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Regiochemistry of Disilanylene-Containing Cyclic Compounds. Palladium- and Platinum-Catalyzed Reactions of 1,1-Dimethyl-2,2-diphenyl-1,2-disilacyclopentane

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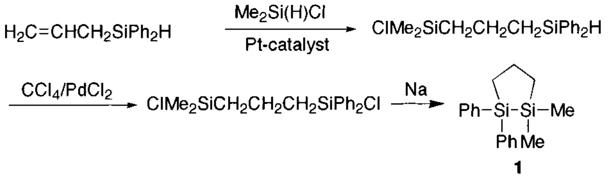
*Summary: The Wurtz-type coupling of 1-chlorodimethylsilyl-3-chlorodiphenylsilylpropane with sodium metal afforded 1,1-dimethyl-2,2-diphenyl-1,2-disilacyclopentane (**1**) in 77% yield. The palladium-catalyzed reaction of **1** with phenylacetylene regiospecifically gave 4,4-dimethyl-1,1,2-triphenyl-1,4-disilacyclohept-2-ene (**2**) in 93% yield. Similar treatment of **1** with tert-butylacetylene and 1-hexyne also proceeded with high regiospecificity to give 2-tert-butyl-4,4-dimethyl-1,1-diphenyl-1,4-disilacyclohept-2-ene (**3**) and 2-n-butyl-4,4-dimethyl-1,1-diphenyl-1,4-disilacyclohept-2-ene (**4**) in 93% and 90% yields, respectively. The platinum-catalyzed reactions of **1** with phenylacetylene, tert-butylacetylene, and 1-hexyne regiospecifically afforded the same products as those obtained from palladium-catalyzed reactions in high yields.*

Introduction

Activation of an Si−Si bond by a transition-metal catalyst and the subsequent reactions with organic unsaturated compounds offer useful methods for synthesizing organic silicon compounds. Many papers concerning the bis-silylation of alkenes and alkynes have been reported to date.[1] However, little interest has been shown in the regiochemistry of the bis-silylation reactions. Ozawa et al. reported that the reactions of phenylacetylene and 1-octyne with Me_3SiSiF_2Ph in the presence of a palladium catalyst proceeded regiospecifically to give the bis-silylation products.[1c] They also reported that cis-$Pt(SiR_3)_2(PMe_2Ph)_2$ reacted with phenylacetylene to give cis-$Pt\{C(Ph){=}CH(SiR_3)\}(SiR_3)(PMe_2Ph)_2$.[1a]

Recently, we have found that the palladium-catalyzed reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane with mono- and disubstituted acetylenes proceed to give the respective *cis*- and *trans*-5,6-benzo-1,4-disilacyclohexa-2,5-dienes with high stereospecificity.[2] It is of interest to us to investigate the regiochemistry of insertion of alkynes into a silicon−silicon bond in the disilacycloalkane system. In this paper, we report the first synthesis and regiochemistry of 1,1-dimethyl-2,2-diphenyl-1,2-disilacyclopentane.

Scheme 1



Results and Discussion

Synthesis. The starting compound, 1,1-dimethyl-2,2-diphenyl-1,2-disilacyclopentane (**1**), was prepared by a series of the reactions shown in Scheme 1. Hydrosilylation of allyldiphenylsilane[3] with chlorodimethylsilane in the presence of a catalytic amount of hydrogen hexachloroplatinate hexahydrate produced 1-chlorodimethylsilyl-3-diphenylsilylpropane in 89% yield. The Cl−H exchange reaction of the resulting hydrosilylation product with carbon tetrachloride in the presence of a palladium chloride catalyst gave 1-chlorodimethylsilyl-3-chlorodiphenylsilylpropane in 90% yield. Finally, Wurtz-type coupling of the resulting 1-chlorodimethylsilyl-3-chlorodiphenylsilylpropane with sodium metal in refluxing toluene afforded 1,2-disilacyclopentane **1** in 77% yield as a colorless liquid. The structure of **1** was verified by mass and ^1H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis (see Experimental Section).

Palladium-Catalyzed Reaction. First we carried out the palladium-catalyzed reactions of **1** with monosubstituted alkynes to investigate the regiochemistry of insertion of the alkynes into an Si−Si bond in the disilacyclopentane. Thus, the reaction of **1** with a 1.5-fold excess of phenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in a sealed glass tube at 150 °C produced 4,4-

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(1) (a) Ozawa, F.; Kamite, J. *Organometallics* **1998**, *17*, 5630 and references therein. (b) Tsuji, Y.; Funato, M.; Ozawa, M.; Ogiyama, H.; Kajita, S.; Kawamura, T. *J. Org. Chem.* **1996**, *61*, 5779. (c) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237. (d) Obora, Y.; Tsuji, Y.; Kawamura, T. *Organometallics* **1993**, *12*, 2853. (e) Murakami, M.; Oike, H.; Sugawara, M. Suginome, M.; Ito, Y. *Tetrahedron* **1993**, *49*, 3933. (f) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487. (g) Finckh, W.; Tang, B.; Lough, A.; Manner, I. *Organometallics* **1992**, *11*, 2904. (h) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353. (i) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241. (j) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948. (k) Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987. (l) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280. (m) Hayashi, T.; Kawamoto, A. M.; Kobayashi, T. Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1990**, 563.

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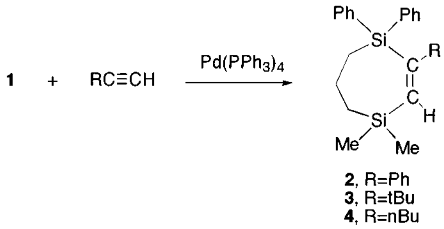
(3) Mironov, V. F.; Petrov, A. D. *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.* **1957**, 383.

10.1021/om001058p CCC: $20.00

Scheme 2

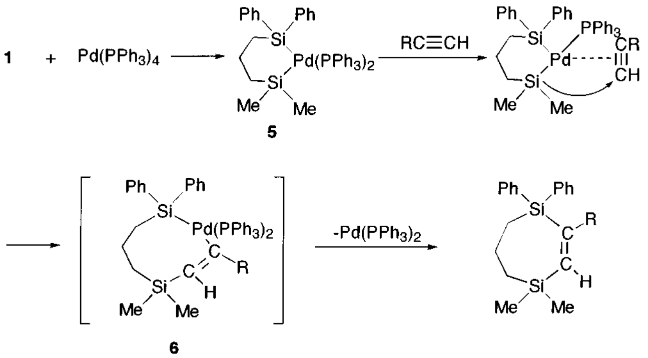


dimethyl-1,1,2-triphenyl-1,4-disilacyclohept-2-ene (**2**) in 93% yields (Scheme 2). No other regioisomer was detected in the reaction mixture. The ^{1}H NMR spectrum of **2** shows the presence of a single resonance at 0.11 ppm due to methylsilyl protons and three resonances at 0.78, 1.49, and 1.81 ppm attributed to three different kinds of methylene protons, in addition to an olefinic proton at 7.02 ppm and phenyl ring protons at 7.27−7.34 ppm. The ^{13}C NMR spectrum of **2** reveals a signal at −1.42 ppm due to the methyl silyl carbon atoms and three signals at 16.85, 17.55, and 17.62 ppm attributed to methylene carbons, along with phenyl ring carbons and olefinic carbons. The location of the olefinic proton on the 1,4-disilacycloheptene ring was confirmed by NOE−FID difference experiments at 500 MHz. Thus, irradiation of the methyl silyl protons at 0.11 ppm resulted in a strong enhancement of the olefinic proton at 7.02 ppm, as well as methylene protons at 0.78 ppm, indicating that the sp^{2}-hybridized carbon atom bearing the hydrogen atom is attached to the dimethylsilyl group but not to the diphenylsilyl group.

Similar treatment of **1** with *tert*-butylacetylene in a degassed sealed tube at 150 °C regiospecifically produced 2-*tert*-butyl-4,4-dimethyl-1,1-diphenyl-1,4-disilacyclohept-2-ene (**3**) in 93% yield. The structure of **3** was also verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis. The ^{1}H NMR spectrum of **3** shows three singlet resonances at 0.06, 0.98, and 6.89 ppm attributed to methylsilyl protons, *tert*-butyl protons, and an olefinic proton, along with resonances due to methylene protons and phenyl ring protons. In the similar NOE−FID difference experiments for **3**, irradiation of the olefinic proton at 6.89 ppm resulted in enhancement of methylsilyl protons at 0.06 ppm and *tert*-butyl protons at 0.98 ppm. Saturation of methylsilyl protons at 0.06 ppm caused a positive NOE of the methylene protons at 0.59 ppm and the olefinic proton at 6.89 ppm, while irradiation of *tert*-butyl protons at 0.98 ppm led to an enhancement of the olefinic proton at 6.89 ppm and the phenyl ring protons at 7.55−7.57 ppm. Again, these results clearly show that the regiochemistry of this reaction must be the same as that of the reaction with phenylacetylene. The reaction of **1** with 1-hexyne under the same conditions gave 2-*n*-butyl-4,4-dimethyl-1,1-diphenyl-1,4-disilacyclohept-2-ene (**4**). Again, the reaction proceeded to give the adduct with high regiospecificity. No other regioisomers were detected in the reaction mixture by spectrometric analysis. The structure of **4** was verified by spectrometric analysis, as well as by elemental analysis.

The regiospecific formation of the products **2**, **3**, and **4** in the palladium-catalyzed reactions of **1** with monosubstituted acetylenes can best be explained by a series of the reaction shown in Scheme 3. The first step involves oxidative addition of an Si−Si bond in **1** to a palladium species to give a bis(silyl)-complex, 2-pallada-1,3-disilacyclohexane (**5**), followed by coordination of a monosubstituted acetylene to the palladium atom in **5**.[1a,1h,4] Regiospecific addition of a Pd−SiMe$_2$ bond across the carbon−carbon triple bond of the coordinated alkyne affords 2-pallada-1,5-disilacyclooct-3-ene (**6**), as an intermediate, although evidence for the formation of **6** has not yet been obtained at present. Finally, reductive elimination of the palladium species gives the product, 1,4-disilacyclohept-2-ene.[2−4]

Scheme 3



It has been reported that introduction of electron-withdrawing substituents on the silicon atom in the silyl-platinum complexes strengthens the Pt−Si bond, and the stronger Pt−Si bond possesses the lower reactivity toward insertion because of the higher activation barrier for the silyl migration.[1a,5]Like the silyl-platinum complexes, in the present palladium complex **5**, the Pd−SiMe$_2$ bond is probably weaker than the Pd−SiPh$_2$ bond, and therefore the dimethylsilyl group, but not the diphenylsilyl group, migrates to the less hindered carbon atom in the coordinated monosubstituted acetylene to give the insertion product **6** with high regiospecificity.

To get more information about the reactive intermediate in the present reaction, we carried out the stoichiometric reaction of **1** and tetrakis(triphenylphosphine)palladium(0). The reaction of **1** with 1 equiv of tetrakis(triphenylphosphine)palladium(0) in refluxing benzene for 12 h led to the recovery of the starting compound **1**. When a similar reaction was carried out in a sealed glass tube at 150 °C for 24 h, again **1** was recovered. In all cases, no evidence for the formation of complex **5** was obtained, and the starting compound **1** was recovered quantitatively. Presumably, the equilibrium between reactants and products lies far to the reactants. The reversibility of the formation of the bis(silyl)palladium has been reported.[4c]

Next, we carried out the platinum-catalyzed reaction of **1** with monosubstituted acetylenes under the same conditions as those of the palladium-catalyzed reactions. Thus, treatment of **1** with a 3.6-fold excess of phenyl-

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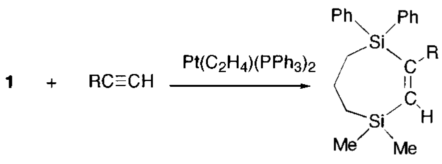
(6) Ozawa, F.; Hikida, T. *Organometallics* **1996**, *15*, 4501.

Scheme 4



2, R=Ph
3, R=tBu
4, R=nBu

acetylene in the presence of a catalytic amount of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube produced **2** in 65% yield, in addition to 25% of the unchanged starting compound **1** (Scheme 4). No other regioisomers were detected by GLC and GPC analysis.

In this reaction, no phenylacetylene was recovered, but the nonvolatile products were produced. Presumably, oligomerization of the acetylene takes place, concomitantly by the reaction with **1**. The low yield of the product **2**, compared with that of the palladium-catalyzed reaction, may be responsible for this oligomerization.

The reaction of **1** with *tert*-butylacetylene and 1-hexyne in the presence of the platinum catalyst under the same conditions afforded compounds **3** and **4** in 89% and 85% yields, respectively. Again, no other isomers were detected in the reaction mixture. All spectral data for products **2**−**4** obtained from the platinum-catalyzed reactions were identical to those of compounds formed from the palladium-catalyzed reactions.

In conclusion, Wurtz-type condensation of 1-chlorodimethylsilyl-3-chlorodiphenylsilylpropane afforded 1,1-dimethyl-2,2-diphenyl-1,2-disilacyclopentanes **1** in high yields. The palladium-catalyzed reactions of **1** with phenylacetylene, *tert*-butylacetylene, and 1-hexyne proceeded regiospecifically to give the respective adducts arising from insertion of a triple bond into a silicon−silicon bond in **1**. The reactions of **1** with monosubstituted acetylenes in the presence of the platinum catalyst gave the same products, 1,4-disilacyclohept-2-enes, with high regiospecificity in high yields.

Experimental Section

General Procedure. All palladium- and platinum-catalyzed reactions were carried out in a degassed sealed tube (1.0 cm × 15 cm). Yields of the products were determined by analytical GLC with the use of *n*-pentadecane as an internal standard, on the basis of the starting material used. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Low- and high-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. Pure *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane were separated by a TSA-SB2 spinning band type distillation column (Taika Kogyo). Melting points were measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Tetrahydrofuran, diethyl ether, and toluene used as a solvent were dried over sodium/benzophenone under a nitrogen atmosphere and distilled just before use. Carbon tetrachloride was dried over diphosphorus pentoxide and distilled before use. Allyldiphenylsilane was prepared according to the method reported previously.[3]

Preparation of 1-Chlorodimethylsilyl-3-diphenylsilylpropane. In a 100-mL two-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 5.710 g (60.4 mmol) of chlorodimethylsilane and 0.1 mL (0.02 mmol) of an isopropyl alcohol solution of hydrogen hexachloroplatinate hexahydrate. To this was added 7.425 g (33.1 mmol) of allyldiphenylsilane at room temperature over a period of 1 h. The mixture was stirred at room temperature for 2 h. The mixture was fractionally distilled under reduced pressure to give 9.341 g (29.3 mmol) of 1-chlorodimethylsilyl-3-diphenylsilylpropane (89% yield): bp 158−160 °C/2 Torr; MS *m*/*z* 318 (M^+); IR 3068, 3048, 3018, 2956, 2917, 2869, 2115 (Si−H), 1589, 1486, 1429, 1332, 1253, 1139, 1114, 908, 806, 730, 698 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.39 (s, 6H, Me_2Si), 0.98 (t, 2H, CH_2, $^3J = 7.9$ Hz), 1.29 (dt, 2H, CH_2, $^3J = 7.9$ Hz, $^3J = 3.7$ Hz), 1.66 (quint, 2H, CH_2, $^3J = 7.9$ Hz), 4.91 (t, 1H, HSi, $^3J = 3.7$ Hz), 7.37−7.44 (m, 6H, phenyl ring protons), 7.58−7.60 (m, 4H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ 1.70 (Me_2Si), 15.95, 18.27, 22.78 (CH_2), 127.99, 129.56, 134.29, 135.10 (phenyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −14.8, 31.1. Anal. Calcd for $C_{17}H_{23}Si_2Cl$: C, 64.01; H, 7.27. Found: C, 64.19; H, 7.35.

Preparation of 1-Chlorodimethylsilyl-3-chlorodiphenylsilylpropane. In a 100-mL two-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 0.052 g (0.293 mmol) of palladium chloride and 50 mL of carbon tetrachloride. To this solution was added 9.341 g (29.3 mol) of 1-chlorodimethylsilyl-3-diphenylsilylpropane at room temperature over a period of 1 h. The mixture was heated to reflux for 6 h, and then the resulting chloroform and carbon tetrachloride were evaporated off. The residue was distilled under reduced pressure to give 9.332 g (26.4 mmol) of 1-chlorodimethylphenylsilyl-3-chlorodiphenylsilylpropane (90% yield): 162−165 °C/2 Torr; MS *m*/*z* 317 (M^+-Cl); IR 3072, 3052, 3000, 2960, 2927, 1429, 1255, 1116, 989, 908, 732, 649 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.38 (s, 6H, Me_2Si), 0.96 (t, 2H, CH_2, $^3J = 8.2$ Hz), 1.47 (t, 2H, CH_2, $^3J = 7.9$ Hz), 1.66−1.73 (m, 2H, CH_2), 7.41−7.49 (m, 6H, phenyl ring protons), 7.64−7.66 (m, 4H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ 1.70 (Me_2Si), 16.92, 20.09, 22.69 (CH_2), 128.12, 130.53, 133.57, 134.27 (phenyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ 9.8, 31.0. Anal. Calcd for $C_{17}H_{22}Si_2Cl_2$: C, 57.77; H, 6.27. Found: C, 57.85; H, 6.45.

Preparation of 1,1-Dimethyl-2,2-diphenyl-1,2-disilacyclopentane (1). In a 200-mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 2.522 g (0.110 mol) of sodium and 80 mL of toluene. The mixture was heated to reflux and stirred to prepare a sodium dispersion. To this was added 9.332 g (26.4 mmol) of 1-chlorodimethylsilyl-3-chlorodiphenylpropane over a period of 1 h. After the mixture was heated to reflux for 3 h, the resulting mixture was hydrolyzed with ethanol. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined and washed with water and then dried over magnesium sulfate. The solvents were evaporated off, and the residue was fractionally distilled under reduced pressure to give 5.769 g (20.4 mmol) of **1** (77% yield): bp 126−128 °C/2 Torr; MS *m*/*z* 282 (M^+); IR 3066, 3048, 2954, 2900, 2848, 1427, 1251, 1106, 908, 840, 732, 698 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.22 (s, 6H, Me_2Si), 0.89 (t, 2H, CH_2, $^3J = 6.9$ Hz), 1.31 (t, 2H, CH_2, $^3J = 6.9$ Hz), 1.91 (quint, 2H, CH_2, $J = 6.9$ Hz), 7.33−7.41 (m, 6H, phenyl ring protons), 7.49−7.52 (m, 4H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ −3.00 (Me_2Si), 17.03, 19.21, 23.05 (CH_2), 127.85, 128.67, 134.65, 135.31 (phenyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −14.9, −11.6. Anal. Calcd for $C_{17}H_{22}Si_2$: C, 72.27; H, 7.85. Found: C, 71.91; H, 7.89.

Palladium-Catalyzed Reaction of 1 with Phenylacetylene. A mixture of 0.130 g (0.460 mmol) of **1**, 0.0702 g (0.687 mmol) of phenylacetylene, and 0.0272 g (0.0235 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **2** (93% yield). The palladium species in the resulting mixture was removed by passing the mixture through a short silica gel column. Compound **2** was isolated by column chromatography: MS *m*/*z* 384 (M^+); IR 3068, 3048, 3021, 2950, 2894, 1486, 1427, 1247, 1108, 908, 840, 698 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.11 (s, 6H, Me_2Si), 0.78 (t, 2H, CH_2, ^3J = 6.7 Hz), 1.49 (t, 2H, CH_2, ^3J = 6.7 Hz), 1.81 (quint, 2H, CH_2, ^3J = 6.7 Hz), 6.99−7.01 (m, 5H, phenyl ring protons), 7.02 (s, 1H, HC═C), 7.27−7.34 (m, 6H, phenyl ring protons), 7.46−7.48 (m, 6H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ −1.42 (Me_2Si), 16.85, 17.55, 17.62 (CH_2), 125.88, 127.05, 127.44, 127.60, 128.99, 135.44, 136.42, 148.00 (phenyl ring carbons), 153.57, 159.11 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −9.3, −6.3. Anal. Calcd for $C_{25}H_{28}Si_2$: C, 78.06; H, 7.34. Found: C, 78.06; H, 7.25.

Palladium-Catalyzed Reaction of 1 with *tert*-Butylacetylene. A mixture of 0.073 g (0.258 mmol) of **1**, 0.0916 g (1.12 mmol) of *tert*-butylacetylene, and 0.0152 g (0.0132 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **3** (93% yield). The palladium species in the resulting mixture was removed by passing the mixture through a short silica gel column. Compound **3** was isolated by column chromatography: MS *m*/*z* 364 (M^+); IR 3068, 2960, 2865, 1427, 1361, 1245, 1106, 908, 850, 738, 700 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.06 (s, 6H, Me_2Si), 0.59 (t, 2H, CH_2, ^3J = 6.7 Hz), 0.98 (s, 9H, t-Bu), 1.47 (t, 2H, CH_2, ^3J = 6.7 Hz), 1.68 (quint, 2H, CH_2, ^3J = 6.7 Hz), 6.89 (s, 1H, HC═C), 7.33−7.39 (m, 6H, phenyl ring protons), 7.55−7.57 (m, 4H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ −1.14 (Me_2Si), 16.11, 17.59, 19.13 (CH_2), 31.03 (Me_3C), 40.16 (CMe_3), 126.46, 128.77, 136.04, 138.73 (phenyl ring carbons), 145.00, 167.54 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −11.1, −7.1. Anal. Calcd for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.88; H, 9.18.

Palladium-Catalyzed Reaction of 1a with 1-Hexyne. A mixture of 0.082 g (0.290 mmol) of **1a**, 0.0681 g (0.829 mmol) of 1-hexyne, and 0.0176 g (0.0152 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **4** (90% yield). The palladium species in the resulting mixture was removed by passing the mixture through a short silica gel column. Compound **4** was isolated by column chromatography: MS *m*/*z* 364 (M^+); IR 3066, 3048, 2954, 2925, 2858, 1427, 1245, 1108, 908, 844, 738, 700 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.06 (s, 6H, Me_2Si), 0.67−0.74 (m, 5H, CH_2, CH_3), 1.02−1.26 (m, 4H, CH_2), 1.46 (t, 2H, CH_2, ^3J = 6.7 Hz), 1.80 (quint, 2H, CH_2, ^3J = 6.7 Hz), 2.07 (t, 2H, CH_2, ^3J = 6.7 Hz), 6.72 (s, 1H, HC═C), 7.32−7.46 (m, 6H, phenyl ring protons), 7.48−7.55 (m, 4H, phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ −1.30 (Me_2Si), 13.73, 16.59, 17.24, 17.64, 22.44, 31.31, 41.81 (CH_2, CH_3), 127.63, 129.02, 135.39, 136.79 (phenyl ring carbons), 147.41, 159.35 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −9.9, −7.3. Anal. Calcd for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.43; H, 8.81.

Platinum-Catalyzed Reaction of 1 with Phenylacetylene. A mixture of 0.073 g (0.258 mmol) of **1**, 0.0943 g (0.923 mmol) of phenylacetylene, and 0.0109 g (0.0146 mmol) of (η_2-ethylene)bis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was analyzed by GLC and was found to be **2** (65% yield) and the starting compound **1** (25%). The platinum species in the resulting mixture was removed by passing the mixture through a short silica gel column. Compound **2** was isolated by column chromatography. All spectral data for **2** were identical with those of an authentic sample obtained from the palladium-catalyzed reaction.

Platinum-Catalyzed Reaction of 1 with *tert*-Butylacetylene. A mixture of 0.080 g (0.283 mmol) of **1**, 0.0777 g (0.946 mmol) of *tert*-butylacetylene, and 0.0110 g (0.0147 mmol) of (η_2-ethylene)bis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was analyzed by GLC and was found to be **3** (89% yield). The platinum species in the resulting mixture was removed by passing the mixture through a short silica gel column. Compound **3** was isolated by column chromatography. All spectral data for **3** were identical with those of an authentic sample obtained from the palladium-catalyzed reaction.

Platinum-Catalyzed Reaction of 1 with 1-Hexyne. A mixture of 0.083 g (0.294 mmol) of **1**, 0.0799 g (0.973 mmol) of 1-hexyne, and 0.0112 g (0.0150 mmol) of (η_2-ethylene)bis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was analyzed by GLC and was found to be **4** (85% yield). The platinum species in the resulting mixture was removed by passing the mixture through a short silica gel column. Compound **4** was isolated by column chromatography. All spectral data for **4** were identical with those of an authentic sample obtained from the palladium-catalyzed reaction.

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