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Silicon–Carbon Unsaturated Compounds. 43. Nickel-Catalyzed Reactions of Disilanyl-Substituted Enynes with Methyldiphenylsilane

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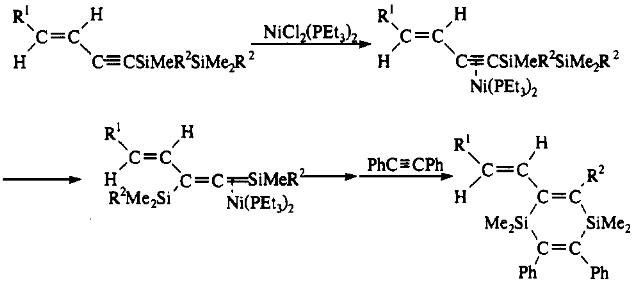
The nickel-catalyzed reactions of 1,4-bis(disilanyl)but-1-en-3-ynes, 4-(disilanyl)-1-(silyl)but-1-en-3-ynes, and 1-(disilanyl)-4-(silyl)but-1-en-3-yne with methyldiphenylsilane have been investigated. Treatment of (*E*)-1,4-bis(pentamethyldisilanyl)but-1-en-3-yne with methyldiphenylsilane in the presence of a catalytic amount of $NiCl_2(PEt_3)_2$ at 200 °C gave *trans*-1,1-dimethyl-2-(2,2-diphenyltrimethyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene. Similar reaction of (*E*)-1-(pentamethyldisilanyl)-4-(1-phenyltetramethyldisilanyl)but-1-en-3-yne produced a *trans*-1-silacyclopent-3-ene, while (*E*)-1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne afforded two isomers of the 1-silacyclopent-3-ene. The reactions of (*E*)-1-(methyldiphenylsilyl)-4-(pentamethyldisilanyl)but-1-en-3-yne, (*E*)-1-(methyldiphenylsilyl)-4-(1-phenyltetramethyldisilanyl)but-1-en-3-yne, and (*E*)-1,4-bis(methyldiphenylsilyl)but-1-en-3-yne with methyldiphenylsilane produced silylallene derivatives arising from 1,4-addition of the silane to enynes. Similar treatment of 1-(disilanyl)-4-(silyl)but-1-en-3-yne afforded nonvolatile substances.

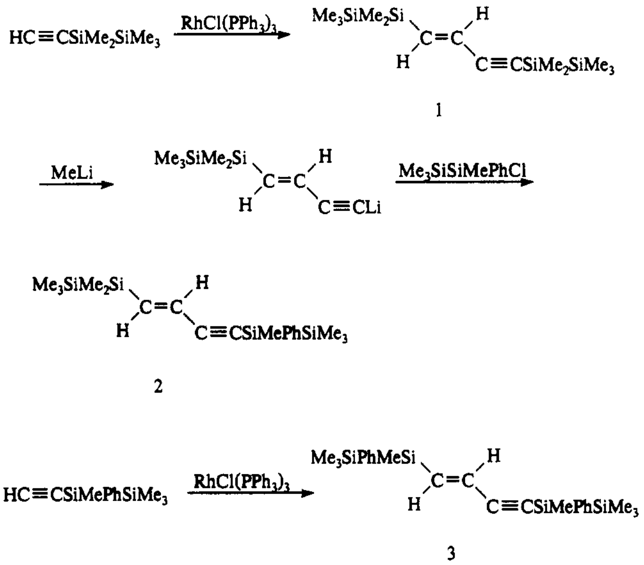
Introduction

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] We recently found that 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(triethylphosphine)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.

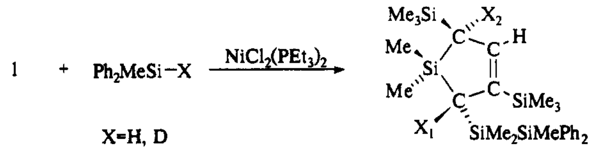


It is of interest to us to investigate the nickel-catalyzed reaction of the bis(disilanyl) enynes with a hydrosilane, because the products expected from addition of an Si–H bond to the silapropadienes might be obtained. In this paper we report the reactions of 1,4-bis(disilanyl)but-1-en-3-ynes, 4-(disilanyl)-1-(silyl)but-1-en-3-ynes, 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.

Scheme I



Scheme II



4a, $X_1=X_2=H$
4b, $X_1=D, X_2=H$
4c, $X_1=H, X_2=D$
4d, $X_1=X_2=D$

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)but-1-en-3-ynes 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-

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[2] Ishikawa, M.; Nomura, Y.; Tozaki, E.; Kunai, A.; Ohshita, J. *J. Organomet. Chem.* 1990, *399*, 205.
[3] Ishikawa, M.; Nishimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* 1992, *11*, 483.
[4] Ohshita, J.; Naka, A.; Ishikawa, M. *Organometallics* 1992, *11*, 602.
[5] Ohshita, J.; Furumori, K.; Matsuguchi, A.; Ishikawa, M. *J. Org. Chem.* 1990, *55*, 3277.

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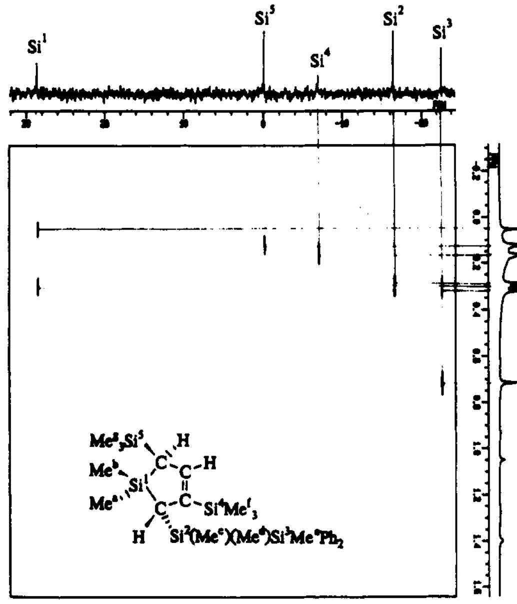


Figure 1. ^{1}H–^{29}Si COSY NMR spectrum of **4a**.

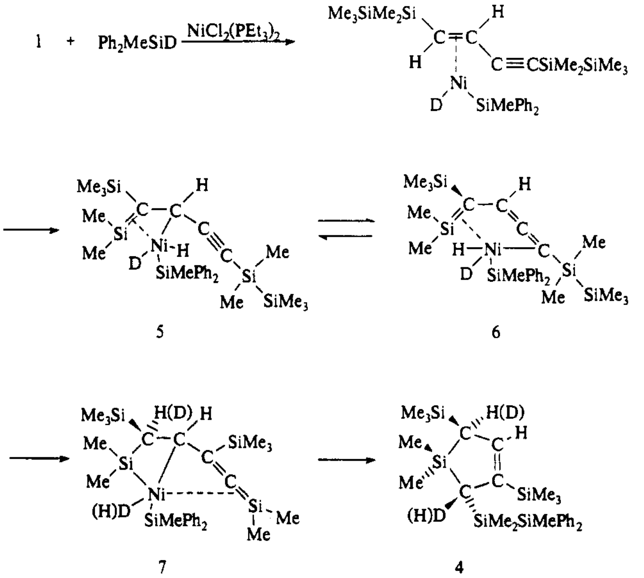
1-en-3-yne (**1**), (*E*)-1-(pentamethyldisilanyl)-4-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**2**), and (*E*)-1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**3**), employed as starting compounds (Scheme I).

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 could be readily isolated by preparative GLC methods 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 atoms in the ring, respectively, while hydrogen on an olefinic carbon atom at 6.07 ppm couples with the C-4 atom.

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.

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**.

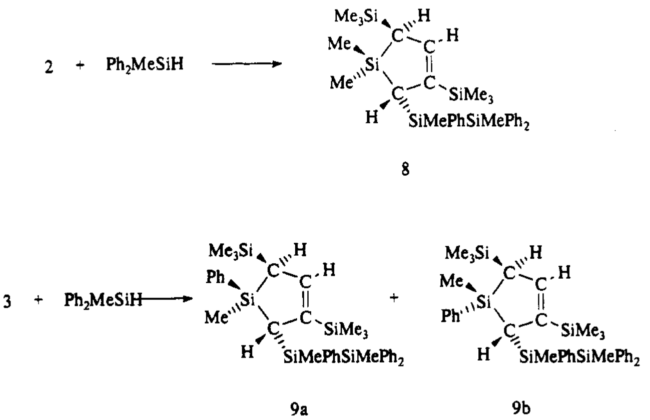
Scheme III



As can be seen in the ^{1}H 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 a 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 ^{2}H NMR spectrometric analysis. The ^{2}H 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 ^{2}H 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 ^{1}H 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 the silene–nickel complex **5**, which would be transformed into the silylnickel complex **6**. The silyl–nickel complex **6** undergoes intramolecular isomerization, giving the silapropadiene–nickel complex **7**. Finally, hydrosilylation at a silicon–carbon double bond and then formation of the five-membered ring, accompanied by the reductive elimination of the nickel species, produces product **4**. The similar nick-

Scheme IV



el-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-(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 in the first step. The nickel complex thus obtained 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.

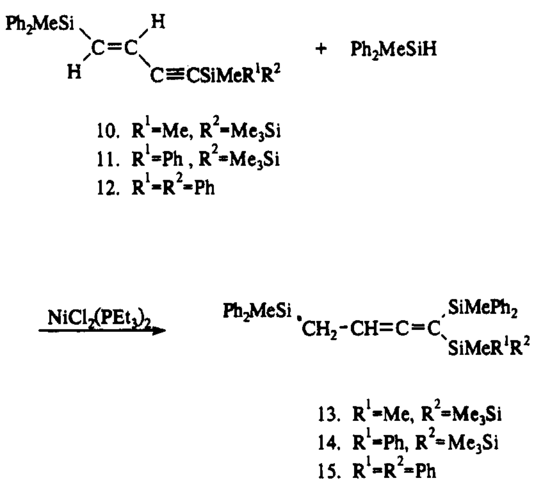
The presence of deuterium atoms on sp^3 carbons in the silacyclopentenyl ring and of methyldiphenylsilane in the recovered deuteriomethyldiphenylsilane can be understood by hydrogen–deuterium exchange between Ni–D and C–H bonds in the nickel complex **5**–**7** and by exchange between coordinated methyldiphenylsilane (MePh$_2$Si–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 reactions 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 ^{1}H NMR spectrometric 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**).

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.

Scheme V



Next we turned our attention to 1-(silyl)-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 a method similar 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 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 by either 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 an sp^2 carbon were detected by either spectrometric analysis or GLC analysis. In contrast to the similar reactions of **1**–**3**, the nickel species probably coordinates to a carbon–carbon triple bond in the enynes in the initial step. It has been reported that the hydrosilylation of 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 reactions 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 1-(disilanyl)-4-(silyl)but-1-en-3-yne produced nonvolatile substances.

Experimental Section

General Procedure. All reactions for the synthesis of the starting compounds **1**–**3** and **10**–**12** were carried out under a purified argon atmosphere. The nickel-catalyzed reactions of compounds **1**–**3**, **10**–**12**, and **16** were carried out in a degassed, sealed glass tube (1.0 cm × 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 instrument. 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 instrument (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**), and (*E*)-1,4-bis(methyldiphenylsilyl)but-1-en-3-yne (**12**) were prepared as reported previously.[4,5]

(*E*)-1-(Pentamethyldisilanyl)-4-(1-phenyltetramethyldisilanyl)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 warmed 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, which was then stirred for 5 h at room temperature. The mixture was hydrolyzed with water, and then 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 with hexane as eluent, to give 0.6579 g (39% yield) of **2**: MS *m/e* 374 (M$^+$); IR $\nu_{C\equiv C}$ 2148 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.08 (s, 9 H, Me$_3$Si), 0.14 (br s; 6 H, Me$_2$Si; 9 H, Me$_3$Si), 0.48 (s, 3 H, MeSi), 5.99 (d, 1 H, HC=C, J = 19 Hz), 6.75 (d, 1 H, HC=C, J = 19 Hz), 7.33–7.37 (m, 3 H, ring protons), 7.55–7.59 (m, 2 H, ring protons); ^{13}C NMR (CDCl$_3$) δ −4.62 (Me$_3$Si), −4.15 (MeSi), −2.37 (Me$_3$Si), −2.32 (Me$_3$Si), 90.80 and 109.24 (C≡C), 123.37 (C=C), 127.85, 128.81, 134.12, and 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 with hexane as eluent, to remove nickel species from the reaction mixture. The product **4a** (63% yield) was isolated by preparative GLC: MS *m/e* 510 (M$^+$); ^{1}H NMR (C$_6$D$_6$) δ 0.06 (s, 3 H, MeSi), 0.12 (s, 9 H, Me$_3$Si), 0.17 (s, 9 H, Me$_3$Si), 0.29 (s, 3 H, MeSi), 0.30 (s, 3 H, MeSi), 0.32 (s, 3 H, MeSi), 0.72 (s, 3 H, MeSi), 1.05 (br s, 1 H, HC), 1.40 (br d, 1 H, HC, J = 1.5 Hz), 6.07 (br d, 1 H, HC=C, J = 1.5 Hz), 7.22–7.68 (m, 10 H, ring protons); ^{13}C NMR (C$_6$D$_6$) δ −4.22 (MeSi), −3.26 (MeSi), −2.10 (MeSi), −0.86 (MeSi), 0.28 (Me$_3$Si), 0.46 (MeSi), 0.51 (Me$_3$Si), 20.35 and 26.35 (HC), 129.08 (phenyl ring carbon), 129.11 (olefinic ring carbon), 135.22 and 135.30 (phenyl ring carbons), 140.76 (olefinic ring carbon), 147.17 (phenyl ring carbon); ^{29}Si NMR (C$_6$D$_6$) δ −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 flask was introduced hydrogen chloride for 3 h. After the solvent benzene and excess 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 for 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 chromatographed on a short Florisil column to remove nickel species from the reaction mixture. A mixture of **4b–d** (57% yield) was isolated by preparative GLC: MS *m/e* 511 (M$^+$) for **4b**,**c** and 512 (M$^+$) for **4d**; ^{1}H NMR (C$_6$D$_6$) δ 0.05 (s, 3 H, MeSi), 0.12 (s, 9 H, Me$_3$Si), 0.17 (s, 9 H, Me$_3$Si), 0.29 (s, 3 H, MeSi), 0.30 (s, 3 H, MeSi), 0.32 (s, 3 H, MeSi), 0.72 (s, 3 H, MeSi), 1.05 (br s, 0.24 H, HC), 1.40 (br d, 0.17 H, HC, J = 1.5 Hz), 6.07 (br d, 1 H, HC=C, J = 1.5 Hz), 7.24–7.73 (m, 10 H, ring protons); ^{13}C NMR (C$_6$D$_6$) δ −4.22 (MeSi), −3.26 (MeSi), −2.10 (MeSi), −0.86 (MeSi), 0.28 (Me$_3$Si), 0.46 (MeSi), 0.51 (Me$_3$Si), 20.35 and 26.35 (HC), 129.08 (phenyl ring carbon), 129.11 (olefinic ring carbon), 135.22 and 135.30 (phenyl ring carbons), 140.76 (olefinic ring carbon), 147.17 (phenyl ring carbon); ^{2}H NMR (C$_6$D$_6$) δ 1.02, 1.38.

***trans*-1,1-Dimethyl-2-(1,2-dimethyltriphenyldisilanyl)-3,5-bis(trimethylsilyl)-1-silacyclopent-3-ene (8).** A mixture of 0.2473 g (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 chromatographed on a short Florisil column to remove nickel species from the reaction mixture. The product **8** (66% yield) was isolated by preparative GLC: MS *m/e* 572 (M$^+$); ^{1}H NMR (C$_6$D$_6$) δ −0.08 (s, 9 H, Me$_3$Si), 0.19 (s, 3 H, MeSi), 0.22 (s, 9 H, Me$_3$Si), 0.35 (s, 3 H, MeSi), 0.36 (s, 3 H, MeSi), 0.71 (s, 3 H, MeSi), 1.22 (br s, 1 H, HC), 2.03 (br d, 1 H, HC, J = 2.0 Hz),

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6.21 (br d, 1 H, HC$=$C, J = 2.0 Hz), 7.24–7.68 (m, 15 H, ring protons); ^{13}C NMR (C$_6$D$_6$) δ −4.31 (MeSi), −3.30 (MeSi), −2.62 (MeSi), −1.76 (MeSi), 0.37 (2 Me$_3$Si), 17.17 and 27.05 (HC), 129.10 and 129.13 (phenyl ring carbon), 129.80 (olefinic ring carbon), 135.04, 135.22, 135.28, 135.33, and 138.17 (phenyl ring carbons), 140.54 (olefinic 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-triphenyldisilanyl)-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 chromatographed on 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/e 572 (M$^+$); ^{1}H NMR (C$_6$D$_6$) δ −0.12 (s, 9 H, Me$_3$Si), −0.09 (s, 9 H, Me$_3$Si), 0.06 (s, 3 H, MeSi), 0.16 (s, 9 H, Me$_3$Si), 0.16 (s, 3 H, MeSi), 0.19 (s, 9 H, Me$_3$Si), 0.40 (s, 3 H, MeSi), 0.58 (s, 3 H, MeSi), 0.67 (s, 3 H, MeSi), 0.69 (s, 3 H, MeSi), 1.14 (br s, 1 H, HC), 1.17 (br s, 1 H, HC), 2.23 (br d, 1 H, HC, J = 1.7 Hz), 2.34 (br d, 1 H, HC, J = 1.7 Hz), 6.40 (br d, 1 H, HC$=$C, J = 1.7 Hz), 6.46 (br d, 1 H, HC$=$C, J = 1.7 Hz), 6.90–7.61 (m, 40 H, ring protons); ^{13}C NMR (C$_6$D$_6$) δ −5.37 (MeSi), −4.02 (MeSi), −3.84 (MeSi), −3.71 (MeSi), −2.85 (MeSi), −2.55 (MeSi), 0.33 (Me$_3$Si), 0.47 (Me$_3$Si), 0.51 (Me$_3$Si), 0.82 (Me$_3$Si), 18.33, 18.89, 26.98, 27.21 (HC), 127.84, 128.25, 128.90, 129.17 (2 C), 129.24, 129.51, 129.80, 134.69, 134.94, 135.12, 135.17, 135.43, 135.46, 135.53 (2 C), 137.11, 137.20, 137.33, 137.56, 137.94 (2 C), 138.05, 138.33, 141.19, 141.57, 146.78 (2 C) (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-(pentamethyldisilanyl)-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 chromatographed on a short Florisil column to remove nickel species from the reaction mixture. The product **13** (73% yield) was isolated by preparative GLC: MS m/e 576 (M$^+$); IR $\nu_{C=C=C}$ 1908 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 0.14 (s, 9 H, Me$_3$Si), 0.16 (s, 3 H, MeSi), 0.22 (s, 3 H, MeSi), 0.44 (s, 3 H, MeSi), 0.67 (s, 3 H, MeSi), 1.97 (d, 2 H, HC, J = 8.0 Hz), 4.52 (t, 1 H, HC$=$C, J = 8.0 Hz), 7.22–7.26 (m, 10 H, ring protons), 7.46–7.51 (m, 5 H, ring protons), 7.66–7.70 (m, 5 H, ring protons); ^{13}C NMR (C$_6$D$_6$) δ −4.47 (MeSi), −1.97 (MeSi), −1.58 (Me$_3$Si and MeSi), −1.31 (MeSi), 13.91 (CH$_2$), 72.58 (HC$=$), 84.39, (C$=$), 129.46 (2 C), 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 for GLC and mass fragmentation pattern obtained for chloropentamethyldisilane and chloromethyldiphenylsilane were identical with those of the authentic samples.

1,4-Bis(methyldiphenylsilyl)-1-(1-phenyltetramethyldisilanyl)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 chromatographed on a short Florisil column to remove nickel species from the reaction mixture. The product **14** (50% yield) was isolated by preparative MPLC: MS m/e 638 (M$^+$); IR $\nu_{C=C=C}$ 1908 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 0.15 (s, 9 H, Me$_3$Si), 0.17 (s, 9 H, Me$_3$Si), 0.30 (s, 3 H, MeSi), 0.32 (s, 3 H, MeSi), 0.34 (s, 3 H, MeSi), 0.36 (s, 3 H, MeSi), 0.42 (s, 3 H, MeSi), 0.48 (s, 3 H, MeSi), 2.01 (d, 2 H, HC, J = 8.0 Hz), 4.55 (t, 1 H, HC$=$C, J = 8.0 Hz), 7.14–7.56 (m, 25 H, ring protons); ^{13}C NMR (C$_6$D$_6$) δ −4.56 (MeSi), −3.77 (MeSi), −1.54 (Me$_3$Si), −1.41 (MeSi), 13.75 and 14.02 (HC), 72.73 and 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, and 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 0.0291 g (0.10 mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 200 °C for 20 h. The mixture was chromatographed on 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/e 642 (M$^+$); IR $\nu_{C=C=C}$ 1911 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 0.29 (s, 3 H, MeSi), 0.54 (s, 6 H, 2 MeSi), 1.83 (d, 2 H, HC, J = 8.0 Hz), 4.49 (t, 1 H, HC$=$C, J = 8.0 Hz), 7.11–7.62 (m, 30 H, ring protons); ^{13}C NMR (C$_6$D$_6$) δ −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, and 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, and the mixture was cooled to −78 °C for 2 min. The mixture was warmed to 0 °C, and 0.50 g (4.61 mmol) of chlorotrimethylsilane in 5 mL of ether was added. After the mixture was stirred for 5 h at room temperature, it 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 with hexane as eluent, to give 0.6599 g (77% yield) of **16**: MS m/e 316 (M$^+$); IR $\nu_{C\equiv C}$ 2154 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.15 (s, 9 H, Me$_3$Si), 0.24 (s, 9 H, Me$_3$Si), 0.42 (s, 3 H, MeSi), 5.85 (d, 1 H, HC$=$C, J = 19 Hz), 6.60 (d, 1 H, HC$=$C, J = 19 Hz), 7.08–7.45 (m, 5 H, ring protons); ^{13}C NMR (CDCl$_3$) δ −5.88 (MeSi), −1.93 (Me$_3$Si), −0.09 (Me$_3$Si), 94.99 and 105.38 (C$\equiv$C), 124.94 (C$=$C), 127.92, 128.84, 134.42, and 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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