Carbohydrate-metallocene conjugates: selective formation of a zirconadioxacyclopentane-type dimer from the reaction of a bis(enolate)$ZrCp_2$ reagent with a glucofuranoside derivative

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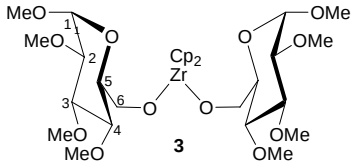
Supporting Information:



3

Preparation of **3**: A solution of 1,2,3,4-*O*-tetramethyl-α-D-glucopyranoside [**2**, 470 mg (2.00 mmol)] in 30 mL of dry dichloromethane was added dropwise with stirring to a solution of 335 mg (1.00 mmol) of bis(2-propenolato)$ZrCp_2$ (**1**) in 30 ml CH_2Cl_2 at room temperature. After 2h the solvent was removed in vacuo, the residue washed with pentane and dried in vacuo to yield 600 mg (86%) of **3** as an off white solid, m.p. (decomp.) 171°C (DSC), $[\alpha]_D^{25}$= +121 (c=0.24, CH_2Cl_2). Anal. calcd. for $C_{30}H_{48}O_{12}Zr$ (691.9): 52.08% C, 6.99% H, found: 51.77% C, 7.09% H. IR (KBr): $\tilde{\nu}$ = 3083, 2974, 2926, 2878, 2835, 2700, 2087, 1735, 1652, 1561, 1439, 1365, 1265, 1161, 1100, 1035, 1009, 896, 796, 709, 583, 513, 478 cm^{-1}.

^1H NMR (CD_2Cl_2, 298 K, 600 MHz): δ^1H = 6.32 (s, 10H, Cp); 4.81 (d, $^3J_{1,2}$ = 3.5 Hz, 2H, 1-H); 4.05 (dd(ABM), ^2J = 11.8 Hz, $^3J_{6,5}$ = 3.4 Hz, 2H, 6-H); 4.02 (dd, ^2J = 11.8 Hz, $^3J_{6',5}$ = 2.3 Hz, 2H, 6-H'); 3.56 (s, 6H, 3-OCH_3); 3.53 (s, 6H, 4-OCH_3); 3.46 (s, 6H, 2-OCH_3); 3.41 (m, 2H, 3-H); 3.39 (s, 6H, 1-OCH_3); 3.32 (ddd, $^3J_{5,4}$ = 9.9 Hz, $^3J_{5,6}$ = 3.4 Hz, $^3J_{5,6'}$ = 2.3 Hz, 2H, 5-H); 3.14 (dd, $^3J_{2,3}$ = 9.6 Hz, $^3J_{2,1}$ = 3.5 Hz, 2H, 2-H); 3.06 (dd, $^3J_{4,5}$ = 9.9 Hz, $^3J_{4,3}$ = 9.0 Hz, 2H, 4-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 151 MHz): $\delta^{13}C$ = 112.3 (Cp); 97.4 (C-1); 83.8 (C-3); 82.3 (C-2); 79.7 (C-4); 73.0 (C-5); 72.2 (C-6); 60.7 (3-OCH_3); 60.4 (4-OCH_3); 58.6 (2-OCH_3); 55.1 (1-OCH_3). ^1H / ^{13}C ghsqc (CD_2Cl_2, 298 K, 600 MHz / 151 MHz): δ^1H / $\delta^{13}C$ = 6.32 / 112.3 (Cp); 4.81 / 97.4 (1-H / C-1); 4.05, 4.02 / 72.2 (6-H, 6-H' / C-6); 3.56 / 60.7 (3-OCH_3); 3.53 / 60.4 (4-OCH_3); 3.46 / 58.6 (2-OCH_3); 3.41 / 83.8 (3-H / C-3); 3.39 / 55.1 (1-OCH_3); 3.32 / 73.0 (5-H / C-5); 3.14 / 82.3 (2-H / C-2); 3.06 / 79.7 (4-H / C-4). ^1H / ^{13}C ghmbc (CD_2Cl_2, 298 K, 600 MHz / 151 MHz): δ^1H / $\delta^{13}C$ = 6.32 / 112.3 (Cp / Cp); 4.81 / 83.8, 73.0, 55.1 (1-H / C-3, C-5, 1-OCH_3); 4.05 / 79.7, 73.0 (6-H / C-4, C-5); 3.56 / 83.8 (3-OCH_3 / C-3); 3.53 / 79.7 (4-OCH_3 / C-4); 3.46 / 82.3 (2-OCH_3 / C-2); 3.41 / 97.4, 82.3, 79.7, 60.7 (3-H / C-1, C-2, C-4, 3-OCH_3); 3.14 / 83.8, 58.6 (2-H / C-3, 2-OCH_3); 3.06 / 83.8, 73.0, 72.2, 60.4 (4-H / C-3, C-5, C-6, 4-OCH_3).

Crystal data for $(C_{15}H_{24}O_6)_2Zr$ (**3**), M = 691.90, monoclinic, space group $C2$ (No. 5), a = 18.157(1), b = 11.380(1), c = 8.664(1) Å, β = 109.32(1)°, V = 1689.4(3) $Å^3$, D_c = 1.360 g cm^{-3}, μ= 0.383 cm^{-1}, Z = 2, λ= 0.71073 Å, T = 198 K, 5832 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 $Å^{-1}$, 3534 independent (R_{int} = 0.024) and 3379 observed reflections [$I \geq 2\ \sigma(I)$], 199 refined parameters, R = 0.036, wR^2 = 0.064.

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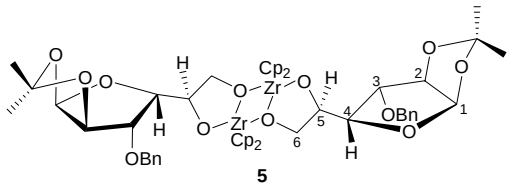

5

Preparation of **5**: Analogous procedure as described for **3**: 372 mg (1.20 mmol) of 3-*O*-benzyl-1,2-*O*-isopropylidene-glucofuranoside (**4**) was reacted with 403 mg (1.20 mmol) of bis(2-propenolato)-zirconocene (**1**) to give 623 mg (90%) of **5** as a slightly yellowish solid, m.p. 274°C (DSC), $[\alpha]_D^{25}$=-26.5 (c=0.29, CH_2Cl_2), Anal. calcd. for $C_{52}H_{60}O_{12}Zr_2$ (1059.5): 58.95% C, 5.71% H, found: 58.87% C, 5.81% H. IR (KBr): $\tilde{\nu}$ = 3083, 2987, 2930, 2852, 1713, 1544, 1500, 1457, 1374, 1213, 1165, 1074, 1013, 804, 736, 700, 587, 544 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K, 600 MHz): δ^1H = 7.49 (pd (AA'BB'C), 2H, o-Ph); 7.40 (pt (AA'BB'C), 2H, m-Ph); 7.32 (pt (AA'BB'C), 1H, p-Ph); 6.18 (s, 5H, Cp_A); 6.10 (s, 5H, Cp_B); 5.91 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, 1-H); 4.79 (AB, ^2J = 12.3 Hz, 1H, 3-OCH_2Ph); 4.70 (AB, ^2J = 12.3 Hz, 1H, 3-OCH_2Ph); 4.61 (d, $^3J_{2,1}$ = 3.8 Hz, 1H, 2-H); 4.09 (ddd, $^3J_{5,6'}$ = 9.9 Hz, $^3J_{5,4}$ = 8.6 Hz, $^3J_{5,6}$ = 4.3 Hz, 1H, 5-H); 4.05 (d, $^3J_{3,4}$ = 3.3 Hz, 1H, 3-H); 3.92 (dd, ^2J = 8.6 Hz, $^3J_{6,5}$ = 4.3 Hz, 1H, 6-H); 3.84 (dd, $^3J_{4,5}$ = 8.6 Hz, $^3J_{3,4}$ = 3.3 Hz, 1H, 4-H); 3.48 (dd, $^3J_{6',5}$ = 9.9 Hz, ^2J = 8.6 Hz, 1H, 6-H'); 1.51 (s, 3H, CH_3 (endo)); 1.32 (s, 3H, CH_3 (exo)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 151 MHz): $\delta^{13}C$ = 138.3 (ipso-Ph); 128.8 (m-Ph); 128.0 (o-Ph, p-Ph); 113.0 (Cp_A); 111.7 ($\underline{C}(CH_3)_2$); 111.6 (Cp_B); 105.9 (C-1); 84.2 (C-4); 82.1 (C-3); 82.0 (C-2); 78.9 (C-6); 74.4 (C-5); 71.8 (3-OCH_2Ph); 26.9 (CH_3 (endo)); 26.3 (CH_3 (exo)). ^1H / ^{13}C ghsqc (CD_2Cl_2, 298 K, 600 MHz / 151 MHz): δ^1H / $\delta^{13}C$ = 7.49, 7.32 / 128.0 (o-Ph, p-Ph); 7.40 / 128.8 (m-Ph); 6.18 / 113.0 (Cp_A); 6.10 / 111.6 (Cp_B); 5.91 / 105.9 (1-H / C-1); 4.79, 4.70 / 71.8 (3-OCH_2Ph); 4.61 / 82.0 (2-H / C-2); 4.09 / 74.4 (5-H / C-5); 4.05 / 82.1 (3-H / C-3); 3.92, 3.48 / 78.9 (6-H, 6-H' / C-6); 3.84 / 84.2 (4-H / C-4); 1.51 / 26.9 (CH_3 (endo)); 1.32 / 26.3 (CH_3 (exo)). ^1H / ^{13}C ghmbc (CD_2Cl_2, 298 K, 600 MHz / 151 MHz): δ^1H / $\delta^{13}C$ = 7.49 / 128.0, 71.8 (o-Ph / o-Ph, p-Ph, 3-OCH_2Ph); 7.40 / 128.0, 71.8 (m-Ph / o-Ph, p-Ph, 3-OCH_2Ph); 6.18 / 113.0 (Cp_A / Cp_A); 6.10 / 111.6 (Cp_B / Cp_B); 5.91 / 111.7, 84.2, 82.2, 82.0 (1-H / $\underline{C}(CH_3)_2$, C-4, C-3, C-2); 4.79 / 138.3, 128.0, 82.1 (3-OCH_2Ph / ipso-Ph, o-Ph, C-3); 4.70 / 138.3, 128.0, 82.1 (3-OCH_2Ph / ipso-Ph, o-Ph, C-3); 4.61 / 105.9, 84.2 (2-H / C-1, C-4); 4.09 / 84.2 (5-H / C-6); 4.05 / 105.9, 84.2, 82.0, 71.8 (3-H / C-1, C-4, C-2, 3-OCH_2Ph); 3.92 / 111.682.1, 74.4 (6-H / CpB, C-4, C-5); 3.84 / 82.1, 78.9, 74.4 (4-H / C-3, C-6, C-5); 3.48 / 82.1, 74.4 (6-H' / C-4, C-5); 1.51 / 111.7, 26.3 (CH_3 (endo) / $\underline{C}(CH_3)_2$, CH_3 (exo)); 1.32 / 111.7, 26.9 (CH_3 (exo) / $\underline{C}(CH_3)_2$, CH_3 (endo)). $^{13}C\{apt\}$ (CD_2Cl_2, 248 K, 150.8 MHz): $\delta^{13}C_{up}$ = 128.8 (CH, m-Ph); 128.0 (CH, o-Ph, p-Ph); 113.0 (CH, Cp_A); 111.6 (CH, Cp_B); 105.9 (CH, C-1); 84.2 (CH, C-4); 82.1 (CH, C-3); 82.0 (CH, C-2); 74.4 (CH, C-5); 26.9 (CH_3, CH_3 (endo)); 26.3 (CH_3, CH_3 (exo)). $\delta^{13}C_{down}$ = 138.3 (C, ipso-Ph); 111.7 (C, $\underline{C}(CH_3)_2$); 78.9 (CH_2, C-6); 71.8 (CH_2, 3-OCH_2Ph). ^1H {^1H, noe} (CD_2Cl_2, 298 K, 599.8 MHz): $\delta^1H_{(irr)}$ / $\delta^1H_{(res)}$ = 6.18 / 3.48 (Cp_A / 6-H'); 6.10 / 7.49, 4.09, 3.92 (Cp_B / o-Ph, 5-H, 6-H); 4.61 / 7.49, 5.91, 4.79, 4.70, 4.05, 1.32 (H-2 / o-Ph, 1-H, 3-OCH_2Ph, 3-OCH_2Ph, 3-H, CH_3 (exo)); 1.51 / 3.84 (CH_3 (endo) / 4-H); 1.32 / 5.91, 4.61 (CH_3 (exo) / 1-H, 2-H).

Crystal data for $(C_{26}H_{30}O_6Zr)_2$ * C_7H_8 (**5**), M = 1151.57, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 9.213(1), b = 19.258(1), c = 30.126(1) Å, V = 5345.1(7) $Å^3$, D_c = 1.431 g cm^{-3}, μ= 0.453 mm^{-1}, Z = 4, λ= 0.71073 Å, T = 198 K, 42406 reflections collected (±h, ±k, ± l), [(sinθ)/λ] = 0.62 $Å^{-1}$, 10820 independent (R_{int} = 0.076) and 8818 observed reflections [$I \geq 2\ \sigma(I)$], 651 refined parameters, R = 0.048, wR^2 = 0.083.

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