

Silicon–Carbon Unsaturated Compounds. 56. Nickel-Catalyzed Reaction of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with Bis(trimethylsilyl)acetylene

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The reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) with bis(trimethylsilyl)acetylene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel (**0**) in a sealed glass tube at 150 °C for 24 h gave 5,6-benzo-1,1,4,4-tetraethyl-2,3-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**2**), 4,5-benzo-1,1,3,3-tetraethyl-2-[bis(trimethylsilyl)methylene]-1,3-disilacyclopent-4-ene (**3**), 5,5,6,6,11,11,12,12-octaethyl-5,6,11,12-tetrasilanaphthacene (**4**), and 1,1'-bis(3,4-benzo-2,2,5,5-tetraethyl-2,5-disilacyclopent-3-enylidene) (**5**), in 10%, 21%, 41%, and 9% yields, in addition to a 34% yield of hexamethyldisilane. Similar reaction of **1** with bis(trimethylsilyl)acetylene in the presence of dimethylphenylsilane produced 5,6-benzo-1,1,4,4-tetraethyl-2-(dimethylphenylsilyl)-1,4-disilacyclohexa-2,5-diene (**12**) in 7% yield, along with **2** and **3**. Treatment of **2** with dimethylphenylsilane in the presence of the nickel catalyst afforded **12** in 29% yield, together with a 28% yield of hexamethyldisilane and a trace amount of 4,5-benzo-1,1,3,3-tetraethyl-2-[(dimethylphenylsilyl)methylene]-1,3-disilacyclopent-4-ene (**13**). Similar treatment of **3** with dimethylphenylsilane again gave **12** and **13** in 30% and 1% yields, respectively, in addition to a 32% yield of hexamethyldisilane.

Introduction

The reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) with organic substrates, such as aromatic compounds, carbonyl compounds, alkenes, and alkynes, in the presence of a catalytic amount of transition-metal complexes afford various types of products¹ as shown in Figure 1. The types of products thus formed depend highly on the nature of the metal in the reactive species formed from the reaction of **1** with the transition-metal complexes used as the catalyst. For example, the palladium(0)- and platinum(0)-catalyzed reactions of **1** with alkynes, such as 1-hexyne, phenylacetylene, 3-hexyne, and diphenylacetylene, produce 5,6-benzo-1,4-disilacyclohexa-2,5-dienes, arising from formal insertion of a triple bond into a silicon–silicon bond in **1**, as the sole product. In marked contrast to these reactions, the nickel-catalyzed reactions of **1** with monosubstituted acetylenes afford no adducts; only polymeric substances are produced. However, with disubstituted acetylenes such as 3-hexyne and diphenylacetylene in the presence of the nickel catalyst, **1** gives two isomers of adducts, 5,6-benzo-1,4-disilacyclohexa-2,5-dienes and 5,6-benzo-1,2-disilacyclohexa-3,5-dienes, derived from formal insertion of a triple bond into a

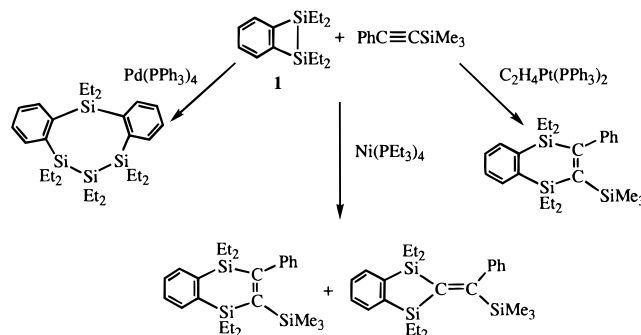


Figure 1.

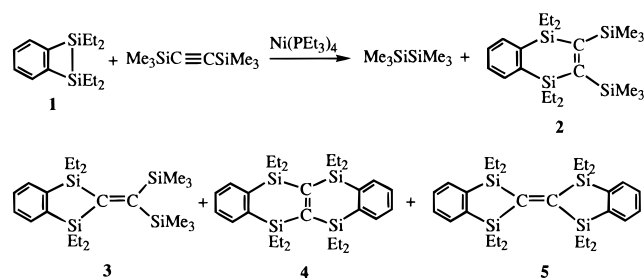
silicon–phenylene bond.² The reaction of **1** with phenyl(trimethylsilyl)acetylene in the presence of the palladium(0) catalyst gives no adduct but produces a dimer of **1** in high yield.^{1e} The platinum-catalyzed reaction of **1** with the same alkyne proceeds smoothly to give an adduct, 5,6-benzo-1,4-disilacyclohexa-2,5-diene, as the sole product.^{1d} The similar reaction of **1** in the presence of the nickel(0) catalyst affords two products, 5,6-benzo-1,4-disilacyclohexa-2,5-diene and 4,5-benzo-2-[phenyl(trimethylsilyl)methylene]-1,3-disilacyclopentene derived from a 1,2-trimethylsilyl shift in phenyl(trimethylsilyl)acetylene.²

We were interested in the formation of the product involving a 1,2-silyl shift and investigated the transition-metal-catalyzed reactions of **1** with silyl-substituted alkynes. In this paper we report the nickel(0)-catalyzed reaction of **1** with bis(trimethylsilyl)acetylene.

* Abstract published in *Advance ACS Abstracts*, January 15, 1996.
(1) (a) Ishikawa, M.; Naka, A. *Synlett* **1995**, 794. (b) Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135. (c) Ishikawa, M.; Naka, A.; Okazaki, S.; Sakamoto, H. *Organometallics* **1993**, *12*, 87. (d) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1993**, *12*, 4987. (e) Naka, A.; Hayashi, M.; Okazaki, S.; Ishikawa, M. *Organometallics* **1994**, *13*, 4994. (f) Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawauchi, S.; Yamabe, T. *Organometallics* **1995**, *14*, 114.

(2) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *499*, 35.

Scheme 1



Results and Discussion

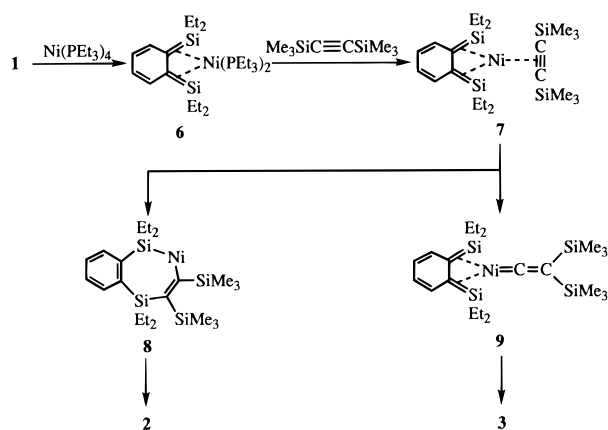
In contrast to the palladium(0)- and platinum(0)-catalyzed reaction of **1** with bis(trimethylsilyl)acetylene, in which no adduct was detected in the resulting mixture under the various conditions, the nickel-catalyzed reaction proceeds readily to give five products. Thus, treatment of **1** with 1.4 equiv of bis(trimethylsilyl)acetylene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in a degassed sealed glass tube at 150 °C for 24 h gave 5,6-benzo-1,1,4,4-tetraethyl-2,3-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**2**), 4,5-benzo-1,1,3,3-tetraethyl-2-bis(trimethylsilyl)methylene-1,3-disilacyclopent-4-ene (**3**), 5,5,6,6,11,11,12,12-octaethyl-5,6,11,12-tetrasilanaphthacene (**4**), and 1,1'-bis(3,4-benzo-2,2,5,5-tetraethyl-2,5-disilacyclopent-3-enylidene) (**5**), in 10%, 21%, 41%, and 9% yields, respectively, along with a 34% yield of hexamethyldisilane (Scheme 1). Products **2**–**5** were isolated by recycling HPLC, after treatment of the reaction mixture with a short column to remove the nickel catalyst. The structures of products **2**–**5** were verified by spectrometric and elemental analysis (see Experimental Section).

The mass spectrum for **4** shows a parent ion at m/z 520, corresponding to the calculated molecular weight for $\text{C}_{30}\text{H}_{48}\text{Si}_4$ (2:1 adduct – $\text{Me}_3\text{SiSiMe}_3$). ^1H , ^{13}C , and ^{29}Si NMR spectra for **4** exhibit simple resonance patterns. Its ^{13}C NMR spectrum shows two resonances at 7.6 and 8.2 ppm, attributed to four equivalent EtSi groups, three resonances at 127.6, 132.8, and 143.2 ppm, due to phenylene carbons, and a single resonance at 188.2 ppm, attributed to olefinic carbons. The ^{29}Si NMR spectrum of **4** reveals a single resonance at –20.6 ppm whose chemical shift is consistent with that of the silicon atoms in the 5,6-benzo-1,4-disilacyclohexa-2,5-diene rings. The resonances of the silicon atoms in the 5,6-benzo-1,4-disilacyclohexa-2,5-dienes observed so far always appear at higher field (–19 to –12 ppm) than those of the 4,5-benzo-1,3-disilacyclopent-4-ene rings (–0.5 to 4 ppm).

The mass spectrum of **5** shows a parent ion at m/z 520, corresponding to the same molecular weight as that of **4**. Its ^{13}C NMR spectrum reveals two resonances at 7.8 and 8.2 ppm, three resonances at 128.3, 132.4, and 148.1 ppm, and a single resonance at 191.2 ppm, due to Et_2Si carbons, phenylene ring carbons, and olefinic carbons, respectively. The ^{29}Si NMR spectrum shows a single resonance at –2.7 ppm at much lower field than that of the silicon atoms in the 5,6-benzo-1,4-disilacyclohexa-2,5-diene rings, indicating that compound **5** must have a 4,5-benzo-1,3-disilacyclopent-4-ene structure.

As reported recently in the nickel-catalyzed reaction of **1** with disubstituted acetylenes,² the formation of

Scheme 2



product **2** can be best understood by a series of reactions including coordination of bis(trimethylsilyl)acetylene to (*o*-quinodisilane)nickel complex **6** to produce complex **7**, followed by insertion of a triple bond into a silicon–nickel bond to give 3,4-benzo-2,2,5,5-tetraethyl-6,7-bis(trimethylsilyl)-1-nickela-2,5-disilacyclohepta-3,6-diene (**8**) and then reductive elimination of the nickel species from intermediate **8**, as shown in Scheme 2. Product **3** may be explained in terms of oxidative addition of an *sp*-hybridized C–Si bond of the coordinated bis(trimethylsilyl)acetylene in complex **7** to the nickel atom, followed by a shift of the trimethylsilyl group from this nickel atom to the trimethylsilyl-substituted *sp* carbon, giving (vinylidene)nickel complex (**9**). Such a trimethylsilyl shift has been observed in the nickel-catalyzed reaction of **1** with the trimethylsilyl-substituted acetylene as mentioned above² and also in the reaction of transition-metal complexes with silyl-substituted acetylenes.^{3–5} At present, evidence for the formation of intermediates **7**–**9** has not yet been obtained.

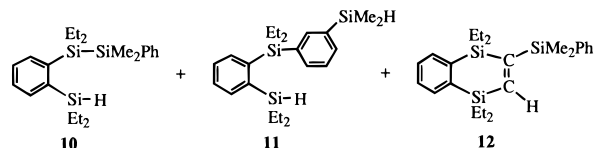
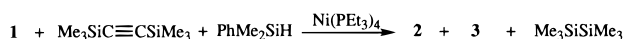
The formation of products **4** and **5** is of considerable interest, because elimination of hexamethyldisilane from bis(trimethylsilyl)acetylene must be involved in the present nickel-catalyzed reaction. In order to learn more about the formation of **4** and **5**, we carried out the same reaction in the presence of a hydrosilane in the hope of trapping the reactive nickel species. Thus, the nickel-catalyzed reaction of **1** with bis(trimethylsilyl)acetylene in the presence of 5.6 equiv of dimethylphenylsilane under the same conditions afforded products **2**, **3**, 1-[(1,1-diethyl-2,2-dimethylphenyl)disilanyl]-2-(diethylsilyl)benzene (**10**), 1-[diethyl(*m*-(dimethylsilyl)phenyl)silyl]-2-(diethylsilyl)benzene (**11**), and 5,6-benzo-1,1,4,4-tetraethyl-2-(dimethylphenylsilyl)-1,4-disilacyclohexa-2,5-diene (**12**) in 7%, 23%, 21%, 6%, and 7% yields, respectively, in addition to a 6% yield of hexamethyldisilane (Scheme 3). No detectable amount of products **4** and **5** was observed in this reaction. Products **10** and **11** can be expected to be produced from a direct reaction of (*o*-quinodisilane)nickel complex **6** with the hydrosilane. To confirm this, we carried out the reaction of **1** with dimethylphenylsilane in the presence

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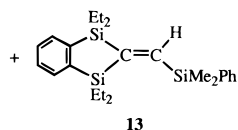
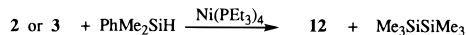
(4) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089.

(5) Sakurai, H.; Hiram, K.; Nakadaira, Y.; Kabuto, C. *J. Am. Chem. Soc.* **1987**, *109*, 6880.

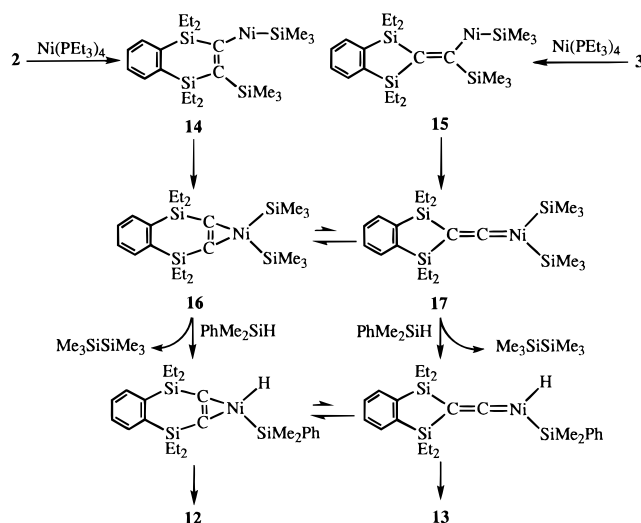
Scheme 3



Scheme 4



Scheme 5



of tetrakis(triethylphosphine)nickel(0) under the same conditions. Adduct **10** was obtained in 52% yield, in addition to a 3% yield of **11**. The structures of **10** and **11** were confirmed by spectrometric and elemental analysis (see Experimental Section). The formation of **10** can be explained in terms of 1,4-addition of a Si–H bond to **6**, while **11** may be understood by oxidative addition of a C–H bond of the phenyl ring in dimethylphenylsilane to **6**. Such sp^2 -hybridized C–H bond activation of the aryl ring has been observed in the nickel-catalyzed reactions of **1** with aromatic compounds.^{1b,6}

The ²⁹Si NMR spectrum for **12** shows two resonances at –19.9 and –13.0 ppm due to the ring silicon atoms and a single resonance at –9.2 ppm attributed to the (dimethylphenyl)silyl silicon atom. The chemical shifts at –19.9 and –13.0 ppm due to the ring silicon atoms in **12** clearly indicates that this compound must have a 5,6-benzo-1,4-disilacyclohexa-2,5-diene structure. Furthermore, all spectral data for **12** were identical with those of the authentic sample prepared from the palladium-catalyzed reaction of **1** with [(dimethylphenyl)silyl]acetylene.⁷

The formation of product **12** is interesting, because this compound seems to have been produced from the reaction of a reactive intermediate involving a nickel atom with the hydrosilane. In order to learn more about the reactive species which is involved in the present reaction, we treated compounds **2** and **3** with (dimethylphenyl)silane in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0). Treatment of **2** with (dimethylphenyl)silane in the presence of the nickel catalyst in a sealed tube at 190 °C for 24 h afforded product **12** and hexamethyldisilane in 29% and 28% yields, respectively, along with 52% of the unreacted starting compound **2** (Scheme 4). A trace amount of the other isomer of **12** (less than 1% yield) was detected by mass spectrometric analysis of the reaction mixture. The reaction of **3** with (dimethylphenyl)silane under the same conditions again gave **12** and hexamethyldisilane in 30% and 32% yields, together with 10% of the unchanged starting compound **3**. In this reaction, the compound identified as 4,5-benzo-1,1,3,3-

tetraethyl-2-[(dimethylphenyl)silyl]methylene]-1,3-disilacyclohexa-2,5-diene (**13**) was obtained in ca. 1% yield. Mass fragmentation patterns of **13** thus obtained were identical with those of the isomer of **12**, which was detected in the above reaction. Products **12** and **13** were readily isolated by recycling HPLC.

In an effort to prepare compound **13** by an independent route, we found that the reaction of **1** with [(dimethylphenyl)silyl]acetylene in the presence of a catalytic amount of (η^2 -ethylene)bis(triphenylphosphine)platinum(0) in refluxing benzene for 3 h afforded adduct **13** in 70% yield, along with a 23% yield of **12** whose spectral data were identical with those of compound obtained by the palladium-catalyzed reaction of **1** with [(dimethylphenyl)silyl]acetylene. The mass spectrum of **13** reveals a parent ion at m/z 408, corresponding to the same molecular weight as **12**. All spectral data for the compound obtained from the platinum-catalyzed reaction of **1** with [(dimethylphenyl)silyl]acetylene were identical with those of **13** isolated from the reaction of **3** with (dimethylphenyl)silane in the presence of the nickel catalyst.

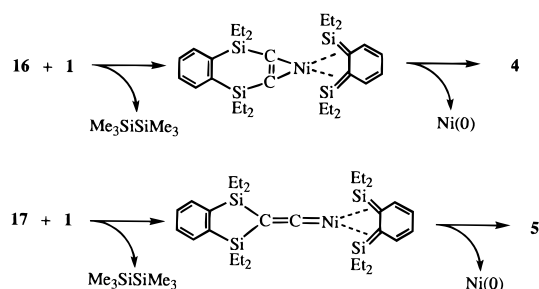
On the other hand, treatment of compounds **2** and **3** with a catalytic amount of tetrakis(triethylphosphine)nickel(0) under the same conditions afforded no isomerization products, but the starting compounds **2** and **3** were recovered unchanged. The result indicates that no equilibrium between **2** and **3** in the presence of the nickel catalyst is involved in the present reaction. Similar reactions of **4** and **5** with the nickel catalyst gave no isomers, but again the starting compounds **4** and **5** were recovered unchanged.

The formation of **12** and **13** in the reactions of **2** and **3** with (dimethylphenyl)silane in the presence of the nickel catalyst can best be explained by a series of the reactions shown in Scheme 5. Insertion of a nickel species into one of two trimethylsilyl–carbon bonds in **2** and **3** gives nickel complexes **14** and **15**, respectively. A trimethylsilyl shift from sp^2 -hybridized carbon to a nickel atom in **14** and **15** would produce the reactive nickelacyclopropene derivative **16** and vinylidene carbene–nickel complex **17**, respectively. The reaction of these nickel species with (dimethylphenyl)silane affords the observed products **12** and **13** and also hexamethyldisilane. Presumably, nickelacyclopropene derivative **16** is thermodynamically more favored than vinylidene

(6) For C–H bond activation by transition-metal catalysts, see: Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. Tanaka, M.; Sakakura, T. *Pure Appl. Chem.* **1990**, *62*, 1147.

(7) Naka, A.; Okada, T.; Ishikawa, M. Manuscript in preparation. The palladium-catalyzed reactions of **1** with alkynes always afford 5,6-benzo-1,4-disilacyclohexa-2,5-dienes as the sole product.

Scheme 6



carbene–nickel complex **17**. This may be ascribed to the higher yield of **12** than **13**. In fact, the synthesis of various types of three-membered nickelacycles with the general formula $L_2Ni(RC\equiv CR')$, analogous to **16**, has been reported by Bartik et al.⁸ and also by Rosenthal et al.⁹

One might consider the possibility that the nickel catalyst reacts with bis(trimethylsilyl)acetylene to give a reactive ethynylene–nickel species and hexamethyldisilane and the resulting ethynylene–nickel species inserts into a silicon–silicon bond in **1** to give nickel-containing cyclic system analogous to **16**. To confirm this, we carried out the reaction of bis(trimethylsilyl)acetylene with 45 mol % of tetrakis(triethylphosphine)nickel(0) under the same conditions. However, no hexamethyldisilane was detected at all by GC–mass spectrometric analysis of the reaction mixture, although a small amount of a product whose mass spectrum shows an ion peak at m/z 367 (dimer – Me_3Si). In this reaction, 85% of the starting compound **1** was recovered unchanged.

On the basis of the results obtained so far, we propose the mechanism for the formation of products **4** and **5**, as shown in Scheme 6. For compound **4**, isomerization of 3,4-benzo-1-nickeladisilacycloheptadiene (**8**), formed from the reaction of (*o*-quinodisilane)nickel complex **6** with bis(trimethylsilyl)acetylene, to another nickelacyclopentadiene derivative **16**, would be involved. Addition of a silicon–silicon bond of **1** to complex **16**, with simultaneous elimination of hexamethyldisilane, and then reductive elimination of nickel species from the resulting complex would produce **4**. On the other hand, the production of **5** can be understood by the reaction of carbene–nickel complex **17** with **1**. As we reported previously, that the carbene–nickel complexes are produced in the nickel-catalyzed reaction of **1** with a non-enolizable ketone such as benzophenone and insert into a silicon–silicon bond in **1** has been observed.^{1c}

In conclusion, the nickel-catalyzed reaction of benzo-disilacyclobutene **1** with bis(trimethylsilyl)acetylene afforded two isomers of a 1:1 adduct and two isomers composed of two molecules of **1** and a C_2 moiety arising from formal elimination of hexamethyldisilane from bis(trimethylsilyl)acetylene. Reactive nickel complexes, nickelacyclopentadiene **16** and carbene–nickel complex **17**, could be trapped by the use of (dimethylphenyl)silane.

Experimental Section

General Procedure. All nickel-catalyzed reactions were carried out in a degassed sealed glass tube (1.0 cm \times 10 cm). Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard, on the basis of the starting compounds used. 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. Gel permeation chromatographic separation was performed with a Model LC-908 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.).

Materials. 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) was prepared as reported previously.¹⁰

Reaction of 1 with Bis(trimethylsilyl)acetylene. A mixture of 0.605 g (2.43 mmol) of **1**, 0.583 g (3.42 mmol) of bis(trimethylsilyl)acetylene, and 0.061 g (0.012 mmol) of tetrakis(triethylphosphine)nickel(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was treated with a short silica gel column to remove the nickel species from the reaction mixture. The mixture was analyzed by GLC as being **2** and **3** (31% combined yield), **4** and **5** (50% combined yield), and hexamethyldisilane (34%). The ratios of **2** and **3** and **4** and **5** were determined to be 1:2.1 and 4.6:1, respectively, by ¹H NMR spectrometric analysis. Compounds **2**–**5** were isolated by recycling HPLC. Data for **2**: mp 78–80 °C; MS m/z 418 (M^+); IR 3037, 2952, 2878, 1458, 1421, 1249, 1117, 998, 839, 761, 670 cm^{-1} ; ¹H NMR δ ($CDCl_3$) 0.34 (s, 18H, Me_3Si), 0.71–1.01 (m, 20H, EtSi), 7.24–7.46 (m, 4H, phenylene ring protons); ¹³C NMR δ ($CDCl_3$) 5.1 (Me_3Si), 8.2, 8.3 (EtSi), 127.6, 131.9, 144.5 (phenylene ring carbons), 186.1 (olefinic carbons); ²⁹Si NMR δ ($CDCl_3$) –18.5, –12.9. Anal. Calcd for $C_{22}H_{42}Si_4$: C, 63.08; H, 10.11. Found: C, 63.05; H, 10.09. Data for **3**: mp 43–45 °C; MS m/z 418 (M^+); IR 3037, 2956, 2878, 1459, 1421, 1250, 1124, 1000, 843, 759, 600 cm^{-1} ; ¹H NMR δ ($CDCl_3$) 0.30 (s, 18H, Me_3Si), 0.79–0.99 (m, 20H, EtSi), 7.34–7.57 (m, 4H, phenylene ring protons); ¹³C NMR δ ($CDCl_3$) 4.5 (Me_3Si), 8.5, 9.1 (EtSi), 128.1, 131.8, 148.9 (phenylene ring carbons), 179.4, 193.2 (olefinic carbons); ²⁹Si NMR δ ($CDCl_3$) –9.1, –2.3. Anal. Calcd for $C_{22}H_{42}Si_4$: C, 63.08; H, 10.11. Found: C, 63.07; H, 10.07. Data for **4**: mp 170–171 °C; MS m/z 520 (M^+); IR 3045, 2954, 1459, 1417, 1224, 1120, 1060, 998, 794, 753, 655 cm^{-1} ; ¹H NMR δ ($CDCl_3$) 0.79–1.04 (m, 40H, EtSi), 7.32–7.53 (m, 8H, phenylene ring protons); ¹³C NMR δ ($CDCl_3$) 7.6, 8.2 (EtSi), 127.6, 132.8, 143.2 (phenylene ring carbons), 188.2 (olefinic carbon); ²⁹Si NMR δ ($CDCl_3$) –20.6. Anal. Calcd for $C_{30}H_{48}Si_4$: C, 69.15; H, 9.29. Found: C, 69.00; H, 9.29. Data for **5**: mp 171–173 °C; MS m/z 520 (M^+); IR 3044, 2948, 2876, 1458, 1422, 1260, 1122, 1014, 996, 803, 755, 695, 605 cm^{-1} ; ¹H NMR δ ($CDCl_3$) 0.75–0.94 (m, 40H, EtSi), 7.33–7.56 (m, 8H, phenylene ring protons); ¹³C NMR δ ($CDCl_3$) 7.8, 8.2 (EtSi), 128.3, 132.4, 148.1 (phenylene ring carbons), 191.2 (olefinic carbon); ²⁹Si NMR δ ($CDCl_3$) –2.7. Anal. Calcd for $C_{30}H_{48}Si_4$: C, 69.15; H, 9.29. Found: C, 69.11; H, 9.03.

Reaction of 1 with Bis(trimethylsilyl)acetylene in the Presence of (Dimethylphenyl)silane. A mixture of 0.331 g (1.33 mmol) of **1**, 0.263 g (1.54 mmol) of bis(trimethylsilyl)acetylene, 0.061 g (0.012 mmol) of tetrakis(triethylphosphine)nickel(0), and 1.015 g (7.46 mmol) of (dimethylphenyl)silane in a sealed glass tube was heated at 150 °C for 24 h. The mixture was treated with a short silica gel column and analyzed by GLC as being **2** and **3** (30% combined yield), **10** (21% yield), **11** (6% yield), **12** (7% yield), and hexamethyldisilane (6% yield). The ratio of **2** and **3** was determined to be 1:3.3 by ¹H NMR spectrometric analysis. Compound **2**, **3**, and **10**–**12** was isolated by recycling HPLC. All spectral data for **2** and **3** were identical with those of the authentic samples.

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Data for **10**: MS m/z 369 ($M^+ - Me$); IR 3045, 2953, 2872, 2142, 1459, 1426, 1376, 1242, 1106, 1009, 972, 834, 808, 753, 698 cm^{-1} ; 1H NMR δ ($CDCl_3$) 0.37 (s, 18H, Me_2Si), 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 ($CDCl_3$) –2.0 (Me_2Si), 4.4, 5.2, 8.2, 8.3 (EtSi), 127.1, 127.5, 127.9, 128.1, 133.9, 135.0, 135.8, 140.1, 143.2, 144.0 (phenyl and phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) –21.6, –12.9, –9.8. Anal. Calcd for $C_{22}H_{36}Si_3$: C, 68.67; H, 9.43. Found: C, 68.68; H, 9.46. Data for **11**: MS m/z 384 (M^+); IR 3043, 2952, 2873, 2151, 2120, 1456, 1416, 1364, 1249, 1106, 1056, 1008, 972, 881, 816, 806, 776, 739, 679 cm^{-1} ; 1H NMR δ ($CDCl_3$) 0.28 (d, 6H, Me_2Si , $J = 3.9$ Hz), 0.31–1.25 (m, 20H, EtSi), 4.21 (quint, 1H, HEt_2Si , $J = 3.3$ Hz), 4.36 (sep, 1H, HMe_2Si , $J = 3.9$ Hz), 7.25–7.65 (m, 8H, phenyl and phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) –3.8 (Me_2Si), 4.2, 5.0, 7.6, 8.2 (EtSi), 126.9, 127.8, 127.9, 134.2, 135.0, 135.9, 136.1 (2C), 137.7, 140.6, 143.1, 143.6 (phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) –17.2, –9.7, –3.4. Anal. Calcd for $C_{22}H_{36}Si_3$: C, 68.67; H, 9.43. Found: C, 68.80; H, 9.37. Data for **12**: MS m/z 408 (M^+); IR 2954, 2872, 1458, 1246, 1112, 1000, 887, 810, 733, 700 cm^{-1} ; 1H NMR δ ($CDCl_3$) 0.45 (s, 6H, Me_2Si), 0.55–0.90 (m, 20H, EtSi), 7.30–7.55 (m, 9H, phenyl and phenylene ring protons), 7.76 (s, 1H, olefinic protons); ^{13}C NMR δ ($CDCl_3$) –1.5 (Me_2Si), 6.0, 7.0, 7.6, 7.7 (EtSi), 127.5, 127.6, 127.9, 128.8, 133.0, 133.1, 134.1, 139.1, 142.8, 144.0 (phenyl and phenylene ring carbons), 164.7, 165.6 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) –19.9, –13.0, –9.2. Anal. Calcd for $C_{24}H_{36}Si_3$: C, 70.51; H, 8.88. Found: C, 70.48; H, 9.17.

Reaction of 1 with (Dimethylphenyl)silane. A mixture of 0.111 g (0.447 mmol) of **1**, 0.011 g (0.021 mmol) of tetrakis(triethylphosphine)nickel(0), and 0.192 g (1.41 mmol) of (dimethylphenyl)silane in a sealed glass tube was heated at 150 °C for 24 h. The mixture was treated with a short silica gel column, and the resulting solution was analyzed by GLC as being **10** (52% yield), **11** (3% yield), and the starting compound **1** (4%). Compounds **10** and **11** were isolated by recycling HPLC. All spectral data for **10** and **11** were identical with those of products **10** and **11** obtained from the reaction described above.

Reaction of 1 with [(Dimethylphenyl)silyl]acetylene in the Presence of a Platinum(0) Catalyst. Into a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.039 g (0.157 mmol) of **1**, 0.061 g (0.381 mmol) of ((dimethylphenyl)silyl)acetylene, and 0.006 g (0.008 mmol) of (η^2 -ethylene)bis(triphenylphosphine)platinum(0) in 5 mL of dry benzene. The mixture was heated to reflux for 3 h and then treated with a short silica gel column. The mixture was analyzed by GLC as being **12** and **13** (93% combined yield). The ratio of **12** and **13** was determined to be 1:3 by 1H NMR spectrometric analysis. Compounds **12** and **13** was isolated by recycling HPLC. All spectral data for **12** were identical with those of an authentic sample obtained from the above reaction. Data for **13**: MS m/z 408 (M^+); IR 3046, 2955, 2861,

1461, 1414, 1243, 1120, 1009, 961, 829, 808, 735, 697 cm^{-1} ; 1H NMR δ ($CDCl_3$) 0.45 (s, 6H, Me_2Si), 0.57–0.93 (m, 20H, EtSi), 7.35–7.58 (m, 9H, phenyl and phenylene ring protons), 7.86 (s, 1H, olefinic proton); ^{13}C NMR δ ($CDCl_3$) –1.4 (Me_2Si), 6.0, 7.1, 7.6, 7.9 (EtSi), 127.8, 128.2, 128.5, 129.1, 132.7, 132.8, 134.1, 138.9, 147.5, 149.1 (phenyl and phenylene ring carbons), 165.1, 165.7 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) –15.2, –1.6, 2.6. Anal. Calcd for $C_{24}H_{36}Si_3$: C, 70.51; H, 8.88. Found: C, 70.30; H, 8.71.

Reaction of 2 with (Dimethylphenyl)silane. A mixture of 0.023 g (0.055 mmol) of **2**, 0.003 g (0.005 mmol) of tetrakis(triethylphosphine)nickel(0), and 0.071 g (0.522 mmol) of (dimethylphenyl)silane in a sealed glass tube was heated at 190 °C for 24 h. After the resulting mixture was treated with a short silica gel column, the mixture was analyzed by GLC as being **12** and **13** (29% combined yield), hexamethyldisilane (28% yield), and the starting compound **2** (52%). The ratio of **12** (29% yield) and **13** (less than 1%) was determined by 1H NMR spectrometric analysis. Compounds **12** and **13** were isolated by recycling HPLC. All spectral data for **12** were identical with those of the authentic samples. Fragmentation patterns of the mass spectrum for **13** were identical with those of an authentic sample.

Reaction of 3 with (Dimethylphenyl)silane. A mixture of 0.036 g (0.086 mmol) of **3**, 0.004 g (0.008 mmol) of tetrakis(triethylphosphine)nickel(0), and 0.048 g (0.353 mmol) of (dimethylphenyl)silane in a sealed glass tube was heated at 190 °C for 24 h. The mixture was treated with a short silica gel column and analyzed by GLC as being **11** and **12** (31% yield), hexamethyldisilane (32% yield), and the starting compound **3** (10%). The ratio of **12** (30% yield) and **13** (1%) was determined by 1H NMR spectrometric analysis. Compounds **12** and **13** were isolated by recycling HPLC. All spectral data for **12** and **13** were identical with those of the authentic samples.

Reaction of Bis(trimethylsilyl)acetylene with 45 mol% of Nickel Catalyst. A mixture of 0.073 g (0.429 mmol) of bis(trimethylsilyl)acetylene and 0.103 g (0.194 mmol) of tetrakis(triethylphosphine)nickel(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was analyzed by GC–mass spectrometry as being a dimer (10% yield, MS m/z 367) and the starting compound (85%).

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