Supporting Information for:

Group 4 Complexes of a New [OSSO]-Type Dianionic Ligand. Coordination Chemistry and Preliminary Polymerization Catalysis Studies

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General

All experiments employing metal complexes were performed under an atmosphere of dry nitrogen in a nitrogen-filled glove box. Ether and THF were purified by reflux and distillation under dry argon atmosphere from Na/benzophenone. 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, bromine, paraformaldehyde, 1,2-ethanedithiol and triethylamine were purchased from Aldrich Inc and used as received. $Ti(Oi\text{-}Pr)_4$ and $Zr(Ot\text{-}Bu)_4$ were purchased from Strem Inc. 2-(Bromomethyl)-4,6-bis(1,1-dimethylethyl)phenol[1] and $ZrBn_4$[2] were synthesized according to published procedures. NMR data for the ligand and 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). For conducting Variable-temperature NMR measurements, the complexes were dissolved in d^8-toluene. The barriers for enantiomer interconversion were calculated from fitting the coalescence temperature to a simulated spectrum generated by the gNMR Program – ADEPT Scientific (UK). 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,[3] and were refined by full-matrix least squares with SHELXL-97.[4]

Synthesis of the ligand precursor $[OSSO]H_2$

To a stirred solution of 2-(bromomethyl)-4,6-bis(1,1-dimethylethyl)phenol (6.44 g, 21.5 mmol) in dry THF (25 mL) at room temperature was added dropwise 1,2-ethanedithiol (1.12 g, 11.3 mmol). After complete dissolution triethylamine (2.17 g, 21.5 mmol) was added dropwise. A white precipitate had formed and the flask had warmed up. The flask was left to stir at room temperature for 24 h in the dark. The white solid was removed by filtration, and the solvent was removed under vacuum yielding a yellow solid. The solid was dissolved in 20 mL of dichloromethane and the

solution was washed thrice with 50 mL of water. The organic layer was dried over sodium sulfate and filtered. The solvent was removed under reduced pressure to yield an orange solid that was recrystallized from methanol as a white solid, and collected by vacuum filtration (4.99 g, 82% yield). ^{1}H NMR (400 MHz, C_6D_6), δ 7.45 (d, *J* = 2.4 Hz, 2H), 6.81 (d, *J* = 2.4 Hz, 2H), 3.33 (s, 4H), 2.13 (s, 4H), 1.61 (s, 18H), 1.29 (s, 18H); ^{13}C NMR (100.63 MHz, C_6D_6), δ 153.4, 143.1, 138.3, 126.2 (*C*H), 124.7 (*C*H), 122.5, 36.0, 35.0, 34.8 (*C*H_2), 32.4 (*C*H_3), 31.2 (*C*H_2), 30.1 (*C*H_3). Anal. Calcd. for $C_{32}H_{50}O_2S_2$: C, 72.40; H, 9.49; S, 12.09. Found: C, 72.28; H, 9.65; S, 12.40.

Synthesis of the complex [OSSO]Ti(Oi-Pr)$_2$

The ligand precursor [OSSO]H_2 (68 mg, 0.13 mmol) was dissolved in *ca*. 2 mL of ether and added dropwise to a solution of Ti(Oi-Pr)$_4$ (37 mg, 0.13 mmol) in ether. The solution was stirred at RT for 2 h. The solvent was removed under vacuum forming 87 mg of a yellow solid that was pure according to ^{1}H NMR (97%). ^{1}H NMR (400 MHz, C_6D_6), δ 7.53 (d, *J*=2.4 Hz, 2H), 6.67 (d, *J*=2.3 Hz, 2H), 5.05 (sept, *J*= 6 Hz, 2H), 3.49 (s, 4H), 1.91 (s, 4H), 1.86 (s, 18H), 1.39 (d, *J*=6 Hz, 12H), 1.31 (s, 18H); ^{13}C NMR (100.63 MHz, C_6D_6), δ 162.0, 140.9, 139.0, 125.5 (*C*H), 124.8 (*C*H), 123.1 (*C*), 79.8 (*C*H), 36.9 (*C*H_2), 36.4 (*C*), 35.0 (*C*), 33.0 (*C*H_2), 32.6 (*C*H_3), 31.5 (*C*H_3) 26.8 (*C*H_3). Anal. Calcd. for $C_{38}H_{62}O_4S_2Ti$: C, 65.56; H, 8.99. Found: C, 65.11; H, 9.47.

Synthesis of the complex [OSSO]Zr(Ot-Bu)$_2$

The ligand precursor [OSSO]H_2 (47 mg, 0.09 mmol) was dissolved in *ca*. 2 mL of ether and added dropwise to a bright solution of Zr(Ot-Bu)$_4$ (34 mg, 0.09 mmol) in ether. The solution was stirred at RT for 2 h. The solvent was removed under vacuum, and the resulting colorless oil was dissolved in pentane (*ca*. 2 mL). Removal of the pentane under vacuum gave a white solid in a yield of 97% (66 mg). ^{1}H NMR (400 MHz, C_6D_6), δ 7.55 (d, *J* = 2.5 Hz, 2H), 6.70 (d, *J* = 2.5 Hz, 2H), 4.05 (d, *J* = 13.6 Hz, 2H, AB system), 3.26 (d, *J* = 13.6 Hz, 2H, AB system), 1.97 (dd, *J* = 12.5 Hz, *J* = 3.7 Hz, 2H), 1.84 - 1.82 (m + s, 20H), 1.50 (s, 18H), 1.32 (s, 18H); ^{13}C NMR (100.63 MHz, C_6D_6), δ 160.0, 140.1, 139.1, 121.8 (8C, *C*), 126.0, 125.1 (4C, *C*H), 36.9 (2C, *C*H_2), 36.42 (2C, *C*), 34.92 (2C, *C*), 33.8 (6C, *C*H_3), 32.6 (6C, *C*H_3), 31.9 (2C, *C*) 31.7 (2C, *C*H_2), 31.47 (6C, *C*H_3). Anal. Calcd. for $C_{40}H_{66}O_4S_2Zr$: C, 62.69; H, 8.68. Found: C, 63.27; H, 9.15.

Crystal data for complex [OSSO]Zr(Ot-Bu)$_2$: $C_{40}H_{66}O_4S_2Zr$; M = 766.31; monoclinic; space group $P2_1/n$; a = 13.0210(2) Å, b = 17.7530(2) Å, c = 19.5070(4) Å, β = 93.0590(5)°, V = 4502.85(13) Å^3; T = 110(2) K; Z = 4; D_c = 1.183 g cm^{-3}; μ (Mo Kα) = 0.373 mm^{-1}; R_1 = 0.0495 and wR_2 = 0.1263 for 7745 reflections with $I > 2\sigma(I)$; R_1 = 0.0792 and wR_2 = 0.1443 for all 10709 unique reflections.

Synthesis of the complex [OSSO]ZrBn$_2$:

The ligand precursor [OSSO]H$_2$ (66 mg, 0.12 mmol) was dissolved in *ca*. 2 mL of toluene and added dropwise to a solution of ZrBn$_4$ (58 mg, 0.12 mmol) in toluene. The solution was stirred at RT for 2 h. The solvent was removed under vacuum and pentane (*ca*. 2 mL) was added. Removal of the pentane under vacuum gave 89 mg of product as a yellow solid (90%). ^{1}H NMR (400 MHz, C_6D_6), δ 7.44 (d, J = 2.4 Hz, 2H), 7.22 (d, J = 7.3 Hz, 4H), 7.13 (t, J = 7.4 Hz, 4H), 6.95 (t, J = 7.2 Hz, 2H), 6.49 (d, J = 2.3 Hz, 2H), 3.02 (d, J = 14.5 Hz, 2H, AB system), 2.84 (d, J = 14.5 Hz, 2H, AB system), 2.60 (d, J = 9.3 Hz, 2H, AB system), 2.10 (d, J = 9.0 Hz, 2H, AB system), 1.85 (d, J = 9.3 Hz, 2H, AB system), 1.74 (s + m, 20H), 1.23 (s, 18H); ^{13}C NMR (100.63 MHz, C_6D_6), δ 158.2, 145.1, 140.9, 137.8, 129.8, 128.0, 124.8 (*C*H), 124.0, 123.7, 123.2 (*C*H), 59.5 (*C*H$_2$), 36.3, 35.8, 35.4, 34.0 (*C*H$_2$), 31.5, 30.7 (*C*H$_3$).

Polymerization of neat 1-hexene procedure.

B(C$_6$F$_5$)$_3$ (8 mg, 0.16 mmol) was dissolved in *ca.* 1 mL of 1-hexene and added to a stirred solution of complex [OSSO]ZrBn$_2$ (10 mg, 0.12 mmol) in 4 mL of 1-hexene. The reaction mixture was stirred at room temperature until the resulting polymer had become viscous. The remaining olefin was evaporated under vacuum yielding 3.14 g poly(1-hexene) as a yellow-white sticky oil 93%. ^{13}C NMR of the polymer revealed that it was stereoirregular. ^{13}C NMR (100.63 MHz, CDCl$_3$) δ 40.4 (br, *C*H$_2$), 34.4 (br, *C*H$_2$), 32.4 (*C*H), 29.8 (br, *C*H$_2$), 23.4 (*C*H$_2$), 14.3 (*C*H$_3$).

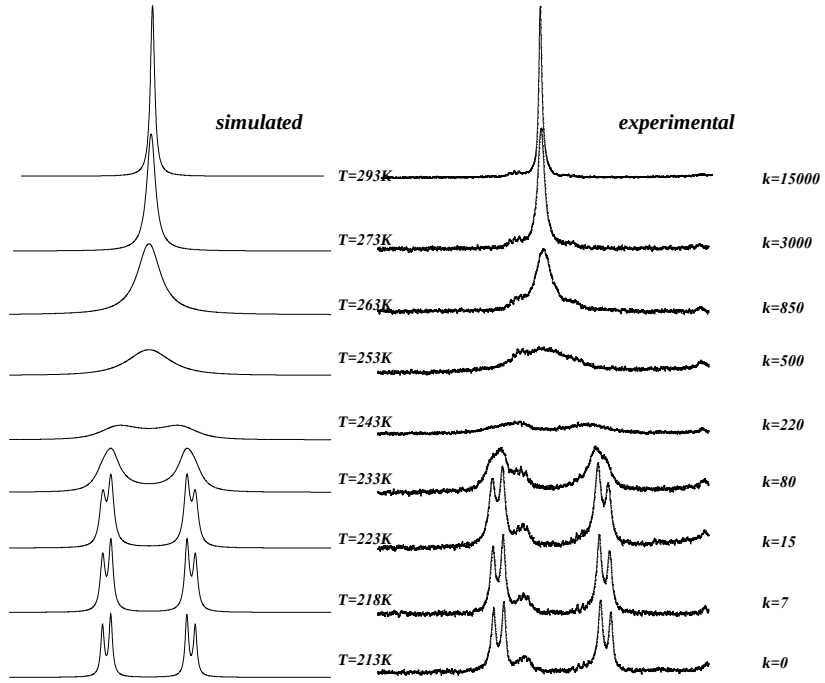

Figure 1: Experimental (right) and simulated (left) variable-temperature ^{1}H NMR spectra of [OSSO]Ti(Oi-Pr)$_2$ in toluene-d_8, 400MHz. Showing the SCH$_2$Ar (δ 3.2 and δ 3.9) resonances.

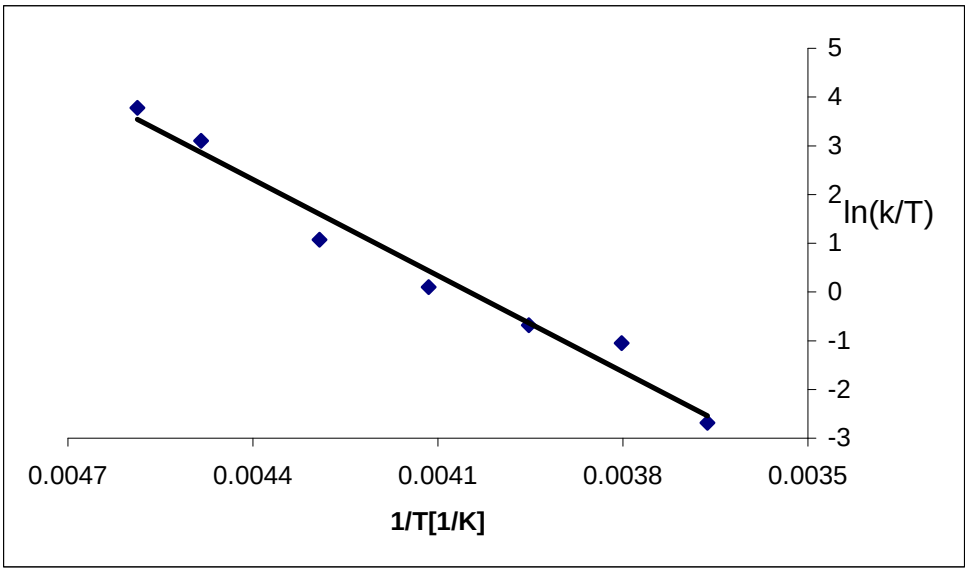

Figure 2: Eyring plot for [OSSO]Ti(Oi-Pr)$_2$ in toluene-d_8, 400MHz. (R^2=0.973)

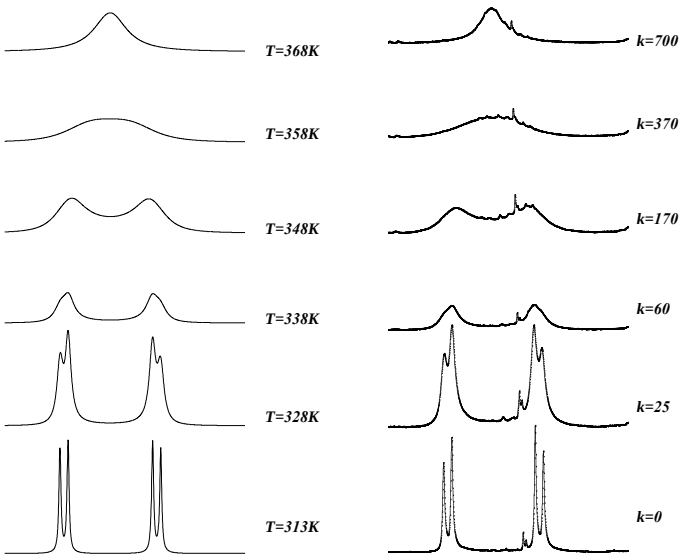

Figure 3: Experimental (right) and simulated (left) variable-temperature ^{1}H NMR spectra of [OSSO]Zr(Ot-Bu)$_2$ in toluene-d_8, 400MHz. Showing the SCH_2Ar (δ 3.4 and δ 4.2) resonances.

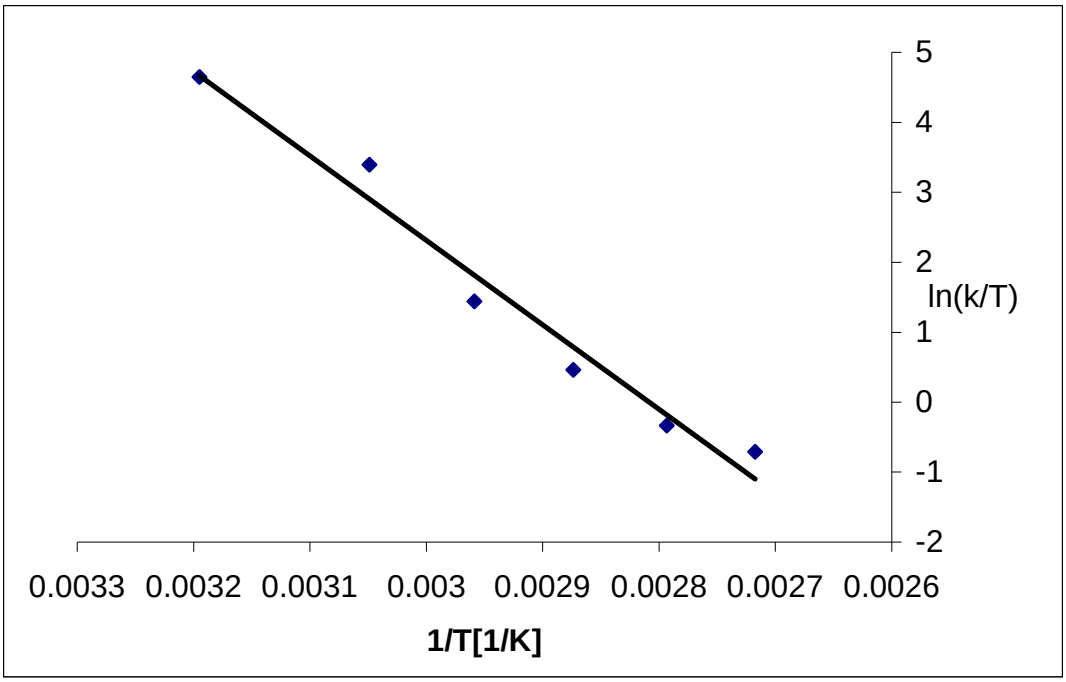

Figure 4: Eyring plot for [OSSO]Zr(Ot-Bu)$_2$ in toluene-d_8, 400MHz. (R^2=0.971).

References

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