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Torsional isomerism of bent metallocene complexes. The structures of *meso*- and *rac*-bis(1-cyclohexyltetrahydroindenyl)zirconium dichloride in the solid state

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Abstract

Two molar equivalents of 1-cyclohexylindenyllithium were treated with $ZrCl_4(thf)_2$ to give a *ca.* 1:1 mixture of *meso*- and *rac*-bis(1-cyclohexylindenyl)$ZrCl_2$ (*meso-/rac*-**4**). Catalytic hydrogenation yielded a corresponding mixture of the bis(1-cyclohexyl-4,5,6,7-tetrahydroindenyl)$ZrCl_2$ diastereoisomers *meso*-**5** and *rac*-**5**. In both cases the diastereomers were separated by fractional crystallization. Complexes *meso*- and *rac*-**5** were characterized by an X-ray crystal structure study. In the crystal the molecular structure of complex *rac*-**5** is C_2-symmetric, with the annulated six-membered ring systems arranged towards the open front side of the bent metallocene wedge and the cyclohexyl substituents oriented *anti*-periplanarly in the lateral sectors. In contrast complex *meso*-**5** has only one of the cyclohexyltetrahydroindenyl ligands arranged in this way, the cyclohexyl substituent of the other one pointing towards a central front position and the annulated six-membered ring being situated in the lateral position (C_1-symmetry).

1. Introduction

Bent metallocene complexes of the early transition metals usually display very low torsional activation barriers for the Cp–M moieties. Thus the interconversions of the rotameric forms of, for example, mono-Cp-substituted $(RCp)_2MX_2$ systems are usually fast in solution but molecular structures corresponding to the favoured local conformational minima may be frozen out in the crystal and hence be observed experimentally by X-ray diffraction [1].

Bent metallocene complexes bearing two mono-alkyl-substituted η^5-cyclopentadiene ring systems are known to exhibit torsional isomerism in the solid state, the isomers having idealized geometries with (a) both R-groups oriented either towards the open side of the bent metallocene wedge (bis-central: *syn* orientation, **A**), or both R-groups oriented towards the lateral sectors (bis-lateral: *anti* orientation, **B**), or (b) one R-group oriented centrally in the front and the other laterally (lateral/central: *gauche*-like orientation, **C**). The **A**-type conformer is favoured for small primary alkyl substituents (methyl, benzyl) [2], whereas the **B**-type arrangement is found when bulky tert-alkyl groups are attached to the Cp-rings [3]. Secondary alkyl substituents seem to allow all three conformational substituent positions. There is even one example, namely bis(isopropylcyclopentadienyl)zirconium dichloride, for which all three torsional isomers were observed to be present in a single crystal and characterized by an X-ray diffraction study [4].

A similar overall conformational situation should apply to pseudotetrahedral bis(indenyl)metaldihalide or bis(tetrahydroindenyl)MX_2 systems. An *a priori* analysis predicts the possible existence of three tor-

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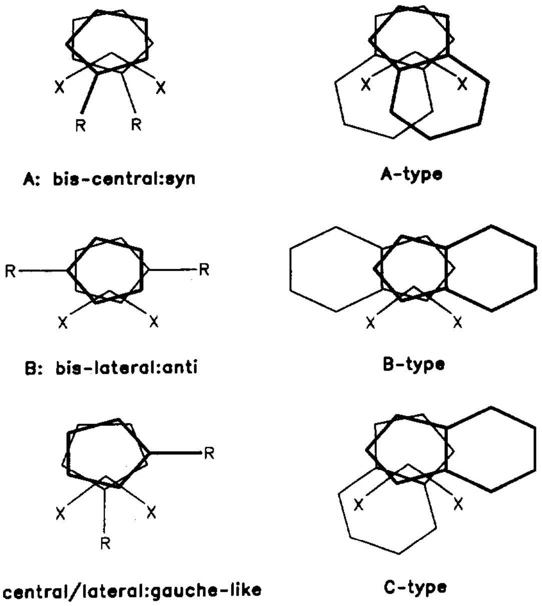
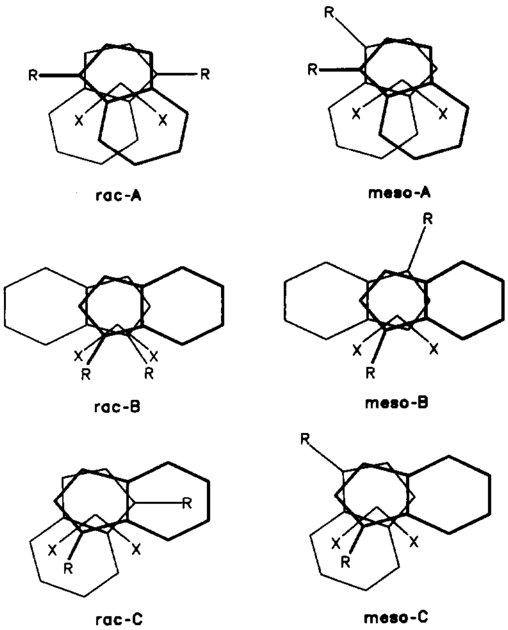
sional isomers that are very similar to the bis-central: *syn*-, bis-lateral: *anti*-, and lateral/central: *gauche*-type $(RCp)_2MX_2$-structures **A**, **B**, and **C**. There is expected to be an **A**-type conformer having both annulated six-membered rings oriented towards the open front side of the bent metallocene wedge and a **B**-type rotational isomer having the annulated rings pointed towards the lateral positions. The series should be completed by a third local minimum on the torsional hypersurface which has one of the six-membered rings pointing to a central position with the other annulated ring oriented laterally. We thus expect an equilibrium system of three conformational isomers of which two have C_2-symmetry and the remaining one being less symmetric (C_1), as found for the $(RCp)_2MX_2$ systems (see Scheme 1).

The situation becomes more complicated when a substitutent R is placed in the 1-position at the five-membered ring of each of the indenyl or tetrahydroindenyl ligands. Now the substituted ligand system is prochiral, and attachment of the metal can occur from either enantiotopic face of the five-membered ring system. Attaching two of such monosubstituted indenyl (or tetrahydroindenyl) ligands to the early transition metal centre gives rise to two diastereomeric bent metallocene complexes. The conformational analysis indicated above has to be applied to each diastereomer, *i.e.* to the complexes belonging to the *rac*- or *meso*-series.



Scheme 1.



Scheme 2.

The conformational analysis suggests the possible existence of a total of six different torsional isomers, three of which belong to the *rac*- and three to the *meso*-series. Their idealized structures are depicted in Scheme 2. The presence of the additional alkyl groups at the **A**, **B**, and **C**-type bis(indenyl)MX_2 or bis(tetrahydroindenyl)MX_2 complexes does not appear to impose any additional steric constraints on the *rac*-series; the R-groups can be conveniently located in the bis-lateral: *anti* orientation in *rac*-**A** and in the bis-central: *syn* position in the rac-**B** conformer. The central/lateral orientation of the R-substituent that gives rise to the *rac*-**C** torsional isomer likewise appears not to present steric problems.

This is probably also true for the central/lateral: *gauche*-type orientation of the R-groups in the corresponding diastereomeric *meso*-**C** torsional isomer. In contrast, in the remaining conformers of the *meso*-series the R-groups lie in sterically unfavourable positions. Thus one of the attached R-substituents of the *meso*-**B** conformer has to be placed at the narrow side of the bent metallocene wedge. In *meso*-**A** both R-groups are brought into close contact since they both occupy the same lateral sector at the bent metallocene framework.

We wished to confirm this qualitative conformational analysis experimentally, and for this purpose we prepared the *meso*- and *rac*-diastereomers of bis(indenyl)- and bis(tetrahydroindenyl)zirconium dichloride and carried out X-ray crystal structure analyses of the latter two complexes. As expected these turn out to belong to different conformational types.

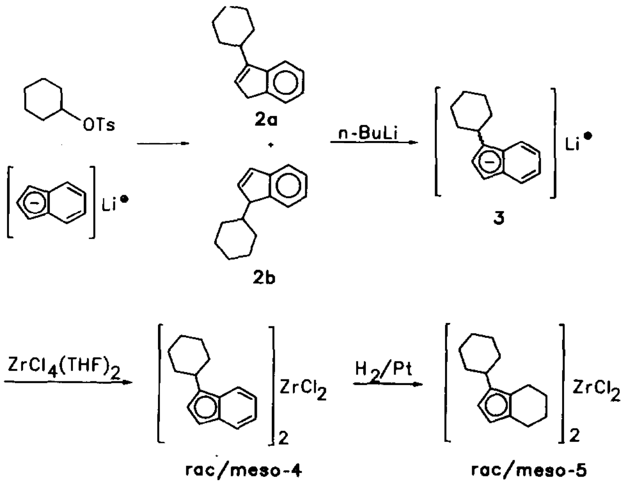
2. Results and discussion

We prepared the bis(1-cyclohexylindenyl)zirconocene dichloride isomers (*rac*-**4**, *meso*-**4**) by the following route. Cyclohexyl tosylate (**1**) was treated with one molar equivalent of indenyllithium in tetrahydrofuran. Distillation gave a 40% yield of a 60:40 mixture of 1-cyclohexylindene (**2b**) and 3-cyclohexylindene (**2a**). The **2a**/**2b** mixture was then treated with n-butyllithium in ether/hexane to give 1-(cyclohexyl)indenyllithium (**3**) (characterized by ^{1}H and ^{13}C NMR spectroscopy at ambient temperature, see Experimental section). The lithium reagent **3** was then treated with $ZrCl_4(thf)_2$ in a 2:1 molar ratio to give a *ca.* 1:1 mixture of the metallocene diastereoisomers *rac*-**4** and *meso*-**4**. The bis(1-cyclohexylindenyl)$ZrCl_2$ mixture of isomers was then subjected to catalytic hydrogenation [5] (PtO_2, H_2-pressure: 60 bar) to afford the corresponding mixture of the bis(1-cyclohexyl-4,5,6,7-tetrahydroindenyl)$ZrCl_2$ isomers *rac*-**5** and *meso*-**5**.

Fractional crystallization from methylene chloride gave *rac*-**4** and *meso*-**4** each in > 96% diastereomeric purity. Due to their averaged overall molecular symmetry in solution (*rac*-**4**: C_2; *meso*-**4**: C_s) each of these complexes contains a pair of symmetry-equivalent 1-cyclohexylindenyl ligands. For the two diastereomeric complexes these give rise to two sets of NMR resonances which of course differ from each other but which are of the same general spectroscopic type and appearance. Thus one complex exhibits an AX-type pattern for the 2-H and 3-H methylene protons at the five-membered ring system at δ 6.30 and 5.81 (in $CDCl_3$ solution), whereas the other isomer shows corresponding 2-H, 3-H AX-pattern at δ 5.90 and 5.83. We tentatively assigned the former as *meso*-**4** and the latter as *rac*-**4** [6*].

The *rac*- and *meso*-**5** diastereomers were also separated by fractional crystallization from CH_2Cl_2 and characterized spectroscopically (see Experimental section). For both diastereomers single crystals suitable for X-ray diffraction studies were obtained. Thus the absolute diastereomeric assignments of the complexes *rac*- and *meso*-bis(1-cyclohexyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride were achieved by X-ray crystallography, and their preferred conformations in the solid state were determined.

In the crystal complex *rac*-**5** shows a pseudotetrahedral coordination geometry around zirconium. Two chloride ligands (*d* Zr–Cl = 2.443(1) Å) and two cyclohexyl-substituted η^5-tetrahydroindenyl ligands are bonded to the central metal centre, which is situated on a twofold rotational axis. The Cl–Zr–Cl* angle is 95.8(1)°. The "bite angle" of the bent metallocene (D–Zr–D*, where D and D* denote the centroids of the symmetry-equivalent η^5-coordinated Cp-structural subunits of the tetrahydroindenyl ring systems) is 130.8°. Such a value is typical for non-bridged Group 4 metallocenes [7]. The angle is larger by *ca.* 5° than those in the ethylene-bridged ansa-metallocene complexes of zirconium [*e.g.* ethylene-bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride [8] has a D–Zr–D* angle of 125.2(1)°, and the Cl–Zr–Cl* angle is 98.58(2)°].



Scheme 3.

The cyclohexyl-substituents in *rac*-**5** adopt a chair conformation, with the tetrahydroindenyl five-membered ring system bonded in an equatorial position. The angle between the mean planes of the Cp-framework and the adjacent cyclohexyl substituent sums to

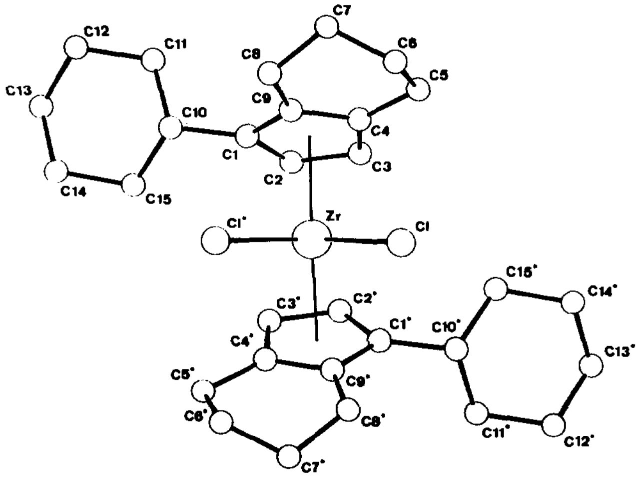


Fig. 1. View of molecular structure of complex *rac*-**5** (with non-systematic numbering scheme).

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* Reference number with an asterisk indicates a note in the list of references.

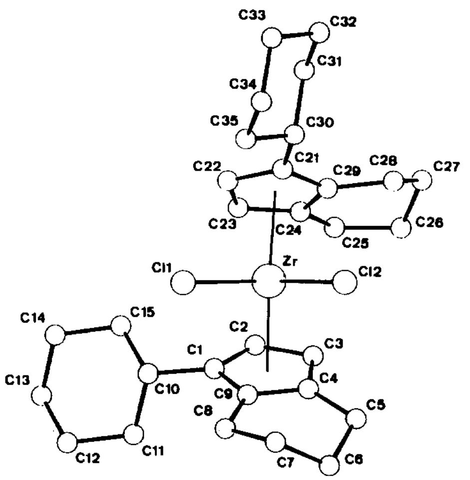

Fig. 2. View of the molecular structure of complex *meso*-**5** (with non-systematic numbering scheme).

69°. The annulated six-membered rings of the tetrahydroindenyl ligands adopt a twist conformation. The arrangement of these ring systems is influenced by the bulky chloride ligands. The sp^3-carbon atoms C5–C8 are pushed away from the halide atoms and are therefore located outside the cyclopentadienyl mean plane (C5: +0.196; C6: +0.052; C7: +0.656; C8: +0.059 Å).

Both annulated six-membered ring systems are oriented C_2-symmetrically towards the open front section of the bent metallocene wedge. In the projection (see Fig. 3) the annulated rings can be seen effectively to shield the chloride ligands from one enantiotopic face. Carbon atom C6 is seen to be almost eclipsed with respect to the Cl-atom in this view (the C8–D–D*–C8* dihedral angle characterizing this conformational situation at the bent metallocene is −31.8°). Consequently the cyclohexyl substituents lie in the lateral positions of the bent metallocene wedge (bis-lateral: *anti* orientation). The corresponding C10–D–D*–C10* dihedral angle is 179.1°. Thus complex *rac*-**5** adopts one of the three conformations that were suggested to correspond to energetically favourable situations in the *a priori* assessment. In the crystal the bis(1-cyclohexyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride complex *rac*-**5** exhibits a C_2-symmetric molecular geometry that comes close to the idealized conformational bent metallocene structure *rac*-**A** depicted in Scheme 2.

In *meso*-**5** the zirconium centre is again pseudotetrahedrally coordinated. The Zr–Cl1 and Zr–Cl2 distances are 2.444(1) and 2.432(1) Å. The Cl1–Zr–Cl2 angle in *meso*-**5** is 97.2(1)° and the D1–Zr–D2 angle 130.5°. The cyclohexyl substituents adopt a chair conformation. The overall geometry of each of the tetrahydroindenyl ligands in *meso*-**5** is very similar to that in *rac*-**5** (twist conformation of the annulated six-membered rings of the C1–C9 and C21–C29 frameworks).

TABLE 1. Selected bond lengths and angles in *rac*-**5**

Zr–D(1)	2.228	Zr–Cl	2.443(1)
Zr–C(1)	2.554(2)	Zr–C(2)	2.466(2)
Zr–C(3)	2.462(2)	Zr–C(4)	2.583(2)
Zr–C(9)	2.599(2)	C(1)–C(2)	1.420(3)
C(1)–C(9)	1.429(3)	C(1)–C(10)	1.506(3)
C(4)–C(5)	1.509(3)	C(4)–C(9)	1.408(3)
C(8)–C(9)	1.503(3)	C(10)–C(11)	1.536(3)
C(10)–C(15)	1.527(3)		
D(1)* –Zr–D(1)	130.8(1)	D(1)–Zr–Cl	107.6(1)
C(1)–Zr–Cl	127.5(1)	C(10)–C(1)–C(9)	125.8(2)
C(10)–C(1)–C(2)	127.1(2)	C(9)–C(4)–C(5)	122.6(2)
C(9)–C(4)–C(3)	107.9(2)	C(8)–C(9)–C(1)	127.9(2)
C(4)–C(9)–C(1)	108.9(2)	C(15)–C(10)–C(11)	110.0(2)
C(15)–C(10)–C(1)	114.5(2)	C(11)–C(10)–C(1)	109.1(2)

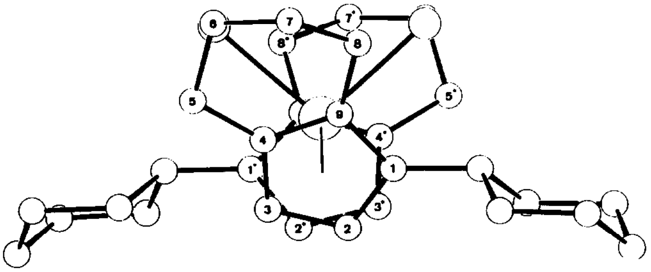

Fig. 3. A projection of the molecular geometry (top view) of complex *rac*-**5**.

TABLE 2. Positional parameters for *rac*-**5**

Atom	*x*	*y*	*z*
Zr	0.7500	1.0300(1)	0.7500
D(1)	0.9246	1.1675	0.7195
Cl	0.6720(1)	0.7872(1)	0.6610(1)
C(1)	0.9763(2)	1.1619(3)	0.7794(1)
C(2)	0.8954(2)	1.3142(3)	0.7483(1)
C(3)	0.8539(2)	1.2624(3)	0.6782(1)
C(4)	0.9126(2)	1.0816(3)	0.6646(1)
C(5)	0.9148(2)	0.9773(4)	0.5961(1)
C(6)	0.9805(3)	0.7765(5)	0.6059(2)
C(7)	1.0949(3)	0.7724(5)	0.6601(2)
C(8)	1.0645(2)	0.8323(3)	0.7315(1)
C(9)	0.9848(2)	1.0170(3)	0.7267(1)
C(10)	1.0538(2)	1.1645(3)	0.8504(1)
C(11)	1.1795(2)	1.2733(4)	0.8465(1)
C(12)	1.2631(2)	1.2840(4)	0.9167(1)
C(13)	1.1933(2)	1.3751(4)	0.9714(1)
C(14)	1.0726(2)	1.2618(4)	0.9767(1)
C(15)	0.9862(2)	1.2560(4)	0.9071(1)

The structures of *rac*-**5** and *meso*-**5** are characteristically different in respect of the relative arrangement of the substituted tetrahydroindenyl ligand systems. In complex *meso*-**5** these ligands are not symmetry equivalent. One of the ligand systems is arranged in such a way that the annulated six-membered ring is positioned towards the front of the bent metallocene wedge whereas its cyclohexyl substituent is oriented in a lateral sector. In contrast, the cyclohexyl group of the other R–C_9H_{10} system points towards the open front section. This ligand thus has its annulated six-membered ring system placed in the lateral sector of the bent metallocene, opposite to that occupied by the R-group of the other R–C_9H_{10} ligand. The C9–D1–D2–C29 dihedral angle is 105.1°. The molecular structure of meso-**5** in the crystal exhibits a C_1-conformation very close to the idealized geometry *meso*-**C** shown in Scheme 2.

We conclude that planarly chiral bent metallocene complexes derived from the bis(indenyl)MX_2 series tend to adopt characteristic conformational orientations. These show similarities to the well established conformational isomers observed for the monosubstituted bent metallocene complexes $(RCp)_2MX_2$. Which of the bis(1-sec-alkyl-4,5,6,7-tetrahydroindenyl)$ZrCl_2$ conformers is favoured in the solid state seems to be determined at least in part by the averaged overall molecular symmetries of the systems concerned, *i.e.* it depends on whether the particular complex belongs to the *rac*- or *meso*-diastereomeric series.

TABLE 3. Selected bond lengths and angles in *meso*-**5**

Zr–D(1)	2.233	Zr–D(2)	2.229
Zr–Cl(1)	2.444(1)	Zr–Cl(2)	2.432(1)
C(1)–C(2)	1.407(1)	C(1)–C(9)	1.429(1)
C(1)–C(10)	1.508(1)	C(3)–C(4)	1.405(1)
C(4)–C(5)	1.509(2)	C(4)–C(9)	1.411(1)
C(8)–C(9)	1.500(1)	C(10)–C(11)	1.537(2)
C(10)–C(15)	1.518(2)	C(21)–C(22)	1.408(1)
C(21)–C(29)	1.420(1)	C(21)–C(30)	1.512(1)
C(23)–C(24)	1.418(1)	C(24)–C(25)	1.510(1)
C(24)–C(29)	1.407(1)	C(28)–C(29)	1.509(1)
C(30)–C(31)	1.524(2)	C(30)–C(35)	1.525(2)
D(2)–Zr–D(1)	130.5(1)	Cl(2)–Zr–Cl(1)	97.2(1)
C(10)–C(1)–C(9)	125.2(1)	C(10)–C(1)–C(2)	127.3(1)
C(9)–C(1)–C(2)	107.0(1)	C(9)–C(4)–C(5)	122.5(1)
C(9)–C(4)–C(3)	107.8(1)	C(5)–C(4)–C(3)	129.4(1)
C(8)–C(9)–C(4)	123.1(1)	C(8)–C(9)–C(1)	128.4(1)
C(4)–C(9)–C(1)	108.2(1)	C(15)–C(10)–C(11)	109.6(1)
C(15)–C(10)–C(1)	114.5(1)	C(11)–C(10)–C(1)	109.1(1)
C(30)–C(21)–C(29)	124.6(1)	C(30)–C(21)–C(22)	128.2(1)
C(29)–C(21)–C(22)	106.5(1)	C(29)–C(24)–C(25)	122.9(1)
C(29)–C(24)–C(23)	107.0(1)	C(25)–C(24)–C(23)	129.3(1)
C(28)–C(29)–C(24)	122.3(1)	C(28)–C(29)–C(21)	128.3(1)
C(24)–C(29)–C(21)	109.2(1)	C(35)–C(30)–C(31)	109.8(1)
C(35)–C(30)–C(21)	114.9(1)	C(31)–C(30)–C(21)	109.2(1)

TABLE 4. Positional parameters for *meso*-**5**

Atom	*x*	*y*	*z*
Zr	0.3335(1)	0.1344(1)	0.2156(1)
D(1)	0.3740	0.1832	0.3309
D(2)	0.3151	0.2186	0.1117
Cl(1)	0.4834(1)	0.0051(1)	0.2006(1)
Cl(2)	0.1505(1)	0.0331(1)	0.2149(1)
C(1)	0.4837(1)	0.1754(1)	0.3235(1)
C(2)	0.4104(1)	0.2560(1)	0.3041(1)
C(3)	0.2872(1)	0.2356(1)	0.3203(1)
C(4)	0.2845(1)	0.1442(1)	0.3535(1)
C(5)	0.1809(1)	0.0951(1)	0.3911(1)
C(6)	0.2312(1)	0.0140(1)	0.4408(1)
C(7)	0.3223(1)	−0.0483(1)	0.4021(1)
C(8)	0.4377(1)	0.0085(1)	0.3859(1)
C(9)	0.4042(1)	0.1048(1)	0.3530(1)
C(10)	0.6223(1)	0.1683(1)	0.3239(1)
C(11)	0.6768(1)	0.1928(1)	0.4009(1)
C(12)	0.8172(1)	0.1861(1)	0.4055(1)
C(13)	0.8730(1)	0.2508(1)	0.3498(1)
C(14)	0.8209(1)	0.2272(1)	0.2735(1)
C(15)	0.6814(1)	0.2316(1)	0.2676(1)
C(21)	0.2762(1)	0.1483(1)	0.0785(1)
C(22)	0.4008(1)	0.1745(1)	0.0910(1)
C(23)	0.4075(1)	0.2593(1)	0.1325(1)
C(24)	0.2856(1)	0.2899(1)	0.1447(1)
C(25)	0.2413(1)	0.3847(1)	0.1746(1)
C(26)	0.1014(1)	0.3843(1)	0.1803(1)
C(27)	0.0326(1)	0.3371(1)	0.1183(1)
C(28)	0.0673(1)	0.2327(1)	0.1088(1)
C(29)	0.2055(1)	0.2209(1)	0.1118(1)
C(30)	0.2229(1)	0.0691(1)	0.0296(1)
C(31)	0.1933(1)	0.1098(1)	−0.0468(1)
C(32)	0.1335(1)	0.0355(1)	−0.0982(1)
C(33)	0.2129(1)	−0.0539(1)	−0.1025(1)
C(34)	0.2430(1)	−0.0947(1)	−0.0273(1)
C(35)	0.3042(1)	−0.0202(1)	0.0243(1)

3. Experimental section

Reactions with organometallic compounds were carried out under argon using Schlenk-type glassware or a glove-box. Solvents were dried and distilled under argon prior to use. The NMR spectra were recorded with a Bruker WP 200 SY (^1H: 200 MHz, ^{13}C: 50 MHz) NMR spectrometer, and IR spectra with a Nicolet 5DXC FT IR spectrometer. Melting points were determined in sealed capillaries using a Büchi SMP 20 apparatus, and are uncorrected. Elemental analyses (C,H) were carried out with a Carlo Erba Elemental Analyzer 1106 or a Perkin Elmer Model 240 instrument. Details of the X-ray crystal structure determinations of the complexes *rac*-**5** and *meso*-**5** are given in Table 5. Cyclohexyl tosylate (**1**) and indenyllithium were prepared by published procedures [9]. The numbering scheme used for the NMR assignments accords with IUPAC nomenclature rules.

3.1. 1- and 3-Cyclohexylindene (2b, 2a)

A solution of 61 g (500 mmol) of indenyllithium is prepared in 600 ml of tetrahydrofuran. A solution of 149 g (446 mmol) of cyclohexyl tosylate (**1**) in 500 ml of tetrahydrofuran is added dropwise at 0°C. The mixture is allowed to warm to ambient temperature with stirring, refluxed for 72 h at 65°C to complete the reaction, and hydrolysed (500 ml of water). Ether (600 ml) is added and the organic phase separated and washed three times with 100 ml portions of water. The aqueous phase is extracted twice with ether (100 ml). The combined organic phases are dried over sodium sulphate. Solvent is removed *in vacuo* and the residue distilled (95°C, 0.1 torr) to give 36 g (41%) of a product mixture of 1- and 3-cyclohexylindene in a 40:60 ratio. Anal. Found: C 88.71, H 9.12. $C_{15}H_{18}$ (198.3) calcd.: C 90.85, H 9.15%. ^{1}H NMR ($CDCl_3$): δ 7.50–7.10 (m, 8H, 4-H–7-H, **2a,b**), 6.80 [m, 1H, 3-H, **2a**, $^3J = 5.6$ Hz (3-H, 2-H), $^4J = 1.5$ Hz (3-H, 1-H)], 6.54 [m, 1H, 2-H, **2a**, $^3J = 1.8$ Hz (2-H, 1-H)], 6.20 [m, 1H, 2-H, **2b**, $^3J = 1.0$ Hz (2-H, 1-H)], 3.44 (bs, 1H, 1-H, **2a**), 3.34 (bs, 2H, 1-H′, **2b**), 2.63 (m, 2H, cyclohexyl-CH of **2a** and **2b**), 2.10–1.12 (m, 20 H, cyclohexyl-CH_2 of **2a** and **2b**).

3.2. 1-(Cyclohexyl)indenyllithium (3)

The 1- and 3-cyclohexylindene product mixture (19.8 g, 100 mmol) is dissolved in 150 ml of ether. A 1.55 M solution of n-butyllithium in ether (64.5 ml, 100 mmol) is added dropwise with stirring. The mixture is then stirred for 2 h at ambient temperature. Solvent is removed *in vacuo* and the white residue washed twice with pentane (50 ml each). Drying *in vacuo* gives 18.6 g (91%) of **3**, which was characterized spectroscopically. ^{1}H NMR [benzene-d_6/THF-d_8 (9:1)]: δ 7.76 (m, 2H, 4-H, 7-H), 6.97 (m, 2H, 5-H, 6-H), 6.64 [X part of AX, 1H, 2-H, $^3J = 3.3$ Hz (2-H, 3-H)], 6.16 (A part of AX, d, 1H, 3-H), 3.10 (m, 1H, cyclohexyl-C*H*), 2.3–1.7 (m, 10H, cyclohexyl-CH_2). ^{13}C NMR [benzene-d_6/THF-d_8 (9:1), *J*(CH) in Hz]: δ 120.6 ($^1J = 154$), 118.8 ($^1J = 149$), 115.8 ($^1J = 154$), 114.8 ($^1J = 154$) (C-4–C-7), 114.1 (C-1), 112.0 ($^1J = 155$, $^2J = 5$, C-2), 88.0 ($^1J = 162$, C-3), 38.1 ($^1J = 131$, cyclohexyl-*C*H), 36.5 ($^1J = 125$), 28.1 ($^1J =$

TABLE 5. Crystal data and experimental details for the X-ray crystal structure analyses of *rac*-**5** and *meso*-**5**

	rac-**5**	*meso*-**5**
formula	$C_{30}H_{42}Cl_2Zr$	$C_{30}H_{42}Cl_2Zr$
mol wt	564.8	564.8
crystal size (mm)	0.13 × 0.47 × 0.40	0.14 × 0.35 × 0.35
a (Å)	10.626(1)	10.858(1)
b (Å)	6.7436(6)	13.849(1)
c (Å)	19.4493(8)	18.262(1)
β (°)	98.027(8)	92.91(1)
V (Å^3)	1380.1	2742.4
D_{calcd} (g cm^{-3})	1.36	1.37
μ (cm^{-1})	6.02	6.06
F(000) (*e*)	592	1184
Z	2	4
space group (no.)	*P*2/*n* (non-standard 13)	$P2_1/c$ (14)
diffractometer	Enraf-Nonius CAD4	
Mo Kα radiation, λ (Å)	0.71069	0.71069
abs. correction	none	none
no. of measd. reflcns.	8911 ($\pm h$, $\pm k$, $+l$)	6698 ($\pm h$, $+k$, $+l$)
$[(\sin\theta)/\lambda]_{max}$ (Å^{-1})	0.70	0.65
R_{av}	0.02	–
no. of indep. reflcns.	4027	6231
no. of obsd. reflcns. ($I > 2\sigma(I)$)	3574	4869
no. of refined params.	150	298
R	0.032	0.038
R_w ($w = 1/\sigma^2(F_o)$)	0.042	0.039
max. resid. electron dens. (*e* Å^{-3})	0.88	0.46

Structures were solved using heavy-atom methods, H-atom positions were found and kept fixed in the final refinement stages.

125), 27.4 ($^1J = 127$) (cyclohexyl-CH_2), C-8 and C-9 hidden under solvent.

3.3. *Bis(1-cyclohexylindenyl)zirconium dichloride (rac-/meso-4)*

To a suspension of $ZrCl_4(thf)_2$ (3.85 g, 10.2 mmol) in 80 ml of toluene is added dropwise a cold solution of 4.17 g (20.4 mmol) of 1-cyclohexylindenyllithium in 250 ml of THF at −78°C. When the addition is complete the mixture is allowed to warm to room temperature over 6 h with stirring then stirred for an additional 12 h at ambient temperature. A small sample is taken for determination of the ratio of diastereomers by ^1H NMR spectroscopy during the reaction (*meso*-**4** : *rac*-**4** = 52 : 48). The solvent is removed from the remaining reaction mixture *in vacuo*. The resulting yellow powder is washed twice with pentane (50 ml each) and then extracted with 150 ml of methylene chloride and filtered from the LiCl residue. The solvent is removed *in vacuo* to give 4.1 g (72%) of the *rac-/meso*-**4** mixture. Fractional crystallization from methylene chloride gives > 96% pure samples of each of the diastereoisomers. *Rac*-**4**: yield 1.8 g (32%), mp = 212°C. Anal. Found C 64.58, H 4.95. $C_{30}H_{34}Cl_2Zr$ (556.7) calcd.: C 64.72, H 6.15%. ^1H NMR ($CDCl_3$): δ 7.61 [m, 1H, 7-H, $^3J = 8.8$ Hz (7-H, 6-H), $^4J = 0.9$ Hz (7-H, 5-H)], 7.53 [m, 1H, 4-H, $^3J = 8.8$ Hz (4-H, 5-H), $^4J = 0.7$ Hz (4-H, 6-H)], 7.33 (m, 1H, 5-H), 7.17 (m, 1H, 6-H), 5.90 [X part of AX, 1H, 2-H, $^3J = 3.1$ Hz (2-H, 3-H)], 5.83 (A part of AX, 1H, 3-H), 3.13 (m, 1H, cyclohexyl-C*H*), 2.01–0.79 (m, 10H, cyclohexyl-CH_2). ^{13}C NMR [$CDCl_3$, *J*(CH) in Hz]: δ 131.4, 127.2, 124.0 (C-1, C-8, C-9), 126.7 ($^1J = 162$, $^2J = 8$), 126.0 ($^1J = 163$, $^2J = 7$), 125.1 ($^1J = 163$, $^2J = 8$), 124.3 ($^1J = 165$, $^2J = 7$) (C-4–C-7), 118.8 ($^1J = 172$, $^2J = 5$, C-2), 96.7 ($^1J = 175$, $^2J = 5$, C-3), 36.9 ($^1J = 130$, cyclohexyl-*C*H), 35.4 ($^1J = 129$), 30.3 ($^1J = 122$), 26.8 ($^1J = 124$), 26.4 (double intensity, $^1J = 124$) (cyclohexyl-CH_2). IR (KBr): $\nu = 3098, 2920, 2847, 1444, 1351, 808, 750, 745$ cm^{-1}. *Meso*-**4**: yield 1.9 g (34%), mp = 188°C. Anal. Found. C : 63.35, H 5.63. $C_{30}H_{34}Cl_2Zr$ (556.7) calcd.: C 64.72, H 6.15%. ^1H NMR ($CDCl_3$): δ 7.57 [m, 1H, 7-H, $^3J = 8.5$ Hz (7-H, 6-H), $^4J = 1.0$ Hz (7-H, 5-H)], 7.40 (m, 1H, 4-H, $^3J = 8.4$ Hz (4-H, 5-H), $^4J = 1.1$ Hz (4-H, 6-H)], 7.29 (m, 1H, 5-H), 7.21 (m, 1H, 6-H), 6.30 [X part of AX, 1H, 2-H, $^3J = 3.2$ Hz (2-H, 3-H)], 5.81 (A part of AX, 1H, 3-H), 3.18 (m, 1H, cyclohexyl-C*H*), 2.05-0.82 (m, 10H, cyclohexyl-CH_2). ^{13}C NMR [$CDCl_3$, *J*(CH) in Hz]: δ 130.9, 128.7, 123.8 (C-1, C-8, C-9), 126.6 ($^1J = 161$, $^2J = 10$), 126.0 ($^1J = 163$, $^2J = 7$), 125.1 ($^1J = 165$, $^2J = 9$), 124.1 ($^1J = 166$, $^2J = 7$) (C-4–C-7), 117.3 ($^1J = 170$, $^2J = 5$, C-2), 98.1 ($^1J = 174$, $^2J = 5$, C-3), 37.1 ($^1J = 126$, cyclohexyl-*C*H), 35.7 ($^1J = 129$), 30.7 ($^1J = 128$), 26.8 ($^1J = 124$), 26.4 (^1J not resolved), 26.3 ($^1J = 124$) (cyclohexyl-CH_2). IR (KBr) $\nu = 3093, 2917, 2848, 1443, 1351, 1335, 799, 759, 741$ cm^{-1}.

3.4. *Bis(1-cyclohexyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (rac-/meso-5)*

A sample of the mixture of the *meso*- and *rac*-bis(1-cyclohexylindenyl)zirconium dichloride diastereomers (*rac-/meso*-**4**; 1.75 g, 3.14 mmol) is dissolved in 80 ml of methylene chloride and catalytically hydrogenated at 60 bar H_2-pressure using 80 mg PtO_2 during 12 h. The catalyst is removed by filtration. The diastereomers of the resulting product **5** are separated by fractional crystallization from CH_2Cl_2 at −28°C. The first fraction (0.55 g, 31%, mp = 290°C) is diastereomerically pure *rac*-**5** (crystals of this fraction were used for the X-ray structural analysis of rac-**5**). The filtrate is concentrated *in vacuo* and submitted to a second crystallization at −28°C. The resulting precipitate (0.43 g, 24%) is filtered off. It consists of a mixture of *rac*- and *meso*-**5**. The filtrate is further concentrated and further solid allowed to crystallize, eventually to yield 0.58 g (33%) of *meso*-**5** (mp = 172°C). A crystal from this fraction was used for the X-ray crystal structure analysis of *meso*-**5**. Characterization of the pure diastereoisomers: *rac*-**5**, anal. found C 63.84, H 7.23 $C_{30}H_{42}Cl_2Zr$ (564.8) calcd.: C 63.80, H 7.49%. ^1H NMR ($CDCl_3$): δ 6.04 [X part of AX, 1H, 2-H, $^3J = 2.8$ Hz (2-H, 3-H)], 5.54 (A part of AX, 1H, 3-H), 2.90–2.72 (m, 2H), 2.58–2.35 (m, 3H), 2.09–1.49 (m, 9H), 1.45–1.10 (m, 4H), 1.05–0.80 (m, 1H). ^{13}C NMR [$CDCl_3$, *J*(CH) in Hz]: δ 138.1, 135.4, 127.9 (C-1, C-8, C-9), 104.8 ($^1J = 175$, $^2J = 5.5$), 101.7 ($^1J = 176$, $^2J = 5.5$) (C-2, C-3), 37.0 ($^1J = 126$, cyclohexyl-*C*H), 35.5 ($^1J = 133$), 31.1 ($^1J = 126$), 27.7 ($^1J = 124$), 26.3 ($^1J = 126$), 26.1 ($^1J = 125$), 24.6 ($^1J = 127$), 23.1 ($^1J = 127$), 22.4 ($^1J = 134$), 21.8 ($^1J = 127$) (C-4–C-7 and cyclohexyl-CH_2). IR (KBr): $\nu = 3094, 2925, 2851, 1448, 1263, 886, 822, 805$ cm^{-1}. *Meso*-**5**, anal. found C 65.46, H 7.19 $C_{30}H_{42}Cl_2Zr$ (564.8) calcd.: C 63.80, H 7.49%. ^1H NMR ($CDCl_3$): δ 6.06 [d, 1H, 2-H, $^3J = 2.9$ Hz (2-H, 3-H)], 5.39 (d, 1H, 3-H), 2.87–2.30 (m, 5H), 1.90–0.73 (m, 14 H). ^{13}C NMR [$CDCl_3$, *J*(CH) in Hz]: δ 137.1, 130.0, 129.6 (C-1, C-8, C-9), 110.8 ($^1J = 170$, $^2J = 5.5$), 103.5 ($^1J = 170$, $^2J = 5.5$) (C-2, C-3), 37.2 ($^1J = 126$, cyclohexyl-*C*H), 35.2 ($^1J = 131$), 31.2 ($^1J = 129$), 26.8 ($^1J = 125$), 26.4 ($^1J = 122$), 26.4 ($^1J = 124$), 24.7 ($^1J = 128$), 23.4 ($^1J = 130$), 22.5 ($^1J = 130$), 22.1 ($^1J = 127$) (C-4–C-7 and cyclohexyl-CH_2). IR (KBr): $\nu = 3113, 2927, 2850, 1447, 1262, 816, 805$ cm^{-1}.

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