

# Nickel-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with Carbonyl Compounds

Mitsuo Ishikawa,\* Akinobu Naka, Shougo Okazaki, and Hiromu Sakamoto

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan

Received June 9, 1992

The reaction of 3,4-benzo-1,1,2,2-tetraethyl-disilacyclobut-3-ene (1) with benzaldehyde in the presence of a catalytic amount of  $\text{Ni}(\text{PEt}_3)_4$  at 150 °C afforded 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene in 75% yield. Similar nickel-catalyzed reaction of 1 with acetone gave 5,6-benzo-1,1,4,4-tetraethyl-3,3-dimethyl-2-oxa-1,4-disilacyclohex-5-ene, 1-[diethyl(isopropenyloxy)silyl]-2-(diethylsilyl)benzene, and 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene (6) in 26%, 31%, and 24% yields, respectively. Treatment of 1 with acetophenone, pinacolone, and propiophenone afforded the respective adducts, 1-[diethyl[(1-phenylvinyl)oxy]silyl]-, 1-[[1-(*tert*-butylvinyl)oxy]diethylsilyl]-, and 1-[diethyl[(1-propenyl)oxy]silyl]-2-(diethylsilyl)benzene, in 59%, 27%, and 70% yields, respectively, in addition to 6. Similar treatment of 1 with benzophenone produced 4,5-benzo-1,1,3,3-tetraethyl-2,2-diphenyl-1,3-disilacyclopent-4-ene and 6 in 20% and 57% yields, while with 4,4'-dimethylbenzophenone, 1 gave 4,5-benzo-1,1,3,3-tetraethyl-2,2-di(*p*-tolyl)-1,3-disilacyclopent-4-ene and 6 in 16% and 37% yields. The reaction of 1 with benzophenone in the presence of the nickel catalyst in refluxing cyclohexene gave 7,7-diphenylnorcaradiene and 6 in 39% and 57% yields.

## Introduction

3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (1) shows interesting chemical behavior. Thermolysis of this compound affords an *o*-quinodisilane which reacts with acetylenes to give [4 + 2] cycloadducts.<sup>1,2</sup> The photolysis of 1, however, gives a different reactive intermediate from the *o*-quinodisilane, 1-ethyl-1-[*o*-(diethylsilyl)phenyl]-1-silapropene derived from homolytic scission of a silicon-silicon bond, followed by intramolecular disproportionation of the resulting diradical.<sup>3</sup> Recently we have found that the reaction of 1 with arenes such as benzene, toluene, and xylene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) produces 1-(arenyldiethylsilyl)-2-(diethylsilyl)benzenes arising from C-H bond activation of arenes.<sup>4</sup> In these reactions, we proposed the formation of the reactive intermediates, 3,4-benzo-1,1-bis(triethylphosphonio)-2,2,5,5-tetraethyl-1-nickela-2,5-disilacyclopent-3-ene and an *o*-quinodisilane-nickel complex, in which an arene molecule can coordinate to the nickel atom. In order to get more information about the chemical behavior of the nickel complex, we initiated systematic investigation concerning the nickel-catalyzed reaction of 1 with various unsaturated compounds. In this paper we report the reaction of 1 with carbonyl compounds in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0).

## Results and Discussion

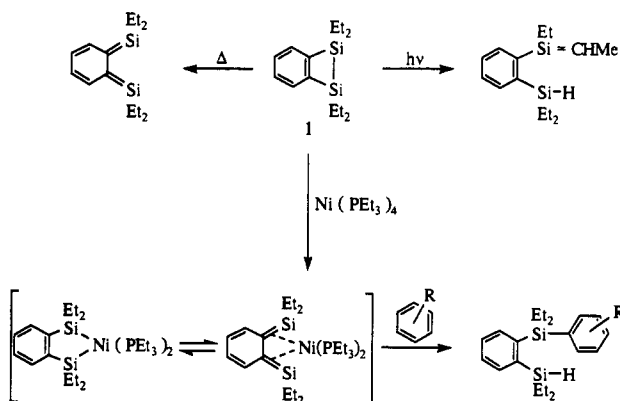
When a mixture of 3,4-benzo-1,1,2,2-tetraethyl-disilacyclobut-3-ene (1) and benzaldehyde in the presence of a

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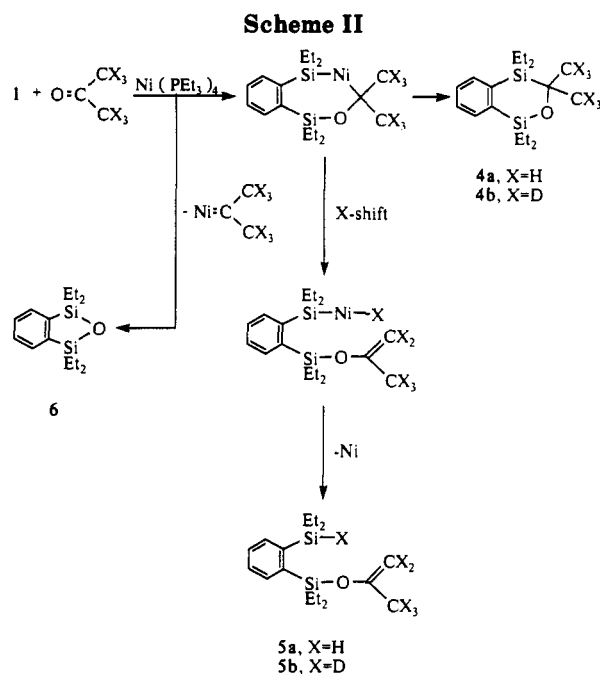
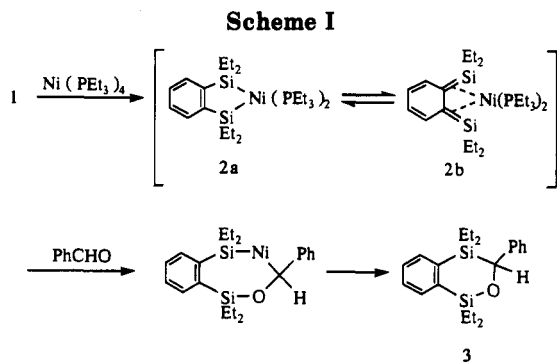
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catalytic amount of tetrakis(triethylphosphine)nickel(0) was heated in a sealed glass tube at 150 °C for 24 h, 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene (3) was obtained in 75% yield as the sole product. All spectral data obtained from 3 were identical with those of the authentic sample prepared from the thermal reaction of 1 with benzaldehyde.<sup>1</sup>

The formation of 3 can be best explained by the reaction of 3,4-benzo-2,2,5,5-tetraethyl-1-nickela-2,5-disilacyclopent-3-ene (2a) or *o*-quinodisilane-nickel complex (2b) with benzaldehyde. Nickel complex 2a may be produced by the reaction of 1 with tetrakis(triethylphosphine)nickel(0), while 2b would be formed by either isomerization of 2a or a direct reaction of the *o*-quinodisilane with tetrakis(triethylphosphine)nickel(0). Since dimer of 1 is obtained in the absence of the nickel catalyst, the *o*-quinodisilane seems to be produced under the conditions used (see below). The reaction of 2a or 2b with benzaldehyde would produce 5,6-benzo-4,7-disila-1-nickela-3-oxacyclohept-6-ene. Finally, reductive elimination of a nickel species affords product 3 (Scheme 1). The formation of 3,4-benzo-1-metalla-2,5-disilacyclopent-3-enes,<sup>5-9</sup> analogous to 2a,



and the reaction of silyl-substituted transition metal complexes with carbonyl compounds, in which a silyl group is transferred from a transition metal to the oxygen atom of a carbonyl group giving an  $\alpha$ -siloxyalkyl complex,<sup>5,10,11</sup> have been reported to date.

To confirm that product 3 was formed by a catalytic process, we carried out the same reaction in the absence of the nickel catalyst. Thus, heating 1 with 1.3 equiv of benzaldehyde at 150 °C for 24 h afforded a dimer of 1, 4,5,7,8-dibenzo-1,1,2,2,3,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene,<sup>1</sup> and 3 in 26% and 8% yields, in addition to 56% unchanged starting compound 1, indicating that product 3 was formed mainly by the catalytic process. Furthermore, in the nickel-catalyzed reaction, no dimerization product was detected in the reaction mixture.

The reaction of 1 with acetone in the presence of the nickel catalyst at 150 °C, gave three products, 5,6-benzo-1,1,4,4-tetraethyl-3,3-dimethyl-2-oxa-1,4-disilacyclohex-5-ene (4a), 1-[diethyl(isopropenyloxy)silyl]-2-(diethylsilyl)benzene (5a), and 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene (6), in 26%, 31%, and 24% yields, respectively. The products, 4a, 5a, and 6, could readily be isolated by preparative GLC. All spectral data for 5 and 6 were identical with those of authentic samples.<sup>1,3</sup> In order to confirm whether or not the hydrogen atom attached to a silicon atom in product 5a was originated from a methyl group of acetone, we carried out the reaction of 1 with acetone- $d_6$ . Thus, the reaction of 1 with acetone- $d_6$  in a degassed sealed tube under the same conditions produced 5,6-benzo-3,3-bis(trideuteriomethyl)-1,1,4,4-tetraethyl-2-oxa-1,4-disilacyclohex-5-ene (4b) and 2-(deuteriodiethylsilyl)-1-[(pentadeuterioisopropenyloxy)diethylsilyl]benzene (5b) in 44% and 20% yields, in addition to a 13% yield of 6. The formation of 5b clearly indicates that the hydrogen on the silicon atom comes from a methyl group of acetone (Scheme II). In the absence of the nickel catalyst, the dimer of 1 was obtained in 12% yield as the sole reaction product, along with 66% unchanged starting compound 1. Neither compound 4a nor 5a was detected in the reaction mixture.

A similar nickel-catalyzed reaction of 1 with acetophenone, however, afforded two products, compound 6 and

1-[diethyl[(1-phenylvinyl)oxy]silyl]-2-(diethylsilyl)benzene (7), in 17% and 59% yields, respectively. No C–O insertion product, 5,6-benzo-2-oxa-1,4-disilacyclohex-5-ene, analogous to 4, was detected in the reaction mixture. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra for product 7 were also identical with those of compound isolated from the phtolysis of 1 in the presence of acetophenone.<sup>3</sup> The reaction of 1 with pinacolone in the presence of the nickel(0) catalyst again afforded two products, compound 6 and 1-[(1-tert-butylvinyl)oxy]diethylsilyl-2-(diethylsilyl)benzene (8), in 18% and 27% yields, while with propiophenone, 1 gave 6 and 1-[diethyl[(1-phenyl-1-propenyl)oxy]silyl]-2-(diethylsilyl)benzene (9) in 24% and 70% yields, respectively. In both cases, again no 5,6-benzo-2-oxa-1,4-disilacyclohex-5-ene derivatives were detected in the reaction mixture. Presumably, the presence of bulky substituents on the carbonyl carbon prevents the formation of the 5,6-benzo-2-oxa-1,4-disilacyclohex-5-ene (Scheme III).

In marked contrast to the enolizable ketones, nonenolizable ketones produce quite different products. Thus, treatment of 1 with benzophenone in the presence of the nickel catalyst at 150 °C afforded 4,5-benzo-1,1,3,3-tetraethyl-2,2-diphenyl-1,3-disilacyclopent-4-ene (10) in 20% yield, in addition to a 57% yield of compound 6. In this reaction, again no C–O insertion product, 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3,3-diphenyl-1,4-disilacyclohex-5-ene, was detected in the reaction mixture. Similarly, the reaction of 1 with 4,4'-dimethylbenzophenone gave 4,5-benzo-1,1,3,3-tetraethyl-2,2-di(*p*-tolyl)-1,3-disilacyclopent-4-ene (11) in 16% yield, along with a 37% yield of 6. The structure of 10 and 11 were verified by mass, IR, and <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra. The mass spectrum of 10 shows a parent ion at *m/e* 414, corresponding to the calculated molecular weight of  $\text{C}_{27}\text{H}_{34}\text{Si}_2$ . The <sup>13</sup>C NMR spectrum of 10 reveals two resonances at 6.33 and 8.45 ppm, attributed to ethylsilyl carbons, and a single resonance at 41.30 ppm, due to diphenyl-substituted carbon, as well as seven resonances attributable to phenylene and phenyl ring carbons. The <sup>29</sup>Si spectrum shows a single resonance due to two equivalent silicon atoms. The mass spectrum of 11 reveals a parent ion at *m/e* 442. Its <sup>13</sup>C

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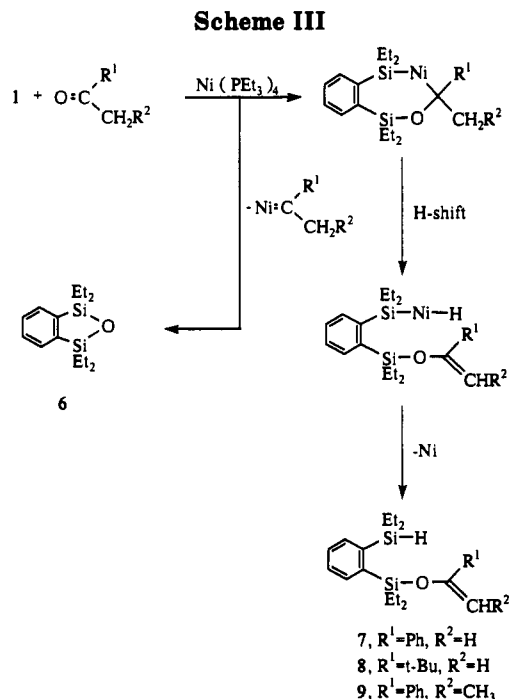
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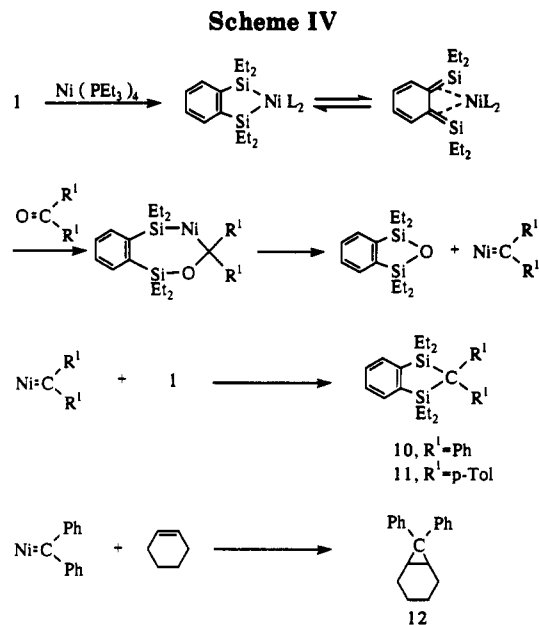


NMR spectrum shows resonances at  $\delta$  6.27 and 8.47 ppm attributed to ethyl carbons and at 20.88 and 39.97 ppm due to methyl carbons and a di(*p*-tolyl)-substituted carbon, as well as seven resonances attributable to tolyl and phenylene ring carbons. The <sup>29</sup>Si NMR spectrum exhibits a single resonance at  $\delta$  12.71 ppm. These results are wholly consistent with the structures proposed for 10 and 11.

The formation of compound 6 is of considerable interest, because the oxygen atom in this molecule must come from carbonyl compounds. Consequently, carbenes, probably carbene-nickel complexes, must be extruded in the reaction of 2 with carbonyl compounds. In fact, the formation of 10 and 11 can be best understood in terms of the reaction of 1 with a diphenylcarbene-nickel complex and di(*p*-tolyl)carbene-nickel complex. For the formation of the carbene-transition metal complex, Gladysz and co-workers have reported that the reaction of (CO)<sub>4</sub>FeSiMe<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub> with benzaldehyde produces 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane and iron carbene species that can be trapped by triphenylphosphine.<sup>11</sup>

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

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



## Experimental Section

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

**Materials.** The starting compound, 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (1), was prepared as reported previously.<sup>1</sup>

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

**Reaction of 1 with Acetone.** A mixture of 0.2811 g (1.13 mmol) of 1, 0.1222 g (2.10 mmol) of acetone, and 0.0310 g (0.058 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being 4a (26% yield), 5a (31% yield), 6 (24% yield), and the starting compound 1 (1% yield). The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. Products 4a, 5a, and 6 were isolated by preparative GLC. All spectral data for 5a and 6 were identical with those of authentic samples.<sup>1,3</sup> For 4a: MS *m/e* 264 (*M*<sup>+</sup> - CMe<sub>2</sub>); IR 3046, 2954, 2875, 1462, 1416, 1235, 1120, 1015, 742, 716, 613 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  (CDCl<sub>3</sub>) 0.68–1.04 (m, 20 H, EtSi), 1.33 (s, 6 H, 2Me), 7.32–7.55 (m, 4 H, phenylene ring protons); <sup>13</sup>C NMR  $\delta$  (CDCl<sub>3</sub>) 2.55, 7.05, 7.77, 8.05 (EtSi), 28.77 (Me), 67.03 (CO), 128.0, 128.1, 132.7, 134.6, 141.7, 143.7 (phenylene ring carbons); <sup>29</sup>Si NMR  $\delta$  (CDCl<sub>3</sub>) -6.62, 1.80. Anal. Calcd for C<sub>17</sub>H<sub>30</sub>OSi<sub>2</sub>: C, 66.60; H, 9.86. Found: C, 66.53; H, 9.73.

**Reaction of 1 with Acetone-*d*<sub>6</sub>.** A mixture of 0.4204 g (1.69 mmol) of 1, 0.4435 g (6.93 mmol) of acetone-*d*<sub>6</sub>, and 0.0395 g (0.074 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. GLC analysis of the reaction mixture indicated

the presence of **4b** (44% yield), **5b** (20% yield), and **6** (13% yield). Products **4b**, **5b**, and **6** were isolated by preparative GLC. For **4b**: MS *m/e* 312 ( $M^+$ ); IR 2956, 2912, 2876, 2208, 1461, 1414, 1236, 1120, 1087, 1035, 1009, 935, 773, 743, 718  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ) 0.75–1.16 (m, 20 H, EtSi), 7.26–7.54 (m, 4 H, phenylene ring protons);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ) 2.94, 7.37, 7.97, 8.54 (EtSi), 28.29 ( $\text{CD}_3$ ), 66.71 ( $\text{C}(\text{CD}_3)$ ), 128.49, 128.54, 133.2, 135.0, 141.8, 144.2 (phenylene ring carbons);  $^2\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ) 1.32 ( $\text{CD}_3$ ).

For **5b**: MS *m/e* 283 ( $M^+ - \text{Et}$ ); IR 2956, 2876, 2227, 1602, 1560, 1459, 1415, 1233, 1119, 1007, 738, 719  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ) 0.80–1.29 (m, 20 H, EtSi), 7.24–7.87 (m, 4 H, phenylene ring protons);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ) 4.75, 7.14, 7.36, 8.56 (EtSi), 128.7, 129.1, 132.0, 135.3, 135.5, 143.2 (phenylene ring carbons), 156.0 ( $\text{C}=\text{CD}_2$ );  $^2\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ) 1.85 ( $\text{CD}_3$ ), 4.18 ( $\text{CD}_2$ ), 4.82 (SiD).

All spectral data for **6** were identical with those of the authentic sample.<sup>1</sup>

**Reaction of 1 with Acetophenone.** A mixture of 0.2409 g (0.97 mmol) of **1**, 0.1981 g (1.65 mmol) of acetophenone, and 0.0200 g (0.038 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. Products **6** (17% yield) and **7** (59% yield) were isolated by preparative GLC. For **7**: MS *m/e* 368 ( $M^+$ ); IR 3060, 2955, 2874, 2146, 1618, 1458, 1317, 1118, 917, 812, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ) 0.79–1.32 (m, 20 H, EtSi), 4.44 (d, 1 H,  $\text{CH}_2=\text{C}$ ,  $J = 2.0$  Hz), 4.80 (quintet, 1 H, HSi,  $J = 3.3$  Hz), 4.90 (d, 1 H,  $\text{CH}_2=\text{C}$ ,  $J = 2.0$  Hz), 7.10–7.95 (m, 9 H, phenyl and phenylene ring protons);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 4.47, 6.65, 6.95, 8.28 (EtSi), 90.53 ( $\text{CH}_2=\text{C}$ ), 125.3, 128.0, 128.1, 128.4, 131.6, 134.9, 135.2, 137.7, 142.4, 142.9 (phenyl and phenylene ring carbons), 155.5 ( $\text{C}=\text{CH}_2$ );  $^{29}\text{Si}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –8.26, 9.53. Anal. Calcd for  $\text{C}_{22}\text{H}_{32}\text{OSi}_2$ : C, 71.68; H, 8.75. Found: C, 71.48; H, 8.71.

All spectral data for **6** were identical with those of the authentic sample.<sup>1</sup>

**Reaction of 1 with Pinacolone.** A mixture of 0.3155 g (1.25 mmol) of **1**, 0.2104 g (2.10 mmol) of pinacolone, and 0.0340 g (0.064 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. GLC analysis of the reaction mixture indicated the presence of **6** (18% yield), **8** (27% yield), and the starting compound **1** (1% yield). Products **6** and **8** were isolated by preparative GLC. For **8**: MS *m/e* 319 ( $M^+ - \text{Et}$ ); IR 3044, 2956, 2146, 1618, 1459, 1415, 1296, 1221, 1184, 1118, 1008, 816, 775, 742, 709, 613  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.76–1.09 (m, 20 H, EtSi), 1.15 (s, 9 H, 3Me), 3.75 (d, 1 H,  $\text{CH}_2=\text{C}$ ,  $J = 1.6$  Hz), 4.02 (d, 1 H,  $\text{CH}_2=\text{C}$ ,  $J = 1.6$  Hz), 4.48 (quintet, 1 H, HSi,  $J = 3.3$  Hz), 7.32–7.76 (m, 9 H, phenylene ring protons);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 4.53, 7.03 (2C), 8.30 (EtSi), 28.34 (Me), 36.77 ( $\text{CMe}_3$ ), 85.75 ( $\text{CH}_2=\text{C}$ ), 128.0, 128.1, 134.7, 135.2, 142.1, 143.6 (phenylene ring carbons), 166.6 ( $\text{C}=\text{CH}_2$ );  $^{29}\text{Si}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –9.26, 6.30. Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{OSi}_2$ : C, 68.89; H, 10.41. Found: C, 68.69; H, 10.37. All spectral data for **6** were identical with those of the authentic sample.<sup>1</sup>

**Reaction of 1 with Propiophenone.** A mixture of 0.4852 g (1.95 mmol) of **1**, 0.3832 g (2.86 mmol) of propiophenone, and 0.0530 g (0.100 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150 °C for 24 h. GLC analysis of the reaction mixture indicated the presence of **6** (20% yield) and **9** (70% yield, *E:Z* = 1:4.8). Products **6** and **9** were isolated by preparative GLC. For **9**: MS *m/e* 382 ( $M^+$ ); IR 3047, 2955, 2875, 2145, 1651, 1456, 1415, 1322, 1233, 1119, 1059, 1007, 969, 917, 807, 738, 720, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 0.66–1.25 (m, 20 H, EtSi), 1.63 (d, 3 H, Me (*Z*),  $J = 6.9$  Hz), 4.52 (quintet, 1 H, HSi (*E*),  $J = 3.3$  Hz), 4.61 (quintet, 1 H, HSi (*Z*),  $J = 3.3$  Hz), 4.99 (q, 1 H,  $\text{HMeC}=\text{C}$  (*E*),  $J = 7.3$  Hz), 5.25 (q, 1 H,  $\text{HMeC}=\text{C}$  (*Z*),  $J = 6.9$  Hz), 7.17–7.79

(m, 9 H, phenyl and phenylene ring protons);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 4.38, 6.94, 7.37, 8.34 (EtSi), 12.09 (Me), 104.9 ( $\text{CHMe}=\text{C}$ ), 125.5, 127.2, 127.8, 127.9, 128.2, 134.9, 135.1, 139.4, 142.3, 143.6 (phenyl and phenylene ring carbons), 150.3 ( $\text{C}=\text{CHMe}$ );  $^{29}\text{Si}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –8.62 (*E*), –8.23 (*Z*), 8.85 (*E* + *Z*). Anal. Calcd for  $\text{C}_{23}\text{H}_{34}\text{OSi}_2$ : C, 72.19; H, 8.95. Found: C, 72.17; H, 8.93.

All spectral data for **6** were identical with those of the authentic sample.<sup>1</sup>

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

All spectral data for **6** were identical with those of the authentic sample.<sup>1</sup>

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

All spectral data for **6** were identical with those of the authentic sample.<sup>1</sup>

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

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

OM920332F