Electronic Supplementary Information for:

Construction of C_1-Symmetric Zirconium Complexes by Designing of New Salan Ligands. Coordination Chemistry and Preliminary Polymerisation Catalysis Studies

Ad Cohen, Adi Yeori, Jacob Kopilov, Israel Goldberg, and Moshe Kol*

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel

General

All experiments employing metal complexes were performed under an atmosphere of dry nitrogen in a nitrogen-filled glovebox. Ether was purified by distillation under dry argon atmosphere from purple Na/benzophenone solution. Pentane was washed with HNO_3/H_2SO_4 prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. 2,4-Di-*tert*-butylphenol, 2,4-dichlorosalicylaldehyde, bromine, paraformaldehyde, *N,N'*-dimethylethylenediamine, *rac*-*N,N'*-dimethyl-1,2-diaminocyclohexane, triethylamine, and $Zr(OtBu)_4$ were purchased from Aldrich and used as received. (*R,R*)-*N,N'*-dimethyl-1,2-diaminocyclohexane,[1] 2-(bromomethyl)-4,6-bis(*tert*-butyl)phenol,[2] and $ZrBn_4$[3] were synthesized according to published procedures. NMR data for the metal complexes were recorded on a Bruker AC-200 and AC-400 spectrometers and referenced to protio impurities in benzene-d_6 (δ 7.15) and to ^{13}C chemical shift of benzene (δ 128.70). NMR data for the poly(1-hexene) samples in $CDCl_3$ were recorded on a Bruker AC-400 spectrometer and referenced to protio impurities in the solvent (δ 77.16). Poly(1-hexene) molecular weights were detrmined by gel permeation chromatography (GPC) using TSKgel GMHHR-M column on Jasco instrument equipped with a refractive index detector. Molecular weight determination was carried out relative to polystyrene standards using tetrahydrofuran (HPLC grade, distilled and filtered under vacuum prior to use) as the eluting solvent. Elemental analyses were performed in the microanalytical laboratory in the Hebrew University of Jerusalem. X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer system, using MoKα (λ = 0.7107 Å) radiation. The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to *ca*. 110 K. The structures were solved by a combination of direct methods and Fourier techniques using SIR-97 software,[4] and were refined by full-matrix least squares with SHELXL-97.[5]

Synthesis of 2,4-dichloro-6-((methyl(2-(methylamino)ethyl)amino)methyl)phenol

To a stirred solution of 3,5-dichlorosalicylaldehyde (4.32 g, 22.6 mmol) in methanol (110 mL), was added drop-wise, a solution of *N,N'*-dimethylethylendiamine (2.0 g, 22.6 mmol) in methanol (40 mL). The solution was stirred for 2 hours, and $NaBH_4$ (2.5 g, 13.4 mmol) was added in small portions. The solution was stirred for another hour, and another portion of $NaBH_4$ (2.5 g, 13.4 mmol) and some of ice were added, leading to a precipitation of a white solid. The reaction mixture was stirred for additional 2 hours. The white solid was collected by vacuum filtration (3.5 g, 51% yield). M.p. 163 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.22 (d, *J*= 2.6 Hz, 1H), 6.86 (d, *J*= 2.6 Hz, 1H), 3.45 (s, 2H), 2.94 (t, *J*= 6.3 Hz, 2H), 2.65 (t, *J*= 6.3 Hz, 2H), 2.49 (s, 3H), 2.25 (s, 3H).; ^{13}C NMR (400 MHz, $CDCl_3$), δ 155.9 (*C*), 128.5 (*C*H), 127.9 (*C*H), 126.2 (*C*), 122.0 (*C*), 120.0 (*C*), 57.7 (CH_2), 53.8 (CH_2), 47.1 (CH_2), 42.4 (CH_3), 34.3 (CH_3).

Synthesis of *rac*-2,4-dichloro-6-{[methyl-(2-methylamino-cyclohexyl)-amino]-methyl}phenol

To a stirred solution of 3,5-dichlorosalicylaldehyde (1.6 g, 6.3 mmol) in methanol (4 mL), was added drop-wise, a solution of *rac-N,N'*-dimethyl-1,2-diaminocyclohexane (1.2 g, 11.0 mmol) in methanol (10 mL). The reaction mixture was stirred for 2 hours at room temperature forming a yellow solution. $NaBH_4$ (0.9 g, 3.5 mmol) was added in small portions. The solution became colorless and a white solid precipitated. After 1 hour another portion of $NaBH_4$ (0.6 g, 2.3 mmol) and 20 mL of cold water (0 °C) were added while the flask was chilled with ice water. The solution was stirred for 30 min, and the white solid was collected by vacuum filtration (2.0 g, 99%). M.p. 187 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ 7.18 (d, *J*= 2.7 Hz, 1H), 6.80 (d, *J*= 2.7 Hz, 1H), 3.93 (d, *J*= 12.0 Hz, 1H, AB system), 3.11 (m, 1H), 2.71 (d, *J*= 12.0 Hz, 1H, AB system), 2.45 (s, 3H), 2.22 (s, 3H), 2.05 (m, 1H), 1.71 (m, 4H), 1.22 (m, 4H); ^{13}C NMR (50.34 MHz, $CDCl_3$), δ 159.0 (*C*), 128.9 (*C*H), 128.6 (*C*), 128.3 (*C*H), 122.6 (*C*), 116.4 (*C*), 63.5 (*C*H), 56.9 (*C*H), 51.5 (CH_2), 39.4 (CH_3), 28.0 (CH_2), 26.7 (CH_3), 25.3 (CH_2), 22.6 (CH_2).

Synthesis of (*R,R*)-2,4-dichloro-6-{[methyl-(2-methylamino-cyclohexyl)-amino]-methyl}phenol

To a stirred solution of 3,5-dichlorosalicylaldehyde (2.4 g, 12.3 mmol) in methanol (60 mL), was added drop-wise a solution of (*R,R*)-*N,N'*-dimethyl-1,2-diaminocyclohexane (1.8 g, 12.3 mmol) in methanol (25 mL). The reaction mixture was stirred overnight. $NaBH_4$ (1.1 g, 28.9 mmol) was added in small

portions and the solution was stirred until the mixture became colorless and a white solid precipitated. The solution was cooled to 0 °C and stirred for 2 hours. The white solid was collected by vacuum filtration (3.4 g, 87%). ^{1}H NMR (200 MHz, $CDCl_3$), δ 7.18 (d, *J*= 2.7 Hz, 1H), 6.80 (d, *J*= 2.7 Hz, 1H), 3.93 (d, *J*= 12.0 Hz, 1H, AB system), 3.11 (m, 1H), 2.71 (d, *J*= 12.0 Hz, 1H, AB system), 2.45 (s, 3H), 2.22 (s, 3H), 2.05 (m, 1H), 1.71 (m, 4H), 1.22 (m, 4H); ^{13}C NMR (50.34 MHz, $CDCl_3$), δ 159.0 (*C*), 128.9 (*C*H), 128.6 (*C*), 128.3 (*C*H), 122.6 (*C*), 116.4 (*C*), 63.5 (*C*H), 56.9 (*C*H), 51.5 (CH_2), 39.4 (CH_3), 28.0 (CH_2), 26.7 (CH_3), 25.3 (CH_2), 22.6 (CH_2). $[\alpha]_D$ = 16°, (45.1 mg/10.0 mL of CH_2Cl_2, *d* = 0.5).

Synthesis of Lig^{1}H$_2$

To a stirred solution of 2-(bromomethyl)-4,6-bis(*tert*-butyl)phenol (3.00 g, 10.0 mmol) was added 2,4-dichloro-6-((methyl(2-(methylamino)ethyl)amino)methyl)phenol (2.64 g, 10.0 mmol) in dry THF (100 mL). After complete dissolution, triethylamine (1.39 mL, 10.0 mmol) was added drop-wise. A white solid formed immediately and the reaction flask had warmed up. The reaction mixture was stirred for 2 hours, and the white solid was removed by filtration. The volatiles were removed THF under reduced pressure forming a yellow solid. The solid was dissolved in 60 mL of dichloromethane, the solution was washed three times with water (100 mL), the organic layer was dried over sodium sulfate and the solvent was removed to yield an orange solid that was precipitated from methanol as a white solid and collected by vacuum filtration. The product was purified by flash column chromatography over silica gel 60H, eluted with a growing concentration of dichloromethane in petroleum ether. Lig^{1}H$_2$ was re-crystallized from pentane and as a white solid. (2.07 g, 43% yield). M.p. 86 °C. ^{1}H NMR (400 MHz, C_6D_6), δ 7.51 (d, *J*= 2.1 Hz, 1H), 7.25 (d, *J*= 2.1 Hz, 1H), 6.90 (d, *J*= 2.0 Hz, 1H), 6.54 (d, *J*= 2.1 Hz, 1H), 3.23 (s, 2H), 2.82 (s, 2H), 2.01 (t, *J*= 6.5 Hz, 2H), 1.92 (t, *J*= 6.7 Hz, 2H), 1.75 (s, 3H), 1.69 (s, 9H), 1.54 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (400 MHz, C_6D_6), δ 154.7 (*C*), 153.4 (*C*), 140.8 (*C*), 136.1 (*C*), 129.0 (*C*H), 128.0 (*C*), 126.6 (*C*H) 124.0 (*C*), 123.4 (*C*H), 123.2 (*C*H), 122.1 (*C*H), 121.3 (*C*H), 62.5 (CH_2), 60.5 (CH_2), 53.6 (CH_2), 52.9 (CH_2), 40.9 (CH_3), 40.7 (CH_3), 35.1 (*C*), 34.2 (*C*), 31.8 (CH_3), 29.8 (CH_3). Anal. Calcd. for $C_{26}H_{38}Cl_2N_2O_2$: C, 64.86; H, 7.95; N, 5.92. Found: C, 65.15; H, 8.05; N, 5.86.

Synthesis of *rac*-Lig^{2}H$_2$

To a stirred solution of 2-(bromomethyl)-4,6-bis(*tert*-butyl)phenol (0.70 g, 2.34 mmol) was added 2,4-dichloro-6-{[methyl-(2-methylamino-cyclohexyl)-amino]-methyl}phenol (0.74 g, 2.34 mmol) in dry THF (30 mL). After complete dissolution, triethylamine (0.33 mL, 2.34 mmol) was added drop-wise. A

white solid formed immediately and the reaction flask had warmed up. The reaction mixture was stirred for 0.5 an hour, and the white solid was removed by filtration. The volatiles were removed leaving a white-yellow solid. The solid was dissolved in 60 mL of dichloromethane, the solution was washed three times with water (100 mL), the organic layer was dried over sodium sulfate, and the solvent was removed to yield an orange solid that was precipitated from methanol to give *rac*-Lig^{2}H$_2$ as a white solid collected by vacuum filtration (0.7 g, 60% yield). ^{1}H NMR (400 MHz, C_6D_6), δ 7.51 (d, *J*= 2.4 Hz, 1H), 7.27 (d, *J*= 2.5 Hz, 1H), 6.95 (d, *J*= 2.4 Hz, 1H), 6.66 (d, *J*= 2.5 Hz, 1H), 3.52 (d, *J*= 13.1 Hz, 1H, AB system), 3.35 (d, *J*= 13.0 Hz, 1H, AB system), 3.15 (d, *J*= 13.7 Hz, 1H, AB system), 2.94 (d, *J*= 13.3 Hz, 1H, AB system), 2.30 (td, *J*= 10.8 Hz, *J*= 3.0 Hz, 1H), 2.10 (td, *J*= 10.8 Hz, *J*= 3.0 Hz, 1H), 1.91 (s, 3H), 1.79 (s, 3H), 1.64 (s, 9H), 1.37 (s, 9H), 0.62 (m, 8H); ^{13}C NMR (400 MHz, C_6D_6), δ 154.6 (*C*), 153.7 (*C*), 140.8 (*C*), 136.5 (*C*), 129.1 (*C*H), 126.9 (*C*H), 124.7 (*C*), 124.0 (*C*H), 123.4 (*C*H), 122.9 (*C*), 122.4 (*C*), 121.9 (*C*), 62.8 (*C*H), 60.8 (*C*H), 58.2 (*C*H$_2$), 56.6 (*C*H$_2$), 35.1 (*C*H$_3$), 34.9 (*C*), 34.5 (*C*H$_3$), 34.1 (*C*), 31.8 (*C*H$_2$), 29.9 (*C*H$_3$), 25.1 (*C*H$_2$), 24.9 (*C*H$_2$), 22.2 (*C*H$_2$), 21.6 (*C*H$_2$). Anal. Calcd. for $C_{30}H_{44}Cl_2N_2O_2$: C, 67.28; H, 8.26; N, 5.23. Found: C, 67.54; H, 8.57; N, 4.95.

Synthesis of (*R,R*)-Lig^{2}H$_2$

The ligand (*R,R*)-Lig^{2}H$_2$ was synthesized by the same procedure employed for *rac*-Lig^{2}H$_2$ by using (*R,R*)-2,4-dichloro-6-{[methyl-(2-methylamino-cyclohexyl)-amino]-methyl}phenol as starting material. M.p. 84 °C. $[\alpha]_D = 53°$, (40.2 mg/10.0 mL of CH_2Cl_2, *d* = 1.0).

Synthesis of Lig^{1}Zr(O-*tert*-Bu)$_2$

Lig^{1}H$_2$ (48.3 mg, 100 mmol) was dissolved in *ca*. 2 mL of ether and added drop-wise to a bright solution of Zr(OtBu)$_4$ (38.5 mg, 100 mmol) in ether. The solution was stirred at room temperature for 2 hours. The solvent was removed under vacuum, and the resulting white oil was washed with pentane (*ca*. 2 mL). The solvent was removed under vacuum to yield a white solid (74.0 mg, 100%). ^{1}H NMR (400 MHz, C_6D_6), δ 7.58 (d, *J*= 2.5 Hz, 1H), 7.40 (d, *J*= 2.4 Hz, 1H), 6.91 (d, *J*= 2.5 Hz, 1H), 6.62 (d, *J*= 2.6 Hz, 1H), 4.59 (d, *J*= 13.2 Hz, 1H, AB system), 4.39 (d, *J*= 13.5 Hz, 1H, AB system), 2.77 (d, *J*= 13.4 Hz, 1H, AB system), 2.74 (td, *J*= 3.3 Hz, *J*= 13.6, 1H, AB system), 2.33 (d, *J*= 13.6 Hz, 1H, AB system), 2.31 (td, *J*= 3.3 Hz, *J*= 13.2 1H, AB system), 2.12 (s, 3H), 1.95 (s, 3H), 1.71 (s, 9H), 1.43 (s, 9H), 1.36 (s, 9H), 1.36 (s, 9H), 0.83 (dd, *J*= 1.8 Hz, *J*= 13.4 1H, AB system), 0.79 (dd, *J*= 1.9 Hz, *J*= 13.5 1H, AB system); ^{13}C NMR (400 MHz, C_6D_6), δ 158.0 (*C*), 156.0 (*C*), 139.0 (*C*), 136.8 (*C*), 129.5 (*C*H), 128.1 (*C*), 127.6 (*C*H) 125.9 (*C*), 124.5 (*C*H), 124.0 (*C*H), 123.3 (*C*), 120.1 (*C*H), 75.8 (*C*), 75.4 (*C*), 65.2 (*C*H$_2$), 63.1 (*C*H$_2$), 51.1 (*C*H$_2$), 50.9 (*C*H$_2$), 46.4 (*C*H$_3$), 45.3 (*C*H$_3$), 35.4 (*C*), 34.1 (*C*), 33.1

(*C*H$_3$), 32.9 (*C*H$_3$), 31.9 (*C*H$_3$), 30.3 (*C*H$_3$). Anal. Calcd. for $C_{34}H_{54}Cl_2N_2O_4Zr$: C, 56.96; H, 7.59; N, 3.91. Found: C, 57.55; H, 8.02; N, 3.70. Crystal data for Lig^{1}Zr(O-*tert*-Bu)$_2$: $C_{39}H_{66}Cl_2N_2O_4Zr$; M = 789.06; monoclinic; space group $P2_1/c$; a = 15.1740(2) Å; b = 15.2550(2) Å; c = 36.9390(5) Å; β = 94.8900(6) °; V = 8519.5(2) Å^3; T = 110(2) K; Z = 8; D_c = 1.230 g cm^{-3}; μ (Mo Kα) = 0.421 mm^{-1}; R_1 = 0.0597 and wR_2 = 0.1408 for 11540 reflection with $I > 2\sigma(I)$; R_1 = 0.1255 and wR_2 = 0.1746 for all 20086 unique reflections.

Synthesis of *rac*-Lig^{2}Zr(O-*tert*-Bu)$_2$:

Lig^{2}H$_2$ (59.0 mg, 0.11 mmol) was dissolved in *ca*. 2 mL of ether and added drop-wise to a bright solution of Zr(OtBu)$_4$ (43.0 mg, 0.11 mmol) in ether. The solution was stirred at room temperature for 72 hours. The solvent was removed under vacuum, and the resulting white oil was washed with pentane (*ca*. 2 mL). The solvent was removed under vacuum to yield a white solid (75 mg, 100%). ^{1}H NMR (400 MHz, C_6D_6), δ 7.56 (d, *J*= 2.4 Hz, 1H), 7.41 (d, *J*= 2.5 Hz, 1H), 6.87 (d, *J*= 2.4 Hz, 1H), 6.71 (d, *J*= 2.5 Hz, 1H), 4.62 (d, *J*= 13.3 Hz, 1H, AB system), 4.48 (d, *J*= 13.4 Hz, 1H, AB system), 2.99 (d, *J*= 13.4 Hz, 1H, AB system), 2.67 (d, *J*= 13.5 Hz, 1H, AB system), 2.57 (dt, *J*= 4.3 Hz, *J*= 11.2, 1H), 2.26 (dt, *J*= 4.2 Hz, *J*= 11.6 1H), 2.23 (s, 3H), 2.15 (s, 3H), 1.75 (s, 9H), 1.49 (s, 9H), 1.44 (s, 9H), 1.36 (s, 9H), 1.28 (m, 2H), 1.03 (m, 2H), 0.35 (m, 4H); ^{13}C NMR (400 MHz, C_6D_6), δ 158.4 (*C*), 156.8 (*C*), 138.8 (*C*), 136.3 (*C*), 129.8 (*C*H), 127.5 (*C*H), 126.3 (*C*), 124.3 (*C*H), 124.0 (*C*H), 123.5 (*C*), 120.1 (*C*), 76.5 (*C*), 75.9 (*C*), 60.9 (*C*H$_2$), 59.2 (*C*H$_2$), 57.1 (*C*H), 56.8 (*C*H), 40.1 (*C*H$_3$), 39.4 (*C*H$_3$), 35.4 (*C*), 34.1 (*C*), 33.1 (*C*H$_3$), 32.8 (*C*H$_3$), 31.8 (*C*H$_3$), 30.3 (*C*H$_3$), 23.8 (*C*H$_2$), 23.7 (*C*H$_2$), 21.2 (*C*H$_2$), 21.1 (*C*H$_2$). Anal. Calcd. for $C_{38}H_{60}Cl_2N_2O_4Zr$: C, 59.19; H, 7.84; N, 3.63. Found: C, 59.42; H, 8.03; N, 3.47. Crystal data for *rac*-Lig^{2}Zr(O-*tert*-Bu)$_2$: $C_{38}H_{60}Cl_2N_2O_4Zr$; M = 771.00; monoclinic; space group $P2_1/c$; a = 19.6465(4) Å; b = 10.6398(2) Å; c = 20.5229(6) Å; β = 110.2014(8) °; V = 4026.10(16) Å^3; T = 110(2) K; Z = 4; D_c = 1.272 g cm^{-3}; μ (Mo Kα) = 0.444 mm^{-1}; R_1 = 0.0645 and wR_2 = 0.1210 for 5678 reflection with $I > 2\sigma(I)$; R_1 = 0.1322 and wR_2 = 0.1438 for all 9543 unique reflections.

Synthesis of Lig^{1}ZrBn$_2$

Lig^{1}H$_2$ (55.3 mg, 0.11 mmol) was dissolved in *ca*. 2 mL of toluene and added drop-wise to a bright yellow solution of ZrBn$_4$ (55.6 mg, 0.11 mmol) in toluene. The solution was stirred at room temperature for 6 hours. The solvent was removed under vacuum, and the product was washed with pentane (*ca*. 2 mL) to yield a yellow solid (82.1 mg, 95%). ^{1}H NMR (400 MHz, C_6D_6), δ 7.61 (d, *J*=2.4 Hz, 1H), 7.42

(m, 2H), 7.33 (d, *J*= 2.5 Hz, 1H), 6.97 (m, 7H), 6.85 (d, *J*=2.4 Hz, 1H), 6.69 (m, 1H), 6.40 (d, *J*= 2.5 Hz, 1H), 4.12 (d, *J*= 13.8 Hz, 1H, AB system), 3.9 (d, *J*= 13.8 Hz, 1H, AB system), 2.83 (d, *J*= 8.1 Hz, 1H, AB system), 2.68 (d, *J*= 8.2 Hz, 1H, AB system), 2.62 (dt, *J*= 3.1 Hz, *J*= 13.8, 1H, AB system), 2.53 (d, *J*= 14 Hz, 1H, AB system), 2.24 (d, *J*= 10.8 Hz, 1H, AB system), 2.15 (dt, *J*= 3.04 Hz, *J*= 13.8, 1H, AB system), 1.82 (d, *J*= 14.1 Hz, 1H, AB system), 1.8 (s, 3H), 1.75 (s, 3H), 1.71 (s, 9H), 1.38 (s, 9H), 0.91 (d, *J*= 10.8 Hz, 1H, AB system), 0.87 (dd, *J*= 2.2 Hz, *J*= 13.5 1H, AB system), 0.64 (dd, *J*= 2.5 Hz, *J*= 13.5 1H, AB system) ; ^{13}C NMR (128.04 MHz, C_6D_6), δ 156.3, 154.6 (2C, *C*), 151.6 (1C, *C*), 141.5, 139.8, 137.2 (3C, *C*), 131.0, 129.9 (4C, *C*H), 129.2, (1C, *C*), 127.0, (2C, *C*H), 125.5, 125.3 (2C, *C*H), 125.0 (1C, *C*), 124.7 (1C, *C*H), 124.3 (1C, *C*), 122.6 (1C, *C*), 120.6, (1C, *C*H) , 65.1 (1C, *C*H_2), 64.3 (1C, *C*H_2), 61.4 (1C,*C*H_2), 60.8 (1C,*C*H_2), 53.1 (1C, *C*H_2), 52.5 (1C, *C*H_2), 45.2 (1C, *C*H_3), 44.4 (1C, *C*H_3), 35.3 (1C, *C*), 34.3 (1C, *C*), 31.7(1C, *C*H_3), 30.1 (1C, *C*H_3). Crystal data for Lig^{1}ZrBn$_2$: $C_{45.5}H_{64}Cl_2N_2O_{3.25}Zr$; M = 853.11; orthorombic; space group *Iba*$_2$; a = 28.4943(3) Å; b = 17.8980(3) Å; c = 17.8230(6) Å; V = 9089.5(4) Å^3; T = 110(2) K; Z = 8; D_c = 1.247 g cm^{-3}; μ (Mo Kα) = 0.399 mm^{-1}; R_1 = 0.0524 and wR_2 = 0.1230 for 4452 reflection with $I > 2\sigma(I)$; R_1 = 0.0703 and wR_2 = 0.1324 for all 5493 unique reflections.

Synthesis of *rac*-Lig^{2}ZrBn$_2$

rac-Lig^{2}H$_2$ (59.0 mg, 0.11 mmol) was dissolved in *ca*. 2 mL of toluene and added drop-wise to a bright yellow solution of $ZrBn_4$ (50.0 mg, 0.11 mmol) in toluene. The solution was stirred at room temperature for 24 hours. The solvent was removed under vacuum, and the product was washed with pentane (*ca*. 2 mL) to yield a yellow solid (50 mg, 57%).

^{1}H NMR (400 MHz, C_6D_6), δ 7.59 (d, *J*=2.3 Hz, 1H), 7.51 (d, *J*=7.3 Hz, 1H), 7.35 (d, *J*= 2.5 Hz, 2H), 7.21 (t, *J*= 7.5 Hz, 3H), 7.04 (m, 5H), 6.78 (d, *J*= 2.3 Hz, 1H), 6.49 (d, *J*= 2.5 Hz, 1H), 4.04 (d, *J*= 13.9 Hz, 1H, AB system), 3.26 (d, *J*= 14.0 Hz, 1H, AB system), 2.93 (d, *J*= 9.1 Hz, 1H, AB system), 2.89 (d, *J*= 9.1 Hz, 1H, AB system), 2.75 (d, *J*= 6.97 Hz, 1H, AB system), 2.73 (d, *J*= 7.0 Hz, 1H, AB system), 2.69 (d, *J*= 10.7 Hz, 1H, AB system), 2.87 (d, *J*= 14.1, 1H, AB system), 1.98 (m, 4H), 1.88 (s, 3H), 1.80 (s, 3H), 1.77 (s, 9H), 1.40 (m, 2H), 1.34 (s, 9H), 0.23 (m, 2H), 0.11 (m, 2H) ; ^{13}C NMR (128.04 MHz, C_6D_6), δ 157.2, 150.9, 141.7 (3C, *C*), 129.9, 129.6, 129.5, 128.8, 128.7, 128.5, 128.4, 127.9, 126.9 (9C, *C*H), 125.7 (1C, *C*), 125.1, 124.6, 123.4, 121.3 (4C, *C*H), 67.5, 67.1, 59.8 (3C, *C*H_2), 58.6, 57.7 (2C, *C*H), 56.9 (1C, *C*H_2), 38.6, 37.9 (2C, *C*H_3), 34.4, 32.1 (2C, *C*), 31.9, 30.4 (2C, *C*H_3), 23.9, 23.7, 21.3, 21.1 (4C, *C*H_2) .

General procedure for the polymerization of neat 1-hexene:

$B(C_6F_5)_3$ (1-2 equiv) was dissolved in *ca.* 1 mL of 1-hexene and added to a stirred solution of the corresponding complexes, $Lig^{1,2}Zrbn_2$ (11 μmol) in 1-hexene. The resulting mixture was stirred until the resulting polymer solution had become viscous, and the remaining 1-hexene was removed under vacuum yielding poly(1-hexene) as a yellow sticky oil. Samples of poly(1-hexene) were analyzed by GPC and ^{13}C NMR. The results are summarized in Table 1. The 13C NMR spectra are shown in Figures ESI-1 and ESI-2.

Table 1: 1-hexene Polymerization Data for $Lig^{1,2}ZrBn_2$

No.	Cat.	1-Hexene (g)	Polymerization Time (min)	Polymer Obtained (g)	Activity ($g\,mmol^{-1}\,h^{-1}$)	Mw (g/mol)	PDI
1	Lig^1ZrBn_2	3.36	6.0	2.07	1330	47,000	1.56
2	Lig^2ZrBn_2	2.50	60	0.66	53	241,000	1.92

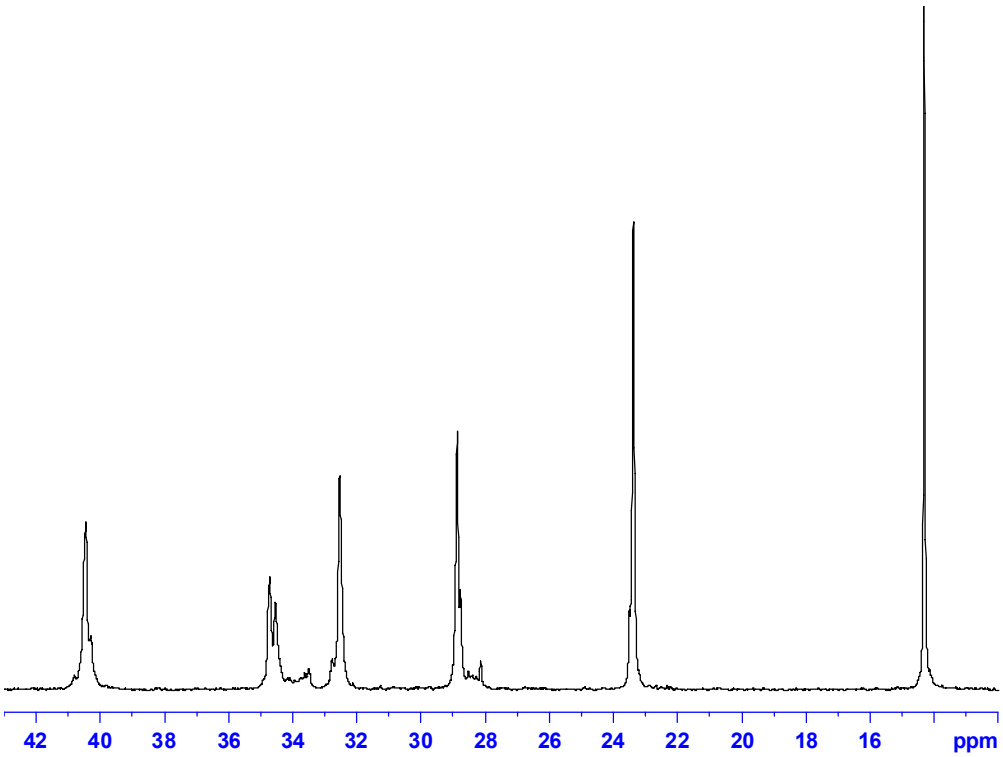

Figure ESI-1. ^{13}C NMR of poly(1-hexene) produced from $Lig^{1}Zrbn_2$.

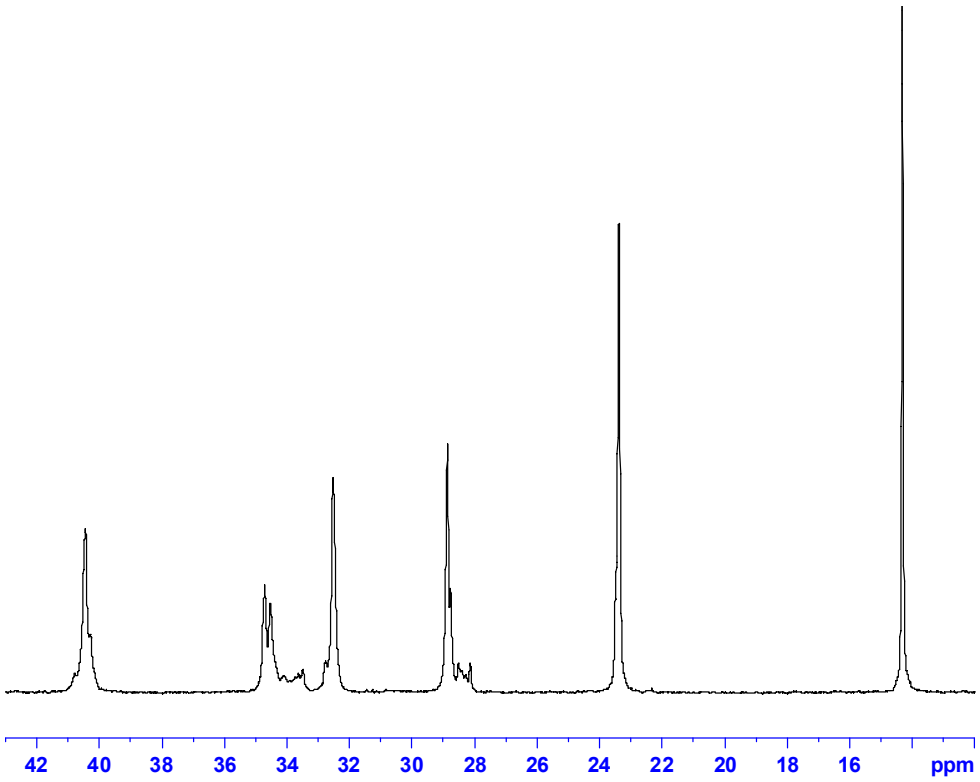

Figure ESI-2. ^{13}C NMR of poly(1-hexene) produced from $Lig^{2}Zrbn_2$.

References

1. A. Yeori, I. Goldberg and M. Kol, *Macromolecules*, 2007, **40**, 8521.

2. W. O. Appiah, A. D. DeGreef, G. L. Razidlo, S. J. Spessard, M. Pink, V. G. Young Jr. and G. E. Hofmeister, *Inorg. Chem*., 2002, **41**, 3656.

3. U. Zucchini, E. Alizzati and U. Giannini, *J. Organomet. Chem*., 1971, **26**, 357.

4. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camali, *J. Appl. Cryst.*, 1994, **27**, 435.

5. G. M. Sheldrick, *SHELXL-97 Program*; University of Göttingen, Germany, 1996.