

# **Formation and structural characterization of a five-membered zirconacycloallenoid**

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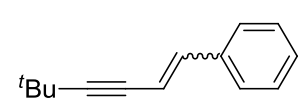
**SUPPORTING INFORMATION**

**General Procedures.** All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried 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. Dichlorobis( $\eta^5$ -cyclopentadienyl)zirconium (J. J. Eisch, F. A. Owuor and P. O. Otieno, *Organometallics*, 2001, **20**, 4132) was prepared according to published procedures and fully characterized by NMR spectroscopy. Purchased starting materials and other chemicals or reagents (Aldrich, TCI and ABCR) were used without further purification. The following instruments were used for physical characterization of the compounds: NMR spectra: Bruker AV 400 spectrometer ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 101 MHz), Agilent DD2 500 ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 126 MHz), Agilent DD2 600 ( $^1\text{H}$ : 600 MHz,  $^{13}\text{C}$ : 151 MHz).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR: chemical shift  $\delta$ , reported in ppm, is given relative to TMS and referenced to the solvent signal {CDCl<sub>3</sub> ( $\delta_{\text{H}}$  = 7.26,  $\delta_{\text{C}}$  = 77.0), [d<sub>2</sub>]-dichloromethane ( $\delta_{\text{H}}$  = 5.32,  $\delta_{\text{C}}$  = 53.8), [d<sub>6</sub>]-benzene ( $\delta_{\text{H}}$  = 7.15,  $\delta_{\text{C}}$  = 128.0), [d<sub>8</sub>]-toluene ( $\delta_{\text{H}}$  = 2.03,  $\delta_{\text{C}}$  = 20.4)}. NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian 3100 FT-IR* (Excalibur Series). Melting points were obtained with a DSC Q20 (*TA Instruments*). Mass spectra were recorded on a Orbitrap LTQ XL (*Thermo Scientific*).

X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (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 30% probability, *R*-values are given for observed reflections, and  $wR^2$  values are given for all reflections. *Exceptions and special features*: For compound **2c** one *t*-Bu group at C1 atom and one Cp group at Zirconium atom were found disordered over two positions. Several restraints (SADI, SIMU, SAME and ISOR) were used in order to improve refinement stability. For the compound **6** an unidentified disordered solvent molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek *J. Appl. Cryst.*, 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. Compound **8** crystallized with two half dimmer molecules in the asymmetric unit. Two

disordered over two positions dichloromethane molecules were found additional in the asymmetrical unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

#### Preparation of compound 4. 5,5-Dimethyl-1-phenyl-hex-1-en-3-yne

 Diethylamine (40 ml) was added to a mixture of bis(triphenylphosphine)palladium(II) dichloride (423 mg, 3 mol%), copper(I) iodide (191 mg, 5 mol%) and 3,3-dimethyl-1-butyne (3 ml, 24.10 mmol, 1.2 eq). The slightly yellow suspension was cooled to 0 °C and  $\beta$ -bromostyrene (2.58 ml, 20.10 mmol, 1 eq) was added. The mixture was warmed to 55 °C and stirred for 18 h. Subsequently the black suspension was filtered over Celite and the brown filtrate was concentrated *in vacuo*. The crude oil was distilled *in vacuo* (44 mbar, 80 °C) yielding the 1,3-ene-yne **4** as yellow oil [3.33 g, 90 %; *E* : *Z* = 84 : 16 (<sup>1</sup>H)].

**MS-Es<sup>+</sup>** (CHCl<sub>3</sub>/CH<sub>3</sub>OH + CF<sub>3</sub>COOAg): *m/z* = calcd. for C<sub>14</sub>H<sub>16</sub>Ag = 291.02922 g/mol, found 291.0297 g/mol.

#### *E*-Isomer

**<sup>1</sup>H NMR** (400 MHz, 295 K, CDCl<sub>3</sub>):  $\delta$  = 7.36 (m, 2H, *o*-Ph), 7.31 (m, 2H, *m*-Ph), 7.25 (m, 1H, *p*-Ph), 6.86 (d, <sup>3</sup>*J*<sub>HH</sub> = 16.2 Hz, 1H, =CH<sup>Ph</sup>), 6.17 (d, <sup>3</sup>*J*<sub>HH</sub> = 16.2 Hz, 1H, =CH), 1.29 (s, 9H, <sup>*t*</sup>Bu). [gbe211\_Nov27-2012\_20]

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, 296 K, CDCl<sub>3</sub>):  $\delta$  = 139.8 (=CH<sup>Ph</sup>), 136.6 (*i*-Ph), 128.6 (*m*-Ph), 128.1 (*p*-Ph), 126.0 (*o*-Ph), 108.9 (=CH), 101.1 (<sup>*t*</sup>BuC $\equiv$ ), 78.2 ( $\equiv$ C), 31.0 (<sup>*t*</sup>Bu), 28.1 (<sup>*t*</sup>Bu). [gbe211\_Nov27-2012\_21]

**<sup>1</sup>H, <sup>1</sup>H GCOSY** (400 MHz / 400 MHz, 296 K, CDCl<sub>3</sub>):  $\delta$  <sup>1</sup>H / <sup>1</sup>H = 6.86 / 6.17 (=CH<sup>Ph</sup> / =CH), 6.17 / 6.86 (=CH / =CH<sup>Ph</sup>). [gbe211\_Nov27-2012\_24]

**<sup>1</sup>H, <sup>13</sup>C GHSQC** (400 MHz / 101 MHz, 295 K, CDCl<sub>3</sub>):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.36 / 126.0 (*o*-Ph), 7.31 / 128.6 (*m*-Ph), 7.25 / 128.1 (*p*-Ph), 6.86 / 139.8 (=CH<sup>Ph</sup>), 6.17 / 108.9 (=CH), 1.29 / 31.0 (<sup>*t*</sup>Bu). [gbe211\_Nov27-2012\_25]

**<sup>1</sup>H, <sup>13</sup>C GHMBC** (400 MHz / 101 MHz, 295 K, CDCl<sub>3</sub>):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 7.36 / 139.8, 128.1, 126.0 (*o*-Ph / =CH<sup>Ph</sup>, *p*-Ph, *o*-Ph), 7.31 / 136.6, 128.6 (*m*-Ph / *i*-Ph, *m*-Ph), 7.25 / 126.0 (*p*-Ph / *o*-Ph), 6.86 / 136.6, 126.0, 108.9, 78.2 (=CH<sup>Ph</sup> / *i*-Ph, *o*-Ph, =CH,  $\equiv$ C), 6.17 / 139.8, 136.6, 101.1, 31.0 (=CH / =CH<sup>Ph</sup>, *i*-Ph, <sup>*t*</sup>BuC $\equiv$ , <sup>*t*</sup>Bu), 1.29 / 101.1, 31.0, 28.1 (<sup>*t*</sup>Bu / <sup>*t*</sup>BuC $\equiv$ , <sup>*t*</sup>Bu, <sup>*t*</sup>Bu). [gbe211\_Nov27-2012\_26]

### Z-Isomer

**$^1\text{H}$  NMR** (400 MHz, 295 K,  $\text{CDCl}_3$ ):  $\delta$  = 7.89 (m, 2H, *o*-Ph), 7.35 (m, 2H, *m*-Ph), n.o. (*p*-Ph), 6.56 (d,  $^3J_{\text{HH}}$  = 11.9 Hz, 1H,  $=\text{CH}^{\text{Ph}}$ ), 5.70 (d,  $^3J_{\text{HH}}$  = 11.9 Hz, 1H,  $=\text{CH}$ ), 1.33 (s, 9H,  $^t\text{Bu}$ ).

[gbe211\_Nov27-2012\_20]

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (101 MHz, 296 K,  $\text{CDCl}_3$ ):  $\delta$  = 137.1 ( $=\text{CH}^{\text{Ph}}$ ), 136.7 (*i*-Ph), 128.5 (*o*-Ph), 128.1 (*p*-Ph), 128.0 (*m*-Ph)<sup>t</sup>, 108.2 ( $=\text{CH}$ ), 105.5 ( $^t\text{BuC}\equiv$ ), 77.9 ( $\equiv\text{C}$ ), 30.7 ( $^t\text{Bu}$ ), 28.5 ( $^t\text{Bu}$ ), [<sup>t</sup>tentative assigned]. [gbe211\_Nov27-2012\_21]

**$^1\text{H}, ^1\text{H}$  GCOSY** (400 MHz / 400 MHz, 296 K,  $\text{CDCl}_3$ ):  $\delta$   $^1\text{H}$  /  $^1\text{H}$  = 7.89 / 7.35 (*o*-Ph / *m*-Ph), 7.35 / 7.89 (*m*-Ph / *o*-Ph), 6.56 / 5.70 ( $=\text{CH}^{\text{Ph}}$  /  $=\text{CH}$ ), 5.70 / 6.56 ( $=\text{CH}$  /  $=\text{CH}^{\text{Ph}}$ ).

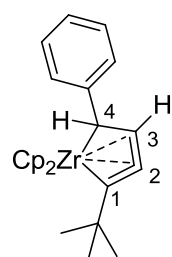
[gbe211\_Nov27-2012\_24]

**$^1\text{H}, ^{13}\text{C}$  GHSQC** (400 MHz / 101 MHz, 295 K,  $\text{CDCl}_3$ ):  $\delta$   $^1\text{H}$  /  $\delta$   $^{13}\text{C}$  = 7.89 / 128.5 (*o*-Ph), 6.56 / 137.1 ( $=\text{CH}^{\text{Ph}}$ ), 5.70 / 108.2 ( $=\text{CH}$ ), 1.33 / 30.7 ( $^t\text{Bu}$ ). [gbe211\_Nov27-2012\_25]

**$^1\text{H}, ^{13}\text{C}$  GHMBC** (400 MHz / 101 MHz, 295 K,  $\text{CDCl}_3$ ):  $\delta$   $^1\text{H}$  /  $\delta$   $^{13}\text{C}$  = 7.89 / 137.1, 128.5, 128.1 (*o*-Ph /  $=\text{CH}^{\text{Ph}}$ , *o*-Ph, *p*-Ph), 6.56 / 136.7, 128.5, 77.9 ( $=\text{CH}^{\text{Ph}}$  / *i*-Ph, *o*-Ph,  $\equiv\text{C}$ ), 5.70 / 137.1, 136.7, 105.5, 30.7 ( $=\text{CH}$  /  $=\text{CH}^{\text{Ph}}$ , *i*-Ph,  $^t\text{BuC}\equiv$ ,  $^t\text{Bu}$ ), 1.33 / 105.5, 30.7, 28.5 ( $^t\text{Bu}$  /  $^t\text{BuC}\equiv$ ,  $^t\text{Bu}$ ,  $^t\text{Bu}$ ). [gbe211\_Nov27-2012\_26]

### Preparation of complex 2c.

At  $-78\text{ }^\circ\text{C}$  *n*-butylmagnesium chloride solution (0.68 ml, 2 M diethyl ether solution, 1.36 mmol, 2 eq) was added to a solution of dichlorobis( $\eta^5$ -cyclopentadienyl)zirconium (200 mg, 0.68 mmol, 1 eq) and 5,5-dimethyl-1-phenyl-hex-1-en-3-yne (153 mg, 0.83 mmol, 1.2 eq) in THF (8 ml). After removal of the dry ice bath, the mixture was allowed to warm to room temperature and then it was stirred for 1 h. Then the orange solution was heated to  $60\text{ }^\circ\text{C}$  for additional 1 h. The deep red mixture was cooled to room temperature and the volatiles were removed *in vacuo*. The resulting residue was extracted with diethyl ether ( $3\times 10$  ml) and filtered. The red coloured filtrate was concentrated and cooled to  $-30\text{ }^\circ\text{C}$ . Compound **2c** was obtained as yellow-orange crystals (161 mg, 58%) which were suitable for an X-ray crystal structure analysis.



**$^1\text{H}$  NMR** (500 MHz, 299 K,  $[d_6]$ -benzene):  $\delta$  = 7.26 (m, 2H, *m*-Ph), 7.21 (m, 2H, *o*-Ph), 6.98 (m, 1H, *p*-Ph), 5.39 (s, 5H,  $\text{Cp}^{\text{A}}$ ), 5.04 (d,  $^3J_{\text{HH}}$  = 13.9 Hz,  $^1J_{\text{CH}}$  = 160.1 Hz, 1H, 3-H), 4.87 (s, 5H,  $\text{Cp}^{\text{B}}$ ), 2.72 (d,  $^3J_{\text{HH}}$  = 13.9 Hz,  $^1J_{\text{CH}}$  = 145.1 Hz, 1H, 4-H), 1.38 (s, 9H,  $^t\text{Bu}$ ). [gbe215\_230113\_299k\_1h]

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz, 299 K,  $[d_6]$ -benzene):  $\delta$  = 162.5 (C-1), 146.4 (*i*-Ph),


128.9 (*m*-Ph), 123.6 (*o*-Ph), 123.0 (*p*-Ph), 116.7 (C-2), 104.8 (Cp<sup>A</sup>), 102.7 (Cp<sup>B</sup>), 92.8 (C-3), 68.5 (C-4), 36.2 (<sup>t</sup>Bu), 33.4 (<sup>t</sup>Bu). [gbe215\_230113\_299k\_13c]

<sup>1</sup>H,<sup>1</sup>H GCSY (500 MHz / 500 MHz, 299 K, [d<sub>6</sub>]-benzene): δ <sup>1</sup>H / <sup>1</sup>H = 7.26 / 7.21, 6.98 (*m*-Ph / *o*-Ph, *p*-Ph), 7.21 / 7.26 (*o*-Ph / *m*-Ph), 6.98 / 7.26 (*p*-Ph / *m*-Ph), 5.04 / 2.72 (3-H / 4-H), 2.72 / 5.04 (4-H / 3-H). [gbe215\_230113\_299k\_gcosy]

<sup>1</sup>H,<sup>13</sup>C GHSQC (500 MHz / 126 MHz, 299 K, [d<sub>6</sub>]-benzene): δ <sup>1</sup>H / δ <sup>13</sup>C = 7.26 / 128.9 (*m*-Ph), 7.21 / 123.6 (*o*-Ph), 6.98 / 123.0 (*p*-Ph), 5.39 / 104.8 (Cp<sup>A</sup>), 5.04 / 92.8 (C-3), 4.87 / 102.7 (Cp<sup>B</sup>), 2.72 / 68.5 (C-4), 1.38 / 33.4 (<sup>t</sup>Bu). [gbe215\_230113\_299k\_ghsqc]

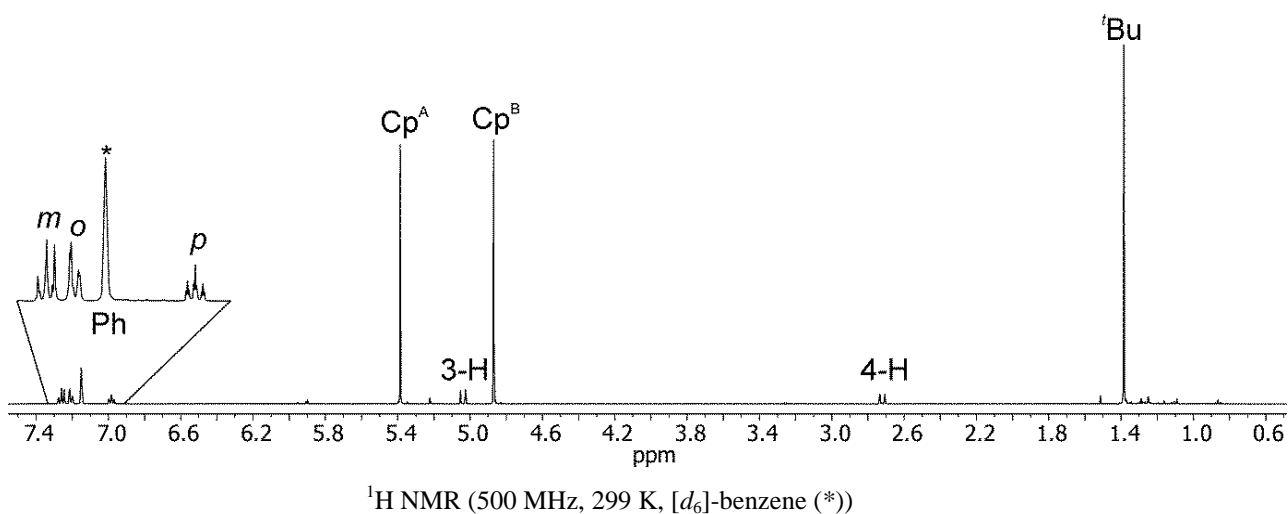
<sup>1</sup>H,<sup>13</sup>C GHMBC (500 MHz / 126 MHz, 299 K, [d<sub>6</sub>]-benzene): δ <sup>1</sup>H / δ <sup>13</sup>C = 7.26 / 146.4, 128.9 (*m*-Ph / *i*-Ph, *m*-Ph), 7.21 / 123.6, 123.0, 68.5 (*o*-Ph / *o*-Ph, *p*-Ph, C-4), 6.98 / 123.6 (*p*-Ph / *o*-Ph), 5.04 / 162.5, 146.4, 116.7, 68.5, 36.2, 33.4 (3-H / C-1, *i*-Ph, C-2, C-4, <sup>t</sup>Bu, <sup>t</sup>Bu), 2.72 / 123.6, 116.7 (4-H / *o*-Ph, C-2), 1.38 / 162.5, 36.2, 33.4 (<sup>t</sup>Bu / C-1, <sup>t</sup>Bu, <sup>t</sup>Bu). [gbe215\_230113\_299k\_ghmbc]

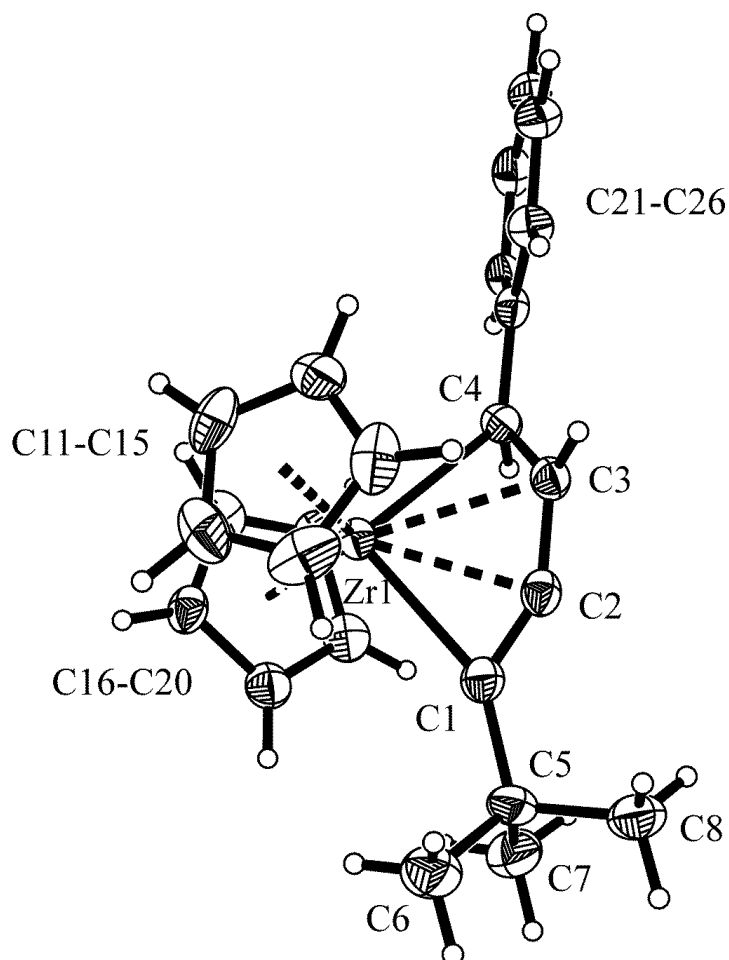
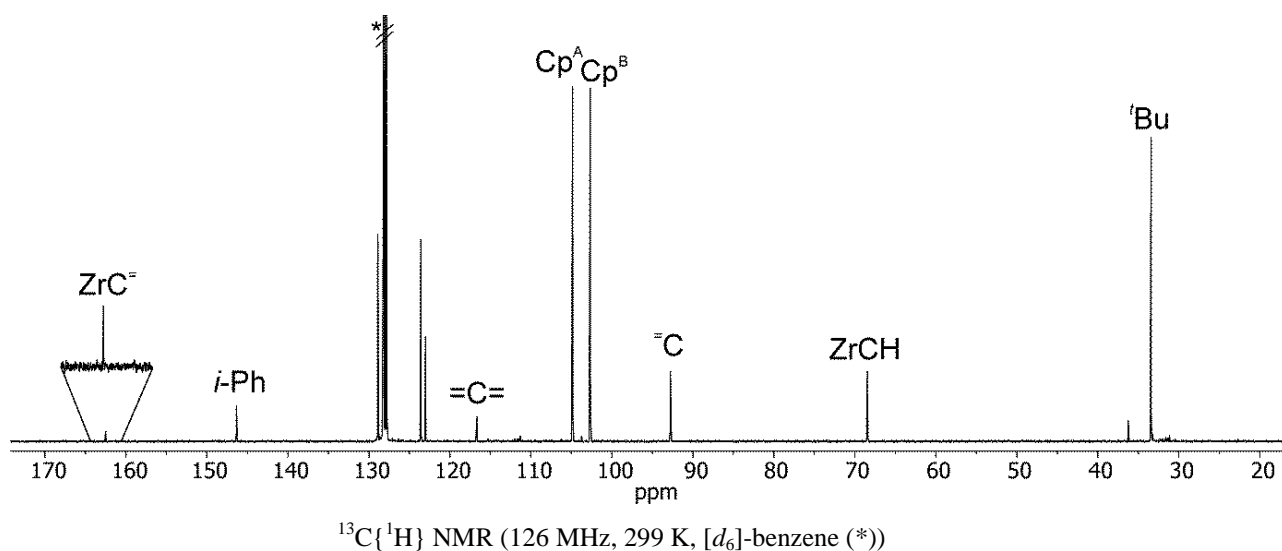
<sup>1</sup>H{<sup>1</sup>H} TOCSY (500 MHz, 299 K, [d<sub>b</sub>]-benzene) [selective experiment]: δ <sup>1</sup>H<sub>irr</sub> / <sup>1</sup>H<sub>res</sub> = 7.26 / 7.21, 6.98 (*m*-Ph / *o*-Ph, *p*-Ph). [gbe215\_230113\_299k\_1dtocsy]

IR (KBr):  [cm<sup>-1</sup>] = 3094 (s), 2956 (s), 2857 (s), 1940 (s), 1811 (s), 1592 (m), 1490 (w), 1340 (m), 1356 (m), 1246 (m), 1154 (s), 1117 (s), 1068 (m), 1014 (w), 892 (w), 863 (w), 788 (br), 747 (m), 698 (m), 643 (m), 554 (s), 522 (s).

**m. p.** (DSC): 102 °C (Decomposition).

**Elemental Analysis:** C<sub>24</sub>H<sub>26</sub>Zr (405.67 g/mol) requires C 71.05, H 6.46, found: C 70.03, H 6.45.



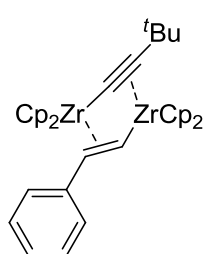


**X-ray crystal structure analysis of 2c (erk7001):** formula  $\text{C}_{24}\text{H}_{26}\text{Zr}$ ,  $M = 405.67$ , yellow-orange crystal,  $0.15 \times 0.07 \times 0.01$  mm,  $a = 14.9219(3)$ ,  $b = 8.0210(2)$ ,  $c = 17.8888(4)$  Å,  $\beta = 112.216(2)^\circ$ ,  $V = 1982.14(8)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.359$  g cm<sup>-3</sup>,  $\mu = 0.557$  mm<sup>-1</sup>, empirical absorption correction ( $0.921 \leq T \leq 0.994$ ),  $Z = 4$ , monoclinic, space group  $P2_1/n$  (No. 14),  $\lambda = 0.71073$  Å,  $T = 223(2)$  K,  $\omega$  and  $\phi$  scans, 12962 reflections collected ( $\pm h, \pm k, \pm l$ ),  $[(\sin\theta)/\lambda] = 0.60$  Å<sup>-1</sup>, 3414 independent ( $R_{\text{int}} = 0.080$ ) and 2696 observed reflections [ $I > 2\sigma(I)$ ], 301 refined

parameters,  $R = 0.072$ ,  $wR^2 = 0.175$ , max. (min.) residual electron density 0.95 (-0.95) e.Å<sup>-3</sup>, the hydrogen atoms at C3 and C4 were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

## Preparation of Complex 6

At -78 °C *n*-butylmagnesium chloride solution (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis( $\eta^5$ -cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and 5,5-dimethyl-1-phenyl-hex-1-en-3-yne (33 mg, 0.18 mmol, 0.5 eq) in THF (5 ml). After removal of the dry ice bath, the mixture was allowed to warm to room temperature and then it was stirred for 1 h. Then the red solution was heated to 60 °C for additional 1 h. The deep red mixture was cooled to room temperature and the volatiles were removed *in vacuo*. The residue was extracted with a mixture of *n*-pentane and toluene (ratio = 20:1, 3×10 ml) and filtered over Celite. The red coloured filtrate was concentrated *in vacuo*. *N*-pentane (3×10 ml) was added to the red residue and the resulting suspension was filtered to obtain complex **6** as red solid (54 mg, 50%). Crystallization from diethyl ether at -30 °C gave the dimer as red crystals, suitable for an X-ray crystal structure analysis.



**<sup>1</sup>H NMR** (500 MHz, 213 K, [*d*<sub>8</sub>]-toluene):  $\delta$  = 9.66 (d,  $^3J_{\text{HH}} = 19.7$  Hz, 1H, ZrCH=), 7.29 (m, 2H, *m*-Ph), 7.18 (m, 2H, *o*-Ph), 7.05 (m, 1H, *p*-Ph), 5.43 (s, 5H, Cp<sup>A</sup>), 5.41 (d,  $^3J_{\text{HH}} = 19.7$  Hz, 1H, CH=), 5.09 (s, 5H, Cp<sup>B</sup>), 5.02 (s, 5H, Cp<sup>C</sup>), 4.62 (s, 5H, Cp<sup>D</sup>), 1.27 (s, 9H, <sup>*t*</sup>Bu). [gbe217g\_250213\_213k\_1h]

**<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, 213 K, [*d*<sub>8</sub>]-toluene):  $\delta$  = 215.0 (ZrC≡), 209.6 (ZrCH=), 170.9 (≡C), 145.8 (*i*-Ph), 128.8 (*m*-Ph), 124.1 (br, *o*-Ph), 124.0 (*p*-Ph), 105.6 (CH=), 104.0 (Cp<sup>A</sup>), 102.44 (Cp<sup>D</sup>), 102.37 (Cp<sup>C</sup>), 102.35 (Cp<sup>B</sup>), 38.1 (<sup>*t*</sup>Bu), 32.7 (<sup>*t*</sup>Bu). [gbe217g\_250213\_213k\_13c]

**<sup>1</sup>H, <sup>1</sup>H GCOSY** (500 MHz / 500 MHz, 213 K, [*d*<sub>8</sub>]-toluene):  $\delta$  <sup>1</sup>H / <sup>1</sup>H = 9.66 / 5.41 (ZrCH= / CH=), 7.29 / 7.18, 7.05 (*m*-Ph / *o*-Ph, *p*-Ph), 7.18 / 7.29 (*o*-Ph / *m*-Ph), 7.05 / 7.29 (*p*-Ph / *m*-Ph), 5.41 / 9.66 (CH= / ZrCH=). [gbe217g\_250213\_213k\_gcosy]

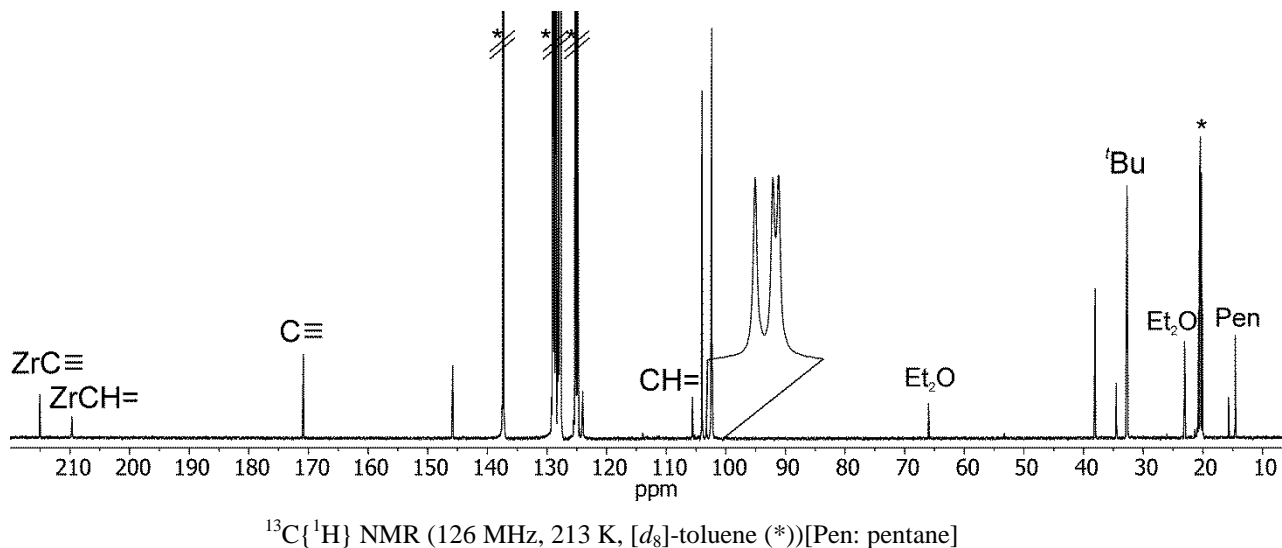
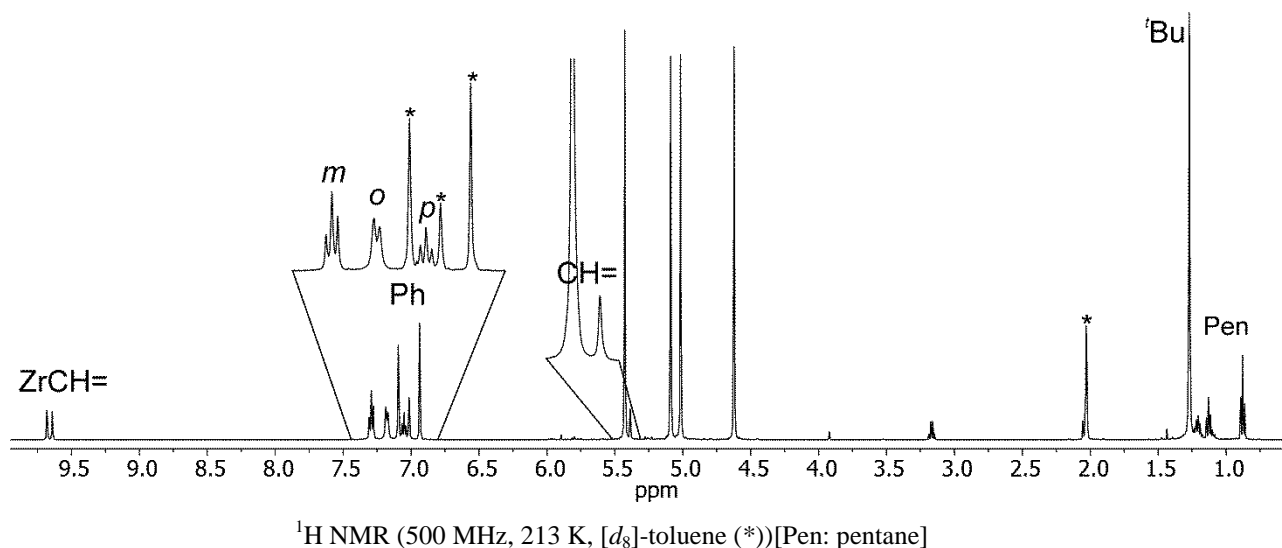
**<sup>1</sup>H, <sup>13</sup>C GHSQC** (500 MHz / 126 MHz, 213 K, [*d*<sub>8</sub>]-toluene):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 9.66 / 209.6 (ZrCH=), 7.29 / 128.8 (*m*-Ph), 7.18 / 124.1 (*o*-Ph), 7.05 / 124.0 (*p*-Ph), 5.43 / 104.0 (Cp<sup>A</sup>), 5.41 / 105.6 (CH=), 5.09 / 102.35 (Cp<sup>B</sup>), 5.02 / 102.37 (Cp<sup>C</sup>), 4.62 / 102.44 (Cp<sup>D</sup>), 1.27 / 32.7 (<sup>*t*</sup>Bu). [gbe217g\_250213\_213k\_ghs qc]

**<sup>1</sup>H, <sup>13</sup>C GHMBC** (500 MHz / 126 MHz, 213 K, [*d*<sub>8</sub>]-toluene):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C = 9.66 / 145.8, 105.6 (ZrCH= / *i*-Ph, CH=), 7.29 / 145.8, 128.8 (*m*-Ph / *i*-Ph, *m*-Ph), 7.18 / 124.0, 105.6 (*o*-Ph

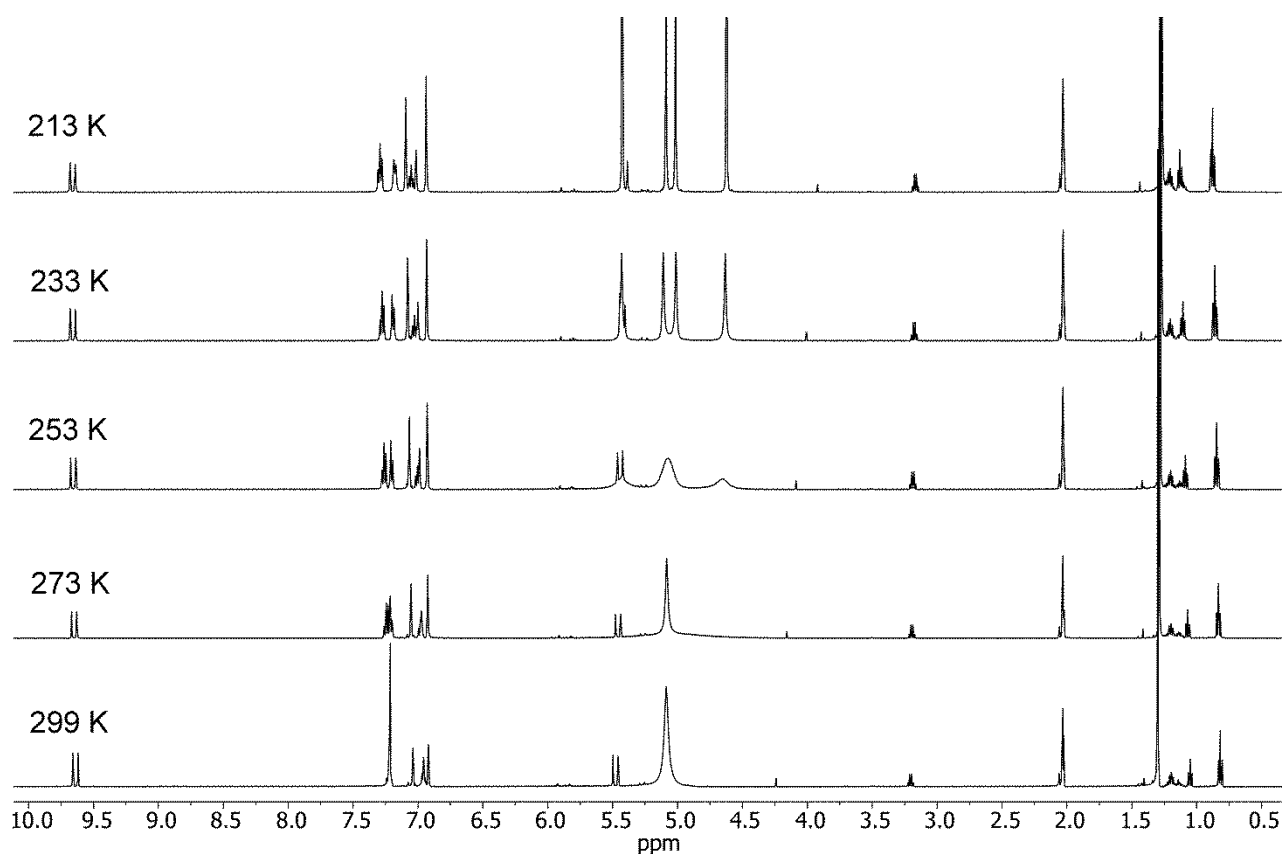
/ *p*-Ph, CH=), 5.41 / 209.6, 145.8 (CH= / ZrCH=, *i*-Ph), 1.27 / 170.9, 38.1, 32.7 (<sup>*t*</sup>Bu / ≡C, <sup>*t*</sup>Bu, <sup>*t*</sup>Bu). [gbe217g\_250213\_213k\_ghmbc]

**IR** (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 2956 (w), 2858 (w), 1789 (m), 1635 (w), 1588 (m), 1483 (m), 1451 (m), 1414 (m), 1384 (w), 1352 (m), 1291 (w), 1273 (m), 1226 (m), 1168 (w), 1126 (w), 1069 (m), 1014 (s), 967 (w), 877 (m), 846 (w), 813 (m), 737 (w), 694 (w), 599 (m), 529 (w), 445 (w).

**m. p.** (DSC): 116 °C (Decomposition).







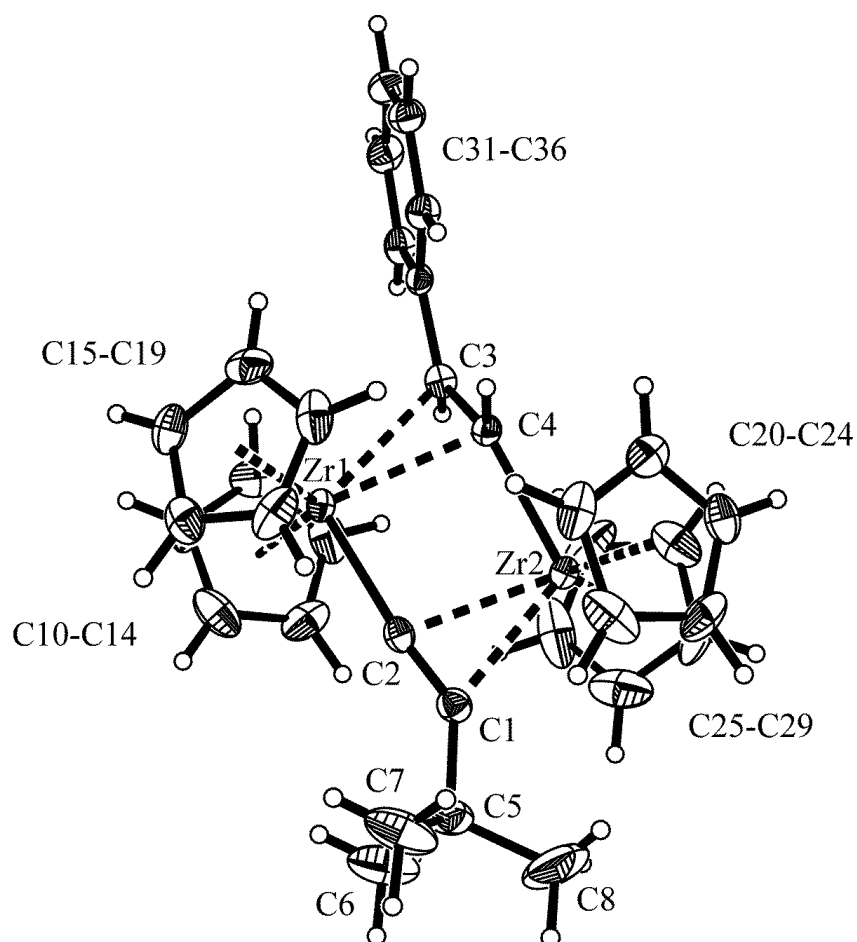
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $[d_8]$ -toluene) of complex **6** at various temperatures.

**Gibbs-Energy:**  $\Delta G = RT_c[22.96 + \ln(T_c/\Delta\nu)]$

$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ;  $1 \text{ cal} = 4.187 \text{ J}$

a)  $\Delta G_{\text{rearr}}^{\ddagger}(T_c = 273 \text{ K}; \Delta\nu(\text{Cp}, 213 \text{ K}) = 402 \text{ Hz}) = 12.2 \text{ kcal}\cdot\text{mol}^{-1}$

b)  $\Delta G_{\text{rearr}}^{\ddagger}(T_c = 243 \text{ K}; \Delta\nu(\text{Cp}, 213 \text{ K}) = 37 \text{ Hz}) = 12.0 \text{ kcal}\cdot\text{mol}^{-1}$

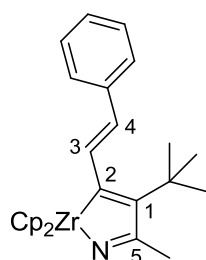


**X-ray crystal structure analysis of 6 (erk6964):** formula  $C_{34}H_{36}Zr_2$ ,  $M = 627.07$  yellow-orange crystal,  $0.08 \times 0.03 \times 0.03$  mm,  $a = 8.2886(2)$ ,  $b = 13.2145(3)$ ,  $c = 15.2253(4)$  Å,  $\alpha = 67.337(1)$ ,  $\beta = 85.182(1)$ ,  $\gamma = 83.609(1)^\circ$ ,  $V = 1527.76(6)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.363$  gcm<sup>-3</sup>,  $\mu = 0.701$  mm<sup>-1</sup>, empirical absorption correction ( $0.946 \leq T \leq 0.979$ ),  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 0.71073$  Å,  $T = 223(2)$  K,  $\omega$  and  $\phi$  scans, 14047 reflections collected ( $\pm h, \pm k, \pm l$ ),  $[(\sin\theta)/\lambda] = 0.60$  Å<sup>-1</sup>, 7350 independent ( $R_{\text{int}} = 0.044$ ) and 5792 observed reflections [ $I > 2\sigma(I)$ ], 336 refined parameters,  $R = 0.054$ ,  $wR^2 = 0.116$ , max. (min.) residual electron density 0.45 (-0.47) e.Å<sup>-3</sup>, the hydrogen atoms at C3 and C4 were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

### Preparation of complex 8

A solution of acetonitrile (24 mg, 0.59 mmol, 3.4 eq) in toluene (2 ml) was added to a solution of complex **2c** (70 mg, 0.17 mmol, 1 eq) in toluene (5 ml). The reaction mixture was stirred over night at room temperature. Then the volatiles of the reaction suspension were removed *in vacuo* and the obtained residue was extracted with dichloromethane (3×5 ml). The orange filtrate was concentrated *in vacuo* and covered with *n*-pentane. Crystallization at  $-30$

°C gave the complex **8** as orange crystals (23 mg, 29%), which were suitable for an X-ray crystal structure analysis.



**$^1\text{H}$  NMR** (600 MHz, 299 K,  $[d_2]$ -dichloromethane):  $\delta$  = 7.42 (m, 2H, *o*-Ph), 7.36 (d,  $^3J_{\text{HH}}$  = 15.8 Hz, 1H, 3-H), 7.32 (m, 2H, *m*-Ph), 7.12 (m, 1H, *p*-Ph), 5.83 (Cp), 5.80 (d,  $^3J_{\text{HH}}$  = 15.8 Hz, 1H, 4-H), 2.46 (s, 3H, Me), 1.42 (s, 9H,  $^t\text{Bu}$ ). [gbe221\_040313\_299k\_13c]

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz, 299 K,  $[d_2]$ -dichloromethane):  $\delta$  = 205.2 (C-2), 193.4 (C-5), 148.7 (C-1), 141.2 (C-3), 140.1 (*i*-Ph), 129.0 (*m*-Ph), 125.8 (*o*-Ph), 125.5 (*p*-Ph), 115.8 (C-4), 110.6 (Cp), 37.7 ( $^t\text{Bu}$ ), 33.8 ( $^t\text{Bu}$ ), 30.4 (Me). [gbe221\_040313\_299k\_13c]

**$^1\text{H}, ^1\text{H}$  GCOSY** (600 MHz / 600 MHz, 299 K,  $[d_2]$ -dichloromethane):  $\delta$   $^1\text{H}$  /  $^1\text{H}$  = 7.42 / 7.32 (*o*-Ph / *m*-Ph), 7.36 / 5.80 (3-H / 4-H), 7.32 / 7.42, 7.12 (*m*-Ph / *o*-Ph, *p*-Ph), 7.12 / 7.32 (*p*-Ph / *m*-Ph), 5.80 / 7.36 (4-H / 3-H). [gbe221\_040313\_299k\_gcosy]

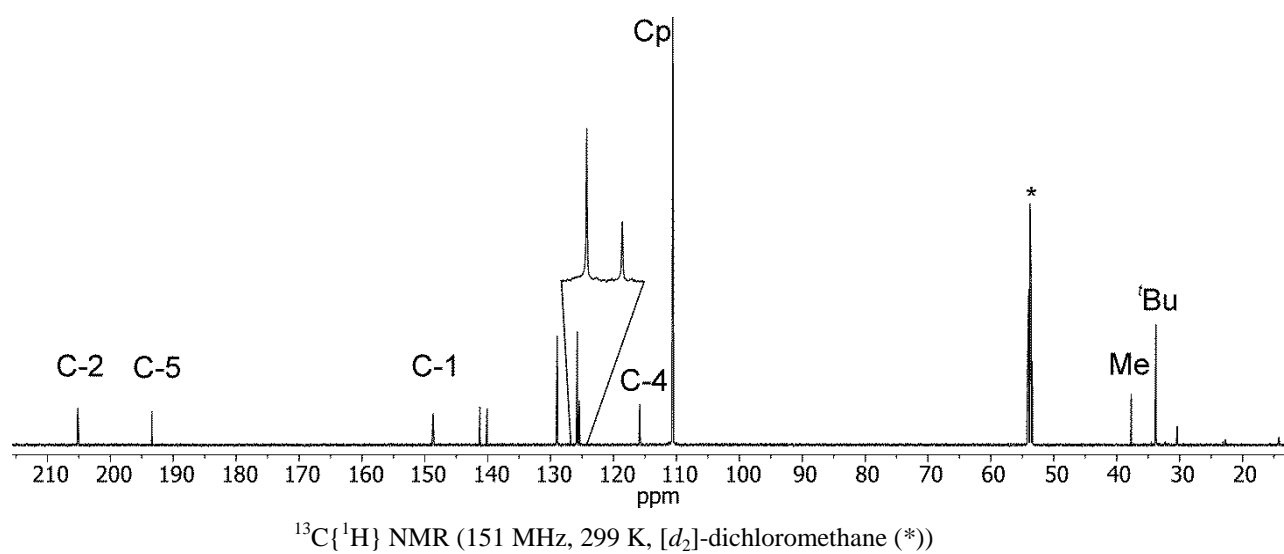
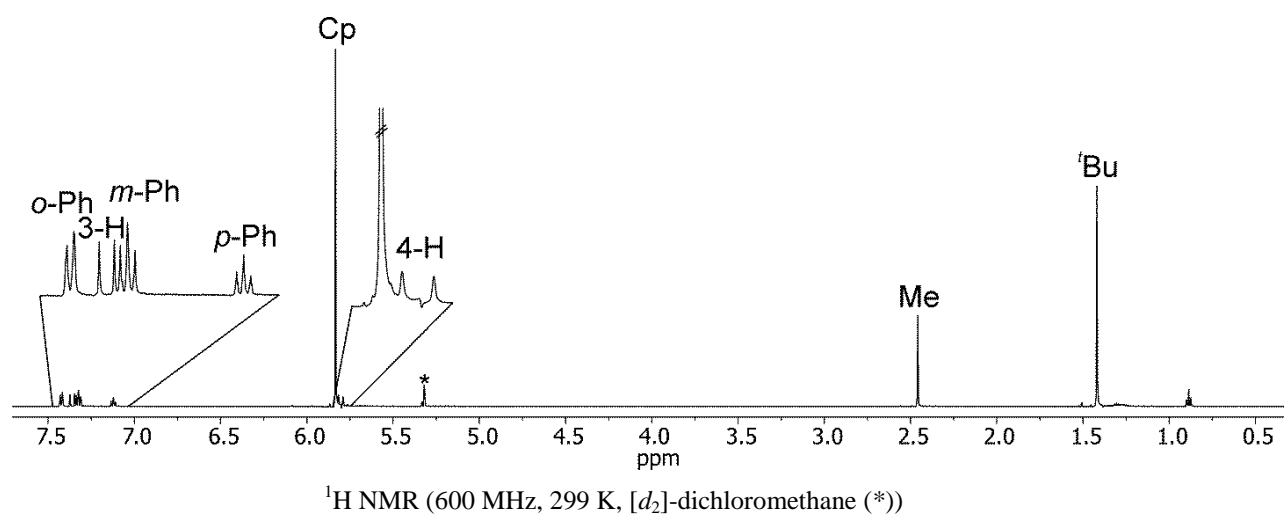
**$^1\text{H}, ^{13}\text{C}$  GHSQC** (600 MHz / 151 MHz, 299 K,  $[d_2]$ -dichloromethane):  $\delta$   $^1\text{H}$  /  $\delta$   $^{13}\text{C}$  = 7.42 / 125.8 (*o*-Ph), 7.36 / 141.2 (3-H), 7.32 / 129.0 (*m*-Ph), 7.12 / 125.5 (*p*-Ph), 5.83 / 110.6 (Cp), 5.80 / 115.8 (4-H), 2.46 / 30.4 (Me), 1.42 / 33.8 ( $^t\text{Bu}$ ). [gbe221\_040313\_299k\_ghsqc]

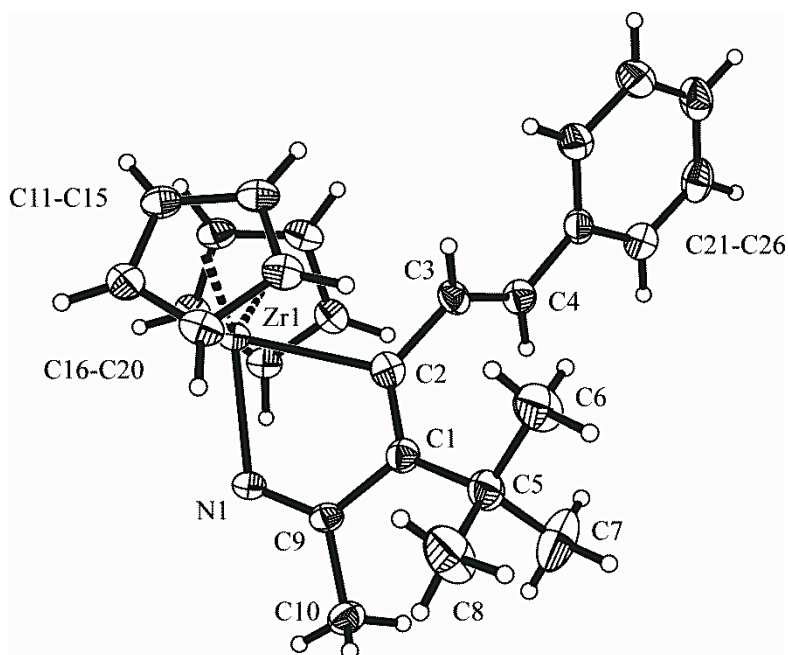
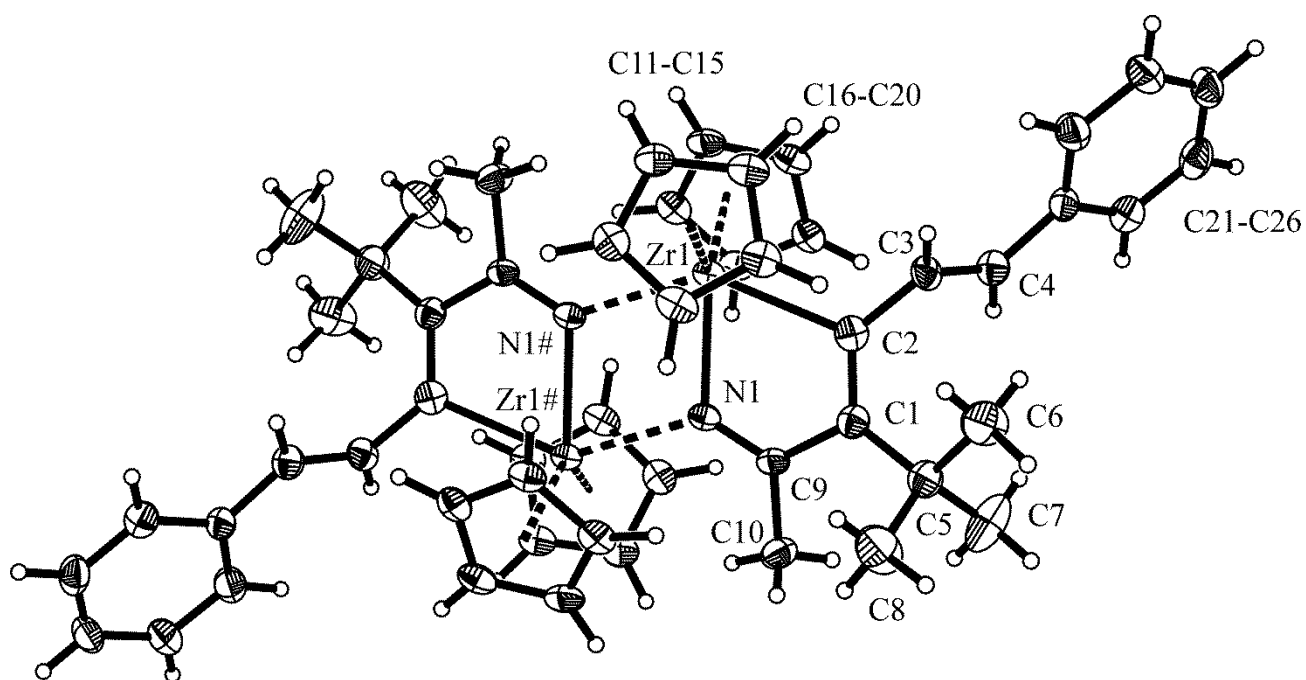
**$^1\text{H}, ^{13}\text{C}$  GHMBC** (600 MHz / 151 MHz, 299 K,  $[d_2]$ -dichloromethane):  $\delta$   $^1\text{H}$  /  $\delta$   $^{13}\text{C}$  = 7.42 / 125.5, 115.8 (*o*-Ph / *p*-Ph, C-4), 7.36 / 148.7, 140.1, 115.8 (3-H / C-1, *i*-Ph, C-4), 7.32 / 140.1, 129.0 (*m*-Ph / *i*-Ph, *m*-Ph), 7.12 / 125.8 (*p*-Ph / *o*-Ph), 5.80 / 205.2, 140.1, 125.8 (4-H / C-2, *i*-Ph, *o*-Ph), 2.46 / 193.4, 148.7 (Me / C-5, C-1), 1.42 / 148.7, 37.7, 33.8 ( $^t\text{Bu}$  / C-1,  $^t\text{Bu}$ ,  $^t\text{Bu}$ ). [gbe221\_040313\_299k\_ghmbc]

**IR** (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 2994 (w), 2956 (w), 1800 (w), 1696 (w), 1591 (m), 1553 (m), 1496 (m), 1442 (m), 1360 (m), 1238 (m), 1198 (m), 1047 (s), 1026 (s), 957 (s), 904 (m), 806 (s), 751 (s), 695 (s), 631 (m), 582 (w), 535 (s), 491 (m), 439 (w).

**m. p.** (DSC): 170 °C (melting point), 175 °C (Decomposition).

**Elemental Analysis:**  $\text{C}_{26}\text{H}_{29}\text{NZr}$  (446.74 g/mol) requires C 69.95, H 6.54, N 3.14, found: C 69.64, H 6.60, N 2.95.





**X-ray crystal structure analysis of 8 (erk7052):** formula  $C_{52}H_{58}N_2Zr_2 \cdot 2 \times CH_2Cl_2$   $M = 1063.30$  orange crystal,  $0.10 \times 0.07 \times 0.02$  mm,  $a = 8.7664(2)$ ,  $b = 15.5494(3)$ ,  $c = 18.6857(6)$  Å,  $\alpha = 96.113(1)$ ,  $\beta = 93.685(1)$ ,  $\gamma = 99.541(1)^\circ$ ,  $V = 2488.84(11)$  Å<sup>3</sup>,  $\rho_{calc} = 1.419$  gcm<sup>-3</sup>,  $\mu = 0.671$  mm<sup>-1</sup>, empirical absorption correction ( $0.935 \leq T \leq 0.986$ ),  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 0.71073$  Å,  $T = 223(2)$  K,  $\omega$  and  $\phi$  scans, 23389 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ),  $[(\sin\theta)/\lambda] = 0.60$  Å<sup>-1</sup>, 8603 independent ( $R_{int} = 0.079$ ) and 6393 observed reflections [ $I > 2\sigma(I)$ ], 602 refined parameters,  $R = 0.071$ ,  $wR^2 = 0.155$ , max. (min.) residual electron density 0.50 (-0.44) e.Å<sup>-3</sup>, hydrogen atoms calculated and refined as riding atoms.