Supplementary Data For:

Stabilizing Zr and Ti Cations by Interaction With a Ferrocenyl Fragment

Alberto Ramos, Edwin Otten and Douglas W. Stephan

All preparations were done under an atmosphere of dry, O₂-free N₂ employing both Schlenk line techniques and M. Braun or Vacuum Atmospheres inert atmosphere glove boxes. Solvents were purified employing a Grubbs’ type column system manufactured by Innovative Technology. ¹H, ¹³C, ³¹P, ¹¹B and ¹⁹F NMR spectroscopy spectra were recorded on Varian 200, 300, 400 MHz and Bruker 400 MHz spectrometers. ¹H and ¹³C NMR spectra are referenced to SiMe₄ using the residual solvent peak impurity of the given solvent. ³¹P, ¹¹B and ¹⁹F NMR spectra were referenced to 85% H₃PO₄, Et₂O·BF₃, and CFCl₃ respectively. Chemical shifts are reported in ppm and coupling constants in Hz. CD₂Cl₂ and BrC₆D₅ were used as the NMR solvents after being dried over CaH₂, vacuum-transferred into Young bombs and freeze-pump-thaw degassed (three cycles). Combustion analyses were performed in house employing a Perkin Elmer 2400 Series II CHNS Analyzer. UV/visible spectra were obtained using a Perkin-Elmer Lambda 900 UV/vis/near-IR spectrophotometer.

Synthesis of [Cp₂ZrMe][MeB(C₆F₅)₃] (I)

This compound was synthesized according to a literature procedure,¹ which was slightly modified. In the glovebox, a vial charged with benzene (10 mL) and a stir bar was placed in the freezer at -35 °C for 2 h. After that time weighed amounts of [Cp₂ZrMe₂] (0.150 g, 0.596 mmol) and B(C₆F₅)₃ (0.307 g, 0.600 mmol) were added in the vial over the frozen benzene. The mixture was left to reach room temperature and was stirred for 2 h. Then, 8 mL of pentane were added and a yellow solid immediately precipitated. Solvents were decanted and the yellow solid was washed with more pentane (2 x 5 mL). After drying under vacuum for 4 h compound 1 was obtained (purity checked by NMR). Yield 0.374 g (82%). ¹H NMR (BrC₆D₅, 400.33 MHz): δ 5.85 (s, Cp, 10H), 0.43 (s, Zr-Me, 3H), 0.25 (s, br, B-Me, 3H) ppm. ¹⁹F{¹H} NMR (BrC₆D₅, 376.64 MHz): δ -133.0 (d, o-F, J = 22 , 6F), -158.7 (s, br, p-F, 3F), -163.5 (m, br, m-F, 6F) ppm. ¹¹B NMR (BrC₆D₅, 128.44 MHz): δ -13.8 (s) ppm.

Synthesis of $\text{[Cp}_2\text{Zr(C}_5\text{H}_4\text{)Fe(C}_5\text{H}_5\text{)] [MeB(C}_6\text{F}_5\text{)]_3}$ (2a)

Ferrocene (0.058 g, 0.314 mmol) was added to a solution of 1 (0.240 g, 0.314 mmol) in 5 mL of BrC$_6$H$_5$. The solution was stirred for 15 h. After this time, pentane was added and the mixture was cooled down to -35 ºC to help precipitate the product. Then, solvents were decanted and the orange solid thus obtained was washed with toluene (2 x 5 mL) and dried under vacuum for 6 h. Yield 0.272 g (93%). Dark orange crystals of 2a were obtained by slow diffusion of a concentrated solution of the compound in BrC$_6$H$_5$ into a layer of hexane at room temperature. Anal. Calcd. for C$_{39}$H$_{22}$BF$_{15}$FeZr: C, 50.18; H, 2.38. Found: C, 49.99; H, 2.11 %. UV-vis: $\lambda_{\text{max}}$ (BrC$_6$H$_5$) = 476 nm ($\varepsilon$ = 615).

$^1$H NMR (BrC$_6$D$_5$, 400.33 MHz, 298 K): $\delta$ 5.92 (s, Zr-Cp, 10H), 4.28, 4.20 (2 x m, C$_5$H$_4$, 2 x 2H), 2.44 (s, Fe-Cp, 5H), 1.10 (s, B-Me, 3H) ppm. $^1$H NMR (BrC$_6$D$_5$, 400.33 MHz, 239 K): $\delta$ 5.85 (s, Zr-Cp, 10H), 4.22, 4.12 (2 x m, C$_5$H$_4$, 2 x 2H), 2.35 (br, $\Delta\nu_{\text{v}_{1/2}}$ = 22 Hz, Fe-Cp, 5H), 1.22 (s, B-Me, 3H) ppm. $^1$H NMR (CD$_2$Cl$_2$, 400.33 MHz, 283 K): $\delta$ 6.57 (s, Zr-Cp, 10H), 4.85, 4.84 (2 x m, C$_5$H$_4$, 2 x 2H), 3.09 (s, Fe-Cp, 5H), 0.46 (s, B-Me, 3H) ppm. $^1$H NMR (CD$_2$Cl$_2$, 400.33 MHz, 298 K): $\delta$ 6.52 (s, Zr-Cp, 10H), 4.79, 4.78 (2 x m, C$_5$H$_4$, 2 x 2H), 3.20 (br, $\Delta\nu_{\text{v}_{1/2}}$ = 600 Hz, Fe-Cp, 5H), 0.33 (s, B-Me, 3H) ppm. $^{19}$F NMR (BrC$_6$D$_5$, 376.64 MHz): $\delta$ -131.5 (d, J = 21, o-F, 6F), -163.2 (t, J = 21, p-F, 3F), -165.8 (m, m-F, 6F) ppm. $^{11}$B NMR (BrC$_6$D$_5$, 128.44 MHz): $\delta$ -14.4 (s) ppm. $^{13}$C{$_1$H} NMR (BrC$_6$D$_5$, 100.46 MHz): $\delta$ 171.0 (s, C$_1$-C$_5$H$_4$), 148.6 (dm, J$_{CF}$ ~ 237, o-C$_5$F$_3$), 137.6 (dm, J$_{CF}$ ~ 244, p-C$_5$F$_3$), 136.5 (dm, J$_{CF}$ ~ 247, m-C$_5$F$_3$), 111.2 (s, Zr-Cp), 85.5 (s, C$_{2/3}$-C$_5$H$_4$), 80.4 (s, Fe-Cp), 74.7 (s, C$_{3/2}$-C$_5$H$_4$), 11.2 (br, B-CH$_3$) ppm.

X-ray Structure of Cation of 2a

Ethylene polymerization protocol

A typical procedure for ethylene polymerization: dry toluene (50 mL) was charged into a 250 mL Schlenk flask in the glovebox. The flask was connected to a Schlenk line and it was placed under ethylene (1 atm) by evacuating it for 5 seconds and refilling it with dry ethylene gas (x 5). Then, $i$-Bu$_3$Al (5 % w. in toluene) was added (0.2 mL, 50 $\mu$mol approx.), and the solution placed in a thermostated water bath at 25 ºC and stirred at 750 rpm for 5 minutes. After that time, a solution containing the catalyst was injected
(1 mL, 2.5 µmol). This was taken to be time zero. The mixture was stirred for 10 min at the same temperature and stir rate, after which time was quenched with an HCl solution in MeOH (1 M), and poured into a beaker containing more of the latter solution (100 mL approx.). The resultant polymer was filtered, washed with MeOH and toluene and dried in vacuo for, at least, 15 h.

Table S1. Ethylene polymerization results

<table>
<thead>
<tr>
<th>Pre-Catalyst</th>
<th>Activity (Trial 1) (g mmol⁻¹ hr⁻¹ atm⁻¹)</th>
<th>Activity (Trial 2) (g mmol⁻¹ hr⁻¹ atm⁻¹)</th>
<th>Average Activity (g mmol⁻¹ hr⁻¹ atm⁻¹)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp₂ZrMe][MeB(C₆F₅)₃] (1)</td>
<td>2802</td>
<td>2850</td>
<td>2826</td>
<td>2</td>
</tr>
<tr>
<td>[Cp₂Zr(C₅H₄)Fe(C₅H₅)] [MeB(C₆F₅)₃] (2a)</td>
<td>2826</td>
<td>3138</td>
<td>2982</td>
<td>11</td>
</tr>
</tbody>
</table>

Synthesis of [Cp₂Zr(C₅H₃Me)Fe(C₅H₄Me)][MeB(C₆F₅)₃] (2b)

Solid 1 (25 mg, 97.7 µmol) was added to a solution of 1,1'-dimethylferrocene (23 mg, 107 µmol) and B(C₆F₅)₃ (50 mg, 97.7 µmol) in 2 mL of BrC₆H₅ at -30 °C. The solution turned dark orange and was stirred for 1 h. After this time, pentane was added to precipitate the product as a dark orange oil. The supernatant was decanted and the oil triturated with pentane to give an orange powder, which was washed with pentane (2 x 2 mL) and dried under vacuum for 6 h. Yield 84 g (89%). Dark orange crystals of 2b were obtained by slow diffusion of a concentrated solution of the compound in BrC₆H₅ into a layer of cyclohexane at room temperature. Despite repeated attempts, a satisfactory elemental analysis could not be obtained.

1H NMR (BrC₆D₅, 400.33 MHz, 298 K): δ 5.92 (s, Zr-Cp, 10H), 4.26 (s, 1H, C₅H₃Me), 4.16 (s, 1H, C₅H₄Me), 3.94 (s, 1H, C₅H₃Me), 3.92 (s, 1H, C₅H₄Me), 3.78 (s, 1H, C₅H₃Me), 1.61 (s, 6H, C₅H₃Me and C₅H₄Me), 1.07 (s, 3H, BMe), 0.86 (s, 1H, C₅H₄Me), -1.29 (s, 1H, C₅H₄Me).

19F NMR (BrC₆D₅, 376.64 MHz): δ -131.6 (d, J = 21, o-F, 6F), -163.3 (t, J = 21, p-F, 3F), -165.9 (m, m-F, 6F) ppm.

11B NMR (BrC₆D₅, 128.44 MHz): δ -1.44 (s) ppm.

13C NMR (BrC₆D₅, 100.46 MHz): δ 171.9 (s, C₅H₃Me ZrC), 148.8 (dm, JCF ~ 237, o-C₆F₅), 137.7 (dm, JCF ~ 244, p-C₆F₅), 136.8 (dm, JCF ~ 247, m-C₆F₅), 111.2 (d, J = 175, Zr-Cp), 93.5 (s, C₅H₃Me MeC), 92.6 (s, C₅H₄Me MeC), 87.4 (d, J = 167, C₅H₄Me CH), 85.7 (d, J = 174, C₅H₃Me CH), 85.4 (d, J = 171, C₅H₄Me CH), 85.0 (d, J = 179, C₅H₃Me CH), 81.3 (d, J = 175, C₅H₄Me CH), 79.6 (d, J = 172, C₅H₃Me CH), 78.2 (d, J = 179, C₅H₃Me CH), 12.8 (q, J = 128, C₅H₃Me), 12.7 (q, J = 128, C₅H₄Me), 11.3 (br, BMe).
X-ray Structure of Cation of 2b
**Synthesis of [Cp₂Zr(C₅H₄)Fe(C₅H₅)(THF)][MeB(C₆F₅)₃] (3)**

THF (3 μL, 0.037 mmol) was added to an orange solution of 2a (0.031 g, 0.033 mmol) in 0.7 mL of BrC₆D₅ giving rise to a deep blue solution containing the adduct 3 as a major product (ca. 90% by NMR). Attempts to isolate 3 as a solid led to deep blue oils containing bigger amounts of unidentified side products. Therefore, compound 3 was only characterized by NMR. UV-vis: λ<sub>max</sub> (BrC₆H₅) = 624 nm (ε = 1240).<sup>1</sup>H NMR (BrC₆D₅, 400.33 MHz): δ 6.14 (s, Zr-Cp, 10H), 4.31 (2 x m, C₅H₅, 2 x 2H), 3.87 (s, Fe-Cp, 5H), 3.14 (br, Δν<sub>β</sub> = 145 Hz, O-CH₂, 4H), 1.36 (br, Δν<sub>β</sub> = 40 Hz, CH₂, 4H), 1.09 (s, B-Me, 3H) ppm.<sup>19</sup>F NMR (BrC₆D₅, 376.64 MHz): δ -131.7 (d, J = 20, o-F, 6F), -163.5 (t, J = 21, p-F, 3F), -166.1 (m, m-F, 6F) ppm.<sup>31</sup>P{<sup>1</sup>H} NMR (BrC₆D₅, 100.46 MHz): δ 6.14 (s, Zr-Cp, 10H), 4.31 (2 x m, C₅H₅, 2 x 2H), 3.82 (s, Fe-Cp, 5H), 1.13 (s, B-Me, 3H), 0.77 (d, J<sub>PH</sub> = 8, P-Me, 9H) ppm.<sup>31</sup>P{<sup>1</sup>H} NMR (BrC₆D₅, 128.44 MHz): δ -7.8 (s, P) ppm.

**Synthesis of [Cp₂Zr(C₅H₄)Fe(C₅H₅)(PMe₃)][MeB(C₆F₅)₃] (4)**

PMe₃ (4 μL, 0.038 mmol) was added to an orange solution of 2a (0.031 g, 0.033 mmol) in 3 mL of BrC₆H₅ giving rise to a purple solution of compound 4. After adding hexane, the product crystallized at room temperature giving rise to purple crystals suitable for an X-ray analysis. Yield 0.031 g (91%).<sup>19</sup>F NMR (BrC₆H₅, 376.64 MHz): δ 5.78 (d, J<sub>CF</sub> = 40 Hz, CH₂, 3H), 3.82 (s, Fe-Cp, 5H), 1.13 (s, B-Me, 3H), 0.77 (d, J<sub>PH</sub> = 8, P-Me, 9H) ppm.

**X-ray Structure of Cation of 4**
Synthesis of [TiCpFc(NP-tBu3)][MeB(C₆F₅)₃] (6)

A solution of [TiCpMe₂(NP-t-Bu₃)] (0.072 g, 0.200 mmol) in 0.5 mL of BrC₆D₅ was added dropwise to a solution of B(C₆F₅)₃ (0.103 g, 0.201 mmol) in 0.5 mL of BrC₆D₅ at -35 °C. The mixture was stirred for 5 minutes to allow the formation of a yellow solution of [TiCpMe(NP-t-Bu₃)][MeB(C₆F₅)₃] 5. Then, ferrocene (0.037 g, 0.199 mmol) was added to this solution and the mixture was stirred for 15 h at room temperature. After this time there is no starting material left in solution, and the mixture contains ~90% of compound 6 by NMR analysis and 10% of uncharacterized impurities. The same mixture was isolated as oil after addition of hexane, storage at -35 °C for 4 h and decanting the mother liquor. The oil was converted into a solid upon washing several times with hexane and drying under vacuum. A small amount of dark red crystals was obtained by cooling a solution in bromobenzene/hexane (ca. 10:1) to -35 °C. ¹H NMR (C₆D₅Br, 399.74 MHz, 295 K): δ 6.19 (s, Ti-Cp, 5H), 4.80 (br, ∆ν½ = 31 Hz, C₅H₄, 2H), 4.31 (s, C₅H₄, 2H), 2.92 (s, Fe-Cp, 5H), 1.17 (d, J₆PH = 14, CH₃-tBu, 27H), 1.12 (s, B-Me, 3H) ppm. ³¹P{¹H} NMR (C₆D₅Br, 161.82 MHz): δ 54.4 (br, 1P) ppm. ¹⁹F NMR (C₆D₅Br, 376.13 MHz): δ -131.7 (d, J₆F = 21, o-C₆F₅, 6F), -163.9 (t, J₆F = 20, p-C₆F₅, 3F), -166.3 (br, m-C₆F₅, 6F) ppm. ¹¹B NMR (C₆D₅Br, 128.26 MHz): δ -14.1 (s, 1B) ppm. ¹³C{¹H} NMR (C₆D₅Br, 100.47 MHz): δ 177.0 (s, C⁴-C₅H₄), 148.7 (dm, J₆CF ~ 238, o-C₆F₅), 137.6 (dm, J₆CF ~ 242, p-C₆F₅), 136.5 (dm, J₆CF ~ 246, m-C₆F₅), 112.5 (s, Ti-Cp), 82.3 (s, C²/C₃-C₅H₄), 79.5 (s, Fe-Cp), 74.2 (s, C³/C₄-C₅H₄), 40.9 (d, J₆PC = 42, C(CH₃)₃), 28.2 (s, CH₃-tBu), 11.3 (br, B-CH₃) ppm.

X-ray Structure of Cation of 6
DFT calculations

Calculations were performed with the Gaussian03 program using density functional theory (DFT).\(^2\) The geometries of \(2a\), \(\text{Cp}_2\text{ZrMe}^+\) and \(\text{Cp}_2\text{ZrPh}^+\) were optimized (for \(2a\): starting from the X-ray structure) at the B3LYP/6-31G(d) level without (symmetry) constraints. NBO analysis for the optimized structures was performed as implemented in Gaussian03. Molecular orbital representations were generated using Molekel 4.3.\(^3\)

---


\(^3\) *MOLEKEL 4.3*, P. Flükinger, H.P. Lüthi, S. Portmann, J. Weber, Swiss National Supercomputing Centre CSCS, Manno (Switzerland), 2000.
Figure S3. $^1$H VT NMR of compound 2a in CD$_2$Cl$_2$. 
Figure S4. $^1$H NMR of compound 2b in C$_6$D$_5$Br.
Figure S5. $^1$H NMR of compound 6 in C$_6$D$_5$Br (crude).
Figure S6. $^1$H NMR of compound 6 in C$_6$D$_5$Br (crystals).