Supplementary Information

Linear or Cross-Shaped Bis(cyclopentadienyltitanium) Compounds with Aryl or Heteroaryl Spacers

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4,4''-Bis(2,3,4,5-tetramethylcyclopentadienyl)terphenyl (3a). In a dry Schlenk tube under nitrogen, a solution of t-BuLi (22 mL, 37.12 mmol) was added dropwise to a slurry of 4,4''-dibromoterphenyl (3.6 g, 9.28 mmol) in diethyl ether (75 mL) at -78°C. The reaction mixture was stirred for 4 h at this temperature and then 1 h at room temperature. It was again cooled to -78°C and a solution of 2,3,4,5-tetramethyl-cyclopent-2-enone (2.56 g, 18.56 mmol) in THF (60 mL) was added dropwise. The reaction mixture was stirred for two days at room temperature. A saturated solution of NH_4Cl was added to quench the reaction and both layers were separated. The aqueous phase was further extracted with diethyl ether and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated and the colourless oil was redissolved in dichloromethane (30 mL). A catalytic amount of p-toluenesulfonic acid was added to the reaction mixture changing the color of the solution to yellow. After stirring at room temperature for 30 min, most of the solvent was evaporated and a small amount of petroleum ether was added to precipitate out the product. After filtration and washing of the precipitates with diethyl ether and petroleum ether, the required product was obtained as a yellow powder. (Yield 43%).

Anal. Calcd for $C_{36}H_{38}$: C, 91.86; H, 8.14 Found: C, 91.15; H, 7.92. NMR ($CDCl_3$) δ_H: 1.00 (6H, d, $^3J_{H-H}$ = 7.5 Hz, Me), 1.89 (6H, s, Me), 1.96 (6H, s, Me), 2.10 (6H, s, Me), 3.25 (2H, q, $^3J_{H-H}$ = 7.5 Hz, CH), 7.33 (4H, d, $^3J_{H-H}$ = 8.1 Hz, CH), 7.65 (4H, d, $^3J_{H-H}$ = 8.1 Hz, CH), 7.72 (4H, s, CH); δ_C: 11.4, 12.2, 13.1, 15.1, 50.2, 126.8, 127.4, 128.9, 135.4, 136.3, 137.7, 137.9, 139.8, 141.3, 142.5.

4,4''-Bis(3,4-dimethylcyclopentadienyl)terphenyl (4a). The same procedure was used as for **(3)** except that 3,4-dimethylcyclopent-2-enone was used instead of 2,3,4,5-tetramethyl-cyclopent-2-enone. (Yield 68%). Due to very low solubility of the compound in all the solvents it was not possible to take its NMR. The product was characterized by its high resolution mass spectrum. m/e calculated = 414.234, Actual = 414.234, Anal. Calcd. For $C_{32}H_{30}$: C, 92.70; H, 7.29. Found: C, 92.17;H, 7.56.

2,5-Bis(3,4-dimethylcyclopentadienyl)-1,4-dioctyloxybenzene (5a). The same procedure was used as for **(3)** except that 2,5-dibromo-1,4-dioctyloxybenzene and 3,4-dimethylcyclopent-2-enone were used instead of 4,4''-dibromoterphenyl and 2,3,4,5-tetramethylcyclopent-2-enone respectively. Recrystallization of the crude product in toluene gave **2** as yellow crystals. (Yield 47%) Anal. Calcd. for $C_{36}H_{54}O_2$: C, 83.34; H, 10.49. Found: C, 82.91; H, 10.56. High resolution mass spectrum: Calculated: 518.411 Found: 518.409 NMR ($CDCl_3$) δ_H: 0.88 (6H, t, $^3J_{H-H}$ = 6.5 Hz, Me), 1.29-1.50 (20H, m, CH_2), 1.87 (4H, m, CH_2), 1.90 (6H, s, Me), 1.98 (6H, s, Me), 3.36 (4H, s, CH), 3.98 (4H, t, $^3J_{H-H}$ = 6.5 Hz, MeO), 6.90 (2H, s, CH), 6.94 (2H, s, CH); δ_C: 12.9, 13.6, 14.3, 22.9, 26.6, 29.5, 29.6, 29.8, 32.0, 47.6, 69.1, 111.8, 123.8, 135.5, 135.6, 136.0, 139.4, 150.4

5,5'-Bis(2,3,4,5-tetramethylcyclopentadienyl)bithiophene (6a). The same procedure was used as for **(1)** except that 2,2'-bithiophene was used instead of 4,4'-dibromobiphenyl. The reaction mixture was stirred for 24h only. (Yield 49%) Anal. Calcd. for $C_{26}H_{30}S_2$: C, 76.79; H, 7.43. Found: C, 76.47; H, 7.49. High resolution mass spectrum. m/e calculated: 414.234, Actual:

414.234. NMR ($CDCl_3$) δ_H: 1.14 (6H, d, $^3J_{H–H}$ = 7.5 Hz, Me), 1.85 (6H, s, Me), 1.93 (6H, s, Me), 2.15 (6H, s, Me), 3.06 (2H, q, $^3J_{H–H}$ = 7.5 Hz, CH), 6.76 (2H, d, $^3J_{H–H}$ = 3.7 Hz, CH), 7.09 (2H, d, $^3J_{H–H}$ = 3.7 Hz, CH); δ_C: 11.3, 12.3, 13.5, 16.6, 50.6, 123.2, 124.3, 135.2, 135.5, 136.3, 138.4, 138.8, 141.8

(Phenyltetramethylcyclopentadienyl)dimethylsilane (7). To a solution of 2 g (10 mmol) of phenyltetramethylcyclopentadienes in 50 mL of diethyl ether in a Schlenk tube at 0 °C, 4.5 mL (11.2 mmol) of a 2.5 M solution of n-butyllithium were added dropwise. A precipitate was formed immediately. The suspension was stirred for 1 h at RT. The supernatant liquid was removed with a canula equipped with a filter and the solid washed once with 30 mL of diethylether. 50 mL of THF were added to the solid and 1.2 mL of dimethylchlorosilane were added dropwise. The mixture was warmed at 50 °C for 1 h. After evaporation of the solvant, the residu was taken up in 60 mL of pentane. Filtration followed by the evaporation of the solvent gave 2.4 g of (phenyltetramethylcyclopentadienyl)dimethylsilane (yield 94%). Anal. Calcd for $C_{17}H_{24}Si$: C, 79.62; H, 9.43. Found: C, 79.21; H, 9.86. NMR ($CDCl_3$) δ_H: -0.01 (6H, d, $^3J_{H–H}$ = 3.4 Hz, MeSi), 1.78 (6H, br s, Me), 1.92 (6H, s, Me), 4.05 (1H, sept, $^3J_{H–H}$ = 3.7 Hz, HSi), 7.30-7.49 (5H, m, CH); δ_C: -6.7, 12.2, 12.4, 126.2, 128.1, 129.8, 138.2, 141.4. ^{129}Si NMR δ -4.2.

(Phenyltetramethylcyclopentadienyl)titanium trichloride (8). To a solution of 4.8 g (19 mmol) of dimethylsilylphenyltetramethylcyclopentadiene in 100 mL of pentane in a Schlenk tube at - 78 °C, 3.5 g (18.4 mmol) of titanium tetrachloride were added dropwise; The solution was stirred for 1.5 h at RT. The red crystalline precipitate was filtered, washed with 20 mL of pentane and dried. Yield 5.5 g (76%). NMR ($CDCl_3$) δ_H: 2.46 (6H, s, Me), 2.50 (6H, s, Me), 7.32-7.48 (5H, m, CH); δ_C: 14.8, 15.7, 128.5, 128.8, 130.5, 133.1, 136.4, 139.0, 141.1.

Trimethyl(phenyltetramethylcyclopentadienyl)titanium (9). A 1.6 M solution of methyllithium in diethylether (25 mL, 40 mmol) was added to a Schlenk tube charged with a suspension of trichloro(phenyltetramethylcyclopentadienyl)titanium (4.5 g, 12.8 mmol) in 100 mL of diethyl ether at -78 °C. The mixture was allowed to reach RT and stirred for 2h. After evaporation of the solvent, the solids were extracted with 150 mL of pentane. Filtration on Celite followed by evaporation of the solvent gave 3 g (yield 81%) of a yellow-green oil which solidifies on standing. Anal. Calcd for $C_{18}H_{26}Ti$: C, 74.47; H, 9.03. Found: C, 73.57; H, 8.77. NMR ($CDCl_3$) δ_H: 1.13 (9H, s, Me), 1.71 (6H, s, Me), 1.88 (6H, s, Me), 7.08-7.22 (5H, m, CH); δ_C: 11.6, 12.5, 63.1, 126.5, 127.0, 127.5, 128.0, 130.0, 135.7.

Tetramethyl-µ-oxobis(phenyltetramethylcyclopentadienyl)titanium (10). A Schlenk tube charged with a solution of trimethyl(phenyltetramethylcyclopentadienyl)titanium (0.72 g, 2.5 mmol) in 50 mL of pentane was linked to a flask containing 20 mL of water. After 72 h the yellow-green solution was concentrated to give 0.60 g (yield 86%) of bis[dimethyl(phenyltetramethylcyclopentadienyl)titanium]oxide as green crystals upon cooling at -20 °C. Anal. Calcd for $C_{18}H_{26}Ti$: C, 72.08; H, 8.18. Found: C, 72.82; H, 8.62. NMR ($CDCl_3$) δ_H: 0.95 (12H, s, Me), 2.04 (12H, s, Me), 2.07 (12H, s, Me), 7.19-7.38 (5H, m, CH); δ_C: 11.2, 12.2, 54.8, 120.5, 123.5, 126.4, 127.5, 127.7, 128.4, 130.3, 135.3.

Hexa-µ-oxotetrakis(phenyltetramethylcyclopentadienyl)tetratitanium (11). To a solution of trimethyl(phenyltetramethylcyclopentadienyl)titanium (0.50 g, 1.7 mmol) in 200 mL of THF was added excess of water (0.30 g, 16.6 mmol). After 48 h, the solvent was evaporated to give a yellow solid which was recristallized in dichloromethane. (0.32 g, yield 71%). NMR ($CDCl_3$) δ_H: 1.92 (6H, s, Me), 1.97 (6H, s, Me), 7.22-7.51 (5H, m, CH); δ_C: 11.2, 12.2, 122.3, 123.1, 127.7, 128.1, 130.7, 130.9, 135.8.