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Silicon–carbon unsaturated compounds

XXVII. Nickel-catalyzed reactions of 2-phenyl- and 2-(*o*-tolyl)-2-(phenylethynyl)hexamethyltrisilane

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Abstract

The nickel-catalyzed reactions of 2-phenyl- and 2-(*o*-tolyl)-2-(phenylethynyl)hexamethyltrisilane (I and II) with phenyl(trimethylsilyl)acetylene at 180 °C have been examined. The reaction of I with phenyl(trimethylsilyl)acetylene in the presence of tetrakis(triethylphosphine)nickel(0) gave 1,3-diphenyl-2-[phenyl(trimethylsilyl)methylene]-1,4-bis(trimethylsilyl)-1-silacyclobut-3-ene and 1,4,4-trimethyl-1,3,6-triphenyl-2,5-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene. Similar reaction of II produced 3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1-(*o*-tolyl)-1,4-bis(trimethylsilyl)-1-silacyclobut-3-ene and 4,4,5-trimethyl-2,6-diphenyl-1,3-bis(trimethylsilyl)-1-(*o*-tolyl)-1,4-disilacyclohexa-2,5-diene. The results of the reactions of I and II in the presence of a catalytic amount of the nickel(0) complex in the absence of phenyl(trimethylsilyl)acetylene are also described.

Introduction

We recently found that the reactions of (phenylethynyl)polysilanes in the presence of a catalytic amount of nickel complex produce reactive intermediates—silapropadiene-nickel complexes, nickelasilacyclobutenes, and nickeladisilacyclopentenes [1–3]. The silacyclopropenes prepared photochemically from the phenylethynylpolysilanes also react with the nickel complex to give the same intermediates. Thus, treatment of phenylethynyltris(trimethylsilyl)silane with phenyl(trimethylsilyl)acetylene in the presence of the nickel catalyst gives 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene and 1,4,4-trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene. The reaction of the silacyclopropene produced from the photolysis of phenylethynyltris(trimethylsilyl)silane with phenyl(trimethylsilyl)acetylene in the presence of the nickel catalyst

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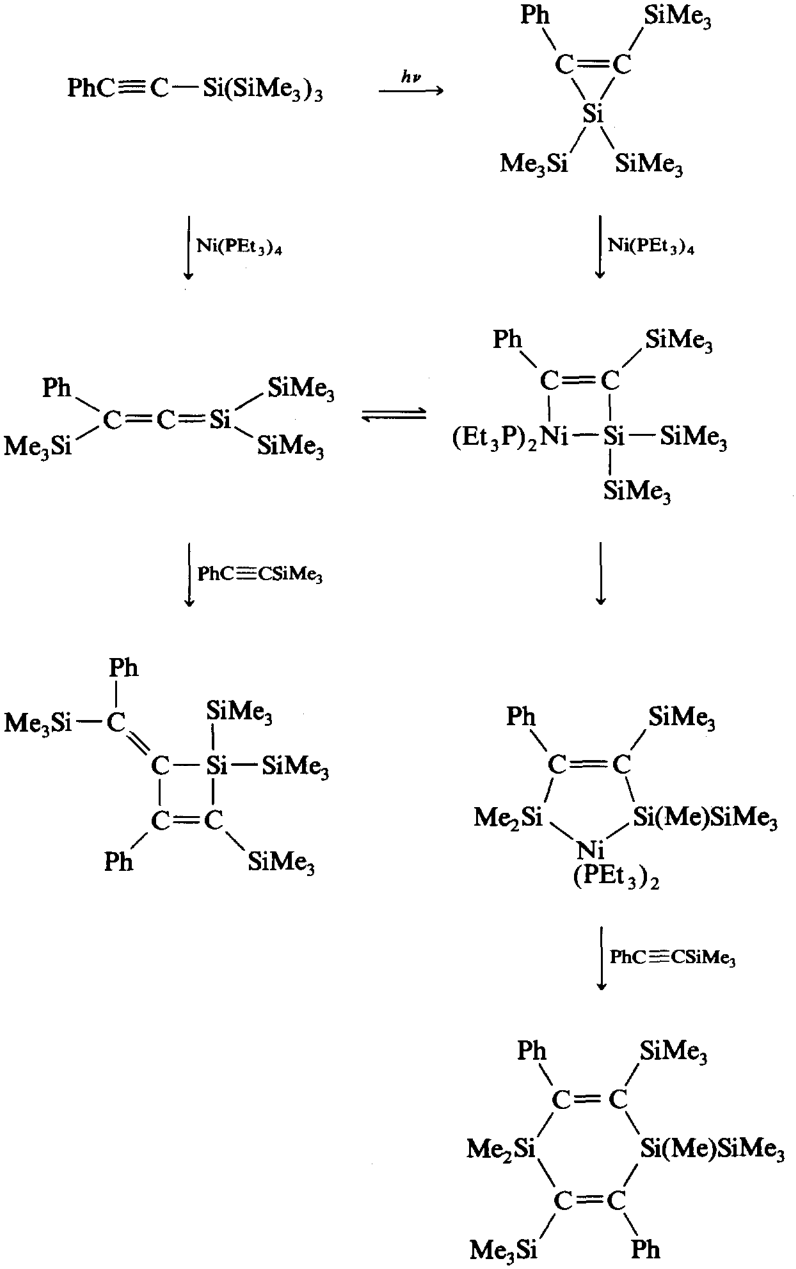
affords the same products, indicating that both reactions involve the same reactive intermediates [2]. We have also found that a nickelasilacyclobutene can readily be transformed into a silapropadiene-nickel complex [4,5].



In order to learn much more about the chemical behavior of nickel-containing reactive intermediates, we have investigated the nickel-catalyzed reaction of 2-phenyl- and 2-(*o*-tolyl)-2-(phenylethynyl)hexamethyltrisilane in the presence or absence of phenyl(trimethylsilyl)acetylene.

Results and discussion

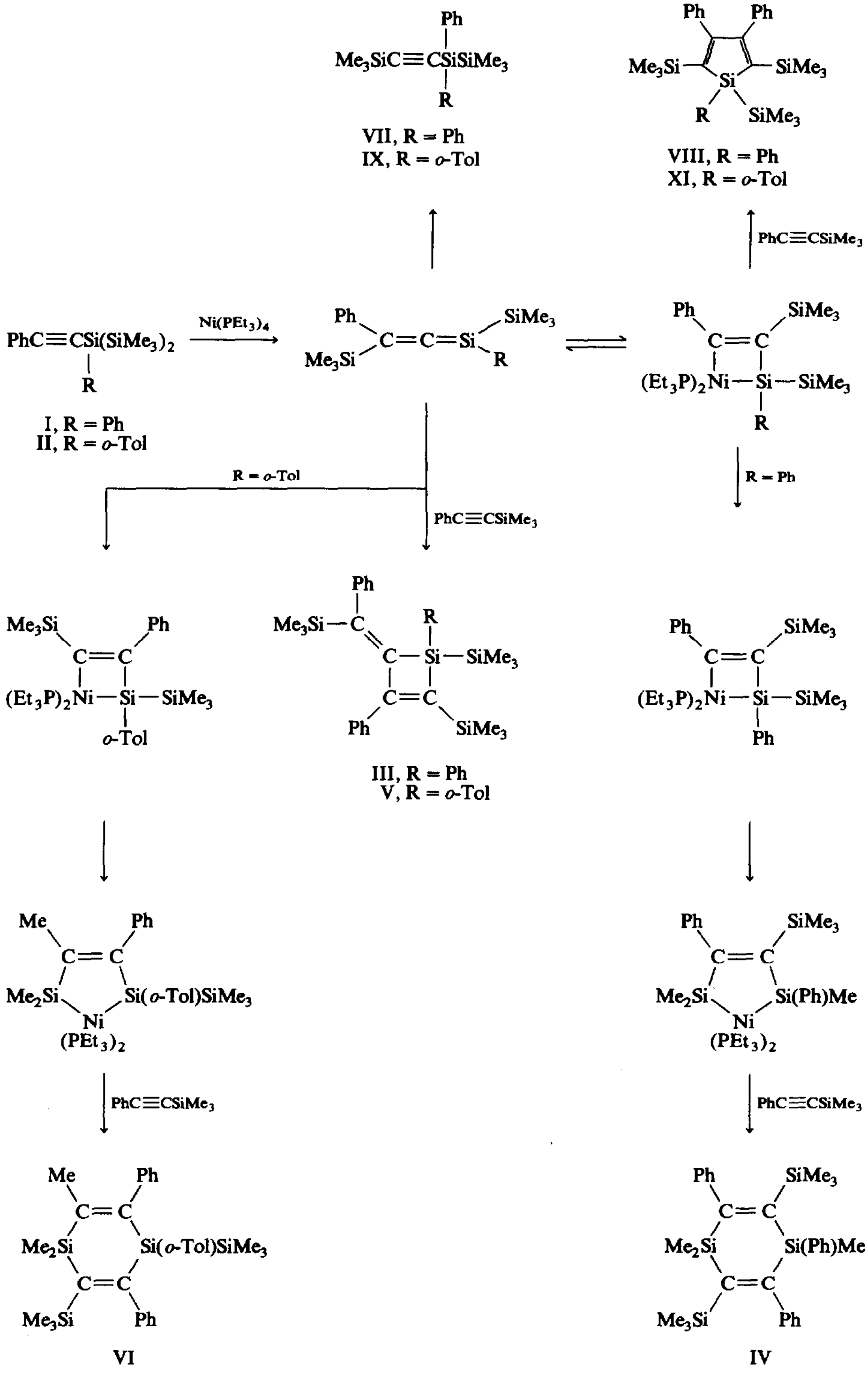
2-Phenyl-2-(phenylethynyl)hexamethyltrisilane (I) was synthesized by the reaction of 2-chloro-2-phenylhexamethyltrisilane with phenylethynyllithium in a mixed solvent consisting of hexane and THF. 2-(Phenylethynyl)-2-(*o*-tolyl)hexamethyltrisilane (II) was prepared by the reaction of 1 equiv. of *o*-tolylmagnesium bromide with 2,2-dichlorohexamethyltrisilane, followed by treatment of the resulting 2-chloro-2-(*o*-tolyl)hexamethyltrisilane with 1 equiv. of phenylethynyllithium in THF.

The nickel-catalyzed reactions of I and II were carried out in a sealed glass tube. Thus, treatment of I with a 2.0-fold excess of phenyl(trimethylsilyl)acetylene in the presence of 4.6 mol% of tetrakis(triethylphosphine)nickel(0) at 180 °C for 20 h resulted in the formation of 1,3-diphenyl-2-[phenyl(trimethylsilyl)methylene]-1,4-bis(trimethylsilyl)-1-silacyclobut-3-ene (III) and 1,4,4-trimethyl-1,3,6-triphenyl-2,5-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (IV) in 21 and 50% yields, respectively. Pure IV was separated from III by MPLC, however, III could not be isolated pure by this method. A mixture consisting of III and IV in the ratio of 7 : 3 was obtained. Since IV was obtained pure, the structure of III could be confirmed by eliminating the signals corresponding to IV in ^{1}H and ^{13}C NMR spectrum of the mixture (see Experimental).

The location of the substituents of the disilacyclohexa-2,5-diene ring for IV was established by NOE-FID difference experiments at 500 MHz. Thus, saturation of trimethylsilyl protons at δ −0.29 ppm caused a positive NOE of one of methyl protons (−0.15 ppm) of a dimethylsilyl group in the six-membered ring, while irradiation of methyl protons at δ −0.15 ppm resulted in strong enhancement of the trimethylsilyl proton (−0.29 ppm) and methyl proton (−0.09 ppm) signals. Similar irradiation of a resonance of the trimethylsilyl protons at δ 0.21 ppm produced a positive NOE for the methyl protons (0.50 ppm) of a methylphenylsilyl group. These results are wholly consistent with the proposed structure.

When compound II was heated with a 2.7-fold excess of phenyl(trimethylsilyl)acetylene in the presence of a nickel(0) catalyst under the same conditions, two products, 3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4-bis(trimethylsilyl)-1-(*o*-tolyl)-1-silacyclobut-3-ene (V) and 4,4,5-trimethyl-2,6-diphenyl-1,3-bis(trimethylsilyl)-1-(*o*-tolyl)-1,4-disilacyclohexa-2,5-diene (VI) in 75 and 18% yields, respectively. The structures of the products V and VI were verified by spectroscopic methods and by elemental analysis. Furthermore, the positions of the various substituents of V and VI were confirmed by NOE-FID difference experiments. Thus, saturation of a resonance of trimethylsilyl protons in V at δ 0.43 ppm led to a positive NOE for the tolyl methyl and trimethylsilyl protons (−0.16 ppm), while irradiation of the trimethylsilyl protons at −0.28 ppm resulted in the enhancement of the phenyl proton signals.

For compound VI, irradiation of the trimethylsilyl protons (−0.13 ppm) on the ring silicon atom produced a positive NOE for the methyl protons (2.54 ppm) of the tolyl group and for the phenyl protons. Irradiaton of the tolyl methyl protons led to enhancement of the signals from one of methyl protons of the dimethylsilyl group, the tolyl ring protons, and the phenyl protons. Irradiation of the methyl protons (2.14 ppm) on sp^2 carbon markedly enhanced the signals from the dimethylsilyl protons as well as those from the protons of the phenyl group. These results are consistent with the proposed structure for V and VI.


VII, R = Ph
IX, R = o-Tol
VIII, R = Ph
XI, R = o-Tol
PhC≡CSiMe3
I, R = Ph
II, R = o-Tol
Ni(PEt3)4
R = o-Tol
R = Ph
III, R = Ph
V, R = o-Tol
VI
IV

Scheme 1

Scheme 1 illustrates a possible mechanistic interpretation of the observed reaction course. The mechanism involves the formation of silapropadiene–nickel complexes. Compounds III and V are probably formed by a [2 + 2] cycloaddition of these complexes to phenyl(trimethylsilyl)acetylene to give the four-membered cyclic system. This type of the reaction has been found to occur in other systems [2,3]. Product IV is probably formed by the isomerization of the silapropadiene-nickel complex first to a nickelasilacyclobutene, by a 1,2-trimethylsilyl shift, and then to a nickeladisilacyclopentene, followed by the reaction with phenyl(trimethylsilyl)-acetylene. Compound VI is probably formed by the reaction of a nickeladisilacyclopentene which is produced from isomerization of a nickelasilacyclobutene with phenyl(trimethylsilyl)acetylene; the nickelasilacyclobutene having been formed from the silapropadiene-nickel complex arising from a 1,2-phenyl shift.

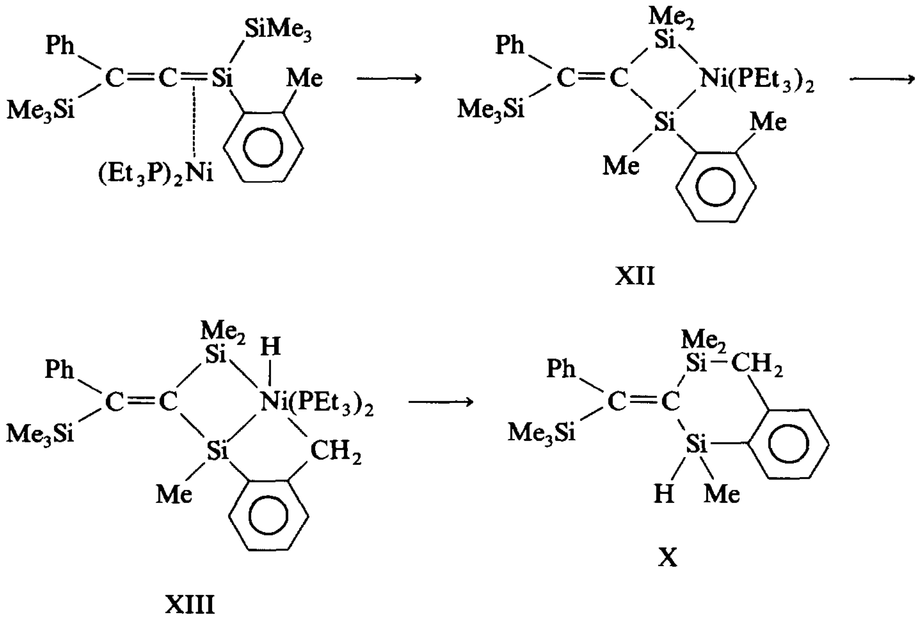
Next, we carried out the nickel-catalyzed reaction of I in the absence of phenyl(trimethylsilyl)acetylene. Thus, heating I in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in a sealed glass tube at 180 °C for 20 h gave four compounds, III, IV, 1,1-diphenyl-1-(trimethylsilylethynyl)trimethyldisilane (VII) and 1,3,4-triphenyl-1,2,5-tris(trimethylsilyl)silole (VIII) in 10, 11, 15, and 29% yields, respectively. Similar reaction of II in the presence of a catalytic amount of the nickel(0) complex afforded compound V, 1-phenyl-1-(*o*-tolyl)-1-(trimethylsilylethynyl)trimethyldisilane (IX), 4,5-benzo-3-hydro-1,1,3-trimethyl-2-[phenyl(trimethylsilyl)methylene]-1,3-disilacyclohexene (X), and 3,4-diphenyl-1-(*o*-tolyl)-1,2,5-tris(trimethylsilyl)silole (XI) in 16, 16, 10, and 17% yields respectively, in addition to the 23% recovery of starting compound II.

All spectral data obtained for VII and IX are identical with those of authentic samples prepared from an independent synthesis. The structures of VIII and XI were readily confirmed by spectroscopic methods, as well as by elemental analysis.

The IR spectrum of X shows a strong absorption band at 2121 cm^{-1}, due to the stretching vibration of an Si–H band at 2121 cm^{-1}. In the NOE-FID difference experiments for X at 500 MHz, irradiation of trimethylsilyl protons (-0.21 ppm) led to the enhancement of the signal from the methyl protons of the hydromethylsilyl group and from the proton of the hydrosilane, while irradiation of methyl protons of the dimethylsilyl group produced a positive NOE for the methylene protons and phenyl protons. These results are wholly consistent with the proposed structure for X.

Products VII and IX are probably formed by the isomerization of the silapropadienenickel complex by a 1,3-phenyl shift from sp^2 carbon onto a sp^2 silicon atom. Indeed, this type of product has been observed in the nickel-catalyzed reaction of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane in the absence of phenyl(trimethylsilyl)acetylene [3]. The fact that compounds III, IV and VIII were obtained from the reactions of I, and V and XI from that with II, clearly indicates that a significant amount of phenyl(trimethylsilyl)acetylene must be formed. This acetylene is probably produced by the elimination of nickel–silylene complexes from nickelasilacyclobutenes, although evidence for the formation of the nickel–silylene complex has not yet been obtained. The formation of the siloles VIII and XI apparently indicates the presence of the nickelasilacyclobutenes. Evidence for the existence of an equilibrium between the silapropadiene-nickel complexes and the nickelasilacyclobutenes has been reported previously [4].

The formation of benzodisilacyclohexene X requires isomerization of the



Scheme 2

silapropadiene-nickel complex to 3-[phenyl(trimethylsilyl)methylene]-1-nickela-2,4-disilacyclobutane (XII). Activation of the carbon–hydrogen bond in the tolyl methyl group of XII gives the intermediate XIII. Subsequent ring expansion to the nickel-containing seven-membered ring compound, and finally reductive elimination of the nickel species takes place (Scheme 2). In marked contrast to the similar nickel-catalyzed reaction of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane in which two isomers of a benzodisilacyclohexene derivative were produced in the ratio of 1 : 1.6, the present reaction afforded only compound X. No other isomer of X was detected in the reaction mixture.

As expected, the nickel(II) complex acts as an effective catalyst. Thus, treatment of II with a catalytic amount of dichlorobis(triethylphosphine)nickel(II) under the same conditions gave V, IX, X and XI in 17, 16, 8, and 12% yields, respectively together with a 25% recovery of the starting compound I.

Experimental

General procedure. All nickel-catalyzed reactions were carried out in 10 cm × 1 cm degassed, sealed glass tubes at 180 °C. ^1H NMR spectra were recorded with a JEOL Model JNM-90-FT spectrometer. NOE-FID difference spectra were recorded with a JEOL Model JNM-GX-500 spectrometer. IR spectra were measured on a Perkin–Elmer 1600 FT-AKA infrared spectrometer. Mass spectra were determined with a Shimadzu Model QP-1000 spectrometer.

Preparation of 2-phenyl-2-(phenylethynyl)hexamethyltrisilane (I). To a solution of phenylethynyllithium prepared from 4.085 g (40 mmol) of phenylacetylene in 100 ml of hexane and 25 ml (40 mmol) of a butyllithium–hexane solution, was slowly added 7.6 g (27 mmol) of 2-chloro-2-phenylhexamethyltrisilane in 50 ml of hexane. The mixture was stirred overnight and then hydrolyzed with water. Organic layer was separated, washed with water, and dried over potassium carbonate. The solvent was distilled off and the residue was fractionally distilled under reduced pressure to give 4.0 g (42% yield) of I: bp 121° C/1 mm Hg; MS *m/e* 352; IR 2145.8 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.29 (Me_3Si, s, 18H), 7.03–7.48 (phenyl ring protons, m, 10H). Anal. Found: C, 68.34; H, 8.19. Calcd.: C, 68.11; H, 8.00%.

*Preparation of 2-(phenylethynyl)-2-(*o*-tolyl)hexamethyltrisilane (II).* To an ether solution of 3 g (12.2 mmol) of 2,2-dichlorohexamethyltrisilane was added 15 ml of an ether solution of *o*-tolyllithium (13.4 mmol) at room temperature, and the mixture was stirred overnight. To this was added 15 ml of a hexane solution containing 14 mmol of phenylethynyllithium. The mixture was hydrolyzed with water. The organic layer was separated and washed with water, and dried over anhydrous magnesium sulfate. The solvents were evaporated off and the product II (4.3 g, 95% yield) was isolated by MPLC: MS *m/e* 366; IR 2145 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.31 (Me_3Si, s, 18H), 2.50 (CH_3, s, 3H), 6.89-7.74 (phenyl and tolyl ring protons, m, 9H); ^{13}C NMR (δ in $CDCl_3$) −0.4 (Me_3Si), 24.1 (CH_3), 90.6, 111.6 (C≡C), 124.4, 125.2, 128.2, 128.3, 128.7, 129.4, 131.8, 133.0, 136.5, 143.2 (phenyl and tolyl carbons). Anal. Found: C, 68.50, H, 8.23. Calcd.: C, 68.77, H, 8.25%.

Preparation of 1,1-diphenyl-1-(trimethylsilylethynyl)trimethyldisilane (VII). To a solution of 0.737 g (7.5 mmol) of trimethylsilylacetylene in 10 ml of THF was added 5 ml of a 1.6 *M* butyllithium–hexane solution while being cooled with ice. The mixture was stirred for 20 min at room temperature, and 2.4 g (8.3 mmol) of 1-chloro-1,1-diphenyltrimethyldisilane in 5 ml of THF was added. The mixture was stirred overnight and then hydrolyzed with water. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave 2.3 g (88% yield) of VII: MS *m/e* 352; ^{1}H NMR (δ in $CDCl_3$) 0.23 (Me_3Si, s, 9H), 0.26 (Me_3Si, s, 9H), 7.31–7.71 (phenyl ring protons, m, 10H); ^{13}C NMR (δ in $CDCl_3$) −2.04 (Me_3Si), −0.03 (Me_3Si), 108.53 (≡C–Si), 120.29 (≡C–C), 127.98, 129.17, 134.10, 135.08 (phenyl ring carbons). Anal. Found: C, 68.03; H, 7.96. Calcd.: C, 68.11; H, 8.00%.

*Preparation of 1-phenyl-1-(*o*-tolyl)-1-(trimethylsilylethynyl)trimethyldisilane (IX).* A solution of *o*-tolyllithium prepared from 1.5 g (8.8 mmol) of *o*-bromotoluene and 0.223 g (32 mmol) of lithium in ca. 10 ml of ether was added to 2.0 g (8.0 mmol) of 1.1-dichloro-1-phenyltrimethyldisilane at room temperature. The mixture was stirred for 2 h at room temperature, and a solution of trimethylsilyllithium, prepared from 0.868 g (8.8 mmol) of trimethylsilylacetylene and butyllithium in hexane (6.0 ml) was added. The mixture was stirred for 2 h and then hydrolyzed with water. Product XI (2.2 g, 75% yield) was isolated by MPLC: MS *m/e* 366; ^{1}H NMR (δ in $CDCl_3$) 0.28 (Me_3Si, s, 9H), 0.29 (Me_3Si, s, 9H), 2.38 (CH_3, s, 3H), 7.11–7.80 (phenyl and tolyl ring protons, m, 9H); ^{13}C NMR (δ in $CDCl_3$) −1.5 (Me_3Si), −0.1 (Me_3Si), 23.5 (CH_3), 109.6, 120.3 (C≡C), 125.0, 128.0, 128.9, 129.9, 130.0, 132.6, 134.7, 134.9, 136.8, 144.8 (phenyl and tolyl ring carbons). Anal. Found: 68.77; H, 8.25 Calcd.: C, 68.71; H, 8.23%.

Reaction of I with phenyl(trimethylsilyl)acetylene in the presence of $Ni(PEt_3)_4$. A mixture of 0.418 g (1.19 mmol) of I, 0.422 g (2.42 mmol) of phenyl(trimethylsilyl)-acetylene and 29 mg (4.6 mol%) of tetrakis(triethylphosphine)nickel(0) in a degassed, sealed tube was heated at 180° C for 20 h. The resulting mixture was chromatographed on silica gel with hexane as eluent to remove any nickel complexes. Hexane was concentrated and the residue was found from GPC, with nonadecane as an internal standard, to consist of III (21% yield) and IV (50% yield). Product IV was isolated pure by MPLC. The product III could not be obtained pure, but a mixture consisting of III and IV in a ratio of 7 : 3 was isolated. For III: MS *m/e* 526; ^{1}H NMR (δ in $CDCl_3$) −0.30 (Me_3Si, s, 9H), −0.15 (Me_3Si, s, 9H), 0.42 (Me_3Si, s, 9H), 6.69–7.75 (phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −0.47 (Me_3Si), 0.18 (two Me_3Si), 124.46, 125.32, 126.57, 126.73, 127.27, 127.87, 128.30, 129.50, 135.08, 137.40, 142.33, 142.55 (phenyl ring carbons), 145.26, 152.90, 162.76, 178.63 (olefinic carbons). For IV: mp 129 °C; MS *m/e* 526; ^{1}H NMR ($CDCl_3$) −0.29 (Me_3Si, s, 9H), −0.21 (Me_3Si, s, 9H), −0.15 (Me–SiMe, s, 3H), −0.09 (Me–SiMe, s, 3H), 0.50 (Me–SiPh, s, 3H), 6.95–7.39 (phenyl ring protons, m, 15H); ^{13}C NMR (δ in $CDCl_3$) −2.58 (Me–SiPh), 0.56 (Me_3Si), 1.59 (Me_3Si), 1.70 (MeSi), 2.35 (MeSi), 125.22, 125.65, 126.73, 126.89, 127.17, 127.44, 128.79, 134.64, 138.43, 146.07, 149.05 (phenyl ring carbons), 156.80, 163.95, 179.77, 180.42 (olefinic carbons). Anal. Found: C, 70.59; H, 7.90. Calcd.: 70.65; H, 8.03%.

Reaction of II with phenyl(trimethylsilyl)acetylene in the presence of Ni(PEt$_3$)$_4$. A mixture of 0.152 g (0.42 mmol) of II, 0.199 g (1.1 mmol) of phenyl(trimethylsilyl)acetylene and 9 mg (4.0 mol%) of $Ni(PEt_3)_4$ was heated at 180 °C for 20 h. The products were chromatographed on silica gel with hexane as eluent to remove nickel complexes. Hexane was concentrated and the residue was found by GPC, with nonadecane as an internal standard, to consist of V (75% yield) and VI (18% yield). Products V and VI were isolated by MPLC. For V: MS *m/e* 540; ^{1}H NMR (δ in $CDCl_3$) −0.28 (Me_3Si, s, 9H), −0.16 (Me_3Si, s, 9H), 0.43 (Me_3Si, s, 9H), 2.62 (MeC, s, 3H), 6.51–7.74 (phenyl and tolyl protons, m, 14H); ^{13}C NMR (δ in $CDCl_3$) −0.7 (Me_3Si), 0.0 (Me_3Si), 0.2 (Me_3Si), 21.6 (Me), 124.5, 125.0, 125.4, 126.6, 126.8, 127.0, 128.1, 129.9, 130.0, 136.2, 142.2, 142.5, 145.5 (phenyl and tolyl carbons), 146.0, 153.9, 162.8, 175.6 (olefinic carbons). Anal. Found: C, 70.97; H, 8.12. Calcd.: C, 71.03; H, 8.20%. For VI: MS *m/e* 540; ^{1}H NMR (δ in $CDCl_3$) −0.44 (Me_3Si, s, 9H), −0.13 (Me_3Si, s, 9H), 0.51 (MeSi, s, 3H), 0.56 (MeSi, s, 3H), 2.41 (MeC, s, 3H), 2.54 (tol-Me, s, 3H), 6.40–7.43 (phenyl and tolyl protons); ^{13}C NMR (δ in $CDCl_3$) −0.9 (Me_3Si), 1.1 (MeSi), 1.7 (MeSi), 2.0 (Me_3Si), 23.5 (Me-C), 28.8 (Me-tol), 124.9, 125.6, 126.9, 127.1, 127.4, 127.6, 129.0, 129.8, 136.5, 136.8, 139.6, 143.5, 142.2 (phenyl and tolyl ring carbons), 147.9, 162.5, 164.2, 179.0 (olefinic carbons). Anal. Found: C, 71.02; H, 8.10. Calcd.: 71.03; H, 8.20%.

Reaction of I with a catalytic amount of Ni(PEt$_3$)$_4$. A mixture of 0.433 g (1.23 mmol) and 31 mg (4.7 mol%) of $Ni(PEt_3)_4$ was heated at 180 °C for 20 h. The mixture was chromatographed on silica gel to remove nickel species, eluting with hexane. The mixture was found by GPC to consist of III (10% yield), IV (11% yield), VII (15% yield), and VIII (29% yield). Products VII and VIII were isolated by MPLC. The spectral data for III, IV, and VII are identical with those of authentic samples. For VIII: mp 159 °C; MS *m/e* 526; ^{1}H NMR (δ in $CDCl_3$) −0.32 (Me_3Si, s, 18H), 0.39 (Me_3Si, s, 9H), 7.01–7.37 (phenyl ring protons, m, 15H). Anal. Found: C, 70.46; H, 7.94. Calcd.: C, 70.65; H, 8.03%.

Reaction of II with a catalytic amount of Ni(PEt$_3$)$_4$. A mixture of 0.440 g (1.20 mmol) of II and 30 mg (4.7 mol%) of $Ni(PEt_3)_4$ was heated at 180 °C for 20 h. Nickel species was removed by a short silica gel column, eluting with hexane. Hexane was evaporated and the residue was analyzed by GPC as being V (16%

yield), IX (16% yield), X (10% yield) and XI (17% yield), in addition to 23% of recovered II. Products V, IX, X and XI were isolated by MPLC. For X: mp 124.9–126.2 °C; MS *m/e* 366; IR 2121 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) -0.37 (MeSi, s, 3H), -0.21 (Me_3Si, s, 9H), 0.05 (MeSi, s, 3H), 0.56 (MeSiH, d, *J* 4.0 Hz, 3H), 2.0 (HC, d, *J* 14.4 Hz, 1H), 2.9 (HC, d, *J* 14.4 Hz, 1H), 4.7 (HSi, q, *J* 4.0 Hz, 1H), 7.0–7.6 (phenyl and tolyl ring protons, m, 9H); ^{13}C NMR (δ in $CDCl_3$) -3.77 (MeSi), -1.60 (MeSi), -1.06 (MeSi), 1.27 (Me_3Si), 27.76 (CH_2), 123.6, 125.8, 127.3, 127.5, 127.9, 130.1, 136.1, 136.8, 146.0, 147.2 (phenyl and tolyl ring carbons), 158.3, 175.2 (olefinic carbons). Anal. Found: C, 68.83; H, 8.25. Calcd.: C, 68.77; H, 8.25%. For XI: MS *m/e* 540; ^{1}H NMR (δ in $CDCl_3$) -0.28 (Me_3Si, s, 18H), 0.41 (Me_3Si, s, 9H), 2.3 (MeC, s, 3H), 6.8–7.8 (phenyl and tolyl ring protons, m, 14H); ^{13}C NMR (δ in $CDCl_3$) 0.78 (Me_3SiSi), 1.1 (Me_3Si), 20.2 (Me), 125.2, 126.1, 126.8, 129.1, 129.5, 129.6, 134.5, 137.2, 142.9, 145.3 (phenyl and tolyl ring carbons), 147.6, 169.4 (olefinic carbons). Anal. Found: C, 71.10; H, 8.28. Calcd.: C, 71.04; H, 8.20%.

Reaction of II with a catalytic amount of $NiCl_2(PEt_3)_2$. A mixture of 0.520 g (1.42 mmol) of II and 17 mg (4.8 mol%) of $NiCl_2(PEt_3)_2$ was heated at 180 °C for 20 h. The resulting mixture was chromatographed on silica gel with hexane as eluent to remove nickel species. The products were found by GPC as to being V (17% yield), IX (16% yield), X (8% yield) and XI (12% yield), in addition to 25% recovery of starting compound II. The spectral data obtained for V, IX, X and XI were identical with those of authentic samples.

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