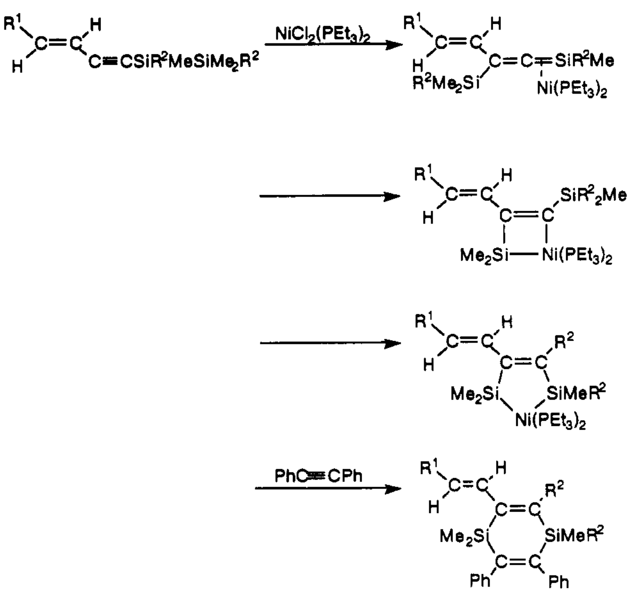
The location of the substituents on the 1,4-disilacyclohexa-2,5-diene ring for compound **7a** was verified by NOE-FID difference experiments at 270 MHz. Thus, saturation of dimethylsilyl protons of the disilacyclohexadienyl ring at −0.02 ppm caused a strong enhancement of an olefin proton and phenyl 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 olefin 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 the phenyl ring protons and a proton on the sp^2 carbon atom attached to the methyldiphenylsilyl group. Irradiation of the methyl protons of a methyldiphenylsilyl group led to the enhancement of two olefin protons, as well as the phenyl protons on this silicon atom.

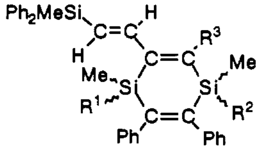
Interestingly, treatment of compound **3** with diphenylacetylene under the same conditions gave the product whose melting point and spectral data were identical with those of compound **8** obtained from the reaction of **2** with diphenylacetylene, in 15% yield as the sole volatile product. Large amounts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

The reaction of 4-[1-(deuteriomethyl)tetramethyldisilanyl]-1-(methyldiphenylsilyl)but-1-en-3-yne (**1b**) with diphenylacetylene under the same conditions yielded a 1,4-disilacyclohexa-2,5-diene derivative. To our surprise, ^1H and ^2H 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 ^1H 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, the 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 ^2H NMR spectrum also reveals the presence of a deuterio-

Scheme V



methyl 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 an 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. The 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 δ −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 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 the 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 the disilanylethynyl group interacted with a nickel catalyst to form the 1,4-disilacyclohexa-2,5-diene structure.

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 intermediates 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**), involving no disilanyl group on the 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; 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 the ethynyldisilanyl unit by the nickel species, as the sole volatile product. No volatile products arising from the activation of the 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

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atmosphere. The nickel-catalyzed reactions of compounds **1**–**5** were carried out in a degassed sealed glass tube (1.0 cm × 20 cm). NMR spectra were determined with a JEOL Model EX-270 spectrometer. Mass spectra were measured on a Shimazdu 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 reported previously.[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 at 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 by MPLC, to give 1.2814 g (66% yield) of **1a**: MS *m/e* 378 (M$^+$); IR $\nu_{C\equiv C}$ 2147 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.13 (s, 9 H, Me$_3$Si), 0.22 (s, 6 H, Me$_2$Si), 0.64 (s, 3 H, MeSi), 6.02 (d, 1 H, HC=C, J = 19 Hz), 6.74 (d, 1 H, HC=C, J = 19 Hz), 7.34–7.54 (m, 10 H, ring protons); ^{13}C NMR δ (CDCl$_3$) −4.04 (MeSi), −3.07 (Me$_2$Si), −2.52 (Me$_3$Si), 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 (4,9 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/e* 381 (M$^+$); IR ν_{C-D} 2120, $\nu_{C\equiv C}$ 2147 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.13 (s, 9 H, Me$_3$Si), 0.21 (s, 3 H, MeSi), 0.64 (s, 3 H, MeSi), 6.02 (d, 1 H, HC=C, J = 19 Hz), 6.74 (d, 1 H, HC=C, J = 19 Hz), 7.34–7.54 (m, 10 H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −4.04 (MeSi), −3.16 (MeSi), −3.11 (CD$_3$Si, J = 17 Hz),[12] −2.53 (Me$_3$Si), 95.33 and 107.17 ($C\equiv C$), 127.31 and 141.42 (olefin α-carbons), 127.92, 129.54, 134.88, 135.29 (phenyl ring carbons).

1-(Methyldiphenylsilyl)-4-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (2). Into 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, cooling with ice. 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/e* 440 (M$^+$); IR $\nu_{C\equiv C}$ 2148 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.19 (s, 9 H, Me$_3$Si), 0.51 (s, 3 H, MeSi), 0.67 (s, 3 H, MeSi), 5.92 (d, 1 H, HC=C, J = 19 Hz), 6.68 (d, 1 H, HC=C, J = 19 Hz), 6.95–7.42 (m, 15 H, ring protons); ^{13}C NMR δ (CDCl$_3$) −4.20 (MeSi), −4.04 (MeSi), −2.36 (Me$_3$Si), 92.93 and 108.75 ($C\equiv C$), 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, cooling with ice. 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**: MS *m/e* 440 (M$^+$); IR $\nu_{C\equiv C}$ 2147 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.19 (s, 6 H, Me$_2$Si), 0.41 (s, 6 H, Me$_2$Si), 0.63 (s, 3 H, MeSi), 6.00 (d, 1 H, HC=C, J = 19 Hz), 6.73 (d, 1 H, HC=C, J = 19 Hz), 7.30–7.53 (m, 15 H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −4.08 (Me$_2$Si and MeSi), −2.96 (Me$_2$Si), 94.97 and 107.62 ($C\equiv C$), 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-phenyltetramethyldisilanyl)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, and the resulting solution was stirred at room temperature for 10 h. The mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The organic layer and extracts were combined, 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/e* 440 (M$^+$); IR $\nu_{C\equiv C}$ 2154 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.12 (s, 9 H, Me$_3$Si), 0.42 (s, 3 H, MeSi), 0.70 (s, 3 H, MeSi), 6.06 (d, 1 H, HC=C, J = 19 Hz), 6.79 (d, 1 H, HC=C, J = 19 Hz), 7.32–7.65 (m, 15 H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −6.02 (MeSi), −2.05 (MeSi), −1.96 (Me$_3$Si), 90.96 and 108.32 ($C\equiv C$), 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-Catalyzed 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 on silica gel, eluting with hexane, using a short column to remove nickel species from the reaction mixture. The product **7a** (0.2624 g, 53% yield) was separated by MPLC (silica gel 40–63 μm) as colorless crystals: mp 155–157 °C (after recrystallization from ethanol); MS *m/e* 556 (M$^+$); ^{1}H NMR δ (CDCl$_3$) −0.02 (s, 6 H, Me$_2$Si), 0.29 (s, 6 H, Me$_2$Si), 0.69 (s, 3 H, MeSi), 2.19 (s, 3 H, MeC), 6.32 (d, 1 H, HC=C, J = 18 Hz), 6.73 (d, 1 H, HC=C, J = 18 Hz), 6.79–7.57 (m, 20 H, ring protons); ^{13}C NMR δ (CDCl$_3$) −3.65 (MeSi), −0.84 (Me$_2$Si), −0.54 (Me$_2$Si), 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 (olefin 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/e* 559 (M$^+$); ^{1}H

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

NMR δ ($CDCl_3$) −0.02 (s, 4.8 H, Me_3Si), 0.29 (s, 4.7 H, Me_2Si), 0.70 (s, 3 H, MeSi), 2.20 (s, 2.5 H, MeC), 6.32 (d, 1 H, HC=C, J = 18 Hz), 6.73 (d, 1 H, HC=C, J = 18 Hz), 6.80–7.58 (m, 20 H, 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/e* 618 (M^+); ^{1}H NMR δ ($CDCl_3$) −0.22 (s, 6 H, Me_2Si), 0.07 (s, 6 H, Me_2Si), 0.61 (s, 3 H, MeSi), 5.82 (d, 1 H, HC=C, J = 18 Hz), 6.92 (d, 1 H, HC=C, J = 18 Hz), 6.74–7.50 (m, 25 H, 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 (olefin 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/e* 490 (M^+); ^{1}H NMR δ ($CDCl_3$) 0.08 (s, 9 H, Me_3Si), 0.17 (s, 6 H, Me_2Si), 0.29 (s, 6 H, Me_2Si), 0.30 (s, 6 H, Me_2Si), 2.14 (s, 3 H, MeC), 6.09 (d, 1 H, HC=C, J = 18 Hz), 6.80 (d, 1 H, HC=C, J = 18 Hz), 6.86–7.09 (m, 10 H, 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 (olefin ring carbon), 148.46 (HC=), 158.22, 160.77, 160.84 (olefin 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/e* 614 (M^+); ^{1}H NMR δ ($CDCl_3$) −0.23 (s, 6 H, Me_2Si), 0.08 (s, 9 H, Me_3Si), 0.28 (s, 3 H, MeSi), 0.39 (s, 3 H, MeSi), 5.70 (d, HC=C, J = 18 Hz), 6.98 (d, 1 H, HC=C, J = 18 Hz), 6.75–7.43 (m, 20 H, 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 (olefin 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 (olefin 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. GLC and GPC analysis of the reaction mixture showed that no volatile product was detected.

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

Registry No. **1a**, 138090-93-4; **1b**, 138091-01-7; **2**, 138090-94-5; **3**, 138090-95-6; **4**, 126615-07-4; **5**, 121001-61-4; **6**, 138090-96-7; **7a**, 138090-97-8; **7b**, 138091-02-8; **7c**, 138091-03-9; **7d**, 138128-55-9; **8**, 138090-98-9; **9**, 138090-99-0; **10**, 138091-00-6; $NiCl_2(PEt_3)_2$, 17523-24-9; PhC≡CPh, 501-65-5; $Me_3SiSiMe_2Cl$, 1560-28-7; $Me_3SiSiMePhCl$, 33559-14-7; $PhMe_2SiSiMe_2Cl$, 941-15-1; $MePh_2SiCl$, 144-79-6; 1,4-bis(methyldiphenylsilyl)but-1-enyne, 121001-63-6.

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[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 environments of the deuteriomethyl groups are also methylsilyl carbons.