Supporting Information for

How big is a Cp? Cycloheptatrienyl Zirconium Complexes with Bulky Cyclopentadienyl and Indenyl Ligands

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1. Computational Details

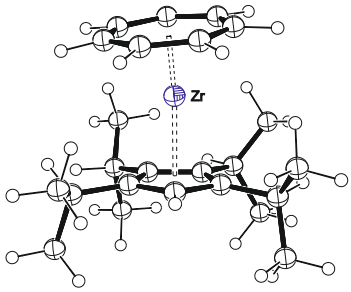
All computations were performed using the DFT functional methods M06 as implemented in the Gaussian09 program.[1] The all-electron triple-ζ basis set (6-311G**)[2] was applied for all main-group elements (C and H), together with the effective core potential double-ζ basis set (Stuttgart RSC 1997 ECP) for the transition metal (Zr).[3]

Energies for the optimized structure:

Compound	E(0 K)[a] [Ha]	H(298 K)[b] [Ha]	G(298 K)[b] [Ha]
[(η^7-C_7H_7)Zr(η^5-^{4}Cp)] (**4**)	-982.267753	-982.238916	-982.322518
Isomer-1	-982.263400	-982.234347	-982.318290
Isomer-2	-982.264612	-982.235497	-982.319720
Isomer-3	-982.261859	-982.233021	-982.316290
[(η^7-C_7H_7)Zr(η^5-^{5}Cp)] (**7**)	-1100.049170	-1100.016005	-1100.107138

[a]DFT energy incl. ZPE.

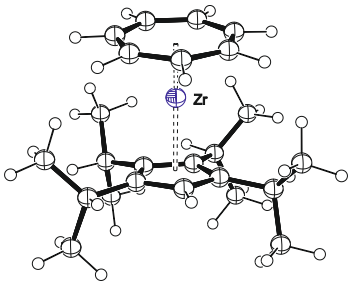
[b]standard conditions T = 298.15 K and p = 1 atm.



(atom, x-, y-, z-positions in Å):

Structure of 4

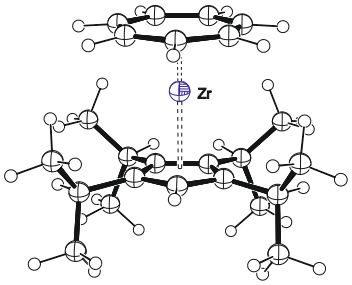
Zr	1.107400	-0.106600	-0.148900
C	2.887800	1.414100	-0.184500
C	2.521500	1.157200	-1.537100
C	2.323600	-0.097800	-2.177500
C	2.436000	-1.401800	-1.622900
C	2.772000	-1.778700	-0.293300
C	3.083700	-0.941300	0.813300
C	3.142700	0.480100	0.858100
C	-0.696500	1.296400	0.913500
C	-1.217200	0.898200	-0.354600
C	-1.400400	-0.523400	-0.332300
C	-0.988400	-0.998000	0.949100
C	-0.558500	0.126800	1.699700
C	-0.471200	2.710300	1.385800
C	-1.805600	3.348100	1.772200
C	0.491200	2.797900	2.561200
C	-1.653600	1.871900	-1.427500
C	-3.178200	1.897900	-1.557900
C	-0.994200	1.695500	-2.793000
C	-2.046400	-1.338700	-1.432100
C	-3.386700	-1.923600	-0.990100
C	-1.140000	-2.408900	-2.033300
C	-1.150100	-2.380100	1.533900
C	-2.332700	-2.388500	2.502000
C	0.101700	-2.893600	2.234000
H	2.887200	2.459700	0.110300
H	2.288600	2.035600	-2.132200
H	1.944200	-0.052500	-3.194900
H	2.136600	-2.216400	-2.275500
H	2.703000	-2.841000	-0.077400
H	3.206900	-1.446500	1.767000
H	3.308800	0.908800	1.842300
H	-0.187100	0.091600	2.718400
H	-0.038700	3.290900	0.555900
H	-2.272700	2.774300	2.582200
H	-2.509100	3.373100	0.934500
H	-1.661900	4.375700	2.124600
H	0.079800	2.291500	3.443000
H	0.659800	3.843500	2.838700
H	1.460200	2.344200	2.332000
H	-1.352700	2.868400	-1.073100
H	-3.560200	0.985500	-2.029600
H	-3.499000	2.744000	-2.175900
H	-3.661000	1.986700	-0.578900
H	0.091300	1.813200	-2.722900
H	-1.372500	2.447100	-3.495600
H	-1.190700	0.710600	-3.230500
H	-2.275400	-0.642300	-2.245800
H	-3.921100	-2.344000	-1.849500
H	-4.022100	-1.154000	-0.537800
H	-3.262900	-2.727700	-0.257600
H	-0.270500	-1.953100	-2.520800
H	-1.679700	-2.995200	-2.786100
H	-0.763400	-3.106300	-1.276100
H	-1.379000	-3.078700	0.719800
H	-2.124700	-1.742700	3.363500
H	-2.524300	-3.399600	2.878700
H	-3.246400	-2.019100	2.025900
H	0.942200	-2.980300	1.537100
H	-0.080700	-3.879700	2.675200
H	0.408300	-2.222600	3.045800



(atom, x-, y-, z-positions in Å):

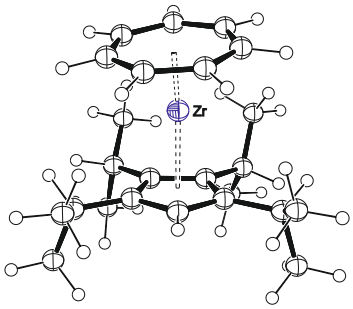
Isomer-1 of (4)

Zr	-1.127400	-0.035200	0.076900
C	-2.970700	-1.362200	-0.535400
C	-3.103600	-0.103500	-1.182900
C	-2.993900	1.200000	-0.622000
C	-2.727800	1.564300	0.728800
C	-2.507300	0.714700	1.847200
C	-2.491600	-0.706100	1.894400
C	-2.691300	-1.631800	0.833600
C	0.789400	1.100200	-1.118800
C	0.593800	-0.161900	-1.733000
C	0.944300	-1.193100	-0.826500
C	1.345000	-0.564600	0.389800
C	1.260900	0.857600	0.205700
C	1.907100	-1.259200	1.611900
C	1.090600	-2.645200	-1.214600
C	0.684300	2.393200	-1.894600
C	1.756400	1.929600	1.153400
C	0.959000	-2.262300	2.264300
C	3.263800	-1.899400	1.315700
C	0.962400	2.057200	2.450500
C	3.257500	1.808600	1.419800
C	-0.145700	3.510100	-1.270200
C	2.081700	2.893000	-2.262400
C	-0.181000	-3.271200	-1.770900
C	2.231800	-2.782800	-2.222100
H	-2.588500	2.626300	0.911700
H	-3.039200	2.018400	-1.334300
H	-3.206200	-0.141300	-2.263500
H	-2.992200	-2.226600	-1.191100
H	-2.527600	-2.676400	1.085200
H	-2.206300	-1.138300	2.848900
H	-2.224200	1.214800	2.768800
H	2.085700	-0.482100	2.363600
H	1.371100	-3.215200	-0.321100
H	0.180300	2.121900	-2.835900
H	1.628100	2.881200	0.626200
H	0.666900	-3.067700	1.581000
H	1.435800	-2.727100	3.135200
H	0.040900	-1.770400	2.605200
H	3.938000	-1.193700	0.818900
H	3.741900	-2.233800	2.243500
H	3.164000	-2.774700	0.665100
H	-0.079300	2.327700	2.242500
H	0.950900	1.125100	3.027800
H	1.392500	2.836300	3.090600
H	3.815300	1.705900	0.482300
H	3.623500	2.703100	1.936300
H	3.503000	0.946600	2.048600
H	-1.170800	3.183000	-1.076800
H	0.271000	3.868900	-0.323400
H	-0.186800	4.368500	-1.950300
H	2.667100	2.102500	-2.742900
H	2.024500	3.744500	-2.949700
H	2.633200	3.221600	-1.373500
H	-0.964600	-3.320100	-1.008400
H	-0.573400	-2.693300	-2.616700
H	0.014500	-4.289000	-2.126500
H	1.969200	-2.298000	-3.169800
H	3.150800	-2.314500	-1.854700
H	2.442000	-3.837400	-2.433600
H	0.256000	-0.300900	-2.756000



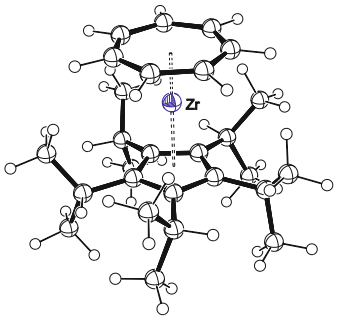
(C_{2v}-Symm.) (atom, x-, y-, z-positions in Å):

Isomer-2 of (4)			
Zr	-1.119300	-0.003300	-0.052700
C	1.002800	-1.154800	0.745700
C	0.813000	0.002400	1.541800
C	0.995100	1.161300	0.746300
C	1.255100	0.723900	-0.584800
C	1.259800	-0.714900	-0.585200
C	1.652600	1.590900	-1.757100
C	1.135400	2.552000	1.317800
C	1.154500	-2.544100	1.317900
C	1.662500	-1.578700	-1.758100
C	0.675000	2.709000	-2.110900
C	3.068700	2.133200	-1.557600
C	3.082600	-2.110800	-1.559900
C	0.693000	-2.704100	-2.111100
C	2.351700	-2.569500	2.267200
C	-0.091200	-3.066400	2.019400
C	-0.117800	3.067800	2.010800
C	2.326900	2.586500	2.273700
C	-2.956600	1.276100	0.682000
C	-3.046900	-0.000600	1.301100
C	-2.945800	-1.285400	0.700600
C	-2.727900	-1.611900	-0.667300
C	-2.556100	-0.732400	-1.771600
C	-2.561100	0.691900	-1.781900
C	-2.739800	1.585300	-0.690000
H	1.689200	0.939900	-2.640600
H	1.362100	3.237900	0.494000
H	1.380900	-3.230000	0.494000
H	1.693300	-0.927200	-2.641600
H	0.512700	3.410600	-1.285800
H	1.055500	3.286500	-2.961300
H	-0.301500	2.301500	-2.391300
H	3.768800	1.324500	-1.319900
H	3.424500	2.637700	-2.463000
H	3.109800	2.859100	-0.737200
H	3.776900	-1.297500	-1.321300
H	3.128900	-2.837500	-0.740500
H	3.441700	-2.611600	-2.466000
H	-0.286300	-2.303900	-2.392300
H	1.078100	-3.279600	-2.960800
H	0.535500	-3.406000	-1.285400
H	3.253500	-2.182600	1.781200
H	2.159900	-1.950000	3.151200
H	2.554900	-3.589600	2.611900
H	-0.921700	-3.179400	1.315300
H	0.103100	-4.041400	2.480300
H	-0.417100	-2.382600	2.813600
H	-0.944400	3.174200	1.301000
H	-0.444500	2.383100	2.803900
H	0.067400	4.044900	2.471200
H	2.134200	1.967300	3.157700
H	3.233800	2.204600	1.793200
H	2.521800	3.608400	2.617900
H	0.620900	0.001400	2.610800
H	-2.577800	-2.667300	-0.879500
H	-2.948400	-2.123200	1.390100
H	-3.112600	0.007200	2.385500
H	-2.967200	2.123600	1.359500
H	-2.598100	2.639000	-0.916200
H	-2.318900	1.152300	-2.735400
H	-2.310200	-1.204500	-2.718400



(atom, x-, y-, z-positions in Å):

Isomer-3 of (4)			
Zr	1.092400	0.007400	-0.246200
C	2.595200	1.765000	-0.624100
C	2.111100	1.337600	-1.893200
C	2.045600	0.012900	-2.410300
C	2.422200	-1.206200	-1.782900
C	2.956900	-1.413900	-0.480700
C	3.270000	-0.439900	0.508100
C	3.117400	0.973800	0.437600
C	-0.764500	1.175600	0.989500
C	-1.369900	0.618400	-0.185200
C	-1.309100	-0.817100	-0.066300
C	-0.655100	-1.117800	1.169500
C	-0.337300	0.103200	1.806800
C	-0.655400	2.635400	1.366500
C	-1.980400	3.161400	1.917700
C	0.439400	2.895700	2.393100
C	-2.013800	1.514300	-1.223800
C	-3.523800	1.668500	-1.012500
C	-1.725300	1.186400	-2.683300
C	-1.886100	-1.932900	-0.923000
C	-1.082100	-2.294000	-2.168700
C	-3.363700	-1.762100	-1.258700
C	-0.464900	-2.486000	1.775000
C	-1.738300	-2.897100	2.514000
C	0.725600	-2.563000	2.721100
H	2.463800	2.820700	-0.402600
H	1.666900	2.110900	-2.513400
H	1.555000	-0.091800	-3.374100
H	2.183100	-2.108000	-2.338200
H	3.065100	-2.450800	-0.175300
H	3.586700	-0.828700	1.471600
H	3.337600	1.509800	1.356300
H	0.166500	0.200700	2.761400
H	-0.406200	3.213800	0.463600
H	-2.297400	2.553500	2.774200
H	-2.781300	3.139400	1.175300
H	-1.871900	4.196500	2.261200
H	0.189400	2.434500	3.356400
H	0.544000	3.971300	2.568800
H	1.409400	2.504900	2.071600
H	-1.574100	2.507800	-1.050200
H	-4.073400	0.801400	-1.386700
H	-3.893900	2.547700	-1.552400
H	-3.780900	1.783900	0.044100
H	-0.650200	1.098000	-2.874100
H	-2.119800	1.980800	-3.326900
H	-2.203600	0.254100	-2.997500
H	-1.840300	-2.823400	-0.283100
H	-1.539300	-3.150600	-2.678300
H	-0.055100	-2.569800	-1.905400
H	-1.033000	-1.469100	-2.885600
H	-3.939400	-1.442200	-0.383300
H	-3.777300	-2.714200	-1.609300
H	-3.524300	-1.030400	-2.056300
H	-0.283400	-3.207700	0.963900
H	-1.929000	-2.198300	3.337600
H	-1.644500	-3.903600	2.937200
H	-2.616000	-2.880600	1.859400
H	1.659100	-2.268500	2.229700
H	0.845800	-3.583800	3.098600
H	0.580800	-1.912100	3.591400

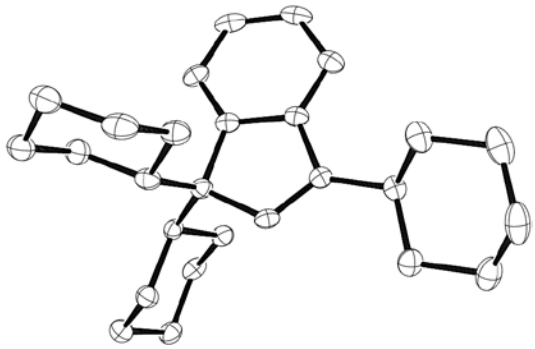


(atom, x-, y-, z-positions in Å):

Structure of (7)			
Zr	1.238300	-0.008700	-0.002900
C	-0.990400	0.824400	0.898500
C	-1.000100	-0.597000	1.057200
C	-1.003100	-1.186000	-0.246000
C	-0.993800	-0.130000	-1.209300
C	-0.991000	1.112800	-0.501300
C	-1.178500	-0.266700	-2.708500
C	-1.211400	-2.650500	-0.582000
C	-1.204800	-1.371600	2.346200
C	-1.170200	1.817700	2.029800
C	-1.187500	2.496300	-1.091400
C	-0.107400	-1.065400	-3.446800
C	-2.579200	-0.780000	-3.049700
C	-0.072900	2.998600	-2.004700
C	-2.557900	2.630200	-1.758900
C	-0.088600	2.886600	2.164200
C	-2.564000	2.449900	1.997900
C	-0.096400	-1.248000	3.387400
C	-2.576900	-1.086300	2.962100
C	-0.114800	-3.602200	-0.111800
C	-2.596700	-3.133100	-0.145800
C	2.928200	-1.581100	0.476100
C	2.942400	-0.615900	1.519600
C	2.929600	0.802700	1.428300
C	2.926000	1.615600	0.260900
C	2.948800	1.199400	-1.098000
C	2.955000	-0.120500	-1.624700
C	2.930500	-1.361000	-0.929300
H	-1.118200	0.746800	-3.119900
H	-1.207800	-2.719100	-1.674500
H	-1.220900	-2.429900	2.065800
H	-1.122400	1.237500	2.957600
H	-1.202600	3.189600	-0.244700
H	-0.026000	-2.099500	-3.096300
H	-0.336500	-1.099300	-4.518300
H	0.876100	-0.602600	-3.326500
H	-3.350400	-0.214800	-2.515500
H	-2.768800	-0.684300	-4.125000
H	-2.704300	-1.836100	-2.789100
H	0.866300	3.096900	-1.450500
H	0.113700	2.333400	-2.855200
H	-0.330800	3.985000	-2.408000
H	-3.352400	2.245400	-1.110000
H	-2.774400	3.682600	-1.975400
H	-2.612600	2.085300	-2.706800
H	0.892000	2.430500	2.330900
H	-0.008500	3.525100	1.278100
H	-0.310100	3.538400	3.017400
H	-3.341900	1.691700	1.860600
H	-2.764100	2.980200	2.936200
H	-2.667500	3.178100	1.186500
H	0.839800	-1.666100	3.005200
H	0.101500	-0.211500	3.682100
H	-0.367000	-1.801100	4.294600
H	-3.369600	-1.137800	2.207700
H	-2.802400	-1.822600	3.742000
H	-2.625900	-0.096700	3.427700
H	0.840500	-3.359700	-0.589500
H	0.044300	-3.567100	0.971500
H	-0.372200	-4.635100	-0.374600
H	-2.678200	-3.245100	0.940000
H	-3.376500	-2.433000	-0.465000
H	-2.814400	-4.110800	-0.590700
H	2.811700	2.683400	0.426800
H	2.831300	1.328300	2.373800
H	2.854400	-1.014300	2.525300
H	2.814100	-2.613400	0.795000
H	2.823000	-2.245800	-1.551500
H	2.880900	-0.187900	-2.705500
H	2.856300	1.991200	-1.835400

2. Experimental Details

1,1,3-Tris(cyclohexyl)indene. Aqueous KOH (50 %; 0.75 L, ca. 10 mol) and Adogen-464 (5 g) were placed in a 2-L three neck round bottom flask fitted with a condenser, mechanical stirrer, heating mantle, and a dropping funnel. Indene (24.9 g, 0.21 mol) and cyclohexyl bromide (139.7 g, 105 mL, 0.86 mol) were added under rapid stirring to the reaction mixture via an addition funnel at a rate that the reaction temperature did not exceed 40 °C. After complete addition the reaction mixture was stirred under reflux for 24 h. The reaction mixture was allowed to cool to room temperature and extracted with diethyl ether (2 x 500 mL). The organic layers were combined, dried over anhydrous Mg_2SO_4, filtered and the solvent was evaporated. The obtained residue was allowed to stand at room temperature overnight upon which a colorless crystalline solid formed which was isolated and washed with cold diethyl ether. Yield: 18.3 g (0.05 mmol, 24 %). The colorless crystals were analyzed by X-ray crystallography and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 24 °C): δ 7.30-7.24 (m, 4H, 4H-7H), 5.89 (s, 1H, 2-H), 2.77-2.50 (m, 3H, cyclohexyl-C*H*), 2.08-0.61 (m, 30H, cyclohexyl-CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ 150.6, 148.3, 145.9 ($3C_{ipso}$), 133.9, 125.7, 124.0, 122.7, 118.7 (5C, C_9H_5), 61.7 (1C, C_{indene}(cyclohexyl)$_2$), 40.5 (2C, cyclohexyl-*C*H), 36.8 (1C, cyclohexyl-*C*H), 32.7 (2C, cyclohexyl-*C*H_2), 28.0 (2C, cyclohexyl-*C*H_2), 27.4 (2C, cyclohexyl-*C*H_2), 27.14 (3C, cyclohexyl-*C*H_2), 27.1 (3C, cyclohexyl-*C*H_2), 26.82 (2C, cyclohexyl-*C*H_2), 26.77 (3C, cyclohexyl-*C*H_2), 26.6 (1C, cyclohexyl-*C*H_2). GC-MS: *m/e* = 362 (M^+).



Empirical formula	$C_{27}H_{38}$	
Formula weight	362.57	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 11.5611(4) Å	α = 90°
	b = 13.3654(4) Å	β = 96.061(2)°
	c = 13.8835(4) Å	γ = 90°
Volume	2133.27(12) $Å^3$	
Z	4	
Density (calculated)	1.129 Mg/m^3	
Absorption coefficient	0.063 mm^{-1}	
F(000)	800	
Crystal size	0.27 x 0.22 x 0.20 mm^3	

Theta range for data collection	2.34 to 26.37°
Index ranges	-14<=h<=14, -16<=k<=16, -17<=l<=17
Reflections collected	69085
Independent reflections	4355 [R(int) = 0.0504]
Completeness to theta = 26.37°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4355 / 0 / 244
Goodness-of-fit on F^2	0.954
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0873
R indices (all data)	R1 = 0.0598, wR2 = 0.0912
Largest diff. peak and hole	0.249 and -0.168 e.Å^{-3}

3. Measurement of Θ and Ω

Values used for the determination of Θ or Ω are highlighted in yellow.

[(η^7-C_7H_7)Zr(η^5-C_5H_5)]

Centroid-Zr-H			
	44.44		
	44.16	**Theta:**	**88.23**
	44.44		
	43.77		
	43.77		

[(η^7-C_7H_7)Zr(η^5-$C_5H_4CH_3$)]

Centroid-Zr-H			
H8	43.49		
H9	44.29	**Theta:**	**95.14**
H10	45.56		
H11	44.35		
Me	60.16		
	56.33		
	48.23		

C13-C12-H			
	23.48		
	26.16	**Omega:**	**49.03**
	23.91		

[(η^7-C_7H_7)Zr(η^5-$C_5H_4Si(CH_3)_3$)]

Centroid-Zr-H			
H8	43.59		
H9	43.61	**Theta:**	**104.29**
H10	44.35		
H11	44.08		

Si(CH3)3			
1. CH3	85.09		
	69.68		
	75.93		
2. CH3	63.31		
	72.13		
	80.66		
3. CH3	37.79		
	38.62		
	49.05		

Si-C12-Me			
1. CH3	47.84		
	47.37	**Omega:**	**95.62**
	27.17		
2. CH3	47.21		
	27.17		
	47.07		
3. CH3	48.38		
	27.57		
	46.16		

[(η^7-C_7H_7)Zr(η^5-C_5H_4(allyl))]

Centroid-Zr-H			
H8	44.05		
H9	45.10	**Theta:**	**105.95**
H10	44.89		
H11	43.53		
Allyl			
H	57.70		
H	41.75		
CH=CH2	87.30		

C13-C12-H			
C-C-H	25.79		
C-C-H	27.35	**Omega:**	**68.61**
CH=CH2	49.77		

[(η^7-C_7H_7)Zr(η^5-Cp‘‘)]

Centroid-Zr-H			
H9	44.05		
H11	44.80	**Theta:**	**116.21**
H12	43.99		
tBu on C8			
1. Me	78.94		
	69.13		
	61.54		
2. Me	75.79		
	66.71		
	57.39		
3. Me	45.59		
	34.24		
	32.57		
tBu on C10			
1. Me	78.75		
	69.15		
	60.84		
2. Me	77.31		
	68.66		
	59.21		
3. Me	46.02		
	34.13		
	33.39		

C(alpha)-C(ipso)-H			
tBu on C8			
1. Me	49.52	**Omega:**	**100.71**
	49.49		
	24.69		
2. Me	49.75		
	49.28		
	24.68		
3. Me	51.53		
	51.21		
	26.58		

tBu on C10	
1. Me	49.71
	49.55
	24.78
2. Me	49.93
	48.96
	24.62
3. Me	51.68
	51.50
	26.79

[(η^7-C_7H_7)Zr(η^5-Cp‘‘‘)]

Centroid-Zr-H			
H10	44.10		
H12	43.33	**Theta:**	**132.01**

tBu on C8	
1. Me	83.49
	76.24
	74.37
2. Me	61.53
	57.84
	43.09
3. Me	49.44
	46.57
	33.21
tBu on C9	
1. Me	79.34
	69.16
	62.96
2. Me	75.04
	67.13
	56.49
3. Me	45.68
	34.71
	32.40
tBu on C11	
1. Me	79.76
	68.94

	62.01		
2. Me	76.46		
	68.50		
	57.14		
3. Me	46.49		
	35.01		
	33.38		

C(alpha)-C(ipso)-H

tBu on C8			
1. Me	48.27	**Omega:**	**99.81**
	47.75		
	23.44		
2. Me	50.04		
	49.58		
	25.26		
3. Me	49.65		
	47.12		
	23.98		
tBu on C9			
1. Me	47.28		
	46.88		
	22.35		
2. Me	50.39		
	49.03		
	25.08		
3. Me	51.28		
	50.34		
	26.15		
tBu on C11			
1. Me	50.48		
	48.16		
	24.59		
2. Me	50.46		
	48.79		
	24.85		
3. Me	51.30		
	51.03		
	26.36		

[(η^7-C_7H_7)Zr(η^5-^{4}Cp)]

Centroid-Zr-H			
H12	44.1		
		Theta:	**146.36**
iPr on C8			
1. Me	76.88		
	67.24		
	59.04		
2. Me	45.38		
	33.93		
	32.45		
H	59.1		
iPr on C9			
1. Me	82.08		
	71.21		
	69.74		
2. Me	45.71		
	40.09		
	29.85		
H	53.21		
iPr on C10			
1. Me	83.39		
	73.03		
	72.49		
2. Me	47.67		
	42.67		
	31.49		
H	53.35		
iPr on C11			
1. Me	79.45		
	68.31		
	66.24		
2. Me	43.62		
	35.95		
	28.74		
H	54.31		

C(alpha)-C(ipso)-H

iPr on C8			
1. Me	48.18	**Omega:**	**85.89**
	48.1		
	23.11		
2. Me	51.13		
	50.9		
	26.17		
H	27.35		
iPr on C9			
1. Me	47.39		
	46.43		
	22.07		
2. Me	51.66		
	46.56		
	24.77		
H	28.08		
iPr on C10			
1. Me	49.53		
	45.89		
	23.14		
2. Me	50.96		
	46.27		
	24.2		
H	27.91		
iPr on C11			
1. Me	53.34		
	41.77		
	25.53		
2. Me	52.45		
	49.76		
	26.37		
H	27.36		

[(η^7-C_7H_7)Zr(η^5-$C_5(CH_3)_5$)]

Centroid-Zr-H			
Me on C5	59.33		
	59.33	**Theta:**	**122.37**
	43.93		
Me on C6	61.59		
	59.44		
	44.28		
Me on C6B	61.59		
	59.44		
	44.28		
Me on C7	43.09		
	59.80		
	61.71		
Me on C7B	43.09		
	59.80		
	61.71		

C(alpha)-C(ipso)-H			
Me on C5	24.83		
	24.83	**Omega:**	**51.20**
	26.42		
Me on C6	24.45		
	26.43		
	26.44		
Me on C7	24.60		
	25.53		
	26.50		
Me on C6B	24.45		
	26.43		
	26.44		
Me on C7B	24.60		
	25.53		
	26.50		

[(η^7-C_7H_7)Zr(η^5-^{5}Cp)]

Centroid-Zr-H			
iPr on C2			
1. Me	83.84	**Theta:**	**167.42**
	71.31		
	71.31		
2. Me	46.03		
	40.70		
	28.56		
H	53.49		
iPr on C3			
1. Me	83.49		
	78.83		
	71.05		
2. Me	45.93		
	41.55		
	28.41		
H	52.54		
iPr on C4			
1. Me	83.68		
	72.38		
	71.22		
2. Me	45.99		
	41.03		
	28.49		
H	52.80		
iPr on C5			
1. Me	84.01		
	71.55		
	71.42		
2. Me	46.32		
	40.45		
	28.88		
H	53.68		
iPr on C6			
1. Me	83.52		
	72.89		

	71.14
2. Me	45.93
	41.45
	28.40
H	52.39

C(alpha)-C(ipso)-H

iPr on C2	
1. Me	48.41
	48.09
	20.92
2. Me	54.34
	47.67
	24.58
H	29.98

iPr on C3	
1. Me	49.02
	47.42
	20.98
2. Me	54.21
	47.34
	24.42
H	30.00

iPr on C4	
1. Me	48.97
	47.99
	21.18
2. Me	54.07
	47.74
	24.39
H	29.93

iPr on C5	
1. Me	48.31
	48.28
	20.95
2. Me	53.97
	48.21
	24.45

Omega: **88.56**

H	29.95
iPr on C6	
1. Me	48.96
	47.68
	21.05
2. Me	54.12
	47.70
	24.43
H	29.98

[(η^7-C_7H_7)Zr(η^5-C_9H_7)]

Centroid-Zr-H			
H9	45.14		
H10	44.47	**Theta:**	**102.56**
H11	45.56		
H14	60.72		
H15	60.51		

[(η^7-C_7H_7)Zr(η^5-Ind‘‘)] (1st molecule in the asymmetric unit)

Centroid-Zr-H			
H9	43.54		
		Theta:	**130.72**
H14	61.52		
H15	61.52		

tBu on C8	
1. Me	46.45
	38.54
	31.2
2. Me	70.09
	64.86
	51.72
3. Me	82.64

	71.4
	68.19

tBu on C10	
1. Me	77.59
	68.52
	60.98
2. Me	74.54
	65.16
	56.07
3. Me	43.72
	33.35
	30.61

C(alpha)-C(ipso)-H

tBu on C8			
1. Me	51.83	**Omega:**	**101.26**
	50.66		
	26.51		
2. Me	48.87		
	47.38		
	23.33		
3. Me	51.34		
	48.57		
	25.31		

tBu on C10	
1. Me	52.52
	51.58
	27.31
2. Me	50.00
	49.57
	24.98
3. Me	49.21
	46.06
	23.01

[(η^7-C_7H_7)Zr(η^5-Ind‘‘)] (2^{nd} molecule in the asymmetric unit)

Centroid-Zr-H			
H9’	42.62		
		Theta:	**131.76**
H14’	61.98		
H15’	63.11		

tBu on C8’	
1. Me	44.41
	33.83
	31.60
2. Me	74.86
	65.89
	56.49
3. Me	77.67
	67.96
	60.86

tBu on C10’	
1. Me	84.03
	73.86
	72.86
2. Me	65.98
	60.02
	46.56
3. Me	62.45
	43.09
	62.45

C(alpha)-C(ipso)-H			
tBu on C8’			
1. Me	51.43	**Omega:**	**100.19**
	51.37		
	29.60		
2. Me	49.82		
	49.54		
	24.87		
3. Me	48.50		
	47.27		

	23.08
tBu on C10’	
1. Me	51.67
	49.62
	26.01
2. Me	50.43
	49.02
	24.89
3. Me	49.18
	48.22
	23.93

[(η^7-C_7H_7)Zr(η^5-Ind^{cHexyl})] (1st molecule in the asymmetric unit)

Centroid-Zr-H	
H9	43.68
H14	61.94
H15	61.10

Theta: **130.96**

cHexyl on C8	
CH	61.69
CH2	79.10
	60.84
CH2	79.07
	78.24
CH2 middle	65.62
	57.71
CH2	58.47
	48.08
CH2	37.30
	35.92

cHexyl on C10	
CH	60.47
CH2	81.57
	63.78
CH2	80.07

	79.01
CH2 middle	65.87
	58.98
CH2	57.38
	47.65
CH2	36.88
	36.05

C(alpha)-C(ipso)-H

cHexyl on C8			
CH	27.96	**Omega:**	**84.89**
CH2	49.11		
	48.76		
CH2	30.23		
	18.31		
CH2 middle	29.82		
	13.24		
CH2	31.05		
	19.15		
CH2	49.97		
	49.34		

cHexyl on C10	
CH	27.97
CH2	49.55
	48.42
CH2	29.99
	18.83
CH2 middle	28.77
	12.05
CH2	30.75
	19.51
CH2	50.10
	49.21

[(η^7-C_7H_7)Zr(η^5-Ind^{cHexyl})] (2^{nd} molecule in the asymmetric unit)

Centroid-Zr-H

H9’	42.49		
		Theta:	**131.70**
H14’	61.25		

H15’	61.17

cHexyl on C8’	
CH	61.47
CH2	75.16
	56.65
CH2	76.00
	73.53
CH2 middle	62.30
	53.66
CH2	57.44
	46.18
CH2	37.54
	23.52

cHexyl on C10’	
CH	47.52
CH2	81.51
	84.11
CH2	88.32
	73.70
CH2 middle	77.61
	73.59
CH2	53.93
	57.44
CH2	50.13
	39.61

C(alpha)-C(ipso)-H			
cHexyl on C8’			
CH	27.92	**Omega:**	**84.20**
CH2	48.59		
	50.07		
CH2	19.93		
	31.25		
CH2 middle	13.26		
	28.93		
CH2	29.68		
	28.23		
CH2	48.60		
	48.12		

cHexyl on C10'	
CH	27.76
CH2	49.09
	48.90
CH2	29.85
	29.55
CH2 middle	11.50
	28.04
CH2	18.94
	29.20
CH2	47.76
	49.60

3. Comparison between cone angles Θ based on calculated (DFT) and experimental structures (X-ray) for [(η^7-C_7H_7)Zr(η^5-^{4}Cp)]

Comparison of cone angles for [(η^7-C_7H_7)Zr(η^5-^{4}Cp)] based on calculated and experimental structures.
Only the conformers without methyl-methyl contacts are compared. Distances are given in Å, angles are given in °.

	Experimental data (X-ray)	C_s symmetry (as exp.)	C_s symmetry	C_{2v} symmetry
Centroid-Zr	2.207	2.218	2.225	2.226
Centroid-Zr-H (for H)	44.10	46.41	46.15	45.82
Centroid-Zr-H (for iPr)	79.45	83.81	82.87	82.69
Centroid-Zr-H (for iPr)	82.08	84.87	84.95	83.85
Centroid-Zr-H (for iPr)	83.39	84.15	83.76	83.84
Centroid-Zr-H (for iPr)	76.88	77.25	83.61	82.61
Cone angle	**146.4**	**150.60**	**152.54**	**151.52**

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