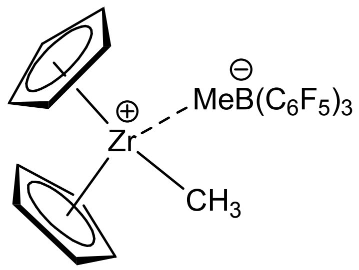
Supplementary Data For:

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, O_2-free N_2 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. ^{1}H, ^{13}C, ^{31}P, ^{11}B and ^{19}F NMR spectroscopy spectra were recorded on Varian 200, 300, 400 MHz and Bruker 400 MHz spectrometers. ^{1}H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR spectra were referenced to 85% H_3PO_4, $Et_2O{\cdot}BF_3$, and $CFCl_3$ respectively. Chemical shifts are reported in ppm and coupling constants in Hz. CD_2Cl_2 and BrC_6D_5 were used as the NMR solvents after being dried over CaH_2, 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.

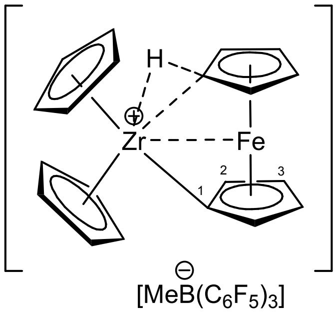
Synthesis of $[Cp_2ZrMe][MeB(C_6F_5)_3]$ (1)



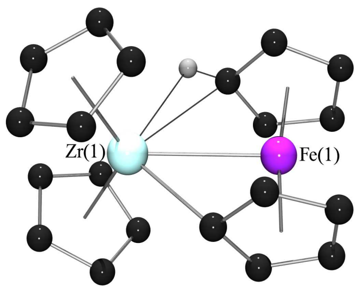
This compound was synthesized according to a literature procedure,[1] which was slightly modified. In the glovebox, a vial charged with benzene (10 mL) and a stir bar was placed in the freezer at -35 ºC for 2 h. After that time weighed amounts of $[Cp_2ZrMe_2]$ (0.150 g, 0.596 mmol) and $B(C_6F_5)_3$ (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%). **^{1}H NMR** (BrC_6D_5, 400.33 MHz): δ 5.85 (s, Cp, 10H), 0.43 (s, Zr-Me, 3H), 0.25 (s, br, B-Me, 3H) ppm. **^{19}F{^{1}H} NMR** (BrC_6D_5, 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. **^{11}B NMR** (BrC_6D_5, 128.44 MHz): δ -13.8 (s) ppm.

[1] Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.,* **1994**, *116*, 10015.

Synthesis of [$Cp_2Zr(C_5H_4)Fe(C_5H_5)$][$MeB(C_6F_5)_3$] (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_6H_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_6H_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: λ_{max} (BrC_6H_5) = 476 nm (ε = 615). **^{1}H NMR** (BrC_6D_5, 400.33 MHz, 298 K): δ 5.92 (s, Zr-Cp, 10H), 4.28, 4.20 (2 x m, C_5H_4, 2 x 2H), 2.44 (s, Fe-Cp, 5H), 1.10 (s, B-Me, 3H) ppm. **^{1}H NMR** (BrC_6D_5, 400.33 MHz, 239 K): δ 5.85 (s, Zr-Cp, 10H), 4.22, 4.12 (2 x m, C_5H_4, 2 x 2H), 2.35 (br, $\Delta\nu_{½}$ = 22 Hz, Fe-Cp, 5H), 1.22 (s, B-Me, 3H) ppm. **^{1}H NMR** (CD_2Cl_2, 400.33 MHz, 283 K): δ 6.57 (s, Zr-Cp, 10H), 4.85, 4.84 (2 x m, C_5H_4, 2 x 2H), 3.09 (s, Fe-Cp, 5H), 0.46 (s, B-Me, 3H) ppm. **^{1}H NMR** (CD_2Cl_2, 400.33 MHz, 238 K): δ 6.55 (s, Zr-Cp, 10H), 4.82, 4.81 (2 x m, C_5H_4, 2 x 2H), 3.05 (br, $\Delta\nu_{½}$ = 22 Hz, Fe-Cp, 5H), 0.40 (s, B-Me, 3H) ppm. **^{1}H NMR** (CD_2Cl_2, 400.33 MHz, 193 K): δ 6.52 (s, Zr-Cp, 10H), 4.79, 4.78 (2 x m, C_5H_4, 2 x 2H), 3.20 (br, $\Delta\nu_{½}$ = 600 Hz, Fe-Cp, 5H), 0.33 (s, B-Me, 3H) ppm. **^{19}F NMR** (BrC_6D_5, 376.64 MHz): δ -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_6D_5, 128.44 MHz): δ -14.4 (s) ppm. **^{13}C{^{1}H} NMR** (BrC_6D_5, 100.46 MHz): δ 171.0 (s, C^1-C_5H_4), 148.6 (dm, J_{CF} ~ 237, *o*-C_6F_5), 137.6 (dm, J_{CF} ~ 244, *p*-C_6F_5), 136.5 (dm, J_{CF} ~ 247, *m*-C_6F_5), 111.2 (s, Zr-Cp), 85.5 (s, $C^{2/3}$-C_5H_4), 80.4 (s, Fe-Cp), 74.7 (s, $C^{3/2}$-C_5H_4), 11.2 (br, B-CH_3) ppm.



X-ray Structure of Cation of 2a

Ethylene polymerization protocol

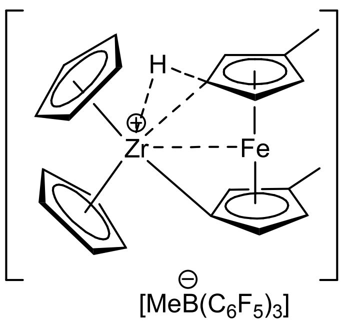
A typical procedure for ethylene polymerization: dry toluene (50 mL) was charged into a 250 mL Schlenk flask in the glovebox. The flask was connected to a Schlenk line were it was placed under ethylene (1 atm) by evacuating it for 5 seconds and refilling it with dry ethylene gas (x 5). Then, *i*-Bu_3Al (5 % w. in toluene) was added (0.2 mL, 50 μmol 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.

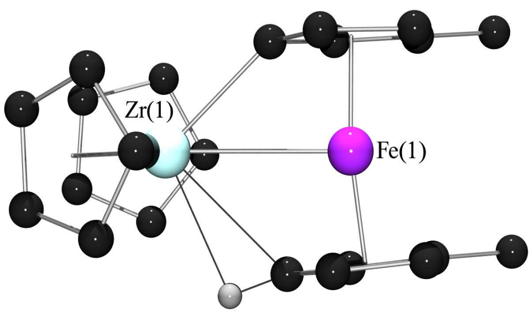
Table S1. Ethylene polymerization results

Pre-Catalyst	**Activity (Trial 1) (g mmol^{-1} hr^{-1} atm^{-1})**	**Activity (Trial 2) (g mmol^{-1} hr^{-1} atm^{-1})**	**Average Activity (g mmol^{-1} hr^{-1} atm^{-1})**	**% Difference**
$[Cp_2ZrMe][MeB(C_6F_5)_3]$ (**1**)	2802	2850	2826	2
$[Cp_2Zr(C_5H_4)Fe(C_5H_5)][MeB(C_6F_5)_3]$ (**2a**)	2826	3138	2982	11

Synthesis of $[Cp_2Zr(C_5H_3Me)Fe(C_5H_4Me)][MeB(C_6F_5)_3]$ (2b)

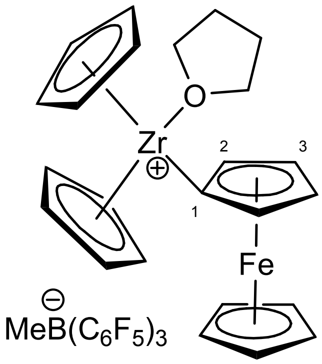


Solid **1** (25 mg, 97.7 µmol) was added to a solution of 1,1'-dimethylferrocene (23 mg, 107 µmol) and $B(C_6F_5)_3$ (50 mg, 97.7 µmol) in 2 mL of BrC_6H_5 at -30 °C. The solution turned dark orange and was stirred for 1 h. After this time, pentane was added to precipitate the product as a dark orange 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 BrC_6H_5 into a layer of cyclohexane at room temperature. Despite repeated attempts, a satisfactory elemental analysis could not be obtained. **^{1}H NMR** (BrC_6D_5, 400.33 MHz, 298 K): δ 5.92 (s, Zr-Cp, 10H), 4.26 (s, 1H, C_5H_3Me), 4.16 (s, 1H, C_5H_3Me), 3.94 (s, 1H, C_5H_4Me), 3.92 (s, 1H, C_5H_3Me), 3.78 (s, 1H, C_5H_4Me), 1.61 (s, 6H, C_5H_3*Me* and C_5H_4*Me*), 1.07 (s, 3H, BMe), 0.86 (s, 1H, C_5H_4Me), -1.29 (s, 1H, C_5H_4Me). **^{19}F NMR** (BrC_6D_5, 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. **^{11}B NMR** (BrC_6D_5, 128.44 MHz): δ -14.4 (s) ppm. **^{13}C NMR** (BrC_6D_5, 100.46 MHz): δ 171.9 (s, C_5H_3Me ZrC), 148.8 (dm, J_{CF} ~ 237, *o*-C_6F_5), 137.7 (dm, J_{CF} ~ 244, *p*-C_6F_5), 136.8 (dm, J_{CF} ~ 247, *m*-C_6F_5), 111.2 (d, *J* = 175, Zr-Cp), 93.5 (s, C_5H_3Me MeC), 92.6 (s, C_5H_4Me MeC), 87.4 (d, *J* = 167, C_5H_4Me CH), 85.7 (d, *J* = 174, C_5H_3Me CH), 85.4 (d, *J* = 171, C_5H_4Me CH), 85.0 (d, *J* = 179, C_5H_3Me CH), 81.3 (d, *J* = 175, C_5H_4Me CH), 79.6 (d, *J* = 172, C_5H_3Me CH), 78.2 (d, *J* = 179, C_5H_3Me CH), 12.8 (q, *J* = 128, C_5H_3*Me*), 12.7 (q, *J* = 128, C_5H_4*Me*), 11.3 (br, BMe).



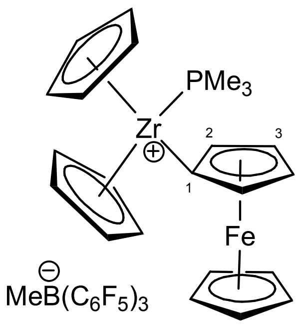
X-ray Structure of Cation of 2b

Synthesis of [$Cp_2Zr(C_5H_4)Fe(C_5H_5)(THF)$][$MeB(C_6F_5)_3$] (3)

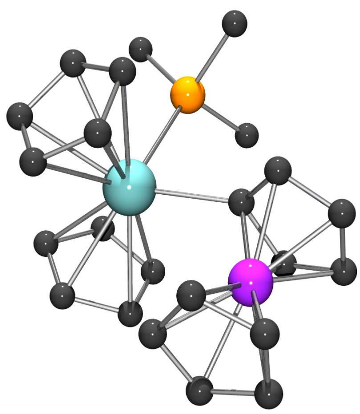


THF (3 μL, 0.037 mmol) was added to an orange solution of **2a** (0.031 g, 0.033 mmol) in 0.7 mL of BrC_6D_5 giving rise to a deep blue solution containing the adduct **3** as a major product (ca. 90% by NMR). Attempts to isolate **3** as a solid led to deep blue oils containing bigger amounts of unidentified side products. Therefore, compound **3** was only characterized by NMR. UV-vis: λ_{max} (BrC_6H_5) = 624 nm (ε = 1240). **^{1}H NMR** (BrC_6D_5, 400.33 MHz): δ 6.14 (s, Zr-Cp, 10H), 4.31 (2 x m, C_5H_4, 2 x 2H), 3.87 (s, Fe-Cp, 5H), 3.14 (br, $\Delta\nu_{½}$ = 145 Hz, O-CH_2, 4H), 1.36 (br, $\Delta\nu_{½}$ = 40 Hz, CH_2, 4H), 1.09 (s, B-Me, 3H) ppm. **^{19}F NMR** (BrC_6D_5, 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. **^{11}B NMR** (BrC_6D_5, 128.44 MHz): δ -14.4 (s) ppm. **^{13}C{^{1}H} NMR** (BrC_6D_5, 100.46 MHz): δ 148.5 (dm, J_{CF} ~ 237, *o*-C_6F_5), 137.6 (dm, J_{CF} ~ 244, *p*-C_6F_5), 136.5 (dm, J_{CF} ~ 246, *m*-C_6F_5), 123.9 (s, C^1-C_5H_4), 113.3 (s, Zr-Cp), 85.5 (s, $C^{2/3}$-C_5H_4), 80.4 (s, Fe-Cp), 74.7 (s, $C^{3/2}$-C_5H_4), 11.0 (br, B-CH_3) ppm.

Synthesis of [$Cp_2Zr(C_5H_4)Fe(C_5H_5)(PMe_3)$][$MeB(C_6F_5)_3$] (4)

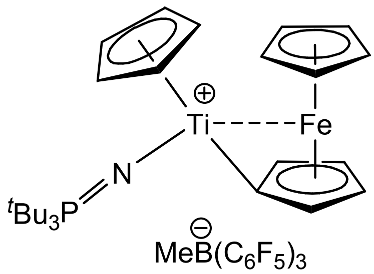


PMe_3 (4 μL, 0.038 mmol) was added to an orange solution of **2a** (0.031 g, 0.033 mmol) in 3 mL of BrC_6H_5 giving rise to a purple solution of compound **4**. After adding hexane, the product crystallized at room temperature giving rise to purple crystals suitable for an X-ray analysis. Yield 0.031 g (91%). **Anal. Calcd.** for $C_{42}H_{31}BF_{15}FePZr\cdot0.5(C_6H_5Br)$: C, 50.13; H, 3.34. Found: C, 49.93; H, 3.15 %. UV-vis: λ_{max} (BrC_6H_5) = 528 nm (ε = 1164). **^{1}H NMR** (BrC_6D_5, 400.33 MHz): δ 5.78 (d, J_{PH} = 1.5, Zr-Cp, 10H), 4.35, 3.49 (2 x m, C_5H_4, 2 x 2H), 3.82 (s, Fe-Cp, 5H), 1.13 (s, B-Me, 3H), 0.77 (d, J_{PH} = 8, P-Me, 9H) ppm. **^{31}P{^{1}H} NMR** (BrC_6D_5, 162.06 MHz): δ -7.8 (s, P) ppm. **^{19}F NMR** (BrC_6D_5, 376.64 MHz): δ -131.5 (d, J = 21, *o*-F, 6F), -163.4 (t, J = 21, *p*-F, 3F), -165.9 (m, *m*-F, 6F) ppm. **^{11}B NMR** (BrC_6D_5, 128.44 MHz): δ -14.3 (s) ppm. **^{13}C{^{1}H} NMR** (BrC_6D_5, 100.46 MHz): δ 148.7 (d, J_{PC} = 17, C^1-C_5H_4), 148.6 (dm, J_{CF} ~ 237, *o*-C_6F_5), 137.6 (dm, J_{CF} ~ 244, *p*-C_6F_5), 136.5 (dm, J_{CF} ~ 246, *m*-C_6F_5), 109.2 (s, Zr-Cp), 80.8 (s, $C^{2/3}$-C_5H_4), 74.8 (s, $C^{3/2}$-C_5H_4), 68.9 (s, Fe-Cp), 16.0 (d, J_{PC} = 25, P-Me), 11.0 (br, B-CH_3) ppm.

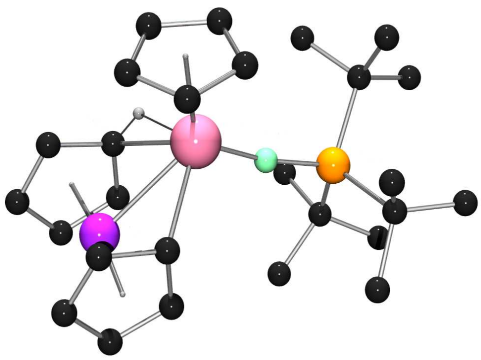


X-ray Structure of Cation of 4

Synthesis of [TiCpFc(NP*t*Bu$_3$)][MeB(C$_6$F$_5$)$_3$] (6)

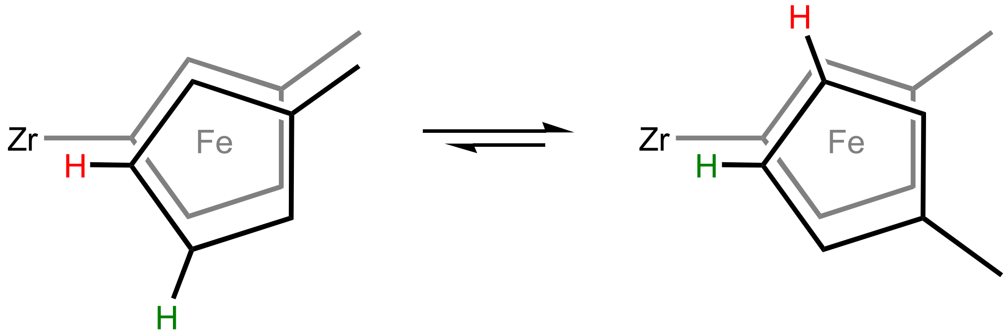


A solution of [TiCpMe$_2$(NP*t*-Bu$_3$)] (0.072 g, 0.200 mmol) in 0.5 mL of BrC$_6$D$_5$ was added dropwise to a solution of B(C$_6$F$_5$)$_3$ (0.103 g, 0.201 mmol) in 0.5 mL of BrC$_6$D$_5$ at -35 ºC. The mixture was stirred for 5 minutes to allow the formation of a yellow solution of [TiCpMe(NP*t*Bu$_3$)][MeB(C$_6$F$_5$)$_3$] **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 ºC 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 ºC. **^{1}H NMR** (C$_6$D$_5$Br, 399.74 MHz, 295 K): δ 6.19 (s, Ti-Cp, 5H), 4.80 (br, $\Delta\nu_{½}$ = 31 Hz, C$_5$H$_4$, 2H), 4.31 (s, C$_5$H$_4$, 2H), 2.92 (s, Fe-Cp, 5H), 1.17 (d, J_{PH} = 14, CH$_3$-*t*Bu, 27H), 1.12 (s, B-Me, 3H) ppm. **^{31}P{^{1}H} NMR** (C$_6$D$_5$Br, 161.82 MHz): δ 54.4 (br, 1P) ppm. **^{19}F NMR** (C$_6$D$_5$Br, 376.13 MHz): δ -131.7 (d, J_{FF} = 21, *o*-C$_6$F$_5$, 6F), -163.9 (t, J_{FF} = 20, *p*-C$_6$F$_5$, 3F), -166.3 (br, *m*-C$_6$F$_5$, 6F) ppm. **^{11}B NMR** (C$_6$D$_5$Br, 128.26 MHz): δ -14.1 (s, 1B) ppm. **^{13}C{^{1}H} NMR** (C$_6$D$_5$Br, 100.47 MHz): δ 177.0 (s, C^1-C$_5$H$_4$), 148.7 (dm, J_{CF} ~ 238, *o-C$_6$*F$_5$), 137.6 (dm, J_{CF} ~ 242, *p-C$_6$*F$_5$), 136.5 (dm, J_{CF} ~ 246, *m-C$_6$*F$_5$), 112.5 (s, Ti-Cp), 82.3 (s, C$^{2/3}$-C$_5$H$_4$), 79.5 (s, Fe-Cp), 74.2 (s, C$^{3/2}$-C$_5$H$_4$), 40.9 (d, J_{PC} = 42, *C*(CH$_3$)$_3$), 28.2 (s, CH$_3$-*t*Bu), 11.3 (br, B-CH$_3$) ppm.



X-ray Structure of Cation of 6

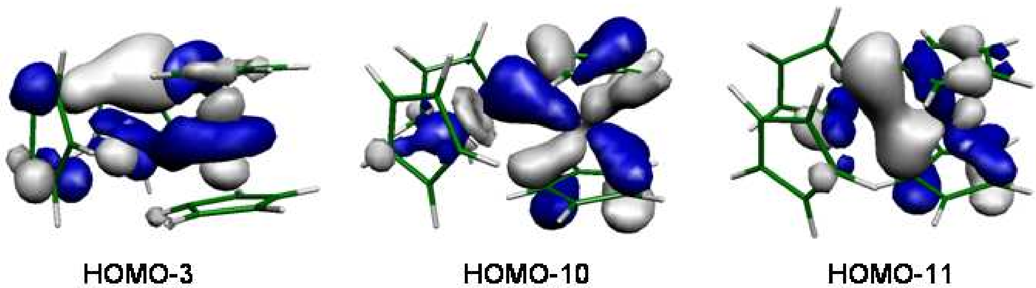
Figure S1



DFT calculations

Calculations were performed with the Gaussian03 program using density functional theory (DFT).[2] The geometries of **2a**, Cp_2ZrMe^+ and Cp_2ZrPh^+ 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]

Figure S2. Orbitals involved in Fe-Zr interaction (Cp_2Zr fragment left, $(C_5H_4)FeCp$ fragment right)



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[2] *Gaussian 03, Revision E.01*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

[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_2Cl_2.

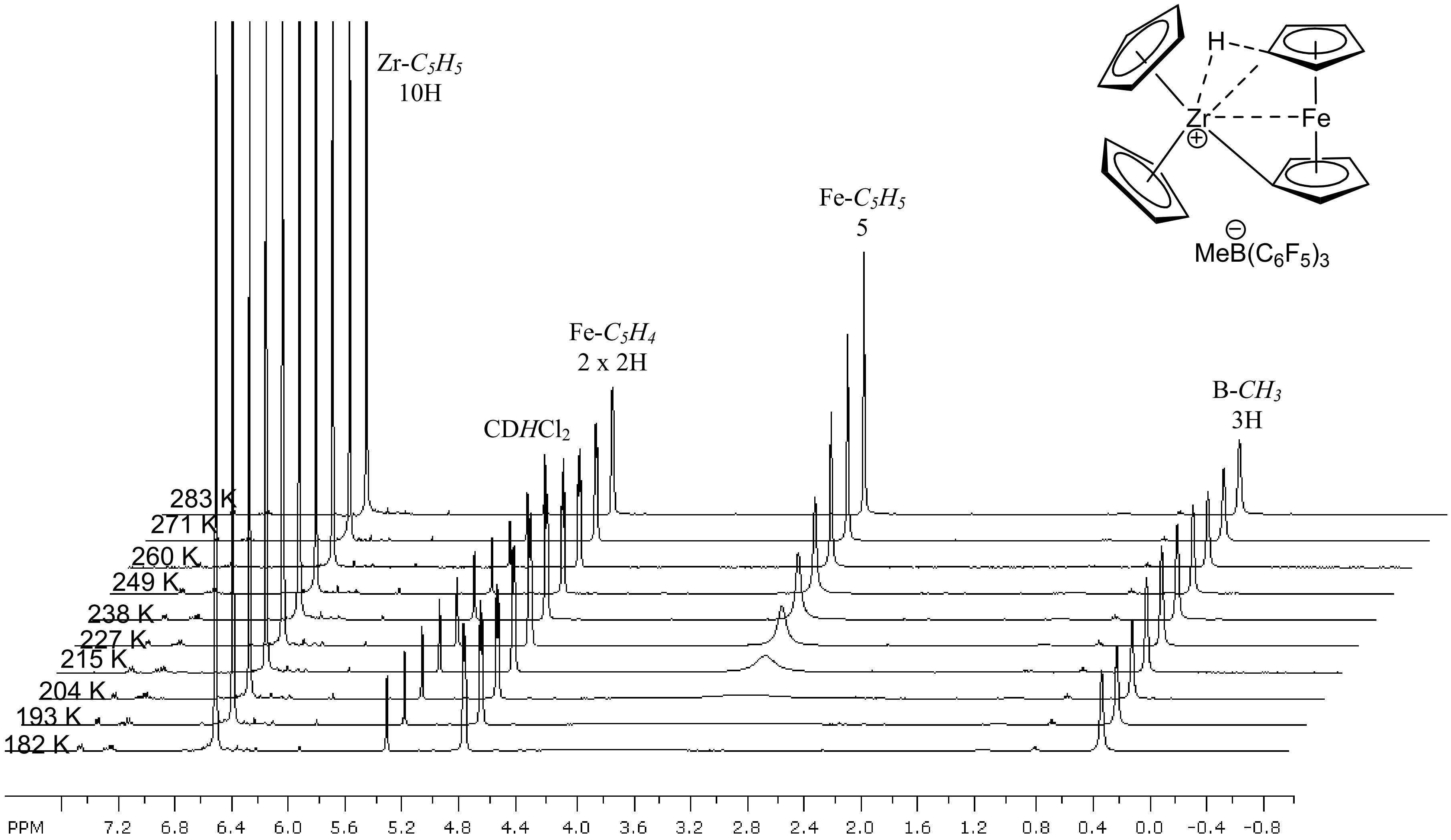

Figure S4. ^{1}H NMR of compound **2b** in C_6D_5Br.

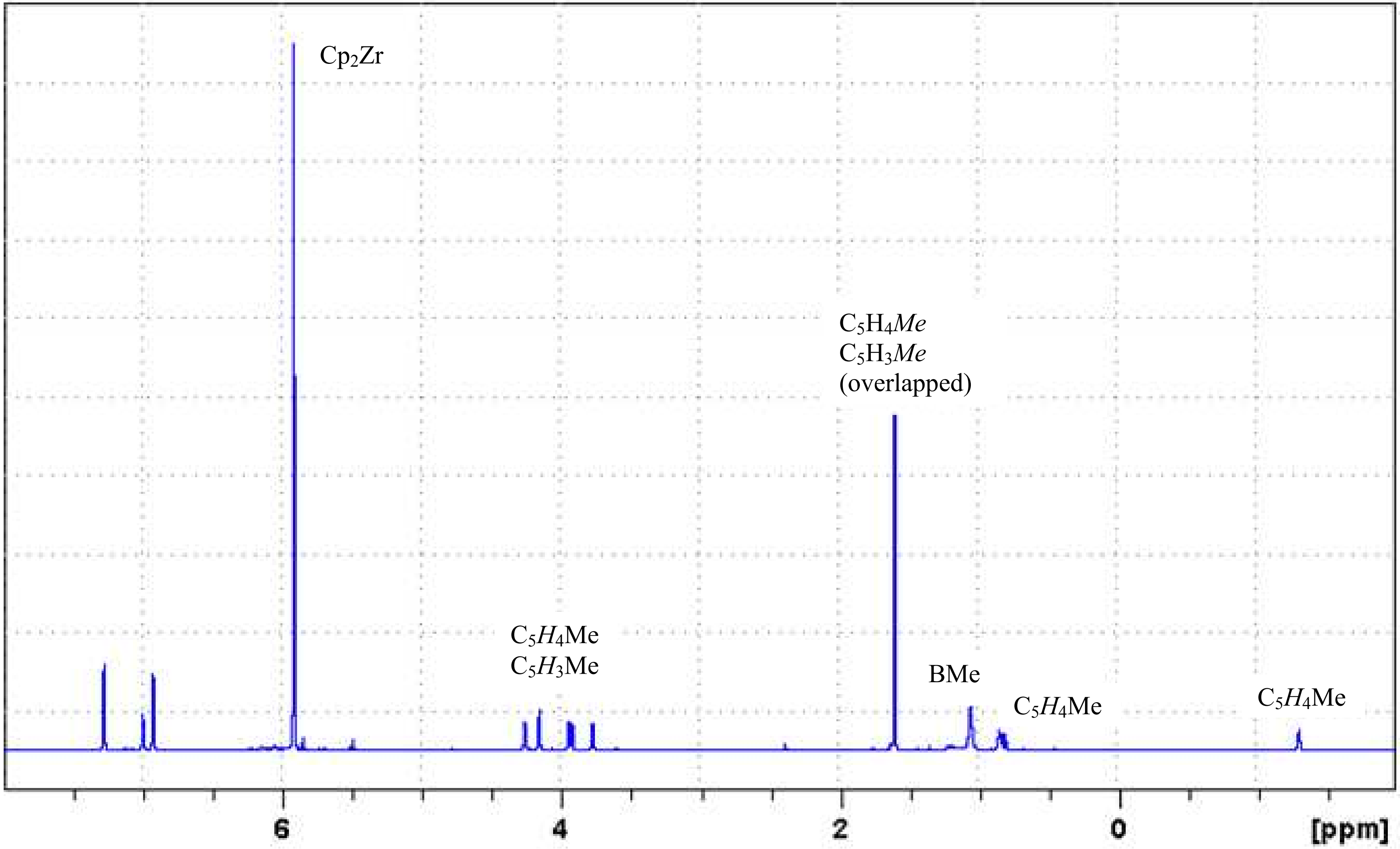

Figure S5. ^{1}H NMR of compound **6** in C_6D_5Br (crude).

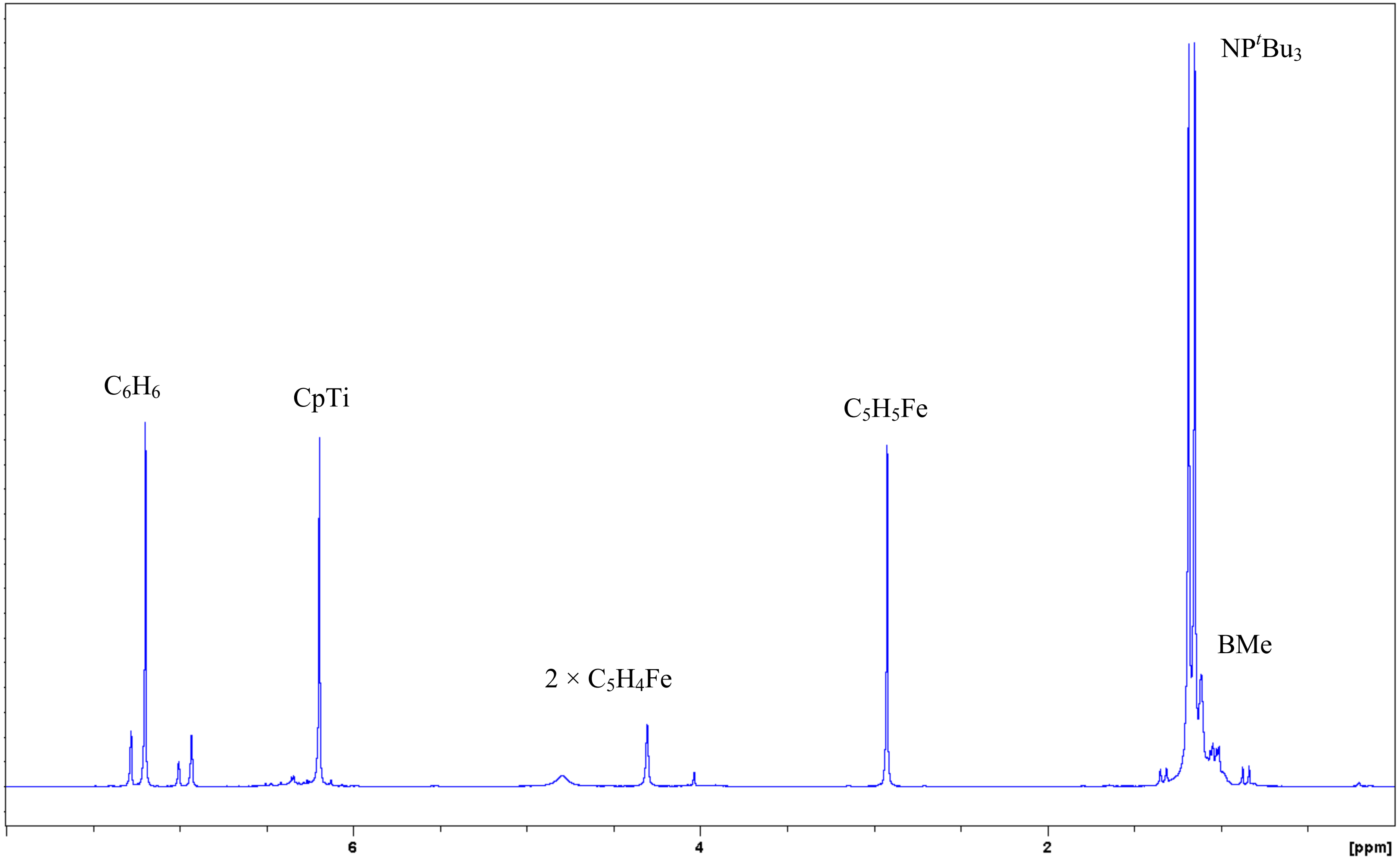

Figure S6. [1]H NMR of compound **6** in C_6D_5Br (crystals).