Chiral Epoxides as Building Blocks for Ethylene-Bridged *ansa*-Metallocene Complexes – Synthesis of C_1-Symmetrical Zirconocene Dichlorides with Two Different Cyclopentadienyl Units

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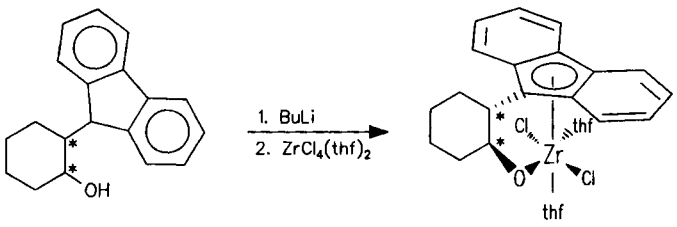
Epoxystyrene undergoes ring opening on treatment with tetraphenylcyclopentadienyl- and fluorenyllithium to give the corresponding chiral alcohols **3** and **4** in high yield. Their trifluoromethanesulfonate derivatives **5** react with one equivalent of cyclopentadienylsodium to form the ligand precursors 1-cyclopentadienyl-1-phenyl-2-(tetraphenylcyclopentadienyl)ethane (L^1H_2) and 1-cyclopentadienyl-2-(9-fluorenyl)-1-phenylethane (L^2H_2). The zirconocenes L^1ZrCl_2 (**7a**) and L^2ZrCl_2 (**7b**) are prepared from the dilithio salts L^1Li_2 and L^2Li_2, respectively. A low-temperature X-ray structure investigation of complex **7a** demonstrates the chiral arrangement of the four phenyl substituents of the tetraphenylcyclopentadienyl (C_5Ph_4) unit. A ^{1}H-NMR study shows that the phenyl groups rotate rapidly on the NMR time scale at room temperature. The dependence of phenyl rotation on temperature is discussed.

As part of interdisciplinary research on new polyolefin materials chiral *ansa*-zirconocene dichlorides have attracted much interest as polymerization catalysts[2]. Our current work is focused on the synthesis of ethylene-bridged metallocene dichlorides bearing two different cyclopentadienyl fragments and their polymerization properties. Only few of those catalysts with single carbon bridges are known[3], albeit they are the first to produce either syndiotactic polypropylene[4] or polyolefins with elastomeric properties[5].

We have recently reported on the preparation of alcohol **1** and its corresponding zirconium(IV) complex **2**[6].



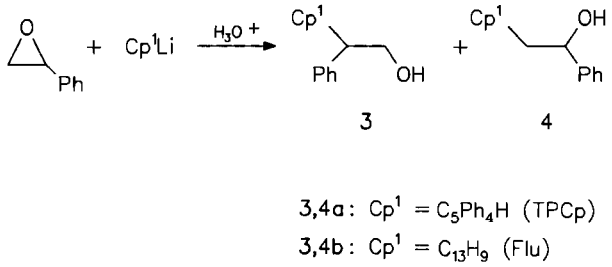
1 2

Chiral **1** results from nucleophilic ring opening of epoxycyclohexene. We now report on the synthesis and properties of *ansa*-zirconocene dichlorides with two different cyclopentadienyl units using epoxystyrene as a building block.

Results and Discussion

Epoxystyrene reacts quantitatively with one equivalent of tetraphenylcyclopentadienyllithium to give the alcohols **3a** and **4a**. Fluorenyllithium opens epoxystyrene to **3b** and **4b**, as depicted in Scheme 1. The reaction of fluorenyllithium has to be performed in diisopropyl ether. In diethyl ether or in tetrahydrofuran (THF) epoxystyrene is polymerized, probably due to the high solubility of the lithium alkoxide intermediate. The alcohols **3a** and **4a** and the fluorenyl derivatives **3b** and **4b** are formed in a ratio of 3:1 independent of the reaction temperature. Pure **3a** and **3b** can be obtained by recrystallization of the crude product from toluene/hexane. Compounds **4a** and **4b** have to be purified by column chromatography over silica.

Scheme 1



Treatment of the alcohols **3a, b** with trifluoromethanesulfonic anhydride and pyridine in CH_2Cl_2 results in the formation of the trifluoromethanesulfonates **5a** and **5b**, which can be transformed into the ligand precursors **6a** and **6b** by the reaction with NaCp · dioxane in dimethylformamide (DMF) at −20°C[7] (Scheme 2).

An interesting feature in the preparation of **6a, b** is the migration of the phenyl substituent. Phenyl group migration followed by a hydride shift is already known for substitution reactions with weak nucleophiles[8]. Solvents of high polarity like DMF support such anchimerically assisted reaction paths[9,10]. However, more detailed work is required for a genuine clarification of that migration reaction.

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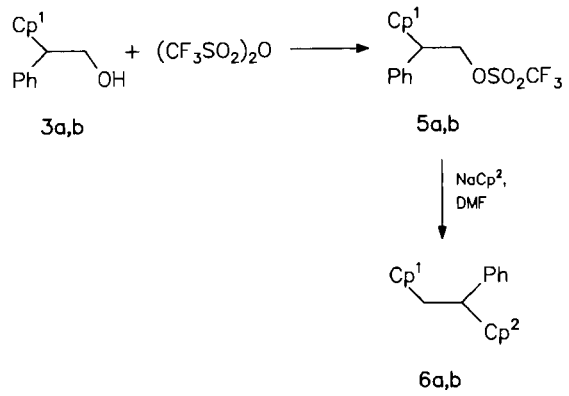
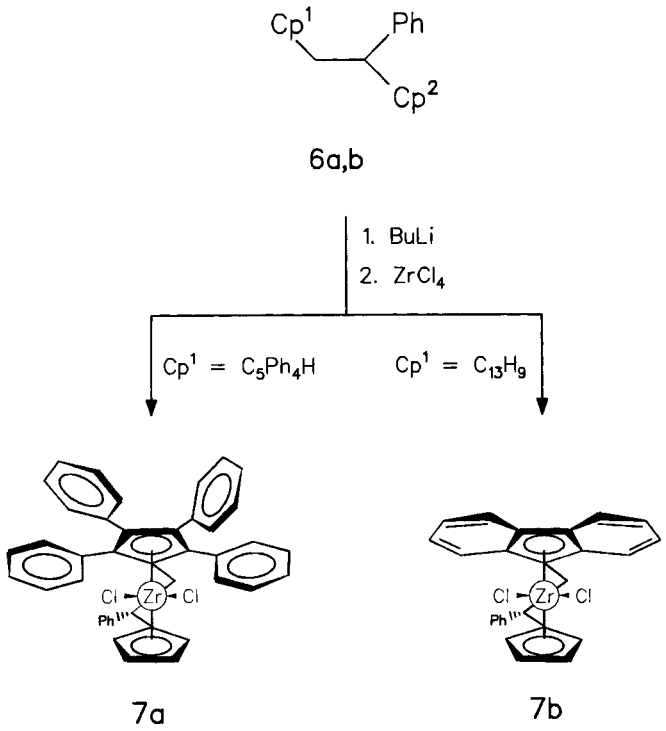
Scheme 2



3a,b 5a,b 6a,b

Complexes **7a** and **7b** have been prepared from the dilithio salts of **6a, b** by reaction with $ZrCl_4$ (Scheme 3).

Scheme 3



6a,b 7a 7b

Solid-State and Solution Structure of 7a

In order to ascertain the structure of the complexes and to collect information on the phenyl arrangement of **7a** an X-ray study has been performed. Figure 1 shows an ORTEP plot of **7a**.

Compound **7a** is the first complex which contains a single tetraphenylcyclopentadienyl ligand integrated in an *ansa*-framework. Figure 1 demonstrates the chiral array defined by the phenyl substituents around the metal center in the solid state at −100°C. Only phenyl groups 2[11] and 4 possess equal torsion angles of 135° with the Cp plane. Ring 3 exhibits a slightly enlarged angle due to nonbonding interactions with Cl^2 (Cl^2-C^{31} distance is 28 pm shorter than the Cl^1-C^{41} distance). Ring 5 interacts with the backbone phenyl substituent which results in a reduction of the torsion angle to −79.4°.

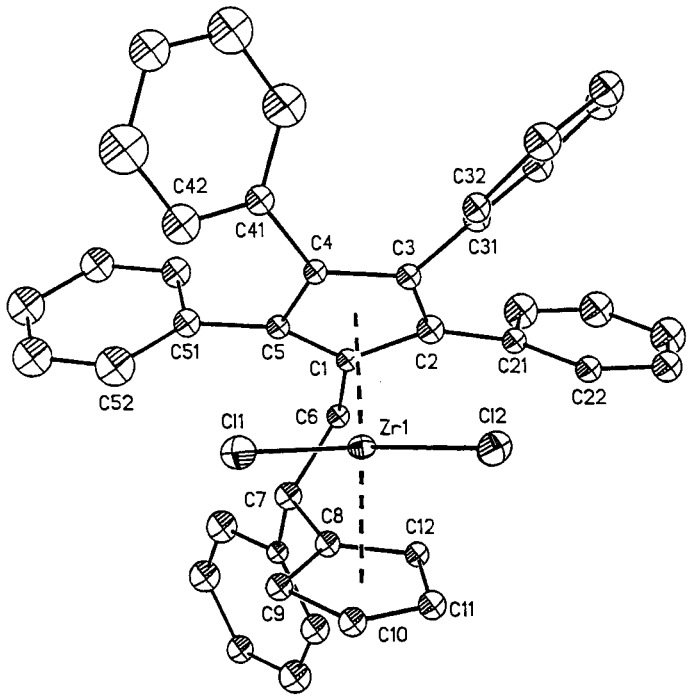


Figure 1. ORTEP plot of complex **7a** in the crystal at −100°C. Thermal ellipsoide are drawn on the 30% level. Selected bond distances [pm]: Zr(1)−Cl(1) 242.9, Zr(1)−Cl(2) 242.9, Zr(1)−TPCp(centroid) 227.4, Zr(1)−Cp(centroid) 221.4; bond angles [°]: Cl(1)−Zr(1)−Cl(2) 95.2, TPCp(centroid)−Zr(1)−Cp(centroid) 124.6; torsion angles [°]: C(1)−C(2)−C(21)−C(22) −135.9, C(2)−C(3)−C(31)−C(32) −141.5, C(3)−C(4)−C(41)−C(42) −135.4, C(4)−C(5)−C(51)−C(52) −79.4

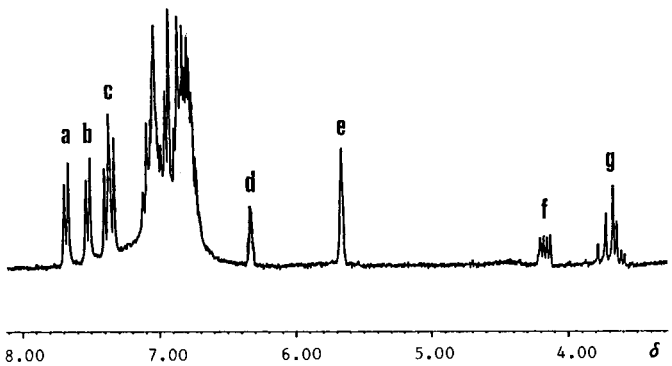


Figure 2. ^{1}H-NMR spectrum of complex **7a** in [D_8]toluene at room temperature

The ethylene bridge with the stereogenic carbon center forces the Cp fragments in a staggered conformation. Figure 1 shows the backbone phenyl group in an equatorial position of the metallacycle.

In solution the bridge is expected to flip between the λ- and δ-conformation[12], allowing both Cp fragments to twist relative to each other around their Cp(centroid)−Zr bonds. However, the conformation of the metallacycle in the solid state might also be preferred in solution.

The ^{1}H-NMR spectrum of **7a** (Figure 2) consists of two doublets (a, b) and a triplet (c) with relative areas of 2:2:4. At lower temperature c splits into two doublets as expected. These peaks are assigned to the *ortho* protons of the four C_5Ph_4-phenyl substituents according to an integration of the spectrum and by a comparison with previous work on bis(tetraphenylcyclopentadienyl)titanium dichloride[13]. The multiplets d, e belong to the Cp fragment and f, g to an ABX-spin system, arising from the protons of the ethylene bridge. Multiplett g can be assigned to the diastereotopic protons of the methylene group (AB part) and f to the methine proton (X part).

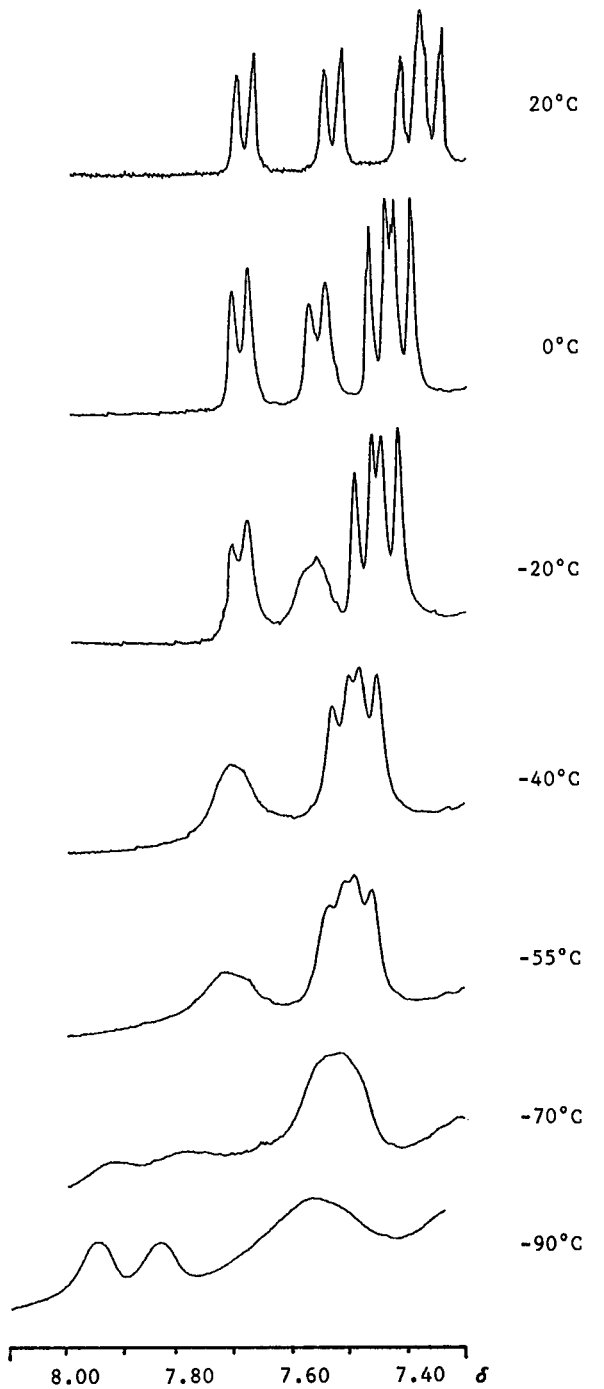


Figure 3. Variable-temperature NMR of the *ortho* proton region of complex **7a**

These assignments imply that the phenyl groups rotate rapidly on the NMR time scale. The *ortho* protons of each C_5Ph_4-phenyl substituent are equivalent.

In analogy to work based on bis(tetraphenylcyclopentadienyl)titanium dichloride[13a] the well-resolved resonances can be used to study the temperature-dependent phenyl ring rotations. In Figure 3 several ^{1}H-NMR spectra of the *ortho* proton region are displayed between 20 and −90°C. At −20°C doublets a and b begin to recede. Between −40 and −60°C a and b disappear suggesting that the two crowded phenyl rings 3 and 4 freeze out in a conformation where the *ortho* protons become inequivalent, one pointing inside and one outside the sandwich. The sterically less hindered rings 2 and 5 start to freeze at −40°C. Comparable temperatures for a slowed phenyl group rotation were found for bis(tetraphenylcyclopentadienyl)titanium dichloride[13a] and bis(tetraphenylcyclopentadienyl)iron(II)[13b].

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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. Tetraphenylcyclopentadiene[14], $ZrCl_4(thf)_2$[15], an NaCp · dioxane[16] were prepared by literature procedures.

NMR: AC 250 spectrometer. Standards: internal TMS. – MS: Finnigan MAT-711A, modified by AMD Intectra (FD, FAB) and Finnigan TSQ70 (EI, FAB), 70 eV. – X-ray structure determination: Siemens P4 diffractometer, SHELXTL-PC program for structure solution and refinement. – Elemental analyses: Microanalytical laboratory of the Institute (Carlo Erba, Model 1106).

2-Phenyl-2-(tetraphenylcyclopentadienyl)ethanol (**3a**): *n*-Butyllithium (30.4 ml, 1.6 M in hexane) was added to a suspension of tetraphenylcyclopentadiene (18.0 g, 48.6 mmol) in 200 ml of diethyl ether at 0°C. A colorless solid precipitated. Epoxystyrene (5.6 ml, 48.6 mmol) was slowly dropped to the suspension, keeping the temp. at 0°C. After stirring overnight the yellow reaction mixture was heated to reflux for 2 h. Then 200 ml of a saturated NH_4Cl/H_2O solution was added. The organic layer was separated and the aqueous phase washed twice with ether. The combined organic phases were dried with Na_2SO_4. Evaporation of the solvent gave a 3:1 mixture of **3a** and **4a** as a colorless solid (23.1 g, 47.1 mmol, 97%). Recrystallization from hot toluene/hexane (2:3) resulted in the crystallization of pure **3a** (11.4 g, 23.2 mmol, 49%), m.p. 146–147°C. – ^{1}H NMR ($CDCl_3$): δ = 3.43 (dt, *J* = 7.9/3.1 Hz, 1H, CH_{bridge}), 3.60–3.85 (m, 2H, CH_2), 4.91 (d, *J* = 3.1 Hz, 1H, $CH_{C_5Ph_4}$), 6.6–7.4 (m, 25H, aromatic H). – EI-MS (120°C), *m/z*: 490.3 [M^+], 472.2 [$M^+ - H_2O$].

$C_{37}H_{30}O$ (490.6) Calcd. C 90.57 H 6.17
Found C 90.62 H 6.15

1-Phenyl-2-(tetraphenylcyclopentadienyl)ethanol (**4a**) (5.0 g) was separated by column chromatography over silica (1 m high, 3 cm diameter, eluent: toluene/hexane, 7:3) from a 1:1 mixture of **3a** and **4a** (10.0 g). The first fraction contained **4a**, m.p. 154–156°C. – ^{1}H NMR ($CDCl_3$): δ = 3.91 (m, 1H, CH_{bridge}), 2.60–3.00 (m, 2H,

CH_2), 4.62 (dd, J = 5.3/2.5 Hz, 2H, $CH_{C_5Ph_4}$), 6.5–7.4 (m, 25H, aromatic H). – EI-MS (120°C), *m/z*: 490.3 [M^+], 472.2 [$M^+ - H_2O$].

$C_{37}H_{30}O$ (490.6) Calcd. C 90.57 H 6.17
Found C 90.62 H 6.15

2-(9-Fluorenyl)-2-phenylethanol (**3b**): The synthesis of **3b** was performed according to the route used for the preparation of **3a**. Starting from 20.0 g (120 mmol) of fluorene in 200 ml of diisopropyl ether, we obtained **3b** in 49% (16.8 g) yield after recrystallization, m.p. 96–97°C. – ^{1}H NMR ($CDCl_3$): δ = 3.46 (dt, J = 8.2/5.6 Hz, 1H, CH_{bridge}), 3.8–4.0 (m, 2H, CH_2), 4.33 (d, J = 5.6 Hz, 1H, CH_{Flu}), 7.0–7.6 (m, 25H, aromatic H). – EI-MS (120°C), *m/z*: 285.1 [M^+], 267.1 [$M^+ - H_2O$].

$C_{21}H_{18}O$ (286.4) Calcd. C 88.08 H 6.34
Found C 88.17 H 6.25

2-(9-Fluorenyl)-1-phenylethanol (**4b**) (5 g) was also separated by column chromatography over silica (eluent: toluene/hexane, 2:3) from a 1:1 mixture (10.0 g) of **3b** and **4b**. The first fraction contained **4b**, m.p. 106–107°C. – ^{1}H NMR ($CDCl_3$): δ = 4.23 (dd, J = 5.1/7.9, 1H, CH_{bridge}), 2 diastereotopic protons: 2.11 (ddd, J = 4.1/7.9/15.2 Hz, 1H, CH_2), 2.56 (ddd, J = 5.1/9.3/15.2 Hz, 1H, CH_2), 4.91 (dd, J = 9.3/4.1 Hz, 1H, CH_{Flu}), 7.2–7.8 (m, 13H, aromatic H). – EI-MS (120°C), *m/z*: 285.4 [M^+], 267.5 [$M^+ - H_2O$].

$C_{21}H_{17}O$ (285.4) Calcd. C 88.37 H 6.00
Found C 88.43 H 5.98

2-Phenyl-2-(tetraphenylcyclopentadienyl)ethyl Trifluoromethanesulfonate (**5a**): Trifluoromethanesulfonic anhydride (2.61 ml, 15.9 mmol) was added to a solution of **3a** (7.8 g, 15.9 mmol) and pyridine (1.29 ml, 15.9 mmol) in CH_2Cl_2 (75 ml) at 0°C. The reaction mixture was stirred for 15 min. The organic layer was washed with ice/water (four times) and dried with Na_2SO_4. Evaporation of the solvent at 0°C gave 8.7 g (14.0 mmol, 88%) of **5a** as a colorless solid. – ^{1}H NMR: ($CDCl_3$): δ = 3.67 (dt, J = 2.5/8.0 Hz, 1H, CH_{bridge}), 2 diastereotopic protons: 4.48 (m, 1H, CH_2), 4.68 (m, 1H, CH_2), 4.87 (d, J = 2.5 Hz, 1H, CH_{Flu}), 6.6–7.3 (m, 25H, aromatic H).

$C_{38}H_{29}F_3O_3S$ (622.7) Calcd. C 73.29 H 4.69
Found C 72.98 H 4.31

2-(9-Fluorenyl)-2-phenylethyl Trifluormethanesulfonate (**5b**): The synthesis of **5b** was carried out according to the route used for the preparation of **5a**. Starting from 9.5 g (33.3 mmol) of **3b**, we obtained **5b** in 84% (11.7 g, 28 mmol) yield as slightly yellow solid. **5b** decomposed rapidly at temperatures above 0°C. No satisfying analytical results could be obtained. **5b** was used for the preparation of **6b** without isolation.

1-Cyclopentadienyl-1-phenyl-2-(tetraphenylcyclopentadienyl)ethane (**6a**): **5a** (7.7 g, 12.4 mmol) was suspended in dry DMF (100 ml, –20°C), and a colorless solution of NaCp · dioxane (3.3 g, 18.6 mmol) in 30 ml of DMF (0°C) was added. The color changed instantly from pale yellow to dark red, and a homogeneous solution formed. The solvent was evaporated after stirring at –20°C for 3 d, and the brownish residue was dissolved in 200 ml of a saturated NH_4Cl/H_2O solution and 200 ml of diethyl ether. The ether layer was decanted and the aqueous phase washed twice with diethyl ether. The combined organic phases were dried with Na_2SO_4, and the solvent was evaporated, giving crude **6a** as a pale yellow powder (6.58 g). Pure **6a** resulted from chromatography over silica (eluent: toluene/hexane, 2:3). Yield 5.3 g (10.4 mmol, 65%)[17]. The ^{1}H-NMR spectra of **6a** gave no reasonable structural information due to double bond tautomerism of the Cp unit. The ligands were characterized by NMR after preparation of the zirconium complexes. – FD-MS (CH_2Cl_2), *m/z* (%): 538.7 (100) [M^+].

$C_{42}H_{34}$ (538.7) Calcd. C 93.64 H 6.36
Found C 93.73 H 6.28

Table 1. Atomic coordinates (· 10^4) and equivalent isotropic thermal parameters (· 10^3 Å^2) of *rac*-**7a**; [C(7A) and C(7B) refer to a resolved disorder of the ethylene bridge of the second molecule]

	x	y	z	U_{eq}
Zr(1)	1745(8)	8921(9)	4903(9)	31(1)
Cl(1)	87(4)	8572(9)	6010(5)	52(2)
Cl(2)	-381(6)	9129(9)	3278(5)	56(2)
C(1)	4486(82)	8739(6)	4639(86)	29(3)
C(2)	3566(79)	8812(6)	3344(84)	42(4)
C(3)	2410(81)	8550(6)	3072(86)	32(4)
C(4)	2563(82)	8316(7)	4060(87)	27(3)
C(5)	3836(82)	8436(6)	5072(87)	29(4)
C(6)	5844(83)	8954(6)	5392(88)	32(3)
C(7)	5394(80)	9067(6)	6639(85)	43(4)
C(8)	3789(79)	9243(6)	6363(84)	38(4)
C(9)	2531(18)	9187(6)	7061(85)	38(4)
C(10)	1303(80)	9401(6)	6351(86)	39(4)
C(11)	1717(79)	9571(6)	5420(84)	41(4)
C(12)	3241(81)	9473(6)	5373(86)	32(4)
C(22)	2861(89)	9308(7)	1793(90)	39(4)
C(23)	3252	9526	855	54(5)
C(24)	4770	9522	599	80(7)
C(25)	5897	9301	1281	72(6)
C(26)	5507	9084	2220	71(6)
C(21)	3989	9088	2476	35(4)
C(32)	-150(12)	8414(7)	1648(1)	39(4)
C(33)	-1034	8347	452	62(5)
C(34)	-338	8368	-618	54(5)
C(35)	1242	8456	-490	51(5)
C(36)	2126	8523	708	50(5)
C(31)	1431	8502	1777	39(4)
C(42)	1120(82)	7821(7)	4966(89)	71(6)
C(43)	617	7475	4916	103(8)
C(44)	862	7260	3921	77(6)
C(45)	1610	7392	2978	105(9)
C(46)	2114	7739	3029	92(8)
C(41)	1869	7954	4024	41(4)
C(52)	3958(85)	8158(6)	7254(87)	84(7)
C(53)	4752	7949	8227	88(8)
C(54)	6181	7797	8115	81(7)
C(55)	6817	7856	7031	75(6)
C(56)	6024	8066	6060	52(5)
C(51)	4595	8218	6172	41(4)
C(62)	6465(88)	9642(7)	7694(89)	55(5)
C(63)	7559	9821	8587	73(6)
C(64)	8857	9644	9256	52(4)
C(65)	9061	9289	9032	70(6)
C(66)	7968	9112	8140	64(5)
C(61)	6670	9289	7472	30(4)
Zr(2)	289(2)	885	2011(1)	33(1)
Cl(3)	-1844(6)	638(1)	496(5)	56(2)
Cl(4)	-1445(5)	1217(2)	3100(4)	56(2)
C(1A)	2907(19)	1082(4)	1545(14)	34(4)
C(2A)	2165(19)	1399(4)	2025(14)	32(4)
C(3A)	844(18)	1502(4)	1111(13)	28(3)
C(4A)	728(20)	1247(4)	75(15)	40(4)
C(5A)	2012(18)	1002(3)	394(14)	30(4)
C(6A)	4331(19)	895(5)	2226(14)	43(4)
C(7A)	4039(38)	732(8)	3427(28)	34(7)
C(7B)	4179(37)	546(7)	2630(28)	34(7)
C(8A)	2530(27)	548(5)	3279(20)	64(6)
C(9A)	1601(33)	644(7)	4078(26)	92(8)
C(10A)	200(31)	465(6)	3835(23)	79(7)
C(11A)	270(32)	275(7)	2868(24)	82(7)
C(12A)	1627(26)	313(5)	2422(20)	60(5)
C(22A)	2302(14)	1669(4)	4174(14)	84(7)
C(23A)	3056	1881	5156	106(9)
C(24A)	4513	2027	5095	79(7)
C(25A)	5216	1960	4051	61(5)
C(26A)	4462	1748	3069	57(5)
C(21A)	3005	1602	3131	39(4)
C(32A)	-689(26)	1949(5)	2043(16)	169(16)
C(33A)	-1293	2287	2017	240(28)
C(34A)	-1098	2515	1047	82(7)
C(35A)	-298	2406	102	95(8)
C(36A)	307	2068	128	87(7)
C(31A)	111	1839	1098	47(4)
C(42A)	-1962(13)	1352(3)	-1218(9)	60(5)
C(43A)	-2952	1396	-2388	61(5)
C(44A)	-2352	1372	-3504	60(5)
C(45A)	-763	1304	-3451	63(5)
C(46A)	226	1261	-2281	40(4)
C(41A)	-373	1285	-1165	37(4)
C(52A)	1323(12)	484(3)	-1148(11)	42(4)
C(53A)	1726	271	-2092	63(5)
C(54A)	3199	302	-2423	74(6)
C(55A)	4269	546	-1812	85(7)
C(56A)	3866	760	-869	54(5)
C(51A)	2393	728	-537	43(4)
C(62A)	5797(18)	126(4)	3413(11)	91(7)
C(63A)	6928	-84	4147	69(6)
C(64A)	7685	31	5336	63(5)
C(65A)	7312	355	5791	75(6)
C(66A)	6182	565	5058	75(6)
C(61A)	5424	451	3869	92(7)
O(1)	4201(29)	2477(6)	8502(22)	121(7)
C(85)	4476(64)	1848(12)	9488(49)	199(23)
C(86)	3729(52)	2210(11)	8522(45)	176(16)
C(87)	3663(79)	2680(11)	7835(60)	274(33)
C(88)	3980(25)	3129(5)	7539(19)	60(5)

1-Cyclopentadienyl-2-(9-fluorenyl)-1-phenylethane (**6b**): Synthesis and characterization of **6b** were performed according to the route used for the preparation of **6a**. Starting from 19.8 g (47.3 mmol) of **5b**, we obtained solid **6b** in 68% (10.4 g, 32.1 mmol) yield after chromatography. – FD-MS (CH_2Cl_2), *m/z* (%): 334.4 (100) [M^+].

$C_{26}H_{22}$ (334.4) Calcd. C 93.37 H 6.63
Found C 93.45 H 6.52

rac-[1-(η^5-Cyclopentadienyl)-1-phenyl-2-(tetraphenyl-η^5-cyclopentadienyl)ethane]zirconium Dichloride (**7a**): **6a** (5.0 g, 9.3 mmol) was deprotonated in 50 ml of THF with two equivalents of *n*-butyllithium (11.6 ml, 1.6 M in hexane) at 0°C. Solid $ZrCl_4(thf)_2$ (3.51 g, 9.3 mmol) was added to the slightly yellow solution, which was then heated under reflux for 3 h. The solvent was removed in vacuo and the residue suspended in 50 ml of dichloromethane. The suspension was filtered over Celite, and the volume of the resulting dark brown solution was reduced to 25 ml. Then 20 ml of diethyl ether were added. Crystallization at −30°C gave **7a** as pale yellow needles (2.9 g, 4.2 mmol, 45%). – ^{1}H NMR (C_6D_6): δ = 4.26 (dd, *J* = 6.0/12.7 Hz, 1H, CH_{bridge}), 3.7–3.9 (m, 2H, CH_2), 5.6–5.7 (m, 2H, CH_{Cp}), 6.37–6.38 (m, 1H, CH_{Cp}), 6.7–7.8 (m, 26H, aromatic H). – FAB-MS (NBA), *m/z*: 698.2 [M^+], 663.2 [M^+ – Cl].

$C_{42}H_{32}Cl_2Zr \cdot 0.5(C_2H_5)_2O$ (735.9)
Calcd. C 71.81 H 5.07 Cl 9.64
Found C 72.08 H 5.16 Cl 9.51

rac-[1-(η^5-Cyclopentadienyl)-1-phenyl-2-(η^5-9-fluorenyl)ethane]zirconium Dichloride (**7b**): **6b** (3.0 g, 9.0 mmol) was deprotonated with two equivalents of *n*-butyllithium (11.3 ml, 1 M in hexane) in 50 ml of THF at 0°C. The solvent was removed in vacuo and the yellow solid residue dissolved in 50 ml of CH_2Cl_2. Then $ZrCl_4$ (2.1 g, 9 mmol) was added at 0°C, and the suspension was stirred overnight. The orange yellow solution was filtered over Celite, and the volume of the filtrate was reduced to 25 ml. Then 10 ml of hexane was added. A grey solid precipitated which was filtered off. From the clear yellow solution microcrystalline orange **7b** (2.1 g, 4.3 mmol, 48%) crystallized at −30°C. – ^{1}H NMR ($CDCl_3$): δ = 5.61 (dd, *J* = 5.7/5.8 Hz, 1H, CH_{bridge}), 2 diastereotopic protons: 4.12 (dd, *J* = 13.4/14.0, 1H, CH_2), 3.87 (dd, *J* = 7.3/14.0, 1H, CH_2), CH_{Cp}: 5.74, 6.03, 6.16, 6.47 (m, 1H each), 7.0–8.1 (m, 13H, aromatic H). – FAB-MS (NBA), *m/z*: 494.4 [M^+], 459.1 [M^+ – Cl].

$C_{26}H_{20}Cl_2Zr$ (494.5) Calcd. C 63.14 H 4.08 Cl 14.34
Found C 63.25 H 4.00 Cl 14.11

X-ray Structure Determination: The sample was mounted on a glass fiber. Graphite-monochromated Mo-K_α radiation was used. Cell parameters were determined from the setting angles of 17 high-angle centered reflections. Data collection was performed at −100°C by using Wyckoff scans with scan speeds varying from 10 to 30°/min in ω. 2 check reflections were monitored after every 58 intensity measurements. The structure was solved by Patterson synthesis. Calculations used full-matrix least squares methods. Zr and Cl atoms were described anisotropically. Hydrogen atoms were included in the final refinement with fixed U_i. Phenyls were treated as rigid groups. Atomic coordinates and equivalent isotropic factors are summarized in Table 1[18].

7a: Single crystals were grown from CH_2Cl_2/diethyl ether solution, formula: $C_{42}H_{32}Cl_2Zr \cdot 0.5\ (C_2H_5)_2O$ (735.9), crystal size: 0.25 × 0.4 × 0.5 mm^3, *a* = 868.4(4), *b* = 3828(2), *c* = 1073.9(6) pm, β = 100.61(4)°, *V* = 3.510(3) nm^3, monoclinic space group $P2_1$ (No. 4), *F*(000) = 1500. ϱ_{calc} = 1.458 g · cm^{-3}, *U* = 0.50 mm^{-1}; 2Θ = 4–45 in ±*h*, ±*k*, ±*l*, max./min. transmissions 0.593/0.521. L_p and absorption corrections (ψ scan) were applied, 16000 reflections measured, 9207 unique and 6046 considered observed [$F > 4\sigma(F)$], 294 variables, *R* = 0.0876, R_w = 0.1070, *g* = 0.0008. – The compound crystallizes as a solvate with one molecule diethyl ether for the two independent enantiomeric molecules of **7a**. The thermal parameters of the second independent molecule indicate disorder in the phenyl substituent of the ethylene bridge. Calculation with a split model did not improve the result.

[1] X-ray structure determination.
[2] Cf. J. Okuda, *Angew. Chem.* **1992**, *104*, 49; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 47.
[3] [3a] J. A. Ewen, R. L. Jones, A. Razavi, J. D. Ferrara, *J. Am. Chem. Soc.* **1988**, *110*, 6255. – [3b] D. T. Mallin, M. D. Rausch, Y. G. Lin, J. C. W. Chien, *J. Am. Chem. Soc.* **1990**, *112*, 2030. – [3c] G. S. Herrmann, H. G. Alt, M. D. Rausch, *J. Organomet. Chem.* **1991**, *401*, C5.
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[6] B. Rieger, *J. Organomet. Chem.* **1991**, *420*, C17. Only one enantiomer of **2** is shown.
[7] If the methanesulfonic acid derivatives are used instead, no dicyclopentadiene product could be isolated. The corresponding spirocyclopropyl compounds are formed quantitatively by intramolecular replacement of the mesyl group by the fluorenyl substituent.
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[10] The anchimeric effect of the phenyl group can be used to introduce even a second C_5Ph_4 group. 1-Phenyl-1,2-bis(tetraphenylcyclopentadienyl)ethane was prepared in quantitative yield by starting from **5a**.
[11] The phenyl groups are numbered with respect to their corresponding Cp carbons.
[12] For the nomenclature of chiral chelates compare: *IUPAC-Bulletin* **1968**, *33*, 68.
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[17] Two fractions can be separated which are both converted into complex **7a** by deprotonation and subsequent reaction with $ZrCl_4(thf)_2$.
[18] Further details on the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56275, the names of the authors, and the journal citation.

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CAS Registry Numbers

3a: 143007-34-5 / **3b**: 143007-30-1 / **4a**: 143007-36-7 / **4b**: 143007-31-2 / **5a**: 143007-38-9 / **5b**: 143007-32-3 / **6a**: 143007-40-3 / **6b**: 143007-41-4 / **7a**: 143007-42-5 / **7a** · 0.5 $(C_2H_5)_2O$: 143007-44-7 / **7b**: 143007-43-6 / tetraphenylcyclopentadiene: 15570-45-3 / epoxystyrene: 96-09-3 / fluorene: 86-73-7 / $ZrCl_4$ $(thf)_2$: 21959-01-3 / cyclopentadienylsodium: 4984-82-1