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Supporting Information

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Formation of Zirconocene Fluoro Complexes - No Deactivation in Polymerization of Olefins by Contact Ion Pair Catalysts $[Cp'_2ZrR]^+[RB(C_6F_5)_3]^-$ (R = Me, H)

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Experimental Section

General:

All experiments were conducted under exclusion of oxygen and moisture. Solvents were freshly distilled from sodium tetraethylaluminate prior to use. Deuterated solvents (toluene-d_8, benzene-d_6)) were treated with sodium tetraethylaluminate, distilled and stored under argon. The following spectrometers were used: Mass spectra: AMD 402 – NMR spectra: Bruker AV 300 and AV 400. Chemical shifts ^1H, ^{13}C: relative to $SiMe_4$, referenced to signals of the solvent (toluene-d_8, δ_H = 2.03, δ_C = 20.4; benzene-d_6, δ_H = 7.16, δ_C = 128.0; the spectra were assigned with the help of DEPT and shift correlation experiments); ^{19}F: relative to $CFCl_3$; ^{11}B: relative to $X(^{11}B)$ = 32.083971 MHz, $BF_3{\cdot}OEt_2$ in $CDCl_3$. Melting points: sealed capillaries, Büchi 535 apparatus. – Elemental analyses: Leco CHNS-932 elemental analyzer.

*X-ray Crystallographic Study of Complexes **3**, **4** and **5**:*

STOE-IPDS diffractometer using graphite-monochromated Mo-Kα radiation, λ = 0.71069 Å, structures were solved by direct methods [SHELXS-97: G. M. Sheldrick, University of Göttingen, Germany, **1997**.] and refined by full-matrix least-squares techniques against F^2 [SHELXL-97: G. M. Sheldrick, University of Göttingen, Germany, **1997**.], structural representations: XP (BRUKER AXS).

Complex **3**: 0.2 × 0.2 × 0.1 mm, orange prisms, space group $P2_1/n$, monoclinic, a = 10.946(2), b = 20.243(4), c = 22.602(5) Å, β = 100.86(3)°, V = 4918.5(17) $Å^3$, Z = 4, ρ_{calcd} = 1.656 g · cm^{-3}, 17564 reflections measured, 5159 were independent of symmetry, of which 3562 were observed ($I > 2\sigma(I)$), R1 = 0.057, wR^2 (all data) = 0.141, 696 parameters. Terminal hydride atoms have not been located.

Complex **4**: 0.4 × 0.3 × 0.2 mm, yellow prisms, space group $P2_12_12_1$, orthorhombic, a = 11.562(2), b = 12.493(2), c = 22.206(4) Å, V = 3207.5(10) $Å^3$, Z = 4, ρ_{calcd} = 1.759 g · cm^{-3}, 17145 reflections measured, 5104 were independent of symmetry, of which 3749 were observed (I > 2σ(I)), R1 = 0.034, wR^2 (all data) = 0.061, 487 parameters.

Complex **5**: 0.3 × 0.2 × 0.1 mm, colorless prisms, space group *P*-3, hexagonal, a = 23.082(3), c = 12.474(3) Å, V = 5755.5(16) $Å^3$, Z = 6, ρ_{calcd} = 1.537 g · cm^{-3}, 16976 reflections measured, 5992 were independent of symmetry, of which 2908 were observed (I > 2σ(I)), R1 = 0.053, wR^2 (all data) = 0.153, 507 parameters.

CCDC 295535 (**3**), CCDC 295534 (**4**), CCDC 295536 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/depositing.html.

*NMR observation of **1***:

Complex **2** [8a] (80 mg, 0.11 mmol) and $B(C_6F_5)_3$ (57 mg, 0.11 mmol) were mixed in a NMR tube, solved in toluene-d_8 and heated (90°C) for 14 days. Complex **1** was identified as the main product by ^{1}H NMR ((toluene-d_8): δ = 5.33, 5.89 (2 d, 2 x 2 H, CH- ebthi) and ^{19}F NMR (toluene-d_8): δ = 22.9 (s, Zr-F), according to the data published in ref. 6b and 6c.

*Preparation of **3**, **4** and **5*** :

Preparative: Complex **2** [6b] (280 mg, 0.39 mmol) was dissolved in 10 mL of toluene and slowly added to a solution of $B(C_6F_5)_3$ (201 mg, 0.39 mmol) in 15 mL of toluene at r.t. Immediately orange red crystals of **3** were formed, which were directly collected by filtration and washed with *n*-pentane to give complex **3**. Yield: 442 mg (92 %).

Alternatively, a mixture of **2** (420 mg, 0.58 mmol, 10 mL of toluene) and $B(C_6F_5)_3$ (601 mg, 1.17 mmol, 15 mL of toluene) was stirred for 5 h at 60 °C until **3** disappered and the colour of the solution changed to light yellow. After evaporation to dryness, the oily residue was washed once with 3 mL of *n*-pentane and extracted 3 times with a 3 to 1 mixture of *n*-hexane and toluene (60 °C). Upon cooling to - 30°C for 72 h the collected extracts had formed yellow crystals of **4**. Yield 330 mg (33 %). Mp.: 162-165 °C (dec.). Anal. calcd. for $C_{38}H_{25}BF_{14}Zr$ (848): C, 53.72; H, 2.97. Found: C, 53.22; H, 2.79. ^{1}H NMR (benzene-d_6): δ = 1.27 (1 H, μ-H); CH_2-ebthi not analyzed; 4.11, 5.22, 5.44 (3 d, *J* = 3 Hz, 1 H each, CH-ebthi); 6.19 (dt, $J_{H,F}$ = 2.0 Hz, $J_{H,H}$ = 3 Hz, 1 H, CH-ebthi). - $^{13}C\{^1H\}$ NMR (benzene-d_6): δ = 21.3, 22.1, 22.9, 22.9, 23.6, 23.7, 24.8, 25.2, 28.7, 29.9 (all CH_2); 112.6, 114.2, 116.8, 116.8 (all CH); C_{quart} were not detected. ^{19}F NMR (toluene-d_8): δ = -118.5 (dd, 1 F, F_{11}), -122.15 (quint, 1 F, F_{14}), -130.7 (br,

2 F, F_1, F_5); -132.1 (br, 2 F, F_6, F_{10}); -155.0 (tr, 1 F, F_3); -156.3 (tr, 1 F, F_8), -156.8 (tr, 1 F, F_{13}); -157.1 (dd, 1 F, F_{12}); -163.4 (br, 4 F, F_2, F_4, F_7, F_9,); - ^{11}B NMR (toluene-d_6): δ = -12.8. - MS (70eV, m/z): 846 $[M]^+$, 864 $[C_{38}H_{24}BF_{15}Zr]^+$ (**5**), 372 $[C_{20}H_{24}ZrF]$. Crystals for X-ray structure analysis: solution of toluene.

The mother liquid was reduced in vacuum to give at -32 °C pure colourless crystals of **5**. Yield 98 mg (10 %). Mp.: 162-165 °C (dec.). Anal. Calcd. for $C_{38}H_{24}BF_{15}Zr$ (867.61): C, 52.61; H, 2.79. Found: C, 51.95; H, 2.61. ^{1}H NMR (toluene-d_8): δ = CH_2-ebthi not analyzed; 4.85 (br, 1 H, CH-ebthi), 5.08, 6.44 (2 d, J = 3 Hz, 1 H each, CH-ebthi). - $^{13}C\{^1H\}$ NMR (toluene-d_8): δ = 21.7, 21.8, 23.6, 23.8, 23.6, 25.0, 25.5, 26.3, 28.0, 29.6 (all CH_2); 112.6, 115.9, 118.0, (all CH); C_{quart} were not detected. - MS (70eV) m/z (%): 866 $[M]^+$. Crystals for X-ray structur analysis: solution of *n*-pentane.