Electronic Supplementary Material (ESI) for Dalton Transactions.

Reaction of Five-membered Zirconacycloallenoids with the Strong Lewis Acid $B(C_6F_5)_3$

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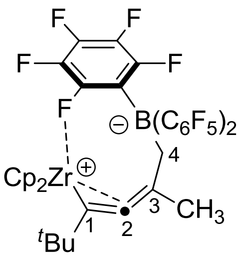
SUPPORTING INFORMATION

General Procedures. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. Dichlorobis(η^5-cyclopentadienyl)zirconium (J. J. Eisch, F. A. Owuor and P. O. Otieno, *Organometallics*, 2001, **20**, 4132), Tris(pentafluorophenyl)borane (A. G. Massey, A. J. Park and F. G. A. Stone, *Proc. Chem. Soc.*, 1963, 212; A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245; A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1966, **5**, 218), 2,5,5-trimethyl-1-hexen-3-yne (G. Bender, G. Kehr, R. Fröhlich, J. L. Petersen and G. Erker, *Chem. Sci.*, 2012, **3**, 3534) and 1,1-Bis(η^5-cyclopentadienyl)-2-*tert*-butyl-5-phenyl-1-zirconacyclopenta-2,3-diene (**6b**) (G. Bender, G. Kehr, C. G. Daniliuc, B. Wibbeling and G. Erker, *Dalton Trans.*, 2013, **42**, 14673) were prepared according to published procedures and fully characterized by NMR spectroscopy. Purchased starting materials and other chemicals or reagents (Aldrich, TCI and ABCR) were used without further purification. The following instruments were used for physical characterization of the compounds: NMR spectra: Agilent DD2 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ, reported in ppm, is given relative to TMS and referenced to the solvent signal {[d_8]-toluene (δ_H = 2.03, δ_C = 20.4)}. NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (*TA Instruments*). Mass spectra were recorded on a Orbitrap LTQ XL (*Thermo Scientific*).

X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.*, 2003, **A59**, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For the compound **7a** one disordered over two positions *t*-Bu group was found in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Compound **7b** crystallized with two disordered over two positions toluene molecules in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

Complex 7a



At –78 °C *n*-butylmagnesium chloride (0.34 mL, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a THF (5 mL) solution of dichlorobis(**η^5**-cyclopentadienyl)zirconium (100 mg, 0.34 mmol) and 2,5,5-trimethyl-1-hexen-3-yne (42 mg, 0.34 mmol). After removal of the dry ice bath, the mixture was allowed to warm to rt and stirred for 1 h. Then the yellow solution was heated at 60 °C for another 1 h. The dark red-brown reaction mixture was cooled to rt and 1,4-dioxane (0.2 mL) was added. After the reaction solution was stirred for 30 min at rt, all volatiles were removed *in vacuo*. The obtained residue was suspended in *n*-pentane (3×5 mL) and the insoluble material was filtered off through *Celite*. After removing the solvent of the filtrate *in vacuo*, complex **6a** was obtained as a yellow oil. Subsequently compound **6a** was dissolved in toluene (7 mL) and $B(C_6F_5)_3$ (150 mg, 0.29 mmol, 0.9 eq) was added. The reaction mixture was stirred overnight at rt. The reaction mixture was concentrated *in vacuo* and *n*-pentane (6 mL) was added. The resulting precipitate was filtered through a glass frit and the obtained solid was dried *in vacuo* to give complex **7a** as a yellow solid (216 mg, 74%). After drying complex **7a** became insoluble in solution (toluene, benzene). Since the isolated compound could not be further purified due to it low solubility, the elemental analysis varied slightly among different preparations. The best obtained value is given below:

IR (KBr): $\tilde{\nu}$ = 3547 (w), 2965 (s), 2868 (m), 2362 (w), 1870 (w), 1643 (s), 1602 (m), 1521 (s), 1362 (s), 1275 (s), 1205 (m), 1167 (m), 1090 (s), 977 (s), 806 (s), 682 (s), 609 (m), 562 (m), 520 (m), 460 (m).

Decomp.: 184 °C.

Elemental Analysis: calcd. for $C_{37}H_{24}BF_{15}Zr$: C 51.94, H 2.83; found: C 51.00, H 2.95.

In situ experiment (NMR-scale)

At –78 °C *n*-butylmagnesium chloride (0.17 mL, 2 M diethyl ether solution, 0.34 mmol, 2 eq) was added to a THF (5 mL) solution of dichlorobis(**η^5**-cyclopentadienyl)zirconium (50 mg, 0.17 mmol) and 2,5,5-trimethyl-1-hexen-3-yne (21.0 mg, 0.17 mmol). The mixture was allowed to warm to rt and stirred for 1 h. After stirring the suspension for another 1 h at 60 °C all volatiles were removed *in vacuo*. The obtained residue was suspended in *n*-pentane (2×10 mL) and the insoluble material was filtered off through *Celite*. All volatiles of the filtrate were removed *in vacuo* and the resulting yellow oil was dissolved in deuterated toluene (1 mL). B(C_6F_5)$_3$ (80 mg, 0.16 mmol, 0.9 eq) was added and the reaction mixture was stirred for 50 min at rt. Then the reaction mixture was characterized by NMR experiments.

^{1}H NMR (500 MHz, 299 K, C_7D_8): δ = 5.53 (s, 5H, Cp^{a}), 5.28 (s, 5H, Cp^{b}), 1.45 (s, 3H, Me), 0.98, 0.51 (each br, each 1H, 4-H), 0.87 (s, 9H, ^{t}Bu).

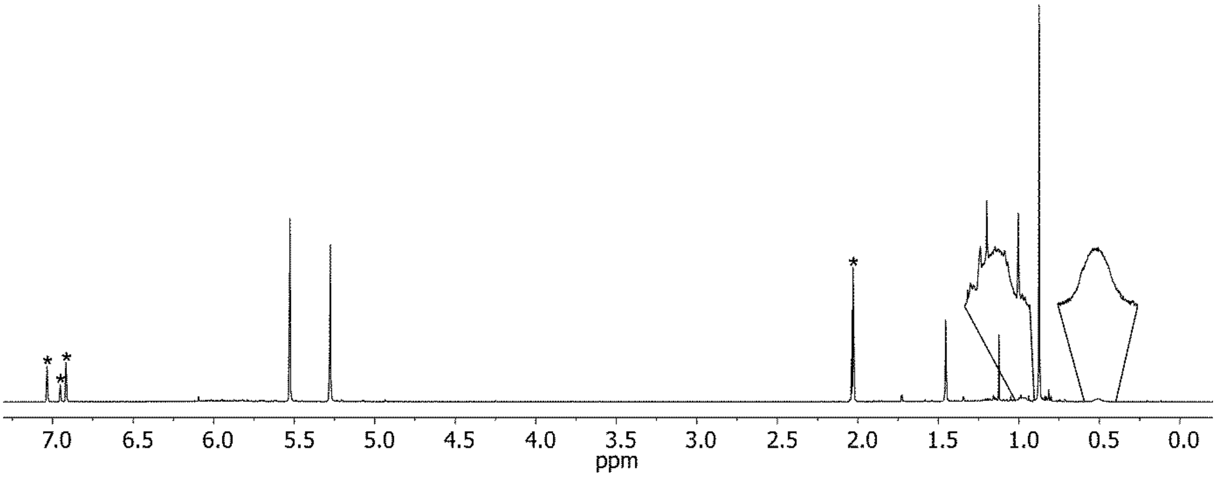
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_7D_8): δ = 159.7 (C-1), 139.0 (C-2)^{t}, 121.2 (br, C-3)^{t}, 111.0 (Cp^{a}), 110.6 (Cp^{b}), 37.6, 32.6 (^{t}Bu), 21.6 (br, C-4), 21.0 (Me), [C_6F_5 not listed, ^{t} tentative assignment].

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_7D_8): δ ^{1}H / δ ^{13}C = 5.53 / 111.0 (Cp^{a}), 5.28 / 110.6 (Cp^{b}), 1.45 / 21.0 (Me), 0.98 / 21.6 (4-CH_2), 0.87 / 32.6 (^{t}Bu).

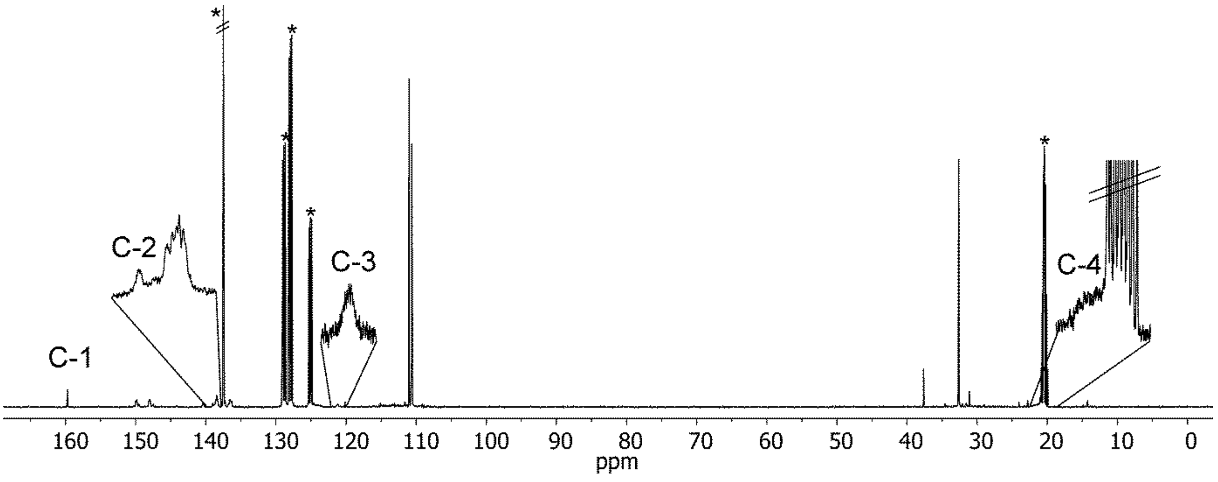
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_7D_8)[selected traces]: δ ^{1}H / δ ^{13}C = 1.45 / 139.0, 121.2, 21.6 (Me / C-2, C-3, C-4), 0.87 / 159.7, 37.6, 32.6 (^{t}Bu / C-1, ^{t}Bu, ^{t}Bu).

^{19}F NMR (470 MHz, 299K, C_7D_8): δ = -134.4 (br, 2F, *o*-C_6F_5), -159.5 (m, 1F, *p*-C_6F_5), -164.3 (br, 2F, *m*-C_6F_5); [$\Delta\delta^{19}F_{m,p}$ = 4.8].

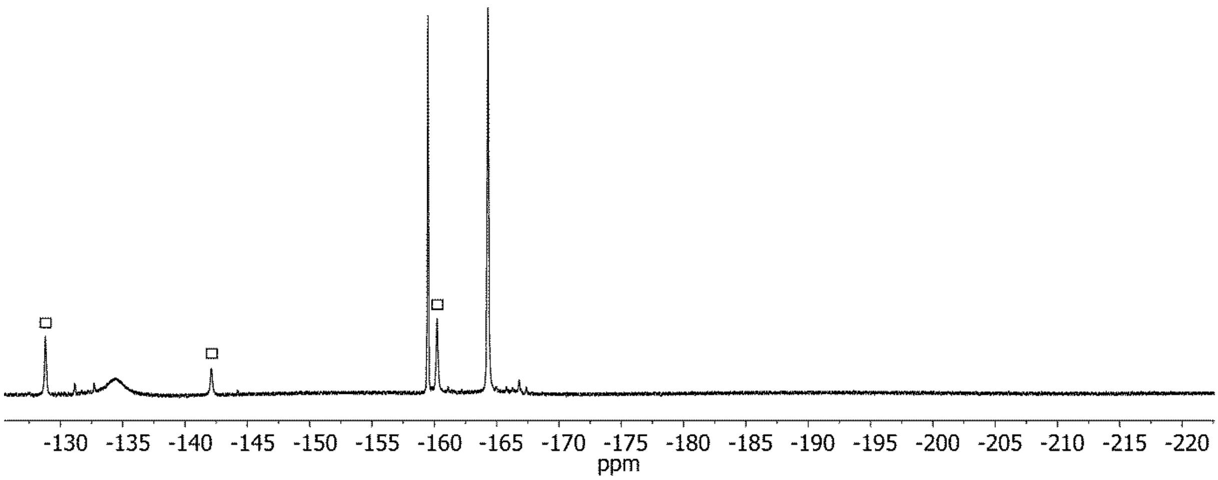
^{11}B{^{1}H} NMR (160 MHz, 299 K, C_7D_8): δ = -13.6 ($\nu_{1/2} \approx$ 30 Hz).



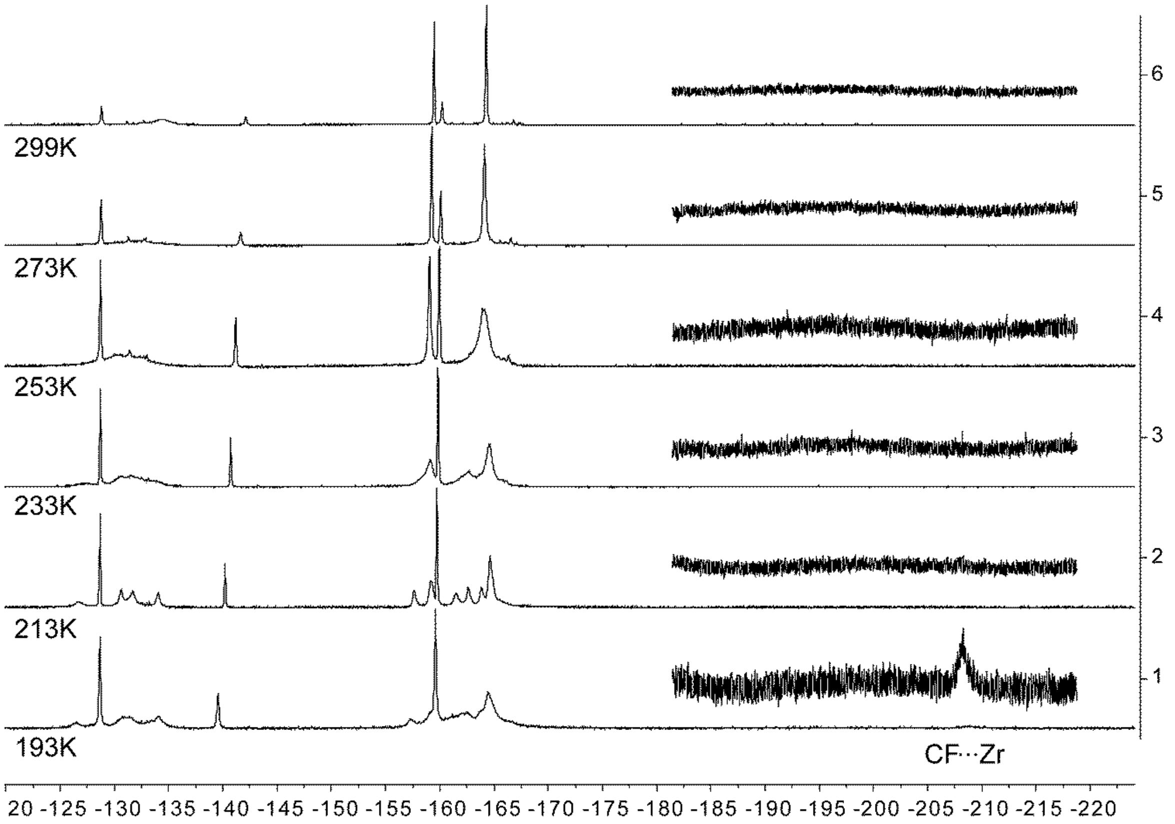
^{1}H NMR (500 MHz, 299 K, C_7D_8 (*)).



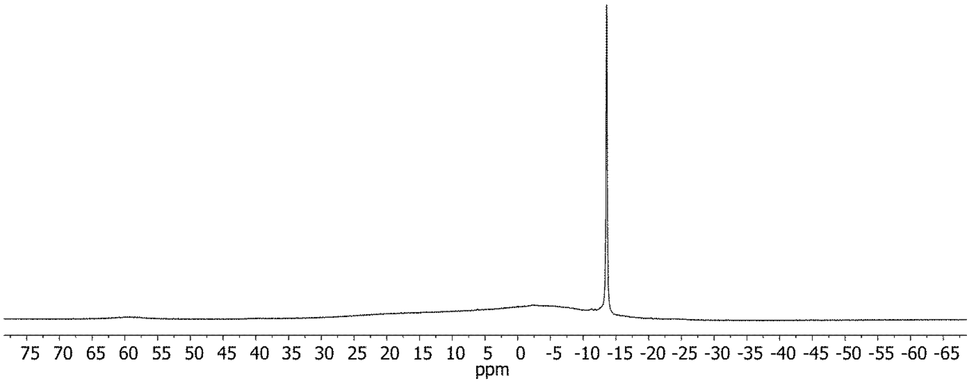
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_7D_8 (*)).



^{19}**F NMR** (470 MHz, 299 K, C_7D_8, $B(C_6F_5)_3$ (□)).



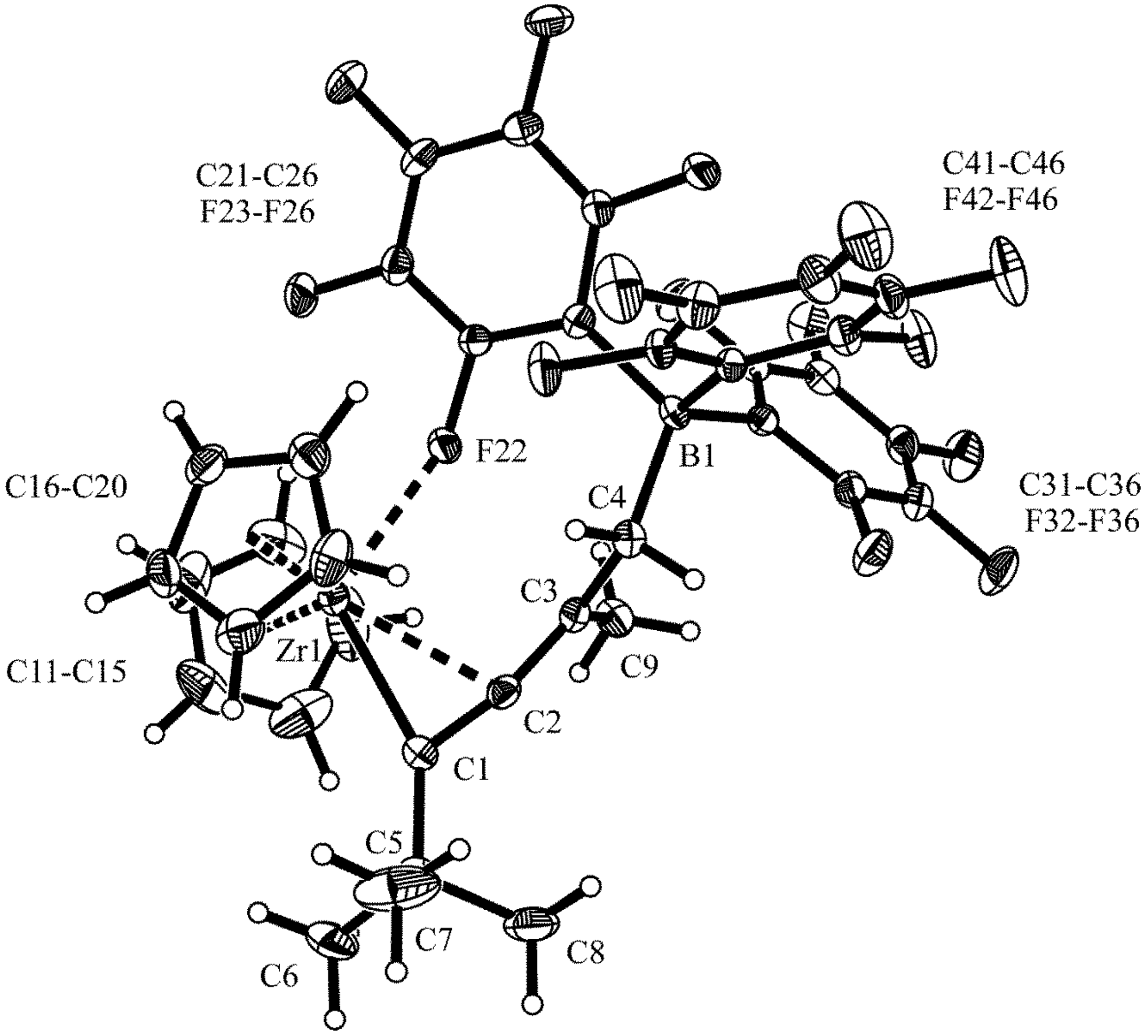
^{19}F NMR (470 MHz, C_7D_8) of complex **7a** at different temperatures.



^{11}B{^{1}H} NMR (160 MHz, 299 K, C_7D_8).

Single crystals for X-ray crystal structure analysis

The analogous procedure and the same reaction scale as described for the preparation of **7a** was used (see above). Instead of using toluene, the *in situ* prepared complex **6a** and $B(C_6F_5)_3$ were dissolved in benzene (5 mL). The benzene solution of compound **7a** was stored 2 days at rt giving the zwitterionic complex **7a** as yellow crystals which were suitable for the X-ray crystal structure analysis.



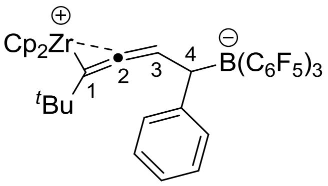
X-ray crystal structure analysis of compound 7a. formula $C_{37}H_{24}BF_{15}Zr$, M = 855.59, colourless crystal, 0.10 x 0.02 x 0.01 mm, a = 8.3106(2), b = 12.2167(3), c = 17.4089(4) Å, α = 107.973(1), β = 90.090(1), γ = 97.935(2) °, V = 1663.3(1) Å^3, ρ_{calc} = 1.708 gcm^{-3}, μ = 0.444 mm^{-1}, empirical absorption correction ($0.957 \leq T \leq 0.995$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 15086 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å^{-1}, 5742 independent (R_{int} = 0.051) and 4793 observed reflections [I>2σ(I)], 516 refined parameters, R = 0.055, wR^2 = 0.121, max. (min.) residual electron density 0.54 (-0.44) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Ethylene polymerization with complex 7a

Complex **7a** (25 mg, 29.2 µmol) was placed in a Schlenk flask (50 mL) and dissolved in toluene (5 mL). Then the evacuated Schlenk flask was filled with ethylene (2 bar) and stirred for 75 min at rt. Subsequently the obtained suspension was filtered through a glass frit and the polymer was washed with 3 N methanolic HCl (10 mL). The polymer was stored in the drying oven at 80 °C for overnight to give polyethylene (17 mg). **Melting point** (DSC): 134 °C.

Complex 7b

Single crystals for X-ray crystal structure analysis



Complex **6b** (30.0 mg, 73.95 µmol) and $B(C_6F_5)_3$ (37.9 mg, 73.95 µmol) were mixed in a vial and dissolved in toluene (3 mL). Then the light orange reaction solution was stored at –30 °C for several days to give the zwitterionic compound **7b** as yellow crystals (45.0 mg, 66%), which were suitable for the X-ray crystal structure analysis.

IR (KBr): $\tilde{\nu}$ = 3671 (m), 3629 (m), 3546 (m), 3126 (w), 3026 (w), 2959 (s), 2867 (m), 2360 (m), 1646 (s), 1523 (m), 1446 (m), 1366 (m), 1287 (m), 1237 (m), 1090 (s), 1019 (m), 969 (m), 820 (m), 673 (w), 606 (w), 516 (w), 425 (w).

Decomp.: 80 °C.

Elemental Analysis: calcd. for $C_{42}H_{26}BF_{15}Zr$: C 54.97, H 2.86; found: C 55.26, H 3.33.

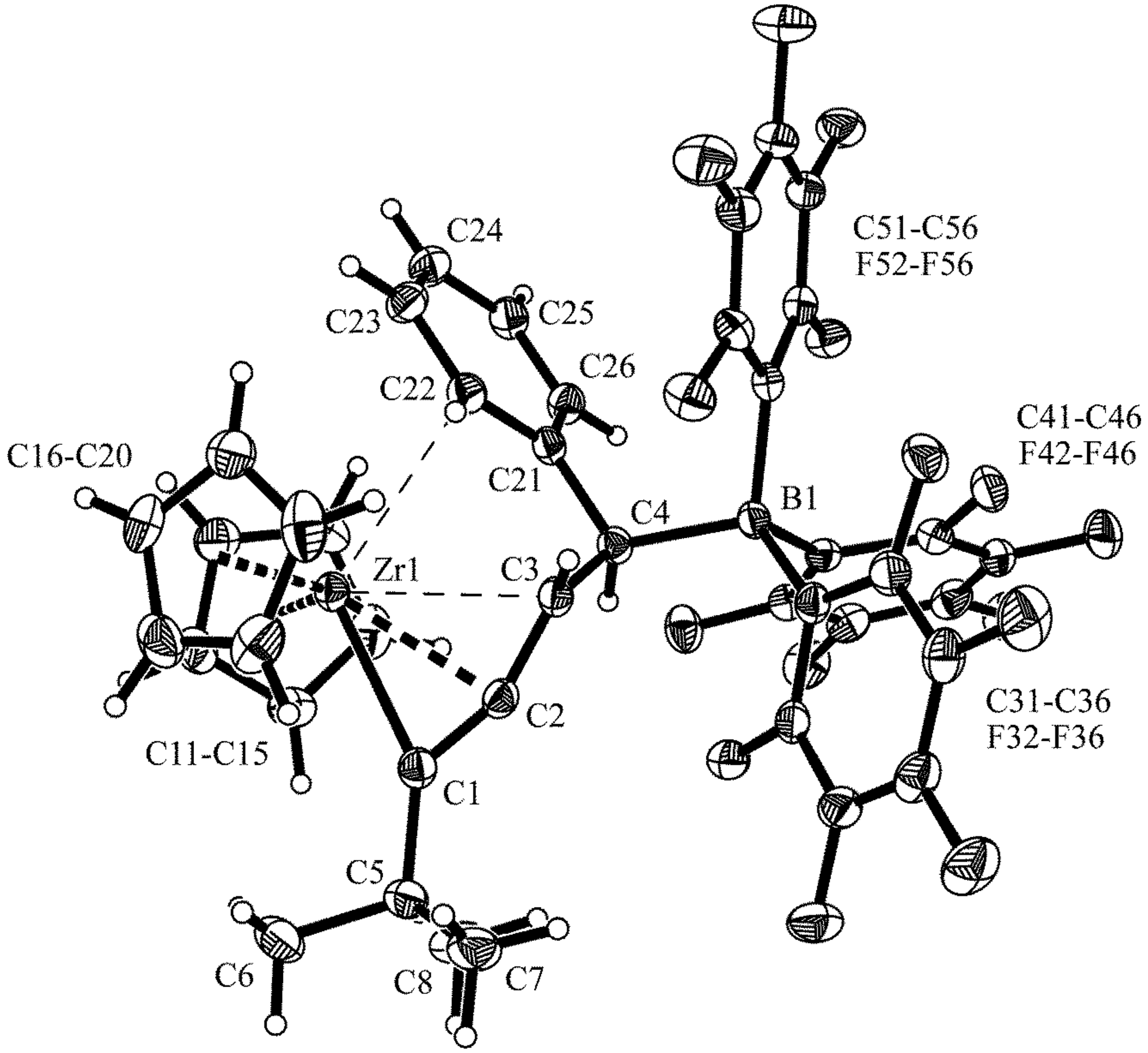


Figure 2: X-ray structure analysis of compound 7b. formula $C_{42}H_{26}BF_{15}Zr \cdot 2 \times C_7H_8$, M = 1101.93, orange crystal, 0.28 x 0.22 x 0.16 mm, a = 11.9272(2), b = 22.9097(3), c = 18.2983(2) Å, β = 106.009(1)°, V = 4806.1(1) Å^3, ρ_{calc} = 1.523 gcm^{-3}, μ = 0.326 mm^{-1}, empirical absorption correction ($0.914 \leq T \leq 0.949$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 28779 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å^{-1}, 8319 independent (R_{int} = 0.038) and 7076 observed reflections [$I > 2\sigma(I)$], 797 refined parameters, R = 0.038, wR^2 = 0.089, max. (min.) residual electron density 0.36 (-0.33) e.Å^{-3}, the hydrogen atoms at C3 and C22 were refined freely; others were calculated and refined as riding atoms.

In situ experiment (NMR-scale)

Due to the fact that complex **7b** is sparingly soluble in hydrocarbons (toluene, benzene) after a little while at rt or at low temperature, the NMR data were collected from an *in situ* generated reaction mixture: compound **6b** (20.0 mg, 49.3 µmol) and $B(C_6F_5)_3$ (25.2 mg, 49.3 µmol) were mixed in deuterated toluene (2 mL). Then the reaction mixture was directly characterized by NMR experiments. (*Comment:* It had not gone to completion when it was measured, so small amounts of both starting materials were still visible in the NMR spectra. Longer reaction times led to precipitation)

Mixture of compound **6b** and **7b** (ratio ca. 1 : 7 [^{1}H NMR]):

^{1}H NMR (500 MHz, 299 K, C_7D_8): δ = 6.72 (m, 2H, *m*-Ph), 6.53 (m, 1H, *p*-Ph), 6.27 (br, 2H, *o*-Ph), 5.67 (m, 1H, 3-H), 5.23 (s, 5H, Cp^a), 4.85 (br, 1H, 4-H), 4.70 (s, 5H, Cp^b), 0.94 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_7D_8): δ = 149.0 (*i*-Ph), 141.9 (C-1), 138.5 (*m*-Ph), n.o. (o-Ph), 133.0 (C-2), 126.2 (*p*-Ph), 111.5 (Cp^b), 109.2 (Cp^a), 91.0 (C-3), 41.0 (br, C-4), 36.8, 32.4 (^{t}Bu), [C_6F_5 not listed].

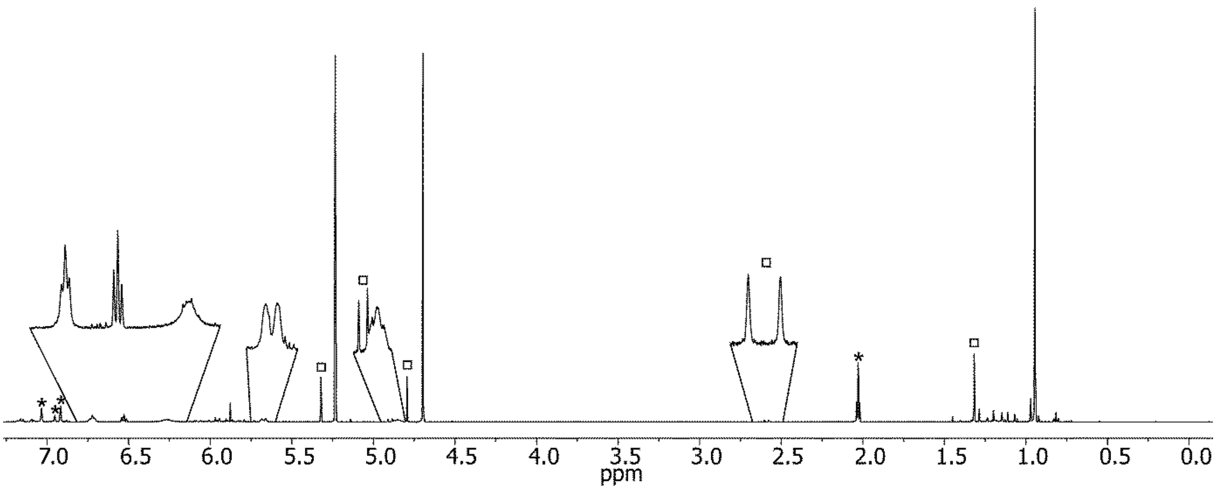
^{1}H{^{1}H} TOCSY (500 MHz MHz, 299 K, C_7D_8)[selected experiments]: δ ^{1}H$_{irr}$ / δ ^{1}H$_{res}$ = 6.53 / 6.72, 6.27 (*p*-Ph / *m*-Ph, *o*-Ph), 5.67 / 4.85 (3-H / 4-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_7D_8): δ ^{1}H / δ ^{13}C = 6.72 / 138.5 (*m*-Ph), 6.53 / 126.2 (*p*-Ph), 5.67 / 91.0 (3-CH), 4.85 / 41.0 (4-CH), 5.23 / 109.2 (Cp^A), 4.70 / 111.5 (Cp^B), 0.94 / 32.4 (^{t}Bu).

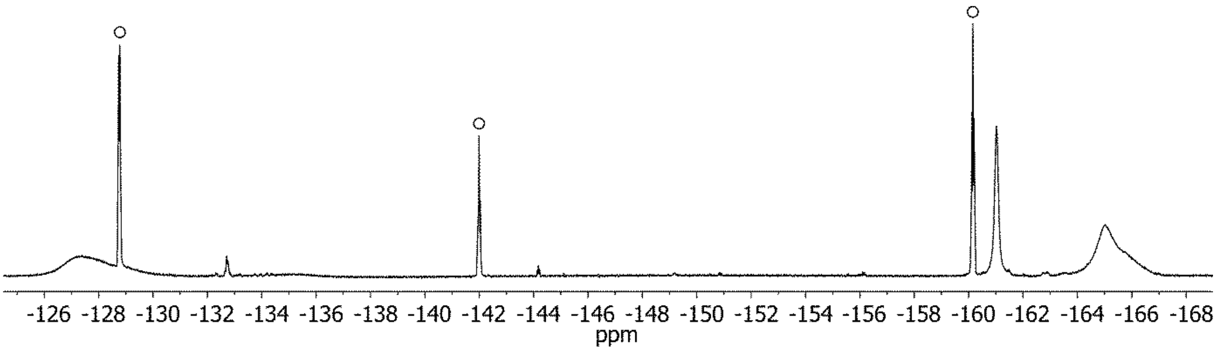
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_7D_8)[selected traces]: δ ^{1}H / δ ^{13}C = 6.72 / 149.0, 138.5 (*m*-Ph / *i*-Ph, *m*-Ph), 5.67 / 141.9 (3-H / C-1), 4.85 / 149.0, 133.0 (4-H / *i*-Ph, C-2), 0.94 / 141.9, 36.8, 32.4 (^{t}Bu / C-1, ^{t}Bu, ^{t}Bu).

^{19}F NMR (470 MHz, 299K, C_7D_8): δ = -127.4 (br, 2F, *o*-C_6F_5), -161.0 (br, 1F, *p*-C_6F_5), -165.0 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p} = 4.0$].

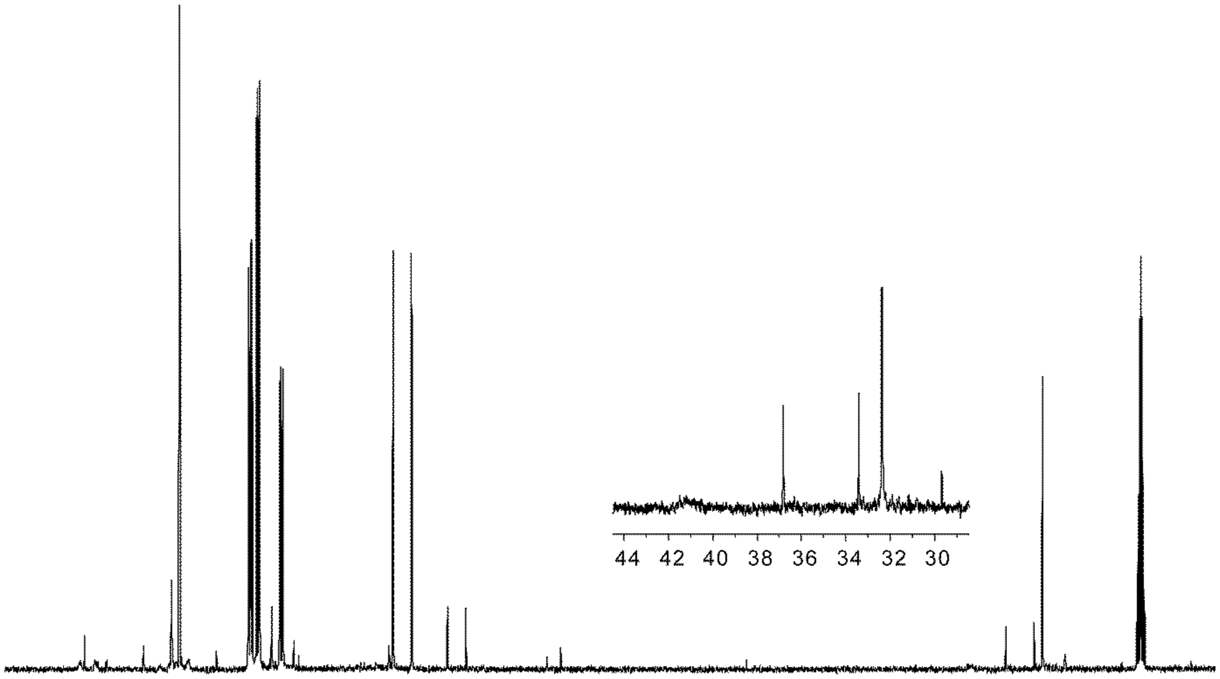
^{11}B{^{1}H} NMR (160 MHz, 299 K, C_7D_8): δ = -9.8 ($\nu_{1/2} \approx 15$ Hz).



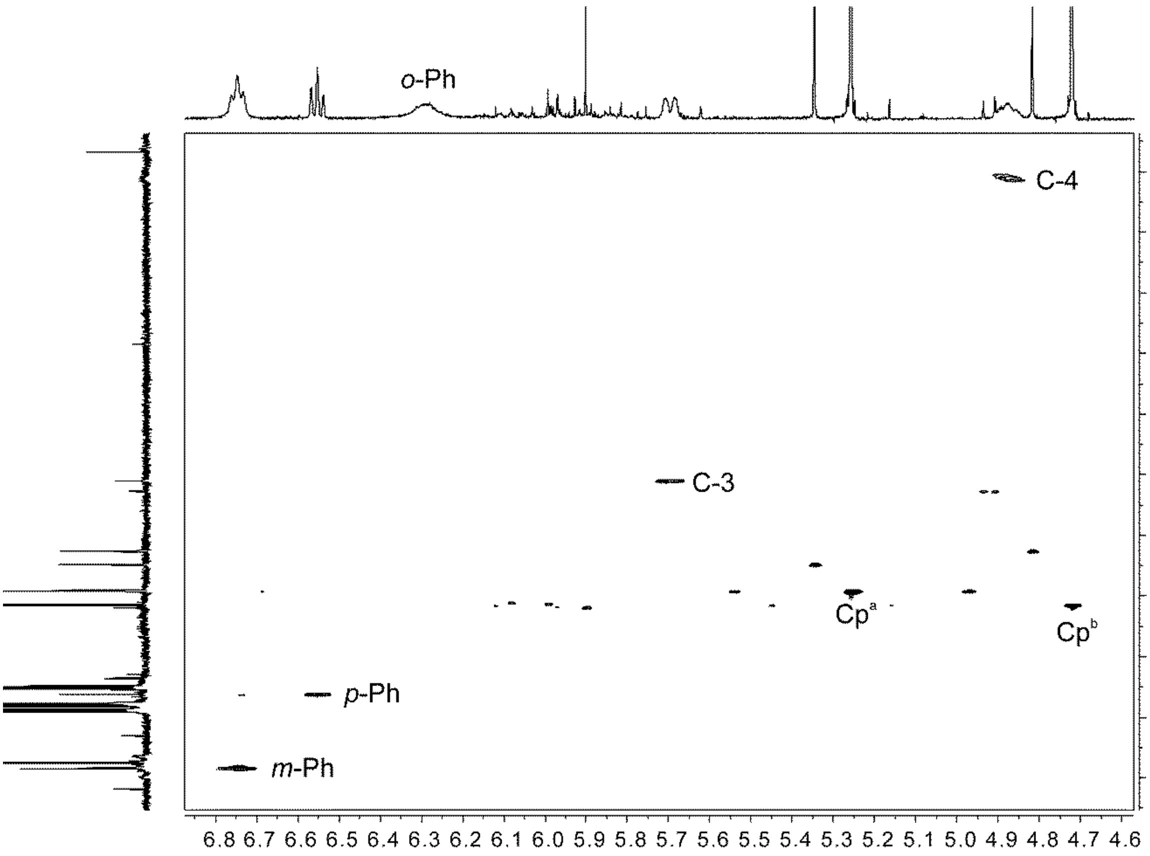
^{1}H NMR (500 MHz, 299 K, C_7D_8 (*), complex **6b** (□)).



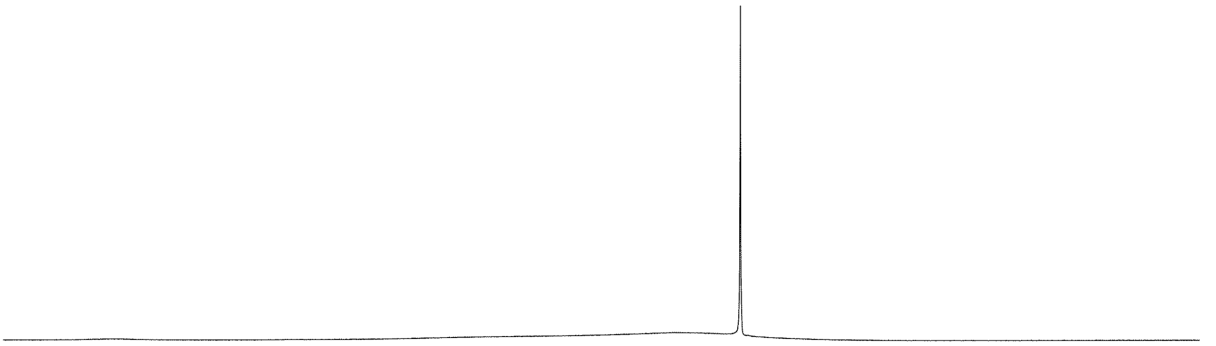
^{19}F NMR (470 MHz, 299 K, C_7D_8, $B(C_6F_5)_3$ (○)).



^{13}C{^{1}H} NMR (126 MHz, 299 K, C_7D_8).



^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_7D_8)



^{11}B{^{1}H} NMR (160 MHz, 299 K, C_7D_8).

Control experiment (NMR scale): in situ generation of compound 7b followed by THF-d_8 addition

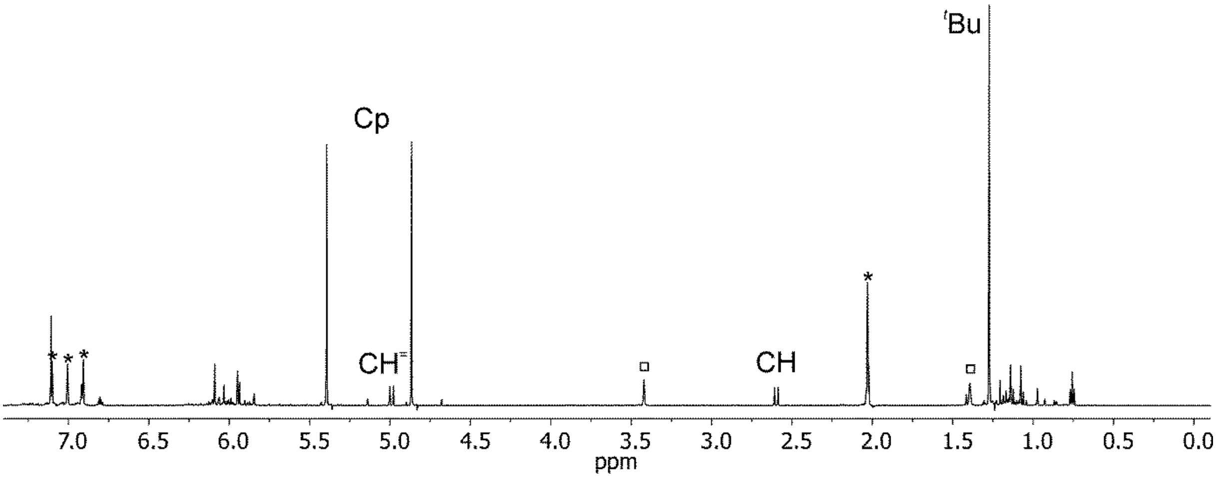
We tried to dissolve compound **7b** in THF-d_8, however this has resulted in reversion of the $B(C_6F_5)_3$ addition with liberation of the starting material **6b** plus the $B(C_6F_5)_3$-THF-d_8-adduct:

Procedure: Complex **6b** (20.0 mg, 49.3 μmol) and $B(C_6F_5)_3$ (25.2 mg, 49.3 μmol) were placed in a Schlenk flask and dissolved in deuterated toluene (2 mL). After 10 min at rt, complex **7b** precipitated as a yellow solid. Then deuterated THF (0.1 mL) was added to the suspension and the reaction suspension became a yellow solution immediately. After stirring for 2 h at rt, the reaction mixture was characterized by NMR experiments. The formation of complex **6b** and the TDF-$B(C_6F_5)_3$-adduct[1] was detected.

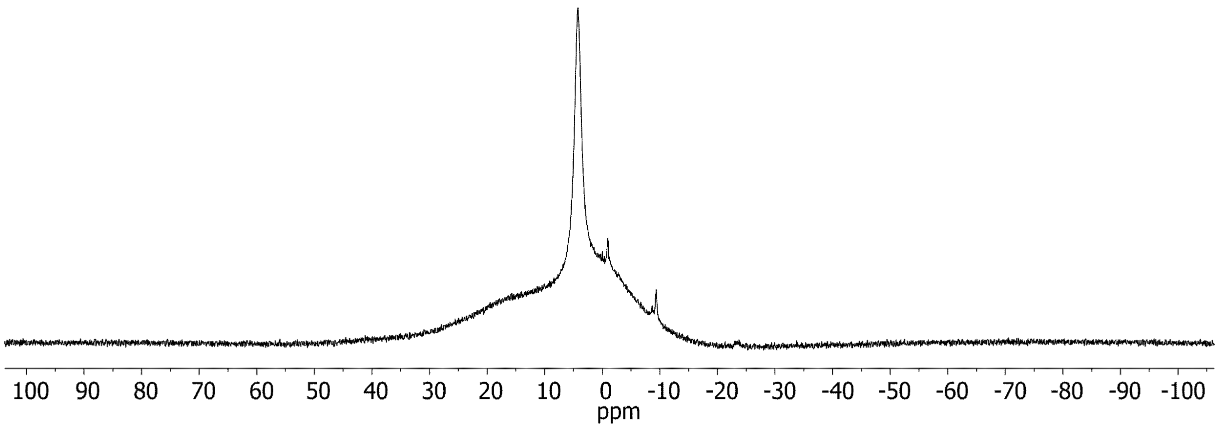
Complex 6b[2]*:* **^{1}H NMR** (500 MHz, 299 K, C_6D_6): δ = 7.26 (m, 2H, *m*-Ph), 7.21 (m, 2H, *o*-Ph), 6.98 (m, 1H, *p*-Ph), 5.39 (s, 5H, Cp^a), 5.04 (d, $^3J_{HH}$ = 13.9 Hz, 3-H), 4.87 (s, 5H, Cp^b), 2.72 (d, $^3J_{HH}$ = 13.9 Hz, 4-H), 1.38 (s, 9H, ^{t}Bu).

THF-d_8-$B(C_6F_5)_3$-adduct: **^{19}F NMR** (564 MHz, 299K, C_7D_8): δ = -133.3 (d, $^3J_{FF}$ = 21 Hz, 2F, *o*-C_6F_5), -156.3 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-C_6F_5), -163.7 (m, 2F, *m*-C_6F_5); [$\Delta\delta$ $^{19}F_{m,p}$ = 7.4].

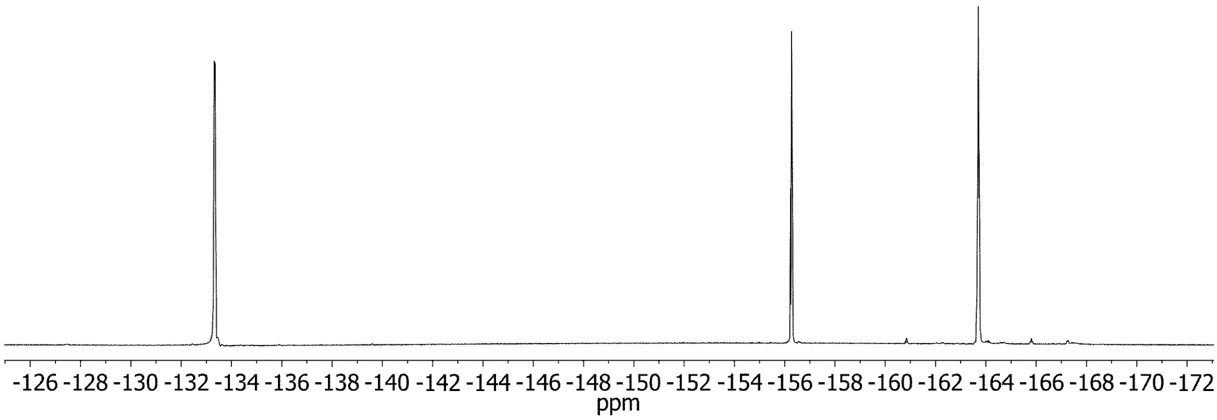
$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_7D_8): δ = 4.2 ($\nu_{1/2} \approx$ 354 Hz).



^{1}H NMR (600 MHz, 299 K, C_7D_8 (*), C_4D_8O (□)).



^{11}B{^{1}H} NMR (192 MHz, 299 K, C_7D_8).



^{19}F NMR (564 MHz, 299 K, C_7D_8).

Ethylene polymerization with compound 7b

Complex **6b** (11.9 mg, 29.3 μmol) and $B(C_6F_5)_3$ (15.0 mg, 29.3 μmol) were placed in a Schlenk flask (50 mL) and dissolved in toluene (5 mL). The evacuated Schlenk flask was filled with ethylene (2 bar) and stirred for 75 min at rt. Subsequently the obtained suspension was filtered through a glass frit and the polymer was washed with 3 N methanolic HCl (10 mL). The polymer was stored in the drying oven at 80 °C for overnight to give polyethylene (241.5 mg). **Melting point**: 135 °C.

Literature:

1 THF-$B(C_6F_5)_3$: W. E. Piers, *Adv. Organomet. Chem.*, 2004, **52**, 1; C. Lorber, R. Choukroun, L. Vendier, *Organometallics*, 2008, **27**, 5017.

2 G. Bender, G. Kehr, C. G. Daniliuc, B. Wibbeling and G. Erker, *Dalton Trans.*, 2013, **42**, 14673.