Synthesis of Ethylene Bridged Biscyclopentadiene Ligand Precursor Compounds and Some of their *ansa*-Zirconocene Derivatives *via* Chiral Epoxides: A Synthetic Strategy of High Variability

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The chiral ligand precursor systems [1-Cp^1-1-R^1-2-R^2-2-Cp^2]ethane **5a–d** bearing two different cyclopentadienyl fragments (Cp^1, Cp^2 = Cp, Ind, Flu) and a variable bridge substitution pattern (R^1, R^2 = H, Ph, cyclopentyl, cyclohexyl) were prepared starting from the corresponding epoxides. The solid state structures of six organic intermediates are reported in order to prove the stereochemistry of the ligand forming reactions. Treatment of the dilithio salts of **5a–d** with $ZrCl_4$ in CH_2Cl_2 afforded chiral *ansa*-zirconocene dichlorides (**6a–d**).

Introduction

In recent years chiral *ansa*-metallocene compounds have attracted considerable interest as polymerization catalysts [1] for catalytic hydrogenation [2] and metal-assisted Diels-Alder reactions [3]. These wide-spread applications make it necessary to look for a synthetic approach which allows easy tailoring of the catalyst structures. In a first report we have shown recently that epoxystyrene can serve as cheap starting material for the preparation of ethylene bridged zirconocene dichlorides [4]. We report here on the use of differently substituted epoxides in the preparation of a variety of new, stereorigid biscyclopentadiene ligand precursor systems with variable backbone substitution and some of their *ansa*-zirconocene dichloride complexes. In order to prove the stereochemical course of the ligand forming reactions the solid state structures of six significant organic intermediates are reported.

Results and Discussion

Ligand preparation

The epoxides (**1a–c**) allow the preparation of ethylene bridged biscyclopentadiene ligand precursor systems (**5a–d**) with two different cyclopentadienyl units according to the reaction procedures shown in Schema 1 A and 1 B.

In a first clean ring opening reaction the fluorenyl group is introduced leading to the corresponding alcohols **2a–c,** as reported by us recently [4, 5]. From the cyclic epoxides (**1a,b**) the crystalline alcohols (**2a,b**) are formed nearly quantitatively. The X-ray structure determination of **2b** shows that the fluorenyl group and the OH function are in an *trans*-arrangement, as expected (Fig. 1). The primary alcohol product **2c** can be isolated after ring opening of epoxystyrene in 75% yield. For both alcohols bond lengths and angles are in the range of expectation.

Substitution of the OH function can now be accomplished according to two different routes. Reaction of **2c** with trifluoromethanesulfonic acid anhydride gives the trifluoromethanesulfonate derivative **6.** Subsequent treatment with one equivalent of indenyllithium results in the formation of the ethylene bridged biscyclopentadiene **5d** by direct substitution of the leaving group [6]. The phenyl backbone substituent does not change its position over the entire reaction sequence (**2c**→**5d**).

The methanesulfonate derivatives **3a–c** behave differently. Reaction with on equivalent of a strong sterically hindered base like CpNa or LDA affords the formation of the spiro-cyclopropanes **4a–c** by intramolecular substitution of the leaving group in high yield. Exemplarily the solid state

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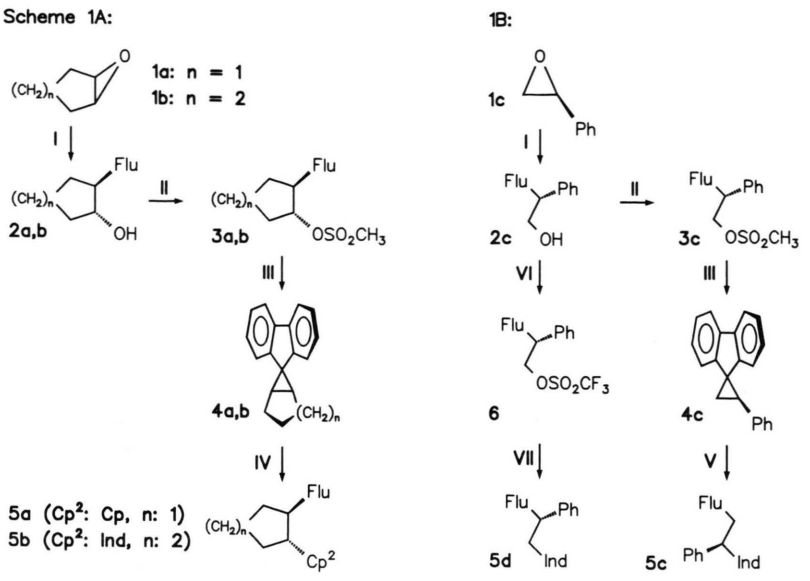


Scheme 1. I. [Flu]Li (1 equiv), $(i\text{-prop})_2O$, 0 °C, 75–86%; II CH_3SO_2Cl (1 equiv), NEt_3 (1 equiv), CH_2Cl_2, 0 °C, ~95%; III LDA (1.2 equiv), THF, ~90%; IV [Cp]Na (1.3 equiv), DMF, 80 °C, 3d, 60%; V [Ind]Li (1.3 equiv), DMF, 80 °C, 3d, 60%; VI $(CF_3SO_2)_2O$ (1 equiv), pyridine (1 equiv), CH_2Cl_2, 0 °C, ~90%; VII [Ind]Li (1.2 equiv), dioxane, ~70%.

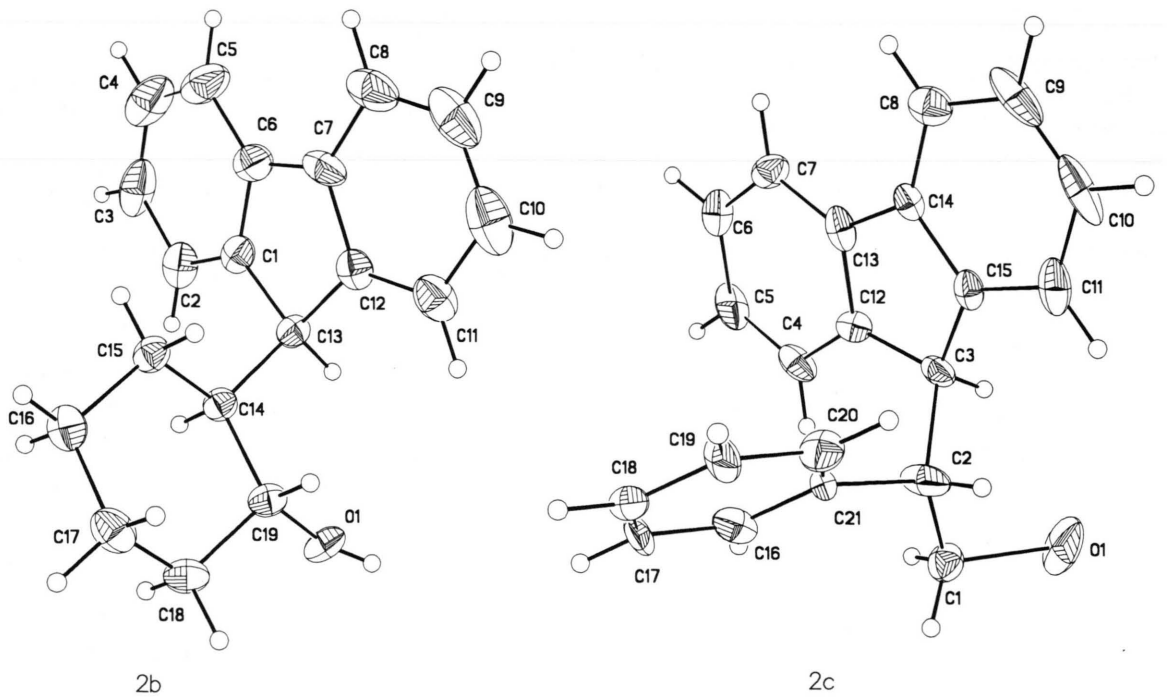


Fig. 1. Molecular structures of the chiral alcohols **2b** and **2c** in the solid state with displacement ellipsoids at the 20% probability level (only the structure of one of the independent molecules is depicted for **2b** and **2c,** respectively). Selected distances (pm): **2b,** C13–C14: 156.4(5); C14–C19: 151.3(6); O1–C19: 144.4(6). **2c,** C1–C2: 139.6(9); C2–C3: 160.9(12); O1–C1: 156(8); C2–C21: 156.3(8).

structures of **4a** and **4c** are shown in Fig. 2. Both compounds encompass two highly constrained cyclopropyl ring systems. The cyclopentyl group in **4a** is nearly planar. The two least-square planes defined by the atoms C1, C2, C3, C4 and C3, C4, C5 have a common angle of 14.5°.

The tension of the cyclopropyl rings of **4a–c** together with the ability of the fluorenyl groups to stabilize a negative charge is used to introduce a second Cp or indenyl fragment. All three spiro compounds undergo a clean opening reaction of the cyclopropyl ring systems with one equivalent of CpNa or Indenyllithium in dimethylformamid (DMF) at 80 °C [7]. The reaction of the cycloalkyl substituted species **4a,b** is expected to happen *via* nucleophilic attack of the Cp^- or Ind^- groups at C1 or C2 (*e.g.* **4a,** Fig. 2) of the spiro-compounds, since the *trans* ligand precursors **5a,b** were isolated exclusively.

The reaction is *fully* regiospecific for **4c** and leads in good yield to **5c** were the phenyl group is located in an α-position to the incoming indenyl fragment. Both reaction paths, i.e. direct substitution (**6**→**5d**) and introduction of the indenyl group *via* ring opening of the spirocyclopropanes (**4c**→**5c**) allow efficient control of the backbone substitution pattern. The synthesis of the cycloalkyl-bridged systems **5a,b** also benefits from the spiro-compounds, since the *trans* ligand precursors with two different cyclopentadienyl units can be prepared from the *trans* alcohols **2a,b.**

The solid state structures of the sterically extremely crowded ethanes **5b** and **5d** are depicted in Fig. 3. The ^{1}H NMR spectrum of **5b** shows significant line broadening for the protons at C1, C2, and C16 (Fig. 3) at ambient temperature, indicating hindered rotation of the fluorenyl- and the indenyl moieties even at room temperature. At −20 °C these rotations are frozen in and two new sets of resonances appear for each of the above mentioned nuclei.

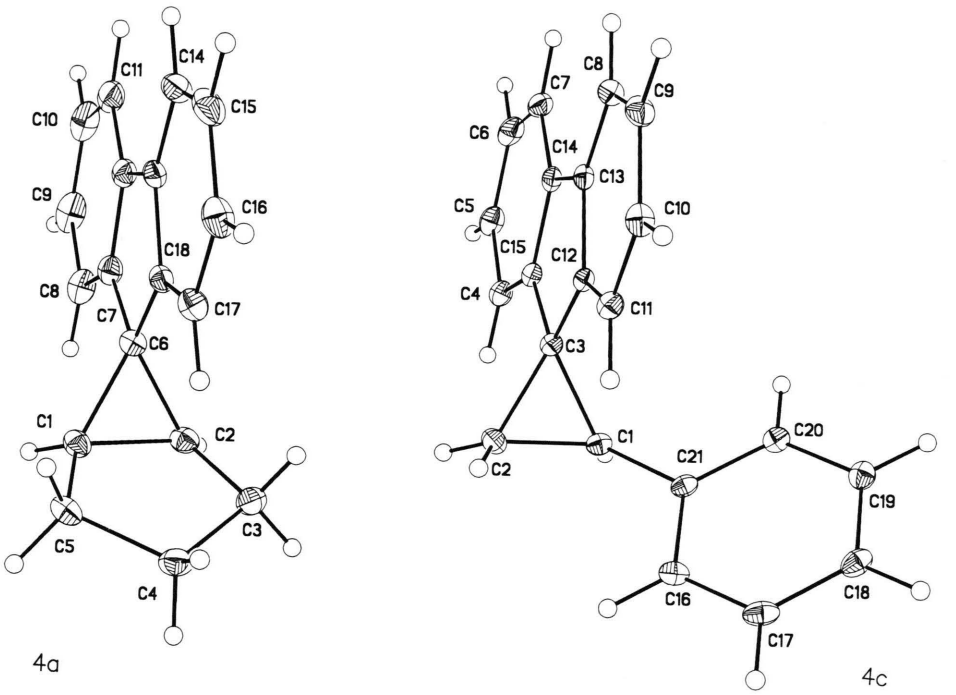


Fig. 2. Molecular structures of the spiro compounds **4a** and **4c.** Selected distances (pm) and angles (°): **4a,** C1–C2: 149.0(2); C2–C3: 151.5(2); C3–C4: 154.5(3); C4–C5: 153.7(3); C1–C5: 151.3(2); C1–C6: 153.3(2); C2–C6: 153.9(2); C1–C6–C2: 58.0(1); C6–C1–C2: 61.2(1); C1–C2–C6: 60.8(1); C7–C6–C18: 104.3(1); **4c:** C1–C2: 148.5(3); C2–C3: 151.7(3); C1–C3: 153.9(2); C1–C21: 149.7(2); C1–C3–C2: 58.2(1); C2–C1–C3: 60.2(1).

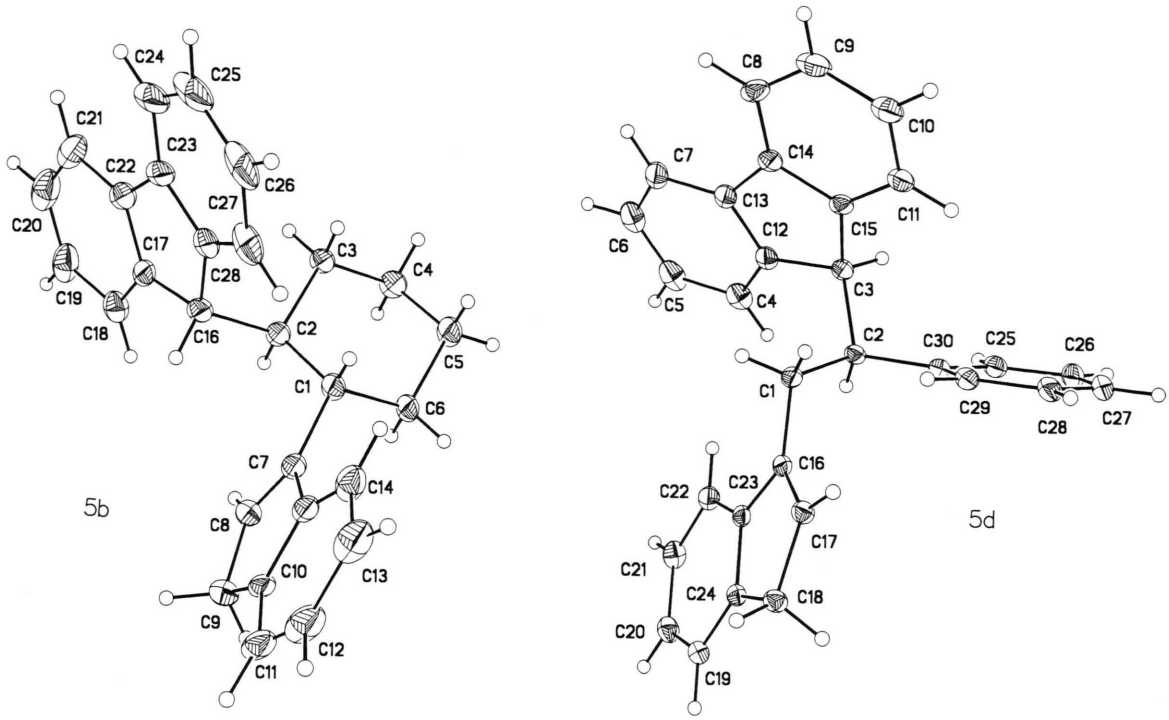
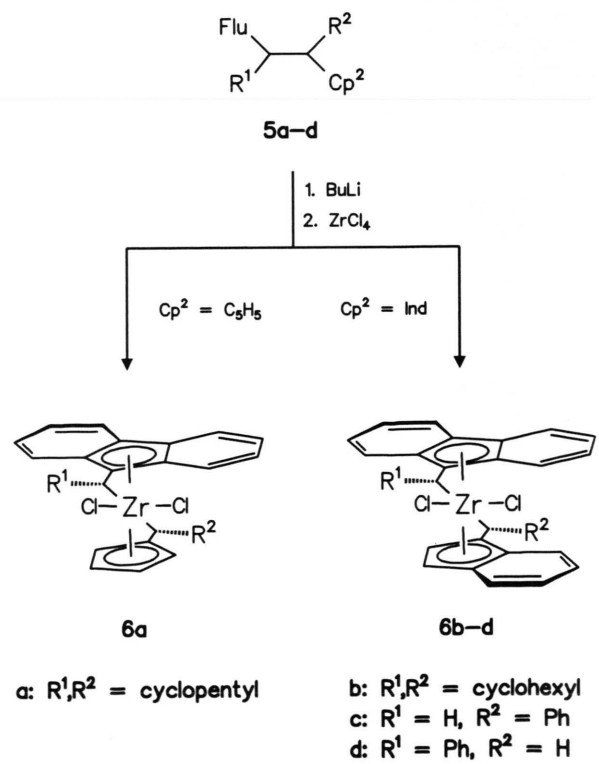


Fig. 3. Molecular structures of the ligand precursors **5b** and **5d.** Selected distances (pm): **5b,** C1–C2: 152.4(5); C1–C7: 151.5(8); C2–C16: 156.4(5); **5d,** C1–C2: 153.9(2); C1–C16: 150.4(2); C2–C3: 156.5(3).

Complex formation

The biscyclopentadienes **5a–d** were transformed into their dilithio salts by reaction with two equivalents of *n*-butyllithium in diethyl ether at 0 °C. Subsequent reaction with $ZrCl_4$ in CH_2Cl_2 at −80 °C afforded the *ansa*-zirconocene dichlorides **6a–d** (Scheme 2). All fluorenyl containing lithio salts gave no products if the reaction was performed in THF or diethyl ether. The complexes **6b–d** were isolated as a mixture of two diastereomeric compounds [8]. Separation and structural characterization of the isomers of **6d** was described by us previously [6]. Efforts to separate the diastereomers of **6b** and **6c** remained unsuccessful.



Experimental

All reactions were carried out under dry argon by using standard Schlenk tube techniques. The hydrocarbon and ether solvents were purified by distillation over $LiAlH_4$. CH_2Cl_2 was distilled from CaH_2. DMF was purified by destillation of the aceotrop with toluene and water, followed by stirring for 12 h over CaO and destillation at reduced

pressure. NaCp(dioxane) [9], **2a,b** [5], **2c, 6** [4], **5d** and **6d** [6] were prepared by literature procedures. Routine ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer at ambient temperature; chemical shifts are referenced with respect to TMS. Mass spectra were acquired with Finnigan instruments (MAT-711A, modified by AMD Intectra (FD, FAB); Finnigan TSQ70 (EI, FAB), 70eV). Elemental analyses: Microanalytical laboratory of the Institute (Carlo Erba, Model 1106).

Preparation of the methanesulfonates (**3a–c**)

To a solution of one of the alcohols **2a–c** (75 mmol) and triethyl amine (10.4 ml, 75 mmol) in CH_2Cl_2 (150 ml) was added methanesulfonyl chloride (5.8 ml, 75 mmol) at 0 °C. After 30 min stirring at this temperature the organic phase was washed with a saturated aqueous solution of NH_4Cl (four times, 50 ml). The CH_2Cl_2 solution was dried (Na_2SO_4) and the solvent removed in vacuo. Stirring of the resulting colorless oil overnight with ethanol at ambient temperature yielded the sulfonates as colorless crystalline materials.

Compound **3a:** 23.8 g, 72.5 mmol, 97%; m.p. 100–101 °C (decomp. > 120 °C); ^1H NMR ($CDCl_3$): δ = 1.38–1.97 (m, 6H, cyclopentyl), 2.42 (s, 3H, O_2S-CH_3), 2.97–3.08 (m, 1H, CH_{bridge}), 4.2 (d, J = 3.3 Hz, 1H, CH_{Flu}), 4.4–4.5 (m, 1H, CH_{bridge}), 7.2–7.8 (m, 8H, CH_{arom}).

Analysis for $C_{19}H_{20}O_3S$

Calcd	C 68.64	H 5.82	S 10.05%,
Found	C 69.48	H 6.14	S 9.77%.

Compound **3b:** 25.3 g, 73.9 mmol, 98%; m.p. 121–122 °C (decomp. > 130 °C); ^1H NMR ($CDCl_3$): δ = 0.6–1.7 (m, 7H, cyclohexyl), 2.3–2.5 (m, 2H, cyclohexyl + CH_{bridge}), 3.06 (s, 3H, O_2S-CH_3), 4.33 (d, J = 2.1 Hz, 1H, CH_{Flu}), 5.1–5.2 (m, 1H, CH_{bridge}), 7.3–7.8 (m, 8H, CH_{arom}).

Analysis for $C_{20}H_{22}O_3S$

Calcd	C 70.15	H 6.48	S 9.37%,
Found	C 70.49	H 7.02	S 8.98%.

Compound **3c:** 26.0 g, 71.3 mmol, 97.7%; m.p. 93–94 °C; ^1H NMR ($CDCl_3$): δ = 2.76 (s, 3H, CH_3), 3.87 (m, 1H, CHPh), 4.3–4.6 (m, 3H, $CH_{2,bridge}$ + CH_{Flu}), 7.0–7.8 (m, 13H, CH_{arom}).

Analysis for $C_{22}H_{20}O_3S$

Calcd	C 72.51	H 5.53	S 8.80%,
Found	C 72.42	H 5.54	S 8.70%.

Preparation of the spiro compounds (**4a–c**)

A solution of diisopropyl amine (8.0 ml, 56.9 mmol) and *n*-butyllithium (1.6 M, 35.6 ml, 56.9 mmol) in 150 ml THF at 0 °C was treated with a solution of one of the methanesulfonates **3a–c** (54.9 mmol) in 100 ml THF over a period of 15 min. After stirring overnight at room temperature the solvents were evaporated and the dark oily residue was suspended in a saturated aqueous solution of NH_4Cl. The mixture was extracted thoroughly with diethyl ether (5 times, 100 ml each). The organic phase was dried (Na_2SO_4) and concentrated in vacuo, leaving a brown oily residue. Chromatography over silica (eluent: toluene/hexane, 2:7) gave **4a–c** as colorless to pale yellow crystals.

Compound **4a:** 11.8 g, 50.8 mmol, 92.5%; m.p. 86–87 °C; ^{1}NMR ($CDCl_3$): δ = 1.78–2.02 (m, 6H, cyclopentyl), 2.15–2.16 (m, 2H, $CH_{cyclopropyl}$), 6.7–7.8 (m, 8H, CH_{arom}).

Analysis for $C_{18}H_{16}$

Calcd	C 93.06	H 6.94%,	
Found	C 93.08	H 7.02%.	

Compound **4b:** 12.0 g, 48.7 mmol, 89.7%; m.p. 933–94 °C; ^{1}NMR ($CDCl_3$): δ = 0.84–1.87 (m, 10H, cyclohexyl), 6.69–7.85 (m, 8H, CH_{arom}).

Analysis for $C_{19}H_{18}$

Calcd	C 92.63	H 7.37%,	
Found	C 92.75	H 7.42%.	

Compound **4c:** 26.0 g, 71.3 mmol, 97.7%; m.p. 133–134 °C; ^1H NMR ($CDCl_3$): δ = 2.22 (d, J = 8.4 Hz, 2H, CH_2), 3.38 (+, J = 8.4 Hz, 1H, CHPh), 6.1–7.7 (m, 13H, CH_{arom}).

Analysis for $C_{21}H_{16}$

Calcd	C 93.99	H 6.01%,	
Found	C 93.91	H 6.17%.	

trans-[1-Cyclopentadienyl-2-(9-fluorenyl)]-cyclopentane (**5a**)

NaCp(dioxane) (10.0 g, 57 mmol) was added to a solution of **4a** (10.4 g, 42.6 mmol) in DMF (200 ml) at −15 °C. The dark red mixture was heated to 80 °C and stirred at this temperature for three days. The solvent was destilled off at reduced pressure and the dark brown residue was suspended in a saturated aqueous solution of NH_4Cl (250 ml). The mixture was extracted thoroughly with diethyl ether (5 times, 100 ml each). The combined organic phases were dried (Na_2SO_4) and the solvent was destilled off leaving a dark brown oil. Column

chromatography over silica (eluent: hexane/toluene = 7:2) gave **5a** (5.8 g, 19.4 mmol, 46%) as colorless oil. The ^{1}H NMR spectrum of **5a** provides no reasonable structural information due to double bond tautomerism of the Cp unit. The ligand was characterized by NMR after preparation of the corresponding zirconium complex. FDMS: 289 (M^+, 100).

Analysis for $C_{23}H_{22}$

Calcd C 92.57 H 7.43%,
Found C 92.32 H 6.92%.

trans-[1-(9-Fluorenyl)-2-(1-indenyl)]cyclohexane (**5b**)

Indene (7.5 ml, 63.8 mmol) in 100 ml diethyl ether was treated with *n*-butyllithium (1.6 M in hexane, 39.8 ml) at 0 °C. When the addition was finished the solvent was evaporated leaving pale yellow solid indenyllithium which was cooled to −80 °C and dissolved in DMF (200 ml, precooled to −50 °C). To the solution **4b** (12.1 g, 49.0 mmol) was added. The brown to yellow solution was warmed to 80 °C and stirred at this temperature for three days. The work up was performed similar to that of **5a** leaving crude **5b** (14.5 g) as yellow to red oil after column chromatography. Crystallization from pentane at room temperature yielded **5b** (10.3 g, 28.4 mmol, 58%). ^{1}H NMR ($CDCl_3$): δ = 0.67−0.75 (m, 1H, $CH_{2,cyclohexyl}$), 0.88−1.00 (m, 1H, $CH_{2,cyclohexyl}$), 1.18−1.34 (m, 3H, $CH_{2,cyclohexyl}$), 1.54−1.58 (m, 1H, $CH_{2,cyclohexyl}$), 1.74 (m, broad signals, 1H, $CH_{2,cyclohexyl}$), 1.9−2.3 (m, broad signals, 1H, $CH_{2,cyclohexyl}$), 2.5−3.0 (m, broad signals, 1H, $CH_{2,cyclohexyl}$), 3.2−3.3 (m, 1H, $CH_{2,cyclohexyl}$), 3.43 (m, broad signal, 2H, $CH_{2,indenyl}$), 4.0−4.5 (m, broad signal, 1H, CH_{Flu}), 6.5 (s, 1H, CH_{Ind}), 6.9−8.0 (m, 12H, CH_{arom}); FDMS: 362 (M^+, 100).

Analysis for $C_{28}H_{26}$

Calcd C 92.77 H 7.23%,
Found C 92.54 H 7.38%.

[1-(9-Fluorenyl)-2-(1-indenyl)-2-phenyl]ethane (**5c**)

4c (8.0 g, 29.8 mmol) was treated with indenyllithium in a manner similar to that of **4b** to yield **5c** (7.0 g, 18.2 mmol, 61%) as pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 2.31−2.65 (m, 2H, $CH_{2,bridge}$), 3.32 (m, 2H, $CH_{2,Ind}$), 3.91 (m, 1H, CH_{Flu}), 4.4 (m, 1H, CH_{bridge}), 6.4 (m, 1H, CH_{Ind}), 7.0−7.7 (m, 17H). FDMS: 384 (M^+, 100).

Analysis for $C_{30}H_{24}$

Calcd C 93.71 H 6.29%,
Found C 93.28 H 6.55%.

Preparation of the zirconocene dichlorides (**6a−c**)

To a solution of one of the ligand precursors **5a−c** (22 mmol) in 50 ml diethyl ether *n*-butyllithium (1.6 M in hexane, 27.5 ml, 44 mmol) was added at room temperature. The solvent was evaporated off and the dry dilithio salt was mixed with $ZrCl_4$ (5.12 g, 22 mmol) followed by the addition of 100 ml CH_2Cl_2 which was precooled to −80 °C. The suspension was warmed up to room temperature and stirred overnight. The mixture was passed through a 1-in. pad of Celite, washing with CH_2Cl_2. Removal of the solvent gave yellow to orange powders from which the zirconocene dichlorides **6a−c** were obtained by recrystallization from toluene solution at −30 °C. The isolated molar ratio was 3:2 for the diastereomers **6b1:6b2** and **6c1:6c2,** respectively [8].

Compound **6a:** 0.8 g, 1.7 mmol, 8%; ^{1}H NMR ($CDCl_3$): δ = 0.7−2.1 (m, 6H, $CH_{2,cyclopentyl}$), 2.4−2.6 (m, 1H, CH_{bridge}), 3.3−3.4 (m, 1H, CH_{bridge}), 6.02, 6.10, 6.28, 6.36 (m, 1H, each, CH_{Cp}), 7.0−7.7 (m, 8H, Ch_{arom}); FABMS: 459 (M^+, 30), 424 (M^+ −Cl, 100).

Analysis for $C_{23}H_{20}Cl_2Zr$

Calcd C 60.25 H 4.40%,
Found C 61.73 H 4.02%.

Compound **6b1,2:** 1.3 g, 2.5 mmol, 11%; ^{1}H NMR ($CDCl_3$): δ = **6b1,2:** 0.7−2.3 (m, 10H, $CH_{2,cyclohexyl}$), 6.8−8.0 (m, 12H, CH_{arom}); **6b1:** 3.84 (m, 1H, CH_{bridge}), 4.21 (m, 1H, CH_{bridge}), 6.30 (d, J = 3.5 Hz, 1H, CH_{Ind}), 6.46 (d, J = 3.5 Hz, 1H, CH_{Ind}); **6b2:** 4.05 (m, 1H, CH_{bridge}), 4.50 (m, 1H, CH_{bridge}), 5.85 (d, J = 3.2 Hz, 1H, CH_{Ind}), 6.14 (d, J = 3.2 Hz, 1H, CH_{Ind}); FABMS: 523 (M^+, 85), 487 (M^+ −Cl, 70).

Analysis for $C_{28}H_{24}Cl_2Zr$

Calcd C 64.35 H 4.63%,
Found C 64.72 H 4.84%.

Compound **6c1,2:** 1.0 g, 1.8 mmol, 8%; ^{1}H NMR ($CDCl_3$): δ = **6c1,2:** 6.8−8.0 (m, 17H, CH_{arom}); **6c1:** 4.15−4.14 (m, 2H, $CH_{2,bridge}$), 5.85−5.95 (m, 1H, CH_{bridge}), 6.51 (d, J = 3.5 Hz, 1H, CH_{Ind}), 6.60 (d, J = 3.5 Hz, 1H, CH_{Ind}); **6c2:** 4.35−5.04 (m, 2H, $CH_{2,bridge}$), 5.75−5.85 (m, 1H, CH_{bridge}), 6.08 (d, J = 3.2 Hz, 1H, CH_{Ind}), 6.23 (d, J = 3.2 Hz, 1H, CH_{Ind}); FABMS: 545 (M^+, 60), 510 (M^+ −Cl, 80).

Analysis for $C_{30}H_{22}Cl_2Zr$

Calcd C 66.16 H 4.07%,
Found C 66.41 H 4.21%.

X-ray structure determinations [10]

All samples were mounted on glass fibers. Graphite-monochromated Mo–K_α radiation was used. Two check reflections were monitored after every 58 intensity measurements. The structures were solved by Direct Methods (Program: SHELXTL-PC). Hydrogen atoms are placed in calculated positions (riding model) and phenyls were treated as rigid groups. All attempts to solve the structure of **2c** in space group $P\bar{1}$ failed. The final cell parameters and specific data collection parameters are summarized in Table I. The final atomic positional parameters can be found in the supplementary material.

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Table I. Crystallographic data for the compounds **2b, c, 4a, c,** and **5b, d.**

	2b	**2c**	**4a**	**4c**	**5b**	**5d**
Formula	$C_{19}H_{20}O$	$C_{21}H_{18}O$	$C_{18}H_{16}$	$C_{21}H_{16}$	$C_{28}H_{26}$	$C_{30}H_{24}$
fw	264.4	286.5	232.3	268.3	362.5	384.5
Cryst. color	colorless	colorless	colorless	colorless	yellow	yellow
Cryst. system	monoclinic	triclinic	tetragonal	monoclinic	triclinic	triclinic
Space group	P2/c (No. 13)	P1 (No. 1)	P4/n (No. 85)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a [pm]	1198.9(2)	1274.0(3)	1642.8(2)	1191.2(2)	910.0(7)	944.8(3)
b [pm]	1396.5(3)	1327.8(3)	1642.8(2)	962.2(1)	1108.2(3)	1118.1(4)
c [pm]	1871.2(4)	1584.9(3)	934.0(2)	1252.2(2)	1158.6(6)	1185.3(5)
α [deg]	90	107.30(3)	90	90	61.99(1)	65.86(3)
β [deg]	105.89(3)	111.08(3)	90	91.44(1)	86.04(1)	66.63(3)
γ [deg]	90	98.12(3)	90	90	78.86(1)	83.74(3)
V [10^6pm^3]	3013.1(10)	2293.6(9)	2520.7(7)	1434.8(3)	1011.9(9)	1046.8(6)
$d_{calcd.}$ [g/cm^3]	1.165	1.240	1.224	1.242	1.190	1.220
Z	8 (2 indep.)	6 (6 indep.)	8	4	2	2
Cryst dimens. [mm]	0.3, 0.5, 0.5	0.3, 0.4, 0.5	0.4, 0.4, 0.5	0.25, 0.4, 0.5	0,25, 0.3, 0.5	0.3, 0.35, 0.4
Abs coeff (μ), [mm^{-1}]	0.065	0.074	0.064	0.070	0.067	0.069
T [K]	298	173	173	173	173	173
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006\,F^2$	$w^{-1} = \sigma^2(F) + 0.0006\,F^2$	$w^{-1} = \sigma^2(F) + 0.0005\,F^2$	$w^{-1} = \sigma^2(F) + 0.0004\,F^2$	$w^{-1} = \sigma^2(F) + 0.0006\,F^2$	$w^{-1} = \sigma^2(F) + 0.004\,F^2$
Scan mode	Wyckoff	Omega	Omega	Wyckoff	Omega	Omega
Scan range, [deg]	1.80	2.40	1.00	1.20	1.25	1.2
2θ Range, [deg]	4–47	4–45	4–50	4–50	4–50	4–50
Scan speed, [deg/min]	10.00–29.30	11.72	10.00–29.30	7.32–29.30	7.32–29.30	7.32–29.30
No. of data collected	9197	11996	15513	9778	7090	7358
No. independ. data	4453	11794	2226	2531	3554	3679
No. of unique data	2152	7838	1580	1583	2133	2578
Obs. criterion	$F > 4\sigma(F)$	$F > 4\sigma(F)$	$F > 4\sigma(F)$	$F > 4\sigma(F)$	$F > 4\sigma(F)$	$F > 4\sigma(F)$
No. of parameters	369	973	163	190	253	271
R	0.061	0.063	0.043	0.036	0.073	0.036
R_w	0.057	0.071	0.041	0.033	0.083	0.044
Residual density [10^{-6}e pm^{-3}]	0.26	0.54	0.15	0.14	0.33	0.16

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[8] **6a** contains two stereogenic carbon centers in the backbone. Due to the *trans*-substitution only the enantiomeric (R,R) or (S,S)-combinations are possible. **6b** encompasses the chirality of the complexed 1-(R,S)-indenyl fragment in addition to the two stereogenic backbone centers. For the bridge only (R,R) or (S,S) are possible again. The two diastereomeric combinations (R)-indenyl-(R,R)-backbone and (S)-indenyl-(R,R)-backbone, as well as their enantiomeric counterparts are allowed, giving rise to two sets of NMR-resonances. The same number of NMR-signals appears for **6c,d** [(R)-indenyl-(R)-backbone and (S)-indenyl-(R)-backbone plus enantiomers].

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[10] Further details on the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57778, the names of the authors, and the journal citation.