J. Org. Chem. 1990, 55, 3277-3280

(q, 2 H), 1.43 (m, 2 H), 0.93 (t, 3 H); ^{13}C NMR (CDCl$_3$) 136.0 (d), 117.2 (d), 116.9 (s), 34.2 (t), 22.0 (t), 20.4 (t), 13.6 (q).

(*Z*)-1-Cyano-2-hexene (5b): ^{1}H NMR (CDCl$_3$) 5.69 (dt, 1 H, J = 10.6 and 7.3 Hz), 5.40 (dt, 1 H, J = 10.6 and 7.0 Hz), 3.10 (d, 2 H, J = 7.0 Hz), 2.04 (q, 2 H), 1.42 (m, 2 H), 0.93 (t, 3 H); ^{13}C NMR (CDCl$_3$) 135.7 (d), 116.9 (d) 116.6 (s), 29.2 (t), 22.1 (t), 15.5 (t), 13.6 (q).

1-Cyano-3-methyl-2-butene (5d): IR (NaCl) 2950, 2250, 1670, 1450, 1380 cm^{-1}; ^{1}H NMR (CDCl$_3$) 5.16 (t, 1 H), 3.03 (d, 2 H), 1.76 (s, 3 H), 1.67 (s, 3 H); ^{13}C NMR (CDCl$_3$) 138.5 (s), 118.4 (s), 111.7 (d), 25.3 (t), 17.9 (q), 16.3 (q).

1-Cyano-3-phenyl-2-propene (5e): IR (NaCl) 3000, 2250, 1650, 1450, 1380 cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.25–7.39 (m, 5 H), 6.74 (d, 1 H, J = 15.4 Hz), 6.06 (dt, 1 H, J = 15.4 and 6.6 Hz), 3.30 (d, 2 H, J = 6.6 Hz); ^{13}C NMR (CDCl$_3$) 135.5 (s), 134.4 (d), 128.5 (d), 128.1 (d), 126.3 (d), 117.2 (s), 116.7 (d), 20.6 (t).

(*E*)-2-Hexenyl Phenyl Sulfone (6a): IR (NaCl) 2920, 1450, 1370, 1310, 1140, 1090, 970 cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.53–7.87 (m, 5 H), 5.51 (dt, 1 H, J = 14.6 and 7.3 Hz), 5.40 (dt, 1 H, J = 14.6 and 7.3 Hz) 3.75 (d, 2 H, J = 7.3 Hz), 1.97 (q, 2 H), 1.28 (m, 2 H), 0.81 (t, 3 H); ^{13}C NMR (CDCl$_3$) 141.4 (d), 138.3 (s), 133.4 (d), 128.8 (d), 128.3 (d), 115.9 (d), 60.1 (t), 34.5 (t), 21.8 (t), 13.5 (q).

(*Z*)-2-Hexenyl Phenyl Sulfone (6b): IR (NaCl) 2960, 1450, 1300, 1140, 1090, 970 cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.20–7.90 (m, 5 H), 5.62 (dt, 1 H, J = 9.1 and 7.3 Hz), 5.42 (dt, 1 H, J = 9.1 and 7.7 Hz), 3.85 (d, 2 H, J = 7.7 Hz), 1.71 (q, 2 H), 1.14 (m, 2 H), 0.74 (t, 3 H); ^{13}C NMR (CDCl$_3$) 139.2 (d), 138.7 (s), 133.5 (d), 128.9 (d), 128.4 (d), 115.2 (d), 55.2 (t), 29.2 (t), 22.0 (t), 13.5 (q).

3-Methyl-2-butenyl Phenyl Sulfone (6d): IR (NaCl) 2950, 1450, 1380, 1310, 1150, 1090 cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.53–7.88 (m, 5 H), 5.19 (t, 1 H), 3.79 (d, 2 H), 1.71 (s, 3 H), 1.30 (s, 3 H); ^{13}C NMR (CDCl$_3$) 142.7 (s), 138.6 (s), 133.4 (d), 128.8 (d), 128.2 (d), 110.3 (d), 56.1 (t), 25.7 (q), 17.7 (q).

(*Z*)-1-Iodo-2-hexene (7): IR (NaCl) 2960, 1460, 1150, 970 cm^{-1}; ^{1}H NMR (CDCl$_3$) 5.75 (dt, 1 H, J = 10.7 and 7.4 Hz), 5.48 (dt, 1 H, J = 10.7 and 8.8 Hz), 3.92 (d, 2 H, J = 8.8 Hz), 2.06 (q, 2 H) 1.45 (m, 2 H), 0.94 (t, 3 H); ^{13}C NMR (CDCl$_3$) 134.4 (d), 126.6 (d), 28.8 (t), 21.9 (t), 13.8 (q), 0.6 (t).

Registry No. **1a**, 928-95-0; **1b**, 928-94-9; **1c**, 4798-44-1; **1d**, 556-82-1; **1e**, 4407-36-7; **1f**, 822-67-3; **2a**, 120990-08-1; **2d**, 72422-42-5; **2e**, 68340-12-5; **2f**, 16717-84-3; **3a**, 126216-29-3; **3d**, 84466-88-6; **4**, 115977-54-3; **5a**, 100596-91-6; **5b**, 80639-55-0; **5d**, 4786-23-6; **5e**, 20068-10-4; **6a**, 98830-70-7; **6b**, 126216-30-6; **6d**, 15874-80-3; **7**, 115977-55-4; hydrogen iodide, 10034-85-2; (*Z*)-2-hexenyl methanesulfonate, 95351-72-7.

Synthesis and Reactions of (*E*)-1,4-Bis(silyl)-Substituted Enynes

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(*E*)-1,4-Bis(silyl)- and (*E*)-1,4-bis(disilanyl)but-1-en-3-ynes have been synthesized by the reaction of ethynyl-substituted mono- and disilanes with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) at room temperature in high yields. Similar reaction of 1-hexyne gave 2-butyloct-1-en-3-yne, while phenylacetylene afforded a mixture of 2,4-diphenylbut-1-en-3-yne and 1,4-diphenylbut-1-en-3-yne in low yields. The reaction of (*E*)-1,4-bis(methyldiphenylsilyl)but-1-en-3-yne (**2a**) with 1 equiv of methyllithium followed by methyl iodide gave (*E*)-1-(methyldiphenylsilyl)pent-1-en-3-yne. Similar treatment of 1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne with methyllithium followed by hydrolysis produced 1-(1-phenyltetramethyldisilanyl)but-1-en-3-yne. The reaction of **2a** with methanol in the presence of a catalytic amount of sodium methoxide afforded 1-(methyldiphenylsilyl)but-1-en-3-yne, which reacted with hydrosilanes in the presence of a platinum catalyst to give (*E*,*E*)-1,4-bis(silyl)buta-1,3-dienes.

Introduction

The C–H bond activation of 1-alkynes by a transition-metal catalyst constitutes one of the most important methods of preparing enynes, which can be used in synthetic routes to many complex compounds including natural products. Many papers that deal with the transition-metal-catalyzed dimerization of 1-alkynes leading to enynes have been reported to date.[1-7] Most of the papers, however, are concerned with head-to-tail dimerization.

The head-to-head couplings with high yields of the enynes were observed when 1-alkynes were heated in benzene in the presence of a catalytic amount of chlorotris(triphenylphosphine)rhodium(I).[2] These couplings, however, are restricted to the 1-alkynes bearing a 3-hydroxy group. Recently, we have discovered that treatment of ethynyl-substituted mono- and disilanes with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) at 100 °C in a sealed glass tube affords (*E*)-enynes arising from head-to-head coupling, as a single regioisomer.[8] We have now found that chlorotris(triphenylphosphine)rhodium(I), a more effective catalyst than the palladium complex, gives head-to-head dimers at room temperature in high yields. Here we report the regio- and stereospecific synthesis of (*E*)-1,4-bis(silyl)- and (*E*)-1,4-bis(disilanyl)butenynes and some reactions of (*E*)-1,4-bis(methyldiphenylsilyl)butenyne obtained from dimerization of ethynylmethyldiphenylsilane.

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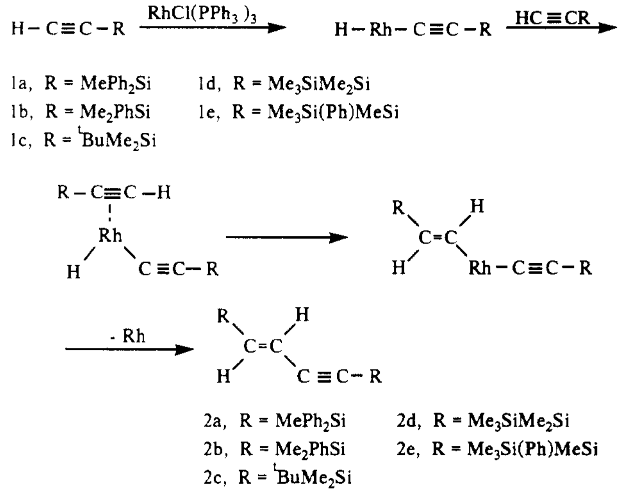
0022-3263/90/1955-3277$02.50/0

Scheme I



1a, R = MePh$_2$Si
1b, R = Me$_2$PhSi
1c, R = ^{t}BuMe$_2$Si
1d, R = Me$_3$SiMe$_2$Si
1e, R = Me$_3$Si(Ph)MeSi

2a, R = MePh$_2$Si
2b, R = Me$_2$PhSi
2c, R = ^{t}BuMe$_2$Si
2d, R = Me$_3$SiMe$_2$Si
2e, R = Me$_3$Si(Ph)MeSi

Results and Discussion

The rhodium-catalyzed dimerization of ethynylsilanes and ethynyldisilanes proceeds readily at room temperature, to give the corresponding head-to-head dimers in high yields. Thus, treatment of a toluene solution of ethynylmethyldiphenylsilane (**1a**) with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) at room temperature for 30 h afforded (*E*)-1,4-bis(methyldiphenylsilyl)butenyne (**2a**) in 94% yield.

Like the palladium-catalyzed head-to-head couplings reported recently,[8] the present reaction also proceeds with remarkable regio- and stereochemical specificity. No other regio- and stereoisomers were detected in the reaction mixture by either GLC or spectrometric analysis. Similar reaction of ethynyldimethylphenylsilane (**1b**) with a catalytic amount of the rhodium complex gave (*E*)-1,4-bis(dimethylphenylsilyl)butenyne (**2b**) in 85% yield.

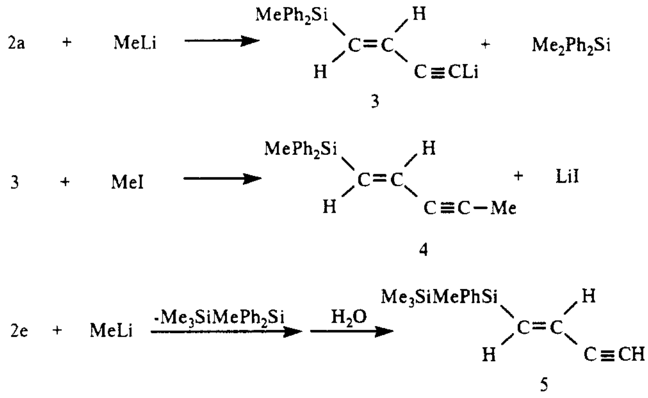
In contrast to the palladium-catalyzed dimerization reaction in which the introduction of at least one phenyl group onto the ethynylsilicon atom is necessary for obtaining the enynes in high yields, the present rhodium-catalyzed reaction gives the enynes in high yields with ethynylsilanes bearing no phenyl group. Thus, treatment of *tert*-butylethynyldimethylsilane (**1c**) with a catalytic amount of the rhodium(I) complex under the same conditions afforded 1,4-bis(*tert*-butyldimethylsilyl)butenyne (**2c**) in 82% yield.

Ethynyl-substituted disilanes can also be used as convenient precursor for enyne synthesis. When 1-ethynylpentamethyldisilane (**1d**) and 1-ethynyl-1-phenyltetramethyldisilane (**1e**) were treated with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) at room temperature, (*E*)-1,4-bis(pentamethyldisilanyl)butenyne (**2d**) and (*E*)-1,4-bis(1-phenyltetramethyldisilanyl)butenyne (**2e**) were obtained in 51 and 88% yields, respectively. Again, no other regio- and stereoisomers were detected by either GLC or spectroscopic analysis. All spectral data obtained for **2a**, **2b**, and **2e** were identical with those of the authentic samples.[8]

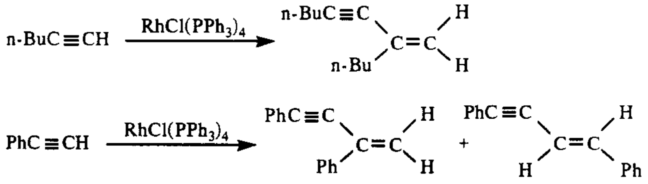
The structure of **2c** and **2d** were verified by mass, IR, and ^{1}H and ^{13}C NMR spectroscopic analyses, as well as by elemental analysis (see Experimental Section). In the ^{1}H NMR spectrum, the coupling constants (J = 19 Hz) of the olefinic protons at δ 6.03 and 6.61 for **2c** and at δ 5.90 and 6.48 for **2d** clearly indicate that compounds **2c** and **2d** must have an *E* configuration.

Scheme I illustrates a possible mechanistic interpretation of the observed reaction course. The mechanism involves the insertion of a rhodium complex into an acetylenic C–H bond, giving an ethynyl–rhodium complex, followed by regiospecific addition of the Rh–H across the triple bond of the coordinated ethynylsilane. Finally, reductive elimination of the rhodium species takes place to give the product. Head-to-head coupling may be ascribed to the steric requirement of a bulky silyl group. Examination of molecular models shows that the steric interaction between two bulky silyl groups in the head-to-tail coupling is much larger than that of the head-to-head coupling.

Scheme II



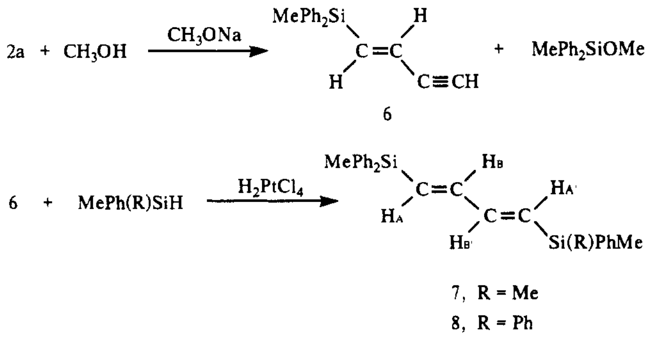
In order to check whether or not organic monosubstituted acetylenes give the head-to-head dimers in the presence of the rhodium complex, we carried out the reaction by using 1-hexyne and phenylacetylene under the same conditions. Thus, treatment of 1-hexyne with a catalytic amount of chlorotris(triphenylphosphine)rhodium afforded a dimer in 64% yield. Proton chemical shifts of the product were identical with those of 2-butyloct-1-en-3-yne reported by Nakamura et al.[4] Furthermore, the coupling constants (J = 2.2 Hz) of two resonances at 5.07 and 5.11 ppm, determined by proton-decoupling, were consistent with the structure of the head-to-tail dimer.



In contrast to the rhodium-catalyzed reaction of 1-hexyne, phenylacetylene gave two isomers of the dimer, 2,4-diphenylbut-1-en-3-yne and 1,4-diphenylbut-1-en-3-yne in 14 and 20% yields, respectively. All attempts to isolate the pure 2,4-isomer by using preparative TLC or GLC were unsuccessful. This compound always decomposed to give nonvolatile products. The structure of the 2,4-isomer, however, could be verified by ^{1}H and ^{13}C NMR spectroscopic analyses of the mixture. The pure 1,4-isomer that was isolated by preparative TLC, followed by recrystallization from ethanol, was characterized by spectroscopic method, as well as by elemental analysis. These results show that only the silyl-substituted monoacetylene undergoes regio- and stereospecific head-to-head coupling.

Next, we carried out the substitution reaction of a silyl group on an acetylenic carbon atom by using enynes **2a** and **2e**, in order to learn the chemical behavior of the present enynes. When 1 equiv of methyllithium was added to a THF solution of **2a** at −78 °C, (*E*)-4-lithio-1-(methyldiphenylsilyl)but-1-en-3-yne (**3**) was formed in almost quantitative yield, as indicated by the fact that treatment of the resulting solution with methyl iodide gave 1-(methyldiphenylsilyl)pent-1-en-3-yne (**4**) in 94% yield. Sim-

Scheme III



ilarly, the reaction of **2e** with 1 equiv of methyllithium at −78 °C in diethyl ether, followed by hydrolysis, gave 1-(1-phenyltetramethyldisilanyl)but-1-en-3-yne (**5**) in 96% yield (Scheme II).

The structure of **4** was verified by IR, mass, and ^{1}H and ^{13}C NMR spectrometric analyses. The ^{1}H NMR spectrum of **4** shows resonances at δ 0.57 and 1.90 due to methylsilyl protons and methyl protons on acetylenic carbon and resonances at δ 5.87, 6.59, and 7.13–7.66, attributed to two nonequivalent vinylic protons (J = 19 Hz) and phenyl ring protons. The ^{13}C NMR spectrum of **4** reveals signals at δ 80.27, 88.02 and 127.90, 139.01, due to acetylenic and vinylic carbons, respectively. The structure of **5** was also verified by mass, ^{1}H, and ^{13}C NMR spectroscopic methods (see Experimental Section).

Treatment of **2a** with methanol in the presence of a catalytic amount of sodium methoxide in diethyl ether at room temperature afforded (*E*)-1-(methyldiphenylsilyl)-butenyne (**6**) in 92% yield (Scheme III). The ^{1}H NMR spectrum of **6** shows a doublet signal at δ 2.65 (J = 2 Hz) due to acetylenic hydrogen, indicating that the only the silyl group on the acetylenic carbon is replaced by hydrogen.

Hydrosilylation of **6** readily produced (*E*,*E*)-1,4-bis(silyl)buta-1,3-dienes in high yields. Thus, the reaction of **6** with dimethylphenylsilane and methyldiphenylsilane in the presence of a catalytic amount of chloroplatinic acid at room temperature gave (*E*,*E*)-1-(dimethylphenylsilyl)-4-(methyldiphenylsilyl)buta-1,3-diene (**7**) and (*E*,*E*)-1,4-bis(methyldiphenylsilyl)buta-1,3-diene (**8**) in 67% and 65% yields, respectively (Scheme III). No other isomers were detected by either GLC or spectroscopic analysis.

The coupling constant ($J_{H_A\text{-}H_B}$ = 18.2 Hz, ($J_{H_A\text{-}H_B}$ = 0.7 Hz, $J_{H_A\text{-}H_A}$ = 0.6 Hz, $J_{H_B\text{-}H_B}$ = 9.7 Hz) of protons at δ 6.21 (H_A, $H_{A'}$) and 6.69 (H_B, $H_{B'}$) for compound 8 clearly shows that 8 must have an *E*,*E* configuration.

In conclusion, the rhodium-catalyzed reactions of (silyl)- and (disilanyl)-substituted acetylenes gave head-to-head dimers stereospecifically. The reactions of the resulting (*E*)-1,4-bis(silyl)- and -bis(disilanyl)but-1-en-3-yne with methyllithium afforded (*E*)-4-lithio-1-(silyl)- and -(disilanyl)but-1-en-3-yne in solution. (*E*)-1-(Silyl)but-1-en-3-yne reacted with hydrosilanes in the presence of a platinum catalyst to give (*E*,*E*)-1,4-bis(silyl)buta-1,3-dienes.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry argon. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Mass spectra were measured on a Shimazu Model GCMS-QP 1000 instrument. ^{1}H NMR (90 MHz) and ^{13}C NMR (22.5 MHz) spectra were determined on a JEOL Model JNM-FX-90A spectrometer.

Materials. All ethynylsilanes used as the starting compounds were synthesized by the reaction of ethynylmagnesium bromide with the corresponding chlorosilanes and chlorodisilanes by the method reported in the literature.[9] Toluene and THF were dried over lithium aluminum hydride and distilled before use.

(*E*)-1,4-Bis(methyldiphenylsilyl)but-1-en-3-yne (2a). In a 200-mL flask was placed a mixture of 5.00 g (22.5 mmol) of ethynylmethyldiphenylsilane (**1a**) and 1.05 g (1.14 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 125 mL of toluene. The mixture was stirred at room temperature for 30 h, and solvent toluene was evaporated under reduced pressure at room temperature. Then, the product was chromatographed on silica gel (200–300 mesh, length 200 mm, i.d. 35 mm), eluting with hexane. Hexane was evaporated to give 4.7 g (94% yield) of **2a**; mp 96.0 °C. Mass, IR, and ^{1}H and ^{13}C NMR spectra obtained for **2a** were identical with those of an authentic sample.[8]

(*E*)-1,4-Bis(dimethylphenylsilyl)but-1-en-3-yne (2b). A mixture of 3.00 g (18.1 mmol) of ethynyldimethylphenylsilane (**1b**) and 0.1896 g (2.05 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 75 mL of toluene was stirred at room temperature for 60 h. The solvent toluene was evaporated under reduced pressure at room temperature, and the residue was chromatographed to remove any rhodium complexes. The product **2b** (2.523 g, 84% yield) was isolated by MPLC (silica gel 40–63 μm, length 310 mm, i.d. 25 mm, flow rate 10 mL/min, eluent hexane) as colorless liquid. All spectral data obtained for **2b** were identical with those of an authentic sample.[8]

(*E*)-1,4-Bis(*tert*-butyldimethylsilyl)but-1-en-3-yne (2c). A mixture of 0.3946 g (2.82 mmol) of *tert*-butylethynyldimethylsilane (**1c**) and 0.134 g (0.145 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 10 mL of toluene was stirred at room temperature for 60 h. Toluene was distilled off under reduced pressure and the residue was chromatographed on silica gel (200–300 mesh, length 200 mm, i.d. 35 mm), eluting with hexane. The hexane was evaporated in vacuo to give 0.321 g (82% yield) of **2c**: subl 80 °C; MS *m*/*e* 227 (M^+ − ^{t}Bu); IR $\nu_{C\equiv C}$ 2155 cm^{-1}; ^{1}H NMR (δ in CCl_4) 0.06 (s, 6 H, MeSi), 0.12 (s, 6 H, MeSi), 0.91 (s, 9 H, ^{t}Bu), 0.96 (s, 9 H, ^{t}Bu), 6.03 (d, 1 H, HC=C, J = 19 Hz), 6.61 (d, 1 H, HC=C, J = 19 Hz); ^{13}C NMR (δ in $CDCl_3$) −6.2, −4.4 (MeSi), 16.8, 16.9 (CMe_3), 26.3, 26.6 (Me_3C), 93.0, 106.2 (acetylenic carbons), 125.0, 144.3 (olefinic carbons). Anal. Calcd for $C_{16}H_{32}Si_2$: C, 68.49; H, 11.49. Found: C, 68.33; H, 11.48.

(*E*)-1,4-Bis(pentamethyldisilanyl)but-1-en-3-yne (2d). A mixture of 0.200 g (1.2810 mol) of ethynylpentamethyldisilane (**1d**) and 0.059 g (6.3810 mol) of chlorotris(triphenylphosphine)rhodium(I) in 5 mL of toluene was stirred at room temperature for 50 h. The mixture was filtered and the product **2d** (0.1028 g, 51%) was isolated by MPLC through a silica gel column (40–63 μm, length 310 mm, i.d. 25 mm, flow rate 10 mL/min, eluent hexane): MS *m*/*e* 312 (M^+); IR $\nu_{C\equiv C}$ 2150 cm^{-1}; ^{1}H NMR (δ in CCl_4) 0.07 (s, 6 H, Me_2Si), 0.12 (s 6 H, Me_2Si), 0.12 (s, 9 H, Me_3Si), 0.18 (s, 9 H, Me_3Si), 5.90 (d, 1 H, HC=C, J = 19 Hz), 6.48 (d, 1 H, HC=C, J = 19 Hz); ^{13}C NMR (δ in $CDCl_3$) −4.4, −2.7, −2.3, −2.1 (MeSi), 93.3, 107.9 (acetylenic carbons), 123.7, 145.6 (olefinic carbons). Anal. Calcd for $C_{14}H_{32}Si_4$: C, 53.77; H, 10.31. Found: C, 53.53; H, 10.34.

(*E*)-1,4-Bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne (2e). A mixture of 13.3 g (60.9 mmol) of 1-ethynyl-1-phenyltetramethyldisilane (**1e**) and 0.850 g (0.0450 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 75 mL of toluene was stirred at room temperature for 14 h. The solvent was evaporated under reduced pressure, and the residue was directly chromatographed on silica gel (200–300 mesh, length 200 mm, i.d. 35 mm) to give 11.8 g (88% yield) of **2e**. All spectral data obtained for **2e** were identical with those of an authentic sample.[8]

2-Butyloct-1-en-3-yne.[4] A mixture of 283 mg (3.45 mmol) of 1-hexyne and 160 mg (0.173 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 5 mL of toluene was stirred at room temperature for 15 h. The mixture was treated with a silica gel column (200–300 mesh, length 200 mm, i.d. 35 mm) to remove any rhodium complexes and was concentrated under reduced pressure. The yield of the product (64% yield) was determined by GLC using tetradecane as an internal standard. Pure product was isolated by preparative GLC (Silicone SE-30): MS *m*/*e* 164 (M^+); IR $\nu_{C\equiv C}$ 2220 cm^{-1}; ^{1}H NMR[4] (δ in $CDCl_3$) 0.86–1.10 (m,

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6 H, CH_3), 1.10–1.77 (m, 8 H, CH_2CH_2), 2.13 (t, 2 H, J = 7 Hz, CH_2CH_2), 2.32 (t, 2 H, J = 7 Hz, $CH_2C{\equiv}C$), 5.12 (br d, 1 H, J = 2.2 Hz, $H_AC(H_B){=}C$), 5.19 (br d, 1 H, J = 2.2 Hz, $H_BC(H_A){=}C$); ^{13}C NMR (δ in $CDCl_3$) 13.5 (CH_3C), 13.8 (CH_3C), 18.9, 22.0, 22.1, 30.3, 30.9, 37.3 (CH_2), 81.1, 89.9 (acetylenic carbons), 119.1, 132.4 (olefinic carbons).

1,4-Diphenylbut-1-en-3-yne. A mixture of 70.3 mg (6.89 mmol) of phenylacetylene and 2 mol % of chlorotris(triphenylphosphine)rhodium(I) in 5 mL of toluene was stirred for 14 h at room temperature. To this was added 50.7 mg (0.275 mmol) of tridecane as an internal standard, and the mixture was then analyzed as being 2,4-diphenylbut-1-en-3-yne (14%) and 1,4-diphenylbut-1-en-3-yne (20%). 1,4-Diphenylbut-1-en-3-yne was isolated by preparative TLC (silica gel) and recrystallized from ethanol: mp 93.8 °C; MS *m/e* 204 (M^+); ^1H NMR (δ in $CDCl_3$) 6.17 (d, 1 H, J = 16 Hz, $H_AC(H_B){=}C$), 6.87 (d, 1 H, J = 16 Hz, $H_BC(H_A){=}C$), 6.99–7.44 (m, 10 H, phenyl ring protons); ^{13}C NMR 89.0, 91.8 (acetylenic carbons), 108.2, 123.4, 126.2, 128.1, 128.3, 128.5, 128.7, 131.4 (phenyl ring carbons), 136.3, 141.2 (olefinic carbons). Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.85; H, 5.85.

2,4-Diphenylbut-1-en-3-yne. A mixture of 1.10 g (10.8 mmol) of phenylacetylene and 1.3 mol % of chlorotris(triphenylphosphine)rhodium(I) in 5 mL of benzene was stirred for 14 h at room temperature. The resulting mixture was treated with a silica gel column (200–300 mesh, length 30 mm, i.d. 35 mm, eluent hexane) to remove any rhodium complexes. After evaporation of hexane, the residue was distilled under reduced pressure (1 Torr) to give a mixture of 2,4-diphenylbut-1-en-3-yne and 1,4-diphenylbut-1-en-3-yne in a ratio of 2:3. For 2,4-diphenylbut-1-en-3-yne: MS *m/e* 204 (M^+); ^1H NMR 5.79 (d, 1 H, J = 0.9 Hz, $H_AC(H_B){=}C$), 6.00 (d, 1 H, J = 0.9 Hz, $H_BC(H_A){=}C$), 7.28–7.82 (m, 10 H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) 88.7, 90.8 (acetylenic carbons), 120.5, 123.0, 126.0, 128.2 (3 carbons), 128.6, 131.5 (phenyl ring carbons), 136.9, 137.1 (olefinic carbons).

(*E*)-1-(Methyldiphenylsilyl)pent-1-en-3-yne (4). In a 10-mL Schlenk tube was placed 0.2120 g (0.48 mmol) of **2a** dissolved in 2 mL of THF. The contents of the Schlenk tube were cooled down to −78 °C. To this solution was added 0.4 mL of an ether solution of methyllithium (0.6 mmol), and the mixture was stirred at room temperature for 6 h. The mixture was again cooled down to −78 °C, and then 0.35 mL (0.60 mmol) of methyl iodide was added to the mixture. The reaction mixture was stirred overnight at room temperature. To this was added 10 mL of hexane, and the resulting precipitates were filtered off. Product **4** (0.1172g, 94% yield) was isolated by MPLC (silica gel 40–63 μm, length 300 mm, i.d. 25 mm, flow rate 10 mL/min, eluent hexane): MS *m/e* 262 (M^+); IR $\nu_{C\equiv C}$ 2215 cm^{-1}; ^1H NMR (δ in $CDCl_3$) 0.57 (s, 3 H, MeSi), 1.90 (d, 3 H, MeC, J = 2 Hz), 5.87 (dq, 1 H, HC=C, J = 19 Hz and 2 Hz), 6.59 (d, 1 H, HC=C, J = 19 Hz), 7.13–7.66 (m, 10 H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.98 (MeSi), 4.26 (MeC), 80.27, 88.02 (acetylenic carbons), 127.90 (olefinic and ring carbon), 139.01 (olefinic carbon), 129.46, 134.87, 135.70 (phenyl ring carbons). Anal. Calcd for $C_{18}H_{18}Si$: C, 82.38; H, 6.91. Found: C, 82.35; H, 6.87.

1-(1-Phenyltetramethyldisilanyl)but-1-en-3-yne (5). To a solution of 5.05 g (11.6 mmol) of **2e** in 20 mL of diethyl ether was added 19.2 mL (28.8 mmol) of a diethyl ether solution of methyllithium at −78 °C. The mixture was stirred at room temperature for 14 h and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The organic layer and extracts were combined and washed with water and then dried over potassium carbonate. The solvent ether was evaporated and the yield of the product was determined by GLC (96% yield). Product **5** was isolated by MPLC (silica gel 40–63 μm, length 310 mm, i.d. 25 mm), eluting with hexane: MS *m/e* 244 (M^+); ^1H NMR (δ in CCl_4) 0.07 (s, 9 H, Me_3Si), 0.35 (s, 3 H, MeSi), 2.74 (d, 1 H, acetylenic proton, J = 1.8 Hz), 5.72 (dd, 1 H, olefinic proton, J = 18.3 Hz, 1.8 Hz), 6.54 (d, 1 H, olefinic proton, J = 18.3 Hz), 7.02–7.35 (m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −6.05 (Me_3Si), −2.04 (MeSi), 77.70, 83.88 (acetylenic carbons), 123.75 (olefinic carbon), 127.92, 128.84, 134.37, 136.21 (phenyl ring carbons), 144.83 (olefinic carbon); exact mass calcd for $C_{14}H_{20}Si_2$ 244.1101, found 244.1093.

(*E*)-4-(Methyldiphenylsilyl)but-1-en-3-yne (6). To a solution of 0.5056 g (1.14 mmol) of **2a** dissolved in 12.5 mL of ether was added 0.25 mL of 0.1 N sodium methoxide–methanol solution. The mixture was stirred for 50 h at room temperature. The mixture was treated with a silica gel column (200–300 μm, length 200 mm, i.d. 35 mm), eluting with hexane, and then the mixture was concentrated under reduced pressure. Product **6** (0.2591 g, 92% yield) was isolated by MPLC (silica gel, 40–63 μm, length 310 mm, i.d. 25 mm, flow rate 10 mL/min, eluent hexane): MS *m/e* 248 (M^+); IR $\nu_{C\equiv C}$ 2097 cm^{-1}; ^1H NMR (δ in $CDCl_3$) 0.62 (s, 3 H, MeSi), 2.65 (d, 1 H, HC≡C), 5.90 (dd, 1 H, HC=C, J = 2 and 19 Hz), 6.82 (d, 1 H, HC=C, J = 19 Hz), 7.10–7.65 (m, 10 H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.08 (MeSi), 78.76, 83.58 (acetylenic carbons), 126.05 (olefinic carbon), 128.00, 129.61, 134.87, 135.07 (phenyl ring carbons), 143.31 (olefinic carbons). Anal. Calcd for $C_{17}H_{16}Si$: C, 82.20; H, 6.49. Found: C, 82.10; H, 6.38.

(*E*,*E*)-1-(Dimethylphenylsilyl)-4-(methyldiphenylsilyl)-buta-1,3-diene (7). A solution of 0.2160 g (0.87 mmol) of **6** and 0.1365 g (1.0 mmol) of dimethylphenylsilane in the presence of chloroplatinic acid catalyst in 2 mL of hexane was stirred for 60 h at room temperature. The reaction mixture was treated with a silica gel column (200–300 mesh, length 200 mm, i.d. 35 mm), eluting with hexane, to remove the platinum catalyst. Product **7** (0.2242 g, 67% yield) was isolated by MPLC under the same conditions as above: MS *m/e* 307 ($M^+ - C_6H_5$); ^1H NMR (δ in $CDCl_3$) 0.38 (s, 6 H, Me_2Si), 0.66 (s, 3 H, MeSi), 5.93–6.70 (m, 4 H, HC=C), 7.30–7.61 (m, 15 H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.74 (MeSi), −2.62 (Me_2Si), 129.02, 130.73, 147.84, 149.79 (olefinic carbons), 127.85 (2 carbons), 129.32, 133.85, 134.87 (2 carbons), 136.39, 138.34 (phenyl ring carbons). Anal. Calcd for $C_{25}H_{28}Si_2$: C, 78.06; H, 7.34. Found: C, 77.98; H, 7.30.

(*E*,*E*)-1,4-Bis(methyldiphenylsilyl)buta-1,3-diene (8). A mixture of 10.00 g (22.5 mmol) of **6** and 5 mL of 0.1 N sodium methoxide–methanol solution in 200 mL of ether was stirred for 2 days. The solvent was evaporated and the residue was directly chromatographed on silica gel (200–300 mesh, length 300 mm, i.d. 35 mm), eluting with hexane. The resulting solution was concentrated to give crude **6**. To the crude **6** dissolved in 40 mL of hexane were added 7.4736 g (22.6 mmol) of methyldiphenylsilane and 2 drops of a solution of chloroplatinic acid–2-propanol. The mixture was stirred for 2 days and the resulting crystals were filtered off. Recrystallization from ethanol gave 6.5273 g (65% yield) of **8**: mp 136 °C; MS *m/e* 446 (M^+); ^1H NMR (δ in $CDCl_3$) 0.63 (s, 6 H, MeSi), 6.04–6.91 (m, 4 H, HC=C), 7.29–7.70 (m, 20 H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.79 (MeSi), 127.85, 129.32, 134.83, 136.24 (phenyl ring carbons), 131.41, 149.55 (olefinic carbons). Anal. Calcd for $C_{30}H_{30}Si_2$: C, 80.66; H, 6.77. Found: C, 80.55; H, 6.70.

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