How big is a Cp? Novel cycloheptatrienyl zirconium complexes with tri-, tetra- and pentasubstituted cyclopentadienyl ligands†

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The new bulky cyclopentadienyl anions 1,2,4-tri(cyclopentyl)cyclopentadienide and 2,3-diisopropyl-1,4-dimethyl-5-trimethylsilyl-cyclopentadienide were prepared. These and the already known 1,2,4-tri(cyclopentyl)-, 1,2,4,5-tetramethyl-5-trimethylsilyl-cyclopentadienide were characterized structurally by elemental analysis and NMR spectroscopy. For five of the sandwich complexes X-ray crystal structure determinations could be carried out; structures of the four others were obtained by DFT calculations. The data serve as a basis for cone angle measurements of cyclopentadienyl ligands to evaluate the steric demand of these ligands.

Introduction

In the late forties of the last century the parent cyclopentadienyl ligand was seized by freshly reduced iron from cyclopentadiene vapors at 300 °C to form a complex later called iron pentamethylcyclopentadienide.2 The authors analyzed a large number of olefin polymerization systems and concluded, in contrast, that steric effects dominate the catalytic activity of zirconocene derivatives17,18 and found “no influ-

†Electronic supplementary information (ESI) available: Details of the electronic structure calculations, X-ray data, the determination of Θ and Ω, and discussions of NMR spectra of five complexes. CCDC 1012756–1012760. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01581a

‡The steric bulk of the cyclopentadienyl ligands in titanocene derivatives was concluded to affect both the angular opening between the two Cp planes corresponding to access of reactants to the metal center and the angular opening in the plane bisecting the two Cp planes, which limits the angle between the Ti–C(polymer) σ bond and the direction of the olefin approach.16 Janiak et al. concluded, in contrast, that steric effects dominate the catalytic activity of zirconocene derivatives17,18 and find “no influ-
ence of ... electronic effects ...". Different methods of substituted cyclopentadienyl bulk quantification have been outlined in the literature, which was later updated in the literature

where steric bulk measures mostly derived from zirconocene or ferrocene derivatives for 35 cyclopentadienyl ligands with 0–1 substituents and for 8 cyclopentadienyl ligands with two isopropyl or cyclohexyl substituents, two or three tBu groups or 2–5 methyl groups have been listed. Another early approach used force field calculations on 24 iron[n] cyclopentadienyl complexes with a fixed Fe–ring centroid distance of 1.73 Å. For most of the bulky cyclopentadienyl ligands with two and more substituents such values are not available. In our research activities bulky alkycyclopentadienyl ligands play a central role, because they can be used to prevent metal complexes from falling into their preferred energetic sink. For our research a systematic evaluation of steric bulk is therefore quite important.

For this reason, we have embarked on an approach, where an average cone angle derived from crystallographic data quantifies the steric bulk of the substituted cyclopentadienyl ligand and additional information on the bulk of the individual substituents is provided by a substituent cone angle adding numerical information on the third dimension. The cycloheptatrienyl-zirconium fragment, which turned out to be a very versatile starting compound for an extensive chemistry, offers good crystallinity and more than one hemisphere of one of the largest transition metals for very bulky cyclopentadienyl ligands. Thus, these CHT–Zr complexes are the materials of choice for the investigation.

Results and discussion

Synthesis of cyclopentadienyl ligands

The synthesis of tricycloheptatrienylcyclopentadienide HCPpent (2-H) from the parent cyclopentadiene followed a variation of the phase-transfer alkylation process in a system consisting of aqueous potassium hydroxide solution and an organic phase containing cyclopentadiene, cyclopentyl bromide, and cyclopentadiene alkylation products (Scheme 1).

Metatation of the 2-H mixture of isomers with sodium amide gave 46% yield of the sodium salt 2-Na.

For the synthesis of potassium 3,4-diisopropyl-2,5-dimethyl-1-trimethylsilylcyclopentadienide KTMS (6-K, Scheme 2) sodium 2,3-diisopropyl-1,4-dimethylcyclopentadienide was silylated with chlorotrimethylsilane in tetrahydrofuran to furnish 61% yield of the silylated cyclopentadiene tautomers 6-H, which could be metalated with potassium hydride to the potassium salt 6-K in 77% yield.

Literature citations regarding the preparation of other cyclopentadienides used in this study can be found in the experimental part.

Synthesis and characterization of cycloheptatrienyl zirconium complexes 2–10

Salt metathesis reaction between the cycloheptatrienyl zirconium chloride 1 and the substituted cyclopentadienides or the indenide was performed in THF solution at –78 °C (Scheme 3). The changing colour of the reaction mixture turned out to be a very good indicator for the progress of the reaction. Whereas a mixture of the dark blue solution of 1 and the brown solution of the cyclopentadienyl salt displays a grey colour, this turns purple after some minutes or hours, depending on the reaction rate.

The synthesis of the cycloheptatrienyl zirconium complex [(C7H7)Zr(C2H5(C5H9)3-1,2,4)] via a reaction between [(CHT)-ZrCl(tmeda)] and 2-Na afforded 53% yield of purple needles. A discussion of proton and 13C NMR spectra of complex 2 can be found in the ESI.

A crystal structure determination reveals the first structural characterization of the 1,2,4-tricycloheptatrienylcyclopentadienyl ligand in complex 2 (Fig. 1). The three cyclopentyl rings show the expected envelope conformation and are rotated such that the methyne hydrogen atom at the α carbon atom is close to the cyclopentadienyl plane, one of the β carbon atoms is above...
and the other below the cyclopentadienyl plane. Both β carbon atoms of all three cyclopentyl substituents point towards a CH group of the cyclopentadienyl ligand, the two vicinal cyclopentyl substituents in 1- and 2-positions are turned away from each other. All three C5 envelopes see the cyclopentadienyl moiety in an exo position and the α (methyne) hydrogen atom in an endo position as expected from a steric point of view. The Zr–CHTcent distance (1.673 Å) is much smaller than the Zr–Cpcent distance (2.191 Å) because of the larger ring diameter of the cycloheptatrienyl ligand and the steric demand of the cyclopentadienyl ring. Due to the arrangement of the cyclopentyl substituents described before, the CHT ligand is tilted towards the two substituents in 1- and 2-positions (CHTcent 1.673, CHTcent–Zr 172.03°).

Other features of the crystallographically determined or theoretically calculated molecular structures of complexes 2–10 are collected in Table 2, details like individual Zr–C distances are listed in the figure caption of Fig. 1.

The tricyclohexylcyclopentadienyl derivative \([\text{C}_{10}H_{12})Zr{(\text{C}_{4}H_{4}i-	ext{C}_{3}H_{7})_{3}-1,2,4}]\) (3) was obtained as purple crystals in 54% yield from 1 and sodium tricyclohexylcyclopentadienide (3-Na)\(^{28}\) by the procedure used also for the synthesis of 2. A discussion of proton and \(^{13}\)C NMR spectra of complex 3 can be found in the ESI.\(^{\dagger}\) The structure of 3 was obtained by DFT calculations (Fig. 2), which arrived at a conformation very similar to that discussed for the crystallographically characterized structure of 2.

The calculated distances (1.684 Å for CHTcent–Zr and 2.213 Å for CPTcent–Zr) are slightly longer than the values for 2, a tendency, which was found for all calculated structures, irrespective of their steric demand (Table 2). The validity of these calculations had been demonstrated for the tetraisopropylcyclopentadienyl derivative \([\text{C}_{10}H_{12})Zr{(\text{C}_{3}H_{3}i-	ext{Pr})_{4}}]\) before.\(^{22}\) In this case the largest difference between the experimental and the calculated Zr–C distances, for example, was found for Zr–C4 (2.346(4) vs. 2.370 Å). For the other eleven Zr–C distances the deviation was found well below 1%.

From sodium 1,2,4-trisopropylcyclopentadienide (1Cp) and the zirconium starting compound the triisopropylcyclopentadienyl derivative \([\text{C}_{10}H_{12})Zr{(\text{C}_{4}H_{4}[i-	ext{C}_{3}H_{7})_{3}-1,2,4}]\) (4) was obtained as purple crystals in 60% yield. The spectroscopic properties of the 1,2,4-trisopropylcyclopentadienyl ligand have been discussed before.\(^{27}\) Since the crystals were found unsuitable for X-ray diffraction, a structure was obtained by DFT calculations (Fig. 3). The calculation shows the expected structure of the complex. The isopropyl substituent in the 4-position is oriented in a way that one methyl carbon atom is close to the ring plane and the methyne proton points towards the zirconium atom to reduce steric strength. Resulting from this orientation, the cycloheptatrienyl ring is tilted towards the...
pentadienide (K₂\text{Zr}(\text{Cp})) type. Even with the almost insoluble sodium 2,3-diisopropyl-1,4-
dimethylocyclopentadienide\(^{26}\) ([\text{ZCp}] the reaction with the blue solution of 1 proceeded smoothly and afforded the sublimable sandwich complex \([\text{C}_2\text{H}_5\text{Zr}][\text{C}_7\text{H}_7\text{Zr}(\text{C}_5\text{H}_2\text{SiMe}_3\text{C}_3\text{H}_7\text{Zr}(\text{C}_5\text{H}_2\text{SiMe}_3\text{C}_3\text{H}_7)]\) (2) as purple crystals in 76% yield. \(^1\text{H}\) and \(^13\text{C}\) NMR spectra exhibit the signals expected for pairs of symmetry-equivalent methyl and isopropyl substituents (the latter with two diastereotopic methyl positions, cf. lit.\(^{27}\)) as well as the CH signals for both ring ligands. The violet prisms of 3 obtained by sublimation at about 120 °C in a sealed glass tube at 10\(^{-3}\) mbar gave X-ray diffraction data of excellent quality (\(\text{wR}_2\) value 0.0473, all data, Table 1) (Fig. 4).

Due to the sterically demanding isopropyl substituents in 2- and 3-positions, the cycloheptatrienyl ligand is tilted towards the substitution gap of the cyclopentadienyl ring (167.98\(^\circ\)). The Zr-CHT\text{cent} distance of 1.677 Å and the Cp\text{cent}-Zr distance of 2.192 Å are in the same range as for other complexes of the [[Zr(CP)](2)] type. The steric bulk of the \(\text{ZCp}\) ligand can be significantly enlarged by replacement of the only hydrogen atom connected to the five-membered ring by a fifth substituent. The trimethylsilyl derivative \([\text{C}_2\text{H}_5\text{Zr}][\text{C}_7\text{H}_7\text{Zr}(\text{C}_5\text{H}_2\text{SiMe}_3\text{C}_3\text{H}_7\text{Zr}(\text{C}_5\text{H}_2\text{SiMe}_3\text{C}_3\text{H}_7)]\) (6) could be obtained in 39% yield from the corresponding potassium 3,4-diisopropyl-2,5-dimethyl-1-trimethylsilylcyclopentadienide (K\text{2Zr}TMES) and the zirconium starting compound 1.

A discussion of proton and \(^13\text{C}\) NMR spectra of complex 6 can be found in the ESL\(^\dagger\).

The crystal structure of the purple orthorhombic blocks obtained by sublimation of 6 in a sealed glass tube under vacuum at 120 °C shows the protruding silyl group (ring C-Si-

### Table 1  Crystallographic data for complexes 2, 5, 6, 8 and 10

<table>
<thead>
<tr>
<th>Complex</th>
<th>2</th>
<th>5</th>
<th>6</th>
<th>8</th>
<th>10</th>
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</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C\text{27H}_{36}\text{Zr}</td>
<td>C\text{20H}_{28}\text{Zr}</td>
<td>C\text{23H}_{36}\text{SiZr}</td>
<td>C\text{46H}_{40}\text{OZr}</td>
<td>C\text{20H}_{22}\text{Zr}</td>
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<tr>
<td>Fw (g mol(^{-1}))</td>
<td>451.78</td>
<td>359.64</td>
<td>431.83</td>
<td>700.00</td>
<td>353.60</td>
</tr>
<tr>
<td>Crystal size (mm(^3))</td>
<td>0.19×0.12×0.04</td>
<td>0.12×0.12×0.04</td>
<td>0.25×0.24×0.06</td>
<td>0.20×0.25×0.04</td>
<td>0.23×0.17×0.10</td>
</tr>
<tr>
<td>Color, habit</td>
<td>Violet, plate</td>
<td>Violet, prism</td>
<td>Violet, plate</td>
<td>Violet, block</td>
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</table>
Table 2  Comparison of selected structural parameters for complexes 2, 5, 6, 8 and 10 (distances in Å, angles in °)\(^a\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Cp</th>
<th>Zr–Cp(_{\text{cent}})</th>
<th>Zr–CHT(_{\text{cent}})</th>
<th>CHT(<em>{\text{cent}})–Zr–Cp(</em>{\text{cent}})</th>
<th>(\alpha)</th>
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<tr>
<td>2</td>
<td>Cp(_{\text{Pent}})</td>
<td>2.191</td>
<td>1.673</td>
<td>172.03</td>
<td>8.36</td>
</tr>
<tr>
<td>3(^b)</td>
<td>Cp(_{\text{Hex}})</td>
<td>2.213</td>
<td>1.684</td>
<td>178.06</td>
<td>1.96</td>
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<tr>
<td>4(^b)</td>
<td>Cp(_{3})</td>
<td>2.205</td>
<td>1.679</td>
<td>174.20</td>
<td>6.51</td>
</tr>
<tr>
<td>5</td>
<td>Cp(_{\text{TMS}})</td>
<td>2.192</td>
<td>1.677</td>
<td>167.98</td>
<td>14.77</td>
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<tr>
<td>6</td>
<td>Cp(_{\text{BigC}})</td>
<td>2.187</td>
<td>1.673</td>
<td>176.75</td>
<td>5.67</td>
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<tr>
<td>7(^c)</td>
<td>Cp(_{1})</td>
<td>2.202</td>
<td>1.683</td>
<td>172.05</td>
<td>8.55</td>
</tr>
<tr>
<td>8(^c)</td>
<td>Cp(_{\text{TMS}})</td>
<td>2.220</td>
<td>1.666</td>
<td>178.90</td>
<td>1.32</td>
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<td>9(^c)</td>
<td>Cp(_{\text{BigC}})</td>
<td>2.233</td>
<td>1.679</td>
<td>179.43</td>
<td>0.62</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ind</th>
<th>Zr–Cp(_{\text{cent}})</th>
<th>Zr–CHT(_{\text{cent}})</th>
<th>CHT(<em>{\text{cent}})–Zr–Cp(</em>{\text{cent}})</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Ind(^d)</td>
<td>2.202</td>
<td>1.661</td>
<td>167.55</td>
<td>13.03</td>
</tr>
</tbody>
</table>

\(^a\) CHT = cycloheptatrienyl, \(\alpha\) = the angle between the two ligand planes. \(^b\) Data are based on the calculated structure.

Fig. 5  ORTEP plot of the molecular structure of 6. Atomic displacement parameters have been drawn at 50% probability. Selected bond length (Å) and angles (°): Zr–C1 2.356(3), Zr–C2 2.345(3), Zr–C3 2.322(3), Zr–C4 2.308(4), Zr–C8 2.488(3), Zr–C9 2.502(2), Zr–C10 2.5121(19), Zr–Cp\(_{\text{cent}}\) 2.187, Zr–CHT\(_{\text{cent}}\) 1.673, CHT\(_{\text{cent}}\)–Zr–Cp\(_{\text{cent}}\) 176.75.

Fig. 6  ORTEP plot of the calculated structure of 7. Calculated bond length (Å) and angles (°): Zr–C1 2.340, Zr–C2 2.349, Zr–C3 2.359, Zr–C4 2.366, Zr–C5 2.358, Zr–C6 2.346, Zr–C7 2.338, Zr–C16 2.518, Zr–C17 2.521, Zr–C18 2.515, Zr–C19 2.517, Zr–C20 2.506, Zr–Cp\(_{\text{cent}}\) 2.202, Zr–CHT\(_{\text{cent}}\) 1.683, CHT\(_{\text{cent}}\)–Zr–Cp\(_{\text{cent}}\) 172.05.

The reaction of sodium pentaphenylcyclopentadienide with 1,2,4-triisopropylcyclopentadienyl (3\(^c\)) as a purple oil, which is almost soluble in dichloromethane. 8 could be crystallized from saturated solutions in tetrahydrofuran by slow evaporation at ambient temperature. This result is interesting because the corresponding pentaisopropylcyclopentadienyl complex could not be obtained with lithium pentaisopropylcyclopentadienide. Another attempt at the synthesis of [(C\(_7\)H\(_8\)-H)\(_2\)] using potassium pentaisopropylcyclopentadienide was also unsuccessful. Thus, it can be supposed that the larger cone angle of the pentaisopropylcyclopentadienide is responsible for the failure of 1 to react, not the reactivity of the alkali cation (Fig. 7).

Through slow evaporation of a saturated THF solution of 8, crystals suitable for X-ray diffraction could be obtained.

During preparation and handling of pentaphenylcyclopentadiene (8-H)\(^{29}\) single crystals of this starting compound suitable for X-ray diffraction were obtained. The data for crystal structure determination were measured at room temperature and solved in \(P2_1/n\) with two independent molecules in the unit cell. In the literature\(^{29}\) there exists another structure of 1,2,3,4,5-pentaphenylcyclopentadiene with one independent molecule in a cell with almost the same cell constants \(b = 6.267(1)\) Å, \(c = 24.517(8)\) Å, \(\beta = 93.49(2)\)° as the structure deter-
indenyl ligand have been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previously, the corresponding mono(d–d) complex of the unsubstituted indenyl ligand has been investigated previous
Table 3 Measured cone angles (°)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\Theta)</th>
<th>(\Omega)</th>
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<tbody>
<tr>
<td>(C_6H_5)</td>
<td>88.2</td>
<td>0</td>
</tr>
<tr>
<td>(C_6H_5CH_3)</td>
<td>95.1</td>
<td>49.0</td>
</tr>
<tr>
<td>(C_6H_5Si(CH_3)_3)</td>
<td>104.3</td>
<td>95.6</td>
</tr>
<tr>
<td>(C_6H_5(\text{allyl}))</td>
<td>106.0</td>
<td>68.6</td>
</tr>
<tr>
<td>(Cp^*)</td>
<td>116.2</td>
<td>100.7</td>
</tr>
<tr>
<td>(Cp^\text{pent})</td>
<td>131.7</td>
<td>86.1</td>
</tr>
<tr>
<td>(Cp^\text{hex})</td>
<td>134.8</td>
<td>89.0</td>
</tr>
<tr>
<td>(Cp\text{″})</td>
<td>132.6</td>
<td>89.1</td>
</tr>
<tr>
<td>(Cp\text{″′})</td>
<td>132.0</td>
<td>99.8</td>
</tr>
<tr>
<td>(Cp^{\text{‡′}})</td>
<td>134.5/134.9</td>
<td>69.2/69.3</td>
</tr>
<tr>
<td>(\text{Cp}^\text{pr})</td>
<td>146.4</td>
<td>85.9</td>
</tr>
<tr>
<td>(\text{Cp}^\text{pp})</td>
<td>122.4</td>
<td>51.2</td>
</tr>
<tr>
<td>(Cp^{\text{TMS}})</td>
<td>150.4</td>
<td>75.0</td>
</tr>
<tr>
<td>(Cp^{\text{pent}})</td>
<td>150.2</td>
<td>75.9</td>
</tr>
<tr>
<td>(Cp^{\text{hex}})</td>
<td>157.4</td>
<td>98.9</td>
</tr>
<tr>
<td>(Cp^{\text{Bisic}})</td>
<td>163.8</td>
<td>104.7</td>
</tr>
<tr>
<td>(\text{Cp}^{\text{Hg}})</td>
<td>167.4</td>
<td>88.6</td>
</tr>
</tbody>
</table>

Complex: \(e\) \(C_6H_5\) \(Cp\) \(Cp^*\) \(Cp\text{″}\) \(Cp\text{″′}\) \(Cp^{\text{‡′}}\) \(\text{Cp}^\text{pr}\) \(\text{Cp}^\text{pp}\) \(Cp^{\text{TMS}}\) \(Cp^{\text{pent}}\) \(Cp^{\text{hex}}\) \(Cp^{\text{Bisic}}\)

Indenyl: \(\text{Ind}\) \(\text{Ind}^\text{"}\) \(\text{Ind}^{\text{"′}}\) \(\text{Ind}^\text{pr}\) \(\text{Ind}^\text{pp}\) \(\text{Ind}^{\text{TMS}}\) \(\text{Ind}^{\text{pent}}\) \(\text{Ind}^{\text{hex}}\) \(\text{Ind}^{\text{Bisic}}\)

\(\theta\) and \(\Omega\) are calculated according to the equations \(\theta = (\theta_1 + \theta_2 + \theta_3 + \theta_4 + \theta_5 + \theta_6 + \theta_7) \times 2/7\) for the \(C_6H_5\) and \(Cp\) groups, respectively. The \(\text{Ind}^{\text{pr}}\) value is approximated as see ref. 22 for details. Data are based on the calculated structure.

an almost identical, but slightly smaller cone angle \(\Theta\) of 131.7° vs. 132.6°. This tendency is more pronounced, when the cone angles of one isopropyl group \(\Omega\) (89.1°) and the cyclopentyl group (86.1°) at the cyclopentadienyl ligand are compared. The reason for the slight appearance of the cyclopentyl group is ring strain visible in the smaller \(\Theta\) – \(\text{C}^\beta – \text{C}^\beta\) angles of the cyclopentadienyl substituent (typically between 101.5° and 102.5° in complex 2) compared to the same angle for the isopropyl substituents of complexes 5 and 6 (between 110.5° and 111.5°). The cone angle \(\Theta\) of the tricyclohexylcyclopentadienyl ligand (134.8°) is larger than that of the tricyclohexyleclopentadienyl ligand (131.7°) and even slightly larger than that of the trisopropylcyclopentadienyl ligand (132.6°). For the \(3\text{Cp}\) ligand, the cone angle \(\Theta\) is comparable even to \(Cp^{\text{TMS}}\) (Table 3), but the ring tilt in 5 is larger than that in the tris(secondary alkyl)cyclopentadienyl complexes 2–4 (Table 2) because the steric bulk of the \(3\text{Cp}\) ligand is concentrated on one edge of the five-membered ring and rather small on the other side of the ring.

The calculated cone angle \(\Theta\) of the \(3\text{Cp}\) ligand (150.2°) is practically identical to that of \(2\text{Cp}^{\text{TMS}}\) (150.3°).

The cone angle \(\Theta\) of 167.4° for the pentaisopropylcyclopentadienyl ligand is significantly larger than the 157.4° angle for the pentaphenyleclopentadienide. This could be an explanation for the failure of 1 to react; another alkali cation does not make a difference.

The calculated cone angle \(\Theta\) (163.8°) of the monobutyl derivative of pentaphenyleclopentadienide (\(Cp^{\text{Bisic}}\)) is significantly larger than the value found for the pentaphenyl derivative 8 (157.4°), which is due to the conformation of the ligand and varies with the rotational orientation of the phenyl ring planes relative to the cyclopentadienyl plane. This cone angle should be viewed with caution. There is no obvious reason why one butyl group in the para position should significantly increase the steric bulk the pentaphenyleclopentadienyl ligand presents to the central atom. The cone angle \(\Theta\) of the 1-tert-butylindenyl ligand was determined to be 119° and is in the expected range between indenyl (102.6°) and 1,3-di(tert-butyl)indenyl (ca. 131°, see Table 3).

Comparison of the values for the cyclopentadienyl ligands listed in the table above results in the following order of bulk:

\[ C_6H_5 < C_6H_5CH_3 < C_6H_7 < C_6H_5Si(CH_3)_3 < C_6H_5(\text{allyl}) < C_6H_5(<\text{Ind}^\text{pr}) < C_6H_5(<\text{Cp}^{\text{TMS}}) < C_6H_5(<\text{Cp}^{\text{pent}}) < C_6H_5(<\text{Cp}^{\text{hex}}) < C_6H_5(<\text{Ind}^{\text{Bisic}}) < C_6H_5(<\text{Cp}^{\text{Bisic}}) < 2\text{Cp} \]

If the cone angle of the cycloheptatrienyl ligand is calculated according to the equation \(\Theta = (\theta_1 + \theta_2 + \theta_3 + \theta_4 + \theta_5 + \theta_6 + \theta_7) \times 2/7\), values of 117°–118° are obtained, which place the steric demand of the CHT ligand between those of 1,3-di(tert-butyl)cyclopentadienyl and 1-tert-butylidenyl ligands.

Conclusion

The cycloheptatrienyliumzirconium fragment accommodates cyclopentadienyl ligands as bulky as tetraisopropylcyclopentadienyl or pentaarylcyclopentadienyl without steric interactions with the cycloheptatrienyl ligand. Up to now sixteen derivatives of the \([\text{CHT}^\text{i}Zr(Cp)\text{]}\) type with different cyclopentadienyl or indenyl ligands coordinated to the cycloheptatrienylium
fragment crystal structures have been obtained and used for data compilation.

The cone angle $\theta$ of the substituted cyclopentadienyl ligand alone in some cases leads to unrealistic conclusions. Tetraisopropylcyclopentadienide, for instance, is bulkier than trisisopropyl-dimethylcyclopentadienide, but the cone angles are reverted. Similarly, diisopropyl-dimethylcyclopentadienide, trisopropylcyclopentadienide, and tri(tert-butyl)cyclopentadienide exhibit very similar cone angles $\theta$ for the ligand, but the cone angles $\Omega$ of the substituents are different. It is therefore necessary to take both values into account when comparing different cyclopentadienyl derivatives. The cone angles found experimentally for the pentaphenylcyclopentadienyl (ECP) ligand and by DFT calculations for its close relative CpBIC with just one $n$-butyl group added in the para position of one phenyl ring differing by ca. 6° are due to different torsion angles of the substituents. This discrepancy may arise from crystal packing forces or may be sensitive to the basis sets used for the calculations.

**Experimental section**

**General**

All preparations and spectroscopic manipulations of air and moisture sensitive compounds were carried out under an atmosphere of nitrogen or argon, using Schlenk line techniques and a glove box (MBraun company, Garching) filled with argon. Solvents were rigorously dried and deoxygenated with argon. Solvents were rigorously dried and deoxygenated in vacuo with pentane (200 mL) and dried in vacuo to yield an ivory solid. Yield: 20.5 g (70.1 mmol, 46%). GC of a hydrolyzed sample: $t_R = 13.2$ min.

**HCP$_2$(2-H).** To a mechanically stirred mixture of an aqueous 50% KOH solution (211 g KOH in 210 mL water) with the quaternary ammonium salt Adogen 464 (3.0 g) and freshly cracked cyclopentadiene (10.0 g, 12.5 mL, 151 mmol) bromocyclopentane (47.0 g, 3.0 mL, 315 mmol) was added dropwise via a dropping funnel. The temperature rose to about 55 °C and the reaction mixture turned brown. After 1 h, more bromocyclopentane (23.0 g, 16.5 mL, 154 mmol) was added dropwise. The mixture was stirred for 18 h at 60 °C and allowed to cool to room temperature. The organic phase was separated and the aqueous phase was extracted twice with petroleum ether (100 mL each). The organic extracts were combined and reduced to an oily residue on a rotary evaporator at 10 mbar and 30 °C. Vacuum distillation of the oily residue at 10$^{-2}$ mbar yielded a yellow oil as the main fraction, which consisted of a mixture of tri(cyclopentyl)cyclopentadiene isomers (30.4 g, 113 mmol, 74%). GC: $t_R = 12.6-13.9$ min.

**NaCp$_2$(2-Na).** Sodium amide (6.0 g, 154 mmol) and tri(cyclopentyl)cyclopentadiene isomers (2-H) (30.0 g, 111 mmol) were refluxed in THF (250 mL) for 70 h under gas evolution. During the reaction, the mixture turned brown and a beige precipitate could be observed. The mixture was filtered hot to remove remaining sodium amide. Volatile components were removed in vacuo and the remaining precipitate was washed with pentane (200 mL) and dried in vacuo to yield an ivory solid. Yield: 20.5 g (70.1 mmol, 46%). GC of a hydrolyzed sample: $t_R = 13.2$ min.

**H$_2$Cp$_{2}$TMS (6-H).** NaCp$_2$ (601 mg, 3.0 mmol) was dissolved in THF (15 mL) and chlorotrimethylsilane (391 µL, 332 mg, 3.06 mmol) was added slowly at room temperature. The colorless suspension was stirred for 24 h at room temperature. The pale yellow solution was decanted from insoluble solids and concentrated in vacuo to a yellow oil. Yield: 457 mg (1.82 mmol, 61%). GC-MS: $t_R = 16.1$ min ($m/z = 250$).

**K$_2$Cp$_{2}$TMS (6-K).** To a solution of H$_2$Cp$_{2}$TMS (6-H) (752 mg, 3.0 mmol) in THF (15 mL) potassium hydride (120 mg, 3.0 mmol) was added at room temperature. The reaction mixture was stirred for 3 d at room temperature resulting in a colourless precipitate. The solvent was removed in a vacuum and the solid was washed with pentane (2 × 20 mL) to yield a pale beige potassium salt. Yield: 670 mg (2.32 mmol, 77%). GC: $t_R = 8.0$ min.

**Synthetic work**

For the DFT calculations of the zirconium complexes a B3LYP functional of the Gaussian09, Revision C.01$^{34}$ was used. A triple zeta basis (6-311G**$^{35}$) for the main group elements (C, H) was combined with a double zeta basis (Stuttgart RSC 1997 ECP)$^{36}$ for zirconium, which also includes the effective core potential.
The reaction mixture changed colour from grey to green and was allowed to warm up to room temperature in 80 minutes. Stirring was continued for 3 hours. The solvent was removed in vacuo, yielding a purple solid. Analytically pure samples could be obtained by crystallization from a concentrated pentane solution at −30 °C or sublimation in a sealed glass tube at 10−3 mbar at 120 °C. Yield: 163 mg (0.45 mmol, 76%).

1H-NMR (400 MHz, C6D6, 298 K): δ 5.22 (s, 7H, C7H7), 5.14 (s, 1H, CpH), 2.66 (sept, 2H, 3J = 7.2 Hz, CH, isopropyl), 1.89 (s, 6H, CH2). 13C{1H}-NMR (151 MHz, C6D6, 298 K): δ 126.1 (Cq, Cp-iso-propyl), 112.0 (Cq, Cp-methyl), 106.0 (CH, 3J), 81.9 (C(−3)H), 26.5 (CH, isopropyl), 24.2 (CH3, iso-propyl), 24.1 (CH3, iso-propyl), 14.6 (CH3). Anal. Caled for C20H28Zr (359.70): C, 66.78; H, 7.86. Found: C, 65.93; H, 7.71.

[(η5-C5H5)Zr(η5-2CpTMS)] (6). K3CpTMS (6-K) (173 mg, 0.60 mmol) was suspended in THF (15 mL) and cooled to −78 °C in a Schlenk flask. A blue solution of [η5-C5H5-ZrCl(tmeda)] (1) (200 mg, 0.60 mmol) in THF (15 mL) was added slowly with a syringe. After addition, the reaction mixture turned purple immediately and was allowed to warm up to room temperature, which took 30 min. Stirring was continued for 1 h at room temperature. The solvent was removed in a vacuum and the resulting purple solid was extracted with pentane (50 mL). An insoluble precipitate was removed by centrifugation. Solvent removal in vacuo yielded a purple solid. Analytically pure samples could be obtained by crystallization from a concentrated pentane solution at −30 °C or sublimation in a sealed glass tube at 10−3 mbar at 120 °C. Yield: 163 mg (0.45 mmol, 76%).

1H-NMR (400 MHz, C6D6, 298 K): δ 5.22 (s, 7H, C7H7), 5.14 (s, 1H, CpH), 2.66 (sept, 2H, 3J = 7.2 Hz, CH, isopropyl), 1.89 (s, 6H, CH2). 13C{1H}-NMR (151 MHz, C6D6, 298 K): δ 126.1 (Cq, Cp-iso-propyl), 112.0 (Cq, Cp-methyl), 106.0 (CH, 3J), 81.9 (C(−3)H), 26.5 (CH, isopropyl), 24.2 (CH3, iso-propyl), 24.1 (CH3, iso-propyl), 14.6 (CH3). Anal. Caled for C20H28Zr (359.70): C, 66.78; H, 7.86. Found: C, 65.93; H, 7.71.

[(η5-C5H5)Zr(η5-2CpTMS)] (6). K3CpTMS (6-K) (173 mg, 0.60 mmol) was suspended in THF (15 mL) and cooled to −78 °C in a Schlenk flask. A blue solution of [η5-C5H5-ZrCl(tmeda)] (1) (200 mg, 0.60 mmol) in THF (15 mL) was added slowly with a syringe. After addition, the reaction mixture turned purple immediately and was allowed to warm up to room temperature, which took 30 min. Stirring was continued for 1 h at room temperature. The solvent was removed in a vacuum and the resulting purple solid was extracted with pentane (50 mL). An insoluble precipitate was removed by centrifugation. Solvent removal in vacuo yielded a purple solid. Analytically pure samples could be obtained by crystallization from a concentrated pentane solution at −30 °C or sublimation in a sealed glass tube at 10−3 mbar at 120 °C. Yield: 163 mg (0.45 mmol, 76%).

1H-NMR (400 MHz, C6D6, 298 K): δ 5.22 (s, 7H, C7H7), 5.14 (s, 1H, CpH), 2.66 (sept, 2H, 3J = 7.2 Hz, CH, isopropyl), 1.89 (s, 6H, CH2). 13C{1H}-NMR (151 MHz, C6D6, 298 K): δ 126.1 (Cq, Cp-iso-propyl), 112.0 (Cq, Cp-methyl), 106.0 (CH, 3J), 81.9 (C(−3)H), 26.5 (CH, isopropyl), 24.2 (CH3, iso-propyl), 24.1 (CH3, iso-propyl), 14.6 (CH3). Anal. Caled for C20H28Zr (359.70): C, 66.78; H, 7.86. Found: C, 65.93; H, 7.71.

[(η5-C5H5)Zr(η5-2CpTMS)] (6). K3CpTMS (6-K) (173 mg, 0.60 mmol) was suspended in THF (15 mL) and cooled to −78 °C in a Schlenk flask. A blue solution of [η5-C5H5-ZrCl(tmeda)] (1) (200 mg, 0.60 mmol) in THF (15 mL) was added slowly with a syringe. After addition, the reaction mixture turned purple immediately and was allowed to warm up to room temperature, which took 30 min. Stirring was continued for 1 h at room temperature. The solvent was removed in a vacuum and the resulting purple solid was extracted with pentane (50 mL). An insoluble precipitate was removed by centrifugation. Solvent removal in vacuo yielded a purple solid. Analytically pure samples could be obtained by crystallization from a concentrated pentane solution at −30 °C or sublimation in a sealed glass tube at 10−3 mbar at 120 °C. Yield: 163 mg (0.45 mmol, 76%).
CH, isopropyl), 1.96 (s, 6H, CH₃, methyl), 1.24 (d, 6H, J = 7.2 Hz, CH₃, isopropyl), 1.18 (d, 6H, J = 7.1 Hz, CH₃, isopropyl), 1.14 (d, 6H, J = 7.2 Hz, CH₃, isopropyl). ¹³C(¹H)-NMR (151 MHz, CD₂O, 298 K): δ 126.5 (Cq, 3Cp), 125.5 (Cq, 3Cp), 111.7 (Cq, 3Cp), 82.1 (C-H), 27.7 (CH, isopropyl), 26.4 (CH, isopropyl), 24.6 (CH₃, isopropyl), 24.2 (CH, isopropyl), 24.1 (CH₂, isopropyl), 12.5 (CH₃, methyl). Anal. calc'd for C₂₃H₃₄Zr (353.64): C, 67.92; H, 6.28. Found: C, 67.13; H, 6.43.

[(η⁵-C₅H₅)Zr(η⁵-C₅Ph)][₈]. To a solution of [(η⁵-C₅H₅)Zr(Cl)[tmeda]] (1) (206 mg, 0.62 mmol) in THF (20 mL) cooled to −78 °C a solution of NaCpBIG (303 mg, 0.65 mmol) in THF (50 mL) was added dropwise over a period of 10 min. The mixture was allowed to thaw to room temperature. Stirring was continued for 2 h, while the colour of the solution turned purple. After removal of solvents by filtration the solvent was evaporated and the residue was washed twice with small amounts of THF. Drying in vacuo afforded 179 mg (0.29 mmol, 46%) of a purple solid.

¹H-NMR (300 MHz, THF-d₈, 297 K): δ 7.26–6.97 (m, 25H, Ph), 5.41 (s, 7H, C-H,₇). ¹³C(¹H)-NMR (151 MHz, THF-d₈, 297 K): δ 135.5 (ipso-C₆H₅), 133.1 (mio-C₅Ph), 128.2 (o/m-C₆H₅), 127.3 (p-C₆H₅), 122.9 (Cp), 86.3 (C-H,₃). MS (EI, 70 eV); m/z 626.1 (M⁺, 100). HR-MS (EI, m/z): calcd for C₃₆H₄₀Zr (577.29): C, 66.43; δ 7.14 (CH₃, isopropyl), 6.78–6.74 (m, 2H, H₅, H₆, Ind'), 5.70 (dd, 1H, J = 3.7 Hz, J = 0.8 Hz, H₃, Ind'), 5.50 (d, 1H, J = 3.7 Hz, H₂, Ind'), 5.01 (s, 7H, C-H,₇), 1.25 (s, 9H, CH₃, tert-butyl). ¹³C(¹H)-NMR (151 MHz, CD₂O, 298 K): δ 124.0 (CH, Ind'), 123.0 (Cq, Ind'), 122.8 (CH, Ind'), 122.4 (Cq, Ind'), 122.1 (CH, Ind'), 121.8 (CH, Ind'), 119.2 (Cq, Ind'), 105.6 (C₃, Ind'), 90.2 (C₂, Ind'), 83.4 (C-H,₇), 32.9 (Cq, tert-butyl), 32.0 (CH₃, tert-butyl). Anal. calcd for C₉₀H₁₂₂Zr (353.64): C, 67.92; H, 6.28. Found: C, 67.13; H, 6.26.

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Notes and references


11 Literature search was carried out in August 2013, only compounds with experimental properties have been counted.

12 C. A. Tolman, Chem. Rev., 1977, 77, 313–348. This article received more than 3700 citations, is still earning more than one hundred citations per year and has been referred to in many textbooks on inorganic chemistry.


