Titanocene-Catalyzed Regioselective *syn*-Hydrosilation of Alkynes

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Supporting Information

Experimental Section

General. All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. NMR spectra were recorded on a JEOL JNM AL-300 spectrometer (^1H , 300 MHz; ^{13}C , 75 MHz). ^1H and ^{13}C chemical shifts are reported in ppm downfield of internal tetramethylsilane. Tetrahydrofuran was distilled from benzophenone-ketyl prior to use. All the other chemicals were obtained from commercial sources and used without further purification.

Titanocene-Catalyzed Hydrosilation of Alkynes. The reaction conditions and results are summarized in Table 1. A typical procedure is given for the preparation of (*E*)-4-(diphenylsilyl)-4-octene (**3a**): To a solution of Cp_2TiCl_2 (50.0 mg, 0.200 mmol) in THF (5 mL) was added *n*-BuLi hexane solution (1.60 mol/L, 0.25 mL, 0.40 mmol) at -78°C . After stirring the solution for 1 h at this temperature, 4-octyne (**1a**; 110 mg, 1.00 mmol) and diphenylsilane (**2a**; 203 mg, 1.10 mmol) were added subsequently by means of syringe. The reaction mixture was warmed to room temperature and stirred for 1 h. After aqueous work-up, GC analysis of the reaction mixture showed formation of **3a** in 87% yield. The alkenylsilane **3a** was isolated as colorless oil in 70% yield by column chromatography on silica gel using hexane as an eluent (Table 1, entry 1). The silanes **3a**,^{1,2} **3c**,² **3e**,² and **4**³ are known compounds and characterized by comparison of their ^1H and ^{13}C NMR spectra with those reported previously. The characterization data of all the other products are listed below.

(*E*)-3-(Diphenylsilyl)-3-hexene (3b): ^1H NMR (300 MHz, CDCl_3): δ 0.81 (t, J = 7.5 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H), 2.06-2.20 (m, 4H), 5.00 (s, 1H), 5.81 (t, J = 6.9 Hz, 1H), 7.23-7.33 (m, 6H), 7.46-7.49 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 14.0, 14.6, 21.9, 23.3, 127.8, 129.4, 134.2, 135.7, 136.0, 147.8. HRMS: calcd for $\text{C}_{18}\text{H}_{22}\text{Si}$ 266.1491; found 266.1482.

(*E*)-1-(Diphenylsilyl)-1-hexene (3d): ^1H NMR (300 MHz, CDCl_3): δ 0.82 (t, J = 6.9 Hz, 3H), 1.19-1.42 (m, 4H), 2.10-2.16 (m, 2H), 5.00 (d, J = 3.0 Hz, 1H), 5.84 (ddt, J = 18.3, 3.0, and 1.5 Hz, 1H), 6.22 (td, J = 18.3 and 6.3 Hz, 1H), 7.25-7.33 (m, 6H), 7.46-7.49 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 13.9, 22.3, 30.6, 36.6, 121.9, 127.9, 129.5, 134.3, 135.4, 153.9. HRMS: calcd for $\text{C}_{18}\text{H}_{22}\text{Si}$ 266.1491; found 266.1488.

(*E*)-1-(Methylphenylsilyl)-1-octene (3f): ^1H NMR (300 MHz, CDCl_3): δ 0.01 (d, J = 3.9 Hz, 3H), 0.49 (t, J = 6.6 Hz, 3H), 0.89-1.10 (m, 8H), 1.74-1.80 (m, 2H), 4.17 (qd, J = 3.9 and 3.3 Hz, 1H), 5.35 (ddt, J = 18.3, 3.3, and 1.5 Hz, 1H), 5.85 (dt, J = 18.3 and 6.3 Hz, 1H), 6.95-6.97 (m, 3H), 7.13-7.16 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ -5.2, 14.1, 22.6, 28.5, 28.9, 31.7, 36.9, 124.0, 127.8, 129.2, 134.5, 136.3, 151.7. HRMS: calcd for $\text{C}_{15}\text{H}_{24}\text{Si}$ 232.1647; found 232.1637.

(E)-1-(Methylphenylsilyl)-1-decene (3g): ^1H NMR (300 MHz, CDCl_3): δ 0.00 (d, J = 3.9 Hz, 3H), 0.49 (t, J = 6.6 Hz, 3H), 0.88-1.04 (m, 12H), 1.73-1.80 (m, 2H), 4.16 (qd, J = 3.9 and 3.0 Hz, 1H), 5.35 (ddt, J = 18.3, 3.0, and 1.5 Hz, 1H), 5.85 (dt, J = 18.3 and 6.3 Hz, 1H), 6.89-6.98 (m, 3H), 7.12-7.17 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ -5.1, 14.1, 22.7, 28.5, 29.2, 29.3, 29.5, 31.9, 36.9, 124.0, 127.8, 129.2, 134.5, 136.4, 151.7. HRMS: calcd for $\text{C}_{17}\text{H}_{28}\text{Si}$ 260.1960; found 260.1965.

(E)-1-(Phenylsilyl)-1-decene (3h): ^1H NMR (300 MHz, CDCl_3): δ 0.81 (t, J = 6.6 Hz, 3H), 1.17-1.35 (m, 12H), 2.07-2.14 (m, 2H), 4.46 (d, J = 3.3 Hz, 2H), 5.68 (ddt, J = 18.3, 3.3 and 1.5 Hz, 1H), 6.17 (dt, J = 18.3 and 6.3 Hz, 1H), 7.28-7.32 (m, 3H), 7.48-7.51 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 14.1, 22.7, 28.4, 29.2, 29.3, 29.4, 31.9, 36.9, 119.8, 128.0, 129.5, 132.4, 135.3, 154.2. HRMS: calcd for $\text{C}_{16}\text{H}_{26}\text{Si}$ 246.1804; found 246.1793.

(E)-1-(Trimethylsilyl)-2-(methylphenylsilyl)-1-propene (3i): ^1H NMR (300 MHz, CDCl_3): δ 0.00 (s, 9H), 0.29 (d, J = 3.9 Hz, 3H), 1.86 (d, J = 6.6 Hz, 3H), 4.51 (q, J = 3.9, 1H), 6.79 (q, J = 6.6 Hz, 1H), 7.23-7.25 (m, 3H), 7.38-7.41 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ -4.1, 0.8, 22.0, 127.7, 129.0, 134.7, 137.3, 137.4, 155.9. HRMS: calcd for $\text{C}_{13}\text{H}_{22}\text{Si}$ 234.1260; found 234.1261.

(E)-1-(Trimethylsilyl)-2-(phenylsilyl)-1-propene (3j): ^1H NMR (300 MHz, CDCl_3): δ 0.00 (s, 9H), 1.84 (d, J = 6.6 Hz, 3H), 4.47 (s, 2H), 6.89 (q, J = 6.6 Hz, 1H), 7.21-7.23 (m, 3H), 7.38-7.42 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 0.3, 21.9, 127.6, 129.1, 133.3, 134.0, 135.2, 158.3. HRMS: calcd for $\text{C}_{12}\text{H}_{20}\text{Si}$ 220.1104; found 220.1100.

Di[(E)-1-deceny]phenylsilane (5): ^1H NMR (300 MHz, CDCl_3): δ 0.81 (t, J = 6.6 Hz, 6H), 1.13-1.36 (m, 24H), 2.06-2.13 (m, 4H), 4.61-4.63 (m, 1H), 5.68 (ddt, J = 18.6, 3.0 and 1.5 Hz, 2H), 6.17 (dt, J = 18.6 and 6.3 Hz, 2H), 7.22-7.29 (m, 3H), 7.45-7.48 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 14.1, 22.7, 28.5, 29.2, 29.3, 29.5, 31.9, 36.9, 122.7, 127.8, 129.2, 135.1, 135.3, 152.8. HRMS: calcd for $\text{C}_{26}\text{H}_{44}\text{Si}$ 384.3212; found 384.3217.

References

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