Electronic Supplementary Material (ESI) for Chemical Communications

Reactions of methylzirconocene cation with Phosphinoalkynes: An alternative pathway for generating $Cp_2Zr(II)$ systems

Xin Xu, Roland Fröhlich,[$] Constantin. G. Daniliuc,[$] Gerald Kehr, Gerhard Erker*

Organisch-Chemisches Institut, Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

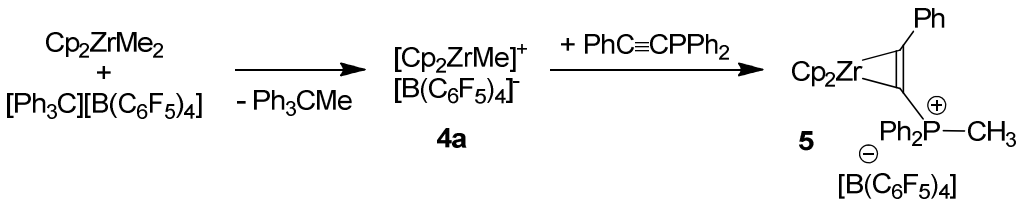
Supporting Information

General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on a Varian 600 MHz UNITY plus, a Bruker AV400, a Bruker DPX300 and a Bruker AC200 NMR spectrometer. Chemical shifts are given in ppm relative to solvents (^{1}H and ^{13}C; $\delta(SiMe_4) = 0$) or an external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR]. Elemental analysis data was recorded on Foss-Heraeus CHNO-Rapid. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series). X-ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); 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). Thermal ellipsoids are shown with 50% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For the compound **6** one dichloromethane molecule disordered over two positions was found in the asymmetric unit. Several restraints (SADI, SAME and SIMU) were used in order to improve refinement stability. Compound **9** present two dichloromethane molecules in the asymmetric unit. The carbon and chlorine atoms displayed irregular displacement ellipsoids, which were therefore constrained to be more regular using the program commands ISOR and SADI. For the compound **10** one cyclopentane molecule was found in the asymmetric unit. The carbon atoms of this cyclopentane molecule and of the phenyl group attached to the C2 atom displayed irregular displacement ellipsoids, which were therefore constrained to be more regular using the program command ISOR. CCDC reference numbers 871479 to 871481.

Materials: Dimethylzirconocene (Cp_2ZrMe_2) [Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263-6267.], Dimethylpermethylzirconocene ($(C_5Me_5)_2ZrMe_2$)

[Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716-2724.], Triphenylcarbenium tetrakis(pentafluorophenyl)borate ($[Ph_3C][B(C_6F_5)_4]$) [Ihara, E.; Young, Jr., V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277-8278.], Diphenyl(phenylethynyl)phosphane [Miller, A. D.; Johnson, S. A.; Tupper, K. A.; McBee, J. L.; Tilley, T. D. *Organometallics* **2009**, *28*, 1252-1262.], Diphenyl(3-methyl-3-en-1-butynyl)phosphane (**7**) [Chattha, M. S. *J. Chem. Eng. Data.* **1978**, *23*, 95-96.].

NMR reaction of $[Cp_2ZrMe]^+[B(C_6F_5)_4]^-$ (4a) with phenyl-diphenylphosphanyl acetylene (7a):



Cp_2ZrMe_2 (5.0 mg, 20 µmol) and $[Ph_3C][B(C_6F_5)_4]$ (18.4 mg, 20 µmol) were mixed in C_6D_5Br (0.3 mL). After standing in the fridge (*ca*. -30°C) for 5 min, the mixture was added to a solution of the respective alkyne **7a** (5.7 mg, 20 µmol) in C_6D_5Br (0.2 mL). The color of the reaction mixture changed into pale yellow immediately.

Data of Ph_3CMe:

^{1}H NMR (600 MHz, C_6D_5Br, 299 K): δ = 7.14 (m, 6H, *m*-Ph), 7.10 (m, 3H, *p*-Ph), 7.07 (m, 6H, *o*-Ph), 2.04 (s, 3H, Me).

^{13}C{^{1}H} NMR (151 MHz, C_6D_5Br, 299 K): δ = 149.2 (*i*-Ph), 128.9 (*o*-Ph), 128.1 (*m*-Ph), 126.1 (*p*-Ph), 52.7 (Ph_3C), 30.6 (Me).

*Data of complex **5**:*

^{1}H NMR (600 MHz, C_6D_5Br, 299 K): δ = 7.37 (m, 2H, *p*-Ph_2P), 7.28 (m, 4H, *m*-Ph_2P), 7.20 (m, 4H, *o*-Ph_2P), 7.11 (m, 2H, *m*-Ph), 7.02 (m, 1H, *p*-Ph), 6.68 (m, 2H, *o*-Ph), 5.59 (s, 10H, Cp), 1.75 (d, $^2J_{PH}$ = 12.7 Hz, 3H, Me).

$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_5Br, 299 K): δ = 233.6 (d, $^{2}J_{PC}$ = 30.2 Hz, PhC=), 148.8 (dm, $^{1}J_{FC}$ ~ 242 Hz, *o*-B(C_6F_5)$_4$), 144.0 (d, $^{3}J_{PC}$ = 10.0 Hz, *i*-Ph), 138.5 (dm, $^{1}J_{FC}$ ~ 244 Hz, *p*-B(C_6F_5)$_4$), 136.7 (dm, $^{1}J_{FC}$ ~ 247 Hz, *m*-B(C_6F_5)$_4$), 133.9 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-Ph_2P), 132.6 (d, $^{1}J_{PC}$ = 7.2 Hz, =CP), 131.5 (d, $^{2}J_{PC}$ = 9.9 Hz, *o*-Ph_2P), 129.9 (d, $^{3}J_{PC}$ = 12.0 Hz, *m*-Ph_2P), 128.7 (*m*-Ph), 127.1 (*p*-Ph), 124.8 (br, *i*-B(C_6F_5)$_4$), 124.1 (d, $^{1}J_{PC}$ = 84.8 Hz, *i*-Ph_2P), 123.5 (d, $^{4}J_{PC}$ = 2.0 Hz, *o*-Ph), 108.7 (Cp), 11.7 (d, $^{1}J_{PC}$ = 59.0 Hz, Me).

$^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_5Br, 299 K): δ = 13.3 ($\nu_{1/2}$ ~ 1 Hz).

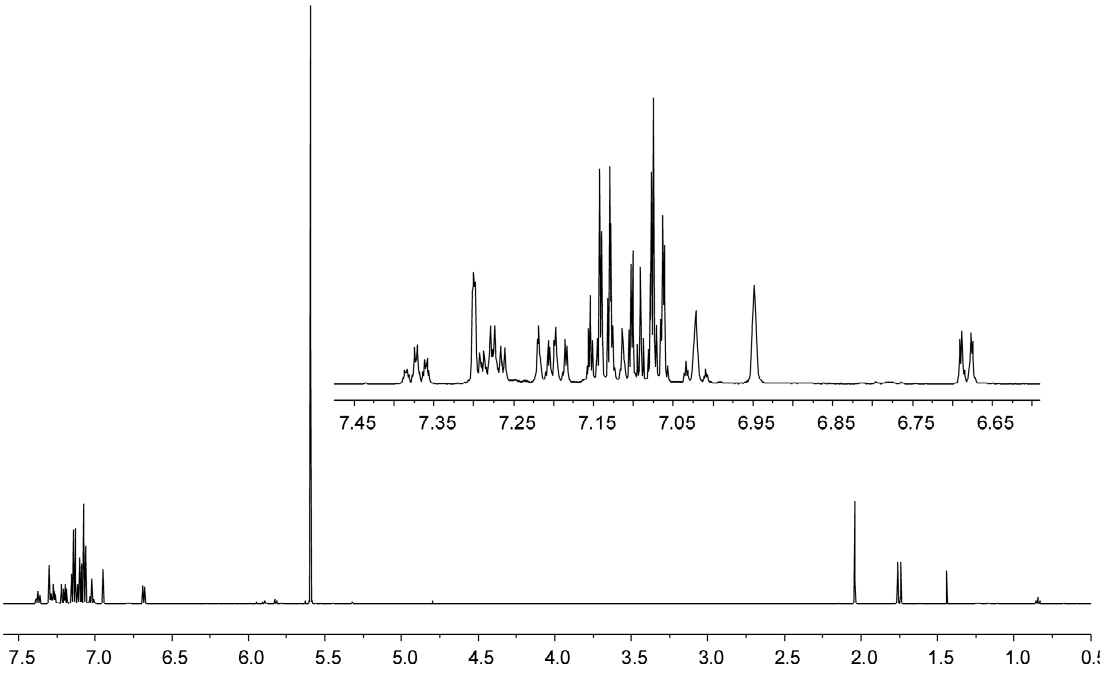
^{19}F NMR (564 MHz, C_6D_5Br, 299 K): δ = -131.4 (br, 2F, *o*-B(C_6F_5)$_4$), -161.8 (t, $^{3}J_{FF}$ = 21.1 Hz, 1F, *p*-B(C_6F_5)$_4$), -165.6 (m, 2F, *m*-B(C_6F_5)$_4$).

$^{11}B\{^{1}H\}$ NMR (192 MHz, C_6D_5Br, 299 K): δ = -15.9 ($\nu_{1/2}$ ~ 20 Hz).

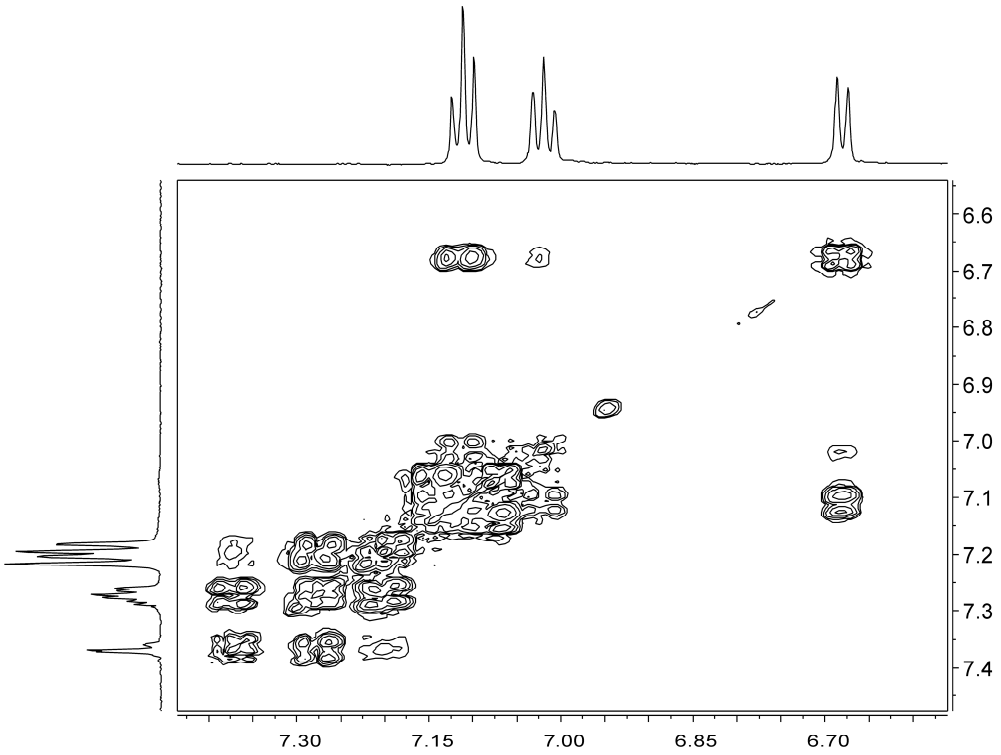
^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, C_6D_5Br, 299 K): $\delta^{1}H$ / $\delta^{1}H$ = 7.37 / 7.28 (*p*-Ph_2P / *m*-Ph_2P), 7.28 / 7.37, 7.20 (*m*-Ph_2P/ *p*-Ph_2P, *o*-Ph_2P), 7.20 / 7.28 (*o*-Ph_2P / *m*-Ph_2P), 7.11 / 7.02, 6.68 (*m*-Ph / *p*-Ph, *o*-Ph), 7.02 / 7.11 (*p*-Ph / *m*-Ph), 6.68 / 7.11 (*o*-Ph / *m*-Ph).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, C_6D_5Br, 299 K): $\delta^{1}H$ / $\delta^{13}C$ = 7.37 / 133.9 (*p*-Ph_2P), 7.28 / 129.9 (*m*-Ph_2P), 7.20 / 131.5 (*o*-Ph_2P), 7.11 / 128.7 (*m*-Ph), 7.02 / 127.1 (*p*-Ph), 6.68 / 123.5 (*o*-Ph), 5.59 / 108.7 (Cp), 1.75 / 11.7 (Me).

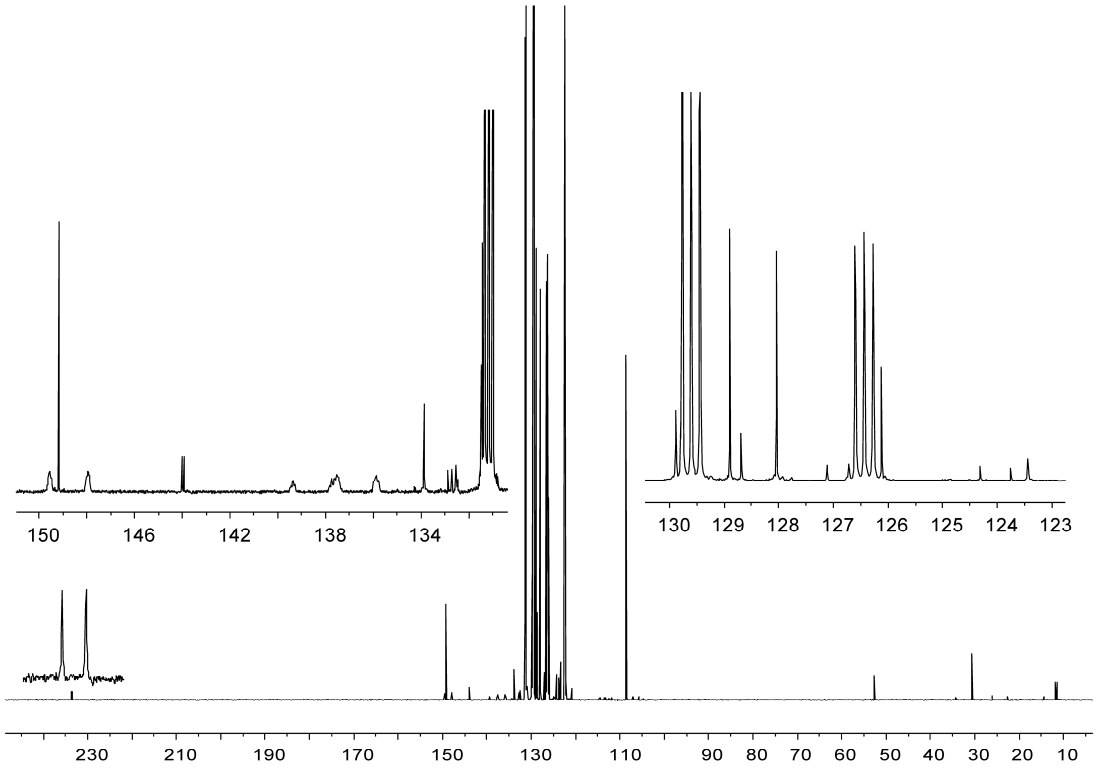
^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, C_6D_5Br, 299 K): $\delta^{1}H$ / $\delta^{13}C$ = 7.37 / 131.5 (*p*-Ph_2P / *o*-Ph_2P), 7.28 / 129.9, 124.1 (*m*-Ph_2P / *m*-Ph_2P, *i*-Ph_2P), 7.20 / 133.9, 131.5 (*o*-Ph_2P / *p*-Ph_2P, *o*-Ph_2P), 7.11 / 144.0, 128.7 (*m*-Ph / *i*-Ph, *m*-Ph), 7.02 / 123.5 (*p*-Ph / *o*-Ph), 6.68 / 233.6, 127.1, 123.5 (*o*-Ph / PhC=, *p*-Ph, *o*-Ph), 5.59 / 108.7 (Cp / Cp), 1.75 / 132.6, 124.1 (Me / =CP, *i*-Ph_2P).



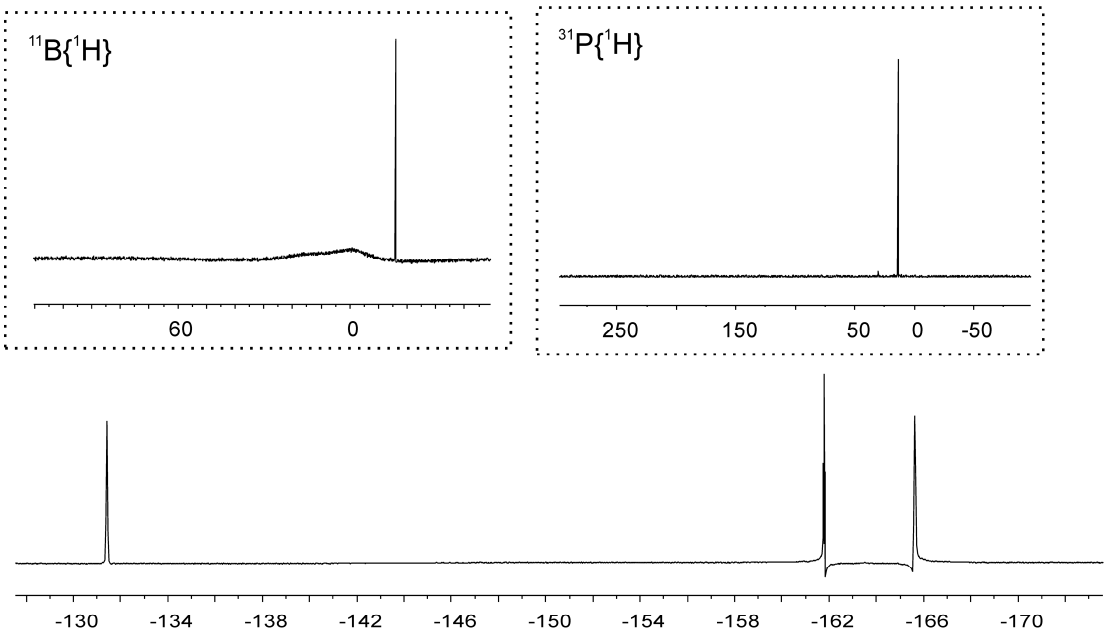
^{1}H NMR (600 MHz, C_6D_5Br, 299 K)



^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, C_6D_5Br, 299 K) [projections ^{1}H tocsy (600 MHz, C_6D_5Br, 299 K): irradiation: δ^{1}H (f1): 7.37 (*p*-Ph_2P), δ^{1}H (f2): 6.68 (*o*-Ph)]

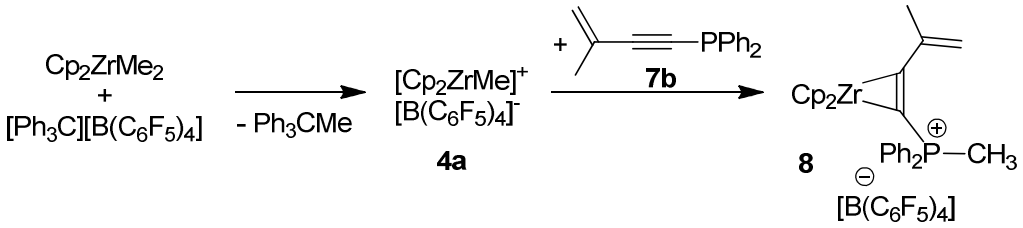


$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_5Br, 299 K)



^{19}F NMR (564 MHz, C_6D_5Br, 299 K), **$^{11}B\{^{1}H\}$ NMR** (192 MHz, C_6D_5Br, 299 K) and **$^{31}P\{^{1}H\}$ NMR** (243 MHz, C_6D_5Br, 299 K)

NMR reaction of $[Cp_2ZrMe]^+[B(C_6F_5)_4]^-$ (4a) with 3-methyl-1-diphenyl-phosphanylbut-3-en-1-yne (7b):



According to the procedure of the *in situ* preparation of complex **5**, the reaction of Cp_2ZrMe_2 (5.0 mg, 20 µmol), $[Ph_3C][B(C_6F_5)_4]$ (18.4 mg, 20 µmol) and enyne **7b** (5.3 mg, 20 µmol) in C_6D_5Br was carried out in an NMR scale to characterize complex **8**. (Comment: complex **8** was not stable at room temperature, so the NMR data were collected at -20°C).

Data of Ph_3CMe:

^{1}H NMR (600 MHz, C_6D_5Br, 253 K): δ = 7.15 (m, 6H, *m*-Ph), 7.11 (m, 3H, *p*-Ph), 7.05 (m, 6H, *o*-Ph), 2.02 (s, 3H, Me).

^{13}C{^{1}H} NMR (151 MHz, C_6D_5Br, 253 K): δ = 149.0 (*i*-Ph), 128.8 (*o*-Ph), 128.0 (*m*-Ph), 126.1 (*p*-Ph), 52.4 (Ph_3C), 30.4 (Me).

*Data of complex **8**:*

^{1}H NMR (600 MHz, C_6D_5Br, 253 K): δ = 7.40 (m, 2H, *p*-Ph_2P), 7.32 (m, 4H, *m*-Ph_2P), 7.19 (m, 4H, *o*-Ph_2P), 5.53 (s, 10H, Cp), 4.26 (br, 1H, $=CH_2^E$), 4.00 (br, 1H, $=CH_2^Z$), 1.83 (d, $^2J_{PH}$ = 12.8 Hz, 3H, MeP), 1.67 (br, 3H, $CH_3C=$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_5Br, 253 K): δ = 234.6 (d, $^2J_{PC}$ = 30.0 Hz, ZrC=), 148.8 (d, $^3J_{PC}$ = 10.2 Hz, =CMe), 148.7 (dm, $^1J_{FC}$ ~ 245 Hz, *o*-$B(C_6F_5)_4$), 138.2 (dm, $^1J_{FC}$ ~ 247 Hz, *p*-$B(C_6F_5)_4$), 136.4 (dm, $^1J_{FC}$ ~ 245 Hz, *m*-$B(C_6F_5)_4$), 133.7 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Ph_2P), 131.3 (d, $^2J_{PC}$ = 10.3 Hz, *o*-Ph_2P), 129.7 (d, $^3J_{PC}$ = 12.0 Hz, *m*-Ph_2P), 128.0 (d, $^1J_{PC}$ = 23.8 Hz, =CP), n.o. (*i*-$B(C_6F_5)_4$), 124.0 (d, $^1J_{PC}$ = 85.6 Hz, *i*-Ph_2P), 108.3 (Cp), 105.0 (br, $=CH_2$), 22.2 (d, $^4J_{PC}$ = 1.2 Hz, $CH_3C=$), 10.8 (d, $^1J_{PC}$ = 56.3 Hz, MeP).

^{31}P{^{1}H} NMR (243 MHz, C_6D_5Br, 253 K): δ = 14.2 ($\nu_{1/2}$ ~ 2 Hz).

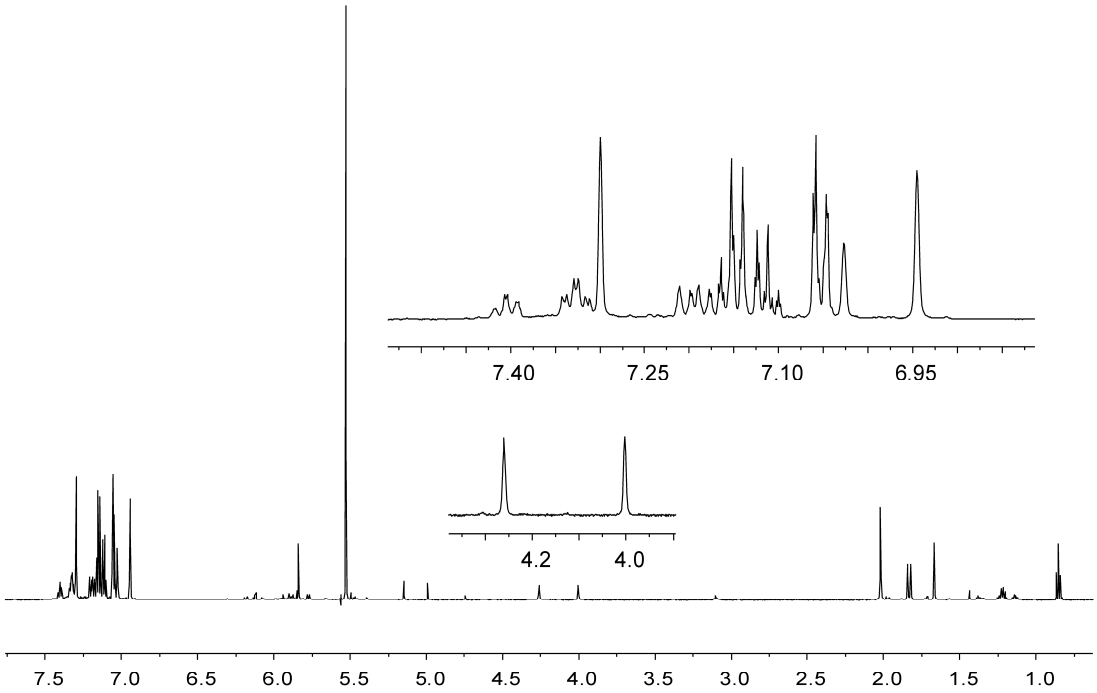
^{19}F NMR (564 MHz, C_6D_5Br, 253 K): δ = -131.6 (br, 2F, *o*-$B(C_6F_5)_4$), -161.2 (br, 1F, *p*-$B(C_6F_5)_4$), -165.1 (br, 2F, *m*-$B(C_6F_5)_4$).

^{11}B{^{1}H} NMR (192 MHz, C_6D_5Br, 253 K): δ = -16.0 ($\nu_{1/2}$ ~ 25 Hz).

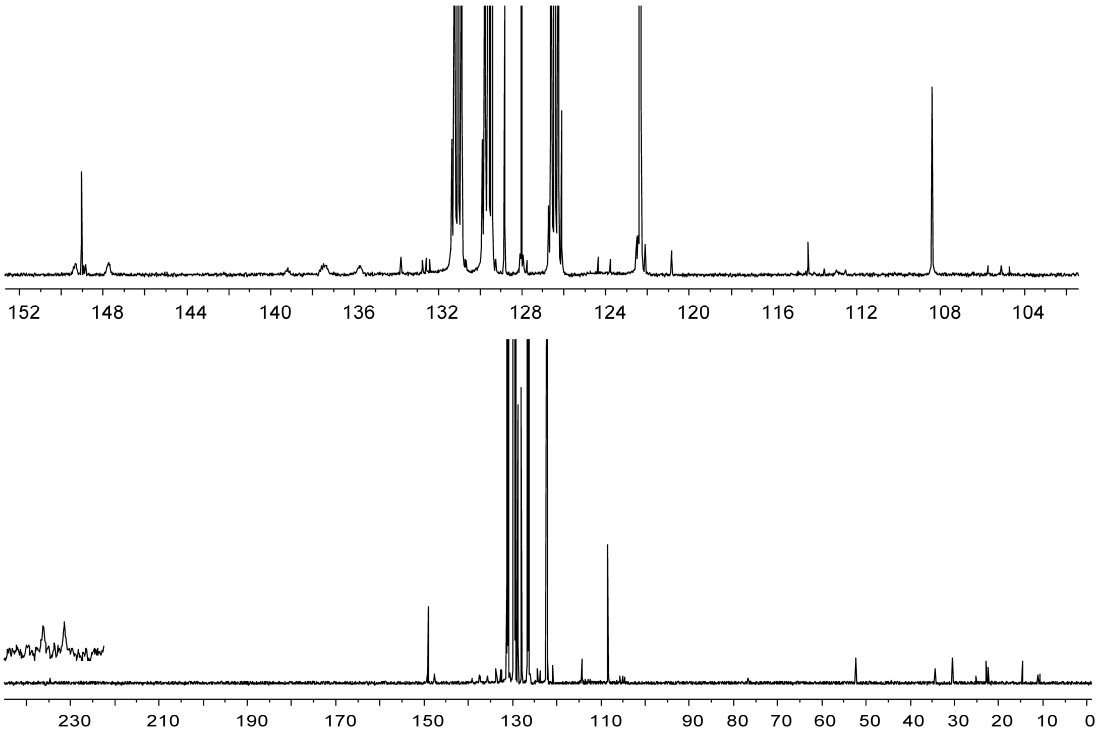
^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, C_6D_5Br, 253 K): δ^1H / δ^1H = 7.40 / 7.32 (*p*-Ph_2P / *m*-Ph_2P), 7.32 / 7.40, 7.19 (*m*-Ph_2P / *p*-Ph_2P, *o*-Ph_2P), 7.19 / 7.32 (*o*-Ph_2P / *m*-Ph_2P), 4.26 / 4.00, 1.67 (=CH_2^E / =CH_2^Z, CH_3C=), 4.00 / 4.26, 1.67 (=CH_2^Z / =CH_2^E, CH_3C=), 1.67 / 4.26, 4.00 (CH_3C= / =CH_2).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, C_6D_5Br, 253 K): δ^1H / δ^{13}C = 7.40 / 133.7 (*p*-Ph_2P), 7.32 / 129.7 (*m*-Ph_2P), 7.19 / 131.3 (*o*-Ph_2P), 5.53 / 108.3 (Cp), 4.26, 4.00 / 105.0 (=CH_2), 1.83 / 10.8 (MeP), 1.67 / 22.2 (CH_3C=).

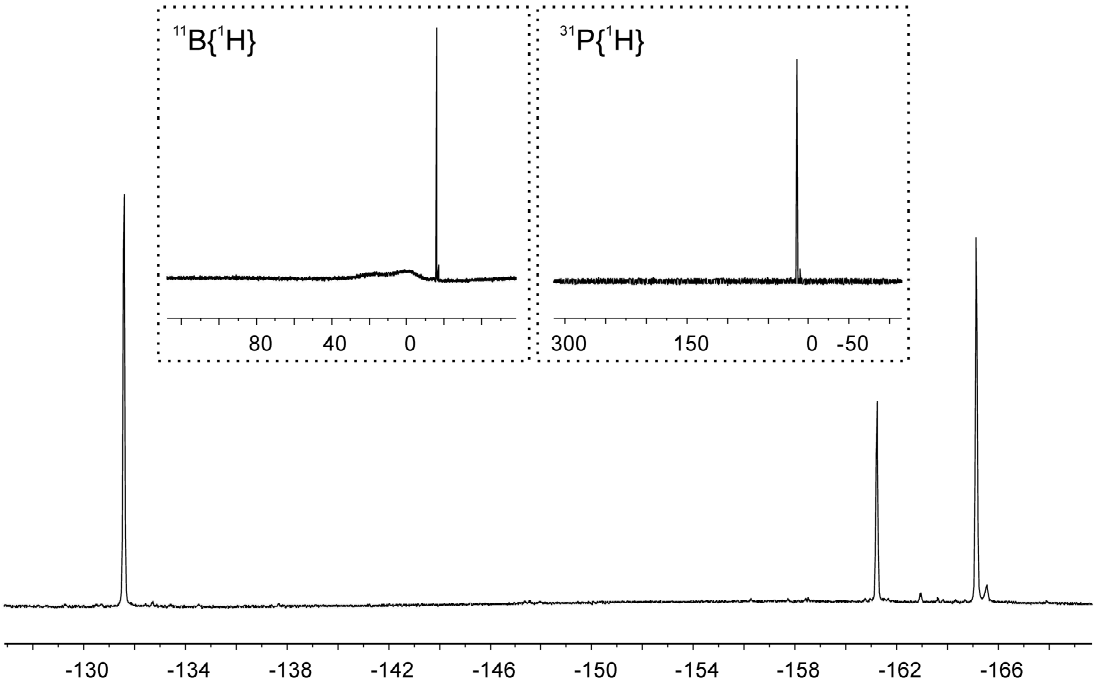
^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, C_6D_5Br, 253 K): δ^1H / δ^{13}C = 7.40 / 131.3 (*p*-Ph_2P / *o*-Ph_2P), 7.32 / 131.3, 129.7, 124.0 (*m*-Ph_2P / *o*-Ph_2P, *m*-Ph_2P, *i*-Ph_2P), 7.19 / 133.7, 131.3 (*o*-Ph_2P / *p*-Ph_2P, *o*-Ph_2P), 5.53 / 108.3 (Cp / Cp), 4.26, 4.00 / 22.2 (=CH_2 / CH_3C=), 1.83 / 128.0, 124.0 (MeP / =CP, *i*-Ph_2P), 1.67 / 148.8, 105.0 (CH_3C= / =CMe, =CH_2).



^{1}H NMR (600 MHz, C_6D_5Br, 253 K)

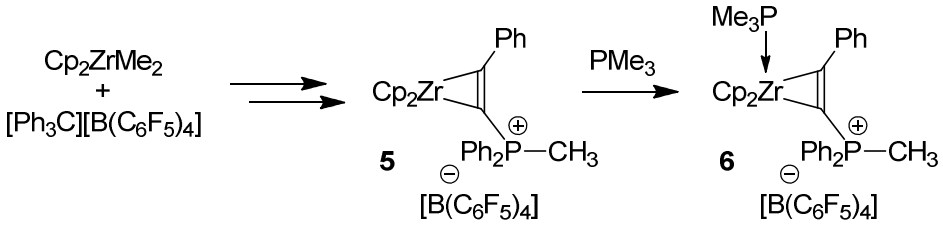


^{13}C{^{1}H} NMR (151 MHz, C_6D_5Br, 253 K)



^{19}F NMR (564 MHz, C_6D_5Br, 253 K), **^{11}B{^{1}H} NMR** (192 MHz, C_6D_5Br, 253 K) and **^{31}P{^{1}H} NMR** (243 MHz, C_6D_5Br, 253 K)

Preparation of the Me_3P stabilized zirconacyclopropene complex 6:



According to the procedure of the *in situ* preparation of complex **5**, Cp_2ZrMe_2 (20.0 mg, 80 µmol) and $[Ph_3C][B(C_6F_5)_4]$ (73.8 mg, 80 µmol) were mixed in 1.0 mL of C_6H_5Br. After standing in the fridge (*ca*. -30°C) for 5 min, the mixture was added to a solution of phenyl-diphenylphosphanyl acetylene (**7a**) (22.9 mg, 80 µmol) in 0.5 mL of C_6H_5Br. After another 1 h, excess of Me_3P (18.3 mg, 240 µmol) was added to the reaction mixture, which then was covered with pentane (3 mL). A beige oil formed overnight. It was crystallized by a two layer procedure using a solution of CH_2Cl_2 and **6** covered by cyclopentane (*ca*. 1:3) to give complex **6** as a pale yellow crystalline solid (82 mg, 76% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at room temperature.

Elemental Analysis: calcd. for $C_{58}H_{37}BF_{20}P_2Zr \cdot CH_2Cl_2$: C, 52.00; H, 2.88. Found: C, 51.99; H, 3.38.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.75 (m, 2H, *p*-Ph_2P), 7.64 (m, 4H, *m*-Ph_2P), 7.57 (m, 4H, *o*-Ph_2P), 7.21 (m, 2H, *m*-Ph), 7.03 (m, 1H, *p*-Ph), 6.58 (m, 2H, *o*-Ph), 5.50 (d, $^3J_{PH}$ = 1.9 Hz, 10H, Cp), 1.99 (d, $^2J_{PH}$ = 12.9 Hz, 3H, MeP), 1.31 (d, $^2J_{PH}$ = 6.9 Hz, 9H, Me_3P).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 213.0 (dd, $^2J_{PC}$ = 31.3 Hz, $^2J_{PC}$ = 20.5 Hz, =CZr), 149.3 (d, $^3J_{PC}$ = 11.6 Hz, *i*-Ph), 148.5 (dm, $^1J_{FC}$ ~ 242 Hz, *o*-$B(C_6F_5)_4$), 147.6 (dd, $^1J_{PC}$ = 13.5 Hz, $^2J_{PC}$ = 2.1 Hz, =CP), 138.6 (dm, $^1J_{FC}$ ~ 247 Hz, *p*-$B(C_6F_5)_4$), 136.7 (dm, $^1J_{FC}$ ~ 246 Hz, *m*-$B(C_6F_5)_4$), 134.3 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Ph_2P), 132.3 (d, $^2J_{PC}$ = 10.1 Hz, *o*-Ph_2P), 130.3 (d, $^3J_{PC}$ = 12.0 Hz, *m*-Ph_2P), 128.8 (*m*-Ph), 124.8 (*p*-Ph), 124.4 (br, *i*-$B(C_6F_5)_4$), 124.1 (d, $^1J_{PC}$ = 86.6 Hz, *i*-Ph_2P), 121.4 (d, $^4J_{PC}$ = 2.0

Hz, *o*-Ph), 105.0 (Cp), 16.9 (d, $^{1}J_{PC}$ = 20.0 Hz, Me_3P), 12.0 (d, $^{1}J_{PC}$ = 51.5 Hz, MeP).

$^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 14.3 (d, $^{3}J_{PP}$ = 12.8 Hz, Ph_2P), -5.1 (d, $^{3}J_{PP}$ = 12.8 Hz, Me_3P).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -133.1 (br, 2F, *o*-$B(C_6F_5)_4$), -163.7 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*-$B(C_6F_5)_4$), -167.6 (m, 2F, *m*-$B(C_6F_5)_4$).

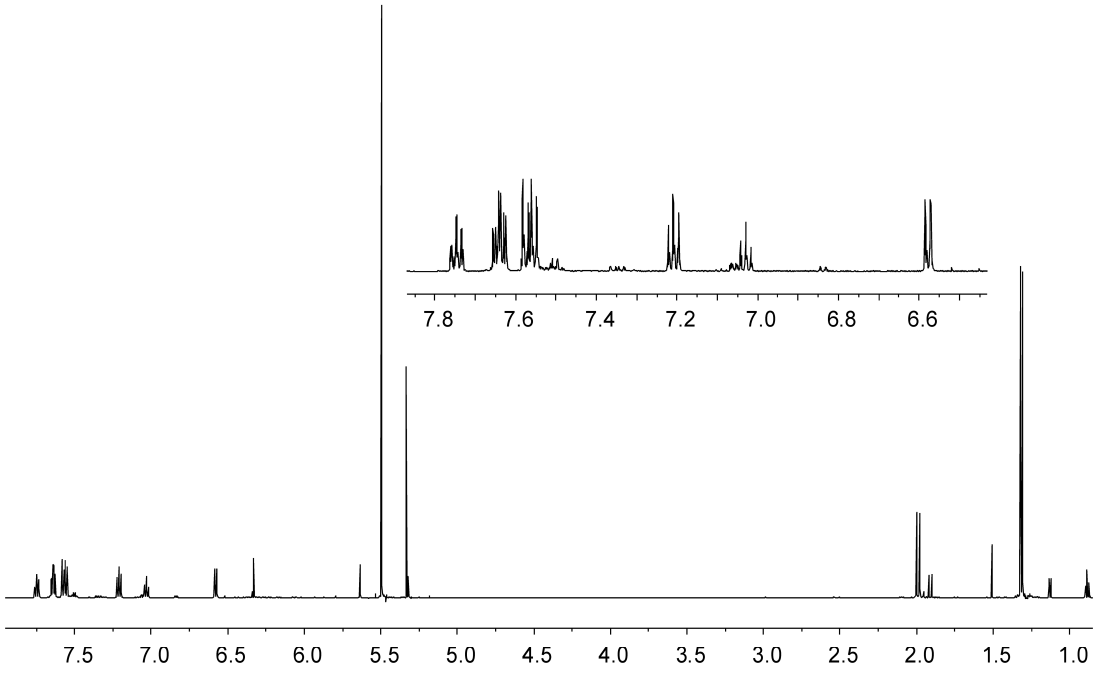
$^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = -16.7 ($\nu_{1/2}$ ~ 20 Hz).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, CD_2Cl_2, 299 K): $\delta^{1}H$ / $\delta^{1}H$ = 7.75 / 7.64 (*p*-Ph_2P / *m*-Ph_2P), 7.64 / 7.75, 7.57 (*m*-Ph_2P / *p*-Ph_2P, *o*-Ph_2P), 7.57 / 7.64 (*o*-Ph_2P / *m*-Ph_2P), 7.21 / 7.03, 6.58 (*m*-Ph / *p*-Ph, *o*-Ph), 7.03 / 7.21 (*p*-Ph / *m*-Ph), 6.58 / 7.21 (*o*-Ph / *m*-Ph).

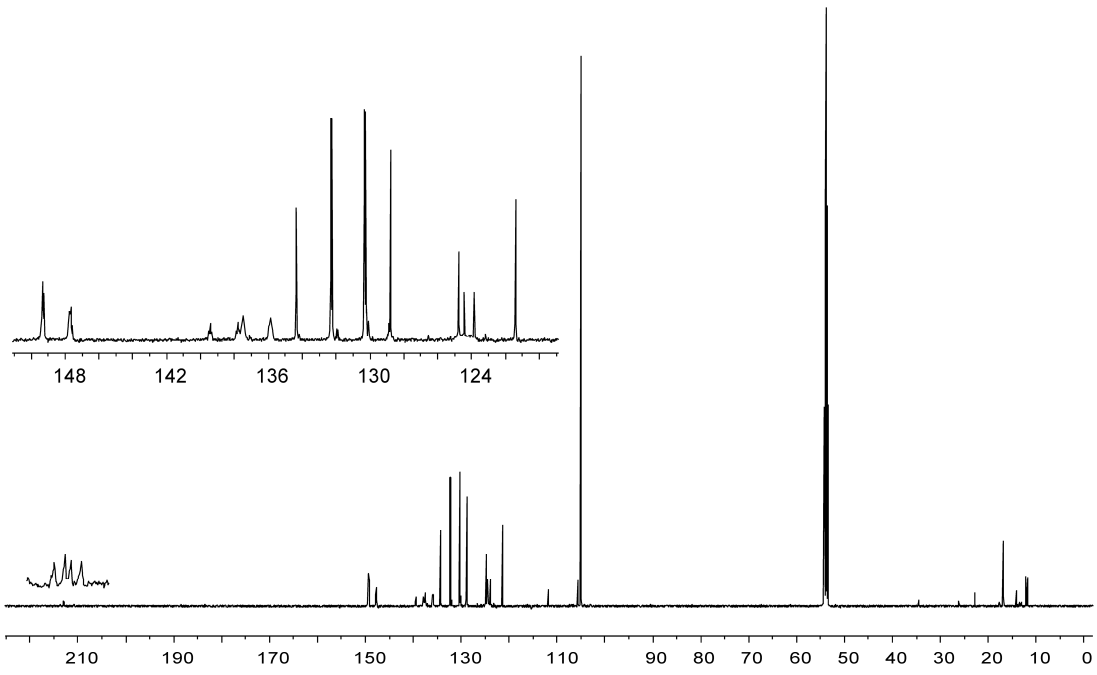
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, CD_2Cl_2, 299 K): $\delta^{1}H$ / $\delta^{13}C$ = 7.75 / 134.3 (*p*-Ph_2P), 7.64 / 130.2 (*m*-Ph_2P), 7.57 / 132.3 (*o*-Ph_2P), 7.21 / 128.8 (*m*-Ph), 7.03 / 124.8 (*p*-Ph), 6.58 / 121.4 (*o*-Ph), 5.50 / 105.0 (Cp), 1.99 / 12.0 (MeP), 1.31 / 16.9 (Me_3P).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, CD_2Cl_2, 299 K): $\delta^{1}H$ / $\delta^{13}C$ = 7.75 / 132.3 (*p*-Ph_2P / *o*-Ph_2P), 7.64 / 130.3, 124.2 (*m*-Ph_2P / *m*-Ph_2P, *i*-Ph_2P), 7.57 / 134.3, 132.3 (*o*-Ph_2P / *p*-Ph_2P, *o*-Ph_2P), 7.21 / 149.3, 128.8 (*m*-Ph / *i*-Ph, *m*-Ph), 7.03 / 121.4 (*p*-Ph / *o*-Ph), 6.58 / 213.0, 124.8, 121.4 (*o*-Ph / =CZr, *p*-Ph, *o*-Ph), 5.50 / 121.4, 105.0 (Cp / *o*-Ph, Cp), 1.99 / 147.6, 124.1 (Me / =CP, *i*-Ph_2P), 1.31 / 16.9 (Me_3P / Me_3P).

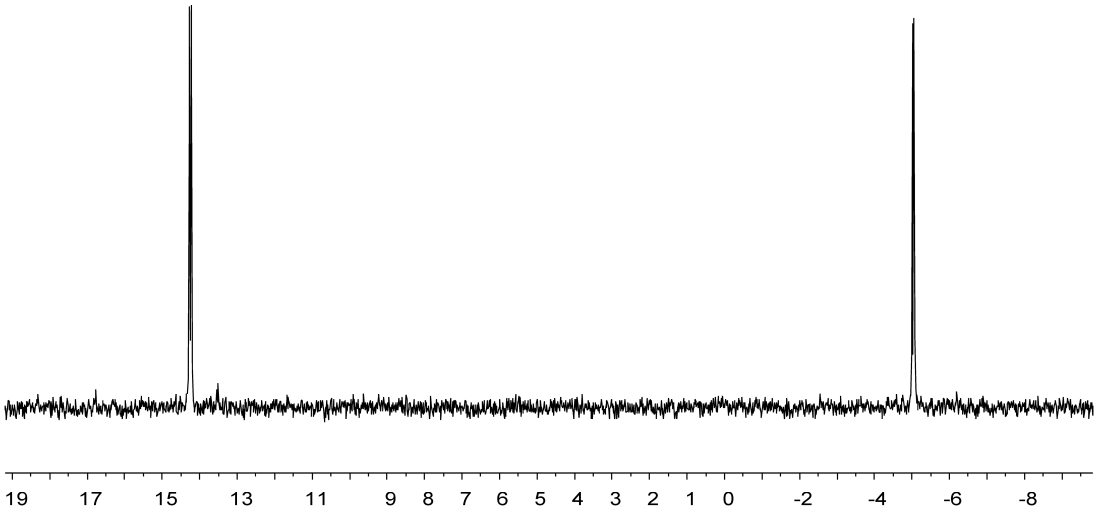
IR (KBr): $\tilde{\nu}$ / cm^{-1} = 1644 (m, C=C).



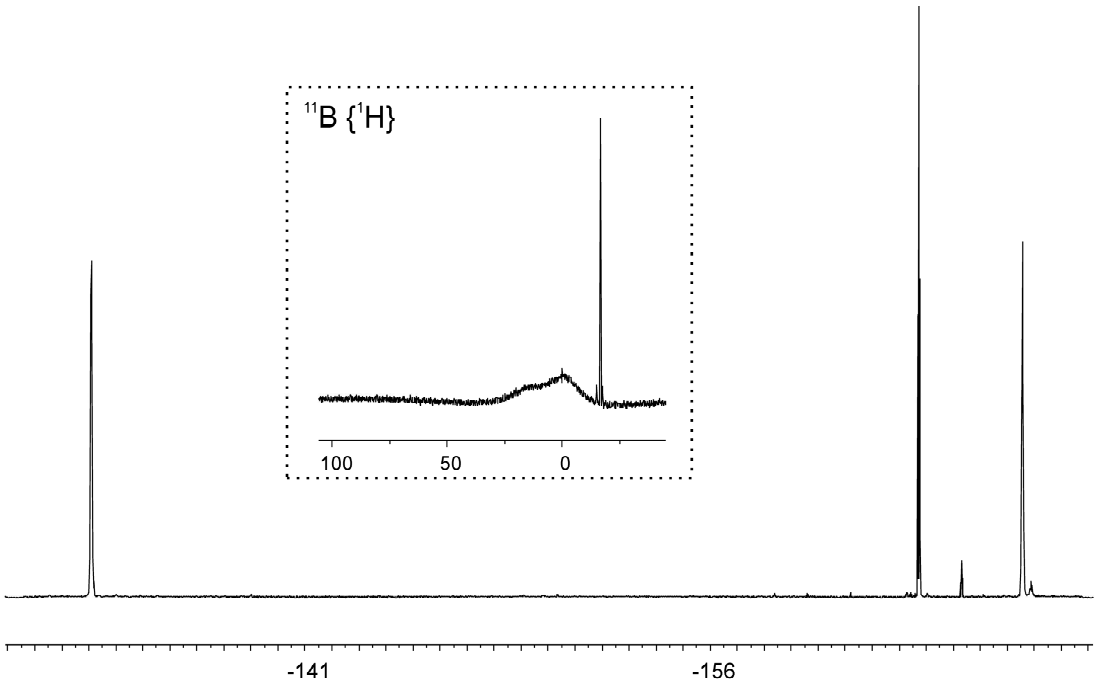
^{1}H NMR (600 MHz, CD_2Cl_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K)



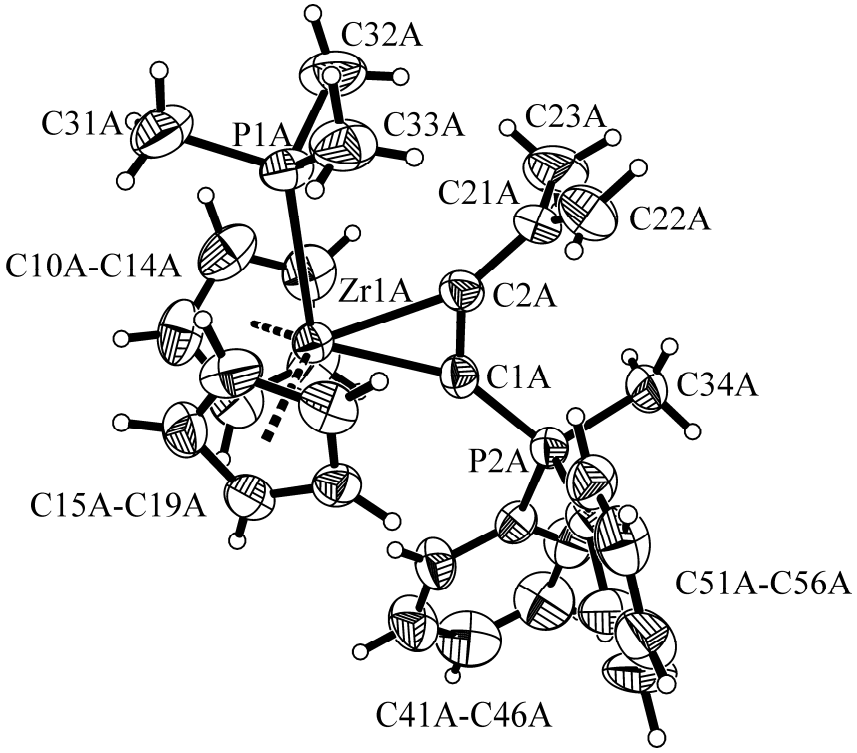
^{31}P{^{1}H } NMR (243 MHz, CD_2Cl_2, 299 K)



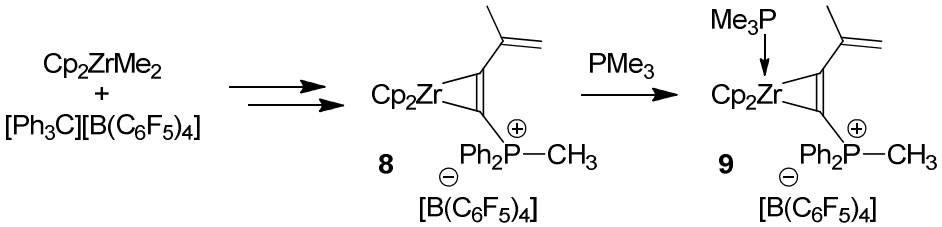
^{19}F NMR (564 MHz, CD_2Cl_2, 299 K) and **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299 K)

X-ray crystal structure analysis of **6** × CH_2Cl_2: formula $C_{59}H_{39}BCl_2F_{20}P_2Zr$, M = 1362.77, colourless crystal, 0.30 x 0.10 x 0.10 mm, a = 18.7974(2), b = 14.7002(1), c = 20.1020(3) Å, V = 5554.70(11) Å^3, ρ_{calc} = 1.630 gcm^{-3}, μ = 0.460 mm^{-1}, empirical absorption correction (0.874 ≤ T ≤ 0.955), Z = 4, orthorhombic, space group Pna2$_1$ (No. 33), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 36266 reflections collected (±h,

±*k*, ±*l*), [(sinθ)/λ] = 0.67 Å^{-1}, 12951 independent (R_{int} = 0.039) and 11896 observed reflections [I>2σ(I)], 783 refined parameters, R = 0.042, wR^2 = 0.087, max. (min.) residual electron density 0.46 (-0.33) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.48(3).



Preparation of the Me_3P stabilized zirconacyclopropene complex 9:



According to the procedure of the *in situ* preparation of complex **5**, Cp_2ZrMe_2 (10.0 mg, 40 µmol) and $[Ph_3C][B(C_6F_5)_4]$ (36.9 mg, 40 µmol) were mixed in 1.0 mL of C_6H_5Br. After standing in the fridge (*ca.* -30°C) for 5 min, enyne **7b** (10.6 mg, 40 µmol) was added to the reaction mixture. After another 1 h in the fridge (*ca.* -30°C),

excess of Me_3P (0.12 mL, 1.0 M in toluene, 120 µmol) was added and then the reaction solution was covered with pentane (3 mL). A beige oil formed overnight. It was crystallized by a two layer procedure using a solution of CH_2Cl_2 and **9** covered by cyclopentane (*ca*. 1:3) to give complex **9** as pale yellow solid (28 mg, 53% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at room temperature.

Elemental Analysis: calcd. for $C_{55}H_{37}BF_{20}P_2Zr \cdot CH_2Cl_2$: C, 50.69; H, 2.96. Found: C, 50.49; H, 2.94.

[*Comment*: Complex **9** was not stable in CD_2Cl_2 at 299 K]

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.78 (m, 2H, *p*-Ph_2P), 7.68 (m, 4H, *m*-Ph_2P), 7.61 (m, 4H, *o*-Ph_2P), 5.44 (d, $^3J_{PH}$ = 1.9 Hz, 10H, Cp), 4.64 (m, 1H, $=CH_2^Z$), 4.25 (m, 1H, $=CH_2^E$), 2.36 (d, $^2J_{PH}$ = 13.0 Hz, 3H, MeP), 1.57 (dd, $^4J_{HH}$ = 1.4 Hz, $^4J_{HH}$ = 0.8 Hz, 3H, $CH_3C=$), 1.53 (d, $^2J_{PH}$ = 6.9 Hz, 9H, Me_3P).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 213.9 (dd, $^2J_{PC}$ = 30.3 Hz, $^2J_{PC}$ = 19.3 Hz,, =CZr), 152.4 (d, $^3J_{PC}$ = 11.2 Hz, =CMe), 148.5 (d, $^1J_{FC}$ ~ 244 Hz, *o*-$B(C_6F_5)_4$), 143.2 (d, $^1J_{PC}$ = 13.2 Hz, =CP), 138.6 (dm, $^1J_{FC}$ ~ 247 Hz, *p*-$B(C_6F_5)_4$), 136.7 (dm, $^1J_{FC}$ ~ 247 Hz, *m*-$B(C_6F_5)_4$), 134.4 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Ph_2P), 132.3 (d, $^2J_{PC}$ = 10.2 Hz, *o*-Ph_2P), 130.3 (d, $^3J_{PC}$ = 11.9 Hz, *m*-Ph_2P), 124.4 (br, *i*-$B(C_6F_5)_4$), 124.3 (d, $^1J_{PC}$ = 85.7 Hz, *i*-Ph_2P), 104.9 (Cp), 103.1 (d, $^4J_{PC}$ = 1.9 Hz, $=CH_2$), 22.7 (d, $^4J_{PC}$ = 1.9 Hz, $CH_3C=$), 16.9 (dd, $^1J_{PC}$ = 19.9 Hz, $^4J_{PC}$ = 1.5 Hz, Me_3P), 11.8 (d, $^1J_{PC}$ = 53.6 Hz, MeP).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = 13.9 (d, $^3J_{PP}$ = 12.9 Hz, Ph_2P), -5.4 (d, $^3J_{PP}$ = 12.9 Hz, Me_3P).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -133.1 (br, 2F, *o*-$B(C_6F_5)_4$), -163.7 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-$B(C_6F_5)_4$), -167.6 (m, 2F, *m*-$B(C_6F_5)_4$).

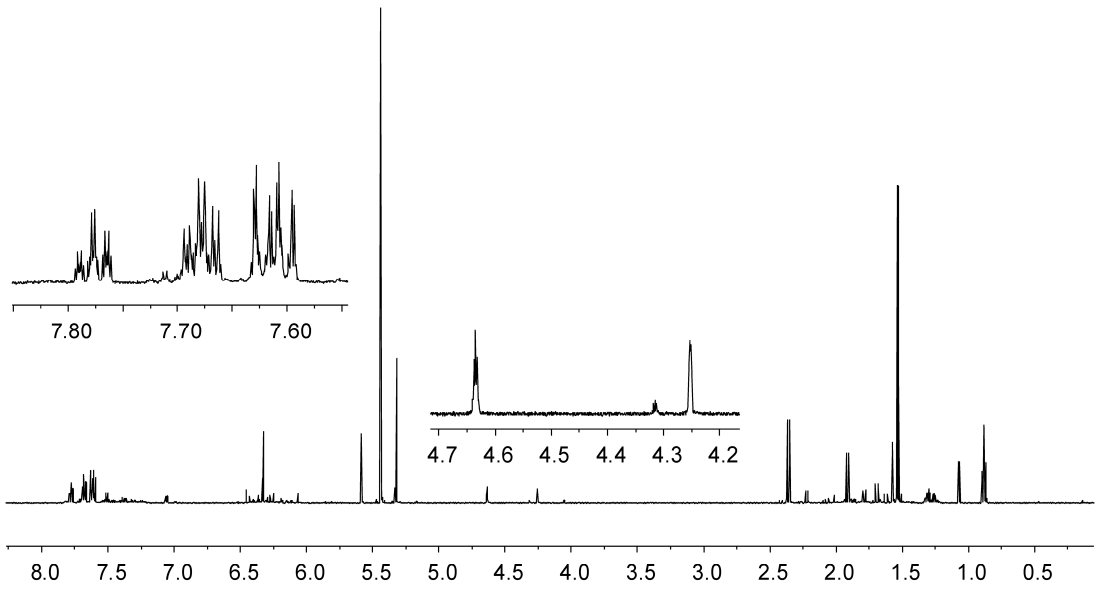
^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = -16.7 ($\nu_{1/2}$ ~ 20 Hz).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, CD_2Cl_2, 299 K): δ^1H / δ^1H = 7.78 / 7.68 (*p*-Ph_2P / *m*-Ph_2P), 7.68 / 7.78, 7.61 (*m*-Ph_2P / *p*-Ph_2P, *o*-Ph_2P), 7.61 / 7.68 (*o*-Ph_2P / *m*-Ph_2P), 4.64 / 4.25, 1.57 ($=CH_2^Z$ / $=CH_2^E$, $CH_3C=$), 4.25 / 4.64, 1.57 ($=CH_2^E$ / $=CH_2^Z$, $CH_3C=$), 1.57 / 4.64, 4.25 ($CH_3C=$ / $=CH_2$).

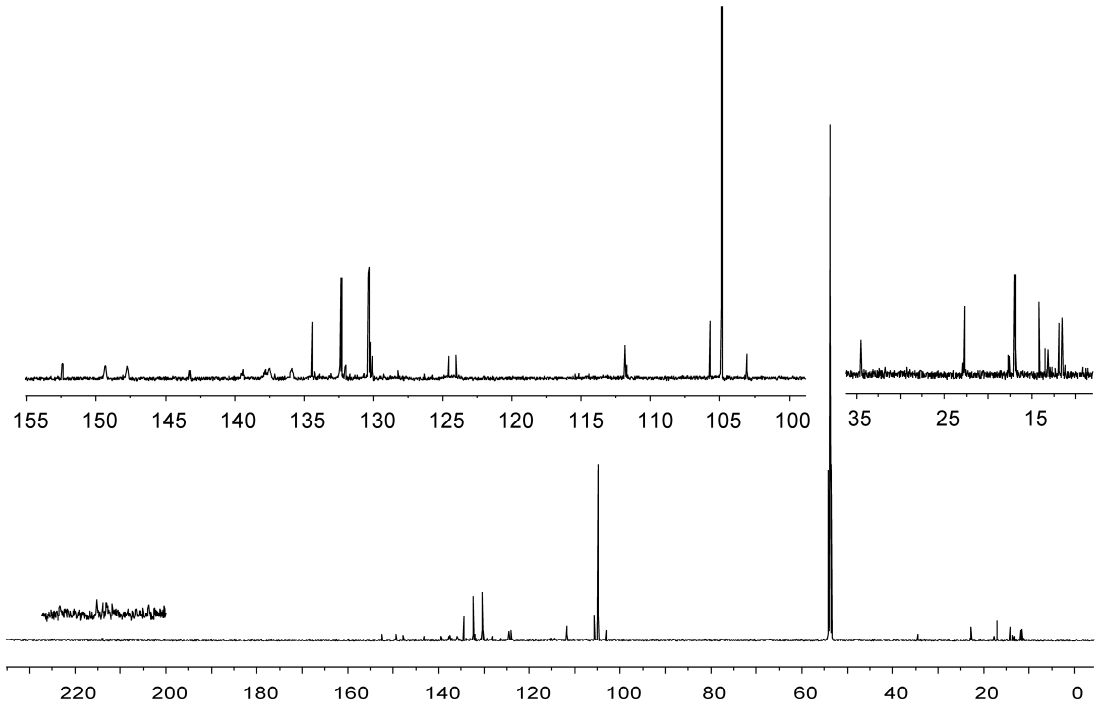
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, CD_2Cl_2, 299 K): δ^{1}H / δ^{13}C = 7.78 / 134.4 (*p*-Ph_2P), 7.68 / 130.3 (*m*-Ph_2P), 7.61 / 132.3 (*o*-Ph_2P), 5.44 / 104.9 (Cp), 4.64, 4.25 / 103.1 (=CH_2), 2.36 / 11.8 (MeP), 1.57 / 22.7 (CH_3C=), 1.53 / 16.9 (Me_3P).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, CD_2Cl_2, 299 K): δ^{1}H / δ^{13}C = 7.78 / 132.3 (*p*-Ph_2P / *o*-Ph_2P), 7.68 / 130.3, 124.3 (*m*-Ph_2P / *m*-Ph_2P, *i*-Ph_2P), 7.61 / 134.4, 132.3 (*o*-Ph_2P / *p*-Ph_2P, *o*-Ph_2P), 5.44 / 104.9 (Cp / Cp), 4.64 / 22.7 (=CH_2^{Z} / CH_3C=), 4.25 / 213.9, 22.7 (=CH_2^{E} / =CZr, CH_3C=), 2.36 / 124.3 (MeP / *i*-Ph_2P), 1.57 / 213.9, 152.4, 103.1 (CH_3C= / =CZr, =CMe, =CH_2), 1.53 / 16.9 (Me_3P / Me_3P).

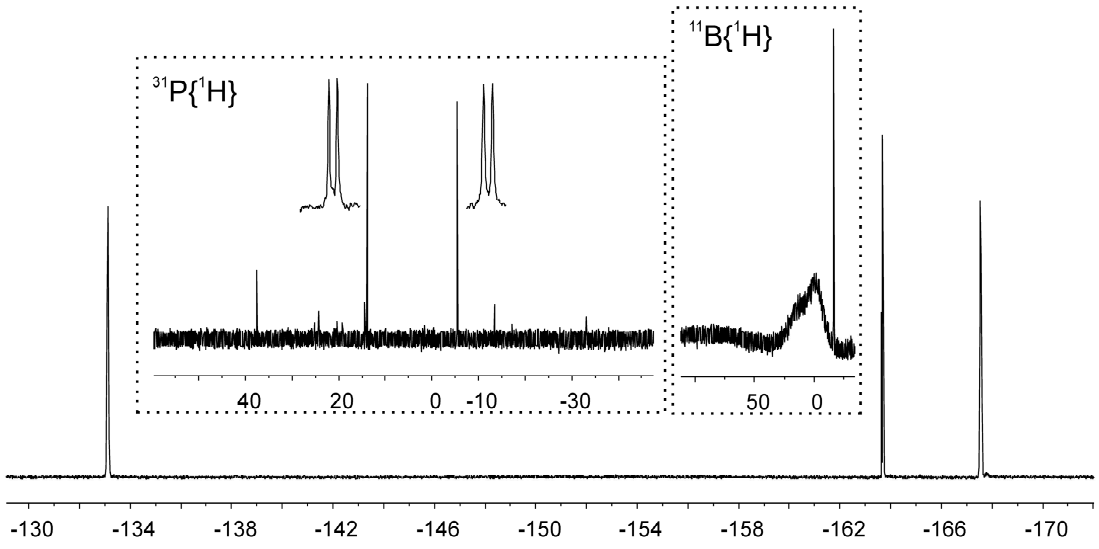
IR (KBr): $\tilde{\nu}$ / cm^{-1} = 1644 (m, C=C).



^{1}H NMR (600 MHz, CD_2Cl_2, 299 K)



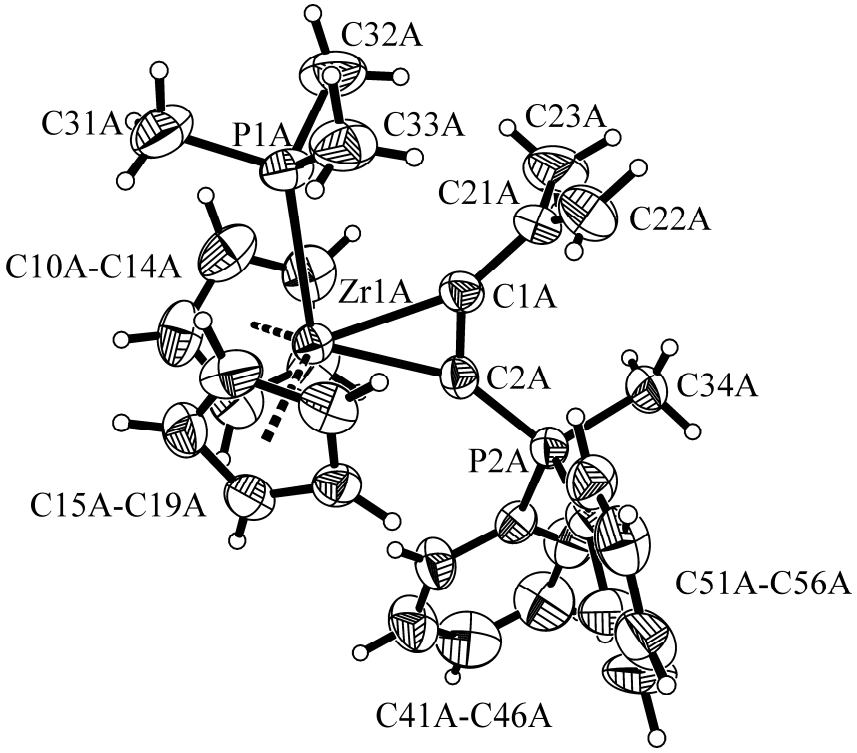
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K)



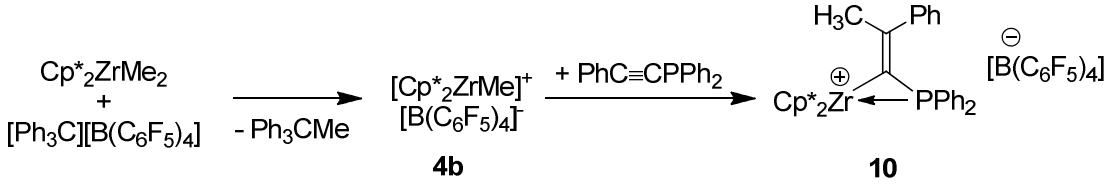
^{19}F NMR (564 MHz, CD_2Cl_2, 299 K) and **^{31}P {^{1}H } NMR** (243 MHz, CD_2Cl_2, 299 K)

X-ray Crystal Structure Analysis of **9**: formula $C_{56}H_{39}BCl_2F_{20}P_2Zr$, M = 1326.74, colourless crystal, 0.38 x 0.20 x 0.15 mm, a = 19.0797(2), b = 14.5742(1), c = 39.3043(4) Å, V = 10929.40(18) Å^3, ρ_{calc} = 1.613 gcm^{-3}, μ = 0.465 mm^{-1}, empirical absorption correction ($0.843 \leq T \leq 0.933$), Z = 8, orthorhombic, space group $Pca2_1$

(No. 29), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 93031 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.66 $Å^{-1}$, 24883 independent (R_{int} = 0.053) and 21569 observed reflections [$I>2\sigma(I)$], 1488 refined parameters, *R* = 0.050, wR^2 = 0.104, max. (min.) residual electron density 0.94 (-0.57) e.$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.50(2).



Preparation of complex 10:



$(C_5Me_5)_2ZrMe_2$ (11.8 mg, 30 µmol) and $[Ph_3C][B(C_6F_5)_4]$ (27.7 mg, 30 µmol) were mixed in 0.8 mL of C_6H_5Br. After standing in the fridge (*ca*. -30°C) for 5 min, the mixture was added to a solution of phenyl-diphenylphosphanyl acetylene (**7a**) (8.6 mg, 30 µmol) in C_6H_5Br (0.2 mL). After another 2 h in the fridge (*ca*. -30°C), pentane (3

mL) was covered over the reaction mixture. A brown solid formed about 2 days. Crystallization of the brown residue by a two layer procedure using a solution of CH_2Cl_2 and **10** covered by cyclopentane (*ca*. 1:3) afforded complex **10** as a red crystalline solid (26 mg, 62% yield). Crystals suitable for X-ray single crystal analysis were grown a two layer procedure using CH_2Cl_2/cyclopentane at -30°C.

Elemental Analysis: calcd. for $C_{65}H_{48}BF_{20}PZr\ C_5H_{10}$: C, 59.54; H, 4.14. calcd. for $C_{65}H_{48}BF_{20}PZr$: C, 58.17; H, 3.61. Found: C, 57.99; H, 4.08. (The lower C content found is probably due to the loss of cyclopentane)

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.55 (m, 2H, *o*-Ph), 7.42 (m, 2H, *m*-Ph)[1], 7.41 (m, 1H, *p*-Ph)[1], 7.40 (m, 2H, *p*-Ph_2P)[2], 7.29 (m, 4H, *m*-Ph_2P), 7.20 (m, 4H, *o*-Ph_2P), 2.00 (br s, 3H, Me), 1.93 (d, $^4J_{PH}$ = 0.57 Hz, 30H, C_5Me_5), [[1] from the ghsqc and ghmbc experiment; [2] from the ^{1}H,^{1}H tocsy experiment].

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 186.2 (d, $^1J_{PC}$ = 103.7 Hz, =CZr), 170.6 (d, $^2J_{PC}$ = 17.3 Hz, C=), 148.6 (dm, $^1J_{FC}$ ~ 245 Hz, *o*-B$(C_6F_5)_4$), 145.4 (d, $^3J_{PC}$ = 7.7 Hz, *i*-Ph), 138.6 (dm, $^1J_{FC}$ ~ 244 Hz, *p*-B$(C_6F_5)_4$), 136.7 (dm, $^1J_{FC}$ ~ 244 Hz, *m*-B$(C_6F_5)_4$), 135.1 (d, $^2J_{PC}$ = 12.5 Hz, *o*-Ph_2P), 132.6 (d, $^1J_{PC}$ = 28.6 Hz, *i*-Ph_2P), 131.3 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Ph_2P), 129.1 (*p*-Ph), 128.9 (*m*-Ph), 128.8 (d, $^3J_{PC}$ = 10.9 Hz, *m*-Ph_2P), 128.1 (*o*-Ph), 126.4 (C_5Me_5), 124.2 (br, *i*-B$(C_6F_5)_4$), 34.0 (d, $^3J_{PC}$ = 21.6 Hz, Me), 12.4 (d, $^3J_{PC}$ = 0.9 Hz, C_5Me_5).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = 17.6 ($\nu_{1/2}$ ~ 2 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -133.1 (br, 2F, *o*-B$(C_6F_5)_4$), -163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-B$(C_6F_5)_4$), -167.7 (m, 2F, *m*-B$(C_6F_5)_4$).

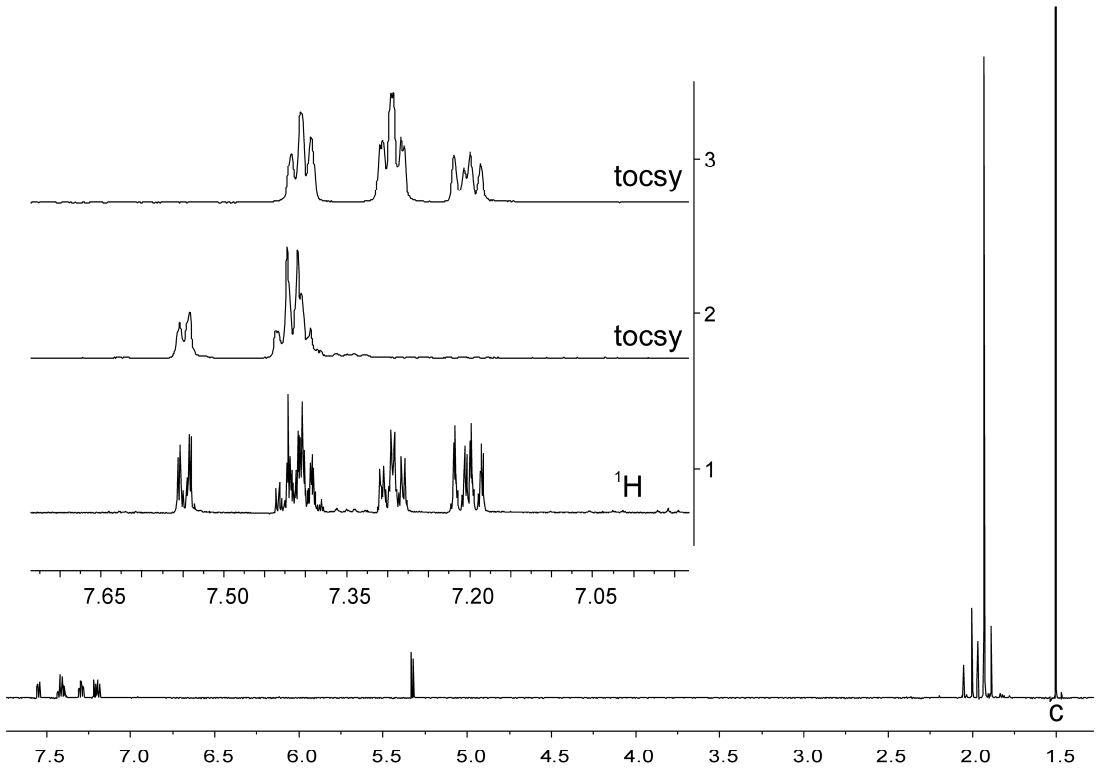
^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = -16.7 ($\nu_{1/2}$ ~ 20 Hz).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, CD_2Cl_2, 299 K): δ^1H / δ^1H = 7.55 / 7.42 (*o*-Ph / *m*-Ph), 7.42 / 7.55, 7.41 (*m*-Ph / *o*-Ph, *p*-Ph), 7.41 / 7.42 (*p*-Ph / *m*-Ph), 7.40 / 7.29 (*p*-Ph_2P / *m*-Ph_2P), 7.29 / 7.40, 7.20 (*m*-Ph_2P / *p*-Ph_2P, *o*-Ph_2P), 7.20 / 7.29 (*o*-Ph_2P / *m*-Ph_2P).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, CD_2Cl_2, 299 K): δ ^{1}H / δ ^{13}C = 7.55 / 128.1 (*o*-Ph), 7.42 / 128.9 (*m*-Ph), 7.41 / 129.1 (*p*-Ph), 7.40 / 131.3 (*p*-Ph_2P), 7.29 / 128.8, (*m*-Ph_2P), 7.20 / 135.1 (*o*-Ph_2P), 2.00 / 34.0 (Me), 1.93 / 12.4 (C_5Me_5).

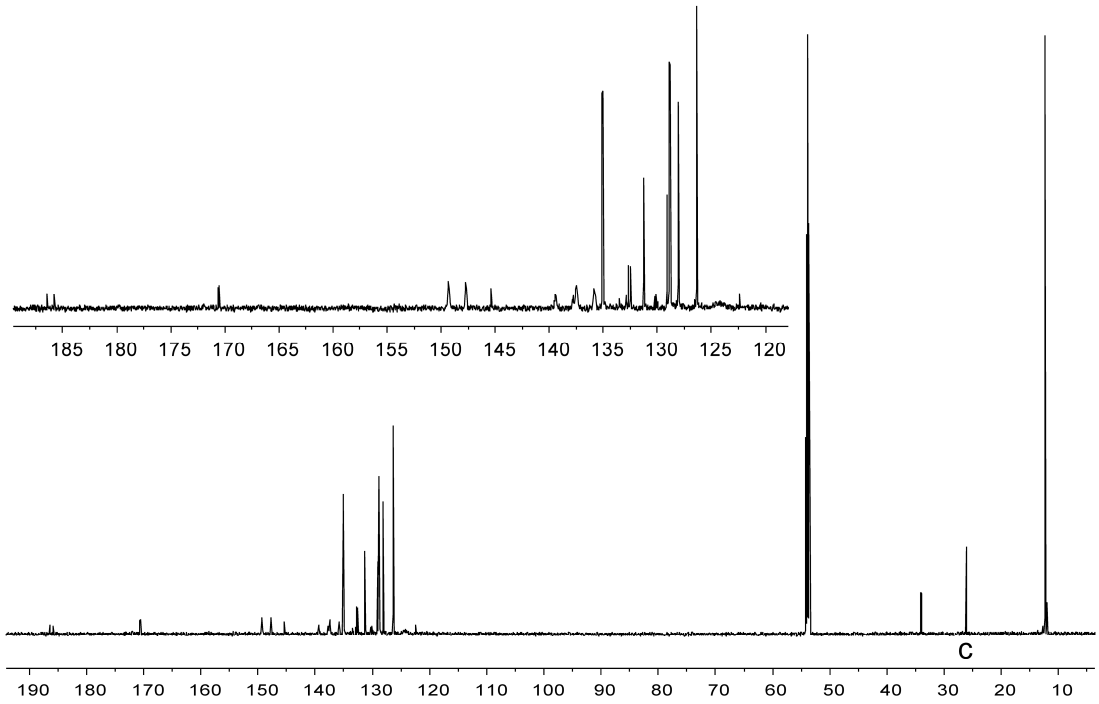
^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, CD_2Cl_2, 299 K): δ^{1}H / δ^{13}C = 7.55 / 170.6, 129.1, 128.1 (*o*-Ph / C=, *p*-Ph, *o*-Ph), 7.42 / 145.4 , 128.9 (*m*-Ph / *i*-Ph, *m*-Ph), 7.41 / 128.1 (*p*-Ph / *o*-Ph), 7.40 / 135.1 (*p*-Ph_2P / *o*-Ph_2P), 7.29 / 132.6, 128.8 (*m*-Ph_2P / *i*-Ph_2P, *m*-Ph_2P), 7.20 / 135.1, 131.3 (*o*-Ph_2P / *o*-Ph_2P, *p*-Ph_2P), 2.00 / 186.2, 170.6, 145.4 (Me / =CZr, C=, *i*-Ph), 1.93 / 126.4 (C_5Me_5 / C_5Me_5).

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 1643 (m, C=C).

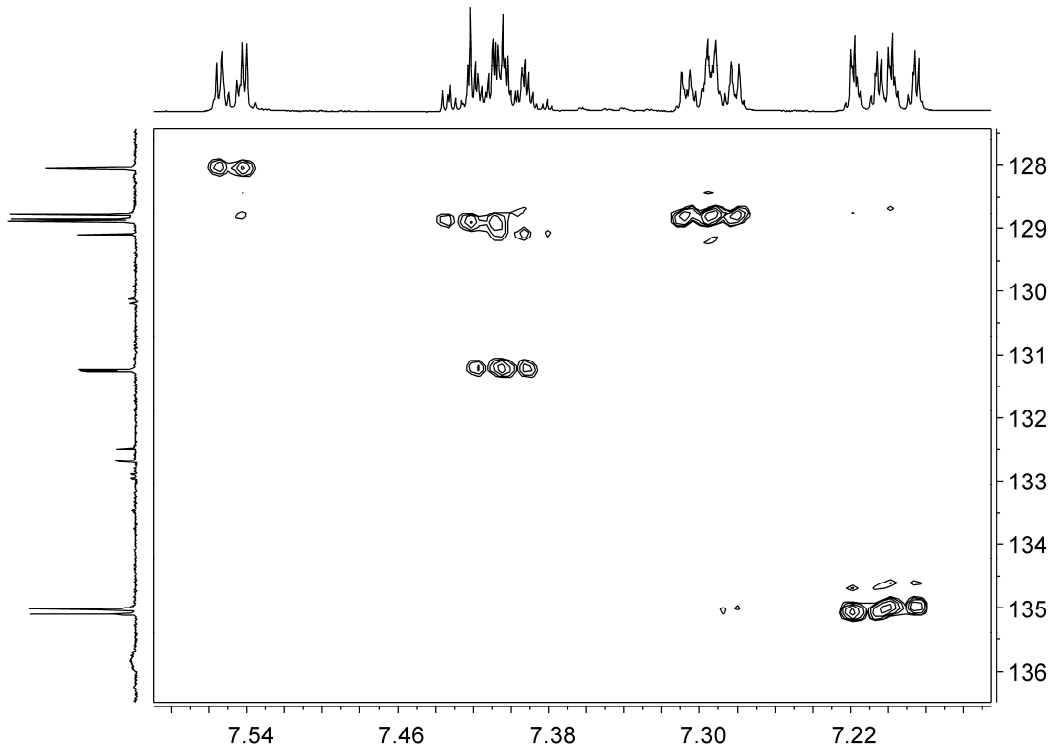


^{1}H NMR (600 MHz, CD_2Cl_2, 299 K)

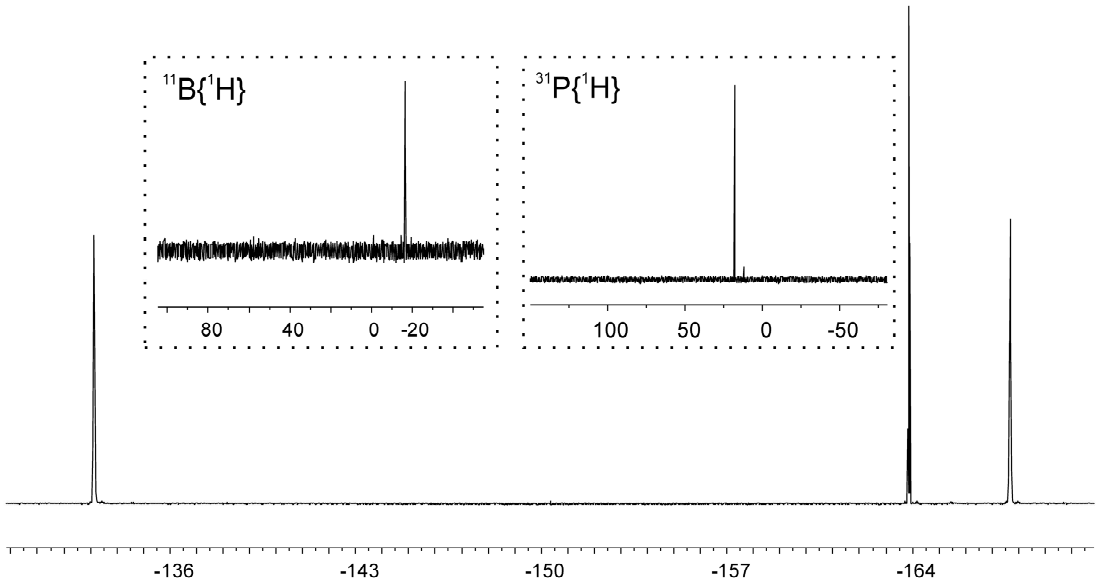
[tocsy 2 $\delta^{1}H_{irr}$: 7.55, tocsy 3 $\delta^{1}H_{irr}$: 7.20; c: cyclopentane]



^{13}C {^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K) [c: cyclopentane]



^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, CD_2Cl_2, 299 K)



$^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K), **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) and **$^{11}B\{^1H\}$ NMR** (192 MHz, CD_2Cl_2, 299 K)

X-ray Crystal Structure Analysis of **10**: formula $C_{70}H_{58}BF_{20}PZr$, M = 1412.16, yellow-orange crystal, 0.43 x 0.30 x 0.07 mm, a = 10.6745(2), b = 15.6839(3), c = 19.2457(3) Å, α = 81.780(1), β = 82.615(1), γ = 83.286(1)°, V = 3146.54(10) Å^3, ρ_{calc} = 1.490 gcm^{-3}, μ = 0.302 mm^{-1}, empirical absorption correction (0.881 ≤ T ≤ 0.979), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 32876 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 15020 independent (R_{int} = 0.045) and 13079 observed reflections [I>2σ(I)], 849 refined parameters, R = 0.055, wR^2 = 0.144, max. (min.) residual electron density 0.82 (-0.66) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.