Supporting Information

Bimetallic Phenylene-Bridged Cp/amide Titanium Complexes and their Olefin Polymerization

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Synthetic details and characterizations of 4, 6, 8, 10-11, 14-15, 16-17, and 19-20

Compound 4. The compound was synthesized from 2,6-dibromo-4-fluoroaniline (1.82 g, 6.77 mmol) using same conditions and procedure as for **3**. Yellow solid was obtained ((1.02 g, 50 %). M.p. 204 ^{o}C. IR (neat): 3440 and 3363 (N-H), 1697 (C=O) cm^{-1}. NMR ($CDCl_3$): δ 2.10 (s, 6H, CH_3), 2.56 (br t, J = 4.4 Hz, 4H, CH_2), 2.72 (br t, J = 3.2 Hz, 4H, CH_2), 3.52 (br s, 2H, NH), 6.65 (d, J = 8.8 Hz, 2H, C_6H_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.64, 32.05, 34.80, 116.61 (d, $^2J_{CF}$ = 22.0 Hz), 119.85 (d, $^3J_{CF}$ = 7.6 Hz), 138.48, 139.05, 154.77 (d, $^1J_{CF}$ = 235.1 Hz), 175.47, 207.09 ppm. Anal. Calc. ($C_{18}H_{18}FNO_2$): C: 72.22; H, 6.06; N, 4.68 %. Found: C, 71.17; H, 6.30; N, 4.81 %.

Compound 6. The compound was synthesized from **4** (0.372 g, 1.24 mmol) using same conditions and procedures as for **5**. Orange solid was obtained (0.209 g, 57 %). M.p. 120 ^{o}C. IR (neat): 3471 and 3379 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 1.79 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.88 (q, J = 2.0 Hz, 3H, CH_3),

1.90 (q, J = 2.0 Hz, 3H, CH_3), 2.76 (s, 4H, CH_2), 3.27 (br s, 2H, NH), 5.91 (s, 2H, Cp-H), 6.79 (s, 1H, C_6H_2), 6.81 (s, 1H, C_6H_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.72, 14.76, 14.82, 44.66, 115.81 (d, $^2J_{CF}$ = 21.3 Hz), 115.89 (d, $^2J_{CF}$ = 21.3 Hz), 123.24 (d, $^3J_{CF}$ = 6.5 Hz), 234.31 (d, $^3J_{CF}$ = 6.5 Hz), 124.94, 124.99, 139.35, 139.51, 139.76, 139.85, 141.52, 141.72, 143.54, 143.67, 155.61 (d, $^1J_{CF}$ = 233.6 Hz), 155.67 (d, $^1J_{CF}$ = 233.6 Hz) ppm. Anal. Calc. ($C_{20}H_{22}FN$): C: 81.32; H, 7.31; N, 4.74 %. Found: C, 81.10; H, 7.25; N, 4.68 %.

Complex 8. The complex was synthesized using same conditions and procedure as for **7**. Overall yield from **6** (0.188 g, 0.64 mmol) was 74 % (0.264 g). ^1H NMR (C_6D_6) for the intermediate bis(dimethylamido)titanium complex: δ 1.93 (s, 12H, CH_3), 3.07 (s, 24H, N-CH_3), 5.66 (s, 4H, Cp-H), 6.86 (s, 1H, C_6H_2), 6.87 (s, 1H, C_6H_2) ppm. Analytically pure crystals of **8** were obtained in toluene solution at -30 ^oC. The analytical data for **8**: ^1H NMR ($CDCl_3$): δ 2.23 (s, 12H, CH_3), 6.72 (s, 4H, Cp-H), 7.01 (d, 1H, J_{HF} = 8 Hz, C_6H_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.41, 115.40 (d, $^2J_{CF}$ = 23.5 Hz), 119.17, 123.55 (d, $^3J_{CF}$ = 9.1 Hz), 128.17, 138.22, 142.82, 160.41 (d, $^1J_{CF}$ = 23.5 Hz) ppm. Anal. Calc. ($C_{20}H_{18}Cl_4NTi_2$): C: 45.42; H, 3.43; N, 2.65 %. Found: C, 45.27; H, 3.39; N, 2.67 %.

4,4'-Oxobis(N-cyclohexylaniline). The compound was synthesized by the same conditions and procedures as for 4,4'-methylenebis(*N*-cyclohexylaniline) from 4,4'-oxobis(aniline) (10.0 g, 49.94 mmol). It was purified by recrystallization in hexane and ethyl acetate (2 : 1). A white solid was obtained (10.05 g, 56 %). M.p. 104 ^oC, IR (neat): 3394 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.87-0.93 (m, 4H, Cy), 1.04-1.19 (m, 6H, Cy), 1.46-1.59 (m, 6H, Cy), 1.88-1.91 (m, 4H, Cy), 2.96-3.00 (m, 2H, N-CH), 2.98 (br s, 2H, NH), 6.39 (d, J = 8.8 Hz, 4H, C_6H_4), 7.07 (d, J = 8.8 Hz, 4H, C_6H_4) ppm. ^{13}C NMR (C_6D_6): δ 25.48, 26.50, 33.81, 52.39, 114.63, 120.04, 143.46, 150.34 ppm. Anal. Calc. ($C_{24}H_{32}N_2O$): C, 79.08; H, 8.85; N, 7.68 %. Found: C, 78.98; H, 8.84 N, 7.34 %.

4,4'-Oxobis(2-bromo-N-cyclohexylaniline) (10). Bromination reaction with Br_2 did not afford the desired compound. Bromination was carried out by the reported method.[1] It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (20 : 1). A yellow solid was obtained (2.44 g, 54 %). M.P. 89 ^oC. IR (neat): 3402 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.93-1.17 (m, 10H, Cy),

1.40-1.56 (m, 6H, Cy), 1.78-1.82 (m, 4H, Cy), 2.98 (br s, 2H, N-CH), 4.08 (br d, J = 4.0 Hz, 2H, NH), 6.38 (d, J = 8.8 Hz, 2H, C_6H_3), 6.88 (dd, J = 9.2 Hz, J = 2.8 Hz, 2H, C_6H_3), 7.34 (d, J = 3.2 Hz, 2H, C_6H_3) ppm. ^{13}C NMR (C_6D_6): δ 25.18, 26.25, 33.31, 52.13, 110.06, 112.64, 119.36, 123.47, 140.79, 149.12 ppm. Anal. Calc. ($C_{24}H_{30}Br_2N_2O$): C, 55.19; H, 5.79; N, 5.36 %. Found: C, 55.59; H, 5.83; N, 5.39 %.

4,4'-o-Phenylenebis(N-cyclohexylaniline). The compound was synthesized by the same conditions and procedures as for 4,4'-methylenebis(*N*-cyclohexylaniline) from 4,4'-*o*-phenylenebis(aniline) (3.84 g, 14.75 mmol). Molecular sieves were removed by filtration while the solution is hot. In the reduction reaction, solvent was MeOH and reaction time was 7 hours. It was purified by recrystallization in hexane (4.41 g, 71 %). M.p. 169-171 ^{o}C. IR (neat): 3432 (N-H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.80-0.85 (m, 4H, Cy), 0.99-1.14 (m, 6H, Cy), 1.44-1.53 (m, 6H, Cy), 1.80-1.82 (m, 4H, Cy), 2.93-2.97 (m, 2H, N-CH), 3.05 (br s, 2H, NH), 6.34 (d, J = 8.4 Hz, 4H, C_6H_4N), 7.27 (d, J = 8.4 Hz, 4H, C_6H_4N), 7.26 (dd, AA'BB', 2H, C_6H_4), 7.55 (AA'BB', 2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 25.26, 26.24, 33.55, 51.43, 112.83, 126.80, 130.83, 130.94, 131.04, 141.01, 146.01 ppm. Anal. Calc. ($C_{30}H_{36}N_2$): C, 84.86; H, 8.55; N, 6.60 %. Found: C, 84.50; H, 8.50; N, 6.42 %.

4,4'-o-Phenylenebis(2-bromo-N-cyclohexylaniline) (11). The compound was synthesized by the same conditions and procedures as for **9** from 4,4'-*o*-phenylenebis(*N*-cyclohexylaniline) (3.26 g, 7.68 mmol). It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (20 : 1). Light yellow solid was obtained in 70 % yield (3.17 g). M.p. 78-80 ^{o}C. IR (neat): 3399 (N-H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.00-1.77 (m, 20H, Cy), 2.89 (m, 2H, N-CH), 4.24 (d, J = 7.6 Hz, 2H, NH), 6.24 (d, J = 8.4 Hz, 2H, C_6H_3), 6.96 (dd, J = 8.4, 2.0 Hz, 2H, C_6H_3), 7.16 (AA'BB', 2H, C_6H_4), 7.28 (AA'BB', 2H, C_6H_4) ppm ^{13}C{^{1}H} NMR (C_6D_6): δ 25.14, 26.17, 33.20, 51.53, 109.79, 111.47, 127.42, 130.77, 130.83, 131.30, 133.79, 139.52, 142.97 ppm. Anal. Calc. ($C_{30}H_{34}Br_2N_2$): C, 61.85; H, 5.88; N, 4.81 %; Found: C, 62.18; H, 5.64; N, 5.07 %.

Compound 13. The compound was synthesized by same conditions and procedures as for **3** using **10** (1.88g, 3.60 mmol). It was purified by column chromatography on silica gel eluting with hexane and

ethyl acetate (3 : 1). A light yellow solid was obtained (1.07 g, 51 %). M.p. 182 ^{o}C. IR (neat): 3448 (N-H), 1502 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.12-1.25 (m, 6H, Cy), 1.31 (d, J = 7.2, 6H, CH_3), 1.36-1.42 (m, 4H, Cy), 1.63-1.75 (m, 6H, Cy), 2.02 (s, 6H, CH_3), 1.98-2.03 (m, 4H, Cy), 2.17 (d, J = 18.0, 2H, CH_2), 2.80 (dd, J = 18.4, 6.4 Hz, 2H, CH_2), 2.91-2.94 (m, 2H, CH), 3.19-3.24 (m, 2H, N-CH), 3.35 (br s, 2H, NH), 6.59 (d, J = 3.2 Hz, 2H, C_6H_3), 6.67 (d, J = 8.8 Hz, 2H, C_6H_3), 6.91 (dd, J = 8.8, 2.8 Hz, 2H, C_6H_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.32, 19.43, 24.92, 25.96, 33.32, 37.75, 43.49, 52.18, 112.75, 118.76, 119.18, 120.81, 138.75, 140.95, 148.48, 179.19, 206.35 ppm. Anal. Calc. ($C_{38}H_{49}N_2O_3$): C, 78.58; H, 8.33; N, 4.82 %. Found: C, 78.75; H, 8.44; N, 4.93 %.

Compound 14. The compound was synthesized by same conditions and procedures as for **3** using **11** (2.50 g, 4.28 mmol). It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (3 : 1). A light yellow solid was obtained (2.47 g, 90 %). M.p. 109-111 ^{o}C. IR (neat): 3386 (N-H), 1695 (C=O) cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.80-0.82 (m, 4H, Cy), 1.18 (d, J = 8.0 Hz, 6H, CH_3), 1.10-1.24 (m, 6H, Cy), 1.43-1.64 (m, 6H, Cy), 1.64 (s, 6H, CH_3), 1.82 (d, J = 18.4 Hz, 2H, CH_2), 1.97 (br s, 4H, Cy), 2.24-2.26 (m, 2H, CH), 2.40 (dd, J = 18.0, 6.4 Hz, 2H, CH_2), 3.12 (br s, 2H, N-CH), 4.17 (s, 2H, NH), 6.61 (d, J = 8.4 Hz, 2H, C_6H_3), 6.96 (s, 2H, C_6H_3), 7.25 (AA'BB', 2H, C_6H_4), 7.34 (dd, J = 8.4, 2.0 Hz, 2H, C_6H_3), 7.53 (AA'BB', 2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 16.22, 19.44, 19.47, 25.25, 26.48, 33.54, 33.80, 37.92, 43.68, 51.71, 112.00, 118.85, 127.00, 130.80, 130.74, 131.00, 131.16, 133.26, 140.16, 141.08, 145.20, 178.03, 205.40 ppm. Anal. Calc. ($C_{44}H_{52}N_2O_2$): C, 82.46; H, 8.18; N, 4.37 %. Found: C, 82.13; H, 8.29; N, 4.58 %.

Compound 16. The compound was synthesized by same conditions and procedures as for **15** using **13** (0.302 g, 0.52 mmol). It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). A white solid was obtained (0.202g, 67 %). M.p. 120 ^{o}C. ^{1}H NMR (C_6D_6): δ 0.89-1.02 (m, 6H, Cy), 1.09-1.19 (m, 4H, Cy), 1.41-1.53 (m, 6H, Cy), 1.79 (s, 6H, CH_3), 1.83 (s, 6H, CH_3), 1.86 (s, 6H, CH_3), 1.88-1.97 (m, 4H, Cy), 2.60 (AB, J = 22.8 Hz, 2H, CH_2), 2.73 (AB, J = 22.4 Hz, 2H, CH_2), 3.07-3.14 (m, 2H, N-CH), 3.60 (d, J = 8.4 Hz, 2H, NH), 6.63 (d, J = 8.8 Hz, 2H, C_6H_3), 7.11 (d, J = 2.8 Hz, 2H, C_6H_3), 7.22 (dd, J = 1.6, 8.8 Hz, 2H, C_6H_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 12.16, 13.83,

14.72, 25.45, 25.49, 26.41, 33.95, 49.01, 52.22, 111.93, 118.81, 121.28, 124.37, 133.22, 136.15, 136.99, 140.54, 141.30, 149.65 ppm. Anal. Calc. ($C_{40}H_{52}N_2O$): C, 83.28; H, 9.09; N, 4.86 %. Found: C, 83.08; H, 9.21; N, 4.85 %.

Compound 17. The compound was synthesized by same conditions and procedures as for **15** using **14** (0.435 g, 0.68 mmol). It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (15 : 1). A light yellow solid was obtained (0.179 g, 41 %). Due to the rotational barrier around C-C bond between the $Me_3C_5H_3$ and C_6H_3N fragment,[2] it was obtained as a mixture of two isomers and some signals were split in the NMR spectra. M.p. 109 ^oC. ^1H NMR (C_6D_6): δ 0.88-1.01 (m, 6H, Cy), 1.08-1.18 (m, 4H, Cy), 1.41-1.53 (m, 6H, Cy), 1.75 (s, 6H, CH_3), 1.85 (s, 6H, CH_3), 1.88 (s, 6H, CH_3), 1.84-1.92 (m, 4H, Cy), 2.68 (AB, *J* = 22.8 Hz, 2H, CH_2), 2.79 (AB, *J* = 22.4 Hz, 2H, CH_2), 3.10-3.12 (m, 2H, N-CH), 3.74 (d, *J* = 5.6 Hz, 2H, NH), 6.59 (d, *J* = 8.4 Hz, 2H, C_6H_3), 7.12 (s, 2H, C_6H_3), 7.23 (AA'BB', 2H, C_6H_4), 7.36 (dd, *J* = 2.0, 8.4 Hz, 2H, C_6H_3), 7.57 (AA'BB', 2H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.15, 13.90, 14.73, 25.47, 26.34, 33.95, 49.07, 51.61, 110.35, 122.43, 126.79, 130.06, 130.69, 130.71, 131.06, 132.42, 132.47, 132.80, 136.54, 136.76, 140.86, 141.61, 143.97 ppm. Anal. Calc. ($C_{46}H_{56}N_2$): C, 86.74; H, 8.86; N, 4.40 %. Found: C, 85.74; H, 9.22; N, 4.42 %.

Complex 19. It was synthesized by same conditions and procedures as for **7** using **16** (0.148 g, 0.26 mmol). It was purified by trituration in pentane. Overall yield from **16** was 78 % (0.161 g). The ^1H NMR (C_6D_6) datum for the intermediate bis(dimethylamido)titanium complex: δ 1.12-1.32 (m, 8H, Cy), 1.36-1.47 (m, 6H, Cy), 1.60-1.62 (m, 2H, Cy), 1.63-1.74 (m, 4H, Cy), 1.78 (s, 6H, CH_3), 1.83-1.87(m, H, Cy), 1.89 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 2.91 (s, 12H, NCH_3), 3.13 (br s, 12H, NCH_3), 5.62 (br s, 2H, Cp-H), 6.68 (br s, 2H, C_6H_3), 7.20 (s, 2H, C_6H_3), 7.23 (d, J = 8.0 Hz, 2H, C_6H_3) ppm. The analytical data for **19**: ^1H NMR (C_6D_6): δ 0.89-0.99 (m, 2H, Cy), 1.40-1.47 (m, 6H, Cy), 1.66-1.93 (m, 8H, Cy), 1.70 (s, 6H, CH_3), 1.82 (s, 6H, CH_3), 2.04-2.15 (m, 4H, Cy), 2.10 (s, 6H, CH_3), 5.54-5.59 (m, 2H, N-CH), 6.05 (s, 2H, Cp-H), 6.62 (d, *J* = 8.8 Hz, 2H, C_6H_3), 7.04 (d, *J* = 9.2 Hz, 2H, C_6H_3), 7.07 (s, 2H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.72, 14.73, 15.13, 26.06, 27.27, 27.29, 27.32, 27.77, 27.84,

59.87, 111.50, 118.23, 118.56, 120.20, 131.63, 133.93, 140.48, 142.30, 142.74, 154.25, 159.84 ppm. Anal. Calc. ($C_{41}H_{50}Cl_4N_2Ti_2$): C, 60.92; H, 6.23; N, 3.47 %. Found: C, 61.14; H, 6.31; N, 3.34 %.

Complex 20. It was synthesized by same conditions and procedures as for **7** using **17** (0.180 g, 0.28 mmol). It was purified by trituration in pentane. Overall yield from **17** was 75 % (0.185 g). It was obtained as a mixture of two diastereomers and some signals were split in the ^1H and ^{13}C NMR spectra. The ^1H NMR (C_6D_6) datum for the intermediate bis(dimethylamido)titanium complex: δ 0.89-1.72 (m, 16H, Cy), 1.80 (s, 6H, CH_3), 1.88 (s, 6H, CH_3), 1.94 (s, 6H, CH_3), 2.76-2.02 (m, 4H, Cy), 2.94 (br s, 12H, NCH_3), 3.13 (s, 12H, NCH_3), 5.65 (br s, 2H, Cp-H), 6.70 (br s, 2H, C_6H_3), 7.27 (br s, 2H, C_6H_3), 7.25 (AA'BB', 2H, C_6H_4), 7.38 (br d, J = 8.0 Hz, 2H, C_6H_3), 7.65 (AA'BB', 2H, C_6H_4) ppm. The analytical data for **20**: ^1H NMR (C_6D_6): δ 0.91-2.18 (m, 20 H, Cy), 1.66 and 1.69 (s, 6H, CH_3), 1.75 and 1.78 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 5.51 (m, 2H, N-CH), 6.05 (s, 2H, Cp-H), 6.52 (d, J = 8.8 Hz, 2H, C_6H_3), 7.10 (d, J = 2.0 Hz, 2H, C_6H_3), 7.24 (dd, J = 2.0, 8.8 Hz, 2H, C_6H_3), 7.30 (AA'BB', 2H, C_6H_4), 7.52 (AA'BB', 2H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.97, 14.76, 15.22, 15.24, 25.87, 30.41, 59.96, 110.86, 118.52, 118.59, 129.87, 130.80, 131.03, 131.82, 131.89, 131.95, 137.06, 140.41, 141.48, 142.55, 142.58, 142.99, 143.07, 162.74 ppm. Anal. Calc. ($C_{46}H_{52}Cl_4N_2Ti_2$): C, 63.47; H, 6.02; N, 3.22 %. Found: C, 63.78; H, 6.31; N, 3.34 %.

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