4524 *Organometallics* **1999,** *18,* 4524−4529

Nickel-Catalyzed Reactions of Benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) with Alkynes and Ketones

Akinobu Naka,[†] Kyung Koo Lee,[†] Kazunari Yoshizawa,[‡] Tokio Yamabe,[‡,§] and Mitsuo Ishikawa*,[†]

Department of Chemical Technology, Kurashiki University of Science and the Arts, 2640 Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan, Department of Molecular Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan, and Institute for Fundamental Chemistry, 34-4 Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan

Received May 12, 1999

Heating a benzene solution of benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) (**1**) with a catalytic amount of tetrakis(triethylphosphine)nickel(0) gave two regioisomers, **2** and **3**, arising from C−H bond activation of benzene in 81% combined yield. The reaction of **1** with diphenylacetylene in the presence of the nickel catalyst afforded benzo[1,2:4,5]bis(1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene) in 91% yield, while with 3-hexyne, **1** yielded benzo[1,2:4,5]bis(1,1,2,3,4,4-hexaethyl-1,4-disilacyclohexa-2,5-diene) and its isomer (**7**) in 64% and 25% yields, respectively. The nickel-catalyzed reaction of **1** with benzophenone gave benzo[1,2](1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene)[4,5](1,1,3,3-tetraethyl-2,2-diphenyl-1,3-disilacyclopent-4-ene) and siloxane (**8**) in 40% and 50% yields. Similarly, with 4,4′-dimethylbenzophenone, **1** produced benzo[1,2](1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene)[4,5](1,1,3,3-tetraethyl-2,2-(*p*-tolyl)-1,3-disilacyclopent-4-ene) in 19% yield, together with a 50% yield of **8**. When the similar treatment of **1** with benzophenone was carried out in cyclohexene, 7,7-diphenylnorcarane was obtained in 14% yield, along with a 54% yield of **8**.

Introduction

Recently, we have found that the palladium- and platinum-catalyzed reactions of benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) (**1**) with alkynes afford 1:2 adducts arising from insertion of a triple bond of alkynes into two silicon−silicon bonds in the benzobis(disilacyclobutene) in high yields.[1] With olefins such as styrene and 1-hexene, the palladium-catalyzed reactions of **1** gave two regioisomers of 1:2 adducts, disubstituted benzo[1,2:4,5]bis(1,4-disilacyclohex-5-ene)s, in which each regioisomer consists of a mixture of cis and trans isomers.[2] The platinum-catalyzed reactions of **1** with styrene and 1-hexene, however, produced 1:2 adducts, disubstituted benzo[1,2:4,5]bis(1,3-disilacyclopent-4-ene)s, consisting of cis and trans isomers, which were derived from terminal sp^2 C−H bond activation of a carbon−carbon double bond of olefins.[2] These results indicate that the patterns of both palladium- and platinum-catalyzed reactions with alkenes and alkynes are similar to those of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene reported previously.[3] Interestingly, the palladium- and platinum-catalyzed reactions of **1** with alkenes and alkynes produces only a 1:2 adduct even in the early stages of the reactions.

It is of interest to us to learn the similarities and dissimilarities between the palladium or platinum catalyst and other transition metal catalysts in the reaction of **1** with unsaturated organic molecules. In this paper we report the nickel-catalyzed reactions of **1** with alkynes and ketones (Chart 1).

Results and Discussion

The starting benzo[1,2;4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) (**1**) was prepared by sodium condensation of 1,2,4,5-tetrakis(chlorodiethylsilyl)benzene as reported previously.[1]

First, we treated **1** with a catalytic amount of a nickel catalyst in benzene to confirm whether C−H bond activation of benzene occurs. When a benzene solution of compound **1** was heated in the presence of 7 mol % of tetrakis(triethylphosphine)nickel(0) in a degassed sealed tube at 150 °C, 1,4-bis(diethylphenylsilyl)-3,6-bis(diethylsilyl)benzene (**2**) and 1,3-bis(diethylphenylsilyl)-4,6-bis(diethylsilyl)benzene (**3**), arising from C−H bond activation of benzene, were obtained in 81% combined yield (Scheme 1). The ratio of isomers was calculated to be 1.2:1 by the ^{1}H NMR spectrometric analysis. All attempts to separate one isomer from the other with the use of recycling HPLC or preparative GLC were unsuccessful. The structures of **2** and **3** were confirmed by spectrometric analysis, as well as by

---

[†] Kurashiki University of Science and the Arts.
[‡] Kyoto University.
[§] Institute for Fundamental Chemistry.

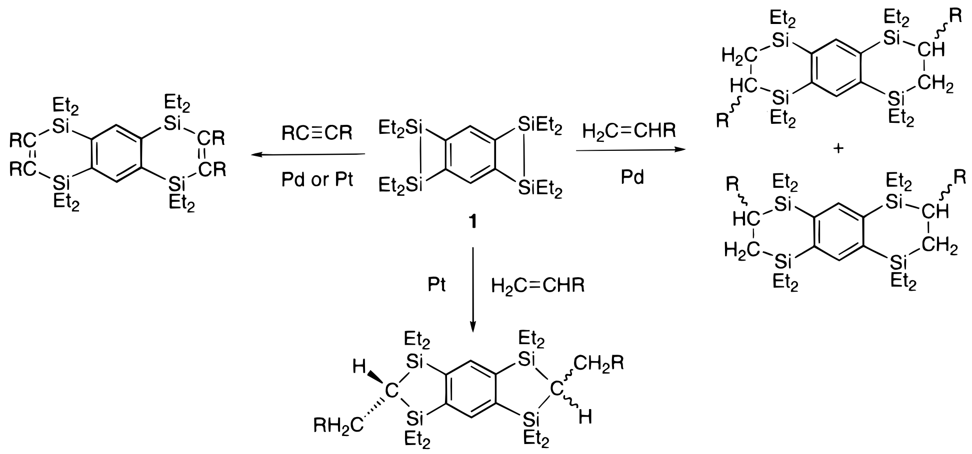
[1] Naka, A.; Yoshizawa, K.; Kang S.; Yamabe, T.; Ishikawa, M. *Organometallics* **1998**, *17*, 5830.

[2] Naka, A.; Lee. K. K.; Yoshizawa, K.; Yamabe, T.; Ishikawa, M. *J. Organomet. Chem.* **1999**, *587*, 1.

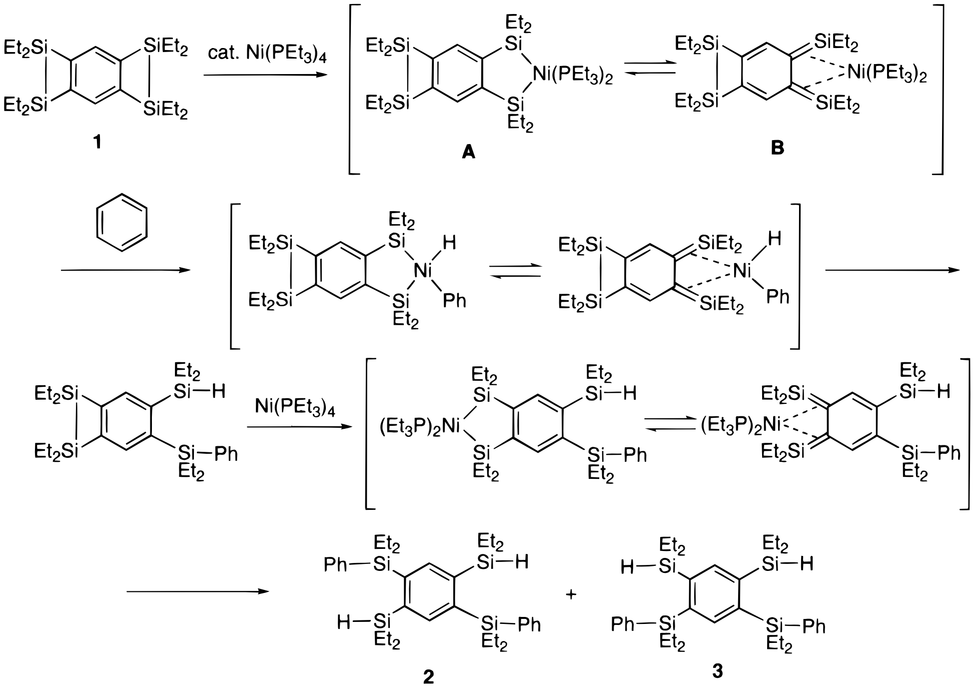
[3] (a) Ishikawa, M.; Naka, A. *SYNLETT* **1995**, 794. (b) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1993**, *12*, 4987. (c) Naka, A.; Hayashi, M.; Ishikawa, M. *Organometallics* **1994**, *13*, 4994.

10.1021/om9903588 CCC: $18.00

Chart 1



Scheme 1



elemental analysis. The IR spectrum of the mixture of **2** and **3** shows a strong absorption band at 2150 cm^{-1}, due to stretching frequencies of the Si−H bonds. Its ^{29}Si NMR spectrum reveals two resonances at −10.10 and −2.90 ppm for one isomer and two resonances at −10.10 and −2.77 ppm for the other.

To confirm that the products **2** and **3** are regioisomers, we carried out the conversion of the Si−H bonds in **2** and **3** into the Si−Ph bonds. Thus, treatment of the mixture of **2** and **3** with carbon tetrachloride in the presence of a catalytic amount of palladium dichloride, followed by the reaction of the resulting dichloro derivatives with 2 equiv of phenyllithium, gave 1,2,4,5-tetrakis(diethylphenylsilyl)benzene (**4**) in 61% yield as the sole product (Scheme 2). In fact, the ^{29}Si NMR spectrum of **4** shows a single resonance at −1.69 ppm, and its ^{13}C NMR spectrum reveals two resonances at 4.91 and 7.49 ppm, due to ethyl carbons, which are consistent with the structure proposed for **4**. These results clearly indicate that **2** and **3** are indeed regioisomers derived from addition of benzene to **1**. The formation of **2** and **3** may be explained in terms of C−H bond activation of benzene by the nickel catalyst. In fact, we found that the reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with benzene in the presence of the nickel catalyst gave the product arising from C−H bond activation of benzene.[4]

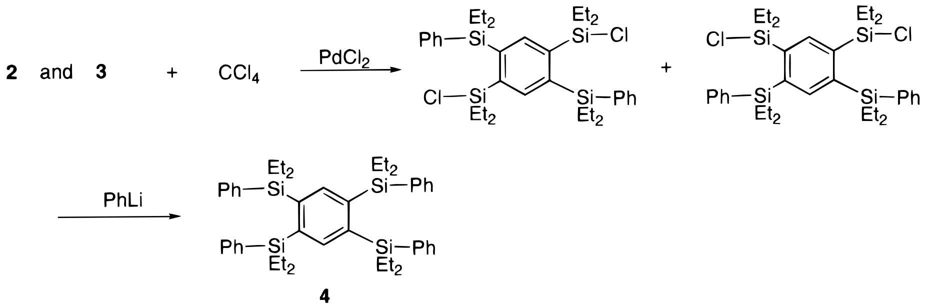
Scheme 1 illustrates a possible mechanistic interpretation of the observed reaction course. We suggest that *o*-quinodisilanenickel complex (**B**) formed from metaladisilacyclopentene derivative (**A**) is involved as the key intermediate in C−H bond activation of benzene, as proposed in the similar nickel-catalyzed reaction of the benzodisilacyclobutene.[4] However, at present, evidence for the formation of intermediates **A** and **B** has not yet been obtained.

Like 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene, compound **1** readily reacts with alkynes in the presence of a catalytic amount of the nickel complex to give 1:2 adducts. Thus, when **1** was treated with diphenylacetylene in the presence of tetrakis(trieth-

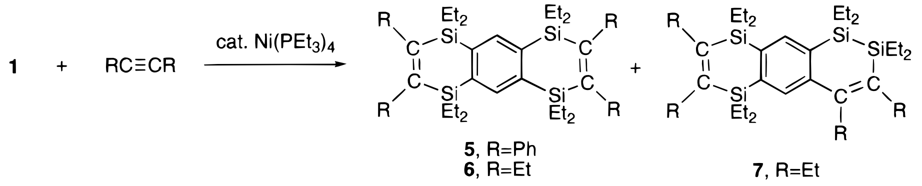
---

[4] Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135.

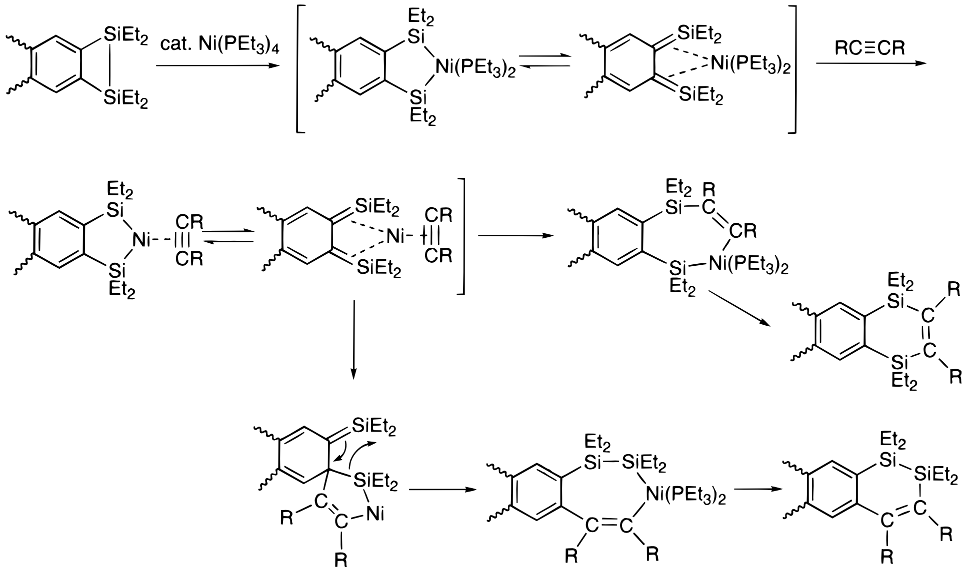
Scheme 2



Scheme 3



Scheme 4



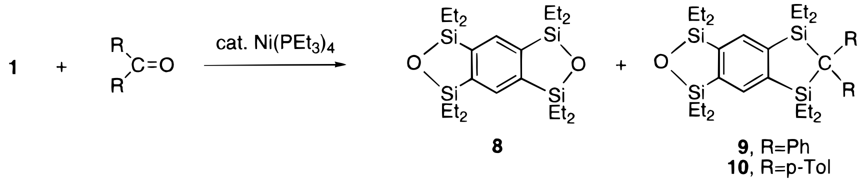
ylphosphine)nickel(0) in a sealed glass tube at 150 °C for 24 h, benzo[1,2:4,5]bis(1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene) (**5**), arising from insertion of a triple bond in diphenylacetylene into the silicon−silicon bonds, was obtained in 91% yield as the sole product. All spectral data for product **5** are identical with those of the authentic sample obtained from the palladium- and platinum-catalyzed reactions of **1** with diphenylacetylene.[1] The similar nickel-catalyzed reaction of **1** with 3-hexyne in a sealed glass tube at 150 °C for 24 h gave two products, benzo[1,2:4,5]bis(1,1,2,3,4,4-hexaethyl-1,4-disilacyclohexa-2,5-diene) (**6**) and its isomer (**7**), in 64% and 25% yield, respectively (Scheme 3). No other products were detected in the reaction mixture by spectrometric analysis and also by GLC analysis. Products **6** and **7** were separated by recycling HPLC. All spectral data for **6** are identical with those of the authentic sample reported previously.[1] The structure of **7** was verified by spectrometric analysis, as well as by elemental analysis (see Experimental Section).

We reported previously that the nickel-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with alkynes produced two regioisomers, 5,6-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene and 5,6-benzo-1,1,2,2-tetraethyl-1,2-disilacyclohexa-3,5-diene, respectively.[5] In these reactions, we proposed that the former product is formed by formal [4 + 2] cycloaddition of an *o*-quinodisilanenickel complex **B** and alkynes, while the latter compound is produced by formal [2 + 2] cycloaddition of **B** and 3-hexyne, followed by ring enlargement of the adduct to the latter compound. In the present reactions, compound **5**−**7** would be produced by a mechanism similar to those of the nickel-catalyzed reactions of the benzodisilacyclobutene with alkynes as shown in Scheme 4.[5] For the formation of **7**, an alternative mechanism involving direct insertion of the nickel species into a silicon−phenylene bond of **1** and then insertion of a triple bond of the 3-hexyne which coordinates to the nickel atom of this intermediate might be considered. However, insertion of the nickel

---

[5] (a) Ishikawa, M.; Sakamoto, H.; Okazaki, S.; Naka, A. *J. Organomet. Chem.* **1992**, *439*, 19. (b) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *499*, 35.

Scheme 5



species into a silicon−phenylene bond seems to be difficult because of the steric hindrance.

In contrast to the palladium- and platinum-catalyzed reactions of **1** with alkenes and alkynes, in which no 1:1 adducts were detected even in the early stages of the reaction, in the present reaction, the 1:1 adducts can be observed in the early stages of the reaction. Thus, treatment of **1** with 3-hexyne in the presence of the nickel catalyst in a sealed tube at 150 °C for 15 min, followed by mass spectrometric analysis of the resulting product, indicated the presence a product whose molecular weight is consistent with that of 1:1 adducts in 28% yield, along with a 19% yield of 1:2 adducts and 33% of the starting compound **1**.

Next, we investigated the nickel-catalyzed reactions of **1** with carbonyl compounds. When the reaction of **1** with benzophenone was carried out in a sealed tube at 150 °C, two products, benzo[1,2:4,5]bis(1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene) (**8**) and benzo[1,2]-(1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene)[4,5]-(1,1,3,3-tetraethyl-2,2-diphenyl-1,3-disilacyclopent-4-ene) (**9**) were obtained in 50% and 40% yields, respectively. No other volatile products were detected by GLC and GPC analysis. The products of **8** and **9** could readily be isolated by column chromatography. All spectral data for **8** were identical with those of the authentic sample reported previously.[1] The similar reaction of **1** with 4,4′-dimethylbenzophenone gave benzo[1,2](1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene)[4,5](1,1,3,3-tetraethyl-2,2-(*p*-tolyl)-1,3-disilacyclopent-4-ene) (**10**) in 19% yield, along with a 50% yield of **8**. Again, compound **10** could be separated from siloxane **8** by a silica gel column. The structures of **9** and **10** were verified by mass, IR, and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis. The ^{13}C NMR spectrum of **9** reveals four resonances at 6.26, 6.69, 7.37, 8.42 ppm, attributed to ethylsilyl carbons, and a single resonance at 41.32 ppm, due to diphenyl-substituted carbon, as well as seven resonances attributed to phenyl and phenylene ring carbons. The ^{29}Si NMR spectrum for **9** shows two resonances at 13.08 and 17.48 ppm. The ^{13}C NMR spectrum of **10** shows resonances at 6.21, 6.69, 7.38, and 8.46 ppm attributed to ethyl carbons and 20.78 and 39.98 ppm due to methyl carbons and di(*p*-tolyl)-substituted carbon, as well as seven resonances attributable to tolyl and phenylene ring carbons. Its ^{29}Si NMR spectrum exhibits two resonances at 12.69 and 17.49 ppm, as expected. These results are wholly consistent with the structures proposed for **9** and **10**.

In both reactions, the siloxane **8** must come from the reaction of **1** with ketones in the presence of the nickel catalyst. Consequently, carbenes, probably, carbene−nickel complexes, must be extruded in the reaction of **1** with ketones. In fact, the production of **9** and **10** can best be understood in terms of the reaction of **1** with a diphenyl carbene−nickel complex and a di(*p*-tolyl)-carbene−nickel complex. For the formation of a carbene−transition metal complex, it has reported that the reaction of $(CO)_4Fe(SiMe_2CH_2CH_2SiMe_2)$ with benzaldehyde gives 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane and an iron carbene complex.[6]

In an attempt to trap the carbene intermediate, we carried out the nickel-catalyzed reaction of **1** with benzophenone in a cyclohexene solution. Thus, when the mixture of **1** and benzophenone was heated to reflux in the presence of the nickel catalyst in cyclohexene for 24 h, 7,7-diphenylnorcarane (**11**) was obtained in 14% yield, in addition to **8** (54% yield) and **9** (4% yield). The formation of **11** clearly indicates that the carbene intermediate is produced in the present reaction as shown in Scheme 6.

Experimental Section

General Procedure. All nickel-catalyzed reactions of compound **1** were carried out in a degassed sealed tube (1.0 cm × 10 cm) with the exception of a carbene trapping experiment. Yields of the products except for a diphenylacetylene adduct were determined by analytical GLC with the use of pentadecane as an internal standard on the basis of the starting compound used. NMR spectra were recorded on a JEOL model JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL model JIR-DIAMOND 20 infrared spectrophotometer. Low-resolution mass spectra were measured on a JEOL model JMS-700 instrument. 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.[7]

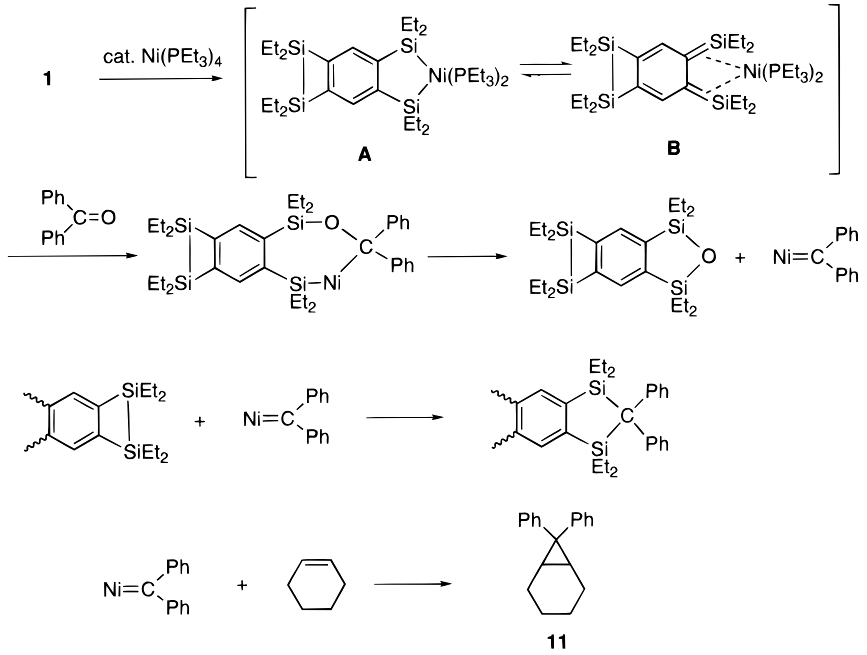
Reaction of 1 with Benzene. A mixture of 0.0858 g (0.205 mmol) of **1** and 0.0073 g (0.0137 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h in a degassed sealed tube. The resulting mixture was passed through a short silica gel column. The mixture was analyzed by GLC as being **2** and **3** (combined yield 81%). The ratio of **2** and **3** was determined to be 1.2:1 by ^{1}H NMR spectrometric analysis. A mixture of **2** and **3** was isolated by recycling HPLC. For **2** and **3**: MS *m/z* 574 (M^+); IR 2953, 2933, 2910, 2873, 2150 (SiH), 1456, 1427, 1232, 1163, 1108, 1007, 972, 800, 709 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.52−0.60 (m, 16H, CH_2Si), 0.79 (m, 24H, CH_3), 0.94 (m, 24H, CH_3), 1.13 (q, 8H, CH_2Si, $J = 7.7$ Hz), 1.16 (q, 8H, CH_2Si, $J = 7.7$ Hz), 4.19 (quint, 2H, SiH, $J = 3.1$ Hz), 4.20 (quint, 2H, SiH, $J = 3.1$ Hz), 7.27−7.31 (m, 5H, phenyl ring protons), 7.43−7.46 (m, 5H, phenyl ring protons), 7.59 (s, 1H, phenylene ring proton), 7.68 (s, 2H, phenylene ring protons), 7.83 (s, 1H, phenylene ring proton); ^{13}C NMR δ ($CDCl_3$) 4.12, 4.17, 5.08 (2C), 7.59 (2C), 8.14 (2C) (EtSi), 127.50 (2C), 128.59, 128.63, 134.95 (2C), 138.28, 138.48, 141.29, 141.74 (2C), 141.97, 142.14, 142.32, 143.17 (phenyl and phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) −10.10 (2Si), −2.90, −2.77. Anal. Calcd for $C_{34}H_{54}Si_4$: C, 71.00; H, 9.46. Found: C, 71.04; H, 9.41.

---

(6) Johnson, D. L.; Gladysz, J. A.; *J. Am. Chem. Soc.* **1979**, *101*, 6433.

(7) Cundy, C. S. *J. Organomet. Chem.* **1974**, *69*, 305.

Scheme 6



Preparation of 4. In a 30 mL flask fitted with a stirrer and reflux condenser was placed 0.1060 g (0.184 mmol) of a mixture of **2** and **3** in 5 mL of carbon tetrachloride. To this was added 0.0004 g (2.3×10^3 mmol) of palladium dichloride, and the mixture was heated to reflux for 40 h. The solvent was evaporated, and then 0.49 mL (0.42 mmol) of a 0.86 M phenyllithium−ether solution was added to the residue at room temperature. After hydrolysis of the resulting mixture 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 magnesium sulfate. The solvent ether was evaporated, and product **4** was isolated by recycling HPLC (61% isolated yield): mp 102−103 °C; MS *m*/*z* 697 (M^+ − Et); IR 3014, 2954, 2869, 1575, 1456, 1427, 1228, 1178, 1108, 1002, 705, 674 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.69−0.80 (m, 40H, EtSi), 7.19−7.34 (m, 20H, phenyl ring protons), 7.89 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 4.91, 7.49 (EtSi), 127.39, 128.61, 134.93, 138.18, 141.25, 146.35 (phenyl and phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) −1.69. Anal. Calcd for $C_{46}H_{62}Si_4$: C, 75.96; H, 8.59. Found: C, 75.79; H, 8.63.

Reaction of 1 with Diphenylacetylene. A mixture of 0.2074 g (0.495 mmol) of **1**, 0.2252 g (1.26 mmol) of diphenylacetylene, and 0.0130 g (0.0245 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h in a degassed sealed tube. The resulting mixture was passed through a short silica gel column to remove nickel species, and product **5** was isolated by recycling HPLC (88% isolated yield). All spectral data for **5** were identical with those of the authentic sample.[1]

Reaction of 1 with 3-Hexyne. A mixture of 0.1768 g (0.422 mmol) of **1**, 0.2010 g (2.45 mmol) of 3-hexyne, and 0.0169 g (0.0318 mmol) of tetrakis(triethylphosphine)nickel (0) was heated at 150 °C for 24 h in a degassed sealed tube. The resulting mixture was passed through a short silica gel column, and the mixture was analyzed by GLC as being **6** (64% yield) and **7** (25% yield). Compounds **6** and **7** were isolated by recycling HPLC. For **7**: mp 133−135 °C; MS *m*/*z* 582 (M^+); IR 2956, 2931, 2908, 2871, 1456, 1413, 1373, 1228, 1149, 1062, 962, 727 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.60 (q, 8H, CH_2Si, $J = 7.6$ Hz), 0.77−1.26 (m, 32H, SiEt), 2.30 (q, 4H, CH_2, $J = 7.6$ Hz), 2.34−2.39 (m, 12H, CH_3), 2.66 (q, 4H, CH_2, $J = 7.6$ Hz), 7.33 (s, 1H, phenylene ring proton), 7.44 (s, 1H, phenylene ring proton); ^{13}C NMR δ ($CDCl_3$) 3.00, 3.81, 6.01, 6.14, 7.70, 7.78, 8.88, 9.06, 13.84, 14.88, 14.90, 14.95, 24.03, 24.07, 25.01, 25.86 (EtSi), 130.81, 133.11, 134.74, 137.94, 139.56, 143.39, 147.42, 151.87, 153.56, 153.86 (phenylene and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −21.96, −19.12, −13.71, 13.39. Anal. Calcd for $C_{34}H_{62}Si_4$: C, 70.02; H, 10.72. Found: C, 69.74; H, 10.60. All spectral data for **6** were identical with those of the authentic sample.[1]

Reaction of 1 with 3-Hexyne for 15 min. A mixture of 0.0440 g (0.105 mmol) of **1**, 0.0273 g (0.333 mmol) of 3-hexyne, and 0.0028 g (0.0053 mmol) of the nickel catalyst was heated at 150 °C for 15 min in a sealed tube. The mixture was passed through a short silica gel column, and then the mixture was analyzed by GC−MS as being **1** (33%), 1:1 adducts (28%), and 1:2 adducts (19%).

Reaction of 1 with Benzophenone. A mixture of 0.3415 g (0.815 mmol) of **1**, 0.3659 g (2.01 mmol) of benzophenone, and 0.0212 g (0.0399 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h in a sealed tube. The resulting mixture was passed through a short silica gel column, and the mixture was analyzed by GLC as being **8** (50% yield) and **9** (40% yield). Compounds **8** and **9** were isolated by column chromatography. For **9**: mp 68−70 °C; MS *m*/*z* 600 (M^+); IR 3025, 2954, 2873, 1594, 1257, 1236, 1006, 916, 798, 728, 700, 526 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.71−1.02 (m, 40H, SiEt), 6.92−7.25 (m, 10H, phenyl ring protons), 7.81 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 6.26, 6.69, 7.37, 8.42 (EtSi), 41.32 (CPh), 124.17, 128.0, 130.53, 136.55, 145.47, 146.07 (phenyl and phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) 13.08, 17.48. Anal. Calcd for $C_{35}H_{52}Si_4O$: C, 69.93; H, 8.72. Found: C, 69.79; H, 8.83. All spectral data for **8** were identical with those of the authentic sample.[1]

Reaction of 1 with 4,4′-Dimethylbenzophenone. A mixture of 0.1890 g (0.451 mmol) of **1**, 0.2178 g (1.04 mmol) of 4,4′-dimethylbenzophenone, and 0.0121 g (0.0228 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h in a sealed tube. The resulting mixture was passed through a short silica gel column, and the mixture was analyzed by GLC as being **8** (50% yield) and **10** (19% yield). Compounds **8** and **10** were isolated by column chromatography. For **10**: mp 133−135 °C; MS *m*/*z* 628 (M^+); IR cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.68−0.92 (m, 28H, SiEt), 1.00 (t, 12H, CH_3, $J = 7.6$ Hz), 2.27 (s, 6H, Me), 6.80 (d, 4H, $J = 7.9$ Hz, phenyl ring protons), 6.95 (d, 4H, $J = 7.9$ Hz, phenyl ring protons), 7.80 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 6.21, 6.69, 7.38, 8.46 (EtSi), 20.78 (Me), 39.98 (Si*C*Si), 128.68, 130.35, 133.38, 136.52, 142.36, 145.89, 148.75 (phenyl and phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) 12.69, 17.49. Anal. Calcd for $C_{37}H_{56}Si_4O$: C, 70.63; H, 8.97. Found: C, 70.62; H, 8.99. All spectral data for **8** were identical with those of the authentic sample.[1]

Reaction of 1 with Benzophenone in Refluxing Cyclohexene. In a 30 mL two-necked flask fitted with a condenser was placed 0.1628 g (0.389 mmol) of **1**, 0.2116 g (1.16 mmol) of benzophenone, and 0.0115 g (0.0216 mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of cyclohexene. The mixture was heated to reflux for 24 h. GLC analysis of the reaction mixture showed the presence of **8** (54% yield), **9** (4% yield), and **11** (14% yield). The solvent cyclohexene was evaporated, and the residue was treated with a short silica gel column to remove nickel species from the reaction mixture. Compounds **8**, **9**, and **11** were isolated by MPLC. All spectral data for **8**, **9**, and **11**[8] were identical with those of the authentic samples.

Acknowledgment. This work was supported in part by a Grant-in-Aid (No. 10133257) from the Ministry of Education, Science, and Culture, and the project of the Institute for Fundamental Chemistry supported by JSPS-Research for the Future Program (JSPS-PFTF96P00206), to which our thanks are due. We also express our appreciation to Toshiba Silicone Co. Ltd., Sumitomo Electric Industry Ltd., and Tokuyama Corp. for financial support.

OM9903588

---

[8] Ishikawa, M.; Naka, A.; Okazaki, S.; Sakamoto, H. *Organometallics* **1993**, *12*, 87.