Supporting Information

Cobalt Catalyzed Three-Component Coupling Reaction of Alkyl Halides, 1,3-Dienes, and Trimethylsilylmethylmagnesium Chloride

Keiya Mizutani, Hiroshi Shinokubo, and Koichiro Oshima*

*Department of Material Chemistry, Graduate School of Engineering, Kyoto University,
Nishikyo-ku, Kyoto 615-8510, Japan*

Instrumentation and Materials

^1H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on Varian GEMINI 300 and Mercury 300 spectrometers. ^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 with the solvent residual peak (CDCl_3 : ^1H = 7.27 ppm, ^{13}C = 77 ppm) as internal reference. IR spectra were recorded on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous CoCl_2 was purchased from Wako Pure Chemicals and was used after removal of water (vide infra). The ligand dppe was purchased from TCI.

Experimental Section

Drying of cobalt chloride

The reaction was quite sensitive to water. Commercially available anhydrous CoCl_2 may contain some water. Completely anhydrous salt is clear blue, whereas purchased CoCl_2 is somewhat reddish-blue. Handling CoCl_2 under air also caused low yield. Hence, in each experiment, CoCl_2 was dried in a reaction flask carefully under reduced pressure (0.5 torr) by heating with a hair drier for 2 min immediately before use.

Typical Procedure for Three-Component Coupling Reaction

Anhydrous cobalt(II) chloride (3.3 mg, 0.025 mmol) was placed in a 25-mL flask and was heated with a hair drier in vacuo for 2 min. After the color of cobalt salt became blue, dppe (11.4 mg, 0.025 mmol) and anhydrous ether (3 mL) were sequentially added under argon. The mixture was stirred for about 30 min. A bright blue mixture was obtained. Bromocyclohexane (0.12 g, 0.75 mmol), 1-phenyl-1,3-butadiene (0.065 g, 0.50 mmol), and trimethylsilylmethylmagnesium chloride (1.0 M ether solution, 1.0 mL, 1.0 mmol) were successively added dropwise to the reaction mixture at 0 °C. The mixture turned brown during the addition of the Grignard reagent. After stirring for 5 h at 20 °C, the reaction mixture was poured into aqueous saturated ammonium chloride. The mixture was extracted with ethyl acetate (20 mL $\times$ 2). The combined organic layer was dried over Na₂SO₄ and was concentrated. Silica gel column purification (hexane) of the crude product provided (*E*)-4-cyclohexyl-1-phenyl-3-trimethylsilylmethyl-1-butene (**2a**, 0.13 g, 0.44 mmol) in 87% yield.

Characterization Data

(*E*)-4-Cyclohexyl-1-phenyl-3-trimethylsilylmethyl-1-butene (2a): IR (neat) 3026, 2922, 2853, 1495, 1448, 1248, 966, 839, 746, 692 cm⁻¹; ¹H NMR (CDCl₃) δ 7.25–7.40 (m, 4H), 7.15–7.25 (m, 1H), 6.20 (d, *J* = 15.6 Hz, 1H), 5.92 (dd, *J* = 9.0, 15.9 Hz, 1H), 2.35–2.50 (m, 1H), 1.70–1.90 (m, 1H), 1.50–1.70 (m, 4H), 1.00–1.40 (m, 6H), 0.75–1.00 (m, 2H), 0.71 (dd, *J* = 5.6, 14.7 Hz, 1H), 0.61 (dd, *J* = 8.7, 14.7 Hz, 1H), 0.01 (s, 9H); ¹³C NMR (CDCl₃) δ 137.90, 137.67, 128.36, 127.76, 126.56, 125.84, 47.15, 36.68, 35.06, 34.24, 32.94, 26.93, 26.43, 26.34, 24.24, –0.40. Found: C, 80.03; H, 10.51%. Calcd for C₂₀H₃₂Si: C, 79.92; H, 10.73%.

(*E*)-1-Phenyl-3-trimethylsilylmethyl-1-dodecene (2b): IR (neat) 3026, 2926, 2855, 1495, 1456, 1248, 966.3, 839, 746, 692 cm⁻¹; ¹H NMR (CDCl₃) δ 7.25–7.40 (m, 4H), 7.05–7.25 (m, 1H), 6.30 (d, *J* = 15.6 Hz, 1H), 5.95 (dd, *J* = 9.0, 15.6 Hz, 1H), 2.20–2.36 (m, 1H), 1.10–1.45 (m, 16H), 0.80–0.92 (m, 3H), 0.74 (dd, *J* = 5.7, 14.7 Hz, 1H), 0.67 (dd, *J* = 8.7, 14.7 Hz, 1H), 0.01 (s, 9H); ¹³C NMR (CDCl₃) δ 137.86, 137.44, 128.36, 128.04, 126.56, 125.84, 39.83, 39.23, 31.98, 29.81, 29.75, 29.72,

29.42, 27.45, 23.81, 22.79, 14.24, -0.449. Found: C, 79.74; H, 11.72%. Calcd for C₂₂H₃₈Si: C, 79.92; H, 11.58%.

(E)-5-Methyl-1-phenyl-3-trimethylsilylmethyl-1-undecene (2c): IR (neat) 3026, 2926, 2856, 1495, 1462, 1377, 966, 839, 746, 692 cm⁻¹; ¹H NMR (CDCl₃) δ 7.24–7.40 (m, 4H), 7.15–7.24 (m, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 5.95 (dd, *J* = 9.3, 13.5 Hz, 0.5H), 5.90 (dd, *J* = 9.3, 13.5 Hz, 0.5H), 2.30–2.48 (m, 1H), 1.00–1.50 (m, 13H), 0.80–1.00 (m, 6H), 0.55–0.79 (m, 2H), 0.00 (s, 9H); ¹³C NMR (CDCl₃) δ 138.04, 137.93, 137.57, 128.45, 128.10, 127.93, 126.66, 125.95, 46.97, 46.72, 37.90, 37.29, 36.38, 31.95, 31.91, 30.41, 30.16, 29.67, 26.89, 26.73, 24.61, 23.65, 22.68, 20.24, 19.34, 14.08, -0.54. Found: C, 80.20; H, 11.74%. Calcd for C₂₂H₃₈Si: C, 79.92; H, 11.58%.

(E)-5,5-Dimethyl-1-phenyl-3-trimethylsilylmethyl-1-hexene (2d): IR (neat) 3026, 2953, 2905, 2866, 1495, 1364, 1248, 968, 837, 748, 692 cm⁻¹; ¹H NMR (CDCl₃) δ 7.23–7.38 (m, 4H), 7.15–7.21 (m, 1H), 6.26 (d, *J* = 15.9 Hz, 1H), 6.00 (dd, *J* = 9.5, 15.9 Hz, 1H), 2.40–2.60 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 2H), 0.90 (s, 9H), 0.60–0.80 (m, 2H), 0.01 (s, 9H); ¹³C NMR (CDCl₃) δ 139.46, 138.00, 128.37, 127.07, 126.48, 125.75, 53.23, 36.94, 31.44, 30.42, 26.82, -0.33. Found: C, 78.76; H, 11.16%. Calcd for C₁₈H₃₀Si: C, 78.75; H, 11.01%.

(E)-4-Cyclohexyl-1-phenyl-3-(dimethylphenylsilylmethyl)-1-butene (2f): IR (neat) 2922, 2851, 1493, 1448, 1427, 1248, 1113, 966, 833, 795, 694 cm⁻¹; ¹H NMR (CDCl₃) δ 7.40–7.55 (m, 2H), 7.00–7.40 (m, 8H), 6.19 (d, *J* = 15.9 Hz, 1H), 5.87 (dd, *J* = 9.3, 15.9 Hz, 1H), 2.30–2.60 (m, 1H), 1.40–1.80 (m, 5H), 1.00–1.50 (m, 6H), 0.99 (dd, *J* = 5.7, 15.0 Hz, 1H), 0.87 (dd, *J* = 8.7, 14.7 Hz, 1H), 0.66–1.00 (m, 2H), 0.29 (s, 3H), 0.27 (s, 3H); ¹³C NMR (CDCl₃) δ 137.77, 137.31, 133.49, 128.54, 128.30, 128.03, 127.56, 126.57, 125.86, 47.10, 36.58, 35.00, 34.12, 32.92, 26.79, 26.39, 26.30, 23.26, 16.01, -1.70, -1.99. Found: C, 82.56; H, 9.23%. Calcd for C₂₅H₃₄Si: C, 82.80; H, 9.45%.

(E)-4-Cyclohexyl-1-(4-methoxyphenyl)-3-trimethylsilylmethyl-1-butene (2g): IR (neat) 2922, 2851,

1608.5, 1512, 1448, 1300, 1248, 1175, 1040, 966, 816, 758, 694 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.20–7.40 (m, 2H), 6.80–7.00 (m, 2H), 6.23 (d, $J = 15.9$ Hz, 1H), 5.78 (dd, $J = 9.3, 15.9$ Hz, 1H), 3.80 (s, 3H), 2.30–2.50 (m, 1H), 1.80–1.90 (m, 1H), 1.55–1.74 (m, 4H), 1.00–1.50 (m, 6H), 0.80–1.00 (m, 2H), 0.71 (d, $J = 5.7, 14.7$ Hz, 1H), 0.62 (dd, $J = 5.4, 11.7$ Hz, 1H), -0.01 (s, 9H); ^{13}C NMR (CDCl_3) δ 158.38, 135.60, 130.78, 127.08, 126.88, 113.83, 55.33, 47.27, 36.64, 35.05, 34.23, 32.96, 26.84, 26.44, 26.35, 24.34, -0.39 . Found: C, 76.28; H, 10.26%. Calcd for $\text{C}_{21}\text{H}_{34}\text{OSi}$: C, 76.30; H, 10.37%.

(*E*)-1-(2-bromophenyl)-4-cyclohexyl-3-trimethylsilylmethyl-1-butene (2h): IR (neat) 2922, 2851, 1466, 1437, 1248, 1022, 966, 839, 748 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.40–7.55 (m, 2H), 7.20–7.30 (m, 1H), 7.00–7.10 (m, 1H), 6.62 (d, $J = 15.6$ Hz, 1H), 5.82 (dd, $J = 9.6, 15.9$ Hz, 1H), 2.40–2.60 (m, 1H), 1.80–1.90 (m, 1H), 1.50–1.80 (m, 4H), 1.00–1.50 (m, 6H), 0.80–1.10 (m, 2H), 0.72 (dd, $J = 5.7, 14.7$ Hz, 1H), 0.63 (dd, $J = 4.7, 14.7$ Hz, 1H), 0.01 (s, 9H); ^{13}C NMR (CDCl_3) δ 140.67, 137.81, 132.64, 127.89, 127.28, 127.01, 126.82, 123.11, 47.0, 36.85, 35.13, 34.30, 32.80, 26.82, 26.47, 26.37, 24.19, -0.39 . Found: C, 63.23; H, 81.12%. Calcd for $\text{C}_{20}\text{H}_{31}\text{SiBr}$: C, 63.48; H, 7.99%.

(*E*)-1-(3-Chlorophenyl)-4-cyclohexyl-3-trimethylsilylmethyl-1-butene (2i): IR (neat) 2922, 2853, 1593, 1564, 1448, 1425, 1248, 1078, 970, 837, 775, 694 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.00–7.40 (m, 4H), 6.23 (d, $J = 15.9$ Hz, 1H), 5.95 (dd, $J = 9.3, 15.7$ Hz, 1H), 2.30–2.50 (m, 1H), 1.70–1.85 (m, 1H), 1.54–1.75 (m, 4H), 1.00–1.35 (m, 6H), 0.75–1.00 (m, 2H), 0.71 (dd, $J = 5.7, 14.7$ Hz, 1H), 0.61 (dd, $J = 8.7, 15.0$ Hz, 1H), -0.01 (s, 9H); ^{13}C NMR (CDCl_3) δ 139.97, 139.48, 134.48, 129.67, 126.68, 126.63, 125.90, 124.14, 46.92, 36.66, 35.11, 34.16, 32.92, 26.73, 26.33, 26.25, 24.12, -0.55 . Found: C, 71.98; H, 9.53%. Calcd for $\text{C}_{30}\text{H}_{31}\text{ClSi}$: C, 71.71; H, 9.33%.

1-Cyclohexyl-2-trimethylsilylmethyl-3-tridecene (2j): IR (neat) 2924, 2853, 1449, 1248, 970, 837 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.17–5.40 (m, 1H), 5.00–5.15 (m, 1H), 1.80–2.15 (m, 4H), 1.50–1.90 (m, 5H), 1.00–1.60 (m, 19H), 0.80–1.00 (m, 5H), 0.40–0.80 (m, 2H), -0.02 (s, 2.7H), -0.03 (s, 6.3H);

^{13}C NMR (CDCl_3) δ 137.99, 128.52, 127.51, 127.14, 47.52, 47.26, 40.59, 39.26, 39.15, 38.28, 34.26, 33.38, 33.08, 32.84, 32.51, 31.95, 29.97, 29.75, 29.67, 29.69, 29.58, 29.38, 29.23, 27.90, 27.75, 27.33, 26.81, 26.70, 26.50, 26.42, 26.39, 24.48, 23.88, 22.70, 14.10, -0.49 , -0.55 . Found: C, 73.92; H, 10.78%. Calcd for $\text{C}_{23}\text{H}_{46}\text{Si}$: C, 73.66; H, 10.68%.

1,5-Dicyclohexyl-4-trimethylsilylmethyl-2-pentene (2k): IR (neat) 2922, 2853, 1448, 1248, 972, 837 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.20–5.40 (m, 1H), 5.00–5.15 (m, 1H), 2.45–2.60 (m, 0.43H), 2.10–2.30 (m, 0.57H), 1.75–2.00 (m, 2H), 1.50–1.80 (m, 10H), 1.00–1.30 (m, 10H), 0.70–0.95 (m, 4H), 0.40–0.65 (m, 2H), -0.02 (s, 3.87H), -0.03 (s, 5.13H); ^{13}C NMR (CDCl_3) δ 138.10, 137.95, 126.87, 125.81, 47.42, 47.18, 40.57, 38.62, 36.24, 35.62, 35.20, 35.15, 34.37, 34.29, 33.52, 33.49, 33.40, 33.05, 32.71, 30.25, 26.90, 26.85, 26.75, 26.71, 26.65, 26.56, 26.51, 26.45, 24.40, 24.36, -0.37 . Found: C, 78.52; H, 12.45%. Calcd for $\text{C}_{21}\text{H}_{40}\text{Si}$: C, 78.67; H, 12.57%.

1-Cyclohexyl-2-trimethylsilylmethyl-3,5-pentadecadiene (2l): IR (neat) 2924, 2853, 1448, 1248, 988, 839 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.80–6.20 (m, 1.6H), 5.45–5.65 (m, 0.8H), 5.20–5.40 (m, 1.2H), 4.90–5.20 (m, 0.4H), 2.20–2.50 (m, 0.4H), 1.80–2.20 (m, 3.6H), 1.50–1.85 (m, 5H), 0.80–1.50 (m, 19H), 0.70–1.20 (m, 5H), 0.40–0.80 (m, 2H), -0.03 (s, 9H); ^{13}C NMR (CDCl_3) δ 139.07, 138.83, 132.15, 131.46, 130.63, 130.47, 128.81, 128.60, 47.02, 40.71, 39.09, 39.00, 38.22, 35.96, 35.01, 34.16, 33.23, 33.17, 32.96, 32.65, 31.92, 29.75, 29.64, 29.59, 29.53, 29.45, 29.34, 29.25, 27.30, 26.79, 26.63, 26.38, 26.27, 24.18, 23.70, 22.68, 14.08, -0.54 , -0.60 . Found: C, 79.70; H, 12.64%. Calcd for $\text{C}_{25}\text{H}_{48}\text{Si}$: C, 79.70; H, 12.84%.

4-Cyclohexyl-1-(dimethylphenylsilyl)-3-trimethylsilylmethyl-1-butene (2m): IR (neat) 3051, 2922, 2853, 1612, 1448, 1427, 1410, 1248, 1113, 993, 837, 781, 758, 729, 689 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.40–7.60 (m, 2H), 7.20–7.40 (m, 3H), 5.83 (dd, $J = 8.4, 18.6$ Hz, 1H), 5.66 (d, $J = 18.6$ Hz, 1H), 2.20–2.50 (m, 1H), 1.50–1.80 (m, 5H), 1.00–1.40 (m, 6H), 0.70–1.00 (m, 2H), 0.50–0.70 (m, 2H), 0.32 (s, 6H), -0.01 (s, 9H); ^{13}C NMR (CDCl_3) δ 155.63, 139.35, 133.76, 128.65, 127.54, 124.99, 46.44,

40.51, 35.23, 34.23, 32.86, 26.84, 26.57, 26.44, 23.52, -0.30, -2.30, -2.32. Found: C, 78.65; H, 13.48%. Calcd for C₂₂H₃₈Si₂: C, 78.77; H, 13.22%.

(E)-1-Phenyl-3-trimethylsilylmethyl-1,7-octadiene (4): IR (neat) 3063, 3016, 2901, 2858, 1641, 1577, 1495, 1448, 1416, 1366, 1248, 966, 908, 837, 786, 787, 749, 692 cm⁻¹; ¹H NMR (CDCl₃) δ 7.18–7.31 (m, 4H), 7.05–7.17 (m, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 5.87 (dd, *J* = 9.0, 15.9 Hz, 1H), 5.60–5.80 (m, 1H), 4.92 (d, *J* = 17.2 Hz, 1H), 4.86 (d, *J* = 11.7 Hz, 1H), 2.15–2.34 (m, 1H), 1.95–2.05 (m, 2H), 1.20–1.60 (m, 4H), 0.50–0.70 (m, 2H), -0.08 (s, 9H); ¹³C NMR (CDCl₃) δ 138.92, 137.76, 137.15, 128.37, 128.23, 126.63, 125.85, 114.23, 39.77, 38.66, 33.93, 26.81, 23.84, -0.46. Found: C, 79.36; H, 10.28%. Calcd for C₁₈H₂₈Si: C, 79.34; H, 10.36%.

5,5-Dimethyl-4-[5-phenyl-3-(trimethylsilylmethyl)pent-4-enyl]dihydrofuran-2-one (7): IR (neat) 3026, 2858, 2341, 1774, 1599, 1493, 1448, 1421, 1389, 1375, 1248, 1121, 1097, 957, 954, 837, 748, 694 cm⁻¹; ¹H NMR (CDCl₃) δ 7.05–7.50 (m, 5H), 6.32 (d, *J* = 15.6 Hz, 0.5H), 6.31 (d, *J* = 15.6 Hz, 0.5H), 5.92 (dd, *J* = 7.5, 9.3 Hz, 0.5H), 5.87 (dd, *J* = 7.1, 8.9 Hz, 0.5H), 2.50–2.70 (m, 1H), 2.10–2.40 (m, 3H), 1.42 (s, 1.5H), 1.41 (s, 1.5H), 1.22 (s, 1.5H), 1.21 (s, 1.5H), 1.20–1.50 (m, 4H), 0.60–0.80 (m, 2H), 0.00 (s, 4.5H), -0.01 (s, 4.5H); ¹³C NMR (CDCl₃) δ 137.50, 137.45, 136.18, 136.08, 129.22, 129.13, 128.56, 127.03, 125.98, 46.04, 45.19, 40.19, 39.67, 37.98, 37.61, 35.24, 35.04, 27.62, 27.58, 27.31, 24.02, 23.84, 21.85, 21.81, -0.65. Found: C, 73.03; H, 9.49%. Calcd for C₂₁H₃₂Si: C, 73.20; H, 9.36%.