Electronic Supplementary Material (ESI) for Chemical Science

Chemistry of the Five-membered Zirconacycloallenoids: Reactions with Unsaturated Substrates**

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SUPPORTING INFORMATION

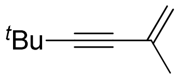
General Procedures. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried with the procedure according to Grubbs (A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.) or were distilled from appropriate drying agents and stored under an argon atmosphere. ***Caution: many isocyanides are toxic compounds that need to be handled with due care***. Dichlorobis(η^5-cyclopentadienyl)zirconium (J. J. Eisch, F. A. Owuor and P. O. Otieno, *Organometallics*, 2001, **20**, 4132.) and trimethyl(3-methyl-but-3-en-1-ynyl)silane (**7c**) (J. Waser, J. C. Gonzalez-Gomez, H. Nambu, P. Huber and E. M. Carreira, *Org. Lett.*, 2005, **7**, 4249) were prepared according to published procedures and fully characterized by NMR spectroscopy. Purchased starting materials and other chemicals or reagents (Aldrich, Fluka, ABCR and Acros) were used without further purification. The following instruments were used for physical characterization of the compounds: NMR spectra: *Bruke*r AV 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz), *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz), *Varian* UnityPlus 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ, reported in ppm, is given relative to TMS and referenced to the solvent signal {$CDCl_3$ (δ_H = 7.26, δ_C = 77.0), [d_6]-benzene (δ_H = 7.15, δ_C = 128.0), [d_8]-toluene (δ_H = 2.03, δ_C = 20.4)}. NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (*TA Instruments*). Mass spectra were recorded on a Orbitrap LTQ XL (*Thermo Scientific*).

X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Bruker, 2008); 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). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: The carbon atom C15 in the compound **8** displayed irregular displacement ellipsoid, which was therefore constrained to be more regular using the program command ISOR. The hydrogen of the N1 atom in compound **10** was refined freely, but with fixed U-value.

2,5,5-Trimethyl-1-hexen-3-yne (7b)

Diethylamine (20 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 2-bromopropene (1.80 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* (64 mbar, 43 °C) yielding the 1,3-ene-yne **7b** as colourless oil (1.48 g, 60 %).



^{1}H NMR (300 MHz, 295 K, $CDCl_3$): δ = 5.17 (m, 1H, $=CH_2$), 5.11 (m, 1H, $=CH_2$), 1.85 (m, 3H, Me), 1.24 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (75 MHz, 295 K, $CDCl_3$): δ = 127.3 (C=), 120.1 ($=CH_2$), 97.5 (^{t}BuC≡), 80.1 (≡C), 31.0 (^{t}Bu), 27.7 (^{t}Bu), 24.0 (Me).

MS-Es$^+$ ($CHCl_3/CH_3OH$ + CF_3COOAg): m/z = calcd. for $C_9H_{14}Ag^+$ = 229.0141 g/mol, found 229.0136 g/mol.

1,1-Bis(η^5-cyclopentadienyl)zirconium[(η^2-2,3)-2-*tert*-butyl-3-(1-methylethenyl)-2-yne] [2-(isocyano-κN)-2-methylpropane] (8)

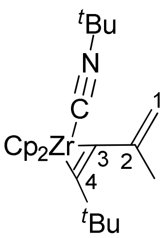
n-Butylmagnesium chloride (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and 2,5,5-trimethyl-1-hexen-3-yne (37 mg, 0.30 mmol, 0.9 eq) in THF (5 ml) at –78 °C. After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1 h. Then the yellow solution was heated to 60 °C for additional 1 h. The deep brown mixture was cooled to room temperature and *tert*-butyl isocyanide (29 mg, 0.35 mmol, 1 eq) was added. The red-brown solution was stirred over night. Subsequently dioxane (0.2 ml) was added and the suspension was stirred for 1 h. The volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. The red coloured filtrate was concentrated *in vacuo* yielding compound **8** as red-brown oil (120 mg, 94%). Crystallization from *n*-pentane at –30 °C gave the complex **8** as yellow crystals (25 mg, 20%), suitable for X-ray crystal structure analysis. Two isomers were detected by NMR experiments: ratio major/minor ≈ 8:1 ([d_6]-benzene, 298 K).

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3067 (s), 2949 (m), 2856 (m), 2159 (w), 1703 (w), 1585 (m), 1456 (m), 1355 (m), 1259 (m), 1210 (w), 1012 (w), 776 (w), 503 (m), 421 (m).

Melting point (DSC): 120 °C.

MS-ESI-EM: Calcd. for [$C_{24}H_{33}NZr$ + H]$^+$: 426.1733 g/mol, found 426.1725 g/mol.

Major isomer



^{1}H NMR (500 MHz, 298 K, [d_6]-benzene): δ = 5.47 (m, 10H, Cp), 4.62 (m, 1H, $=CH_2^E$), 4.26 (m, 1H, $=CH_2^Z$), 1.80 (s, 3H, Me), 1.45 (s, 9H, ^{t}Bu), 1.06 (s, 9H, ^{t}Bu^N).

^{13}C{^{1}H} NMR (126 MHz, 298 K, [d_6]-benzene): δ = 174.4 (C-4), 170.3 (C≡N)^t, 155.3 (C-2)^t, 148.1 (C-3)^t, 102.1 (Cp), 98.1 ($=CH_2$), 56.1, 30.4 (^{t}Bu^N), 39.2, 32.4 (^{t}Bu), 23.7 (Me), [^{t} tentative assignment].

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, [d_6]-benzene): δ ^{1}H / ^{1}H = 4.62 / 4.26, 1.80 ($=CH_2^E$ / $=CH_2^Z$, Me), 4.26 / 4.62, 1.80 ($=CH_2^Z$ / $=CH_2^E$, Me), 1.80 / 4.62, 4.26 (Me / $=CH_2^E$, $=CH_2^Z$).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 5.47 / 102.1 (Cp), 4.62 / 98.2 ($=CH_2$), 4.26 / 98.2 ($=CH_2$), 1.80 / 23.7 (Me), 1.45 / 32.4 (^{t}Bu), 1.06 / 30.4 (^{t}Bu^N).

^{1}H,^{13}C GHMBC (500 MHz / 151 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 4.62 / 148.1, 23.7 ($=CH_2^E$ / C-3, Me), 4.26 / 148.1, 23.7 ($=CH_2^Z$ / C-3, Me), 1.80 / 155.3, 148.1, 98.2 (Me / C-2, C-3, $=CH_2$), 1.45 / 174.4, 39.2 (^{t}Bu / C-4, ^{t}Bu), 1.06 / 56.1 (^{t}Bu^N / ^{t}Bu^N).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 298 K, [d_6]-benzene) [selective experiment]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 1.80 / 5.47, 4.62, 1.45, 1.06 (Me / Cp, $=CH_2^E$, ^{t}Bu, ^{t}Bu^N).

Minor isomer

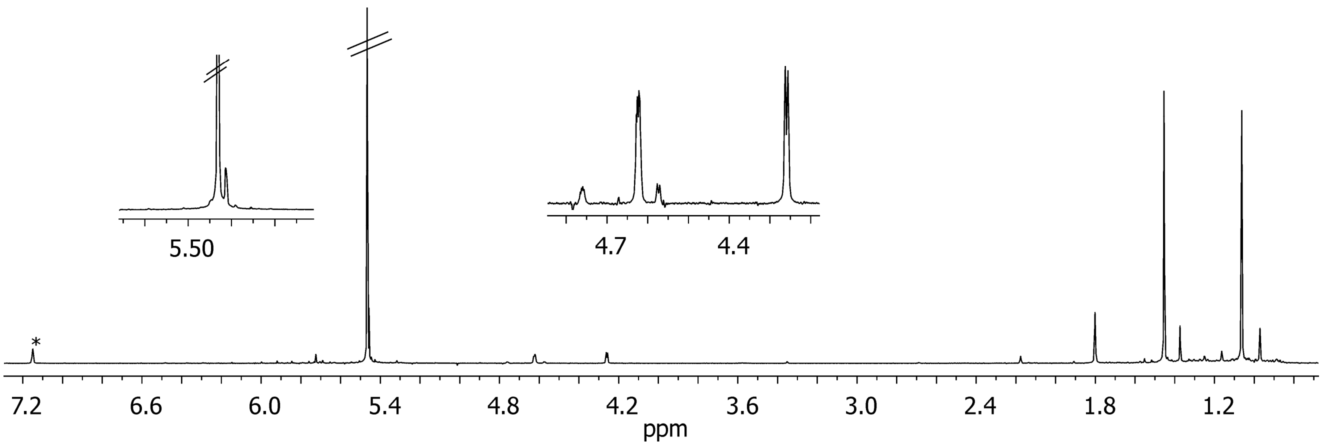
^{1}H NMR (500 MHz, 298 K, [d_6]-benzene): δ = 5.46 (m, 10H, Cp), 4.76 (m, 1H, $=CH_2$), 4.57 (m, 1H, $=CH_2$), 2.18 (s, 3H, Me), 1.37 (s, 9H, ^{t}Bu), 0.97 (s, 9H, ^{t}Bu^N).

^{13}C{^{1}H} NMR (126 MHz, 298 K, [d_6]-benzene): δ = 169.8 (C≡N)[t], 160.7 (C-3)[t], 159.4 (C-4), 156.0 (C-2)[t], 102.9 (Cp), 99.8 (=CH_2), 56.7, 29.5 (^{t}Bu^{N}), 38.5, 31.4 (^{t}Bu), 24.6 (Me), [t tentative assignment].

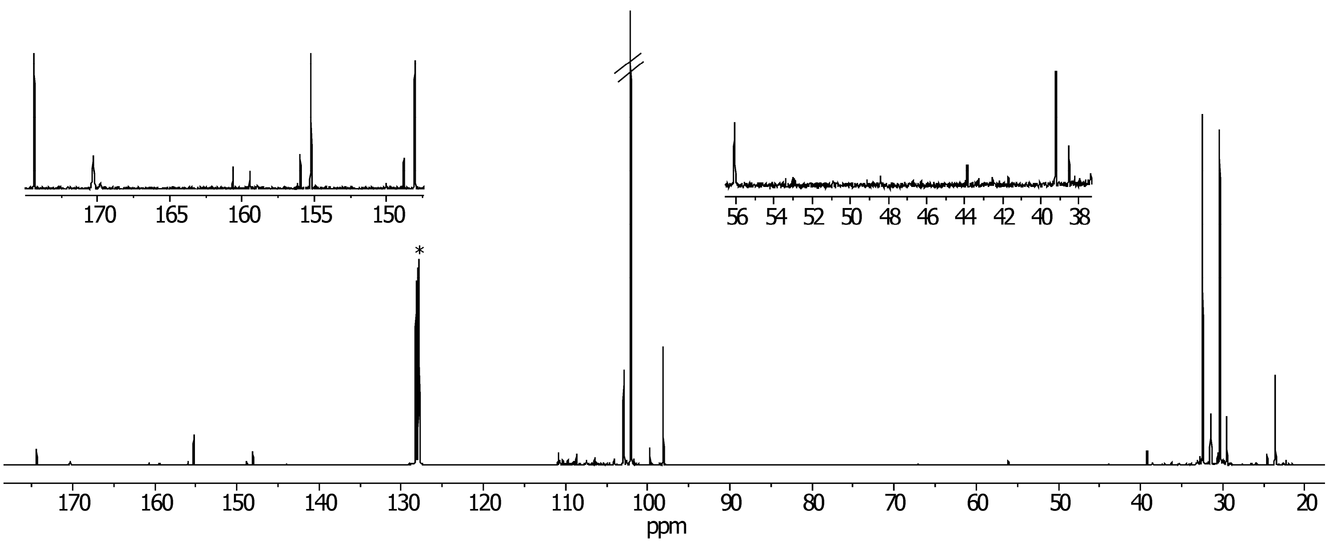
^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, [d_6]-benzene): δ ^{1}H / ^{1}H = 4.76 / 4.57, 2.18 (=CH_2 / =CH_2, Me), 4.57 / 4.76, 2.18 (=CH_2 / =CH_2, Me), 2.18 / 4.76, 4.57 (Me / =CH_2, =CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 5.46 / 102.9 (Cp), 4.76 / 99.8 (=CH_2), 4.57 / 99.8 (=CH_2), 2.18 / 24.6 (Me), 1.37 / 31.4 (^{t}Bu), 0.97 / 29.5 (^{t}Bu^{N}).

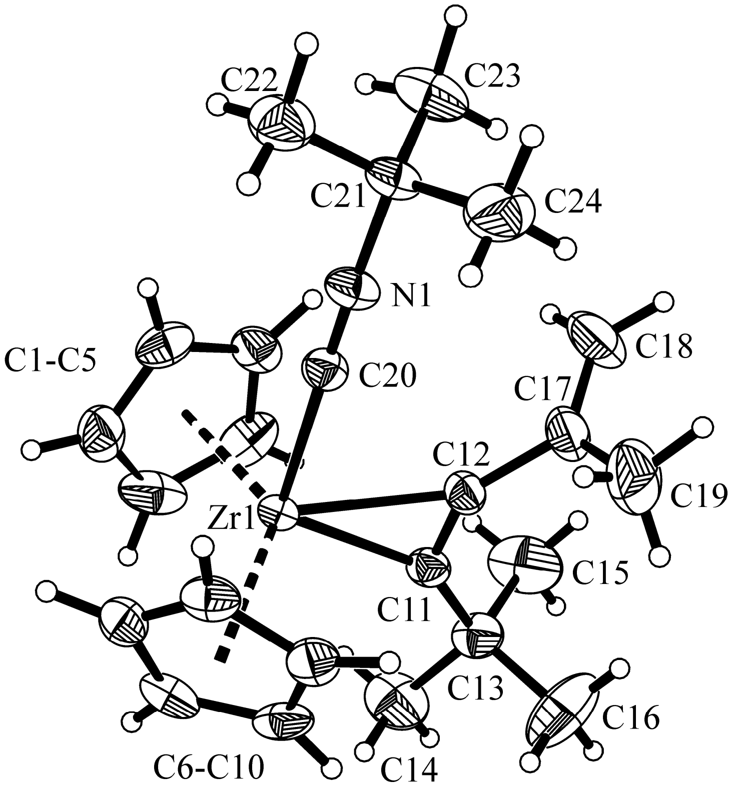
^{1}H,^{13}C GHMBC (500 MHz / 151 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 4.76 / 160.7, 24.6 (=CH_2 / C-3, Me), 4.57 / 160.7, 24.6 (=CH_2 / C-3, Me), 2.18 / 160.7, 156.0, 99.8 (Me / C-3, C-2, =CH_2), 1.37 / 159.5, 38.5 (^{t}Bu / C-4, ^{t}Bu), 0.97 / 56.7 (^{t}Bu^{N} / ^{t}Bu^{N}).



^{1}H NMR (500 MHz, 298 K, [d_6]-benzene (*))



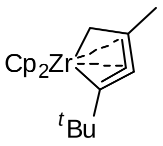
^{13}C{^{1}H} NMR (126 MHz, 298 K, [d_6]-benzene (*))



X-ray crystal structure analysis of 8: formula $C_{24}H_{33}NZr$ * 0.5 C_5H_{12}, M = 462.81, yellow crystal, 0.30 x 0.15 x 0.07 mm, a = 34.6943(5), b = 8.5794(1), c = 17.9781(3) Å, β = 104.784(1)°, V = 5174.14(13) Å^3, ρ_{calc} = 1.188 gcm^{-3}, μ = 0.436 mm^{-1}, empirical absorption correction (0.880 ≤ T ≤ 0.970), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 14052 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 4477 independent (R_{int} = 0.034) and 4019 observed reflections [I>2σ(I)], 253 refined parameters, R = 0.043, wR^2 = 0.113, max. (min.) residual electron density 0.62 (-0.44) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

1,1-Bis(η^5-cyclopentadienyl)-4-methyl-2-*tert*-butyl-1-zirconacyclopenta-2,3-diene (6b)

n-Butylmagnesium chloride (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and 2,5,5-trimethyl-1-hexen-3-yne (37 mg, 0.30 mmol, 0.9 eq) in THF (5 ml) at –78 °C. After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1 h. Then the yellow solution was heated to 60 °C for additional 1 h. The deep red-brown mixture was cooled to room temperature and dioxane (0.2 ml) was added. After the solution was stirred for 30 min the volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. The red-brown coloured filtrate was concentrated *in vacuo* yielding the five-membered compound **6b** as red oil (98 mg, 95%).



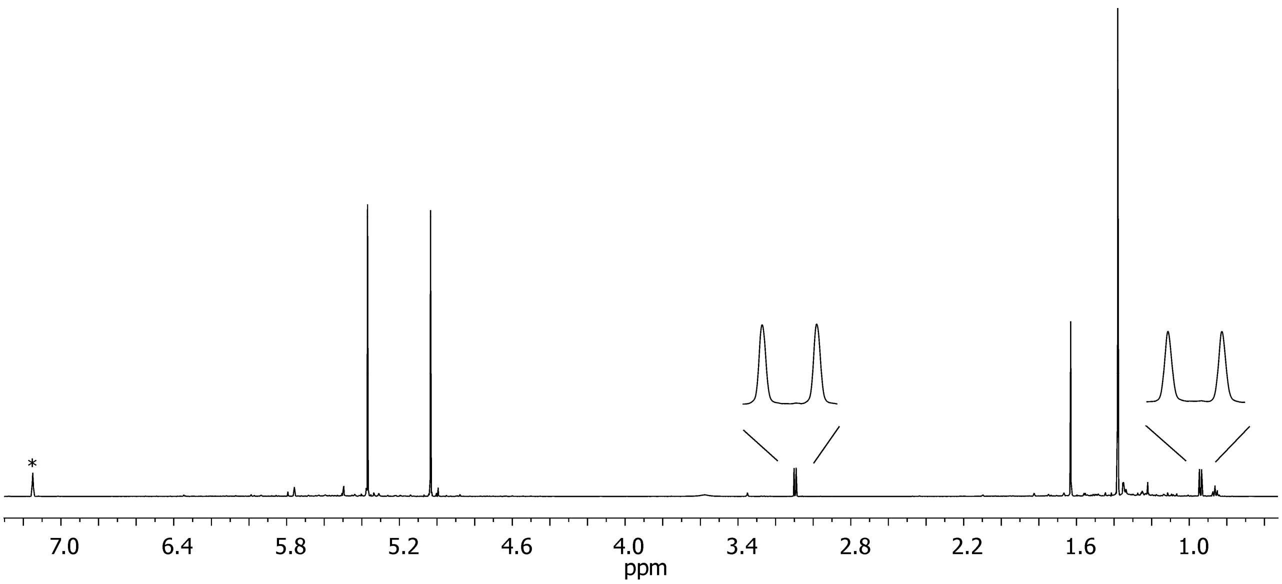
^{1}H NMR (600 MHz, 298 K, [d_6]-benzene): δ = 5.37 (s, 5H, Cp^A), 5.04 (s, 5H, Cp^B), 3.10 (d, $^2J_{HH}$ = 6.7 Hz, 1H, $ZrCH_2$), 1.63 (s, 3H, Me), 1.38 (s, 9H, ^{t}Bu), 0.94 (d, $^2J_{HH}$ = 6.7 Hz, 1H, $ZrCH_2$).

^{13}C{^{1}H} NMR (151 MHz, 298 K, [d_6]-benzene): δ = 161.8 (ZrC=), 124.1 (=C=)^t, 107.4 (=C)^t, 104.0 (Cp^A), 102.3 (Cp^B), 50.3 ($ZrCH_2$), 36.3, 33.5 (^{t}Bu), 26.3 (Me), [^{t} tentative assignment].

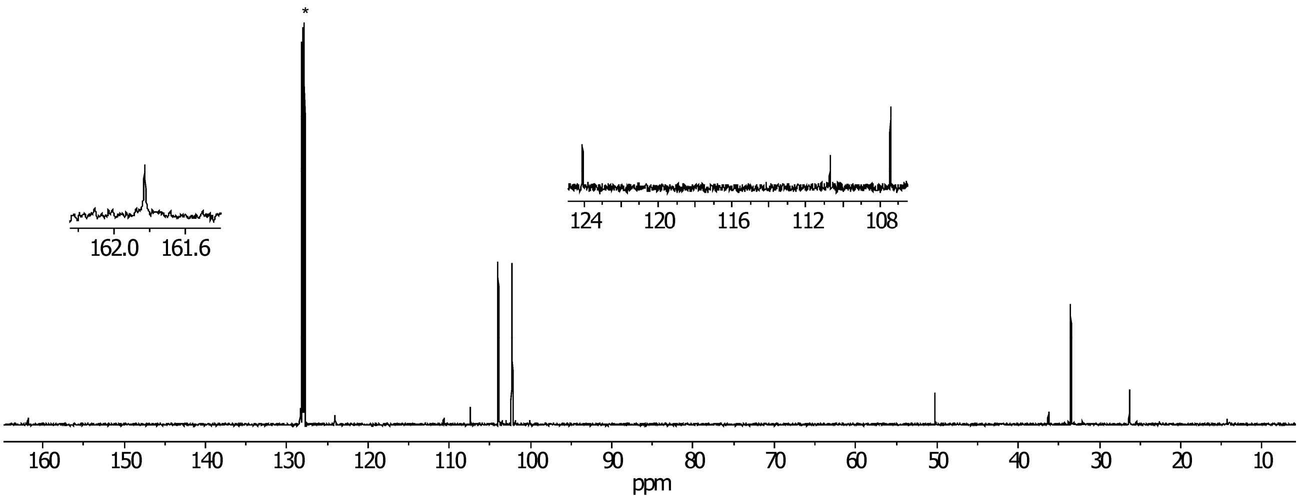
^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 298 K, [d_6]-benzene): δ ^{1}H / ^{1}H = 3.10 / 0.94 ($ZrCH_2$ / $ZrCH_2$), 0.94 / 3.10 ($ZrCH_2$ / $ZrCH_2$).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 5.37 / 104.0 (Cp^A), 5.04 / 102.3 (Cp^B), 3.10 / 50.3 ($ZrCH_2$), 1.63 / 26.3 (Me), 1.38 / 33.5 (^{t}Bu), 0.94 / 50.3 ($ZrCH_2$).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 3.10 / 124.1, 107.4, 26.3 ($ZrCH_2$ / =C=, =C, Me), 1.63 / 124.1, 107.4, 50.3 (Me / =C=, =C, $ZrCH_2$), 1.38 / 161.8, 36.3 (^{t}Bu / ZrC=, ^{t}Bu), 0.94 / 124.1, 26.3 ($ZrCH_2$ / =C=, Me).



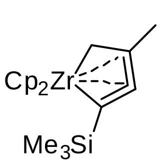
^{1}H NMR (600 MHz, 298 K, [d_6]-benzene (*))



$^{13}C\{^1H\}$ NMR (151 MHz, 298 K, [d_6]-benzene (*))

1,1-Bis(η^5-cyclopentadienyl)-4-methyl-2-trimethylsilyl-1-zirconacyclopenta-2,3-diene (6c)

n-Butylmagnesium chloride (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and trimethyl(3-methyl-but-3-en-1-ynyl)silane (38 mg, 0.27 mmol, 0.8 eq) in THF (5 ml) at –78 °C. After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1 h. Then the orange solution was heated to 60 °C for additional 1 h. The deep brown mixture was cooled to room temperature and dioxane (0.2 ml) was added. After the solution was stirred for 30 min the volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. The brown coloured filtrate was concentrated *in vacuo* to give the five-membered compound **6c** as brown oil.



^{1}H NMR (500 MHz, 298 K, [d_6]-benzene): δ = 5.31 (s, 5H, Cp^A), 5.04 (s, 5H, Cp^B), 2.95 (d, $^2J_{HH}$ = 7.8 Hz, 1H, $ZrCH_2$), 1.62 (s, 3H, Me), 0.85 (d, $^2J_{HH}$ = 7.8 Hz, 1H, $ZrCH_2$), 0.36 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, [d_6]-benzene): δ = 138.2 (=C=)^t, 133.3 ($^1J_{SiC}$ = 69.0 Hz, ZrC=), 104.2 (Cp^A), 102.2 (Cp^B), 94.7 (=C)^t, 48.6 ($ZrCH_2$), 25.1 (Me), 1.7 ($^1J_{SiC}$ = 53.7 Hz, $SiMe_3$), [^{t} tentatively assigned].

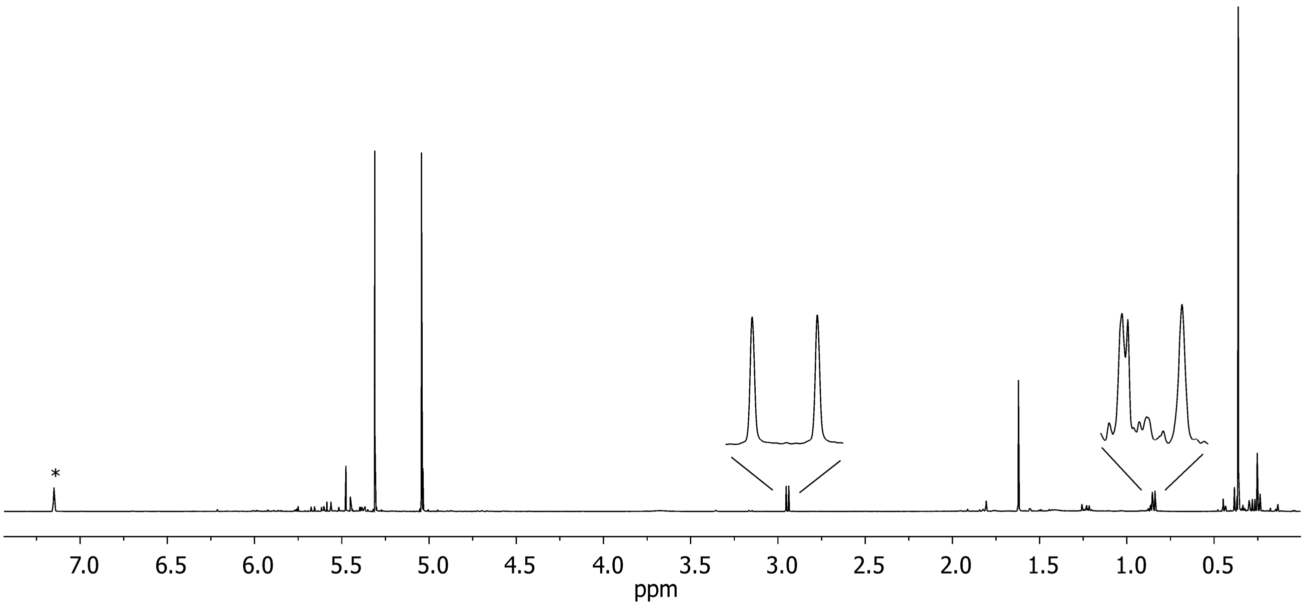
$^{29}Si\{^1H\}$ DEPT NMR (99 MHz, 298 K, [d_6]-benzene): δ = -8.1 ($SiMe_3$).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, [d_6]-benzene): δ ^{1}H / ^{1}H = 2.95 / 0.85 ($ZrCH_2$ / $ZrCH_2$), 0.85 / 2.95 ($ZrCH_2$ / $ZrCH_2$).

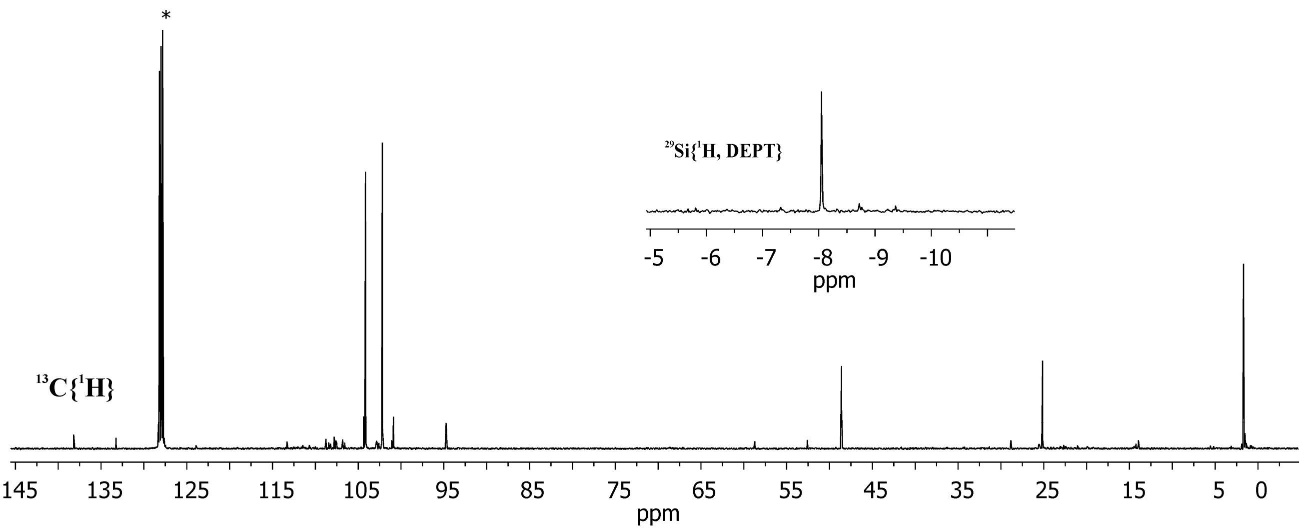
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 5.31 / 104.2 (Cp^A), 5.04 / 102.2 (Cp^B), 2.95 / 48.6 ($ZrCH_2$), 1.62 / 25.1 (Me), 0.85 / 48.6 ($ZrCH_2$), 0.36 / 1.7 ($SiMe_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 2.95 / 138.2, 94.7, 25.1 ($ZrCH_2$ / =C=, =C, Me), 1.62 / 138.2, 94.7, 48.6 (Me / =C=, =C, $ZrCH_2$), 0.85 / 138.2, 25.1 ($ZrCH_2$ / =C=, Me).

^{1}H TOCSY (500 MHz, 298 K, [d_6]-benzene): δ $^1H_{irr}$ / $^1H_{res}$ = 2.95 / 0.85 ($ZrCH_2$ / $ZrCH_2$), 0.85 / 2.95 ($ZrCH_2$ / $ZrCH_2$).



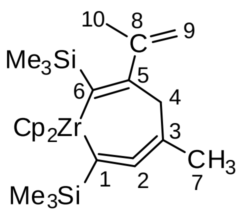
^{1}H NMR (500 MHz, 298 K, [d_6]-benzene (*))



^{13}C{1H} NMR (126 MHz, 298 K, [d_6]-benzene (*)) and ^{29}Si{^{1}H, DEPT} NMR (99 MHz, 298 K, [d_6]-benzene)

1,1-Bis(η^5-cyclopentadienyl)-2,7-bis(trimethylsilyl)-4-methyl-6-(1-methylethenyl)-1-zirconacyclohepta-2,3,6-triene (9)

N-Butylmagnesium chloride (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and trimethyl-(3-methyl-but-3-en-1-ynyl)silane (95 mg, 0.68 mmol, 2 eq) in THF (5 ml) at –78 °C. After 15 min the dry ice bath was removed and the mixture was warmed to room temperature and stirred for further 14 h. Subsequently dioxane (0.2 ml) was added. After the suspension was stirred for 1.5 h the volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (2×10 ml) and filtered. The filtrate was concentrated *in vacuo* to get the crude product as yellow oil. Crystallization from *n*-pentane at –30 °C gave the complex **9** as yellow crystals (85 mg, 50%), suitable for X-ray crystal structure analysis.



^{1}H NMR (500 MHz, 298 K, [d_6]-benzene): δ = 5.58 (s, 5H, Cp^A), 5.56 (s, 5H, Cp^B), 4.83 (br, 1H, 9-H^Z), 4.70 (m, 1H, 9-H^E), 2.93 (d, $^2J_{HH}$ = 14.7 Hz, 1H, 4-H), 2.52 (d, $^2J_{HH}$ = 14.7 Hz, 1H, 4-H), 1.91 (s, 3H, 7-H), 1.76 (s, 3H, 10-H), 0.45 (m, 9H, 6-SiMe$_3$), 0.24 (m, 9H, 1-SiMe$_3$).

^{13}C{^{1}H} NMR (126 MHz, 298 K, [d_6]-benzene): δ = 175.9 (C-6), 171.8 (br, C-5)^t, 153.1 (br, C-8)^t, 143.5 (C-2)^t, 115.3 (C-1), 110.0 ($^1J_{CH}$ ~ 157, 154 Hz, C-9), 108.8 ($^1J_{CH}$ ~ 172 Hz, Cp^A), 106.8 ($^1J_{CH}$ ~ 172 Hz, Cp^B), 94.5 (C-3)^t, 49.3 ($^1J_{CH}$ ~ 127 Hz, C-4), 23.1 ($^1J_{CH}$ ~ 126 Hz, C-10), 22.4 ($^1J_{CH}$ ~ 128 Hz, C-7), 5.6 ($^1J_{CH}$ ~ 118 Hz, $^1J_{SiC}$ = 49.0 Hz, SiMe$_3$-6), 1.4 ($^1J_{CH}$ ~ 120 Hz, $^1J_{SiC}$ = 54.1 Hz, SiMe$_3$-1), [^{t} tentative assignment].

^{29}Si{^{1}H} DEPT NMR (99 MHz, 298 K, [d_6]-benzene): δ = -7.3 (1-SiMe$_3$), -11.7 (6-SiMe$_3$).

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 298 K, [d_6]-benzene): δ ^{1}H / ^{1}H = 4.83 / 4.70, 1.76 (9-H^Z / 9-H^E, 10-H), 4.70 / 4.83, 1.76 (9-H^E / 9-H^Z, 10-H), 2.93 / 2.52, 1.91 (4-H / 4-H, 7-H), 2.52 / 2.93, 1.91 (4-H / 4-H, 7-H), 1.91 / 2.93 (7-H / 4-H), 1.76 / 4.70 (10-H / 9-H^E).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 5.58 / 108.8 (Cp^A), 5.56 / 106.8 (Cp^B), 4.83 / 110.0 (9-CH$_2$), 4.70 / 110.0 (9-CH$_2$), 2.93 / 49.3 (4-CH$_2$), 2.52 / 49.3 (4-CH$_2$), 1.91 / 22.4 (7-CH$_3$), 1.76 / 23.1 (10-CH$_3$), 0.45 / 5.6 (6-SiMe$_3$), 0.24 / 1.4 (1-SiMe$_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 4.70 / 171.8, 23.1 (9-H^E / C-5, C-10), 2.93 / 175.9, 171.8, 143.5, 110.0, 94.5, 22.4 (4-H / C-6, C-5, C-2, C-

Electronic Supplementary Material (ESI) for Chemical Science

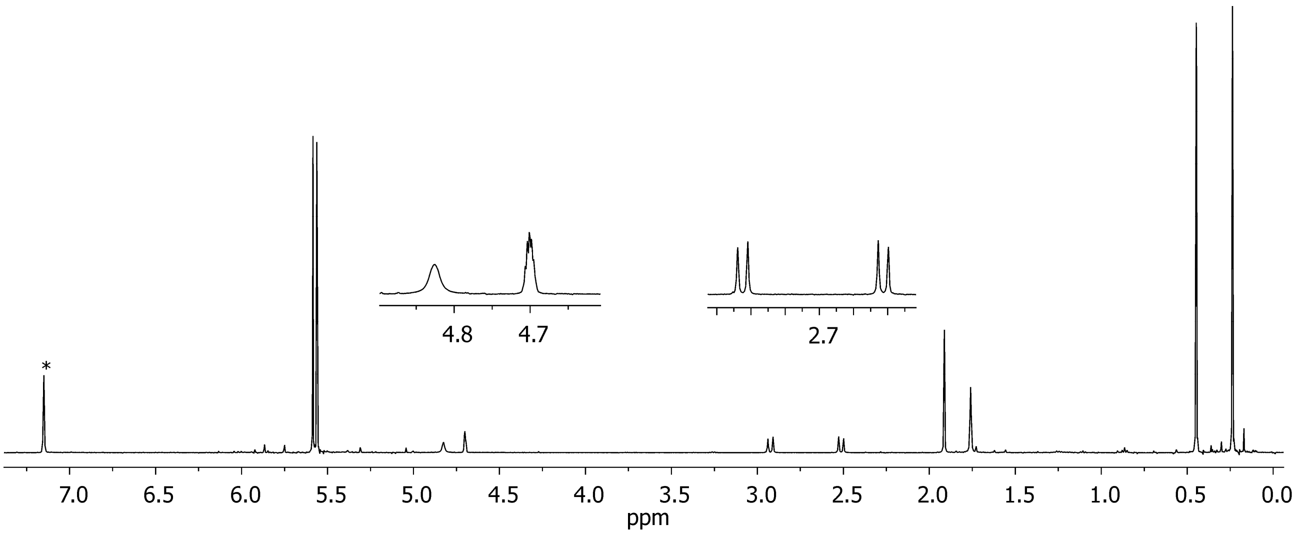
9, C-3, C-7), 2.52 / 175.9, 171.8, 153.1, 143.5, 94.5, 22.4 (4-H / C-6, C-5, C-8, C-2, C-3, C-7), 1.91 / 143.5, 94.5, 49.3 (7-H / C-2, C-3, C-4), 1.76 / 171.8, 153.1, 110.0 (10-H / C-5, C-8, C-9), 0.45 / 175.9 (6-$SiMe_3$ / C-6), 0.24 / 115.3 (1-$SiMe_3$ / C-1).

NOE-DIFF (500 MHz, 298 K, [d_6]-benzene): δ $^1H_{irr}$ / δ $^1H_{res}$ = 1.76 / 4.70, 2.93, 2.52, 0.45 (10-H / 9-H^E, 4-H, 4-H, 6-$SiMe_3$), [selective experiment].

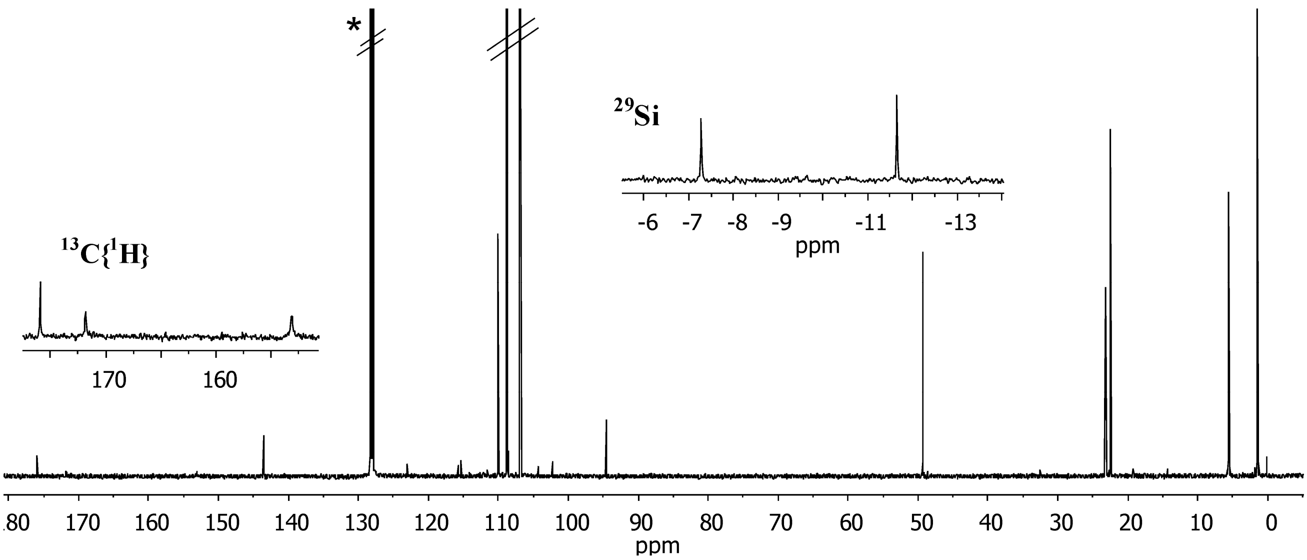
IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3070 (s), 2958 (s), 2879 (s), 2820 (s), 1907 (w), 1622 (s), 1510 (m), 1443 (m), 1370 (m), 1243 (w), 1128 (m), 1063 (s), 1018 (w), 926 (m), 901 (w), 867 (w), 800 (w), 754 (w), 683 (s), 662 (m), 620 (m), 587 (s), 522 (m), 482 (m), 422 (m).

Melting point (DSC): 87 °C.

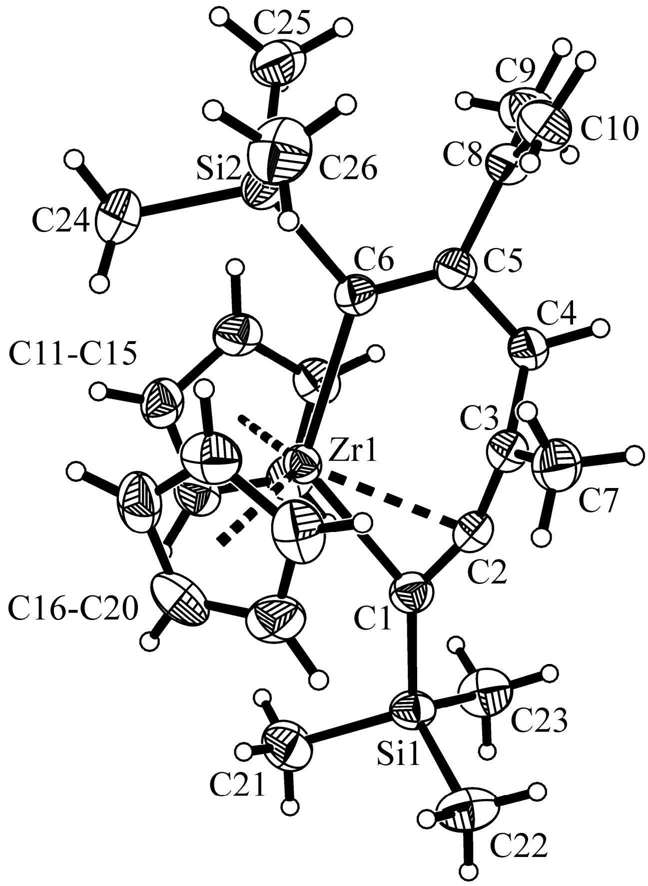
Elemental Analysis: $C_{26}H_{38}Si_2Zr$ (497.97 g/mol) requires C 62.71, H 7.69, found: C 62.52, H 7.35.



^{1}H NMR (500 MHz, 298 K, [d_6]-benzene (*))



^{13}C{^{1}H} NMR (126 MHz, 298K, [d_6]-benzene (*)) and ^{29}Si{^{1}H, DEPT} NMR (99 MHz, 298 K, [d_6]-benzene)

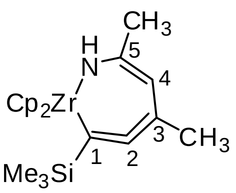


X-ray crystal structure analysis of 9: formula $C_{26}H_{38}Si_2Zr$, M = 497.96 colourless crystal, 0.45 x 0.40 x 0.30 mm, a = 8.2000(2), b = 11.8746(2), c = 14.0316(4) Å, α = 101.443(1), β = 95.903(1), γ = 98.217(2)°, V = 1313.20(5) Å^3, ρ_{calc} = 1.259 gcm^{-3}, μ = 0.520 mm^{-1}, empirical absorption correction (0.799 ≤ T ≤ 0.859), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ =

0.71073 Å, T = 223(2) K, ω and φ scans, 10381 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.66 $Å^{-1}$, 4388 independent (R_{int} = 0.042) and 4280 observed reflections [I>2σ(I)], 270 refined parameters, R = 0.031, wR^2 = 0.08, max. (min.) residual electron density 0.51 (-0.42) e.$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

1,1-Bis(η^5-cyclopentadienyl)-3,5-dimethyl-7-trimethylsilyl-1-zircona-2-azacyclohepta-3,5,6-triene (10)

n-Butylmagnesium chloride (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and trimethyl(3-methyl-but-3-en-1-ynyl)silane (40 mg, 0.29 mmol, 0.85 eq) dissolved in THF (5 ml) at –78 °C. After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1.5 h. Then the orange solution was heated to 60 °C for additional 1 h. The deep brown mixture was cooled to room temperature and acetonitrile (35 mg, 0.85 mmol, 2.5 eq) in THF (2 ml) was added. The mixture was stirred for 16 h and subsequently dioxane (0.2 ml) was added to precipitate magnesium salts. The volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×10 ml) and filtered. The deep red filtrate was concentrated *in vacuo* to get the complex **10** as red oil (112 mg, 0.28 mmol, 96%). Slow evaporation of the *n*-pentane solution gave compound **10** as dark red crystals, suitable for X-ray crystal structure analysis.



^{1}H NMR (500 MHz, 298 K, [d_6]-benzene): δ = 5.51 (s, 10H, Cp), 4.66 (m, 1H, 4-H), 3.44 (br, 1H, NH), 1.86 (m, 3H, 3-Me), 1.75 (s, 3H, 5-Me), 0.34 (s, $^{2}J_{SiH}$ = 6.6 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (126 MHz, 298 K, [d_6]-benzene): δ = 157.6 (C-2)^t, 155.8 (C-5), 137.1 (C-1), 115.3 (C-3)^t, 107.9 (Cp), 94.7 (C-4), 25.1 (Me-5), 21.0 (Me-3), 1.6 ($^{1}J_{SiC}$ = 52.8 Hz, $SiMe_3$), [^{t} tentative assignment].

^{29}Si{^{1}H} DEPT NMR (99 MHz, 298 K, [d_6]-benzene): δ = -4.1 ($SiMe_3$).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, [d_6]-benzene): δ ^{1}H / ^{1}H = 4.66 / 3.44, 1.86, 1.75 (4-H / NH, 3-Me, 5-Me), 1.86 / 4.66, 3.44 (3-Me / 4-H, NH), 1.75 / 4.66, 3.44 (5-Me / 4-H, NH).

$^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 5.51 / 107.9 (Cp), 4.66 / 94.7 (4-CH), 1.86 / 21.0 (3-Me), 1.75 / 25.1 (5-Me), 0.34 / 1.6 ($SiMe_3$).

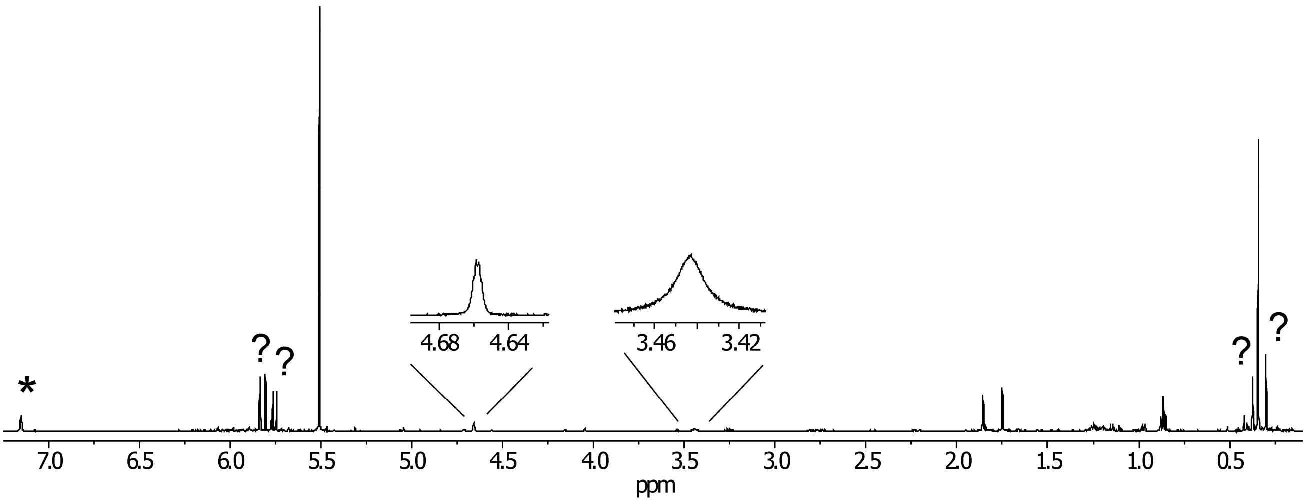
$^{1}H,^{13}C$ GHMBC (500 MHz / 126 MHz, 298 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 4.66 / 157.6, 155.8, 115.3, 25.1, 21.0 (4-H / C-2, C-5, C-3, Me-5, Me-3), 1.86 / 157.6, 137.1, 115.3, 94.7 (3-Me / C-2, C-1, C-3, C-4), 1.75 / 157.6, 155.8, 94.7 (5-Me / C-2, C-5, C-4), 0.34 / 137.1 ($SiMe_3$ / C-1).

NOE-DIFF (500 MHz, 298 K, [d_6]-benzene): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 1.75 / 5.51, 4.66, 3.44 (5-Me / Cp, 4-H, NH), [selective experiment].

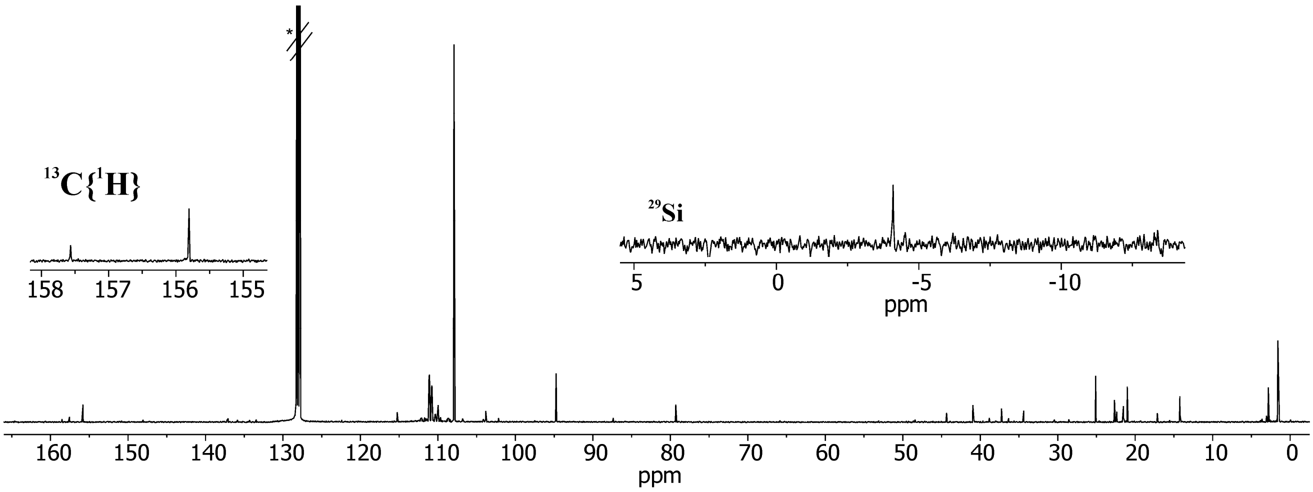
IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3467 (br, surface H_2O), 3328 (s), 2958 (m), 2900 (s), 2167 (s), 1857 (s), 1637 (s), 1438 (s), 1363 (m), 1324 (m), 1248 (w), 1149 (s), 1015 (m), 842 (w), 797 (w), 667 (s), 466 (s).

Melting point (DSC): 116 °C.

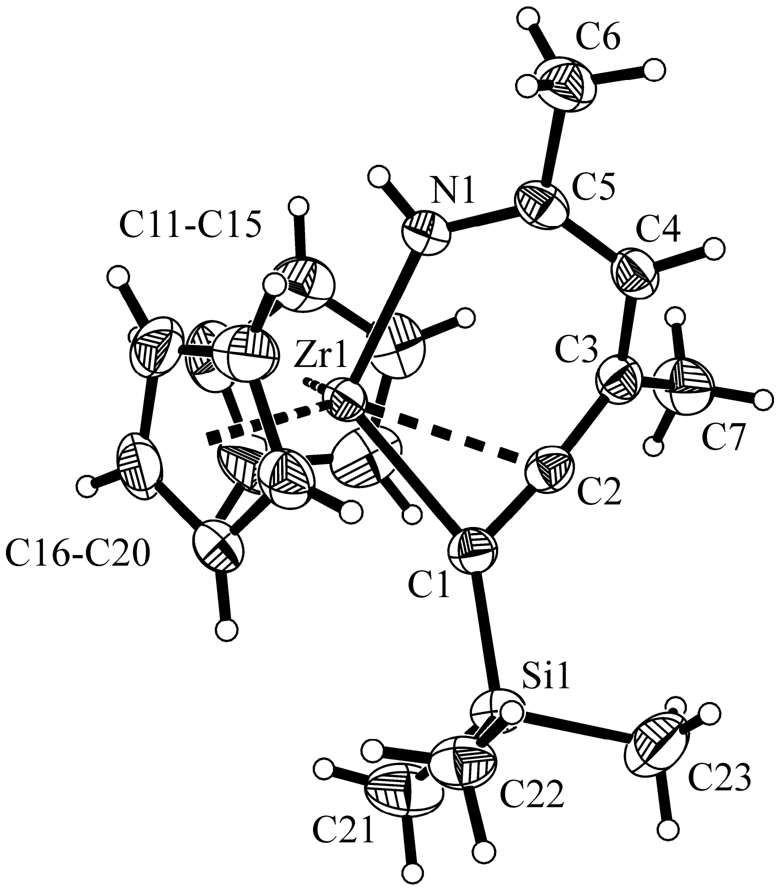
MS-ESI-EM: Calcd. for $[C_{20}H_{27}NSiZr + H]^+$: 400.10326 g/mol, found: 400.10396 g/mol.



^{1}H NMR (500 MHz, 298 K, [d_6]-benzene (*)) [? compound not identified yet]



$^{13}C\{^{1}H\}$ NMR(126 MHz, 298K, [d_6]-benzene (*)) and $^{29}Si\{^{1}H$, DEPT} NMR (99 MHz, 298 K, [d_6]-benzene)



X-ray crystal structure analysis of 10: formula $C_{20}H_{27}NSiZr$, M = 400.74, dark red crystal, 0.41 x 0.16 x 0.10 mm, a = 11.9917(3), b = 9.8277(4), c = 33.0276(16) Å, V = 3892.3(3) Å^3, ρ_{calc} = 1.368 gcm^{-3}, μ = 0.626 mm^{-1}, empirical absorption correction (0.783 ≤ T ≤ 0.940), Z = 8, orthorhombic, space group Pbca (No. 61), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 29274 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 4602 independent (R_{int} = 0.047) and 4087 observed reflections [I>2σ(I)], 216 refined parameters, R = 0.033, wR^2 = 0.089, max. (min.) residual electron density 0.37 (-0.75) e.Å^{-3}, the hydrogen atom at N1 from difmap, others hydrogen atoms calculated and refined as riding atoms.

1,1-Bis(η^5-cyclopentadienyl)-3,8-diphenyl-6-methyl-4-trimethylsilyl-1-zircona-2,9-dioxacyclonona-4,5-diene (12)

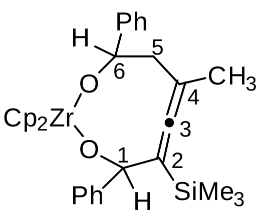
n-Butylmagnesium chloride (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and trimethyl(3-methyl-but-3-en-1-ynyl)silane (38 mg, 0.27 mmol, 0.8 eq) in THF (5 ml) at –78 °C. After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1 h. Then the orange solution was heated to 60 °C for additional 1 h. The mixture was cooled to room temperature and benzaldehyde (73 mg, 0.69 mmol, 2 eq) in THF (1ml) was added. The colour of the solution turned immediately orange. The mixture was stirred over night and subsequently dioxane (0.2 ml) was added to precipitate magnesium salts. After the suspension was stirred for 45 min the volatiles were removed *in vacuo* and the residue was extracted with pentane (2×10 ml) and filtered. The filtrate was cooled to -30 °C and the obtained suspension was filtered yielding the compound **12** as white solid (20 mg, 12%). Two isomers were detected by NMR experiments: ratio major/minor ≈ 9:1 ([d_8]-toluene, 298 K).

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3082 (s), 3028 (s), 2956 (s), 2877 (s), 2820 (s), 1940 (s), 1490 (s), 1450 (m), 1373 (m), 1339 (s), 1246 (m), 1219 (m), 1132 (w), 1091 (w), 1069 (w), 1020 (m), 893 (s), 843 (w), 799 (w), 751 (s), 698 (w), 654 (m), 613 (s), 470 (s), 422 (s).

Melting point (DSC): 143 °C.

MS-ESI-EM: Calcd. for [$C_{32}H_{36}O_2SiZr$ + H]$^+$: 571.1604 g/mol, found 571.1594 g/mol.

Major isomer



^{1}H NMR (500 MHz, 298 K, [d_8]-toluene): δ = 7.39 (m, 2H, *o*-Ph^1), 7.26 (m, 2H, *o*-Ph^6), 7.22 (m, 2H, *m*-Ph^6), 7.17 (m, 2H, *m*-Ph^1), 7.09 (m, 1H, *p*-Ph^6), 7.05 (m, 1H, *p*-Ph^1), 5.97 (m, 5H, Cp^A), 5.89 (m, 5H, Cp^B), 5.35 (s, 1H, 1-H), 5.10 (dd, $^3J_{HH}$ = 10.5, J_{HH} = 1.9 Hz, 1H, 6-H), 2.34 (dm, $^2J_{HH}$ = 15.6 Hz, 1H, 5-CH$_2$), 1.92 (dd, ^2J = 15.6 Hz, $^3J_{HH}$ = 10.5 Hz, 1H, 5-CH$_2$), 1.70 (s, 3H, Me), 0.07 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, SiMe$_3$).

^{13}C{^{1}H} NMR (151 MHz, 298 K, [d_8]-toluene): δ = 203.7 (C-3), 148.0 (*i*-Ph^6), 147.3 (*i*-Ph^1), 128.5 (*m*-Ph^6), 128.4 (*m*-Ph^1), 127.2 (*p*-Ph^1), 127.1 (*o*-Ph^1), 126.8 (*p*-Ph^6), 125.5 (*o*-Ph^6), 112.9 (Cp^A), 111.2 (Cp^B), 107.8 (C-2), 95.6 (C-4), 83.5 (C-1), 80.8 (C-6), 47.0 (C-5), 19.9 (Me), -0.5 ($^1J_{SiC}$ = 52.8 Hz, $SiMe_3$).

^{29}Si{^{1}H} DEPT NMR (99 MHz, 298 K, [d_8]-toluene): δ = -6.2 ($SiMe_3$).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, [d_8]-toluene): δ ^{1}H / ^{1}H = 7.39 / 7.17 (*o*-Ph^1 / *m*-Ph^1), 7.26 / 7.22 (*o*-Ph^6 / *m*-Ph^6), 7.22 / 7.26, 7.09 (*m*-Ph^6 / *o*-Ph^6, *p*-Ph^6), 7.17 / 7.39, 7.05 (*m*-Ph^1 / *o*-Ph^1, *p*-Ph^1), 7.09 / 7.22 (*p*-Ph^6 / *m*-Ph^6), 7.05 / 7.17 (*p*-Ph^1 / *m*-Ph^1), 5.10 / 2.34, 1.92 (6-H / 5-CH_2, 5-CH_2), 2.34 / 5.10, 1.92, 1.70 (5-CH_2 / 6-H, 5-CH_2, Me), 1.92 / 5.10, 2.34, 1.70 (5-CH_2 / 6-H, 5-CH_2, Me), 1.70 / 2.34, 1.92 (Me / 5-CH_2, 5-CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 151 MHz, 298 K, [d_8]-toluene): δ ^{1}H / δ ^{13}C = 7.39 / 127.1 (*o*-Ph^1), 7.26 / 125.4 (*o*-Ph^6), 7.22 / 128.5 (*m*-Ph^6), 7.17 / 128.4 (*m*-Ph^1), 7.09 / 126.8 (*p*-Ph^6), 7.05 / 127.2 (*p*-Ph^1), 5.97 / 112.9 (Cp^A), 5.89 / 111.2 (Cp^B), 5.35 / 83.5 (1-CH), 5.10 / 80.8 (6-CH), 2.34 / 47.0 (5-CH_2), 1.92 / 47.0 (5-CH_2), 1.70 / 19.9 (Me), 0.07 / -0.5 ($SiMe_3$).

^{1}H,^{13}C GHMBC (500 MHz / 151 MHz, 298 K, [d_8]-toluene): δ ^{1}H / δ ^{13}C = 7.39 / 127.1, 83.5 (*o*-Ph^1 / *o*-Ph^1, C-1), 7.26 / 125.5, 80.8 (*o*-Ph^6 / *o*-Ph^6, C-6), 7.22 / 148.0, 128.5 (*m*-Ph^6 / *i*-Ph^6, *m*-Ph^6), 7.17 / 147.3, 128.4 (*m*-Ph^1 / *i*-Ph^1, *m*-Ph^1), 7.09 / 125.5 (*p*-Ph^6 / *o*-Ph^6), 7.05 / 127.1 (*p*-Ph^1 / *o*-Ph^1), 5.35 / 203.7, 147.3, 127.1, 107.8, 47.0, 19.9 (1-H / C-3, *i*-Ph^1, *o*-Ph^1, C-2, C-5, Me), 5.10 / 148.0, 125.5, 95.6, 47.0 (6-H / *i*-Ph^6, *o*-Ph^6, C-4, C-5), 2.34 / 203.7, 95.6, 83.5 (5-CH_2 / C-3, C-4, C-1), 1.92 / 203.7, 148.0, 95.6, 83.5, 80.8, 19.9 (5-CH_2 / C-3, *i*-Ph^6, C-4, C-1, C-6, Me), 1.70 / 203.7, 95.6, 83.5, 47.0 (Me / C-3, C-4, C-1, C-5), 0.07 / 107.8 ($SiMe_3$ / C-2).

Minor isomer

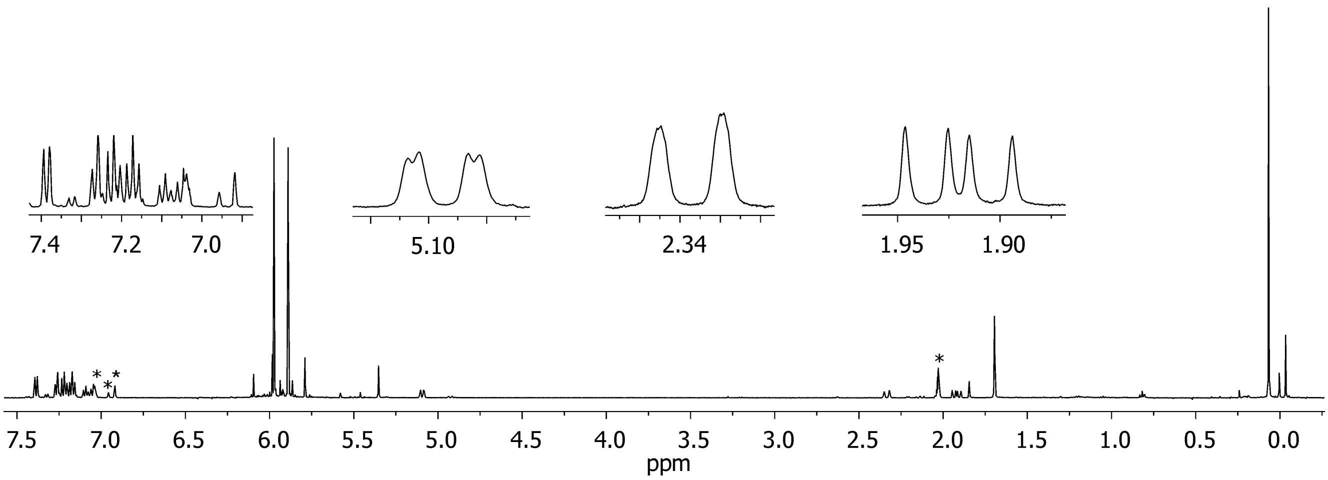
^{1}H NMR (500 MHz, 298 K, [d_8]-toluene): δ = 7.32 (m, 2H, *o*-Ph^1), 7.26 (m, 2H, *o*-Ph^6), 7.21 (m, 2H, *m*-Ph^6), 7.16 (m, 2H, *m*-Ph^1), 7.06 (m, 1H, *p*-Ph^1), 5.98 (m, 5H, Cp^A), 5.79 (m, 5H, Cp^B), 5.46 (s, 1H, 1-H), 4.93 (dm, $^3J_{HH}$ = 10.5 Hz, 1H, 6-H), 2.14 (dd, $^2J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 10.5 Hz, 1H, 5-CH_2), 2.04 (m, 1H, 5-CH_2), 1.85 (s, 3H, Me), -0.03 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $SiMe_3$), n.o. (*p*-Ph^6).

^{13}C{^{1}H} NMR (151 MHz, 298 K, [d_8]-toluene): δ = 204.3 (C-3), 148.3 (*i*-Ph^6), 146.5 (*i*-Ph^1), 128.4, 128.5 (*m*-Ph^{1,6}), 127.5 (*p*-Ph^1)^t, 127.7 (*o*-Ph^1), 125.8 (*o*-Ph^6), 111.7 (Cp^A), 111.6 (Cp^B), 101.7 (C-2), 93.1 (C-4), 85.9 (C-1), 84.3 (C-6), 49.7 (C-5), 18.5 (Me), -0.7 ($SiMe_3$), n.o. (*p*-Ph^6), [^{t} tentative assignment].

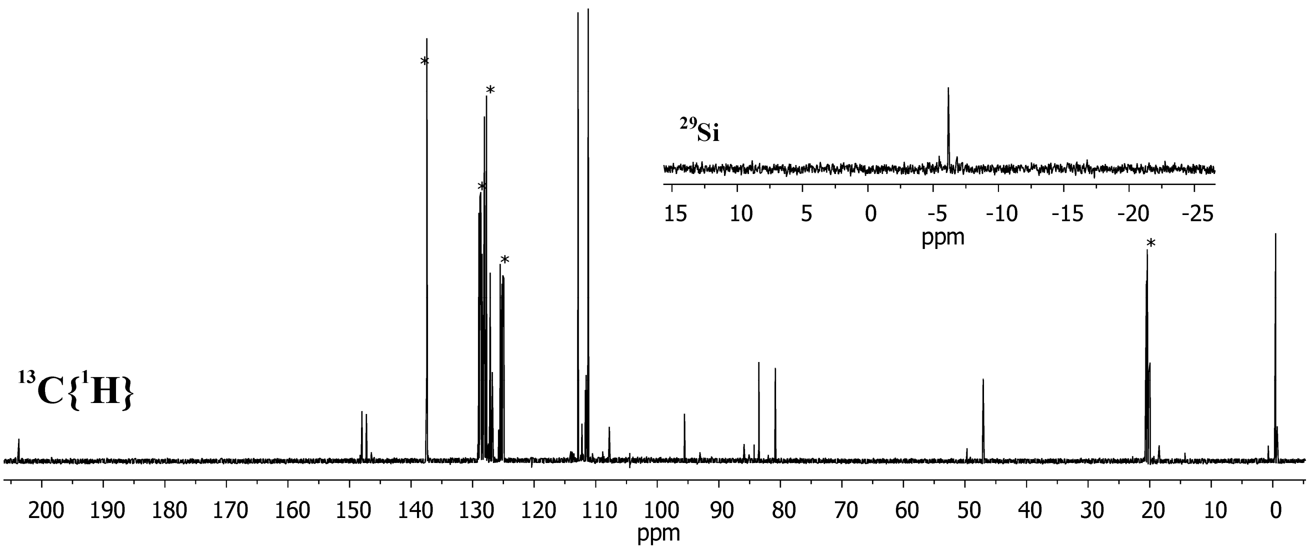
^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, [d_8]-toluene): δ ^{1}H / ^{1}H = 7.32 / 7.16 (*o*-Ph^1 / *m*-Ph^1), 7.16 / 7.32, 7.06 (*m*-Ph^1 / *o*-Ph^1, *p*-Ph^1), 7.06 / 7.17 (*p*-Ph^1 / *m*-Ph^1), 4.93 / 2.14, 2.04 (6-H / 5-CH_2, 5-CH_2), 2.14 / 4.93, 2.04 (5-CH_2 / 6-H, 5-CH_2), 2.04 / 4.93, 2.14, 1.85 (5-CH_2 / 6-H, 5-CH_2, Me), 1.85 / 2.04 (Me / 5-CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 151 MHz, 298 K, [d_8]-toluene): δ ^{1}H / δ ^{13}C = 7.32 / 127.7 (*o*-Ph^1), 7.16 / 128.4 (*m*-Ph^1), 7.06 / 127.5 (*p*-Ph^1), 5.98 / 111.7 (Cp^A), 5.79 / 111.6 (Cp^B), 5.46 / 85.9 (1-CH), 4.93 / 84.3 (6-CH), 2.14 / 49.7 (5-CH_2), 2.04 / 49.7 (5-CH_2), 1.85 / 18.5 (Me), -0.03 / -0.7 ($SiMe_3$).

^{1}H,^{13}C GHMBC (500 MHz / 151 MHz, 298 K, [d_8]-toluene): δ ^{1}H / δ ^{13}C = 7.32 / 127.7, 85.9 (*o*-Ph^1 / *o*-Ph^1, C-1), 5.46 / 204.3, 146.5, 127.7, 101.7, 49.7, 18.5 (1-H / C-3, *i*-Ph^1, *o*-Ph^1, C-2, C-5, Me), 4.93 / 148.3, 125.8, 93.1, 49.7 (6-H / *i*-Ph^6, *o*-Ph^6, C-4, C-5), 2.14 / 204.3, 93.1, 84.3, 18.5 (5-CH_2 / C-3, C-4, C-6, Me), 2.04 / 204.3, 93.1, 18.5 (5-CH_2 / C-3, C-4, Me), 1.85 / 204.3, 93.1, 85.9, 49.7 (Me / C-3, C-4, C-1, C-5), 0.07 / 101.7 ($SiMe_3$ / C-2).



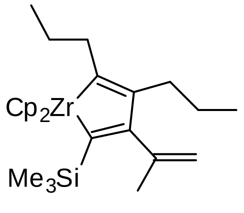
^{1}H NMR (500 MHz, 298 K, [d_8]-toluene (*))



^{13}C{^{1}H} NMR (151 MHz, 298 K, [d_8]-toluene (*)) and ^{29}Si{^{1}H, DEPT} NMR (99 MHz, 298 K, [d_8]-toluene)

1,1-Bis(η^5-cyclopentadienyl)-4,5-dipropyl-3-(1-methylethenyl)-2-trimethylsilyl-1-zirconacyclopenta-2,4-diene (13)

n-Butylmagnesium chloride (0.34 mmol, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and trimethyl(3-methyl-but-3-en-1-ynyl)silane (38 mg, 0.27 mmol, 0.8 eq) in THF (5 ml) at –78 °C. After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1 h. Then the orange solution was heated to 60 °C for additional 1 h. The mixture was cooled to room temperature and 4-octyne (38 mg, 0.34 mmol, 1 eq) in THF (1ml) was added. The mixture was stirred over night and subsequently dioxane (0.2 ml) was added to precipitate magnesium salts. After the suspension was stirred for 45 min the volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml). The filtrate was concentrated to yield compound **13** as a brown oil (120 mg, 91%).



^{1}H NMR (500 MHz, 233 K, [d_8]-toluene): δ = 5.85 (s, 5H, Cp^A), 5.83 (s, 5H, Cp^B), 4.74 (m, 1H, =CH$_2^E$), 4.65 (m, 1H, =CH$_2^Z$), 2.39 (m, 1H, $^=$CH$_2^{Pr(Zr)}$), 2.21 (m, 1H, $^=$CH$_2^{Pr}$), 1.90 (m, 1H, $^=$CH$_2^{Pr(Zr)}$), 1.85 (m, 1H, $^=$CH$_2^{Pr}$), 1.73 (s, 3H, Me), 1.40 (m, 1H, CH$_2^{Pr}$), 1.26 (m, 1H, CH$_2^{Pr}$), 1.22 (m, 2H, CH$_2^{Pr(Zr)}$), 0.97 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH$_3^{Pr(Zr)}$), 0.96 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH$_3^{Pr}$), 0.12 (s, $^2J_{SiH}$ = 6.2 Hz, 9H, SiMe$_3$).

^{13}C{^{1}H} NMR (126 MHz, 233 K, [d_8]-toluene): δ = 195.7 (ZrC=), 192.9 ($^1J_{SiC}$ = 56.7 Hz, ZrC=^{Si}), 152.7 (=C), 150.4 (=C^{Me}), 132.7 (=C^{Pr}), 111.3 (=CH$_2$), 110.5 (Cp^A), 110.3 (Cp^B), 40.1 ($^{=}CH_2^{Pr(Zr)}$), 32.4 ($^{=}CH_2^{Pr}$), 25.5 (Me), 24.5 ($CH_2^{Pr(Zr)}$), 24.1 (CH_2^{Pr}), 15.6 ($CH_3^{Pr(Zr)}$), 15.1 (CH_3^{Pr}), 3.0 ($^1J_{SiC}$ = 50.2 Hz, $SiMe_3$).

^{29}Si{^{1}H} NMR (119 MHz, 298 K, [d_6]-benzene): δ = -18.2 ($SiMe_3$).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 233 K, [d_8]-toluene): δ ^{1}H / ^{1}H = 4.74 / 4.65, 1.73 ($=CH_2^E$ / $=CH_2^Z$, Me), 4.65 / 4.74, 1.73 ($=CH_2^Z$ / $=CH_2^E$, Me), 2.39 / 1.90, 1.22 ($^{=}CH_2^{Pr(Zr)}$ / $^{=}CH_2^{Pr(Zr)}$, $CH_2^{Pr(Zr)}$), 2.21 / 1.85, 1.40, 1.26 ($^{=}CH_2^{Pr}$ / $^{=}CH_2^{Pr}$, CH_2^{Pr}, CH_2^{Pr}), 1.90 / 2.39, 1.22 ($^{=}CH_2^{Pr(Zr)}$ / $^{=}CH_2^{Pr(Zr)}$, $CH_2^{Pr(Zr)}$), 1.85 / 2.21, 1.40, 1.26 ($^{=}CH_2^{Pr}$ / $^{=}CH_2^{Pr}$, CH_2^{Pr}, CH_2^{Pr}), 1.73 / 4.74, 4.65 (Me / $=CH_2^E$, $=CH_2^Z$), 1.40 / 2.21, 1.85, 1.26, 0.96 (CH_2^{Pr} / $^{=}CH_2^{Pr}$, $^{=}CH_2^{Pr}$, CH_2^{Pr} CH_3^{Pr}), 1.26 / 2.21, 1.85, 1.40, 0.96 (CH_2^{Pr} / $^{=}CH_2^{Pr}$, $^{=}CH_2^{Pr}$, CH_2^{Pr} CH_3^{Pr}), 1.22 / 2.39, 1.90, 0.97 (CH_2^{Pr} / $^{=}CH_2^{Pr(Zr)}$, $^{=}CH_2^{Pr(Zr)}$, $CH_3^{Pr(Zr)}$), 0.97 / 1.22 ($CH_3^{Pr(Zr)}$ / $CH_2^{Pr(Zr)}$), 0.96 / 1.40, 1.26 (CH_3^{Pr} / CH_2^{Pr}, CH_2^{Pr}).

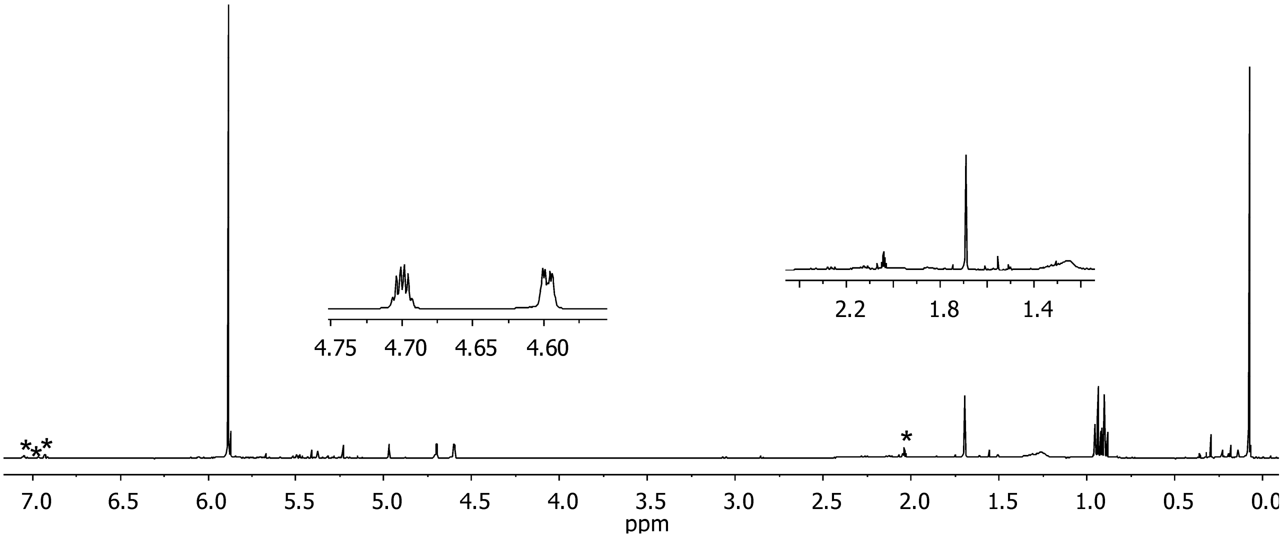
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 233 K, [d_8]-toluene): δ ^{1}H / δ ^{13}C = 5.85 / 110.5 (Cp^A), 5.83 / 110.3 (Cp^B), 4.74 / 111.3 ($=CH_2$), 4.65 / 111.3 ($=CH_2$), 2.39 / 40.1 ($^{=}CH_2^{Pr(Zr)}$), 2.21 / 32.4 ($^{=}CH_2^{Pr}$), 1.90 / 40.1 ($^{=}CH_2^{Pr(Zr)}$), 1.85 / 32.4 ($^{=}CH_2^{Pr}$), 1.73 / 25.5 (Me), 1.40 / 24.1 (CH_2^{Pr}), 1.26 / 24.1 (CH_2^{Pr}), 1.22 / 24.5 ($CH_2^{Pr(Zr)}$), 0.97 / 15.6 ($CH_3^{Pr(Zr)}$), 0.96 / 15.1 (CH_3^{Pr}) 0.12 / 3.0 ($SiMe_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 233 K, [d_8]-toluene): δ ^{1}H / δ ^{13}C = 4.74 / 152.7, 150.4, 25.5 ($=CH_2^E$ / =C, $=C^{Me}$, Me), 4.65 / 152.7, 150.4, 25.5 ($=CH_2^Z$ / =C, $=C^{Me}$, Me), 2.39 / 195.7, 132.7, 24.5, 15.6 ($^{=}CH_2^{Pr(Zr)}$ / ZrC=, $=C^{Pr}$, $CH_2^{Pr(Zr)}$, $CH_3^{Pr(Zr)}$), 2.21 / 195.7, 152.7, 132.7, 24.1, 15.1 ($^{=}CH_2^{Pr}$ / ZrC=, =C, $=C^{Pr}$, CH_2^{Pr}, CH_3^{Pr}), 1.90 / 195.7, 132.7, 24.5, 15.6 ($^{=}CH_2^{Pr(Zr)}$ / ZrC=, $=C^{Pr}$, $CH_2^{Pr(Zr)}$, $CH_3^{Pr(Zr)}$), 1.85 / 195.7, 152.7, 132.7, 24.1, 15.1 ($^{=}CH_2^{Pr}$ / ZrC=, =C, $=C^{Pr}$, CH_2^{Pr}, CH_3^{Pr}), 1.73 / 152.7, 150.4, 111.3 (Me / =C, $=C^{Me}$, $=CH_2$), 1.40 / 132.7, 32.4, 15.1 (CH_2^{Pr} / $=C^{Pr}$, $^{=}CH_2^{Pr}$, CH_3^{Pr}), 1.26 / 132.7, 32.4, 15.1 (CH_2^{Pr} / $=C^{Pr}$, $^{=}CH_2^{Pr}$, CH_3^{Pr}), 1.22 / 195.7, 40.1, 15.6 ($CH_2^{Pr(Zr)}$ / ZrC=, $^{=}CH_2^{Pr(Zr)}$, $CH_3^{Pr(Zr)}$), 0.97 / 40.1, 24.5 ($CH_3^{Pr(Zr)}$ / $^{=}CH_2^{Pr(Zr)}$, $CH_2^{Pr(Zr)}$), 0.96 / 32.4, 24.1 (CH_3^{Pr} / $^{=}CH_2^{Pr}$, CH_2^{Pr}), 0.12 / 192.9 ($SiMe_3$ / $ZrC=^{Si}$).

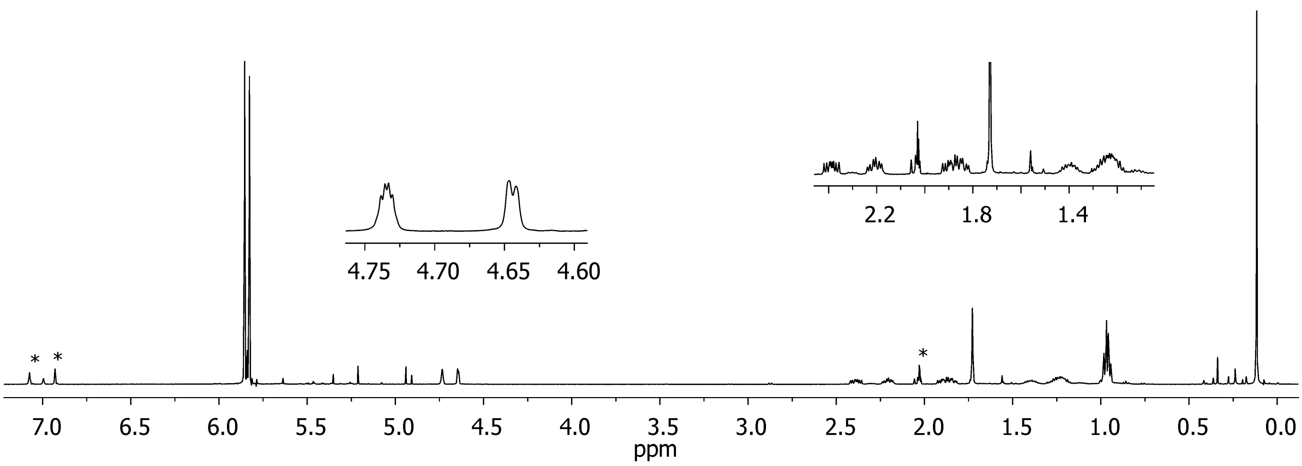
^{1}H TOCSY (500 MHz, 233 K, [d_8]-toluene) [selective experiment]: δ $^1H_{irr}$ / $^1H_{res}$ = 2.39 / 1.90, 1.22, 0.97 ($^{=}CH_2^{Pr(Zr)}$ / $^{=}CH_2^{Pr(Zr)}$, $CH_2^{Pr(Zr)}$, $CH_3^{Pr(Zr)}$), 2.21 / 1.85, 1.40, 1.26, 0.96 ($^{=}CH_2^{Pr}$ / $^{=}CH_2^{Pr}$, CH_2^{Pr}, CH_2^{Pr}, CH_3^{Pr}).

NOE-DIFF (500 MHz, 233 K, [d_8]-toluene): δ $^1H_{irr}$ / δ $^1H_{res}$ = 1.73 / 5.85, 4.74, 0.12 (Me / Cp^A, $=CH_2^E$, $SiMe_3$), [selective experiment].

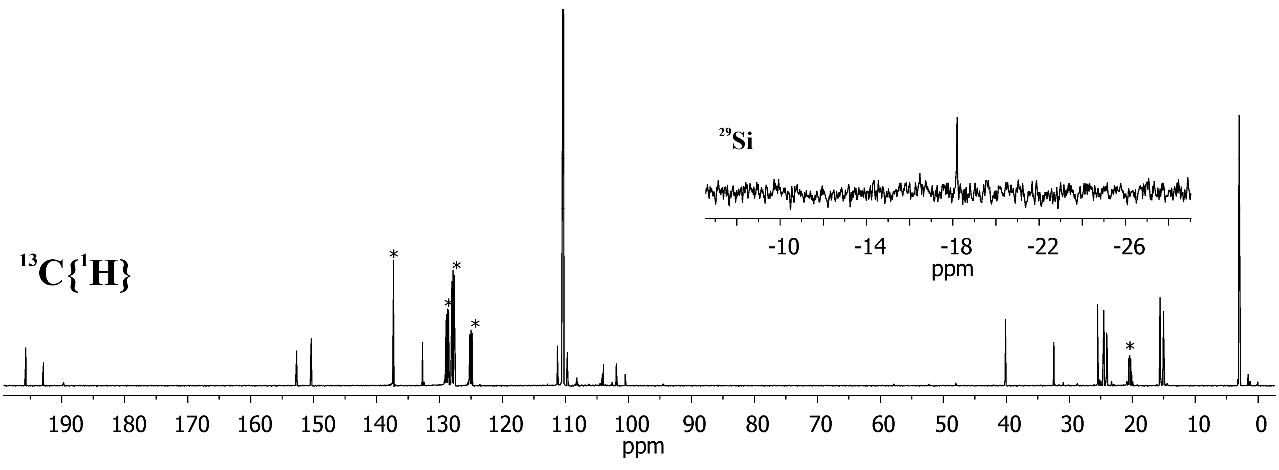
MS-ESI-EM: Calcd. for $[C_{26}H_{38}SiZr + H]^{+}$: 469.1863 g/mol, found 469.1869 g/mol.



^{1}H NMR (500 MHz, 298 K, [d_8]-toluene (*))



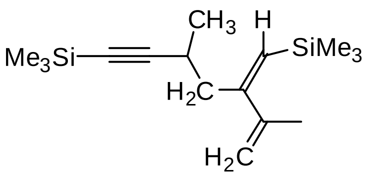
^{1}H NMR (500 MHz, 233 K, [d_8]-toluene (*))



$^{13}C\{^{1}H\}$ NMR (126 MHz, 233 K, [d_8]-toluene (*)) and $^{29}Si\{^{1}H$, DEPT$\}$ NMR (119 MHz, 298 K, [d_6]-benzene)

Synthesis of 11

N-Butylmagnesium chloride (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and trimethyl-(3-methyl-but-3-en-1-ynyl)silane (95 mg, 0.68 mmol, 2 eq) in THF (5 ml) at –78 °C. After 15 min the dry ice bath was removed and the mixture was warmed to room temperature and stirred over night. Subsequently dioxane (0.2 ml) was added. After the suspension was stirred for 40 min the volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. The filtrate was concentrated *in vacuo* to get the crude product **9** as yellow oil. The seven-membered complex was dissolved in diethyl ether (5 ml) and hydrogen chloride (0.18 ml, 2 M diethyl ether solution, 0.34 mmol, 1 eq) was added. The yellow-white slurry was stirred for 2 h. Subsequently the reaction was terminated by addition of water (10 ml). After washing of the organic layer with $NaHCO_3$-solution (5 ml), brine (5 ml) and water (5 ml) the ether solution was dried over magnesium sulfate and concentrated. The residue was purified by column chromatography (silica gel, cyclohexane:ethyl actetate 9:1). The product **11** was obtained as yellow oil (69 mg, 73%).



^{1}H NMR (600 MHz, 298 K, $CDCl_3$): δ = 5.28 (m, 1H, =CH), 4.84 (m, 1H, =CH_2), 4.78 (m, 1H, =CH_2), 2.52 (m, 1H, CH), 2.37 (m, 1H, CH_2), 2.19 (m, 1H, CH_2), 1.80 (m, 3H, $Me^{=}$), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 3H, Me), 0.13 (s, $^2J_{SiH}$ = 7.1 Hz, 9H, $SiMe_3^{\equiv}$), 0.06 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3^{=}$).

^{13}C{^{1}H} NMR (151 MHz, 298 K, $CDCl_3$): δ = 158.6 (C=), 146.5 ($C^{=CH2}$), 127.6 (=CH), 114.3 (=CH_2), 111.6 (≡C), 84.0 (≡C^{Si}), 46.2 (CH_2), 25.3 (CH), 22.0 ($Me^{=}$), 20.2 (Me), 0.4 ($SiMe_3^{C=}$), 0.3 ($SiMe_3^{C\equiv}$).

^{29}Si{^{1}H} DEPT NMR (119 MHz, 298 K, $CDCl_3$): δ = -10.9 ($SiMe_3^{=}$), -19.4 ($SiMe_3^{\equiv}$).

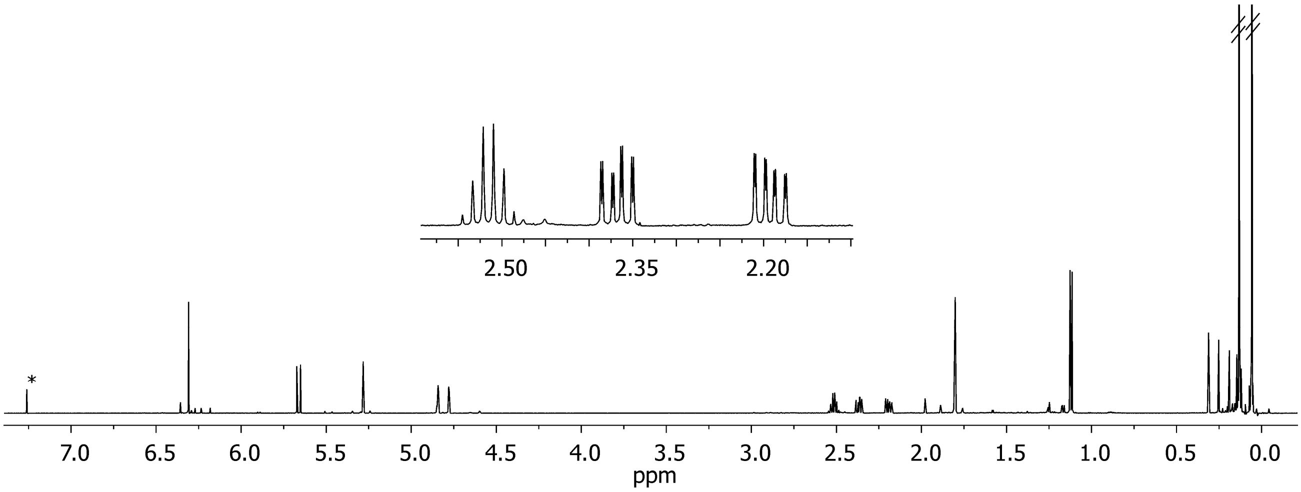
^{1}H, ^{29}Si GHMBC (600 MHz / 119 MHz, 298 K, $CDCl_3$): δ ^{1}H / δ ^{29}Si = 0.13 / -19.4 ($SiMe_3^{C\equiv}$), 0.06 / -10.9 ($SiMe_3^{C=}$).

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 298 K, $CDCl_3$): δ ^{1}H / ^{1}H = 5.28 / 2.37, 2.19 (=CH / CH_2, CH_2), 4.84 / 4.78, 1.80 (=CH_2 /=CH_2, $Me^{=}$), 4.78 / 4.84, 1.80 (=CH_2 /=CH_2, $Me^{=}$), 2.52 / 2.37, 2.19, 1.12 (CH / CH_2, CH_2, Me), 2.37 / 5.28, 2.52, 2.19 (CH_2 / =CH, CH, CH_2), 2.19 / 5.28, 2.52, 2.37 (CH_2 / =CH, CH, CH_2), 1.80 / 4.84, 4.78 ($Me^{=}$ / =CH_2, =CH_2), 1.12 / 2.52 (Me / CH).

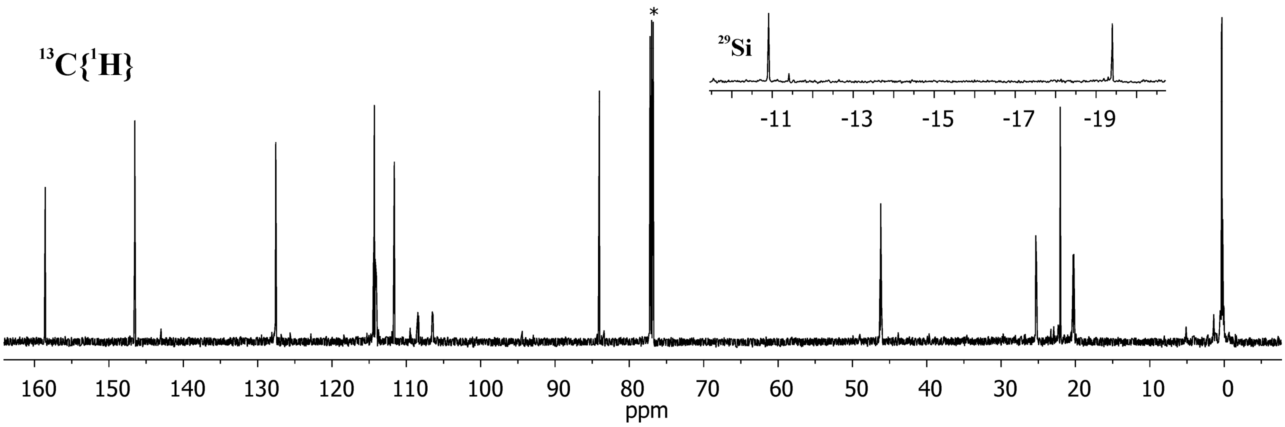
^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, $CDCl_3$): δ ^{1}H / δ ^{13}C = 5.28 / 127.6 (=CH), 4.84 / 114.3 (=CH_2), 4.78 / 114.3 (=CH_2), 2.52 / 25.3 (CH), 2.37 / 46.2 (CH_2), 2.19 / 46.2 (CH_2), 1.80 / 22.0 ($Me^{=}$), 1.12 / 20.2 (Me), 0.13 / 0.3 ($SiMe_3^{C\equiv}$), 0.06 / 0.4 ($SiMe_3^{C=}$).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, $CDCl_3$): δ ^{1}H / δ ^{13}C = 5.28 / 158.6, 146.5, 46.2 (=CH / C=, $C^{=CH2}$, CH_2), 4.84 / 158.6, 22.0 (=CH_2 / C=, $Me^{=}$), 4.78 / 158.6, 22.0 (=CH_2 / C=, $Me^{=}$), 2.52 / 111.6, 46.2 (CH / ≡C, CH_2), 2.37 / 158.6, 146.5, 127.6, 111.6, 25.3 (CH_2 / C=, $C^{=CH2}$, =CH, ≡C, CH), 2.19 / 158.6, 146.5, 127.6, 111.6, 25.3, 20.2 (CH_2 / C=, $C^{=CH2}$, =CH, ≡C, CH, Me), 1.80 / 158.6, 146.5, 114.3 ($Me^{=}$ / C=, $C^{=CH2}$, =CH_2), 1.12 / 111.6, 46.2, 25.3 (Me / ≡C, CH_2, CH), 0.13 / 84.0 ($SiMe_3^{C\equiv}$ / ≡C^{Si}), 0.06 / 127.6 ($SiMe_3^{C=}$ / =CH).

MS-Es^{+} ($CHCl_3$/CH_3OH + CF_3COOAg): m/z = calcd. for $C_{16}H_{30}Si_2Ag^{+}$ = 385.0932 g/mol, found 385.0928 g/mol.



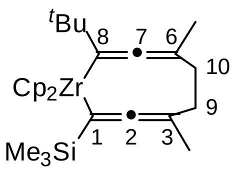
^{1}H NMR (600 MHz, 298 K, $CDCl_3$ (*))



^{13}C{^{1}H} NMR (151 MHz, 298 K, $CDCl_3$ (*)) and ^{29}Si{^{1}H, DEPT} NMR (119 MHz, 298 K, $CDCl_3$)

1,1-Bis(η^5-cyclopentadienyl)-4,7-dimethyl-9-*tert*-butyl-2-trimethylsilyl-1-zirconacyclonona-2,3,7,8-tetraene (14)

n-Butylmagnesium chloride (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and 2,5,5-trimethyl-1-hexen-3-yne (37 mg, 0.30 mmol, 0.9 eq) in THF (5 ml) at –78 °C. After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1 h. Then the yellow solution was heated to 60 °C for additional 1 h. The deep red-brown mixture was cooled to room temperature and dioxane (0.2 ml) was added. After the solution was stirred for 30 min the volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. To the red-brown coloured filtrate was added trimethyl-(3-methyl-but-3-en-1-ynyl)silane (48 mg, 0.35 mmol, 1 eq) in pentane (2 ml). The mixture was stirred over night and subsequently filtered. Crystallization from pentane at –30 °C gave the complex **14** as yellow crystals (41 mg, 28 %).



^{1}H NMR (500 MHz, 299 K, [d_6]-benzene): δ = 5.80 (s, 5H, Cp^A), 5.74 (s, 5H, Cp^B), 1.98 (m, 1H, 9-H), 1.86 (m, 2H, 10-H), 1.79 (m, 1H, 9-H), 1.58 (m, 3H, 3-Me), 1.54 (m, 3H, 6-Me), 1.25 (s, 9H, ^{t}Bu), 0.32 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, SiMe$_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_6]-benzene): δ = 181.1 (C-2), 171.3 (C-7), 142.4 (C-8), 113.7 (C-1), 108.3 (Cp^A), 108.0 (Cp^B), 104.7 (C-6), 85.9 (C-3), 38.3 (^{t}Bu), 34.0 (C-10), 32.8 (^{t}Bu), 31.6 (C-9), 20.6 (Me-6), 18.9 (Me-3), 1.6 ($^1J_{SiC}$ = 52.1 Hz, SiMe$_3$).

^{29}Si{^{1}H} DEPT NMR (99 MHz, 298 K, [d_6]-benzene): δ = -5.6 (SiMe$_3$)

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 299 K, [d_6]-benzene): δ ^{1}H / ^{1}H = 1.98 / 1.86, 1.79, 1.58 (9-H / 10-H, 9-H, 3-Me), 1.86 / 1.98, 1.79, 1.54 (10-H / 9-H, 9-H, 6-Me), 1.79 / 1.98, 1.86, 1.58 (9-H / 9-H, 10-H, 3-Me), 1.58 / 1.98, 1.79 (3-Me / 9-H, 9-H), 1.54 / 1.86 (6-Me / 10-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 5.80 / 108.3 (Cp^A), 5.74 / 108.0 (Cp^B), 1.98 / 31.6 (9-CH$_2$), 1.86 / 34.0 (10-CH$_2$), 1.79 / 31.9 (9-CH$_2$), 1.58 / 18.9 (3-Me), 1.54 / 20.6 (6-Me), 1.25 / 32.8 (^{t}Bu), 0.32 / 1.6 (SiMe$_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 1.98 / 181.1, 104.7, 85.9 (9-H / C-2, C-6, C-3), 1.86 / 171.3, 104.7, 85.9, 31.6 (10-H / C-7, C-6, C-3, C-9),

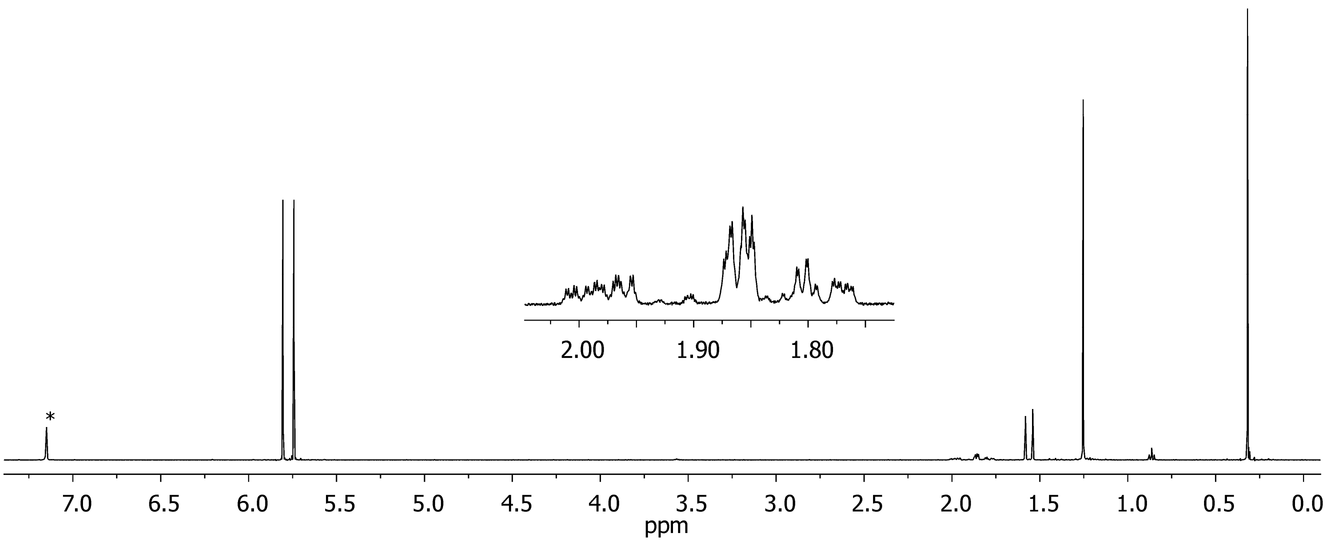
Electronic Supplementary Material (ESI) for Chemical Science

1.58 / 181.1, 85.9, 31.6 (3-Me / C-2, C-3, C-9), 1.54 / 171.3, 104.7, 38.3, 34.0 (6-Me / C-7, C-6, ^{t}Bu, C-10), 1.25 / 142.4, 38.3, 32.8 (^{t}Bu / C-8, ^{t}Bu, ^{t}Bu), 0.32 / 113.7 ($SiMe_3$ / C-1).

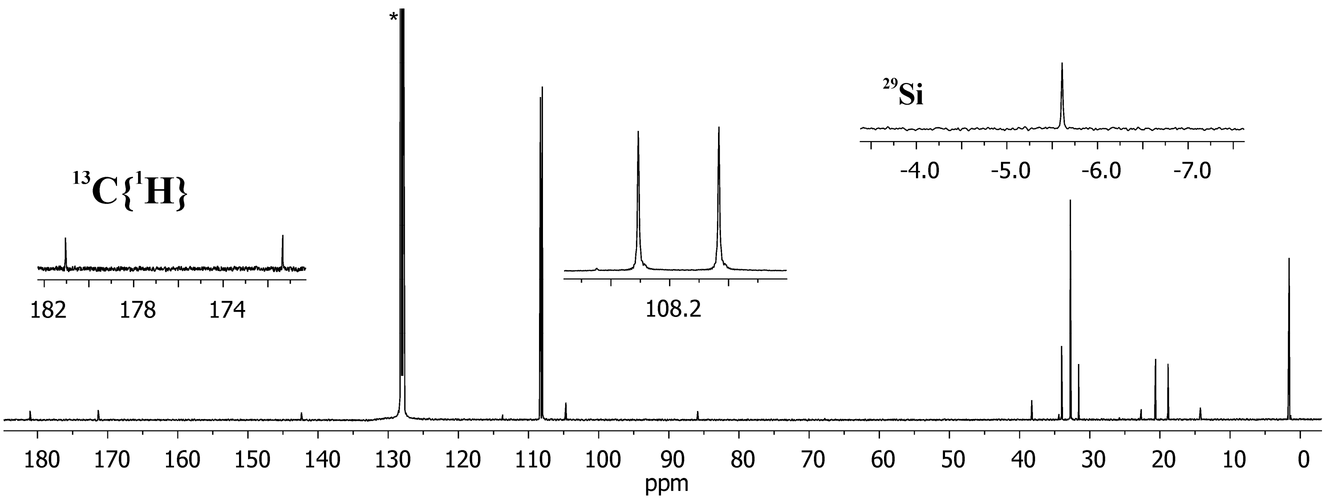
^{1}H TOCSY (500 MHz, 299 K, [d_6]-benzene): δ $^1H_{irr}$ / $^1H_{res}$ = 1.98 / 1.86, 1.79, 1.58, 1.54 (9-H / 10-H, 9-H, 3-Me, 6-Me), 1.86 / 1.98, 1.79, 1.58, 1.54 (10-H / 9-H, 9-H, 3-Me, 6-Me), 1.79 / 1.98, 1.86, 1.58, 1.54 (9-H / 9-H, 10-H, 3-Me, 6-Me), 1.58 / 1.54 (3-Me / 6-Me), 1.54 / 1.58 (6-Me / 3-Me).

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2952 (m), 2869 (m), 2816 (m), 1890 (w), 1693 (s), 1591 (s), 1448 (m), 1361 (m), 1244 (w), 1207 (m), 1017 (w), 956 (s), 933 (s), 910 (m), 855 (m), 803 (m), 785 (m), 681 (s), 619 (s), 554 (s), 480 (m), 455 (m).

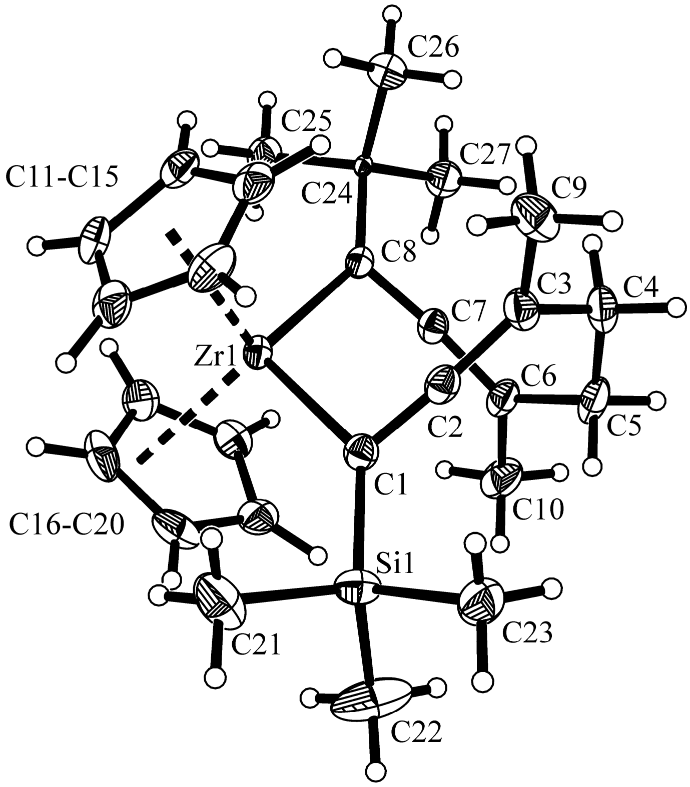
Elemental Analysis: $C_{27}H_{38}SiZr$ (481.90 g/mol) requires C 67.29, H 7.95, found: C 66.87, H 7.81.



^{1}H NMR (500 MHz, 299 K, [d_6]-benzene (*))



^{13}C{^{1}H} NMR (125 MHz, 299 K, [d_6]-benzene (*)) and ^{29}Si{^{1}H, DEPT} NMR (99 MHz, 299 K, [d_6]-benzene)



X-ray crystal structure analysis of 14: formula $C_{27}H_{38}SiZr$, M = 481.88, yellow crystal, 0.40 x 0.35 x 0.25 mm, a = 8.8130(2), b = 9.2076(3), c = 16.7639(6) Å, α = 80.358(2), β = 77.962(2), γ = 72.931(2)°, V = 1263.57(7) Å^3, ρ_{calc} = 1.267 gcm^{-3}, μ = 0.493 mm^{-1}, empirical absorption correction (0.827 ≤ T ≤ 0.886), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 10822 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 4312 independent (R_{int} = 0.035) and 4209 observed reflections [I>2σ(I)], 270 refined parameters, R = 0.033, wR^2 = 0.085, max. (min.) residual electron density 0.50 (-0.75) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.