Cover page for Supporting Information

Title: Synthesis of Multiply Substituted Alkylidene Silacyclohexadiene Derivatives via Palladium-Catalyzed Insertion of Alkynes into Alkylidene Silacyclobutenes

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1) General experimental condition and characterization data for all products except illustrative examples.

General. The reactions of alkylidenesilacyclobutenes with activated alkynes were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk techniques. All the alkylidenesilacyclobutenes¹ and 1-phenylprop-2-yn-1-one² were synthesized by the reported procedure. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Toluene was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. ¹H and ¹³C NMR spectra were recorded at 300 and 75.4 MHz, respectively. The absorption spectra were recorded with Varian Cary 1E UV-vis spectrophotometer. The absorption spectra of alkylidene silacyclohexadienes were studied in THF with concentrations ca. 10⁻⁵ M.

4ba+4bc: A mixture of two isomers in 10:1 molar ratio, combined isolated yield 82% (433 mg); ¹H NMR (CDCl₃, Me₄Si): δ = 3.08 (s, CH₃), 3.40 (s, CH₃), 3.49 (s, CH₃), 3.96 (s, CH₃), 7.16-7.68 (m, CH); ¹³C NMR (CDCl₃, Me₄Si): δ = 51.6, 51.7, 51.7, 52.7, 126.9, 127.0, 127.3, 127.8, 127.9, 128.0, 128.3, 128.4, 128.6, 128.9, 129.6, 129.8, 129.9, 130.1, 130.4, 131.4, 132.3, 132.5, 133.0, 134.8, 135.3, 135.6, 135.9, 136.2, 138.1, 139.6, 141.7, 142.4, 143.1, 143.9, 144.8, 146.6, 166.7, 169.3, 169.7; HRMS calcd. for C₃₄H₂₈O₄Si: 528.1757, found 528.1739.

4ca+4cc: A mixture of two isomers in 6:1 molar ratio, combined isolated yield 95% (410 mg); ¹H NMR (CDCl₃, Me₄Si): δ = 0.42 (s, CH₃), 0.43 (s, CH₃), 0.97-1.42 (m, CH₃), 3.45-4.43 (m, CH₂), 7.11-7.37 (m, CH); ¹³C NMR (CDCl₃): δ = -2.1, -1.1, 13.4, 14.1, 14.2, 15.2, 60.9, 61.1, 61.6, 65.8, 126.5, 126.7, 126.8, 126.9, 128.0, 128.1, 128.3, 128.5, 128.6, 129.5, 129.6, 130.2, 132.5, 132.8, 135.8, 136.0, 136.5, 138.3, 141.3, 141.7, 142.3, 142.4, 143.0, 143.3, 145.0, 145.0, 154.6, 166.5, 166.6, 169.6, 169.7; HRMS calcd. for C₂₆H₂₈O₄Si: 432.1757, found 432.1741.

4da: Colorless liquid, isolated yield 91% (315 mg); ^1H NMR (CDCl_3 , Me_4Si): $\delta = 0.35$ (s, 6H, CH_3), 3.09 (s, 3H, CH_3), 6.98 (s, 1H, CH), 7.23-7.36 (m, 12H, CH); ^{13}C NMR (CDCl_3): $\delta = -1.4$ (2 CH_3), 51.5 (1 CH_3), 126.6 (2 CH), 126.6 (1 CH), 127.8 (1 CH), 128.2 (2 CH), 128.6 (2 CH), 128.9 (2 CH), 133.5 (1 quart C), 137.8 (1 quart C), 139.1 (1 CH), 139.4 (1 quart C), 140.4 (1 CH), 143.0 (1 quart C), 145.0 (1 CH), 145.3 (1 quart C), 168.9 (1 quart C); MS (EI) m/z (rel int) 346 (M^+ , 98), 89 (100); IR (neat): ν ($\text{C}=\text{O}$) = 1723cm^{-1} ; UV/Vis (THF) : λ max : 325 nm; HRMS calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_2\text{Si}$: 346.1389, found 346.1385.

4ea: Colorless liquid, isolated yield 89% (418 mg); ^1H NMR (CDCl_3 , Me_4Si): $\delta = 3.10$ (s, 3H, CH_3), 7.16-7.58 (m, 23H, CH); ^{13}C NMR (CDCl_3 , Me_4Si): $\delta = 51.6$ (1 CH_3), 126.8 (1 CH), 127.1 (2 CH), 128.1 (1 CH), 128.2 (4 CH), 128.3 (2 CH), 128.5 (2 CH), 129.1 (2 CH), 123.0 (2 CH), 133.2 (2 quart C), 133.5 (1 quart C), 135.4 (1 quart C), 135.7 (4 CH), 137.6 (1 quart C), 137.7 (1 CH), 140.6 (1 CH), 142.7 (1 quart C), 145.8 (1 quart C), 147.3 (1 CH), 168.6 (1 quart C); IR (neat): ν ($\text{C}=\text{O}$) = 1725cm^{-1} ; UV/Vis (THF) : λ max : 328 nm; HRMS calcd. for $\text{C}_{32}\text{H}_{26}\text{O}_2\text{Si}$: 470.1702, found 470.1689.

4fa: Colorless liquid, isolated yield 70% (274 mg); ^1H NMR (CDCl_3 , Me_4Si): $\delta = 0.40$ (s, 6H, CH_3), 6.79-7.42 (m, 18H, CH); ^{13}C NMR (CDCl_3): $\delta = -1.1$ (2 CH_3), 126.6 (2 CH), 126.7 (1 CH), 127.4 (2 CH), 127.8 (2 CH), 127.9 (2 CH), 128.6 (4 CH), 129.7 (2 CH), 131.9 (1 CH), 135.3 (1 quart C), 136.7 (1 quart C), 136.8 (1 quart C), 140.0 (1 quart C), 140.2 (1 CH), 140.6 (1 CH), 142.9 (1 quart C), 144.9 (1 CH), 152.5 (1 quart C), 197.0 (1 quart C); IR (neat): ν ($\text{C}=\text{O}$) = 1665cm^{-1} ; HRMS calcd. for $\text{C}_{27}\text{H}_{24}\text{OSi}$: 392.1596, found 392.1590.

4ga+4gc: A mixture of two isomers in 7:1 molar ratio, combined isolated yield 80% (288 mg); ^1H NMR (CDCl_3 , Me_4Si): $\delta = 0.32$ (s, CH_3), 0.35 (s, CH_3), 1.96 (s, CH_3), 2.36 (s, CH_3), 3.82 (s, CH_3), 3.92 (s, CH_3), 6.65 (s, CH), 7.22-7.38 (m, CH), 7.50 (s, CH); ^{13}C NMR (CDCl_3): $\delta = -2.5$, -1.4, 17.9, 19.2, 51.4, 51.8, 126.6, 126.7, 127.5, 127.7, 127.8, 128.1,

128.2, 128.4, 128.5, 129.4, 129.9, 130.1, 130.8, 132.8, 135.5, 136.5, 136.8, 136.9, 137.8, 141.4, 142.9, 143.1, 143.8, 150.8, 170.4; HRMS calcd. for $C_{23}H_{24}O_2Si$: 360.1546, found 360.1537.

4ha+two isomers: A mixture of three isomers in 2:1:1 molar ratio, combined isolated yield 72% (304 mg); 1H NMR ($CDCl_3$, Me_4Si): δ = 0.16 (s, CH_3), 0.17 (s, CH_3), 3.16 (s, CH_3), 3.19 (s, CH_3), 3.20 (s, CH_3), 6.40-7.29 (m, CH); ^{13}C NMR ($CDCl_3$): δ = -2.1, -2.0, -1.4, 51.1, 51.2, 51.4, 126.4, 126.5, 126.6, 126.7, 126.8, 127.0, 127.2, 127.5, 127.8, 128.1, 128.2, 128.5, 128.9, 129.0, 129.7, 130.0, 132.5, 133.8, 136.3, 136.4, 136.6, 136.7, 137.4, 137.5, 137.6, 138.0, 138.3, 140.3, 140.6, 140.8, 141.3, 141.7, 141.9, 142.6, 142.9, 143.1, 143.4, 146.2, 151.4, 156.0, 169.4, 171.2, 171.6; HRMS calcd. for $C_{28}H_{26}O_2Si$: 422.1702, found 422.1708.

5aa+5ac: A mixture of two isomers in 10:1 molar ratio, combined isolated yield 87% (341 mg); 1H NMR ($CDCl_3$, Me_4Si): δ = 0.20 (s, CH_3), 0.37 (s, CH_3), 0.86-0.94 (m, CH_3), 1.02-1.44 (m, CH_2), 2.05-2.39 (m, CH_2), 3.74 (s, CH_2), 3.75 (s, CH_2), 6.71 (s, CH), 7.08 (s, CH); ^{13}C NMR ($CDCl_3$): δ = -3.8, -3.7, 12.9, 13.8, 13.9, 14.2, 22.3, 22.4, 23.0, 23.1, 24.8, 26.2, 29.8, 31.5, 32.0, 32.7, 34.7, 35.3, 36.1, 38.9, 51.5, 51.7, 51.9, 52.1, 127.1, 127.5, 130.1, 134.4, 138.0, 138.1, 138.5, 139.1, 147.2, 151.3, 154.5, 165.8, 168.8, 170.1, 170.2, 170.5; HRMS calcd. for $C_{22}H_{36}O_4Si$: 392.2383, found 392.2392.

5ba+5bc: A mixture of two isomers in 2:1 molar ratio, combined isolated yield 84% (433 mg); 1H NMR ($CDCl_3$, Me_4Si): δ = 0.50 (s, CH_3), 0.70-1.29 (m, CH_3), 2.21-2.34 (m, CH_2), 3.39 (s, CH_3), 3.42 (s, CH_3), 3.74 (s, CH_3), 3.82 (s, CH_3), 7.32-7.71 (m, CH); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 13.1, 13.6, 13.7, 13.8, 13.9, 14.4, 22.3, 22.4, 22.7, 22.9, 25.2, 26.6, 30.0, 30.5, 31.4, 32.6, 34.8, 35.3, 35.6, 40.1, 51.1, 51.5, 52.0, 52.3, 124.1, 126.5, 127.7, 127.8, 127.9, 129.3, 129.8, 130.6, 131.7, 133.9, 134.4, 135.2, 135.5, 135.6, 141.1, 149.1, 153.3, 155.1, 168.5, 168.8, 169.4, 169.6, 170.2; HRMS calcd. for $C_{32}H_{40}O_4Si$: 516.2696, found

516.2700.

5da: Colorless liquid, isolated yield 79% (362 mg); ^1H NMR (CDCl_3 , Me_4Si): δ = 0.72 (t, J = 7.2 Hz, 3H, CH_3), 0.81 (t, J = 7.2 Hz, 3H, CH_3), 1.08 (t, J = 7.5 Hz, 3H, CH_3), 1.13-1.38 (m, 8H, CH_2), 2.00 (t, J = 7.5 Hz, 2H, CH_2), 2.26 (t, J = 7.2 Hz, 2H, CH_2), 2.37 (t, J = 7.5 Hz, 2H, CH_2), 3.77 (s, 3H, CH_3), 6.94 (s, 1H, CH), 7.31-7.54 (m, 11H, CH); ^{13}C NMR (CDCl_3 , Me_4Si): δ = 13.3 (1 CH_3), 13.8 (1 CH_3), 13.8 (1 CH_3), 22.4 (1 CH_2), 23.0 (1 CH_2), 25.5 (1 CH_2), 29.8 (1 CH_2), 31.7 (1 CH_2), 35.4 (1 CH_2), 35.9 (1 CH_2), 52.2 (1 CH_3), 127.9 (2 CH), 128.3 (1 quart C), 129.7 (1 CH), 133.4 (1 quart C), 133.5 (1 quart C), 135.5 (1 quart C), 135.5 (2 CH), 141.0 (1 quart C), 149.1 (1 quart C), 149.7 (1 quart C), 169.9 (1 quart C); IR (neat): ν ($\text{C}=\text{O}$) = 1723 cm^{-1} ; HRMS calcd. for $\text{C}_{30}\text{H}_{38}\text{O}_2\text{Si}$: 458.2641, found 458.2640.

5ea+three isomers: A mixture of four isomers in 6:2:1:1 molar ratio, combined isolated yield 60% (210 mg); ^1H NMR (CDCl_3 , Me_4Si): δ = 0.126 (s, CH_3), 0.131 (s, CH_3), 0.154 (s, CH_3), 0.253 (s, CH_3), 0.86-1.06 (m, CH_3), 1.21-1.50 (m, CH_2), 1.94-2.34 (m, CH_2), 3.17 (s, CH_3), 3.20 (s, CH_3), 3.67 (s, CH_3), 3.73 (s, CH_3), 6.25 (s, CH), 6.41 (s, CH), 7.01 (s, CH), 7.12 (s, CH); ^{13}C NMR (CDCl_3): δ = -4.0, -3.5, -2.3, -0.5, 12.6, 13.0, 13.9, 17.1, 22.2, 22.3, 22.4, 22.5, 22.6, 22.7, 23.0, 23.1, 23.9, 24.6, 25.5, 25.9, 26.0, 29.6, 29.7, 29.8, 29.9, 30.4, 31.4, 31.6, 31.7, 31.7, 31.8, 32.0, 32.0, 32.1, 33.6, 33.7, 33.8, 34.2, 35.8, 35.9, 36.1, 38.4, 38.9, 41.1, 42.0, 50.8, 51.2, 51.6, 51.7, 125.3, 127.7, 130.4, 134.2, 135.2, 138.7, 139.6, 139.7, 140.1, 141.7, 142.6, 142.7, 144.8, 145.6, 160.3, 160.8, 169.6, 170.8, 172.8; HRMS calcd. for $\text{C}_{21}\text{H}_{36}\text{O}_2\text{Si}$: 348.2485, found 348.2482.

6ba: Yellow liquid, isolated yield 78% (423 mg); ^1H NMR (CDCl_3 , Me_4Si): δ = 0.39 (s, 6H, CH_3), 0.66 (t, J = 7.2 Hz, 3H, CH_3), 0.92 (t, J = 7.2 Hz, 3H, CH_3), 1.11-1.49 (m, 8H, CH_2), 1.91 (t, J = 6.6 Hz, 2H, CH_2), 2.20 (t, J = 7.2 Hz, 2H, CH_2), 3.03 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 5.72 (t, J = 7.5 Hz, 1H, CH), 7.20-7.35 (m, 10H, CH), 7.90 (s, 1H, CH); ^{13}C NMR (CDCl_3): δ = -2.2 (2 CH_3), 13.7 (1 CH_3), 14.0 (1 CH_3), 22.6 (1 CH_2), 22.6 (1 CH_2), 27.8 (1

CH₂), 29.9 (1 CH₂), 30.2 (1 CH₂), 31.7 (1 CH₂), 51.5 (1 CH₃), 51.8 (1 CH₃), 126.4 (1 CH), 126.6 (2 CH), 127.7 (2 CH), 128.5 (2 CH), 128.6 (1 CH), 130.9 (1 quart C), 131.0 (1 CH), 132.4 (1 CH), 137.4 (1 quart C), 137.9 (1 quart C), 139.6 (1 quart C), 140.4 (1 quart C), 143.2 (1 quart C), 144.0 (1 CH), 147.0 (1 quart C), 158.5 (1 quart C), 167.7 (1 quart C), 170.2 (1 quart C); ν (C=O) = 1723 cm⁻¹; HRMS calcd. for C₃₄H₄₂O₄Si: 542.2852, found 542.2869.

6ca: Colorless liquid, isolated yield 70% (320 mg); ¹H NMR (CDCl₃, Me₄Si): δ = 0.34 (s, 6H, CH₃), 0.75 (t, J = 7.5 Hz, 3H, CH₃), 1.00 (t, J = 7.5 Hz, 3H, CH₃), 1.22 (q, J = 7.5 Hz, 2H, CH₂), 1.54 (q, J = 7.5 Hz, 2H, CH₂), 1.94 (t, J = 7.5 Hz, 2H, CH₂), 2.22 (t, J = 7.5 Hz, 2H, CH₂), 3.10 (s, 3H, CH₃), 5.75 (t, J = 7.5 Hz, 1H, CH), 6.74 (s, 1H, CH), 7.23-7.34 (m, 10H, CH), 7.93 (s, 1H, CH); ¹³C NMR (CDCl₃): δ = -1.3 (2 CH₃), 14.1 (1 CH₃), 14.3 (1 CH₃), 21.3 (1 CH₂), 22.8 (1 CH₂), 30.2 (1 CH₂), 32.6 (1 CH₂), 51.3 (1 CH₃), 126.2 (1 CH), 126.6 (2 CH), 127.8 (2 CH), 128.1 (1 CH), 128.4 (2 CH), 130.4 (2 CH), 131.0 (1 quart C), 132.0 (1 CH), 136.9 (1 CH), 138.3 (1 quart C), 140.2 (1 quart C), 140.7 (1 quart C), 143.7 (1 quart C), 143.9 (1 CH), 148.4 (1 quart C), 154.7 (1 quart C), 169.6 (1 quart C); MS (EI) m/z (rel int) 456 (M⁺, 100), 397 (92); IR (neat): ν (C=O) = 1726 cm⁻¹; HRMS calcd. for C₃₀H₃₆O₂Si: 456.2485, found 456.2463.

6cc: Colorless liquid, isolated yield 12% (55 mg); ¹H NMR (CDCl₃, Me₄Si): δ = 0.24 (s, 3H, CH₃), 0.33 (s, 3H, CH₃), 0.75 (t, J = 7.5 Hz, 3H, CH₃), 0.92 (t, J = 7.5 Hz, 3H, CH₃), 1.17 (q, J = 7.5 Hz, 2H, CH₂), 1.39 (q, J = 7.5 Hz, 2H, CH₂), 1.85 (t, J = 7.5 Hz, 2H, CH₂), 1.90 (t, J = 7.5 Hz, 2H, CH₂), 3.69 (s, 3H, CH₃), 5.34 (q, J = 4.5 Hz, 1H, CH), 6.66 (s, 1H, CH), 7.10-7.35 (m, 11H, CH); ¹³C NMR (75 MHz, CDCl₃, 25°C): δ = -2.2 (1 CH₃), 0.2 (1 CH₃), 14.1 (1 CH₃), 14.2 (1 CH₃), 21.4 (1 CH₂), 22.7 (1 CH₂), 32.3 (1 CH₂), 36.3 (1 CH₂), 51.7 (1 CH₃), 126.2 (1 CH), 126.5 (2 CH), 127.4 (1 CH), 128.2 (2 CH), 128.4 (2 CH), 129.3 (2 CH), 131.5 (1 quart C), 131.5 (1 CH), 135.9 (1 CH), 139.0 (1 quart C), 139.8 (1 quart C), 141.4 (1 quart C), 141.7 (1 CH), 143.4 (1 quart C), 148.5 (1 quart C), 150.4 (1 quart C), 169.5 (1 quart C).

C); MS (EI) m/z (rel int) 456 (M^+ , 100), 89 (84); IR (neat): ν (C=O) = 1725 cm^{-1} ; HRMS calcd. for $\text{C}_{30}\text{H}_{36}\text{O}_2\text{Si}$: 456.2485, found 456.2474.

6da: Colorless liquid, isolated yield 50% (243 mg); ^1H NMR (CDCl_3 , Me_4Si): δ = 0.33 (s, 6H, CH_3), 0.68 (t, J = 7.2 Hz, 3H, CH_3), 0.92 (t, J = 7.2 Hz, 3H, CH_3), 1.12-1.17 (m, 4H, CH_2), 1.36-1.51 (m, 4H, CH_2), 1.93 (t, J = 6.6 Hz, 2H, CH_2), 2.23 (t, J = 7.2 Hz, 2H, CH_2), 3.09 (s, 3H, CH_3), 5.72 (t, J = 7.5 Hz, 1H, CH), 6.74 (s, 1H, CH), 7.20-7.35 (m, 10H CH), 7.90 (s, 1H, CH); ^{13}C NMR (CDCl_3): δ = -1.3 (2 CH_3), 13.8 (1 CH_3), 14.0 (1 CH_3), 22.6 (1 CH_2), 22.6 (1 CH_2), 27.8 (1 CH_2), 30.1 (1 CH_2), 30.2 (1 CH_2), 31.9 (1 CH_2), 51.3 (1 CH_3), 126.2 (1 CH), 126.6 (2 CH), 127.8 (2 CH), 128.1 (1 CH), 128.4 (2 CH), 130.4 (2 CH), 131.0 (1 quart C), 131.9 (1 CH), 136.9 (1 CH), 138.4 (1 quart C), 140.0 (1 quart C), 140.7 (1 quart C), 143.8 (1 quart C), 144.0 (1 CH), 148.4 (1 quart C), 154.5 (1 quart C), 169.6 (1 quart C); MS (EI) m/z (rel int) 484 (M^+ , 76), 89 (100); IR (neat): ν (C=O) = 1726 cm^{-1} ; UV/Vis (THF) : λ max : 332 nm; HRMS calcd. for $\text{C}_{32}\text{H}_{40}\text{O}_2\text{Si}$: 484.2798, found 484.2786.

6dc: Colorless liquid, isolated yield 14% (68 mg); ^1H NMR (CDCl_3 , Me_4Si): δ = 0.24 (s, 3H, CH_3), 0.32 (s, 3H, CH_3), 0.76 (t, J = 7.2 Hz, 3H, CH_3), 0.91 (t, J = 7.2 Hz, 3H, CH_3), 1.11-1.18 (m, 4H, CH_2), 1.26-1.45 (m, 4H, CH_2), 1.72 (t, J = 6.6 Hz, 2H, CH_2), 1.92 (t, J = 7.2 Hz, 2H, CH_2), 3.69 (s, 3H, CH_3), 5.33 (t, J = 7.5 Hz, 1H, CH), 6.65 (s, 1H, CH), 7.10-7.35 (m, 11H, CH_3), 7.90 (s, 1H, CH_3); ^{13}C NMR (CDCl_3): δ = -2.1 (1 CH_3), 0.2 (1 CH_3), 14.0 (1 CH_3), 14.1 (1 CH_3), 22.6 (1 CH_2), 22.8 (1 CH_2), 30.0 (1 CH_2), 30.5 (1 CH_2), 32.0 (1 CH_2), 33.8 (1 CH_2), 51.7 (1 CH_3), 126.2 (1 CH), 126.5 (2 CH), 127.4 (1 CH), 128.2 (2 CH), 128.4 (2 CH), 129.4 (2 CH), 131.5 (1 quart C), 131.7 (1 CH), 135.9 (1 CH), 138.9 (1 quart C), 139.9 (1 quart C), 141.4 (1 quart C), 141.7 (1 CH), 143.4 (1 quart C), 148.5 (1 quart C), 150.5 (1 quart C), 169.5 (1 quart C); MS (EI) m/z (rel int) 484 (M^+ , 52), 89 (100); IR (neat): ν (C=O) = 1725 cm^{-1} ; HRMS calcd. for $\text{C}_{32}\text{H}_{40}\text{O}_2\text{Si}$: 484.2798, found 484.2791.

References:

- (1) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.; Obora, Y.; Suzuki, N.; Nakajima, K.; Takahashi, T.
J. Am. Chem. Soc. **1997**, *119*, 12842-12848.
- (2) Brandsma, L., Preparative Acetylenic Chemistry, 2nd Eds., Elsevier, Amsterdam, 1988,
pp 281-282.

2) Copies of ^1H NMR and ^{13}C NMR spectra for all new compounds.

4aa

+

4ac

4ba

+

4bc

4ea

4ha

5aa

+

5ac

5da

+ three isomers

6ba

6ca

6da

6dc

3) Copies of ^{13}C NMR spectra showing satellite peaks due to ^{29}Si for products 4da and 6da.

Full ^{13}C -NMR

C¹³satellite-C(2)

Current Data Parameters
 NAME C3357
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
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 Time 10.15
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 NS 1621
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 SWH 27777.777 Hz
 FIDRES 0.847710 Hz
 AQ 0.5898740 sec
 RG 16384
 DW 18.000 usec
 DE 25.71 usec
 TE 300.0 K
 D12 0.00002000 sec
 DL5 22.20 dB
 CPDPRG waltz16
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 SFO1 100.6240000 MHz
 NUCLEUS 13C
 D11 0.03000000 sec

F2 - Processing parameters
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 LB 1.50 Hz
 GB 0
 PC 0.20

1D NMR plot parameters
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 F1 14166.01 Hz
 F2P 139.939 ppm
 F2 14079.63 Hz
 PPMCM 0.04293 ppm/cm
 HZCM 4.31944 Hz/cm

C^{13} satellite-C(6)

Current Data Parameters
NAME C3357
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061212
Time 10.15
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PROBHD 5 mm Multinu
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 1621
DS 0
SWH 27777.777 Hz
FIDRES 0.847710 Hz
AQ 0.5898740 sec
RG 16384
DM 18.000 usec
DE 25.71 usec
TE 300.0 K
D12 0.00002000 sec
DL5 22.20 dB
CPDPRG waltz16
P31 100.00 usec
D1 2.00000000 sec
P1 2.50 usec
DE 25.71 usec
SF01 100.6240000 MHz
NUCLEUS 13C
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 100.6127823 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 0.20

1D NMR plot parameters
CX 20.00 cm
F1P 139.626 ppm
F1 14048.18 Hz
F2P 138.617 ppm
F2 13966.80 Hz
PPMCM 0.04044 ppm/cm
HZCM 4.06905 Hz/cm

C¹³satellite-C(2) and C(6)

Full C¹³-NMR

C^{13} satellite-C(2)

Current Data Parameters
 NAME C33378
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20061214
 Time 7.59
 INSTRUM ARX400
 PROBHD 5 mm Multinu
 PULPROG zgpg
 TD 32768
 SOLVENT CDCl3
 NS 3000
 DS 0
 SMH 27777.777 Hz
 FIDRES 0.84710 Hz
 AQ 0.5698740 sec
 RG 16384
 DM 18.000 usec
 DE 25.71 usec
 TE 300.0 K
 D12 0.0002000 sec
 DL5 22.20 dB
 CPDPRG waltz16
 P31 100.00 usec
 D1 2.0000000 sec
 P1 2.50 usec
 DE 25.71 usec
 SF01 100.624000 MHz
 NUCLEUS 13C
 D11 0.0300000 sec

F2 - Processing parameters
 SI 16384
 SF 100.6127797 MHz
 MDW EM
 SSB 0
 LB 0.80 Hz
 GB 0
 PC 0.30

1D NMR plot parameters
 CX 20.00 cm
 F1P 137.300 ppm
 F1 13814.15 Hz
 F2P 136.323 ppm
 F2 13715.88 Hz
 PPMCM 0.04883 ppm/cm
 HZCM 4.91342 Hz/cm

C¹³satellite-C(6)

Current Data Parameters
NAME C33378
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061214
Time 7.59
INSTRUM APTX400
PROBHD 5 mm Multinu
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 3000
DS 0
SWH 27777.777 Hz
FIDRES 0.847710 Hz
AQ 0.589740 sec
RG 16384
DN 18.000 usec
DE 25.71 usec
TE 300.0 K
D12 0.0002000 sec
DL5 22.20 dB
CPDPRG waltz16
P31 100.00 usec
D1 2.0000000 sec
P1 2.50 usec
DE 25.71 usec
SF01 100.6240000 MHz
NUCLEUS 13C
D11 0.0300000 sec

F2 - Processing parameters
SI 16384
SF 100.6127797 MHz
WDW EM
SSB 0
LB 0.80 Hz
GB 0
PC 0.30

1D NMR plot parameters
CX 20.00 cm
F1P 138.818 ppm
F1 13966.84 Hz
F2P 137.976 ppm
F2 13882.18 Hz
PPMCM 0.04207 ppm/cm
HZCM 4.23309 Hz/cm

4) X-ray Structure and Crystallographic data for 4aa

FIGURE 1. Perspective View of *exo*-Alkylidenesilacyclohexadiene 4aa. Selected bond lengths [Å] and angles [deg]: Si-C1 1.873(2), C1-C2 1.350(3), C2-C3 1.484(3), C3-C4 1.469(3), C4-C5 1.338(3), Si-C5 1.852(2); C1-Si-C5 101.43(10), C2-C3-C4 119.52(19).

Table 1. Crystal data and structure refinement for **4aa**.

Identification code	a
Empirical formula	C ₂₄ H ₂₄ O ₄ Si
Formula weight	404.52
Temperature	293(2) K
Measurement device	Rigaku RAXIS RAPID IP
Measurement method	Oscillation
Wavelength	0.71073 Å
Program for data collection	
Program for cell refinement	
Program for data reduction	
Program for structure solution	
Program for structure refinement	
Program for molecular graphics	
Program for publication material	
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.2495(18) Å alpha = 90 deg. b = 8.9167(18) Å beta = 90.39(3) deg. c = 26.294(5) Å gamma = 90 deg.
Volume	2168.6(7) Å ³
Refls. No. for cell measurement	11134

Theta range for cell measurement	2.41 to 25.02 deg.
Z, Calculated density	4, 1.239 Mg/m ³
Absorption coefficient	0.135 mm ⁻¹
F(000)	856
Crystal shape / Crystal colour	Block / Colourless
Crystal size	0.50 x 0.40 x 0.18 mm
Theta range for data collection	2.41 to 25.02 deg.
Limiting indices	-11<=h<=11, -10<=k<=10, -31<=l<=31
Reflections collected / unique	11134 / 3768 [R(int) = 0.0562]
Reflections with I>2sigma(I)	2468
Completeness to theta = 25.02	98.5 %
Decay correction (%)	?
Absorption correction	Empirical
Max. and min. transmission	0.976 and 0.935
Method for primary solution	direct
Method for secondary solution	difmap
Hydrogen addition / treatment	/
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3768 / 0 / 263
Goodness-of-fit on F ²	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1093
R indices (all data)	R1 = 0.0761, wR2 = 0.1192
Extinction coefficient	0.0066(11)
Largest diff. peak and hole	0.269 and -0.271 e.A ⁻³
Max. and mean shift/sigma	0.000 and 0.000

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4aa**.
 $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Si(1)	3015(1)	3020(1)	385(1)	45(1)
O(1)	2683(2)	6112(2)	1044(1)	71(1)
O(2)	516(2)	5208(2)	1273(1)	59(1)
O(3)	538(2)	2236(2)	2094(1)	61(1)
O(4)	2262(2)	4002(2)	2105(1)	56(1)
C(1)	2312(2)	3485(2)	1033(1)	46(1)
C(2)	2195(2)	2427(2)	1398(1)	44(1)
C(3)	2516(2)	821(2)	1304(1)	45(1)
C(4)	2458(2)	234(2)	782(1)	48(1)
C(5)	2623(2)	987(2)	346(1)	46(1)
C(6)	2509(2)	235(2)	-160(1)	49(1)
C(7)	1525(3)	-920(3)	-249(1)	59(1)
C(8)	1371(3)	-1533(3)	-730(1)	71(1)
C(9)	2168(4)	-1005(3)	-1128(1)	78(1)
C(10)	3165(4)	117(3)	-1048(1)	77(1)
C(11)	3334(3)	720(3)	-566(1)	64(1)
C(12)	2843(2)	-135(2)	1682(1)	50(1)
C(13)	3222(2)	160(2)	2215(1)	47(1)
C(14)	2659(3)	-700(3)	2608(1)	60(1)
C(15)	3070(3)	-459(3)	3107(1)	76(1)
C(16)	4063(3)	635(4)	3226(1)	79(1)
C(17)	4635(3)	1479(3)	2847(1)	74(1)
C(18)	4221(3)	1258(3)	2346(1)	58(1)
C(19)	5001(2)	3387(3)	384(1)	63(1)
C(20)	1974(3)	4114(3)	-95(1)	61(1)
C(21)	1898(3)	5066(2)	1125(1)	50(1)
C(22)	21(3)	6712(3)	1378(1)	80(1)
C(23)	1557(3)	2841(2)	1903(1)	47(1)
C(24)	1722(4)	4537(3)	2587(1)	85(1)

Table 3. Bond lengths [Å] and angles [deg] for **4aa**.

Si (1)–C (5)	1.852 (2)
Si (1)–C (20)	1.859 (2)
Si (1)–C (19)	1.865 (2)
Si (1)–C (1)	1.873 (2)
O (1)–C (21)	1.202 (3)
O (2)–C (21)	1.345 (3)
O (2)–C (22)	1.445 (3)
O (3)–C (23)	1.198 (2)
O (4)–C (23)	1.332 (3)
O (4)–C (24)	1.445 (3)
C (1)–C (2)	1.350 (3)
C (1)–C (21)	1.482 (3)
C (2)–C (3)	1.484 (3)
C (2)–C (23)	1.505 (3)
C (3)–C (12)	1.342 (3)
C (3)–C (4)	1.469 (3)
C (4)–C (5)	1.338 (3)
C (5)–C (6)	1.493 (3)
C (6)–C (11)	1.387 (3)
C (6)–C (7)	1.393 (3)
C (7)–C (8)	1.383 (3)
C (8)–C (9)	1.368 (4)
C (9)–C (10)	1.376 (4)
C (10)–C (11)	1.384 (3)
C (12)–C (13)	1.466 (3)
C (13)–C (18)	1.389 (3)
C (13)–C (14)	1.391 (3)
C (14)–C (15)	1.383 (4)
C (15)–C (16)	1.374 (4)
C (16)–C (17)	1.358 (4)
C (17)–C (18)	1.384 (3)
C (5)–Si (1)–C (20)	112.06 (11)
C (5)–Si (1)–C (19)	111.36 (11)
C (20)–Si (1)–C (19)	114.35 (11)
C (5)–Si (1)–C (1)	101.43 (10)
C (20)–Si (1)–C (1)	108.65 (11)
C (19)–Si (1)–C (1)	108.08 (11)
C (21)–O (2)–C (22)	116.43 (18)
C (23)–O (4)–C (24)	115.78 (19)
C (2)–C (1)–C (21)	121.7 (2)
C (2)–C (1)–Si (1)	121.43 (16)
C (21)–C (1)–Si (1)	116.83 (16)
C (1)–C (2)–C (3)	122.65 (19)
C (1)–C (2)–C (23)	119.38 (19)
C (3)–C (2)–C (23)	117.60 (18)
C (12)–C (3)–C (4)	118.14 (19)

C(12)–C(3)–C(2)	122.3(2)
C(4)–C(3)–C(2)	119.52(19)
C(5)–C(4)–C(3)	128.2(2)
C(4)–C(5)–C(6)	122.1(2)
C(4)–C(5)–Si(1)	117.83(16)
C(6)–C(5)–Si(1)	120.11(16)
C(11)–C(6)–C(7)	117.5(2)
C(11)–C(6)–C(5)	120.7(2)
C(7)–C(6)–C(5)	121.6(2)
C(8)–C(7)–C(6)	120.6(2)
C(9)–C(8)–C(7)	120.7(3)
C(8)–C(9)–C(10)	119.9(3)
C(9)–C(10)–C(11)	119.5(3)
C(10)–C(11)–C(6)	121.7(3)
C(3)–C(12)–C(13)	130.1(2)
C(18)–C(13)–C(14)	117.1(2)
C(18)–C(13)–C(12)	121.3(2)
C(14)–C(13)–C(12)	121.5(2)
C(15)–C(14)–C(13)	121.2(2)
C(16)–C(15)–C(14)	120.3(3)
C(17)–C(16)–C(15)	119.4(3)
C(16)–C(17)–C(18)	120.8(3)
C(17)–C(18)–C(13)	121.1(2)
O(1)–C(21)–O(2)	123.7(2)
O(1)–C(21)–C(1)	123.5(2)
O(2)–C(21)–C(1)	112.59(19)
O(3)–C(23)–O(4)	124.6(2)
O(3)–C(23)–C(2)	125.0(2)
O(4)–C(23)–C(2)	110.45(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4aa**.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Si(1)	46(1)	40(1)	48(1)	3(1)	-3(1)	-4(1)
O(1)	77(1)	37(1)	100(1)	2(1)	12(1)	-10(1)
O(2)	57(1)	40(1)	80(1)	-5(1)	-2(1)	2(1)
O(3)	64(1)	54(1)	66(1)	0(1)	15(1)	-8(1)
O(4)	70(1)	50(1)	48(1)	-9(1)	1(1)	-8(1)
C(1)	49(1)	36(1)	55(1)	1(1)	-6(1)	-6(1)
C(2)	47(1)	38(1)	46(1)	-3(1)	-2(1)	-6(1)
C(3)	49(1)	36(1)	49(1)	2(1)	3(1)	-4(1)
C(4)	53(2)	36(1)	55(2)	-4(1)	-2(1)	-4(1)
C(5)	46(1)	43(1)	49(1)	-4(1)	2(1)	-1(1)
C(6)	53(1)	49(1)	47(1)	-4(1)	-2(1)	4(1)
C(7)	54(2)	59(2)	63(2)	-12(1)	-2(1)	-3(1)
C(8)	70(2)	69(2)	73(2)	-23(2)	-19(2)	4(2)
C(9)	111(3)	73(2)	48(2)	-13(2)	-15(2)	25(2)
C(10)	106(2)	74(2)	52(2)	-2(2)	8(2)	7(2)
C(11)	81(2)	60(2)	51(2)	-4(1)	4(1)	-3(1)
C(12)	58(2)	35(1)	58(2)	3(1)	-2(1)	-3(1)
C(13)	55(2)	37(1)	49(1)	3(1)	-1(1)	4(1)
C(14)	71(2)	44(1)	65(2)	7(1)	2(1)	-4(1)
C(15)	104(2)	67(2)	57(2)	17(2)	9(2)	2(2)
C(16)	101(2)	83(2)	53(2)	3(2)	-13(2)	4(2)
C(17)	72(2)	79(2)	71(2)	0(2)	-19(2)	-14(2)
C(18)	58(2)	58(2)	59(2)	8(1)	-5(1)	-10(1)
C(19)	53(2)	61(2)	74(2)	12(1)	-5(1)	-10(1)
C(20)	59(2)	61(2)	62(2)	5(1)	-7(1)	2(1)
C(21)	60(2)	38(1)	50(1)	-1(1)	-4(1)	-2(1)
C(22)	75(2)	49(2)	116(3)	-15(2)	2(2)	16(1)
C(23)	54(2)	38(1)	50(1)	2(1)	-3(1)	-2(1)
C(24)	119(3)	79(2)	57(2)	-26(2)	13(2)	-11(2)

Table 5. Torsion angles [deg] for **4aa**.

C(5)–Si(1)–C(1)–C(2)	24.0(2)
C(20)–Si(1)–C(1)–C(2)	142.18(19)
C(19)–Si(1)–C(1)–C(2)	–93.2(2)
C(5)–Si(1)–C(1)–C(21)	–156.27(18)
C(20)–Si(1)–C(1)–C(21)	–38.1(2)
C(19)–Si(1)–C(1)–C(21)	86.54(19)
C(21)–C(1)–C(2)–C(3)	176.1(2)
Si(1)–C(1)–C(2)–C(3)	–4.2(3)
C(21)–C(1)–C(2)–C(23)	3.2(3)
Si(1)–C(1)–C(2)–C(23)	–177.05(16)
C(1)–C(2)–C(3)–C(12)	158.6(2)
C(23)–C(2)–C(3)–C(12)	–28.4(3)
C(1)–C(2)–C(3)–C(4)	–22.3(3)
C(23)–C(2)–C(3)–C(4)	150.7(2)
C(12)–C(3)–C(4)–C(5)	–156.3(2)
C(2)–C(3)–C(4)–C(5)	24.6(3)
C(3)–C(4)–C(5)–C(6)	–178.9(2)
C(3)–C(4)–C(5)–Si(1)	1.4(3)
C(20)–Si(1)–C(5)–C(4)	–137.87(18)
C(19)–Si(1)–C(5)–C(4)	92.6(2)
C(1)–Si(1)–C(5)–C(4)	–22.2(2)
C(20)–Si(1)–C(5)–C(6)	42.4(2)
C(19)–Si(1)–C(5)–C(6)	–87.1(2)
C(1)–Si(1)–C(5)–C(6)	158.17(18)
C(4)–C(5)–C(6)–C(11)	–147.2(2)
Si(1)–C(5)–C(6)–C(11)	32.5(3)
C(4)–C(5)–C(6)–C(7)	36.1(3)
Si(1)–C(5)–C(6)–C(7)	–144.20(19)
C(11)–C(6)–C(7)–C(8)	–1.0(4)
C(5)–C(6)–C(7)–C(8)	175.8(2)
C(6)–C(7)–C(8)–C(9)	–0.9(4)
C(7)–C(8)–C(9)–C(10)	2.0(4)
C(8)–C(9)–C(10)–C(11)	–1.1(4)
C(9)–C(10)–C(11)–C(6)	–0.9(4)
C(7)–C(6)–C(11)–C(10)	1.9(4)
C(5)–C(6)–C(11)–C(10)	–174.9(2)
C(4)–C(3)–C(12)–C(13)	168.1(2)
C(2)–C(3)–C(12)–C(13)	–12.8(4)
C(3)–C(12)–C(13)–C(18)	–46.2(4)
C(3)–C(12)–C(13)–C(14)	137.4(3)
C(18)–C(13)–C(14)–C(15)	0.6(4)
C(12)–C(13)–C(14)–C(15)	177.1(2)
C(13)–C(14)–C(15)–C(16)	–0.7(4)
C(14)–C(15)–C(16)–C(17)	0.1(5)
C(15)–C(16)–C(17)–C(18)	0.6(5)
C(16)–C(17)–C(18)–C(13)	–0.7(4)
C(14)–C(13)–C(18)–C(17)	0.1(4)

C (12)–C (13)–C (18)–C (17)	–176.4 (2)
C (22)–O (2)–C (21)–O (1)	–5.4 (4)
C (22)–O (2)–C (21)–C (1)	179.3 (2)
C (2)–C (1)–C (21)–O (1)	127.3 (3)
Si (1)–C (1)–C (21)–O (1)	–52.5 (3)
C (2)–C (1)–C (21)–O (2)	–57.4 (3)
Si (1)–C (1)–C (21)–O (2)	122.88 (18)
C (24)–O (4)–C (23)–O (3)	–0.2 (3)
C (24)–O (4)–C (23)–C (2)	178.3 (2)
C (1)–C (2)–C (23)–O (3)	123.8 (2)
C (3)–C (2)–C (23)–O (3)	–49.4 (3)
C (1)–C (2)–C (23)–O (4)	–54.7 (3)
C (3)–C (2)–C (23)–O (4)	132.1 (2)

Symmetry transformations used to generate equivalent atoms: