Electronic Supplementary Material (ESI) for Dalton Transactions

Reactions of dimethylzirconocene complexes with a vicinal frustrated P/B Lewis pair

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[‡]X-ray crystal structure analyses

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 with the procedure according to Grubbs (A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics* 1996, **15**, 1518) or were distilled from appropriate drying agents and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: NMR spectra: *Agilent* DD2 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz), *Agilent* DD2 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz, ^{31}P: 243 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ is given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shift δ is given relative to $CFCl_3$ (external reference). ^{11}B NMR: chemical shift δ is given relative to $BF_3{\cdot}Et_2O$ (external reference). ^{31}P NMR: chemical shift δ is given relative to H_3PO_4 (85% in H_2O) (external reference). 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*).

X-Ray Crystal Structure Analyses. 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 and W. Minor, *Methods Enzymol.* 1997, **276**, 307); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr*. 2003, **A59**, 228); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. 1990, **A46**, 467); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. 2008, **A64**, 112) 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*: Compound **3a** crystallized with two molecules in the asymmetric unit. The hydrogen atoms at C4 in compound **3b** were refined freely. In compound **6a** one disordered over two positions dichloromethane molecule was found in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For the compound **8a** one disordered over two positions dichloromethane molecule, one C_6F_5 group, one Cp group and one methyl group were found in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

Materials. Dimethylzirconocene Cp_2ZrMe_2 (**1a**) (P. C. Wails, H. Weigold and A. P. Bell, *J. Organomet. Chem.* 1972, **34**, 155. E. Samuel and M. D. Rausch, *J. Am. Chem. Soc.* 1973, **95**, 6263), dimethylpermethylzirconocene $(C_5Me_5)_2ZrMe_2$ (**1b**) (J. M. Manriquez, D. R. McAlister, R. D. Sanner and J. E. Bercaw, *J. Am. Chem. Soc.* 1978, **100**, 2716), dimesitylvinylphosphane (P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.* 2007, 5072), bis(pentafluorophenyl)borane (D. J. Parks, R. E. v. H. Spence and W. E. Piers, *Angew. Chem. Int. Ed.* 1995, **34**, 809; W. E. Piers, D. J. Parks and G. P. A. Yap, *Organometallics* 1998, **17**, 5492) and {2-[bis(pentafluorophenyl)boryl]ethyl}dimesityl-phosphane (**2**) (P. Spies, G. Erker, G. Kehr, K.

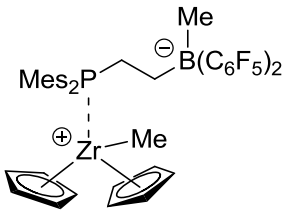
Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.* 2007, 5072) were prepared according to modified literature procedures.

Synthesis of 3a:

Dimesitylvinylphosphane (50.0 mg, 0.17 mmol) and bis(pentafluorophenyl)borane (58.4 mg, 0.17 mmol, 1.0 eq.) were dissolved in benzene (5 mL) and stirred for 10 minutes to give a yellow solution. Then Cp_2ZrMe_2 (**1a**) (42.4 mg, 0.17 mmol, 1.0 eq.) was added to give an orange reaction solution. Subsequently all volatiles were removed *in vacuo* and the obtained orange residue was dried *in vacuo* to yield compound **3a**. Crystals suitable for X-ray single crystal structure analysis were grown by slow diffusion of heptane into a solution of **3a** in toluene at −40 °C.

Yield: 118 mg (0.13 mmol, 78%). [$C_{44}H_{42}BF_{10}PZr$, M = 893.8 g/mol].

Elemental analysis: Calc. for $C_{44}H_{42}BF_{10}PZr$ (893.8 g/mol): C 59.13, H 4.74. Found: C 60.13, H 5.12.



^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.53 (d, $^4J_{PH}$ = 2.5 Hz, 4H, *m*-Mes), 5.71 (s, 10H, Cp), 2.81 (br m, 2H, PCH_2), 1.98 (s, 6H, *p*-CH_3^{Mes}), 1.74 (br, 12H, *o*-CH_3^{Mes}), 1.18 (br m, 2H, BCH_2), 0.99 (br, 3H, BCH_3), –0.01 (s, 3H, $ZrCH_3$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 148.9 (dm, $^1J_{FC}$ ~ 234 Hz, C_6F_5), 140.9 (d, $^2J_{PC}$ = 5.0 Hz, *o*-Mes), 140.5 (*p*-Mes), 137.9 (dm, $^1J_{FC}$ ~ 238 Hz, C_6F_5), 137.3 (dm, $^1J_{FC}$ ~ 247 Hz, C_6F_5), 131.6 (*m*-Mes), 127.6 (*i*-Mes)[1], 113.1 (Cp), 50.1 (br, $ZrCH_3$), 32.0 (br, PCH_2), 24.9 (m, *o*-CH_3^{Mes}), 23.1 (br m, BCH_2), 20.6 (*p*-CH_3^{Mes}), 10.9 (very br, BCH_3), n.o. (*i*-C_6F_5), [[1] from the ghmbc experiment].

^{1}H{^{1}H} 1D-TOCSY (500 MHz, C_6D_6, 298 K) [selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 2.81 / 1.18 (PCH_2 / BCH_2), 0.99 / –0.01 (BCH_3 / $ZrCH_3$)[1], [[1] chemical exchange].

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, C_6D_6, 298 K) [selected trace]: δ ^{1}H / δ ^{1}H = 6.53 / 1.98, 1.74 (*m*-Mes / *p*-CH_3^{Mes}, *o*-CH_3^{Mes}).

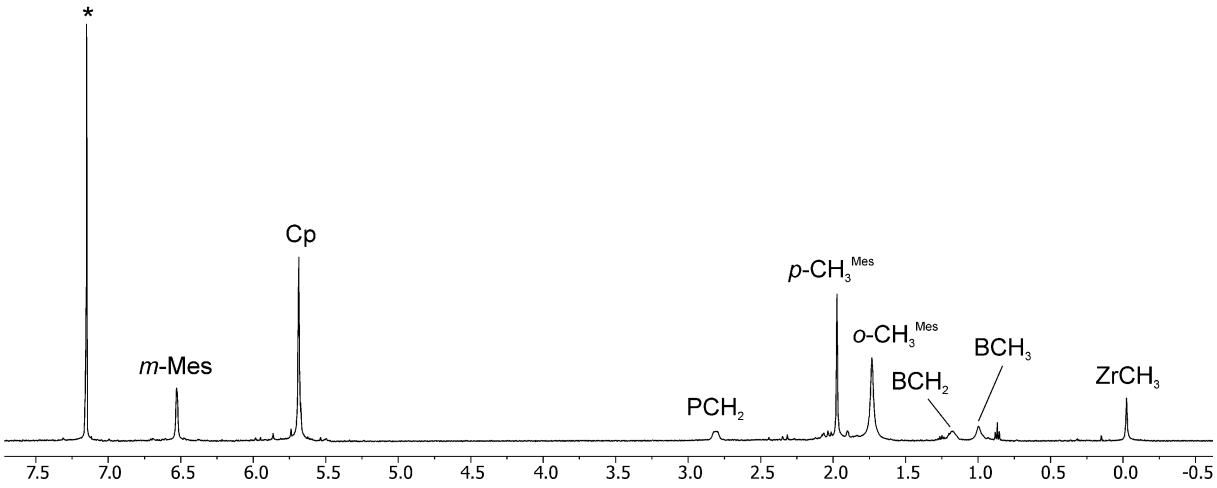
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 6.53 / 131.6 (*m*-Mes), 5.71 / 113.1 (Cp), 2.81 / 32.0 (PCH_2), 1.98 / 20.6 (*p*-CH_3^{Mes}), 1.74 / 24.9 (*o*-CH_3^{Mes}), 1.18 / 23.1 (BCH_2), –0.01 / 50.1 ($ZrCH_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 1.98 / 140.5, 131.6 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes), 1.74 / 140.9, 131.6 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes).

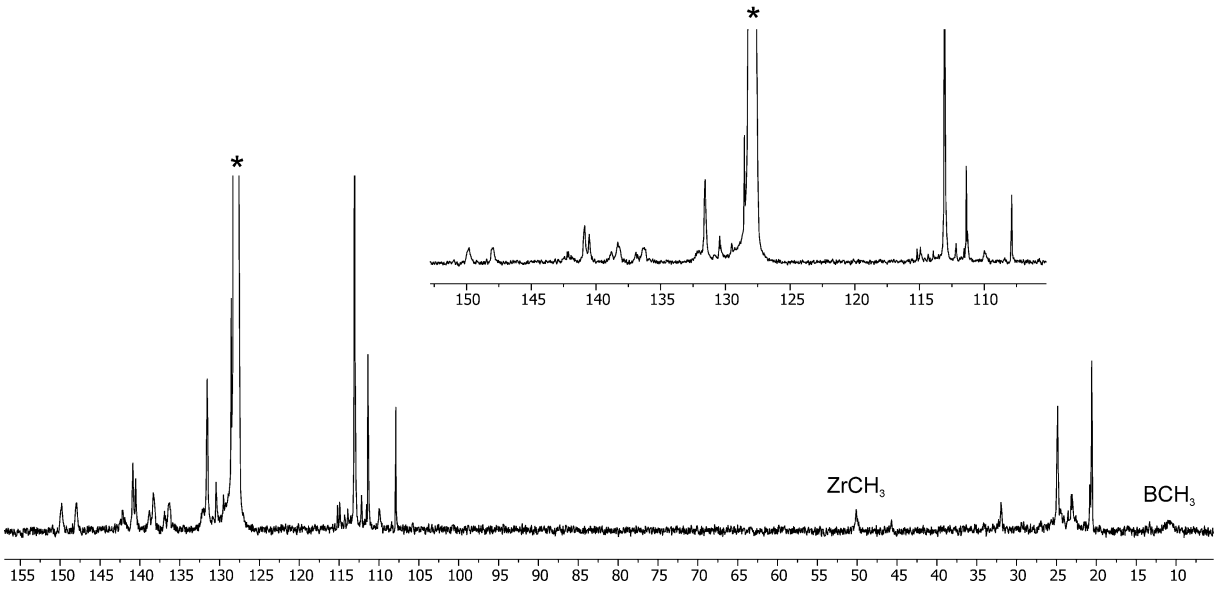
^{19}F NMR (470 MHz, C_6D_6, 298 K): δ = −132.6 (m, 2F, *o*-C_6F_5), −164.2 (br, 1F, *p*-C_6F_5), −166.1 (br, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 1.9].

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ = –11.9 ($\nu_{1/2}$ ~ 120 Hz).

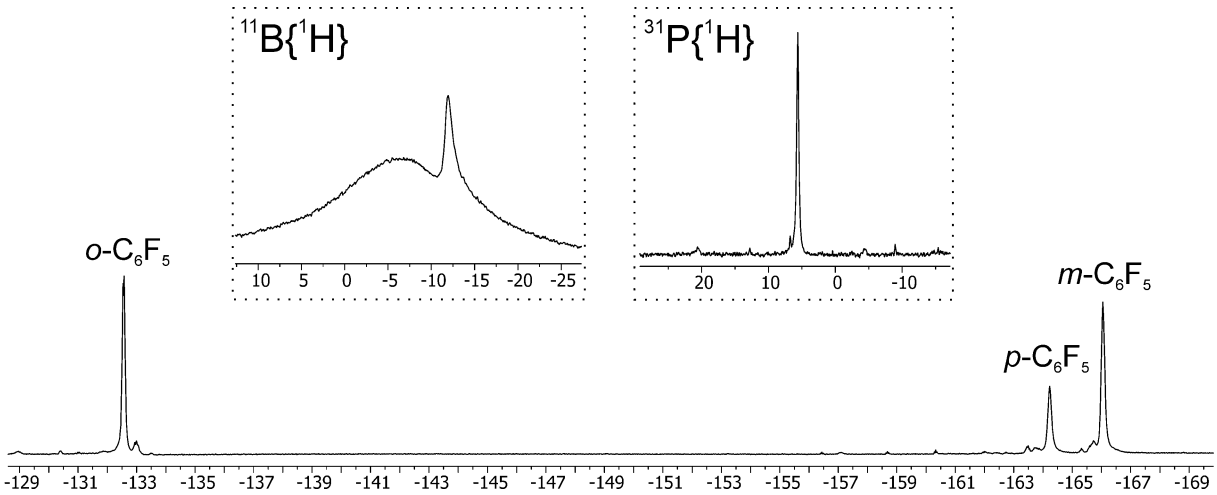
^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K): δ = 5.6 ($\nu_{1/2}$ ~ 60 Hz).



^{1}H NMR (500 MHz, C_6D_6(*), 298 K) of compound **3a**.

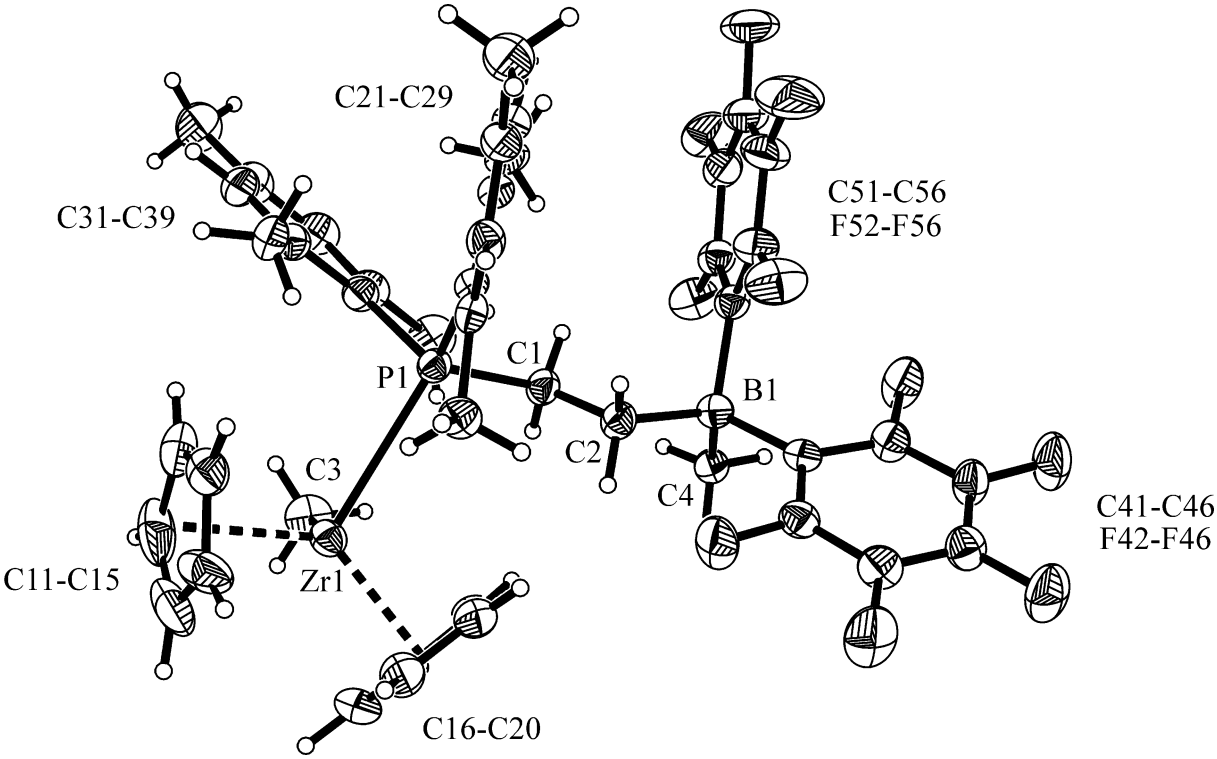


^{13}C{^{1}H} NMR (126 MHz, C_6D_6(*), 298 K) of compound **3a**.



^{19}F NMR (470 MHz, C_6D_6, 298 K), ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K) and ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K) of compound **3a**.

X-ray crystal structure analysis of compound 3a: formula $C_{44}H_{42}BF_{10}PZr$, M = 893.78, yellow crystal, 0.27 x 0.20 x 0.13 mm, a = 24.0134(2), b = 20.4685(3), c = 16.1406(2) Å, V = 7933.4(2) Å^3, ρ_{calc} = 1.497 gcm^{-3}, μ = 0.397 mm^{-1}, empirical absorption correction (0.900≤ T ≤ 0.950), Z = 8, orthorhombic, space group $Pna2_1$ (No. 33), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 46932 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 13311 independent (R_{int} = 0.067) and 11762 observed reflections [I>2σ(I)], 1044 refined parameters, R = 0.055, wR^2 = 0.128, max. (min.) residual electron density 0.60 (-0.49) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms. Flack parameter: 0.44(4).



Synthesis of 3b:

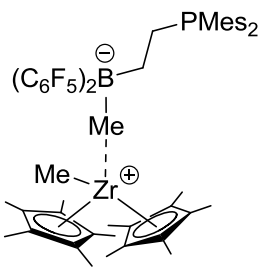
Dimesitylvinylphosphane (50.0 mg, 0.17 mmol) and bis(pentafluorophenyl)borane (58.4 mg, 0.17 mmol, 1.0 eq.) were dissolved in toluene (5 mL) and stirred for 10 minutes until a yellow solution was formed. Then $(C_5Me_5)_2ZrMe_2$ (**1b**) (66.1 mg, 0.17 mmol, 1.0 eq.) was added to give a dark yellow solution after 10 minutes of stirring. After all volatiles were removed *in vacuo*, pentane (5 mL) was added and the obtained reaction mixture was stirred for 10 minutes. Subsequently all volatiles were removed again and the obtained yellow solid was dried *in vacuo* for 60 minutes to give compound **3b**. Crystals suitable for X-ray single crystal structure analysis were grown by slow diffusion of heptane into a solution of **3b** in deuterated toluene at −40 °C.

Yield: 125 mg (0.12 mmol, 72%). [$C_{54}H_{62}BF_{10}PZr$, M = 1034.1 g/mol]

Elemental analysis: Calc. for $C_{54}H_{62}BF_{10}PZr$ (1034.1 g/mol): C 62.72, H 6.04. Found: C 63.15, H 6.47.

Melting point (DSC): 100 °C.

Decomposition point (DSC): 146 °C.



^{1}H NMR (500 MHz, C_7D_8, 233 K): δ = 6.61 (d, $^4J_{PH}$ = 1.7 Hz, 4H, *m*-Mes), 2.67 (m, 2H, PCH_2), 2.43 (s, 12H, *o*-CH_3^{Mes}), 2.09 (s, 6H, *p*-CH_3^{Mes}), 1.36 (s, 30H, C_5Me_5), 1.14 (m, 2H, BCH_2)[1], − 0.38 (s, 3H, $ZrCH_3$), –0.78 (s, 3H, BCH_3), [[1] from the ghsqc experiment].

^{13}C{^{1}H} NMR (126 MHz, C_7D_8, 233 K): δ = 148.1 (dm, $^1J_{FC}$ ~ 237 Hz, C_6F_5), 142.0 (d, $^2J_{PC}$ = 12.6 Hz, *o*-Mes), 138.2 (C_6F_5)[t], 137.1 (dm, $^1J_{FC}$ ~ 248 Hz, C_6F_5), 136.6 (*p*-Mes), 134.9 (d, $^1J_{PC}$ = 23.9 Hz, *i*-Mes), 130.1 (d, $^3J_{PC}$ = 1.9 Hz, *m*-Mes), 126.8 (*i*-C_6F_5)[1], 123.0 (C_5Me_5), 45.0 ($ZrCH_3$), 25.7 (d, $^1J_{PC}$ = 15.2 Hz, PCH_2), 24.9 (br, BCH_2), 23.7 (d, $^3J_{PC}$ = 12.5 Hz, *o*-CH_3^{Mes}), 21.4 (br, BCH_3), 20.9 (*p*-CH_3^{Mes}), 11.1 (C_5Me_5), [[t] tentatively assigned; [1] from the ghmbc experiment].

^{1}H{^{1}H} 1D-TOCSY (500 MHz, C_7D_8, 233 K) [selected experiment]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 2.67 / 1.14 (PCH_2 / BCH_2).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, C_7D_8, 233 K) [selected trace]: δ ^{1}H / δ ^{1}H = 6.61 / 2.43, 2.09 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}).

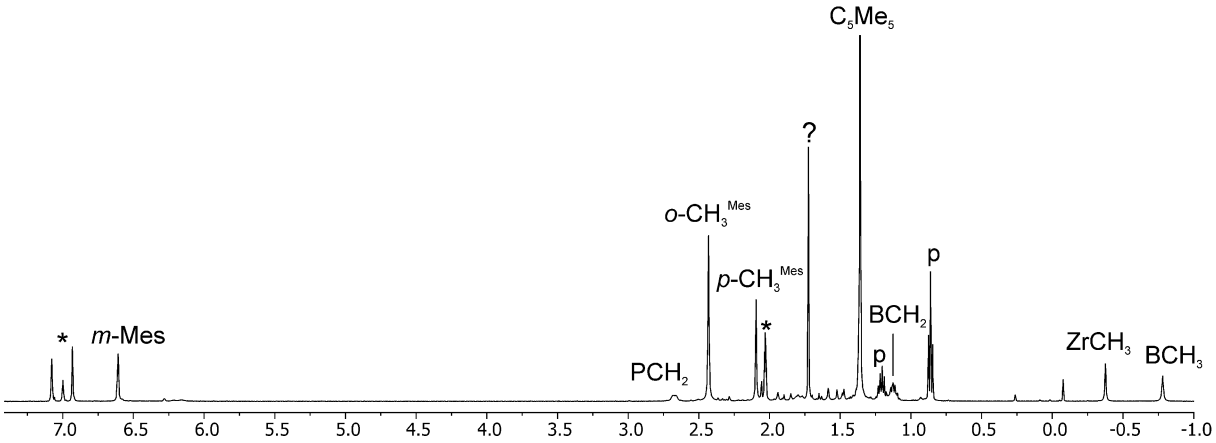
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, C_7D_8, 233 K): δ ^{1}H / δ ^{13}C = 6.61 / 130.1 (*m*-Mes), 2.67 / 25.7 (PCH_2), 2.43 / 23.7 (*o*-CH_3^{Mes}), 2.09 / 20.9 (*p*-CH_3^{Mes}), 1.36 / 11.1 (C_5Me_5), 1.14 / 24.9 (BCH_2), –0.38 / 45.0 ($ZrCH_3$), –0.78 / 21.4 (BCH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, C_7D_8, 233 K): δ ^{1}H / δ ^{13}C = 6.61 / 134.9, 130.1, 23.7, 20.9 (*m*-Mes / *i*-Mes, *m*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 2.43 / 142.0, 134.9, 130.1 (*o*-CH_3^{Mes} / *o*-Mes, *i*-Mes, *m*-Mes), 2.09 / 136.6, 130.1 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes), 1.36 / 123.0 (C_5Me_5 / C_5Me_5), −0.78 / 126.8 (BCH_3 / *i*-C_6F_5).

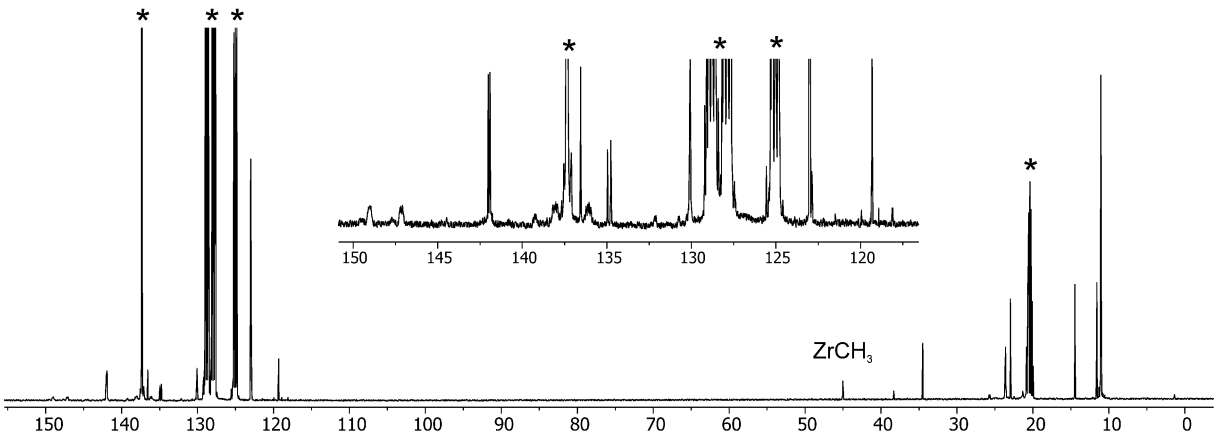
^{19}F NMR (470 MHz, C_7D_8, 233 K): δ = −132.5 (m, 2F, *o*-C_6F_5), −161.1 (t, $^{3}J_{FF}$ = 21.1 Hz, 1F, *p*-C_6F_5), −164.7 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 3.6].

^{11}B{^{1}H} NMR (160 MHz, C_7D_8, 233 K): δ = –10.1.

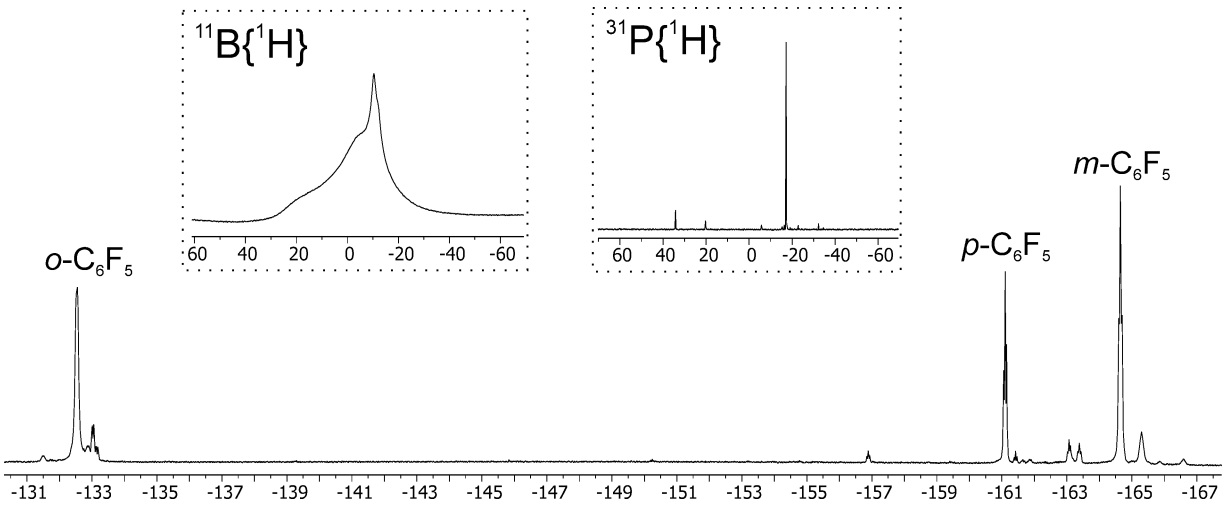
^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 233 K): δ = –17.3 ($\nu_{1/2}$ ~ 10 Hz).



^{1}H NMR (500 MHz, C_7D_8(*), 233 K) of compound **3b** (p = pentane, ? compound not identified yet).

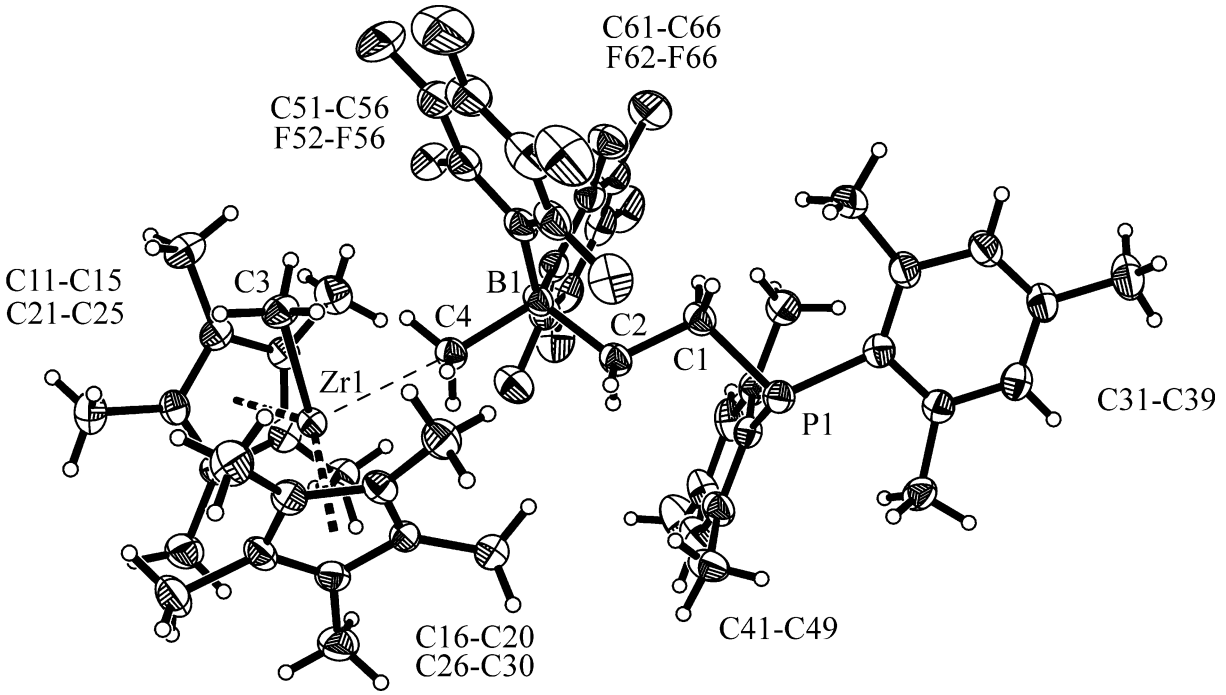


^{13}C{^{1}H} NMR (126 MHz, C_7D_8(*), 233 K) of compound **3b.**



^{19}F NMR (470 MHz, C_7D_8, 233 K), ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 233 K) and ^{11}B{^{1}H} NMR (160 MHz, C_7D_8, 233 K) of compound **3b**.

X-ray crystal structure analysis of compound 3b: formula $C_{54}H_{62}BF_{10}PZr \cdot C_7H_8$, M = 1126.17, yellow crystal, 0.32 x 0.06 x 0.03 mm, a = 17.5025(3), b = 23.0203(7), c = 28.2476(8) Å, V = 11381.3(5) Å^3, ρ_{calc} = 1.314 gcm^{-3}, μ = 2.441 mm^{-1}, empirical absorption correction (0.508≤ T ≤ 0.930), Z = 8, orthorhombic, space group *P*bca (No. 61), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 41458 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 9865 independent (R_{int} = 0.078) and 6508 observed reflections [I>2σ(I)], 696 refined parameters, R = 0.053, wR^2 = 0.125, max. (min.) residual electron density 0.32 (-0.36) e.Å^{-3}, the hydrogen atoms at C4 were refined freely; others were calculated and refined as riding atoms.



Synthesis of 6a:

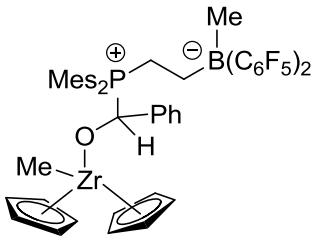
Dimesitylvinylphosphane (20.0 mg, 0.07 mmol) and bis(pentafluorophenyl)borane (23.3 mg, 0.07 mmol, 1.0 eq.) were dissolved in toluene (5 mL) and stirred for 10 minutes until a yellow solution was formed. Then Cp_2ZrMe_2 (**1a**) (16.9 mg, 0.07 mmol, 1.0 eq.) was added to give an orange solution. Then benzaldehyde (7.9 mg, 7.4 µL, 0.07 mmol, 1.1 eq.) was added and the reaction solution turned yellow immediately. After removal of all volatiles *in vacuo* the obtained yellow residue was washed with pentane (5 mL) and dried *in vacuo* to give compound **6a**. Crystals suitable for X-ray single crystal structure analysis were grown by slow concentration of a solution of **6a** in dichloromethane at −40 °C.

Yield: 51.0 mg (0.05 mmol, 76%). [$C_{51}H_{48}BF_{10}OPZr$, M = 999.9 g/mol].

Elemental analysis: Calc. for $C_{51}H_{48}BF_{10}OPZr$ (999.9 g/mol): C 61.26, H 4.84. Found: C 61.31, H 4.92.

Decomposition point (DSC): 142 °C.

[*Comment*: there is a second species in the CD_2Cl_2 solution of **6a**, which was tentatively assigned as $HP^+Mes_2CH_2CH_2B^-Me(C_6F_5)_2$ [ca. 19% (^{31}P)]; the corresponding Zr component was not identified yet]



^{1}H NMR (600 MHz, CD_2Cl_2, 243 K): δ = 7.51, 6.30 (each m, each 1H, *o*-Ph), 7.44 (m, 1H, *p*-Ph), 7.29, 7.23 (each m, each 1H, *m*-Ph), 7.08 (m, 1H, *m*-Mes^A), 7.01 (m, 1H, *m*-Mes^B), 6.78 (m, 1H, *m*'-Mes^A), 6.77 (m, 1H, *m*'-Mes^B), 6.70 (d, $^2J_{PH}$ = 2.7 Hz, 1H, CHO), 5.85, 5.79 (each s, each 5H, Cp), 2.87 (s, 3H, *o*-CH_3^{MesA}), 2.30 (s, 3H, *p*-CH_3^{MesA}), 2.29 (s, 3H, *p*-CH_3^{MesB}), 2.13, 1.94 (each m, each 1H, PCH_2), 1.93 (s, 3H, *o*-CH_3^{MesB}), 1.48 (s, 3H, *o*'-CH_3^{MesA}), 1.40, 0.83 (each m, each 1H, BCH_2), 1.23 (s, 3H, *o*'-CH_3^{MesB}), 0.12 (s, 3H, $ZrCH_3$), −0.08 (br, 3H, BCH_3).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 243 K): δ = 144.2 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Mes^B), 144.12 (d, $^2J_{PC}$ = 9.1 Hz, *o*'-Mes^B), 144.10 (d, $^2J_{PC}$ = 7.8 Hz, *o*-Mes^B), 143.2 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Mes^A), 142.6 (d, $^2J_{PC}$ = 9.0 Hz, *o*-Mes^A), 140.3 (d, $^2J_{PC}$ = 7.6 Hz, *o*'-Mes^A), 138.0 (d, $^2J_{PC}$ = 2.8 Hz, *i*-Ph), 131.9 (d, $^3J_{PC}$ = 11.7 Hz, *m*'-Mes^B), 131.7 (d, $^3J_{PC}$ = 10.7 Hz, *m*-Mes^B), 131.48 (d, $^3J_{PC}$ = 11.8 Hz, *m*'-Mes^A)^t, 131.48 (d, $^3J_{PC}$ = 10.9 Hz, *m*-Mes^A)^t, 130.4 (d, *J* = 3.6 Hz, *p*-Ph), 128.9 (d, $^4J_{PC}$ = 3.3 Hz, *m*-Ph), 128.7 (d, $^3J_{PC}$ = 4.2 Hz, *o*-Ph), 127.9 (d, $^4J_{PC}$ = 1.9 Hz, *m*-Ph), 127.8 (d, $^3J_{PC}$ = 7.6 Hz, *o*-Ph), 120.2 (d, $^1J_{PC}$ = 66.9 Hz, *i*-Mes^A), 115.6 (d, $^1J_{PC}$ = 61.4 Hz, *i*-Mes^B), 111.4, 111.1 (Cp), 85.9 (d, $^1J_{PC}$ = 45.6 Hz, CHO), 28.0 (d, $^1J_{PC}$ = 31.9 Hz, PCH_2), 25.8 (d, $^3J_{PC}$ = 3.0 Hz, *o*-CH_3^{MesB}), 25.5 ($ZrCH_3$), 23.5 (d, $^3J_{PC}$ = 1.6 Hz, *o*'-CH_3^{MesB}), 22.8 (d, $^3J_{PC}$ = 2.2 Hz, *o*-CH_3^{MesA}), 22.5 (d, $^3J_{PC}$ = 4.3 Hz, *o*'-CH_3^{MesA}), 21.0 (d, $^5J_{PC}$ = 1.4 Hz, *p*-CH_3^{MesB}), 20.8 (d, $^5J_{PC}$ = 1.4 Hz, *p*-CH_3^{MesA}), 19.4 (br, BCH_2), 8.7 (br, BCH_3), [C_6F_5 not listed; ^{t} tentatively assigned].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, CD_2Cl_2, 243 K): δ ^{1}H / δ ^{13}C = 7.51 / 127.8 (*o*-Ph), 7.44 / 130.4 (*p*-Ph), 7.29 / 127.9 (*m*-Ph), 7.23 / 128.9 (*m*-Ph), 7.08 / 131.48 (*m*-Mes^{A}), 7.01 / 131.7 (*m*-Mes^{B}), 6.78 / 131.48 (*m*'-Mes^{A}), 6.77 / 131.9 (*m*'-Mes^{B}), 6.70 / 85.9 (CHO), 6.30 / 128.7 (*o*-Ph), 5.85 / 111.4 (Cp), 5.79 / 111.1 (Cp), 2.87 / 22.8 (*o*-CH_3^{MesA}), 2.30 / 20.8 (*p*-CH_3^{MesA}), 2.29 / 21.0 (*p*-CH_3^{MesB}), 2.13, 1.94 / 28.0 (PCH_2), 1.93 / 25.8 (*o*-CH_3^{MesB}), 1.48 / 22.5 (*o*'-CH_3^{MesA}), 1.40, 0.83 / 19.4 (BCH_2), 1.23 / 23.5 (*o*'-CH_3^{MesB}), 0.12 / 25.5 ($ZrCH_3$), –0.08 / 8.7 (BCH_3).

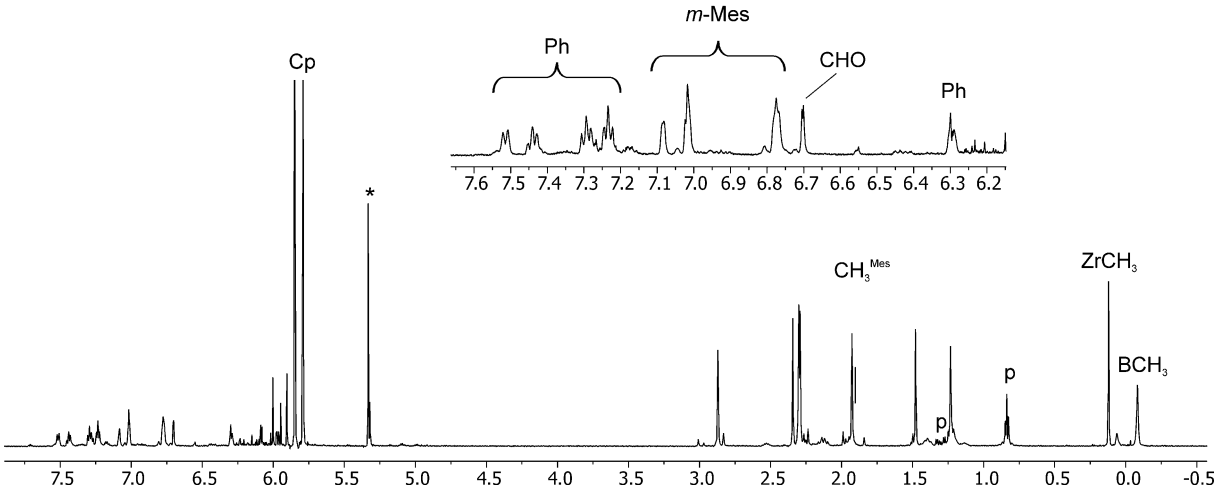
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, CD_2Cl_2, 243 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.29 / 138.0, 128.9 (*m*-Ph / *i*-Ph, *m*-Ph), 7.08 / 131.48, 120.2, 22.8, 20.8 (*m*-Mes^{A} / *m*-Mes^{A}, *i*-Mes^{A}, *o*-CH_3^{MesA}, *p*-CH_3^{MesA}), 7.01 / 131.9, 115.6, 25.8, 21.0 (*m*-Mes^{B} / *m*'-Mes^{B}, *i*-Mes^{B}, *o*-CH_3^{MesB}, *p*-CH_3^{MesB}), 2.87 / 142.6, 131.48, 120.2 (*o*-CH_3^{MesA} / *o*-Mes^{A}, *m*-Mes^{A}, *i*-Mes^{A}), 2.30 / 143.2, 131.48 (*p*-CH_3^{MesA} / *p*-Mes^{A}, *m*-Mes^{A}), 2.29 / 144.2, 131.7 (*p*-CH_3^{MesB} / *p*-Mes^{B}, *m*-Mes^{B}), 1.93 / 144.10, 131.7, 115.6 (*o*-CH_3^{MesB} / *o*-Mes^{B}, *m*-Mes^{B}, *i*-Mes^{B}), 1.48 / 140.3, 131.48, 120.2 (*o*'-CH_3^{MesA} / *o*'-Mes^{A}, *m*-Mes^{A}, *i*-Mes^{A}), 1.23 / 144.12, 131.9, 115.6 (*o*'-CH_3^{MesB} / *o*'-Mes^{B}, *m*'-Mes^{B}, *i*-Mes^{B}), –0.08 / 129.7, 19.4 (BCH_3 / *i*-C_6F_5, BCH_2).

^{19}F NMR (564 MHz, CD_2Cl_2, 243 K): δ = −133.8, −133.9 (each m, each 2F, *o*-C_6F_5), −164.42 (t, $^{3}J_{FF}$ = 20.3 Hz), −164.43 (t, $^{3}J_{FF}$ = 20.6 Hz)(each 1F, *p*-C_6F_5), −166.5 (m, 4F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 2.1, 2.1].

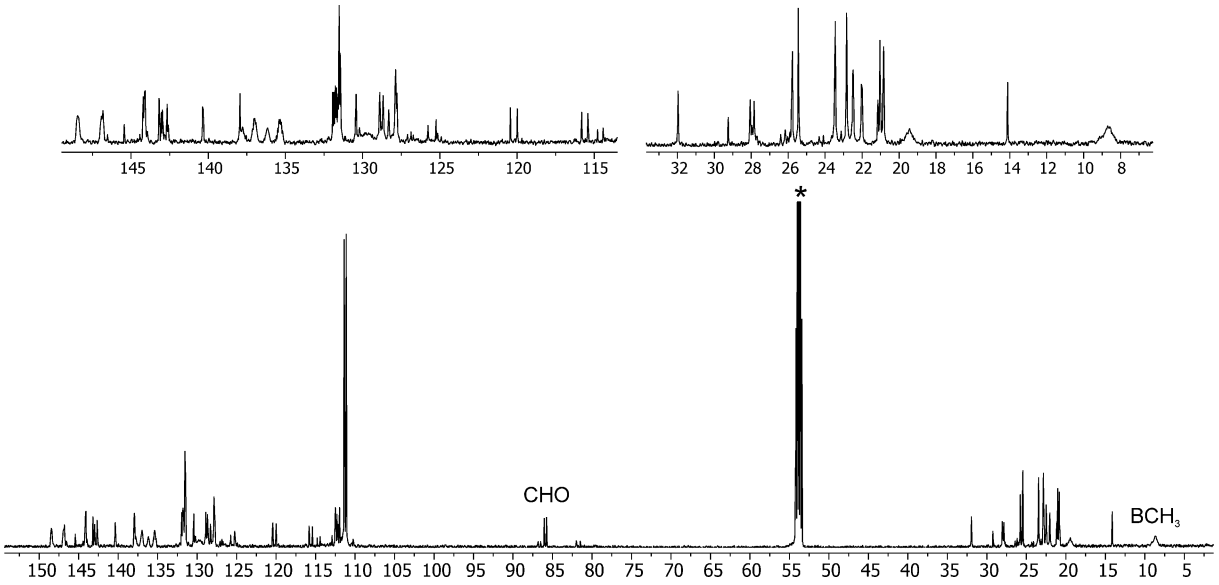
^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 243 K): δ = –12.8 ($\nu_{1/2}$ ~ 180 Hz).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 243 K): δ = 31.6 ($\nu_{1/2}$ ~ 20 Hz), –2.3 ($\nu_{1/2}$ ~ 31 Hz, 19%, PH).

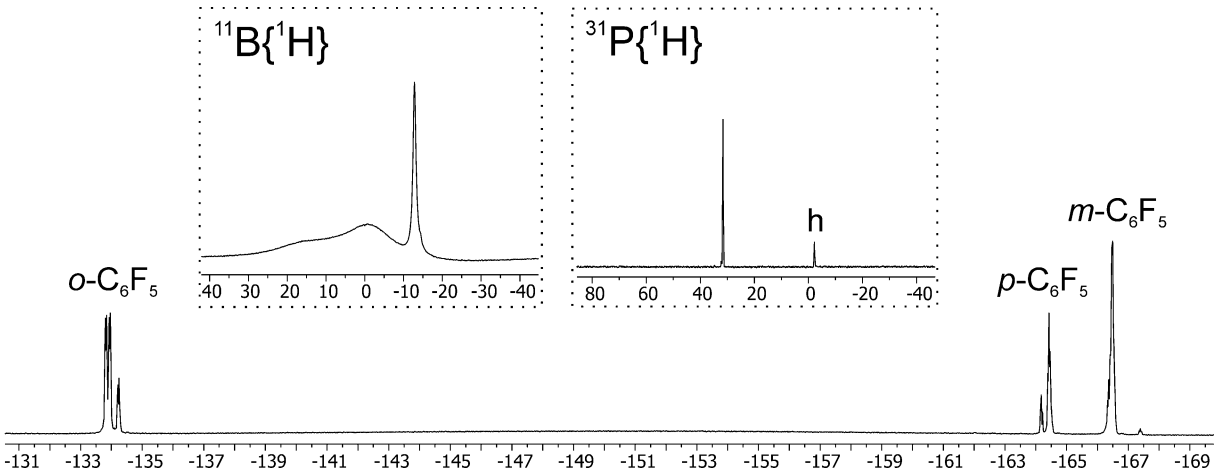
^{31}P NMR (243 MHz, CD_2Cl_2, 243 K): δ = 31.6 ($\nu_{1/2}$ ~ 47 Hz), –2.3 (d, $^{1}J_{PH}$ = 470 Hz, 19%, PH).



^{1}H NMR (600 MHz, CD_2Cl_2(*), 243 K) of compound **6a** (p = pentane).

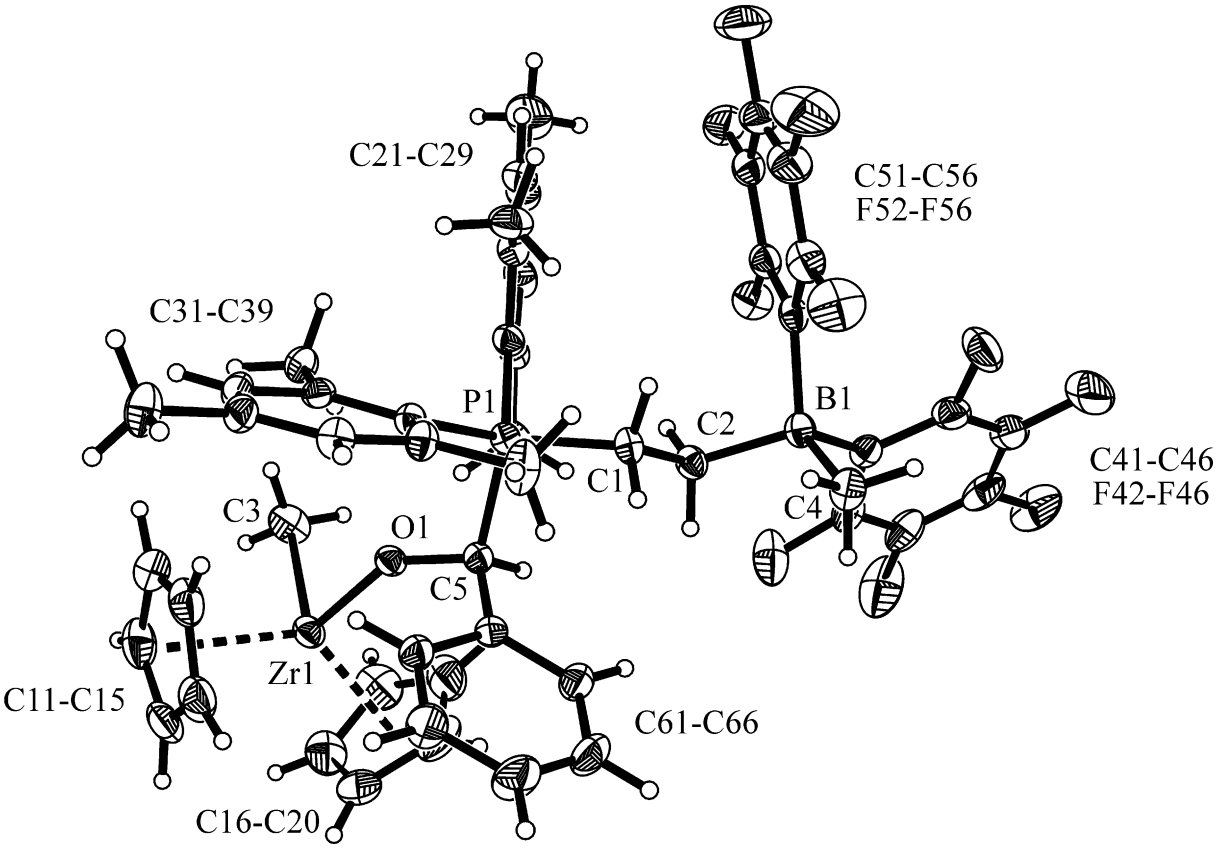


$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2(*), 243 K) of compound **6a**.



^{19}F NMR (564 MHz, CD_2Cl_2, 243 K), $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2, 243 K) and $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 243 K) of compound **6a** (h = PH species, probably caused by hydrolysis).

X-ray crystal structure analysis of compound 6a: formula $C_{51}H_{48}BF_{10}OPZr \cdot CH_2Cl_2$, M = 1084.82, colourless crystal, 0.43 x 0.26 x 0.15 mm, a = 14.8875(2), b = 17.4300(2), c = 19.5656(3) Å, β = 101.034(1)°, V = 4983.2(1) Å^3, ρ_{calc} = 1.446 gcm^{-3}, μ = 0.435 mm^{-1}, empirical absorption correction ($0.835 \leq T \leq 0.937$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 26276 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 8562 independent (R_{int} = 0.032) and 7470 observed reflections [$I>2\sigma(I)$], 649 refined parameters, R = 0.047, wR^2 = 0.123, max. (min.) residual electron density 0.83 (-0.65) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



Synthesis of 7a:

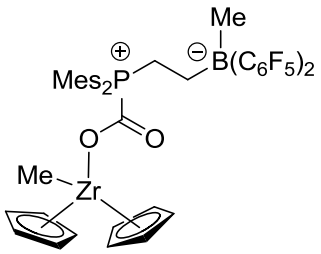
Dimesitylvinylphosphane (50.0 mg, 0.17 mmol) and bis(pentafluorophenyl)borane (58.4 mg, 0.17 mmol, 1.0 eq.) were dissolved in toluene (3 mL) and stirred for 15 minutes until a yellow solution was formed. Then Cp_2ZrMe_2 (**1a**) (42.4 mg, 0.17 mmol, 1.0 eq.) was added to give an orange solution. Subsequently CO_2 gas (1.5 bar) was introduced for 5 minutes and the solution turned light orange. After the reaction mixture was stirred for 1 hour at room temperature the solvent was removed *in vacuo*, the resulting light orange solid was washed with pentane (5 mL) and dried *in vacuo* to give compound **7a**.

Yield: 137 mg (0.15 mmol, 86%). [$C_{45}H_{42}BF_{10}O_2PZr$, M = 937.8 g/mol].

Elemental analysis: Calc. for $C_{45}H_{42}BF_{10}O_2PZr$ (937.8 g/mol): C 57.63, H 4.51. Found: C 56.93, H 4.52.

Decomposition point (DSC): 119 °C.

[*Comment*: compound **7a** was not stable for a prolonged time in C_7D_8 at r.t.]



^{1}H NMR (500 MHz, C_7D_8, 299 K): δ = 6.44 (d, $^4J_{PH}$ = 4.3 Hz, 4H, *m*-Mes), 5.56 (s, 10H, Cp), 2.85 (m, 2H, PCH_2), 2.01 (s, 12H, *o*-CH_3^{Mes}), 1.86 (s, 6H, *p*-CH_3^{Mes}), 1.34 (m, 2H, BCH_2), 0.72 (br, 3H, BCH_3), 0.20 (s, 3H, $ZrCH_3$).

^{13}C{^{1}H} NMR (126 MHz, C_7D_8, 299 K): δ = 168.5 (d, $^1J_{PC}$ = 103.0 Hz, C=O), 144.4 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Mes), 142.6 (d, $^2J_{PC}$ = 9.0 Hz, *o*-Mes), 132.2 (d, $^3J_{PC}$ = 11.1 Hz, *m*-Mes), 117.4 (d, $^1J_{PC}$ = 66.8 Hz, *i*-Mes), 112.5 (Cp), 34.9 ($ZrCH_3$), 29.8 (d, $^1J_{PC}$ = 29.7 Hz, PCH_2), 23.4 (d, $^3J_{PC}$ = 4.1 Hz, *o*-CH_3^{Mes}), 20.8 (br, BCH_2), 20.7 (d, $^5J_{PC}$ = 1.5 Hz, *p*-CH_3^{Mes}), 10.3 (br, BCH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, C_7D_8, 299 K) [selected traces]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 6.44 / 2.01, 1.86 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 2.85 / 1.34 (PCH_2 / BCH_2).

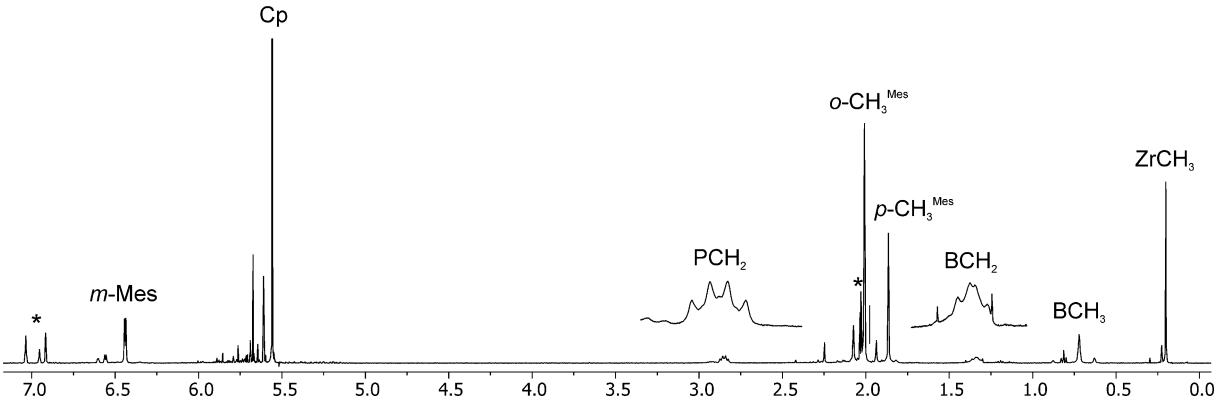
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, C_7D_8, 299 K): δ ^{1}H / δ ^{13}C = 6.44 / 132.2 (*m*-Mes), 5.56 / 112.5 (Cp), 2.85 / 29.8 (PCH_2), 2.01 / 23.4 (*o*-CH_3^{Mes}), 1.86 / 20.7 (*p*-CH_3^{Mes}), 1.34 / 20.8 (BCH_2), 0.72 / 10.3 (BCH_3), 0.20 / 34.9 ($ZrCH_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, C_7D_8, 299 K) [selected traces]: δ ^{1}H / δ ^{13}C = 6.44 / 142.6, 132.2, 117.4, 23.4, 20.7 (*m*-Mes / *o*-Mes, *m*-Mes, *i*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 1.86 / 144.4, 132.2 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes), 0.72 / 131.4, 20.8 (BCH_3 / *i*-C_6F_5, BCH_2), 0.20 / 112.5 ($ZrCH_3$ / Cp).

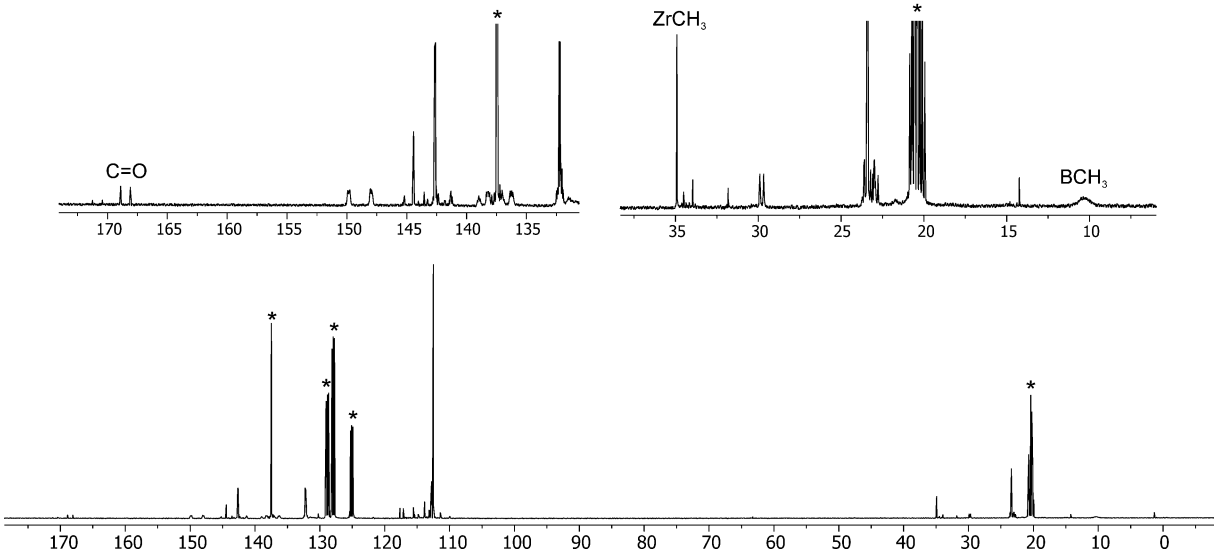
^{19}F NMR (470 MHz, C_7D_8, 299 K): δ = −132.8 (m, 2F, *o*-C_6F_5), −164.1 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), −166.0 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 1.9].

^{11}B{^{1}H} NMR (160 MHz, C_7D_8, 299 K): δ = −12.0 ($\nu_{1/2}$ ~ 140 Hz).

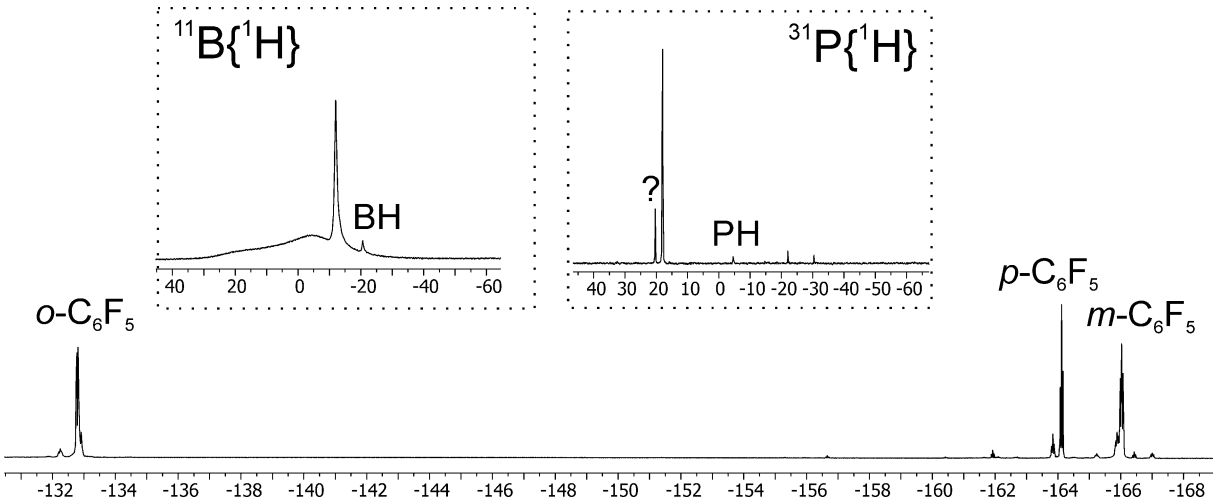
^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 299 K): δ = 18.0 ($\nu_{1/2}$ ~ 30 Hz).



^{1}H NMR (500 MHz, C_7D_8(*), 299 K) of compound **7a**.



^{13}C{^{1}H} NMR (126 MHz, C_7D_8(*), 299 K) of compound **7a.**



^{19}F NMR (470 MHz, C_7D_8, 299 K), ^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 299 K) and ^{11}B{^{1}H} NMR (160 MHz, C_7D_8, 299 K) of compound **7a** (? compound not identified yet).

Synthesis of 7b:

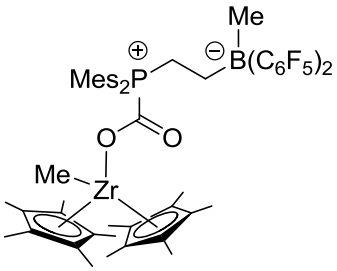
Dimesitylvinylphosphane (50.0 mg, 0.17 mmol) and bis(pentafluorophenyl)borane (58.4 mg, 0.17 mmol, 1.0 eq.) were dissolved in toluene (3 mL) and stirred for 15 minutes until a yellow solution was formed. Then $(C_5Me_5)_2ZrMe_2$ (**1b**) (66.1 mg, 0.17 mmol, 1.0 eq.) was added to give a dark yellow solution. Subsequently CO_2 gas (1.5 bar) was introduced for 5 minutes and the solution turned light yellow. After the reaction mixture was stirred for 1 hour at room temperature all volatiles were removed *in vacuo*, the resulting light yellow solid was washed with pentane (5 mL) and dried *in vacuo* to eventually give compound **7b**. Crystals suitable for X-ray single crystal structure analysis were grown from a dichloromethane solution of compound **7b** which was layered with cyclopentane and stored at −40 °C.

Yield: 161 mg (0.15 mmol, 88%). [$C_{55}H_{62}BF_{10}O_2PZr$, M = 1078.1 g/mol].

Elemental analysis: Calc. for $C_{55}H_{62}BF_{10}O_2PZr$ (1078.1 g/mol): C 61.27, H 5.80. Found: C 61.66, H 6.08.

Decomposition point (DSC): 118 °C.

[*Comment*: compound **7b** was not stable for a prolonged time in C_7D_8 at r.t.]



^{1}H NMR (500 MHz, C_7D_8, 299 K): δ = 6.48 (d, $^4J_{PH}$ = 4.0 Hz, 4H, *m*-Mes), 2.77 (m, 2H, PCH_2), 2.11 (br, 12H, *o*-CH_3^{Mes}), 1.90 (s, 6H, *p*-CH_3^{Mes}), 1.52 (s, 30H, C_5Me_5), 1.51 (br, 2H, BCH_2), 0.68 (br, 3H, BCH_3), –0.05 (s, 3H, $ZrCH_3$).

^{13}C{^{1}H} NMR (126 MHz, C_7D_8, 299 K): δ = 164.2 (d, $^1J_{PC}$ = 105.2 Hz, C=O), 144.0 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Mes), 143.5 (br d, $^2J_{PC}$ = 8.3 Hz, *o*-Mes), 132.3 (d, $^3J_{PC}$ = 11.1 Hz, *m*-Mes), 121.3 (C_5Me_5), 117.4 (d, $^1J_{PC}$ = 67.8 Hz, *i*-Mes), 41.4 ($ZrCH_3$), 29.8 (d, $^1J_{PC}$ = 25.4 Hz, PCH_2), 23.8 (d, $^3J_{PC}$ = 3.5 Hz, *o*-CH_3^{Mes}), 20.7 (*p*-CH_3^{Mes}), 20.5 (br, BCH_2), 10.9 (C_5Me_5), 10.2 (br, BCH_3), [C_6F_5 not listed].

^{1}H{^{1}H} 1D-TOCSY (500 MHz, C_7D_8, 299 K) [selected experiment]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 2.77 / 1.51 (PCH_2 / BCH_2).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, C_7D_8, 299 K) [selected trace]: δ ^{1}H / δ ^{1}H = 6.48 / 2.11, 1.90 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}).

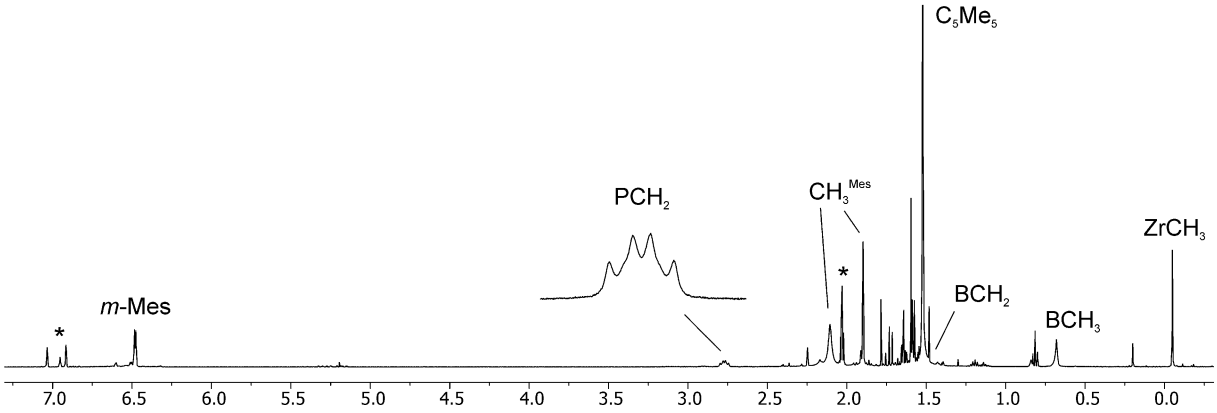
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, C_7D_8, 299 K): δ ^{1}H / δ ^{13}C = 6.48 / 132.3 (*m*-Mes), 2.77 / 29.8 (PCH_2), 2.11 / 23.8 (*o*-CH_3^{Mes}), 1.90 / 20.7 (*p*-CH_3^{Mes}), 1.52 / 10.9 (C_5Me_5), 1.51 / 20.5 (BCH_2), 0.68 / 10.2 (BCH_3), –0.05 / 41.4 ($ZrCH_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, C_7D_8, 299 K) [selected traces]: δ ^{1}H / δ ^{13}C = 6.48 / 143.5, 132.3, 117.4, 23.8, 20.7 (*m*-Mes / *o*-Mes, *m*-Mes, *i*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 1.90 / 144.0, 132.3, 117.4 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes, *i*-Mes), 0.68 / 130.8, 20.5 (BCH_3 / *i*-C_6F_5, BCH_2).

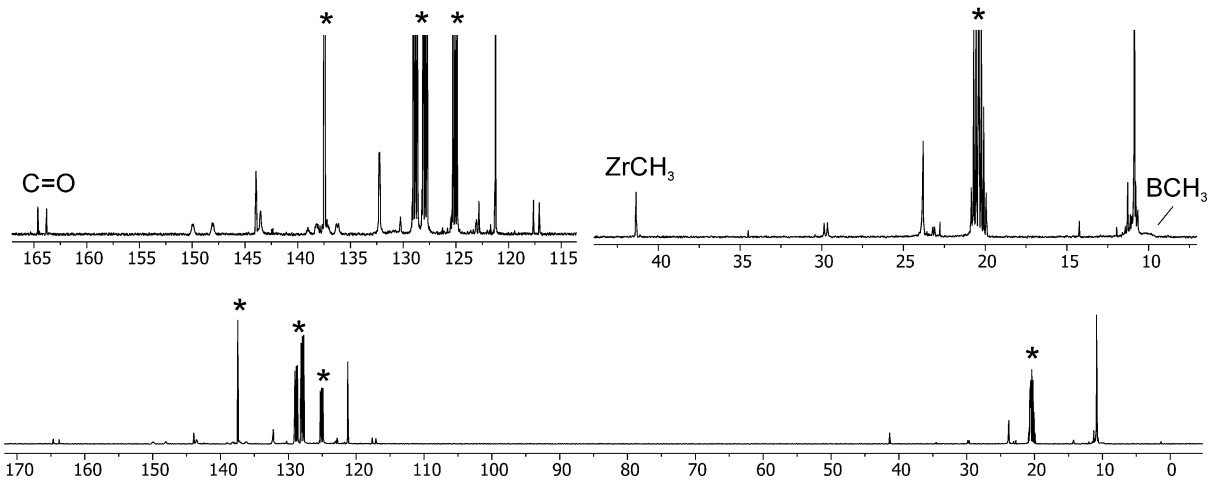
^{19}F NMR (470 MHz, C_7D_8, 299 K): δ = −132.2 (m, 2F, *o*-C_6F_5), −164.3 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), −166.1 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 1.8].

^{11}B{^{1}H} NMR (160 MHz, C_7D_8, 299 K): δ = −12.2 ($\nu_{1/2}$ ~ 180 Hz).

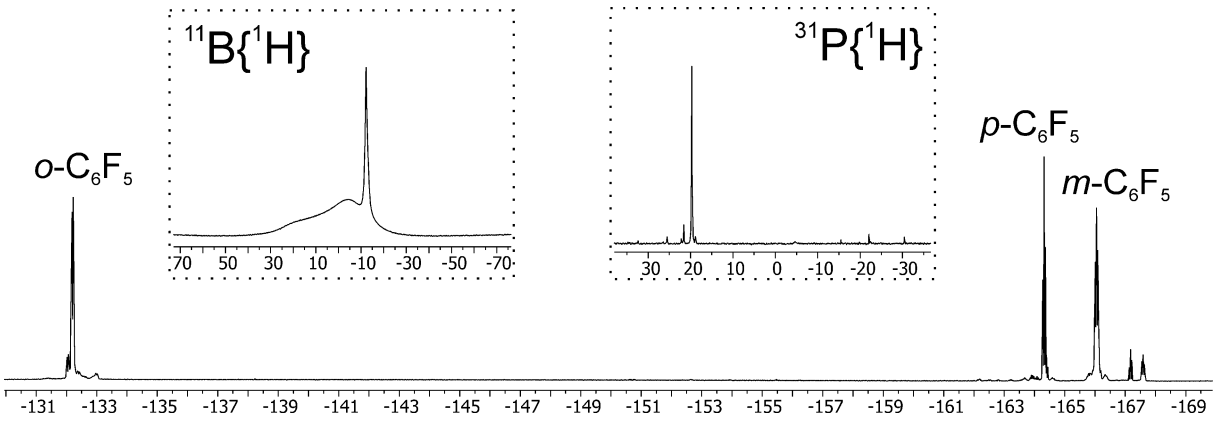
^{31}P{^{1}H} NMR (202 MHz, C_7D_8, 299 K): δ = 19.7 ($\nu_{1/2}$ ~ 20 Hz).



^{1}H NMR (500 MHz, C_7D_8(*), 299 K) of compound **7b**.

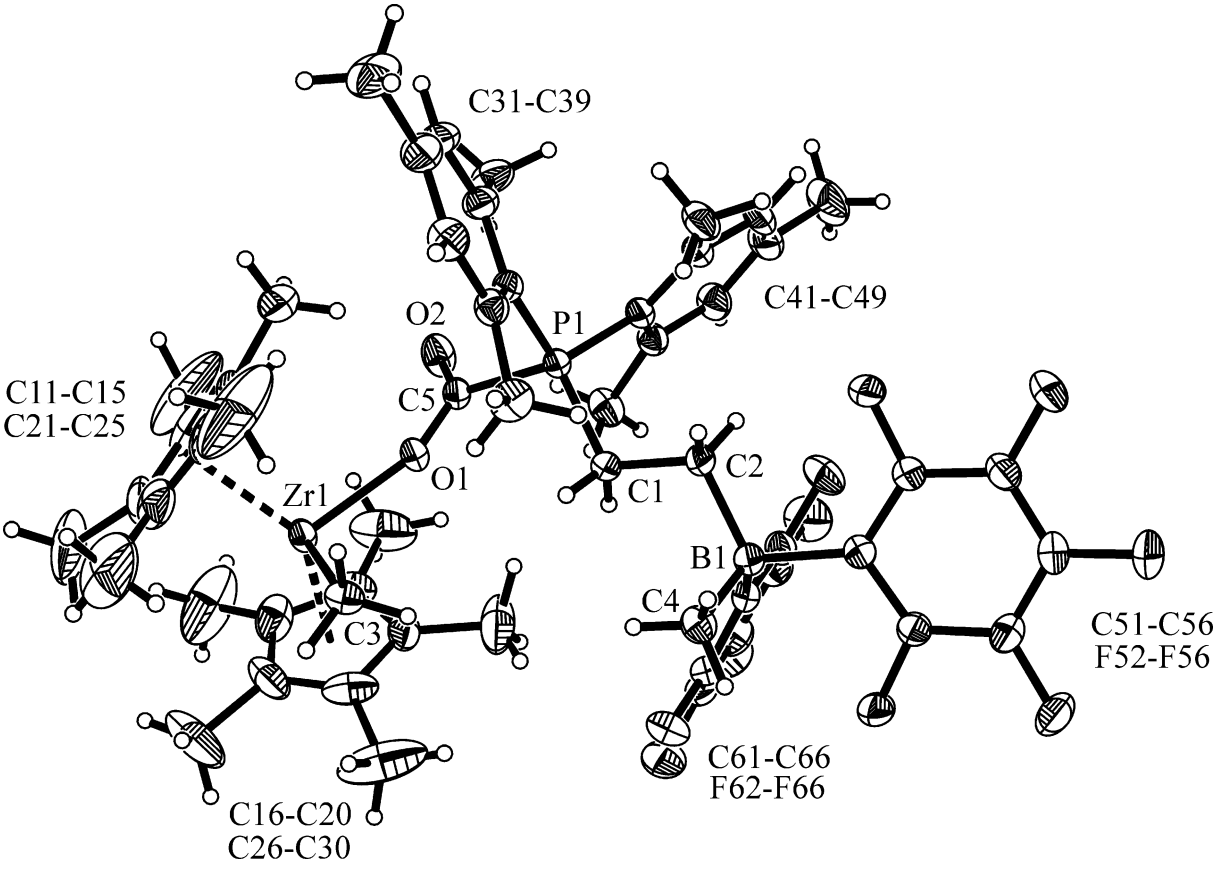


^{13}C{^{1}H} NMR (126 MHz, C_7D_8(*), 299 K) of compound **7b**.



^{19}F NMR (470 MHz, C_7D_8, 299 K), $^{31}P\{^1H\}$ NMR (202 MHz, C_7D_8, 299 K) and $^{11}B\{^1H\}$ NMR (160 MHz, C_7D_8, 299 K) of compound **7b**.

X-ray crystal structure analysis of compound 7b: formula $C_{55}H_{62}BF_{10}O_2PZr \cdot C_5H_{10}$, M = 1148.18, colourless crystal, 0.30 x 0.25 x 0.10 mm, a = 9.0108(1), b = 25.1301(4), c = 24.9895(4) Å, β = 92.989(1)°, V = 5654.4(2) Å^3, ρ_{calc} = 1.349 gcm^{-3}, μ = 0.297 mm^{-1}, empirical absorption correction ($0.916 \leq T \leq 0.970$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 54527 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 9886 independent (R_{int} = 0.052) and 8382 observed reflections [$I>2\sigma(I)$], 684 refined parameters, R = 0.053, wR^2 = 0.149, max. (min.) residual electron density 0.79 (-0.54) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



Synthesis of 8a:

Dimesitylvinylphosphane (49.5 mg, 0.17 mmol) and bis(pentafluorophenyl)borane (57.8 mg, 0.17 mmol, 1.0 eq.) were dissolved in toluene (5 mL) and stirred for 10 minutes until a yellow solution was formed. Then Cp_2ZrMe_2 (**1a**) (42.0 mg, 0.17 mmol, 1.0 eq.) was added to give an orange solution. Then *p*-tolyl isocyanate (24.5 mg, 23.2 µL, 0.18 mmol, 1.1 eq.) was added and the solution turned yellow immediately. After *ca*. 2 minutes a white solid began to precipitate. After 30 minutes of stirring the reaction mixture all volatiles were removed *in vacuo* and the obtained residue was dissolved in dichloromethane (5 mL). This solution was layered with heptane (10 mL) and kept at −32 °C overnight. The resulting white precipitate was separated from the light yellow solution *via* syringe and was dried *in vacuo* to yield a mixture of two isomers tentatively assigned as **8a** (N-inside) and **8a** (N-outside) in a ratio of ca. 2 : 1.

Crystals suitable for X-ray single crystal structure analysis of the isomer **8a** (N-inside) were obtained by slow concentration of a solution of the ca. 2 : 1 mixture of the isomers **8a** (N-inside) : **8a** (N-outside) in deuterated dichloromethane at room temperature.

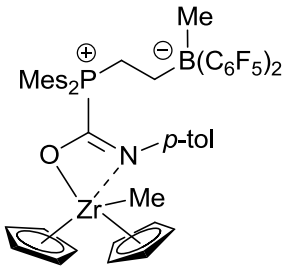
Yield: 147 mg (0.14 mmol, 85%). [$C_{52}H_{49}BF_{10}NOPZr$, M = 1027.0 g/mol].

Melting point (DSC): 129 °C.

Decomposition point (DSC): 136 °C.

$^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 273 K): δ = −12.7 ($\nu_{1/2}$ ~ 140 Hz).

8a (N-inside) [major isomer]:



^1H NMR (500 MHz, CD_2Cl_2, 273 K): δ = 7.30 (m, 2H, *m*-Tol), 7.04 (d, $^4J_{PH}$ = 3.8 Hz, 4H, *m*-Mes), 6.66 (m, 2H, *o*-Tol), 5.62 (s, 10H, Cp), 2.74 (m, 2H, PCH_2), 2.43 (s, 3H, $^{Tol}CH_3$), 2.35 (s, 6H, *p*-CH_3^{Mes}), 2.24 (s, 12H, *o*-CH_3^{Mes}), 0.85 (m, 2H, BCH_2), 0.04 (br, 3H, BCH_3), −0.12 (s, 3H, $ZrCH_3$).

$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 273 K): δ = 155.9 (d, $^1J_{PC}$ = 138.6 Hz, OCN), 144.2 (d, $^4J_{PC}$ = 1.7 Hz, *p*-Mes), 143.2 (d, $^3J_{PC}$ = 20.3 Hz, *i*-Tol), 142.9 (d, $^2J_{PC}$ = 9.8 Hz, *o*-Mes), 134.6 (*p*-Tol), 132.2 (d, $^3J_{PC}$ = 11.2 Hz, *m*-Mes), 130.1 (*m*-Tol), 120.4 (*o*-Tol), 117.8 (d, $^1J_{PC}$ = 71.7 Hz, *i*-Mes), 112.3 (Cp), 31.6 ($ZrCH_3$), 29.5 (dm, $^1J_{PC}$ = 35.4 Hz, PCH_2), 23.9 (d, $^3J_{PC}$ = 3.2 Hz, *o*-CH_3^{Mes}), 21.1 (*p*-CH_3^{Mes}), 21.0 ($^{Tol}CH_3$), 20.4 (br, BCH_2), 9.3 (br, BCH_3)^t, [C_6F_5 not listed; ^{t} tentatively assigned].

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, CD_2Cl_2, 273 K) [selected traces]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.30 / 6.66, 2.43 (*m*-Tol / *o*-Tol, $^{Tol}CH_3$), 7.04 / 2.35, 2.24 (*m*-Mes / *p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 2.74 / 0.85 (PCH_2 / BCH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, CD_2Cl_2, 273 K): δ ^{1}H / δ ^{13}C = 7.30 / 130.1 (*m*-Tol), 7.04 / 132.2 (*m*-Mes), 6.66 / 120.4 (*o*-Tol), 5.62 / 112.3 (Cp), 2.74 / 29.5 (PCH_2), 2.43 / 21.0 ($^{Tol}CH_3$), 2.35 / 21.1 (*p*-CH_3^{Mes}), 2.24 / 23.9 (*o*-CH_3^{Mes}), 0.85 / 20.4 (BCH_2), –0.12 / 31.6 ($ZrCH_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, CD_2Cl_2, 273 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.30 / 143.2, 130.1, 21.0 (*m*-Tol / *i*-Tol, *m*-Tol, $^{Tol}CH_3$), 7.04 / 132.2, 117.8, 23.9, 21.1 (*m*-Mes / *m*-Mes, *i*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 6.66 / 134.6, 120.4 (*o*-Tol / *p*-Tol, *o*-Tol), 2.35 / 144.2, 132.2 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes), 2.24 / 142.9, 132.2, 117.8 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes), 0.04 / 130.8, 20.4 (BCH_3 / *i*-C_6F_5, BCH_2).
^{19}F NMR (470 MHz, CD_2Cl_2, 273 K): δ = −133.8 (m, 2F, *o*-C_6F_5), −165.2 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), −167.1 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 1.9].

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 273 K): δ = 23.4 ($\nu_{1/2}$ ~ 30 Hz).

8a (N-outside) [minor isomer]:

^{1}H NMR (500 MHz, CD_2Cl_2, 273 K): δ = 7.02 (d, $^{4}J_{PH}$ = 4.2 Hz, 4H, *m*-Mes), 6.96 (m, 2H, *m*-Tol), 6.29 (br m, 2H, *o*-Tol), 5.88 (s, 10H, Cp), 2.36 (s, 6H, *p*-CH_3^{Mes})^{t}, 2.28 (s, 3H, $^{Tol}CH_3$), 2.14 (m, 2H, PCH_2), 2.11 (br, 12H, *o*-CH_3^{Mes}), 0.88 (br, 2H, BCH_2), –0.09 (br, 3H, BCH_3), –0.44 (br, 3H, $ZrCH_3$), [^{t} tentatively assigned].

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 273 K): δ = 144.8 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-Mes)^{t}, 136.6 (*p*-Tol), 132.4 (d, $^{3}J_{PC}$ = 11.5 Hz, *m*-Mes), 129.6 (*m*-Tol), 125.0 (*o*-Tol), 110.7 (Cp), 32.8 ($ZrCH_3$), 30.4 (d, $^{1}J_{PC}$ = 24.2 Hz, PCH_2), 23.7 (br d, $^{3}J_{PC}$ = 3.2 Hz, *o*-CH_3^{Mes}), 22.2 (*p*-CH_3^{Mes}), 20.8 (BCH_2)^{t}, 20.5 ($^{Tol}CH_3$), 9.3 (br, BCH_3)^{t}, n.o. (OCN, *i*-Tol, *o*-Mes, *i*-Mes), [C_6F_5 not listed; ^{t} tentatively assigned].

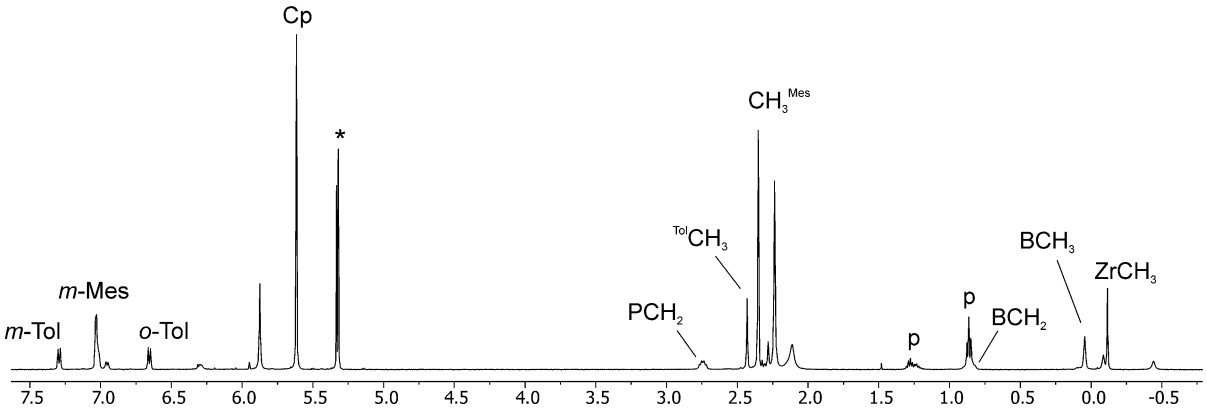
^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, CD_2Cl_2, 273 K) [selected traces]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.96 / 6.29, 2.28 (*m*-Tol / *o*-Tol, $^{Tol}CH_3$), 2.14 / 0.88 (PCH_2 / BCH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, CD_2Cl_2, 273 K): δ ^{1}H / δ ^{13}C = 7.02 / 132.4 (*m*-Mes), 6.96 / 129.6 (*m*-Tol), 6.29 / 125.0 (*o*-Tol), 5.88 / 110.7 (Cp), 2.36 / 22.2 (*p*-CH_3^{Mes}), 2.28 / 20.5 ($^{Tol}CH_3$), 2.14 / 30.4 (PCH_2), 2.11 / 23.7 (*o*-CH_3^{Mes}), –0.44 / 32.8 ($ZrCH_3$).

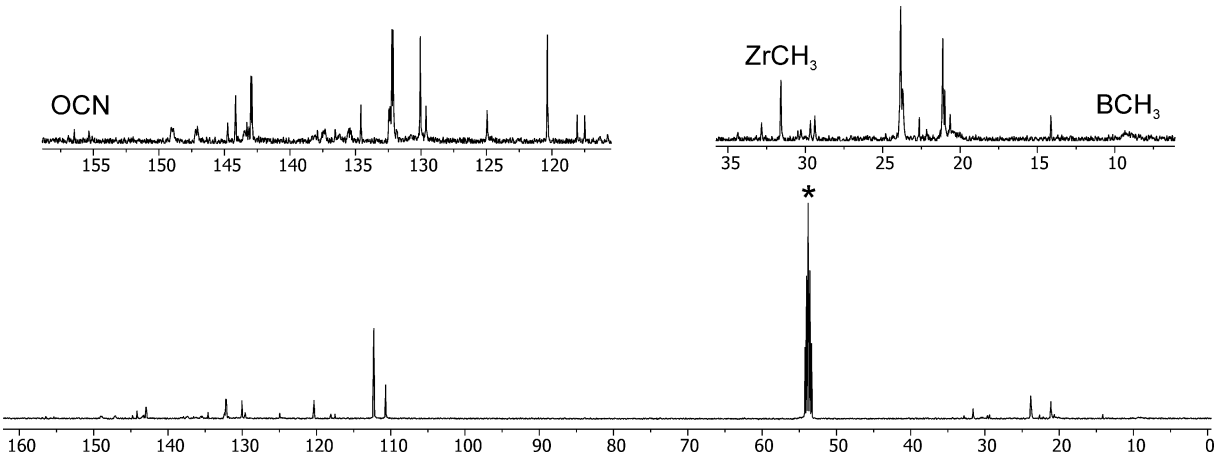
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, CD_2Cl_2, 273 K) [selected trace]: δ ^{1}H / δ ^{13}C = 2.28 / 136.6, 129.6 ($^{Tol}CH_3$ / *p*-Tol, *m*-Tol).

^{19}F NMR (470 MHz, CD_2Cl_2, 273 K): δ = −133.5 (m, 2F, *o*-C_6F_5), −164.6 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), −166.7 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 2.1].

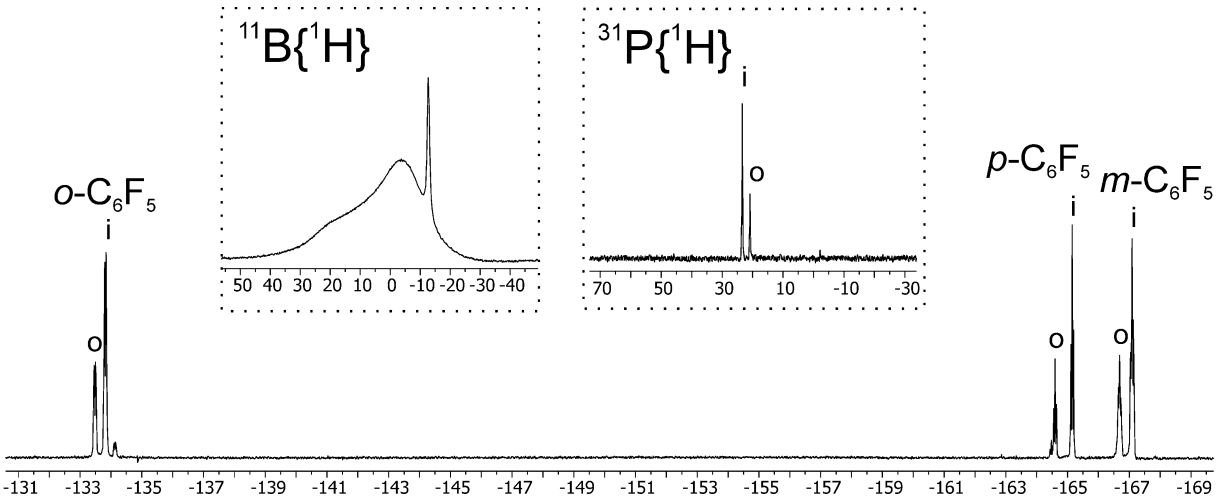
^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 273 K): δ = 20.9 ($\nu_{1/2}$ ~ 35 Hz).



^{1}H NMR (500 MHz, CD_2Cl_2(*), 273 K) of a mixture of isomers of **8a** (p = pentane) (signals of the **8a (N-inside)** isomer are assigned).



^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2(*), 273 K) of a mixture of isomers of **8a** (signals of the **8a (N-inside)** isomer are assigned).



^{19}F NMR (470 MHz, CD_2Cl_2, 273 K), $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 273 K) and $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 273 K) of a mixture of isomers of **8a** (i: N-inside; o: N-outside).

X-ray crystal structure analysis of compound 8a (N-inside): formula $C_{52}H_{49}BF_{10}NOPZr \cdot CH_2Cl_2$, M = 1111.85, colourless crystal, 0.17 x 0.15 x 0.05 mm, a = 18.2150(2), b = 12.6017(2), c = 22.4162(3) Å, β = 100.989(1)°, V = 5051.1(1) Å^3, ρ_{calc} = 1.462 gcm^{-3}, μ = 0.432 mm^{-1}, empirical absorption correction (0.930 ≤ T ≤ 0.978), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 30888 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 8742 independent (R_{int} = 0.042) and 7126 observed reflections [I>2σ(I)], 777 refined parameters, R = 0.052, wR^2 = 0.127, max. (min.) residual electron density 0.74 (-0.42) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.