Reactions of methylzirconocene cation with Phosphinoalkynes: An alternative pathway for generating Cp$_2$Zr(II) systems

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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$_3$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$_2$ZrMe$_2$) [Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* 1973, 95, 6263-6267.], Dimethylpermethylzirconocene ((C$_5$Me$_5$)$_2$ZrMe$_2$)

NMR reaction of [Cp₂ZrMe][B(C₆F₅)₄] (4a) with phenyl-diphenylphosphanyl acetylene (7a):

\[
\begin{align*}
\text{Cp₂ZrMe}_2 + [\text{Ph₃C}][\text{B(C₆F₅)₄}] &\rightarrow [\text{Cp₂ZrMe}]^+ [\text{B(C₆F₅)₄}]^- - \text{Ph₃CMe} \\
\text{Ph₃C-CH₃} &\rightarrow [\text{Cp₂ZrMe}]^+ [\text{B(C₆F₅)₄}]^- + \text{PhC=CPh₂}
\end{align*}
\]

[5]

Cp₂ZrMe₂ (5.0 mg, 20 µmol) and [Ph₃C][B(C₆F₅)₄] (18.4 mg, 20 µmol) were mixed in C₆D₅Br (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 C₆D₅Br (0.2 mL). The color of the reaction mixture changed into pale yellow immediately.

Data of Ph₃CMe:

\[^1H\text{ NMR}\]  (600 MHz, C₆D₅Br, 299 K): \(\delta = 7.14\) (m, 6H, m-Ph), 7.10 (m, 3H, p-Ph), 7.07 (m, 6H, o-Ph), 2.04 (s, 3H, Me).

\[^{13}C[^1H]\text{ NMR}\]  (151 MHz, C₆D₅Br, 299 K): \(\delta = 149.2\) (i-Ph), 128.9 (o-Ph), 128.1 (m-Ph), 126.1 (p-Ph), 52.7 (Ph₃C), 30.6 (Me).

Data of complex 5:

\[^1H\text{ NMR}\]  (600 MHz, C₆D₅Br, 299 K): \(\delta = 7.37\) (m, 2H, p-Ph₂P), 7.28 (m, 4H, m-Ph₂P), 7.20 (m, 4H, o-Ph₂P), 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, \(^2J_{CH} = 12.7\) Hz, 3H, Me).
$^{13}\text{C}^{1}\text{H}$ NMR (151 MHz, C$_6$D$_5$Br, 299 K): $\delta$ = 233.6 (d, $^2$J$_{PC}$ = 30.2 Hz, PhC=), 148.8 (dm, $^1$J$_{PC}$ ~ 242 Hz, o-B(C$_6$F$_5$)$_4$), 144.0 (d, $^3$J$_{PC}$ = 10.0 Hz, i-Ph), 138.5 (dm, $^1$J$_{PC}$ ~ 247 Hz, m-B(C$_6$F$_5$)$_4$), 133.9 (d, $^4$J$_{PC}$ = 3.0 Hz, p-Ph$_2$P), 132.6 (d, $^1$J$_{PC}$ = 7.2 Hz, =CP), 131.5 (d, $^2$J$_{PC}$ = 9.9 Hz, o-Ph$_2$P), 129.9 (d, $^3$J$_{PC}$ = 12.0 Hz, m-Ph$_2$P), 127.1 (p-Ph), 124.8 (br, i-B(C$_6$F$_5$)$_4$), 124.1 (d, $^1$J$_{PC}$ = 84.8 Hz, i-Ph$_2$P), 123.5 (d, $^4$J$_{PC}$ = 2.0 Hz, o-Ph), 108.7 (Cp), 11.7 (Cp).

$^{31}\text{P}^{1}\text{H}$ NMR (243 MHz, C$_6$D$_5$Br, 299 K): $\delta$ = 13.3 ($\nu_{1/2}$ ~ 1 Hz).

$^{19}\text{F}$ NMR (564 MHz, C$_6$D$_5$Br, 299 K): $\delta$ = -131.4 (br, 2F, o-B(C$_6$F$_5$)$_4$), -161.8 (t, $^3$J$_{FF}$ = 21.1 Hz, 1F, p-B(C$_6$F$_5$)$_4$), -165.6 (m, 2F, m-B(C$_6$F$_5$)$_4$).

$^{11}\text{B}^{1}\text{H}$ NMR (192 MHz, C$_6$D$_5$Br, 299 K): $\delta$ = -15.9 ($\nu_{1/2}$ ~ 20 Hz).

$^1\text{H}, ^1\text{H}$ GCOSY (600 MHz / 600 MHz, C$_6$D$_5$Br, 299 K): $\delta^1\text{H} / \delta^1\text{H} = 7.37 / 7.28$ (p-Ph$_2$P / m-Ph$_2$P), 7.28 / 7.37, 7.20 (m-Ph$_2$/ p-Ph$_2$P, o-Ph$_2$P), 7.20 / 7.28 (o-Ph$_2$P / m-Ph$_2$P), 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).

$^1\text{H}, ^{13}\text{C}$ GHSQC (600 MHz / 151 MHz, C$_6$D$_5$Br, 299 K): $\delta^1\text{H} / \delta^{13}\text{C} = 7.37 / 133.9$ (p-Ph$_2$P), 7.28 / 129.9 (m-Ph$_2$P), 7.20 / 131.5 (o-Ph$_2$P), 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).

$^1\text{H}, ^{13}\text{C}$ GHMBC (600 MHz / 151 MHz, C$_6$D$_5$Br, 299 K): $\delta^1\text{H} / \delta^{13}\text{C} = 7.37 / 131.5$ (p-Ph$_2$P / o-Ph$_2$P), 7.28 / 129.9, 124.1 (m-Ph$_2$/ p-Ph$_2$P, i-Ph$_2$P), 7.20 / 133.9, 131.5 (o-Ph$_2$P / p-Ph$_2$P, o-Ph$_2$P), 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$_2$P).
$^1$H NMR (600 MHz, C$_6$D$_5$Br, 299 K)

$^1$H, $^1$H GCOSY (600 MHz / 600 MHz, C$_6$D$_5$Br, 299 K) [projections $^1$H tocsy (600 MHz, C$_6$D$_5$Br, 299 K): irradiation: $\delta^1$H (f1): 7.37 ($p$-Ph$_2$P), $\delta^1$H (f2): 6.68 ($o$-Ph)]
$^{13}$C($^1$H) NMR (151 MHz, C₆D₅Br, 299 K)
NMR reaction of \([\text{Cp}_2\text{ZrMe}]^+[\text{B(C_6F_5)₄}]^-\) (4a) with 3-methyl-1-diphenylphosphanylbut-3-en-1-yne (7b):

According to the procedure of the in situ preparation of complex 5, the reaction of \(\text{Cp}_2\text{ZrMe}_2\) (5.0 mg, 20 µmol), \([\text{Ph}_3\text{C}]\:[\text{B(C_6F_5)₄}]\) (18.4 mg, 20 µmol) and enyne 7b (5.3 mg, 20 µmol) in C₆D₅Br 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 Ph₃CMe:**

\(^1\text{H} \text{NMR}\) (600 MHz, C₆D₅Br, 253 K): \(\delta = 7.15\) (m, 6H, m-Ph), 7.11 (m, 3H, p-Ph), 7.05 (m, 6H, o-Ph), 2.02 (s, 3H, Me).

\(^{13}\text{C}^1\text{H} \text{NMR}\) (151 MHz, C₆D₅Br, 253 K): \(\delta = 149.0\) (i-Ph), 128.8 (o-Ph), 128.0 (m-Ph), 126.1 (p-Ph), 52.4 (Ph₃C), 30.4 (Me).

**Data of complex 8:**

\(^1\text{H} \text{NMR}\) (600 MHz, C₆D₅Br, 253 K): \(\delta = 7.40\) (m, 2H, p-Ph₂P), 7.32 (m, 4H, m-Ph₂P), 7.19 (m, 4H, o-Ph₂P), 5.53 (s, 10H, Cp), 4.26 (br, 1H, =CH₂), 4.00 (br, 1H, =CH₂), 1.83 (d, \(^2J_{PH} = 12.8\) Hz, 3H, MeP), 1.67 (br, 3H, CH₃C=).

\(^{13}\text{C}^1\text{H} \text{NMR}\) (151 MHz, C₆D₅Br, 253 K): \(\delta = 234.6\) (d, \(^2J_{PC} = 30.0\) Hz, ZrC=), 148.8 (d, \(^3J_{PC} = 10.2\) Hz, =CMe), 148.7 (dm, \(^1J_{PC} \sim 245\) Hz, o-B(C₆F₅)₄), 138.2 (dm, \(^1J_{PC} \sim 247\) Hz, p-B(C₆F₅)₄), 136.4 (dm, \(^1J_{PC} \sim 245\) Hz, m-B(C₆F₅)₄), 133.7 (d, \(^4J_{PC} = 2.7\) Hz, p-Ph₂P), 131.3 (d, \(^2J_{PC} = 10.3\) Hz, o-Ph₂P), 129.7 (d, \(^3J_{PC} = 12.0\) Hz, m-Ph₂P), 128.0 (d, \(^1J_{PC} = 23.8\) Hz, =CP), n.o. (i-B(C₆F₅)₄), 124.0 (d, \(^1J_{PC} = 85.6\) Hz, i-Ph₂P), 108.3 (Cp), 105.0 (br, =CH₂), 22.2 (d, \(^4J_{PC} = 1.2\) Hz, CH₃C=), 10.8 (d, \(^1J_{PC} = 56.3\) Hz, MeP).

\(^{31}\text{P}^1\text{H} \text{NMR}\) (243 MHz, C₆D₅Br, 253 K): \(\delta = 14.2\) (ν/₂ ~ 2 Hz).
\( ^{19}\text{F NMR} \) (564 MHz, \( \text{C}_6\text{D}_5\text{Br} \), 253 K): \( \delta = -131.6 \) (br, 2F, \( \alpha\)-B(\( \text{C}_6\text{F}_5\)\( _4 \)), -161.2 (br, 1F, \( \rho\)-B(\( \text{C}_6\text{F}_5\)\( _4 \)), -165.1 (br, 2F, \( \text{m}\)-B(\( \text{C}_6\text{F}_5\)\( _4 \)).

\( ^{11}\text{B}\{^{1}\text{H} \} \) NMR (192 MHz, \( \text{C}_6\text{D}_5\text{Br} \), 253 K): \( \delta = -16.0 \) (\( \nu_{1/2} \approx 25 \text{ Hz} \).

\( ^{1}\text{H,}^{1}\text{H GCOSY} \) (600 MHz / 600 MHz, \( \text{C}_6\text{D}_5\text{Br} \), 253 K): \( \delta^{1}\text{H} / \delta^{1}\text{H} = 7.40 / 7.32 \) (\( \text{p}\)-Ph\( _2\)\( \text{P} / \text{m}\)-Ph\( _2\)\( \text{P} \)), 7.32 / 7.40, 7.19 (\( \text{m}\)-Ph\( _2\)\( \text{P} / \text{p}\)-Ph\( _2\)\( \text{P} \), \( \alpha\)-Ph\( _2\)\( \text{P} \)), 7.19 / 7.32 (\( \alpha\)-Ph\( _2\)\( \text{P} / \text{m}\)-Ph\( _2\)\( \text{P} \)), 4.26 / 4.00, 1.67 (=CH\( _2\)\( ^{\text{E}} \) / =CH\( _2\)\( ^{\text{Z}} \), CH\( _3\)C=), 4.00 / 4.26, 1.67 (=CH\( _2\)\( ^{\text{Z}} \) / =CH\( _2\)\( ^{\text{E}} \), CH\( _3\)C=), 1.67 / 4.26, 4.00 (CH\( _3\)C= / =CH\( _2 \)).

\( ^{1}\text{H,}^{13}\text{C GHSQC} \) (600 MHz / 151 MHz, \( \text{C}_6\text{D}_5\text{Br} \), 253 K): \( \delta^{1}\text{H} / \delta^{13}\text{C} = 7.40 / 133.7 \) (\( \text{p}\)-Ph\( _2\)\( \text{P} \)), 7.32 / 129.7 (\( \text{m}\)-Ph\( _2\)\( \text{P} \)), 7.19 / 131.3 (\( \alpha\)-Ph\( _2\)\( \text{P} \)), 5.53 / 108.3 (Cp), 4.26, 4.00 / 105.0 (=CH\( _2 \)), 1.83 / 10.8 (MeP), 1.67 / 22.2 (CH\( _3\)C=).

\( ^{1}\text{H,}^{13}\text{C GHMBC} \) (600 MHz / 151 MHz, \( \text{C}_6\text{D}_5\text{Br} \), 253 K): \( \delta^{1}\text{H} / \delta^{13}\text{C} = 7.40 / 131.3 \) (\( \text{p}\)-Ph\( _2\)\( \text{P} / \alpha\)-Ph\( _2\)\( \text{P} \)), 7.32 / 131.3, 129.7, 124.0 (\( \text{m}\)-Ph\( _2\)\( \text{P} / \alpha\)-Ph\( _2\)\( \text{P} \), m-Ph\( _2\)\( \text{P} \), i-Ph\( _2\)\( \text{P} \)), 7.19 / 133.7, 131.3 (\( \alpha\)-Ph\( _2\)\( \text{P} / \text{p}\)-Ph\( _2\)\( \text{P} \), \( \alpha\)-Ph\( _2\)\( \text{P} \)), 5.53 / 108.3 (Cp / Cp), 4.26, 4.00 / 22.2 (=CH\( _2 \) / CH\( _3\)C=), 1.83 / 128.0, 124.0 (MeP / =CP, i-Ph\( _2\)\( \text{P} \)), 1.67 / 148.8, 105.0 (CH\( _3\)C= / =CMe, =CH\( _2 \)).
$^{13}\text{C}^{1}\text{H}}$ NMR (151 MHz, C$_6$D$_5$Br, 253 K)

$^{19}\text{F} \text{NMR}$ (564 MHz, C$_6$D$_5$Br, 253 K), $^{11}\text{B}^{1}\text{H}}$ NMR (192 MHz, C$_6$D$_5$Br, 253 K) and $^{31}\text{P}^{1}\text{H}}$ NMR (243 MHz, C$_6$D$_5$Br, 253 K)
Preparation of the Me₃P stabilized zirconacyclopene complex 6:

According to the procedure of the in situ preparation of complex 5, Cp₂ZrMe₂ (20.0 mg, 80 µmol) and [Ph₃C][B(C₆F₅)₄] (73.8 mg, 80 µmol) were mixed in 1.0 mL of C₆H₅Br. 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 C₆H₅Br. After another 1 h, excess of Me₃P (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 CH₂Cl₂ 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 CH₂Cl₂/cyclopentane at room temperature.

**Elemental Analysis:** calcd. for C₅₈H₇₁BF₂₀P₂Zr·CH₂Cl₂: C, 52.00; H, 2.88. Found: C, 51.99; H, 3.38.

**¹H NMR** (600 MHz, CD₂Cl₂, 299 K): δ = 7.75 (m, 2H, p-Ph₂P), 7.64 (m, 4H, m-Ph₂P), 7.57 (m, 4H, o-Ph₂P), 7.21 (m, 2H, m-Ph), 7.03 (m, 1H, p-Ph), 6.58 (m, 2H, o-Ph), 5.50 (d, 3JₚH = 1.9 Hz, 10H, Cp), 1.99 (d, 2JₚH = 12.9 Hz, 3H, MeP), 1.31 (d, 2JₚH = 6.9 Hz, 9H, Me₃P).

**¹³C[¹H] NMR** (151 MHz, CD₂Cl₂, 299 K): δ = 213.0 (dd, 2JₚC = 31.3 Hz, 2JₚC = 20.5 Hz, =CZr), 149.3 (d, 3JₚC = 11.6 Hz, i-Ph), 148.5 (dm, 1JₚC ~ 242 Hz, o-B(C₆F₅)₄), 147.6 (dd, 1JₚC = 13.5 Hz, 2JₚC = 2.1 Hz, =CP), 138.6 (dm, 1JₚC ~ 247 Hz, p-B(C₆F₅)₄), 136.7 (dm, 1JₚC ~ 246 Hz, m-B(C₆F₅)₄), 134.3 (d, 4JₚC = 2.9 Hz, p-Ph₂P), 132.3 (d, 2JₚC = 10.1 Hz, o-Ph₂P), 130.3 (d, 3JₚC = 12.0 Hz, m-Ph₂P), 128.8 (m-Ph), 124.8 (p-Ph), 124.4 (br, i-B(C₆F₅)₄), 124.1 (d, 1JₚC = 86.6 Hz, i-Ph₂P), 121.4 (d, 4JₚC = 2.0 Hz, m-Ph).
$^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ = 14.3 (d, $^3J_{PP}$ = 12.8 Hz, Ph$_2$P), -5.1 (d, $^3J_{PP}$ = 12.8 Hz, Me$_3$P).

$^{19}$F NMR (564 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ = -133.1 (br, 2F, $^3J_{FF}$ = 20.4 Hz, 1F, p-B(C$_6$F$_5$)$_4$), -163.7 (t, $^3J_{FF}$ = 20.4 Hz, 1F, p-B(C$_6$F$_5$)$_4$), -167.6 (m, 2F, m-B(C$_6$F$_5$)$_4$).

$^{11}$B($^1$H) NMR (192 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ = -16.7 ($\nu_{1/2}$ ~ 20 Hz).

$^1$H, $^1$H GCOSY (600 MHz / 600 MHz, CD$_2$Cl$_2$, 299 K): $\delta^1$H / $\delta^1$H = 7.75 / 7.64 (p-Ph$_2$P / m-Ph$_2$P), 7.64 / 7.75, 7.57 (m-Ph$_2$P / p-Ph$_2$P, o-Ph$_2$P), 7.57 / 7.64 (o-Ph$_2$P / m-Ph$_2$P), 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$_2$Cl$_2$, 299 K): $\delta^1$H / $\delta^{13}$C = 7.75 / 134.3 (p-Ph$_2$P), 7.64 / 130.2 (m-Ph$_2$P), 7.57 / 132.3 (o-Ph$_2$P), 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$_3$P).

$^1$H, $^{13}$C GHMBC (600 MHz / 151 MHz, CD$_2$Cl$_2$, 299 K): $\delta^1$H / $\delta^{13}$C = 7.75 / 132.3 (p-Ph$_2$P / o-Ph$_2$P), 7.64 / 130.3, 124.2 (m-Ph$_2$P / m-Ph$_2$P, i-Ph$_2$P), 7.57 / 134.3, 132.3 (o-Ph$_2$P / p-Ph$_2$P, o-Ph$_2$P), 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$_2$P), 1.31 / 16.9 (Me$_3$P / Me$_3$P).

IR (KBr): $\tilde{\nu}$ / cm$^{-1}$ = 1644 (m, C=C).
$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 299 K)

$^{13}$C{$_^1$H} NMR (151 MHz, CD$_2$Cl$_2$, 299 K)
X-ray crystal structure analysis of 6 × CH₂Cl₂: formula C_{59}H_{39}BCl₂F₂O₂P₂Zr, \( M = 1362.77 \), colourless crystal, 0.30 x 0.10 x 0.10 mm, \( a = 18.7974(2) \), \( b = 14.7002(1) \), \( c = 20.1020(3) \) Å, \( V = 5554.70(11) \) Å³, \( \rho_{\text{calc}} = 1.630 \) gcm⁻³, \( \mu = 0.460 \) mm⁻¹, empirical absorption correction (0.874 ≤ \( T \) ≤ 0.955), \( Z = 4 \), orthorhombic, space group \( P\text{na}_{21} \) (No. 33), \( \lambda = 0.71073 \) Å, \( T = 223(2) \) K, \( \omega \) and \( \phi \) scans, 36266 reflections collected (±h,
$\pm k, \pm l$, $[(\sin \theta)/\lambda] = 0.67 \ \textrm{Å}^{-1}$, 12951 independent ($R_{int} = 0.039$) and 11896 observed reflections ($I > 2\sigma(I)$), 783 refined parameters, $R = 0.042$, $wR^2 = 0.087$, max. (min.)
residual electron density 0.46 (-0.33) eÅ$^{-3}$, hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.48(3).

Preparation of the Me$_3$P stabilized zirconacyclopentene complex 9:

According to the procedure of the in situ preparation of complex 5, Cp$_2$ZrMe$_2$ (10.0 mg, 40 µmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (36.9 mg, 40 µmol) were mixed in 1.0 mL of C$_6$H$_5$Br. 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 Me₂P (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 CH₂Cl₂ 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 CH₂Cl₂/cyclopentane at room temperature.

**Elemental Analysis:** calcd. for C₅₅H₃₇BF₂₀P₂Zr·CH₂Cl₂: C, 50.69; H, 2.96. Found: C, 50.49; H, 2.94.

[Comment: Complex 9 was not stable in CD₂Cl₂ at 299 K]

**¹H NMR** (600 MHz, CD₂Cl₂, 299 K): δ = 7.78 (m, 2H, p-Ph₂P), 7.68 (m, 4H, m-Ph₂P), 7.61 (m, 4H, o-Ph₂P), 5.44 (d, ³Jₚₕₚ = 1.9 Hz, 10H, Cp), 4.64 (m, 1H, =CH₂), 4.25 (m, 1H, =CH₂), 2.36 (d, ²Jₚₚ = 13.0 Hz, 3H, MeP), 1.57 (dd, ⁴Jₚₚ = 1.4 Hz, ⁴Jₚₚ = 0.8 Hz, 3H, CH₃C=), 1.53 (d, ²Jₚₙ = 6.9 Hz, 9H, Me₃P).

**¹³C{¹H} NMR** (151 MHz, CD₂Cl₂, 299 K): δ = 213.9 (dd, ²J_Cₚ = 30.3 Hz, ²J_Cₚ = 19.3 Hz, =CZr), 152.4 (d, ³J_Cₚ = 11.2 Hz, =CMe), 148.5 (d, ¹J_Fₐₐ ~ 244 Hz, o-B(C₆F₅)₄), 143.2 (d, ¹J_Cₚ = 13.2 Hz, =CP), 138.6 (dm, ¹J_Fₐₐ ~ 247 Hz, p-B(C₆F₅)₄), 136.7 (dm, ¹J_Fₐₐ ~ 247 Hz, m-B(C₆F₅)₄), 134.4 (d, ²J_Cₚ = 3.0 Hz, p-Ph₂P), 132.3 (d, ²J_Cₚ = 10.2 Hz, o-Ph₂P), 130.3 (d, ³J_Cₚ = 11.9 Hz, m-Ph₂P), 124.4 (br, i-B(C₆F₅)₄), 124.3 (d, ¹J_Cₚ = 85.7 Hz, i-Ph₂P), 104.9 (Cp), 103.1 (d, ⁴J_Cₚ = 1.9 Hz, =CH₂), 22.7 (d, ⁴J_Cₚ = 1.9 Hz, CH₃C=), 16.9 (dd, ¹J_Cₚ = 19.9 Hz, ²J_Cₚ = 1.5 Hz, Me₃P), 11.8 (d, ¹J_Cₚ = 53.6 Hz, MeP).

**³¹P{¹H} NMR** (243 MHz, CD₂Cl₂, 299 K): δ = 13.9 (d, ³J_Pₚ = 12.9 Hz, Ph₂P), -5.4 (d, ³J_Pₚ = 12.9 Hz, Me₃P).

**¹⁹F NMR** (564 MHz, CD₂Cl₂, 299 K): δ = -133.1 (br, 2F, o-B(C₆F₅)₄), -167.6 (m, 2F, m-B(C₆F₅)₄).

**¹¹B{¹H} NMR** (192 MHz, CD₂Cl₂, 299 K): δ = -16.7 (ν₁/₂ ~ 20 Hz).

**¹H, ¹H GCOSY** (600 MHz / 600 MHz, CD₂Cl₂, 299 K): δ¹H / δ¹H = 7.78 / 7.68 (p-Ph₂P / m-Ph₂P), 7.68 / 7.78, 7.61 (m-Ph₂P / p-Ph₂P, o-Ph₂P), 7.61 / 7.68 (o-Ph₂P / m-Ph₂P), 4.64 / 4.25, 1.57 (=CH₂ / =CH₂̧, CH₃C=), 4.25 / 4.64, 1.57 (=CH₂̧ / =CH₂, CH₃C=), 1.57 / 4.64, 4.25 (CH₃C= / =CH₂).
$^1$H, $^{13}$C GHSQC (600 MHz / 151 MHz, CD$_2$Cl$_2$, 299 K): $\delta^1$H / $\delta^{13}$C = 7.78 / 134.4 (p-Ph$_2$P), 7.68 / 130.3 (m-Ph$_2$P), 7.61 / 132.3 (o-Ph$_2$P), 5.44 / 104.9 (Cp), 4.64, 4.25 / 103.1 (=CH$_2$), 2.36 / 11.8 (MeP), 1.57 / 22.7 (CH$_3$C=), 1.53 / 16.9 (Me$_3$P).

$^1$H, $^{13}$C GHMBC (600 MHz / 151 MHz, CD$_2$Cl$_2$, 299 K): $\delta^1$H / $\delta^{13}$C = 7.78 / 132.3 (p-Ph$_2$P / o-Ph$_2$P), 7.68 / 130.3, 124.3 (m-Ph$_2$P / m-Ph$_2$P, i-Ph$_2$P), 7.61 / 134.4, 132.3 (o-Ph$_2$P / p-Ph$_2$P, o-Ph$_2$P), 5.44 / 104.9 (Cp / Cp), 4.64 / 22.7 (=CH$_2^Z$ / CH$_3$C=), 4.25 / 213.9, 22.7 (=CH$_2^E$ / =CZr, CH$_3$C=), 2.36 / 214.3 (MeP / i-Ph$_2$P), 1.57 / 213.9, 152.4, 103.1 (CH$_3$C= / =CZr, =CMe, =CH$_2$), 1.53 / 16.9 (Me$_3$P / Me$_3$P).

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

$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 299 K)
X-ray Crystal Structure Analysis of 9: formula C$_{56}$H$_{39}$BCl$_2$F$_{20}$P$_2$Zr, $M = 1326.74$, 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$^3$, $\rho_{\text{calc}} = 1.613$ g cm$^{-3}$, $\mu = 0.465$ mm$^{-1}$, empirical absorption correction ($0.843 \leq T \leq 0.933$), $Z = 8$, orthorhombic, space group $Pca2_1$
(No. 29), \( \lambda = 0.71073 \, \text{Å}, \, T = 223(2) \, \text{K}, \) \( \phi \) and \( \varphi \) scans, 93031 reflections collected (\( \pm h, \pm k, \pm l \)), \( \langle \sin \theta \rangle / \lambda = 0.66 \, \text{Å}^{-1} \), 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) eÅ\(^{-3} \), hydrogen atoms calculated and refined as riding atoms, Flack parameter 0.50(2).

Preparation of complex 10:

\[
\text{Cp}^*_{2}\text{ZrMe}_2 + [\text{Ph}_3\text{C][B(C}_6\text{F}_5)_4] \rightarrow [\text{Cp}^*_{2}\text{ZrMe}]^+ + \text{PhC\&\&CPPh}_2 \rightarrow \text{Cp}^*_{2}\text{Zr} \rightarrow \text{10} \]

\((\text{C}_5\text{Me}_5)_2\text{ZrMe}_2 (11.8 \, \text{mg}, 30 \, \mu\text{mol}) \) and \([\text{Ph}_3\text{C][B(C}_6\text{F}_5)_4] (27.7 \, \text{mg}, 30 \, \mu\text{mol}) \) were mixed in 0.8 mL of \( \text{C}_6\text{H}_5\text{Br} \). After standing in the fridge (ca. -30°C) for 5 min, the mixture was added to a solution of phenyl-diphenylphosphanyl acetylene \((7a) (8.6 \, \text{mg}, 30 \, \mu\text{mol}) \) in \( \text{C}_6\text{H}_5\text{Br} (0.2 \, \text{mL}) \). 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 CH₂Cl₂ 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 CH₂Cl₂/cyclopentane at -30°C.

**Elemental Analysis:** calcd. for C₆₅H₄₈BF₂₀PZr C₃H₁₀: C, 59.54; H, 4.14. calcd. for C₆₅H₄₈BF₂₀PZr: 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)

**¹H NMR (600 MHz, CD₂Cl₂, 299 K):** δ = 7.55 (m, 2H, o-Ph), 7.42 (m, 2H, m-Ph)¹, 7.41 (m, 1H, p-Ph), 7.40 (m, 2H, p-Ph₂P)², 7.29 (m, 4H, m-Ph₂P), 7.20 (m, 4H, o-Ph₂P), 2.00 (br s, 3H, Me), 1.93 (d, 4J_PH = 0.57 Hz, 30H, C₅Me₅), [¹ from the ghsqc and ghmbc experiment; ² from the ¹H,¹H tocsy experiment].

**¹³C¹H NMR (151 MHz, CD₂Cl₂, 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(C₆F₅)₄), 145.4 (d, ³J_PC = 7.7 Hz, i-Ph), 138.6 (dm, ¹J_FC ~ 244 Hz, p-B(C₆F₅)₄), 136.7 (dm, ¹J_FC ~ 244 Hz, m-B(C₆F₅)₄), 135.1 (d, ²J_PC = 12.5 Hz, o-Ph₂P), 132.6 (d, ¹J_PC = 28.6 Hz, i-Ph₂P), 131.3 (d, ⁴J_PC = 2.9 Hz, p-Ph₂P), 129.1 (p-Ph), 128.9 (m-Ph), 128.8 (d, ³J_PC = 10.9 Hz, m-Ph₂P), 128.1 (o-Ph), 126.4 (C₅Me₅), 124.2 (br, i-B(C₆F₅)₄), 34.0 (d, ³J_PC = 21.6 Hz, Me), 12.4 (d, ³J_PC = 0.9 Hz, C₅Me₅).

**³¹P¹H NMR (243 MHz, CD₂Cl₂, 299 K):** δ = 17.6 (v₁/₂ ~ 2 Hz).

**¹⁹F NMR (564 MHz, CD₂Cl₂, 299 K):** δ = -133.1 (br, 2F, o-B(C₆F₅)₄), -163.9 (t, ³J_FF = 20.3 Hz, 1F, p-B(C₆F₅)₄), -167.7 (m, 2F, m-B(C₆F₅)₄).

**¹¹B¹H NMR (192 MHz, CD₂Cl₂, 299 K):** δ = -16.7 (v₁/₂ ~ 20 Hz).

**¹H,¹H GCOSY (600 MHz / 600 MHz, CD₂Cl₂, 299 K):** δ¹H / δ¹H = 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-Ph₂P / m-Ph₂P), 7.29 / 7.40, 7.20 (m-Ph₂P / p-Ph₂P, o-Ph₂P), 7.20 / 7.29 (o-Ph₂P / m-Ph₂P).

**¹H,¹³C GHSQC (600 MHz / 151 MHz, CD₂Cl₂, 299 K):** δ¹H / δ¹³C = 7.55 / 128.1 (o-Ph), 7.42 / 128.9 (m-Ph), 7.41 / 129.1 (p-Ph), 7.40 / 131.3 (p-Ph₂P), 7.29 / 128.8, (m-Ph₂P), 7.20 / 135.1 (o-Ph₂P), 2.00 / 34.0 (Me), 1.93 / 12.4 (C₅Me₅).
$^1$H, $^{13}$C CPMAS (600 MHz / 151 MHz, CD$_2$Cl$_2$, 299 K): $\delta^1$H / $\delta^{13}$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$_2$P / o-Ph$_2$P), 7.29 / 132.6, 128.8 (m-Ph$_2$P / i-Ph$_2$P, m-Ph$_2$P), 7.20 / 135.1, 131.3 (o-Ph$_2$P / o-Ph$_2$P, p-Ph$_2$P), 2.00 / 186.2, 170.6, 145.4 (Me / =CZr, C=, i-Ph), 1.93 / 126.4 (C$_5$Me$_3$ / C$_5$Me$_5$).

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

**$^1$H NMR** (600 MHz, CD$_2$Cl$_2$, 299 K)

[tocsy 2 $\delta^1$H$_{tr}$: 7.55, tocsy 3 $\delta^1$H$_{tr}$: 7.20; c: cyclopentane]
$^{13}C\{^1H\}$ NMR (151 MHz, CD$_2$Cl$_2$, 299 K) [c: cyclopentane]

$^1H, ^{13}C$ GHSQC (600 MHz / 151 MHz, CD$_2$Cl$_2$, 299 K)
\(^{31}\text{P}[^{1}\text{H}]\) NMR (243 MHz, CD\(_2\)Cl\(_2\), 299 K), \(^{19}\text{F}\) NMR (564 MHz, CD\(_2\)Cl\(_2\), 299 K) and \(^{11}\text{B}[^{1}\text{H}]\) NMR (192 MHz, CD\(_2\)Cl\(_2\), 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, \(\alpha = 81.780(1), \beta = 82.615(1), \gamma = 83.286(1)^\circ\), \(V = 3146.54(10) \) Å\(^3\), \(\rho_{\text{calc}} = 1.490 \) gcm\(^{-3}\), \(\mu = 0.302 \) mm\(^{-1}\), empirical absorption correction (0.881 \(\leq T \leq 0.979\)), \(Z = 2\), triclinic, space group \(P\bar{1}\) (No. 2), \(\lambda = 0.71073 \) Å, \(T = 223(2) \) K, \(\omega\) and \(\phi\) scans, 32876 reflections collected (\(\pm h, \pm k, \pm l\)), \((\sin\theta/\lambda) = 0.67 \) Å\(^{-1}\), 15020 independent \((R_{int} = 0.045)\) and 13079 observed reflections \([I > 2\sigma(I)]\), 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.