Palladium-Catalyzed Bissilylation of Arynes with Cyclic Disilanes: Synthesis of Benzo-Annulated Disilacarbocycles

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Supporting Information

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^1H , 270 MHz; ^{13}C , 67.8 MHz; ^{29}Si , 53.7 MHz) spectrometer or a JEOL Lambda-400 (^1H , 400 MHz; ^{13}C , 99.5 MHz) spectrometer using residual chloroform (^1H) or CDCl_3 (^{13}C) as an internal standard and tetramethylsilane (^{29}Si) as an external standard. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (benzene as an eluent). Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. THF was distilled from Na/K alloy. MeCN was distilled from phosphorus pentoxide. 1,1,2,2-tetramethyl-1,2-(1,8-naphthylene)disilane (**1a**),¹ 1,1,2,2-tetramethyl-1,2-(2,2'-biphenylene)disilane (**1b**),² 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**1c**),³ 2-(trimethylsilyl)phenyl triflate (**2a**),⁴ 5-methyl-2-(trimethylsilyl)phenyl triflate (**2b**),⁵ 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**2e**),⁶ 6-(trimethylsilyl)-5-indanyl triflate (**2f**),⁶ 3-methoxy-2-(trimethylsilyl)phenyl triflate (**2h**),⁷ 6-phenyl-2-(trimethylsilyl)phenyl triflate (**2i**),⁸ 1-(trimethylsilyl)-2-naphthyl triflate (**2j**),⁹ 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**2l**)⁶ and 4-methyl-2-(trimethylsilyl)phenyl triflate (**2m**)⁵ were prepared according to literature procedures. 4-Methoxy-2-(trimethylsilyl)phenyl triflate (**2c**), 4-phenyl-2-(trimethylsilyl)phenyl triflate (**2d**) and 6-methyl-2-(trimethylsilyl)phenyl triflate (**2g**) were prepared from 2-chloro-4-methoxyphenol (Aldrich), 2-chloro-4-phenylphenol (TCI) and 2-bromo-6-methylphenol,¹⁰ respectively, in a similar manner as the preparation of **2a**. 3,4-Dimethoxy-2-(trimethylsilyl)phenyl triflate (**2k**) was synthesized from 3,4-dimethoxyphenol (Aldrich) in a similar manner as the preparation of **2h**.

Bissilylation of Arynes. A General Procedure. A THF solution (1.0 mL) of 1,1,3,3-tetramethylbutyl isocyanide (0.017 g, 0.12 mmol), $\text{Pd}(\text{OAc})_2$ (1.8 mg, 8.0 μmol) and 18-crown-6 (0.32 g, 1.2 mmol) was degassed by three freeze-thaw cycles. To this solution were added a disilane (0.40 mmol), an aryne precursor (0.60 mmol) and KF (0.070 g, 1.2 mmol), and

the resulting mixture was stirred at 20 °C. After the time specified in Table 1 or Scheme 2, the mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated. Silica-gel column chromatography (hexane as an eluent) followed by gel permeation chromatography (benzene as an eluent) gave the corresponding product.

7,7,12,12-Tetramethyl-7,12-dihydro-7,12-disilapleiadene (3aa). Isolated in 66% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.62 (s, 12 H), 7.42-7.49 (m, 4 H), 7.75-7.77 (m, 2 H), 7.86 (dd, J = 8.2, 1.2 Hz, 1 H), 7.94 (dd, J = 6.9, 1.3 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 1.9, 124.3, 128.3, 130.8, 133.6, 133.7, 135.2, 139.3, 140.8, 145.2; ^{29}Si NMR (CDCl_3) δ -7.4; Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{Si}_2$: C, 75.41; H, 6.96. Found: C, 75.22; H, 6.95.

7,7,9,12,12-Pentamethyl-7,12-dihydro-7,12-disilapleiadene (3ab). Isolated in 72% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.57 (s, 6 H), 0.58 (s, 6 H), 2.38 (s, 3 H), 7.22-7.24 (m, 1 H), 7.42-7.46 (m, 2 H), 7.55 (s, 1 H), 7.64 (d, J = 7.5 Hz, 1 H), 7.83 (d, J = 8.2 Hz, 2 H), 7.88-7.91 (m, 2 H); ^{13}C NMR (CDCl_3) δ 2.0, 2.3, 21.8, 124.4, 129.4, 130.9, 131.0, 133.7, 134.1, 134.6, 135.3, 135.4, 138.1, 139.5, 139.7, 140.9, 141.6, 145.2; ^{29}Si NMR (CDCl_3) δ -7.5, -7.4; Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{Si}_2$: C, 75.84; H, 7.27. Found: C, 75.71; H, 7.22.

9-Methoxy-7,7,12,12-tetramethyl-7,12-dihydro-7,12-disilapleiadene (3ac). Isolated in 75% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.60 (s, 6 H), 0.62 (s, 6 H), 3.86 (s, 3 H), 6.95-6.08 (m, 1 H), 7.30-7.35 (m, 1 H), 7.38-7.51 (m, 2 H), 7.63-7.75 (m, 1 H), 7.83-7.94 (m, 4 H); ^{13}C NMR (CDCl_3) δ 1.7, 2.3, 54.9, 113.2, 120.1, 124.2, 124.3, 130.8, 131.0, 133.5, 135.2, 135.3, 135.6, 135.8, 139.0, 139.6, 140.8, 147.0, 159.6; ^{29}Si NMR (CDCl_3) δ -7.6, -7.1; Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{OSi}_2$: C, 72.36; H, 6.94. Found: C, 72.31; H, 7.12.

7,7,12,12-Tetramethyl-9-phenyl-7,12-dihydro-7,12-disilapleiadene (3ad). Isolated in 54% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.64-0.67 (m, 12 H), 7.35-7.42 (m, 1 H), 7.44-7.52 (m, 4 H), 7.63-7.67 (m, 3 H), 7.82-7.88 (m, 3 H), 7.93-7.99 (m, 3 H); ^{13}C NMR (CDCl_3) δ 1.9, 2.0, 124.3, 127.2, 127.3, 127.4, 128.8, 130.95, 130.97, 132.5, 133.6, 134.3, 135.29, 135.33, 139.2, 139.3, 140.8, 141.0, 141.4, 143.9, 145.7; ^{29}Si NMR (CDCl_3) δ -7.3, -7.1; HRMS Calcd for $\text{C}_{26}\text{H}_{26}\text{Si}_2$: M^+ , 394.1573. Found: m/z 394.1569.

7,7,9,10,12,12-Hexamethyl-7,12-dihydro-7,12-disilapleiadene (3ae). Isolated in 77% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.58 (s, 12 H), 2.31 (s, 6 H), 7.44 (t, J = 7.5 Hz, 2 H), 7.50 (s, 2 H), 7.82 (d, J = 7.5 Hz, 2 H), 7.89 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (CDCl_3) δ 2.0, 19.8, 124.2, 130.8, 133.5, 135.2, 135.3, 136.9, 139.6, 140.8, 142.1; ^{29}Si NMR (CDCl_3) δ -7.7; Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{Si}_2$: C, 76.23; H, 7.56. Found: C, 76.07; H, 7.49.

7,7,12,12-Tetramethyl-9,10-propylene-7,12-dihydro-7,12-disilapleiadene (3af).

Isolated in 76% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.68 (s, 12 H), 2.15 (quintet, $J = 7.5$ Hz, 2 H), 3.04 (t, $J = 7.5$ Hz, 4 H), 7.51 (t, $J = 7.5$ Hz, 2 H), 7.74 (s, 2 H), 7.89 (d, $J = 7.5$ Hz, 2 H), 7.99 (d, $J = 7.5$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ 2.1, 24.9, 32.9, 124.2, 130.1, 130.8, 133.5, 135.1, 139.7, 140.8, 142.4, 144.7; ^{29}Si NMR (CDCl_3) δ -7.3; Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{Si}_2$: C, 77.03; H, 7.31. Found: C, 76.75; H, 7.26.

7,7,8,12,12-Pentamethyl-7,12-dihydro-7,12-disilapleiadene (3ag).

Isolated in 40% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.50 (s, 6 H), 0.59 (s, 6 H), 2.56 (s, 3 H), 7.19 (d, $J = 7.5$ Hz, 1 H), 7.29 (t, $J = 7.5$ Hz, 1 H), 7.42-7.48 (m, 2 H), 7.57 (d, $J = 7.5$ Hz, 1 H), 7.80-7.84 (m, 3 H), 7.92 (dd, $J = 7.0, 1.2$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 1.6, 4.6, 24.6, 124.5, 128.2, 130.2, 130.5, 131.1, 131.8, 133.1, 134.2, 135.4, 139.9, 140.2, 143.0, 143.2, 143.6, 145.8; ^{29}Si NMR (CDCl_3) δ -8.2, -7.8; Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{Si}_2$: C, 75.84; H, 7.27. Found: C, 75.63; H, 7.25.

8-Methoxy-7,7,12,12-tetramethyl-7,12-dihydro-7,12-disilapleiadene (3ah).

Isolated in 37% yield as a colorless solid: ^1H NMR (CDCl_3) δ -0.06 (s, 6 H), -0.05 (s, 6 H), 3.26 (s, 3 H), 6.35 (d, $J = 8.2$ Hz, 1 H), 6.68-6.93 (m, 5 H), 7.23-7.27 (m, 2 H), 7.42 (dd, $J = 7.0, 1.2$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 0.3, 3.1, 54.9, 111.0, 124.4, 124.5, 125.6, 130.0, 130.1, 130.6, 132.6, 133.2, 133.9, 135.6, 139.3, 140.4, 143.9, 146.9, 164.2; ^{29}Si NMR (CDCl_3) δ -7.5, -8.5; Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{OSi}_2$: C, 72.36; H, 6.94. Found: C, 72.10; H, 7.08.

7,7,12,12-Tetramethyl-8-phenyl-7,12-dihydro-7,12-disilapleiadene (3ai).

Isolated in 30% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.07 (s, 6 H), 0.62 (s, 6 H), 7.03 (t, $J = 7.7$ Hz, 1 H), 7.24-7.33 (m, 2 H), 7.36-7.51 (m, 5 H), 7.62 (d, $J = 8.2$ Hz, 1 H), 7.70-7.75 (m, 2 H), 7.83 (t, $J = 8.1$ Hz, 2 H), 7.96 (d, $J = 6.8$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 3.0, 4.1, 124.2, 126.8, 127.1, 127.8, 128.6, 128.9, 129.2, 129.8, 130.5, 130.8, 131.4, 133.2, 133.3, 134.7, 135.4, 139.8, 140.5, 143.2, 145.2, 145.4, 147.4, 148.3; ^{29}Si NMR (CDCl_3) δ -8.6, -7.1; HRMS Calcd for $\text{C}_{26}\text{H}_{26}\text{Si}_2$: M^+ , 394.1573. Found: m/z 394.1589.

7,7,14,14-Tetramethyl-7,14-dihydro-7,14-disilabenzok[pleiadene (3aj).

Isolated in 33% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.59 (s, 6 H), 0.76 (s, 6 H), 7.44-7.54 (m, 4 H), 7.80-7.88 (m, 6 H), 8.04 (d, $J = 7.0$ Hz, 1 H), 8.31 (d, $J = 8.2$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 0.9, 5.5, 124.6, 125.1, 125.5, 128.2, 128.7, 129.3, 129.4, 130.2, 130.7, 133.3, 133.6, 133.9, 135.5, 136.6, 139.6, 140.1, 143.4, 144.8, 145.0; ^{29}Si NMR (CDCl_3) δ -8.5, -7.6; Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{Si}_2$: C, 78.20; H, 6.56. Found: C, 78.19; H, 6.54.

8,9-Dimethoxy-7,7,12,12-tetramethyl-7,12-dihydro-7,12-disilapleiadene (3ak).

Isolated in 63% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.49 (s, 6 H), 0.58 (s, 6 H), 3.88 (s, 3 H), 3.91 (s, 3 H), 7.00 (d, $J = 8.2$ Hz, 1 H), 7.41-7.49 (m, 3 H), 7.80-7.83 (m, 3 H), 7.97-8.00 (m, 1 H); ^{13}C NMR (CDCl_3) δ 1.0, 3.5, 55.3, 60.7, 113.2, 124.37, 124.44, 129.9, 130.2, 130.6, 133.2, 134.1, 135.5, 136.6, 137.5, 139.6, 140.4, 143.2, 152.7, 154.1; ^{29}Si NMR (CDCl_3) δ -8.6, -8.0; HRMS Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_2\text{Si}_2$: M^+ , 378.1471. Found: m/z 378.1461.

8,11-Dimethoxy-7,7,12,12-tetramethyl-7,12-dihydro-7,12-disilapleiadene (3al).

Isolated in 72% yield as a colorless solid: ^1H NMR (CDCl_3) δ 0.50 (s, 12 H), 3.78 (s, 6 H), 6.87 (s, 2 H), 7.44 (t, $J = 7.9$ Hz, 2 H), 7.80 (d, $J = 7.9$ Hz, 2 H), 7.91 (d, $J = 7.9$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ 3.2, 55.7, 112.5, 124.5, 130.0, 133.0, 134.6, 134.7, 140.2, 142.7, 158.3; ^{29}Si NMR (CDCl_3) δ -9.2; Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_2\text{Si}_2$: C, 69.79; H, 6.92. Found: C, 69.80; H, 6.96.

1,1,6,6-Tetramethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]disilocine (3ba). Isolated in 81% yield as a colorless solid: ^1H NMR (CDCl_3) δ -0.73 (s, 6 H), 0.63 (s, 6 H), 7.32-7.36 (m, 4 H), 7.39-7.44 (m, 4 H), 7.58-7.60 (m, 2 H), 7.64 (dd, $J = 5.6, 3.4$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ -0.9, 0.3, 126.8, 128.0, 128.6, 129.2, 134.0, 135.5, 137.6, 146.9, 151.1; ^{29}Si NMR (CDCl_3) δ -7.8; Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{Si}_2$: C, 76.68; H, 7.02. Found: C, 76.87; H, 7.09.

1,1,2,6,6-Pentamethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]disilocine (3bg). Isolated in 70% yield as a colorless solid: ^1H NMR (CDCl_3) -0.76 (s, 3 H), -0.59 (s, 3 H), 0.52 (s, 3 H), 0.64 (s, 3 H), 2.45 (s, 3 H), 7.11-7.14 (m, 1 H), 7.21-7.24 (m, 1 H), 7.31-7.36 (m, 2 H), 7.40-7.49 (m, 5 H), 7.53-7.56 (m, 2 H); ^{13}C NMR (CDCl_3) -1.4, -1.3, 2.5, 5.2, 25.1, 126.65, 126.69, 127.4, 127.5, 128.1, 129.0, 129.3, 130.6, 132.0, 135.7, 137.1, 138.9, 140.0, 143.5, 145.8, 149.2, 151.2, 151.4; ^{29}Si NMR (CDCl_3) δ -8.2, -7.4; Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{Si}_2$: C, 77.03; H, 7.31. Found: C, 76.73; H, 7.39.

2-Methoxy-1,1,6,6-tetramethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]disilocine (3bh).

Isolated in 72% yield as a colorless solid: ^1H NMR (CDCl_3) -0.76 (s, 3 H), -0.74 (s, 3 H), 0.61 (s, 3 H), 0.63 (s, 3 H), 3.82 (s, 3 H), 6.88 (dd, $J = 8.2, 2.7$ Hz, 1 H), 7.21 (d, $J = 2.7$ Hz, 1 H), 7.32-7.45 (m, 6 H), 7.59 (d, $J = 7.9$ Hz, 3 H); ^{13}C NMR (CDCl_3) -1.0, -0.7, 0.2, 0.4, 54.9, 112.4, 120.8, 126.73, 126.74, 128.5, 128.6, 129.1, 129.2, 135.4, 135.5, 135.7, 137.3, 137.4, 137.9, 148.8, 151.0, 151.1, 159.2; ^{29}Si NMR (CDCl_3) δ -8.2, -7.4; HRMS Calcd for $\text{C}_{23}\text{H}_{26}\text{OSi}_2$: M^+ , 374.1522. Found: m/z 374.1524.

1,1,3,6,6-Pentamethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]disilocene (3bm). Isolated in 63% yield as a colorless solid: ^1H NMR (CDCl_3) -0.74 (s, 3 H), -0.73 (s, 3 H), 0.62 (s, 3 H), 0.64 (s, 3 H), 2.35 (s, 3 H), 7.17 (d, $J = 7.7$ Hz, 1 H), 7.32-7.36 (m, 2 H), 7.39-7.42 (m, 4 H), 7.46 (s, 1 H), 7.54-7.60 (m, 3 H); ^{13}C NMR (CDCl_3) -0.9, -0.8, 0.3, 21.5, 126.72, 126.74, 128.5, 128.6, 128.9, 129.1, 129.2, 134.2, 135.0, 135.4, 135.5, 137.56, 137.64, 137.8, 143.2, 146.8, 151.08, 151.13; ^{29}Si NMR (CDCl_3) δ -8.1, -7.9; Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{Si}_2$: C, 77.03; H, 7.31. Found: C, 76.83; H, 7.32.

1,1,6,6-Tetramethyl-6,7,8,9-tetrahydro-(1*H*)-benzo[*b*][1,4]disilolepine (3ca). Isolated in 55% yield as a colorless oil: ^1H NMR (CDCl_3) 0.27 (s, 12 H), 0.99 (t, $J = 6.5$ Hz, 4 H), 1.91 (quintet, $J = 6.5$ Hz, 2 H), 7.32 (dd, $J = 5.5, 3.2$ Hz, 2 H), 7.59 (dd, $J = 5.5, 3.2$ Hz, 2 H); ^{13}C NMR (CDCl_3) -0.3, 18.0, 31.6, 127.7, 134.4, 146.9; ^{29}Si NMR (CDCl_3) δ -0.8; Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{Si}_2$: C, 66.59; H, 9.46. Found: C, 66.45; H, 9.30.

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