Synthesis of Enantiomerically Pure Ethylene-Bridged *ansa*-Zirconocene and -Hafnocene Complexes Bearing Fluorenyl, Indenyl, Octahydrofluorenyl, and Tetrahydroindenyl Ligands[1]

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We report on an efficient synthetic route for the preparation of enantiomerically pure ethylene-bridged *ansa*-zirconocene and -hafnocene complexes, bearing different cyclopentadienyl fragments. Ring opening of (*R*)-epoxystyrene (**1**) with fluorenyllithium proceeds enantiospecifically and leads to optically pure 2-(9-fluorenyl)-1-(*S*)-phenylethanol (**2a**) and 2-(9-fluorenyl)-2-(*S*)-phenylethanol (**2b**) in nearly quantitative yield. Treatment of **5**, the trifluoromethanesulfonate derivative of **2b**, with fluorenyl- and indenyllithium results in the formation of 1-(9-fluorenyl)-1-(*S*)-phenyl-2-(1-indenyl)ethane (**6a**) and 1,2-bis(9-fluorenyl)-1-(*S*)-phenylethane (**6b**), respectively. Reaction of the dilithio salts of **6a** with $ZrCl_4$ and of **6b** with MCl_4 (M = Zr, Hf) affords the formation of the enantiomerically pure complexes [1-(η^5-9-fluorenyl)-1-(*R*)-phenyl-2-(η^5-1-(*R*,*S*)-indenyl)ethane]$ZrCl_2$ (**7a** = *R*,*R*; **7b** = *R*,*S*) and of [1,2-bis(η^5-9-fluorenyl)-1-(*R*)-phenylethane]MCl_2 (**7c**, M = Zr; **7d**, M = Hf) in up to 63% yield. Hydrogenation of **7a**−**d** with H_2/PtO_2 gives the complexes **8a**−**d**, bearing octahydrofluorenyl and tetrahydroindenyl ligands. Hydrolysis of **8a**,**b** in basic, aqueous media leads to the formation of C_2-symmetric μ-oxo dimers (**12a**,**b**). The solid-state structures of enantiomerically pure **7b** and **8c** and of **12b** are reported.

Introduction

Racemic *ansa*-metallocene dichlorides are well-known as catalysts for olefin polymerization.[3] The ability of their lanthanide homologues to polymerize even polar monomers, such as methyl methacrylate, by a group transfer mechanism is currently a topic of several research programs.[4] Pure enantiomers of such *ansa*-metallocene complexes[5] have found application in asymmetric cyclopolymerization[6] and are known as enantioselective catalysts for hydrogenation of olefins[7] and imines,[8] for asymmetric oligomerization of olefins,[9] and for an induction of optical activity in Diels−Alder products.[10] Most of the applied catalyst systems have to be isolated by separation from their racemic mixtures via diastereomeric derivatization. For either the *R* or *S* diastereoisomer of [ethylenebis(4,5,6,7-tetrahydroindenyl)]$ZrCl_2$ the separation procedure is well-established,[11] but it has to be adopted for each new racemic metallocene structure. In addition, this synthetic approach requires the preceding separation of undesired *meso* isomers and is, in most of the cases, not suitable for non-hydrogenated fluorenyl and indenyl complexes. Recently, several different strategies have been published for the direct preparation of enantiomerically pure *ansa*-metallocene dichlorides.[12] We report here on a convenient synthesis of enantiomerically pure zirconocene and hafnocene dichlorides, bearing indenyl and fluorenyl as well as tetrahydroindenyl and octahydrofluorenyl ligands.

Results and Discussion

Ligand Formation.[13] A convenient, large-scale synthesis of enantiomerically pure ethylene-bridged ligand precursors of the type $Cp_1CH(Ph)CH_2Cp_2$ (Cp_1 = Flu, Cp_2 = Ind, Flu) is outlined in Scheme 1. Ring opening of (*R*)-epoxystyrene (**1**) by fluorenyllithium in diisopropyl ether affords the formation of the secondary

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(1) Dedicated to Professor Dr. Gottfried Huttner on the occasion of his 60th birthday.

(2) X-ray diffraction studies, Institut für Anorganische Chemie, Universität Tübingen.

(3) Cf.: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255 and literature cited therein.

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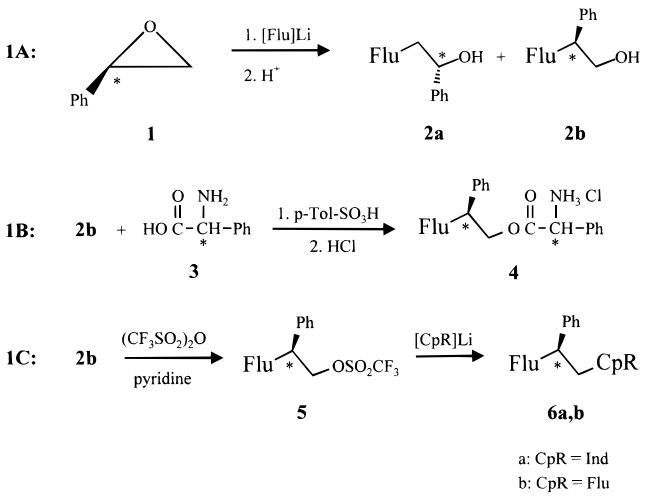
Scheme 1



and primary alcohols **2a** and **2b** (1:3 ratio, Scheme 1A) in 96% yield. **2b** crystallizes in pure form from toluene/hexane, leaving a 1:1 mixture of both alcohols in solution. A quantitative separation can be achieved by column chromatography. In order to determine the enantiospecificity of the ring-opening reaction, **2b** was converted to the ester **4** (1B) by use of the chiral auxiliary (*R*)-α-aminophenylacetic acid (**3**). In the ^{1}H NMR spectrum of **4** only one set of resonances could be detected, indicating the presence of a single diastereoisomer.[14,15]

Ligand formation is completed by converting **2b** into the triflate derivative **5**, followed by the addition of a second cyclopentadienyl fragment (Scheme 1C). With fluorenyl- or indenyllithium the ligand precursors **6a**,**b** are formed in 78 and 85% isolated yields, respectively.

Complexes. Preparation of the metallocene dichlorides **7a**,**b** was accomplished by the reaction of the dilithio salt of **6a** in dichloromethane at −78 °C with $ZrCl_4$ (Scheme 2). The coordination of **6a** leads to the formation of two optically pure diastereoisomers (**7a**,**b**), due to the two different enantiofacial orientations of the indenyl moiety. The isomers **7a**,**b** are obtained as a 1:3 mixture, from which **7b** can be isolated by crystallization. All attempts to separate **7a** from the remaining 1:1 mixture failed.

The fluorenyl and indenyl ligands in **7a**,**b** are readily hydrogenated by H_2/PtO_2 to give the octahydrofluorenyltetrahydroindenyl derivatives **8a**,**b** in high yield. Reaction of **8a**,**b** with pyridine-2,6-dicarboxylic acid, according to a procedure recently reported by Brintzinger et al.,[16] affords the formation of the pyridine carboxylates **9a**,**b**. Also here no separation of the diastereoisomers could be achieved, either by crystallization or by column chromatography. The latter resulted in decomposition of the complexes, and the new ligand precursor **13** was eluted as the only product. **13** is also liberated from a mixture of **8a**,**b** by simple hydrolysis in a basic, aqueous medium. Under mild conditions the μ-oxo dimers **12a**,**b** are formed as stable compounds. A reasonable mechanism involves exchange of the chlorides by hydroxyl groups[17] followed by extrusion of water on the sterically less hindered side.[18] An X-ray structure investigation and a NMR study showed that the two C_2-symmetric complexes **12a**,**b** are formed exclusively, where the oxo bridge connects two identical isomers (**a**,**a** or **b**,**b**). The third possibility, an unsymmetric combination of **8a** and **8b**, could not be detected, probably due to steric effects (see below).

Treatment of the dichloro complexes **7a**,**b** and **8a**,**b** with methyllithium in diethyl ether resulted in the dimethyl- and monomethyl compounds **10a**,**b** and **11a**,**b**, respectively. The monomethylation in case of **8a**,**b** underlines the increased steric demand of the hydrogenated Cp-ring substituents.[19] From **10a**,**b** the enantiomerically pure isomer **10a** can be isolated by crystallization from hexane in good yield.

For the formation of **7c**,**d** the dilithio salt of **6b** was treated with MCl_4 (**c**, M = Zr; **d**, M = Hf) in toluene at −78 °C (Scheme 3). Only one enantiomerically pure bis(fluorenyl) complex exists for either **7c** or **7d**, which can be isolated in moderate to good yield (**7c**, 27.9%; **7d**, 63.1%). Purification is performed by crystallization from toluene. Compounds **7c**,**d** are also converted into the corresponding bis(octahydrofluorenyl) complexes **8c**,**d**, as described above.

Solid-State Structures. The crystal structures of enantiomerically pure **7b**, **8c**, and **12b** were determined by X-ray diffraction (Figure 1, Tables 1−3). All single enantiomers show the expected *R* configuration of the stereogenic backbone center,[20] which forces the bridge into the δ conformation.[21] This, together with the stereochemistry of the indenyl coordination, leads to the formation of one δ-backward and one δ-forward isomer in the case of the enantiomerically pure fluorenyl−indenyl complexes.[22] The solid-state structure of the δ-backward isomer **7b** is depicted in Figure 1.

In contrast to the recently published structures of C_s-symmetric and hence achiral dimethylsilane-bridged bis(fluorenyl) complexes,[23] the present ethylene-bridged bis(fluorenyl) (**7c**,**d**) and bis(octahydrofluorenyl) complexes (**8c**,**d**) are chiral, due to the stereogenic carbon

(13) Synthesis, characterization, and polymerization properties of the racemic ligands and complexes have been reported before: (a) Rieger, B.; Jany, G.; Fawzi, R.; Steimann, M. *Organometallics* **1994**, *13*, 647. (b) Rieger, B. *Polym. Bull.* **1994**, *32*, 41. Cf. also: (c) Guerra, G.; Cavallo, L.; Moscardi, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1996**, *29*, 4834. For a communication of preliminary results concerning the enantiomerically pure compounds, cf.: (d) Rieger, B.; Jany, G. *Chem. Ber.* **1994**, *127*, 2417.

(14) By the use of racemic **2b** two sets of resonance signals appear in the ^{1}H NMR spectrum. All peaks could be assigned to the corresponding protons by ^{1}H/^{1}H COSY NMR experiments.

(15) 2-(9-Fluorenyl)-2-(*R*)-phenylethanol (**2b***) is accessible by starting from (*S*)-epoxystyrene. **2b***: mp 90.9 °C; $[\alpha]^{20}_D = -25.5°$ ($c = 1.50$, toluene).

(16) Niemann, U.; Diebold, J.; Troll, C.; Rief, U.; Brintzinger, H. H. *J. Organomet. Chem.* **1993**, *456*, 195.

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(19) Monomethylation corresponds to the observation that derivatization of **8a**,**b** into a disubstituted diastereomeric acetyl (*R*)-mandelate to verify the optical purity failed, because of the high steric demand of the condensed cyclohexyl rings.

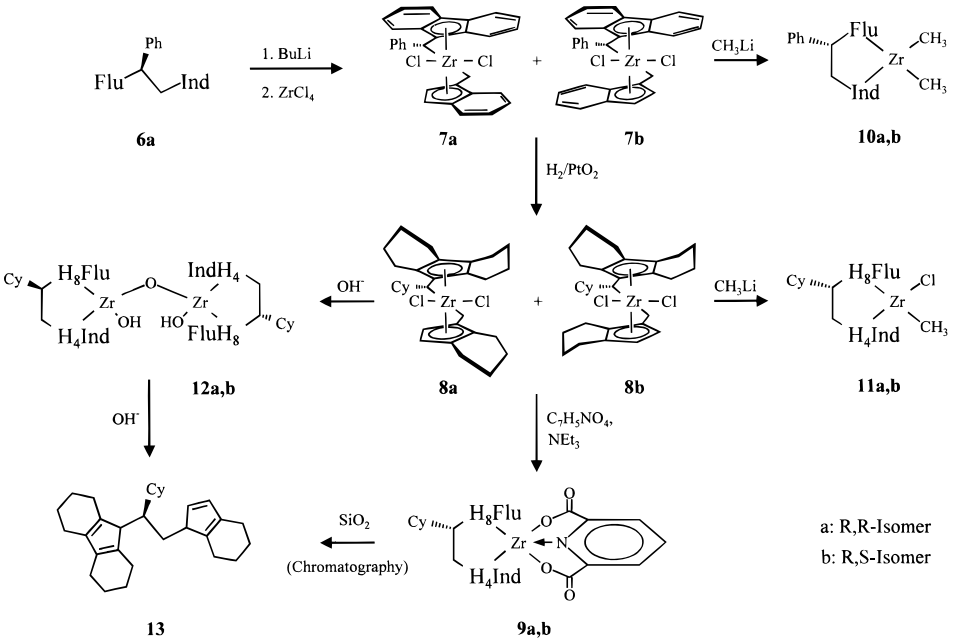
(20) The change from absolute *S* to *R* configuration of the stereogenic backbone center during the conversion of ligands **6a**,**b** to complexes **7a**−**d** is due to a change in the priority of the carbon substituents according to the CIP rules. It is not caused by a chemically induced inversion of the chirality of this particular carbon atom.

(21) For a discussion of different conformations of metallacycles in ethylene-bridged complexes and for a definition of the nomenclature, cf. ref 13a and literature cited therein.

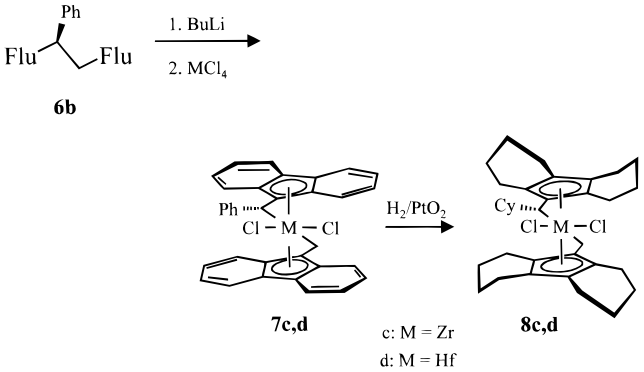
(22) In racemic complexes of this type each diastereoisomer consists of a pair of enantiomers (δ-forward/λ-backward and δ-backward/λ-forward, respectively), due to the four combinatorial possibilities of a stereogenic backbone atom and the two different coordination modes of the indenyl moiety.

(23) (a) Chen, Y. X.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1995**, *497*, 1. (b) Resconi, L.; Jones, R. L.; Rheingold, A. L. *Organometallics* **1996**, *15*, 998.

Scheme 2



Scheme 3



atom in the backbone unit. Since this center originates from optically active (*R*)-epoxystyrene, **7c**,**d** and **8c**,**d** exist as pure enantiomers. The solid-state structure of **8c** (Figure 1) shows the twisted bridge in the expected δ conformation, which pushes the Cp rings of the octahydrofluorenyl ligands into a staggered arrangement, so that a chiral cage around the Cl−Zr−Cl plane is opened by the forward-oriented β-CH_2 substituents C_8 and C_{21}.[24]

Hydrogenation of the indenyl and fluorenyl fragments to give cyclohexyl-substituted Cp-ligands results in an increased steric demand of the tetrahydroindenyl (^{H}Ind) and octahydrofluorenyl (^{H}Flu) complexes, indicated by a significant increase of Zr−Cl bond lengths after hydrogenation (Table 2). The asymmetry of the mixed-ligand system **7b** leads to a slight elongation of the Zr−Cl(1) bond, which points into the open quadrant (Zr−Cl(1), 2.418 Å; Zr−Cl(2), 2.410 Å). Interestingly, the Zr−Ind(centroid) and Zr−^{H}Flu2(centroid) distances of **7b** (2.217 Å) and **8c** (2.228 Å) are comparable, whereas the Zr−^{H}Flu1(centroid) bond (2.237 Å) of **8c** is notably shortened compared to the corresponding Zr−Flu(centroid) distance (2.275 Å) of **7b**.[25]

(24) The chiral arrangement of two fluorenyl units, introduced by a substituted ethylene bridge, was recently demonstrated by the production of isotactic polypropene ([mmmm] up to 63%) with the racemic analogue of **7c**.[13b]

Hydrolysis of a 1:1 mixture of **8a**,**b** in basic aqueous media results in the formation of the two oxo-bridged dimers **12a**,**b**. The structure of **12b** consists of two **8b** ("backward") isomers (Figure 1) which are related by a C_2 symmetry axis through O(1). Only one oxo bridge is formed on the sterically less hindered side, so that each Zr atom still carries an OH group. The condensation of the two OH ligands to give a second oxo bridge is hindered by the high steric demand of the hydrogenated indenyl and fluorenyl groups. The shielding influence of these ligands is also indicated by an elongation of the Zr(1)−O(1)−Zr(2) bonds (Zr(1)−O(1), 1.991 Å; Zr(2)−O(1), 1.989 Å) in comparison with literature values of known species (Zr−O−Zr, ∼1.95 Å).[26]

Experimental Section

All reactions were carried out under a dry argon atmosphere by using standard Schlenk tube techniques. The hydrocarbon and ether solvents were purified by distillation from $LiAlH_4$. CH_2Cl_2 and pyridine were distilled from CaH_2 and dioxane from sodium. $(CF_3SO_2)_2O$[27] and compound **4**[13d] were prepared according to literature procedures. ^{1}H NMR spectra were recorded on Bruker AC 250 and Bruker AMX 400 spectrometers; chemical shifts are referenced with respect to TMS. Mass spectra (FD, FAB) were acquired with a Finnigan MAT-711A, modified by AMD Intectra. Elemental analyses were carried out in the microanalytical laboratory of our institute (Carlo Erba, Model 1106). Optical rotations were measured on a Knauer Chiral Detector A 1000, Na_D line (589 nm).

Preparation of 2-(9-Fluorenyl)-1-(*S*)-phenylethanol (2a) and 2-(9-Fluorenyl)-2-(S)-phenylethanol (2b). *n*-Butyllithium (112.5 mL, 180 mmol, 1.6 M in hexane) was added to

(25) An experimental indication of the higher steric demand of the hydrogenated complexes is given by the results of propene polymerization experiments with racemic catalysts. The hydrogenated complexes show an up to 5 times reduced rate of insertion, in comparison with the nonhydrogenated species. This leads also to a reduction of molecular weight in the polymer products. A detailed report on the polymerization properties of hydrogenated racemic complexes will be published elsewhere.

(26) Cf.: *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 3, p 573, and literature cited therein.

(27) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673.

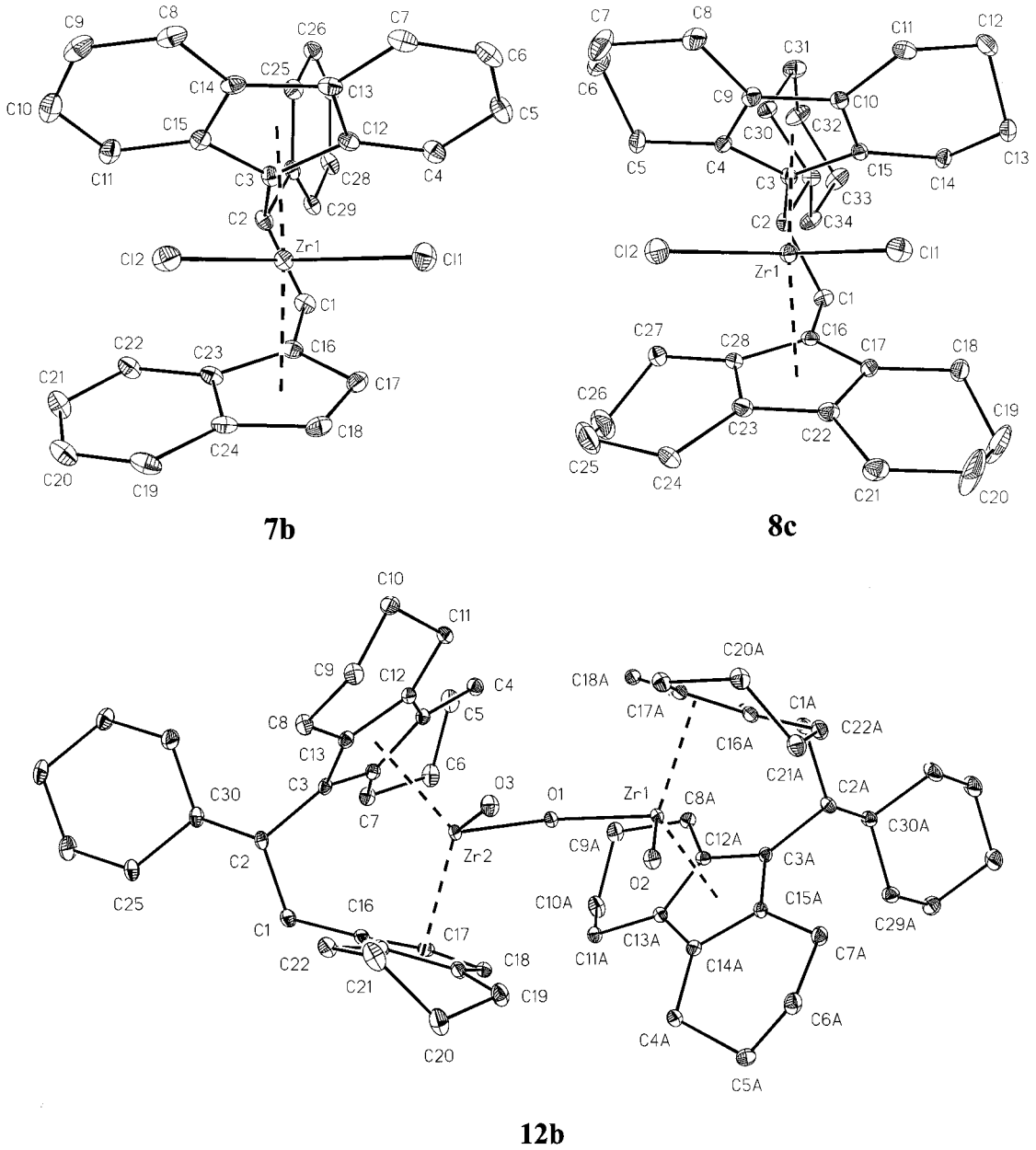


Figure 1. Molecular structures of the enantiomerically pure ethylene-bridged complexes **7b** and **8c** and of the μ-oxo dimer **12b** at −100 °C with 20% probability thermal ellipsoids depicted and H atoms removed for clarity.

a solution of fluorene (30 g, 180 mmol) in diisopropyl ether at 0 °C. A yellow suspension formed, which was slowly treated with a solution of (*R*)-epoxystyrene (**1**; 20.6 mL, 180 mmol) in diisopropyl ether (50 mL) at 0 °C. An orange solid precipitated. The product mixture was neutralized with a saturated aqueous solution of NH_4Cl (350 mL) after being stirred overnight. The organic layer was separated, and the aqueous phase was extracted exhaustively with diisopropyl ether. The combined organic phases were dried over Na_2SO_4 and filtered. Evaporation of the solvent gave **2a** and **2b** in a 1:3 ratio as a colorless solid. The primary alcohol **2b** was obtained by crystallization from toluene/hexane (2:3) at room temperature. The remaining 1:1 mixture of **2a**,**b** was separated by column chromatography over silica. Pure **2a** can be eluted using toluene. Upon addition of 10 vol % diethyl ether **2b** was isolated as the second fraction. **2a**: yield 10.4 g, 36.3 mmol, 20%; mp 117.2 °C. $[\alpha]^{20}_D = +34.4°$ ($c = 2.0$, toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.00 (ddd, $J = 5.3/4.1/3.3/2.0$ Hz, 1H, CH_2(bridge)), 2.45 (ddd, $J = 5.0/4.2/4.9$ Hz, 1H, CH_2(bridge)), 4.11 (dd, $J = 5.1/2.8/5.0$ Hz, 1H, CH(bridge)), 4.80 (dd, $J = 3.8/3.1/2.3$ Hz, 1H, CH(Flu)), 7.1−7.7 (m, 13H, aromatic H) ppm. Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.43; H, 5.98. **2b**: yield 34.6 g, 120.8 mmol, 67%; mp 89.9 °C. $[\alpha]^{20}_D = +26.6°$ ($c = 1.95$, toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.46 (ddd, $J = 5.61/2.6/2.9$ Hz, 1H, CH(bridge)), 3.83 (m, 1H, CH_2(bridge)), 3.99 (m, 1H, CH_2(bridge)), 4.33 (d, $J = 5.5$, 1H, CH(Flu)), 6.9−7.6 (m, 13H, aromatic H) ppm. Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.17; H, 6.25.

Preparation of 1-(9-Fluorenyl)-1-(*S*)-phenyl-2-(1-indenyl)ethane (6a) and 1,2-Bis(9-fluorenyl)-1-(*S*)-phenylethane (6b) via 2-(9-Fluorenyl)-2-(*S*)-phenylethyl Trifluoromethanesulfonate (5). Trifluoromethanesulfonic acid anhydride (2.87 mL, 17.5 mmol) was added dropwise to a mixture of **2b** (5 g, 17.5 mmol) and pyridine (1.41 mL, 17.5 mmol) in CH_2Cl_2 (150 mL) at 0 °C. After the mixture was stirred for 30 min, the organic layer was washed two times with ice-cold water and was then dried over Na_2SO_4. Evaporation of the solvent gave **5** as a colorless solid, which was dissolved in dioxane (50 mL). The solution was added to a suspension of either indenyllithium (2.56 mL of indene, 13.75 mL of *n*-butyllithium) or fluorenyllithium (3.65 g of fluorene, 13.75 mL of *n*-butyllithium) in dioxane (150 mL) without further purification, due to the thermal instability of the triflate **5**. After it was stirred overnight at ambient temper-

Table 1. Crystallographic Data for Enantiomerically Pure 7b, 8c, and 12b[a]

	7b	8c	12b
formula	$C_{30}H_{22}Cl_2Zr$	$C_{41}H_{54}Cl_2Zr$[b]	$C_{67}H_{90}O_3Zr_2$[c]
fw	544.6	708.9	1225.8
cryst color	red	colorless	colorless
cryst syst	orthorhombic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1$	$P1$
a, Å	10.651(2)	9.610(2)	10.767(3)
b, Å	14.354(3)	19.468(3)	12.276(3)
c, Å	15.378(3)	9.765(1)	12.567(3)
α, deg	90.0	90.0	115.95(2)
β, deg	90.0	107.69(1)	107.78(2)
γ, deg	90.0	90.0	90.58(2)
V, Å^3	2351.1(8)	1740.5(5)	1402.1(6)
d_{calcd}, g/cm^3	1.538	1.353	1.333
Z	4	2	1
cryst size, mm	0.3 × 0.2 × 0.2	0.3 × 0.3 × 0.25	0.5 × 0.5 × 0.4
abs coeff (μ), mm^{-1}	0.712	0.498	0.418
T, K	173(2)	173(2)	173(2)
2θ range, deg	4−50	4−50	4−50
no. of rflns collected	15753	12262	9854
no. of indep rflns	4149	6144	9854
GOF on F^2	1.538	1.706	1.308
R (final)[d]	R1 = 0.0227, wR2 = 0.0525	R1 = 0.0374, wR2 = 0.0984	R1 = 0.0283, wR2 = 0.0724
Flack param	−0.05(3)	−0.04(4)	−0.05(2)
extinctn coeff	0.0000(3)	0.005(1)	0.015(1)

[a] **7b**, **8c**, and **12b**: SHELXL 93. [b] Contains one toluene molecule in the unit cell; formula $C_{34}H_{46}Cl_2Zr$, fw = 616.8. [c] Contains one toluene molecule in the unit cell; formula $C_{60}H_{82}O_3Zr_2$, fw 1033.7. [d] The following formulas have been used for calculation of R and w values: $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]]^{1/2}$; $w = [0 + e^{(f((\sin\theta)/\lambda)^2)}]/[\sigma^2(F_o^2) + [g(\max{}^1/_3F_o^2, 0) + {}^2/_3F_c^2]]$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 7b and 8c

7c		8c	
	Distances		
Zr−Cl(1)	2.418(1)	Zr−Cl(1)	2.4449(10)
Zr−Cl(2)	2.410(1)	Zr−Cl(2)	2.4521(9)
Zr−Flu(centr)[a]	2.275	Zr−^{H}Flu(centr)	2.237
Zr−Ind(centr)	2.217	Zr−^{H}Flu(centr)	2.228
C(1)−C(2)	1.546(4)	C(1)−C(2)	1.538(5)
C(1)−C(16)	1.507(4)	C(1)−C(16)	1.508(5)
C(2)−C(3)	1.515(4)	C(2)−C(3)	1.520(5)
C(2)−C(30)	1.531(3)	C(2)−C(30)	1.543(5)
	Angles		
Cl(1)−Zr−Cl(2)	95.6(1)	Zl(1)−Zr−Cl(2)	96.08(4)
Flu(centr)−Zr−Ind(centr)	127.7	^{H}Flu(centr)−Zr^{H}-Flu(centr)	126.1
C(1)−C(2)−C−(3)	110.9(2)	C(1)−C(2)−C−(3)	110.5
C(2)−C(1)−C−(16)	110.8(2)	C(2)−C(1)−C−(16)	111.2(3)
C(3)−C(2)−C−(30)	112.9(2)	C(3)−C(2)−C−(29)	111.9(3)
C(2)−C(3)−C−(12)	125.4(3)	C(2)−C(3)−C−(15)	127.1(3)
C(2)−C(3)−C−(15)	126.8(2)	C(2)−C(3)−C−(4)	125.7(3)
C(15)−C(3)−C−(12)	106.4(2)	C(4)−C(3)−C−(15)	107.1(3)
C(1)−C(16)−C−(23)	77.3(3)	C(1)−C(16)−C−(23)	125.0(3)

[a] ^{H}Flu = octahydrofluorenyl.

ature, the mixture was heated for 30 min at 60 °C. Dioxane was distilled off and the solid residue was suspended in a saturated aqueous solution of NH_4Cl (250 mL). Extraction with diethyl ether (3 × 100 mL) and drying of the collected organic fractions over Na_2SO_4 gave, after evaporation of the solvent and column chromatography over silica (eluent toluene/hexane 2:3), colorless **6a** (5.23 g, 13.6 mmol, 78%) or **6b** (6.44 g, 14.8 mmol, 85%). **6a**: mp 137.6 °C. $[\alpha]^{20}_D = +73.19°$ (c = 1.49, toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.61−2.94 (m, 2H, CH_2(bridge)), 3.16 (d, J = 1.9 Hz, 2H, CH(Ind), 4.00 (ddd, J = 4.88/4.53/5.21/4.03 Hz, 1H, CH(bridge)), 4.39 (d, J = 3.8 Hz, 1H, CH(Flu)), 5.90 (s, 1H, CH(Ind), 7.1−7.7 (m, 17H, aromatic H). MS (FD): m/z 384.1 (M^+, 100%). Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.74; H, 6.30. **6b**: mp 165.8 °C. $[\alpha]^{20}_D = +35.4°$ (c = 1.51, toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.81 (ddd, J = 14.25/9.5/4.2 Hz, 1H, CH_2-(bridge)), 2.57 (ddd, J = 14.5/10.8/4.2 Hz, 1H, CH_2(bridge)), 3.70 (dd, J = 9.5/4.2 Hz, 1H, CH(Flu)), 3.89 (ddd, J = 11.2/4.2/4.3 Hz, 1H, C CH(bridge)), 4.13 (d, J = 4.3 Hz, 1H, CH(Flu)), 7.0−7.6 (m, 21H, aromatic H). MS (FD): m/z 434.3 (M^+, 100%). Anal. Calcd for $C_{34}H_{26}$: C, 93.97; H, 6.03. Found: C, 94.08; H, 6.24.

Preparation of [1-(η^5-9-Fluorenyl)-1-(*R*)-phenyl-2-(η^5-1-(*R*)-indenyl)ethane]zirconium Dichloride (7a) and [1-(η^5-9-Fluorenyl)-1-(*R*)-phenyl-2-(η^5-1-(*S*)-indenyl)ethane]zirconium Dichloride (7b). *n*-Butyllithium (12.5 mL, 20 mmol, 1.6 M in hexane) was added slowly to a solution of the ligand precursor **6a** (3.85 g, 10 mmol) in diethyl ether (100 mL) at 0 °C. The solvent was evaporated off, and the dry dilithio salt was suspended in precooled CH_2Cl_2 (150 mL, −80 °C). $ZrCl_4$ (2.3 g, 10 mmol) was added in one portion with vigorous stirring. Subsequently, the reaction mixture was stirred to ambient temperature overnight. CH_2Cl_2 was removed in vacuo, and the remaining crude product was extracted with hot toluene (5 × 100 mL). The suspension was filtered through a 1-in. pad of Celite. Removal of the solvent and washing of the microcrystalline residue with hexane (5 × 20 mL) gave crude **7a** and **7b** in a 1:3 ratio (total 5.22 g, 9.59 mmol, 96%). Pure **7b** crystallizes from a saturated toluene solution at 0 °C (orange, 2.61 g, 4.79 mmol, 48%).[28] All attempts to separate

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 12b

		Distances	
Zr(1)−O(1)	1.991(2)	C(1)−C(2)	1.549(4)
Zr(1)−O(2)	2.020(2)	C(1)−C(16)	1.502(4)
Zr(2)−O(1)	1.989(2)	C(2)−C(3)	1.511(4)
Zr(2)−O(3)	2.004(2)	C(2)−C(30)	1.556(3)
Zr(1)−^{H}Flu(centr)[a]	2.274	C(1a)−C(2a)	1.550(4)
Zr(1)−^{H}Ind(centr)[a]	1.275	C(1a)−C(16a)	1.510(4)
Zr(2)−^{H}Flu(centr)	2.281	C(2a)−C(3a)	1.513(4)
Zr(2)−^{H}Ind(centr)	2.279	C(2a)−C(30a)	1.543(3)
		Angles	
O(1)−Zr(1)−O(2)	96.52(8)	C(1)−C(16)−C(23)	126.6(3)
O(1)−Zr(2)−O(3)	96.57(8)	C(13)−C(3)−C(14)	107.6(3)
^{H}Flu(centr)−Zr(1)−^{H}Ind(centr)	122.4	C(1a)−C(2a)−C(3a)	110.9(2)
^{H}Flu(centr)−Zr(2)−^{H}Ind(centr)	122.3	C(2a)−C(1a)−C(16a)	113.3(2)
C(1)−C(2)−C(3)	111.2(2)	C(3a)−C(2a)−C(30a)	114.4(2)
C(2)−C(1)−C(16)	112.8(2)	C(2a)−C(3a)−C(15a)	124.9(3)
C(3)−C(2)−C(30)	114.3(2)	C(1a)−C(16a)−C(23a)	126.8(3)
C(2)−C(3)−C(13)	124.4(3)	C(15a)−C(3a)−C(12a)	107.3(2)

[a] ^{H}Flu = octahydrofluorenyl; ^{H}Ind = tetrahydroindenyl.

pure **7a** from the remaining 1:1 mixture failed. **7a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.08 (dd, J = 6.97/7.32/6.97 Hz, 1H, CH_2(bridge)), 4.69 (dd, J = 13.88/13.81 Hz, 1H, CH_2(bridge)), 5.80 (dd, J = 6.96/6.48/6.92 Hz, 1H, CH(bridge)), 6.44 (d, J = 3.47 Hz, 1H, CH(Ind)), 6.57 (d, J = 3.39 Hz, 1H, CH(Ind)), 6.9−8.1 (m, 19H, aromatic H). **7b**: $[\alpha]^{20}_D = +378.5°$ (c = 0.2, toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.39 (ddd, J = 14.08/12.39/7.32/5.88 Hz, 2H, CH_2(bridge)), 5.93 (d, J = 3.25 Hz, 1H, CH(Ind)), 6.20 (d, J = 3.25 Hz, 1H, CH(Ind)), 6.30 (dd, J = 8.34/4.2/8.34 Hz, 1H, CH(bridge)), 6.9−8.1 (m, 19H, aromatic H). MS (FAB): m/z 545.0 (M^+, 100%). Anal. Calcd for $C_{30}H_{22}ZrCl_2$: C, 66.16; H, 4.07; Cl, 13.01. Found: C, 66.04; H, 4.63; Cl, 12.76.

Preparation of [1,2-Bis(η^5-9-fluorenyl)-1-(*R*)-phenylethane]zirconium Dichloride (7c) and [1,2-Bis(η^5-9-fluorenyl)-1-(*R*)-phenylethane]hafnium Dichloride (7d). The dilithio salt of **6b** (4.35 g, 10 mmol) was treated in a manner similar to that for **6a** with MCl_4 (10 mmol; **7c**, M = Zr; **7d**, M = Hf) using toluene instead of CH_2Cl_2 as the reaction medium. Workup of the complexes was also performed by the procedure described above. Crystallization from toluene gave bordeaux red **7c** (1.66 g, 2.79 mmol, 28%) and orange **7d** (4.31 g, 6.31 mmol, 63%). **7c**: $[\alpha]^{20}_D = +569°$ (c = 0.1, toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.65 (dd, J = 14.4/7.7 Hz, 1H, CH_2(bridge)), 5.09 (dd, J = 14.7/12.8 Hz, 1H, CH_2(bridge)), 6.53 (dd, J = 7.8/13.3 Hz, 1H, CH(bridge)), 6.97−8.09 (m, 21H, aromatic H). MS (FAB): m/z 594.1 (M^+, 100%), 558.7 (M^+ − Cl, 94%). Anal. Calcd for $C_{34}H_{24}ZrCl_2$: C, 68.67; H, 4.07; Cl, 11.92. Found: C, 68.52; H, 4.38; Cl, 12.01. **7d**: $[\alpha]^{20}_D = +179°$ (c = 0.2, toluene). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.85 (dd, J = 8.14/6.1/8.14 Hz, 1H, CH_2(bridge)), 4.99 (dd, J = 14.24/13.22 Hz, 1H, CH(bridge)), 6.44 (dd, J = 7.63/5.08/8.14 Hz, 1H, CH_2(bridge)), 6.98−8.11 (m, 21H, aromatic H). Anal. Calcd for $C_{34}H_{24}HfCl_2$: C, 59.88; H, 3.54; Cl, 10.39. Found: C, 59.72; H, 3.83; Cl, 10.39.

Preparation of [1-(*R*)-Cyclohexyl-1-(η^5-octahydro-9-fluorenyl)-2-(η^5-tetrahydro-1-(*R*)-indenyl)ethane]zirconium Dichloride (8a), [1-(*R*)-Cyclohexyl-1-(η^5-octahydro-9-fluorenyl)-2-(η^5-tetrahydro-1-(*S*)-indenyl)ethane]zirconium Dichloride (8b), [1-(*R*)-Cyclohexyl-1,2-bis(η^5-octahydro-9-fluorenyl)ethane]zirconium Dichloride (8c), and [1-(*R*)-Cyclohexyl-1,2-bis(η^5-octahydro-9-fluorenyl)ethane]hafnium Dichloride (8d). A steel autoclave was loaded with one of the complexes **7a**−**d** (5 mmol), $PtO_2 \cdot xH_2O$ (100 mg), and CH_2Cl_2 (150 mL). The vessel was charged with hydrogen (125 bar), and the reaction mixture was stirred for 48 h at constant pressure. The resulting slightly green slurry was filtered through a 1 in. pad of Celite followed by removal of the solvent in vacuo. Crystallization of the solid residue from hexane or hexane/toluene gave the colorless to fluorescent yellow complexes **8a**−**d**.[29] **8a** (1:1 mixture with **8b**): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.6−3.26 (m, 38H, alkyl H), 5.62 (d, J = 3.14 Hz, 1H, CH(Ind)), 6.41 (d, J = 3.15 Hz, 1H, CH(Ind)). **8b**: yield 2.50 g, 4.45 mmol, 89%. $[\alpha]^{20}_D = -10.6°$ (c = 0.58, toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.6−3.26 (m, 38H, alkyl H), 5.34 (d, J = 2.93 Hz, 1H, CH(Ind)), 6.14 (d, J = 2.91 Hz, 1H, CH(Ind)). MS (FD): m/z 561.7 (M^+, 100%). Anal. Calcd for $C_{30}H_{40}ZrCl_2$: C, 64.03; H, 7.16; Cl, 12.60. Found: C, 64.42; H, 7.43; Cl, 12.42. **8c**: yield 2.24 g, 3.65 mmol, 73%. $[\alpha]^{20}_D = +14.0°$ (c = 0.2, toluene). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.6−3.4 (m, 46H, alkyl H). MS (FD): m/z 615.9 (M^+, 100%). Anal. Calcd for $C_{34}H_{46}ZrCl_2$: C, 66.20; H, 7.52; Cl, 11.49. Found: C, 66.58; H, 7.68; Cl, 11.30. **8d**: yield 2.96 g, 4.21 mmol, 84%. $[\alpha]^{20}_D = -5.4°$ (c = 0.35, toluene). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.6−3.3 (m, 46H, alkyl H). MS (FD): m/z 704.6 (M^+, 100%). Anal. Calcd for $C_{34}H_{46}HfCl_2$: C, 57.99; H, 6.58; Cl, 10.07. Found: C, 57.45; H, 6.87; Cl, 10.11.

Preparation of [1-(*R*)-Cyclohexyl-1-(η^5-octahydro-9-fluorenyl)-2-(η^5-tetrahydro-1-(*R*)-indenyl)ethane]zirconium 2,6-Pyridindicarboxylate (9a) and [1-(*R*)-Cyclohexyl-1-(η^5-octahydro-9-fluorenyl)-2-(η^5-tetrahydro-1-(*S*)-indenyl)ethane]zirconium 2,6-Pyridindicarboxylate (9b). A 1:1 mixture of **8a**,**b** (0.33 g, 0.59 mmol) and 2,6-pyridinedicarboxylic acid (0.1 g, 59 mmol) was suspended in 30 mL of toluene at 80 °C. Over a 20 min period a solution of Et_3N (0.17 mL, 1.2 mmol) in toluene (10 mL) was added dropwise. The reaction mixture was stirred for 5 h at 80 °C and at ambient temperature overnight. After evaporation of the toluene solvent CH_2Cl_2 (30 mL) and water (20 mL) were added and the suspension was stirred for another 6 h. The organic layer was separated, dried (Na_2SO_4) and filtered. The solvent was evaporated, and the solid residue was washed with pentane (30 mL), leaving **9a**,**b** as a colorless powder (0.27 g, 0.42 mmol, 69%). MS (FAB): m/z 651.3 (M^+, 100%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.35−5.05 (m, 76H, alkyl H), 5.32 (d, J = 2.91 Hz, 1H, CH(Ind)), 5.64 (d, J = 3.19 Hz, 1H, CH(Ind)), 5.67 (d, J = 2.91 Hz, 1H, CH(Ind)), 5.73 (d, J = 3.07 Hz, 1H, CH(Ind)), 8.16−8.24 (m, 6H, arom H(pyridine)) ppm. IR (KBr): ν 1676, 1598 (CO) cm^{-1}.

Preparation of [1-(η^5-9-Fluorenyl)-1-(R)-phenyl-2-(η^5-1-(*R*)-indenyl)ethane]zirconium Dimethyl (10a). A solution of **7a**,**b** (1:1.3 mixture, 1.23 g, 2.2 mmol) in diethyl ether (150 mL) was cooled to −78 °C and treated with methyllithium

(28) A different diastereoselectivity can be achieved by the use of toluene instead of CH_2Cl_2 as reaction medium. In this case **7a** and **7b** are formed in a 1:1 ratio.

(29) No formation of partially hydrogenated structures was observed under the conditions applied here.[13d] Complexes **8a**−**d** contain variable amounts of solvent after recrystallization. Elemental analysis was performed after vacuum drying of the powdered materials at 50−60 °C overnight.

(8 mL, 4.9 mmol, 0.62 M in diethyl ether). The reaction mixture warmed to ambient temperature, and the solvent was evaporated in vacuo. The residue was extracted with hexane (2 × 25 mL) and was filtered through a 1 in. pad of Celite. The enantiomerically pure δ-forward isomer **10a** has been obtained as a yellow powder by crystallization from hexane at −30 °C: yield 0.4 g, 0.8 mmol, 70%. ^{1}H NMR (250 MHz, C_6D_6): δ −2.29 (s, 3H, CH_3), −1.07 (s, 3H, CH_3), 3.34 (dd, J = 6.4/7.6 Hz, 1H, CH_2), 4.0−4.1 (m, 1H, CH_{Ph}), 4.84 (dd, J = 6.4/7.0 Hz, 1H, CH_2), 5.75 (d, J = 3.4 Hz, 1H, CH(Ind)), 6.17 (d, J = 3.4 Hz, 1H, CH(Ind)), 6.7−7.8 (m, 17H, arom H) ppm.[30]

Preparation of [1-(*R*)-Cyclohexyl-1-(η^5-octahydro-9-fluorenyl)-2-(η^5-tetrahydro-1-(*R*)-indenyl)ethane]zirconium Methyl Chloride (11a) and of [1-(*R*)-Cyclohexyl-1-(η^5-octahydro-9-fluorenyl)-2-(η^5-tetrahydro-1-(*S*)-indenyl)ethane]zirconium Methyl Chloride (11b). 8a,b (1:1 mixture, 2.2 g, 3.9 mmol) were treated with methyllithium (13.8 mL, 8.5 mmol, 0.62 M in diethyl ether) as described above. After evaporation of the solvent, the residue was extracted with hexane (40 mL), filtered through a 1 in. pad of Celite, and crystallized from hexane at −30 °C. A 1:1 mixture of the monomethylated diastereoisomers **11a**,**b** was obtained as a colorless powder: yield 1.5 g, 2.8 mmol, 73.5%. ^{1}H NMR (250 MHz, C_6D_6): δ 0.20 (s, 3H, CH_3), 0.23 (s, 3H, CH_3), 0.6−3.3 (m, 76 H, alkyl H), 4.68 (d, J = 2.93 Hz, 1H, CH(Ind)), 4.91 (d, J = 3.17 Hz, 1H, CH(Ind)), 6.06 (d, J = 2.78 Hz, 1H, CH(Ind)), 6.28 (d, J = 3.17 Hz, 1H, CH(Ind)) ppm. Anal. Calcd for $C_{31}H_{43}ZrCl$: C, 68.65; H, 7.99; Cl, 6.54. Found: C, 67.24; H, 7.92; Cl, 6.26.

Preparation of (μ-Oxo)bis{[1-(*R*)-cyclohexyl-1-(η^5-octahydro-9-fluorenyl)-2-(η^5-tetrahydro-1-(*S*)-indenyl)-ethane]zirconium hydroxide} (12b). A solution of **8a**,**b** (2 g, 3.55 mmol, 1:1 mixture) in diethyl ether (200 mL) was added to an aqueous solution of Na_3PO_4 (200 mL, 0.2 M). The suspension was heated to reflux for 3 h. After it was cooled to room temperature, the organic layer was extracted with diethyl ether (3 × 100 mL). After drying over Na_2SO_4 and evaporation of the solvent a slightly yellow solid remained. Crystallization from acetone/toluene (1:1) gave colorless **12b** (0.6 g, 0.58 mmol, 33%). **12b**: $[\alpha]^{20}_D$ = +78.4° (c = 0.19, toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.65−3.20 (m, 76H, alkyl H), 3.30 (s, 2H, OH), 5.23 (d, J = 2.68 Hz, 2H, CH(Ind)), 5.82 (d, J = 2.7 Hz, 2H, CH(Ind)). MS (FD): m/z 1032.8 (M^+, 100%). Anal. Calcd for $C_{60}H_{82}Zr_2O_3$: C, 69.71; H, 7.99. Found: C, 70.74; H, 8.62.

(30) The methyl and dimethyl complexes are too air and moisture sensitive to give satisfactory mass spectra or elemental analysis results.

Preparation of 1-Cyclohexyl-1-(octahydro-9-fluorenyl)-2-(tetrahydro-1-indenyl)ethane (13). A solution of **8a**,**b** (2 g, 3.55 mmol, 1:1 mixture) in diethyl ether (200 mL) was treated in a manner similar to that applied for the synthesis of **12a**,**b**. Heating to reflux was carried out for 48 h. After it was cooled to room temperature, the organic layer was extracted with diethyl ether (3 × 100 mL). After purification by column chromatography over silica (eluent toluene/hexane, 1:1) **13** was obtained as a pale beige powder: yield 0.85 g, 2.1 mmol, 59%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.6−3.4 (m, 40H, alkyl H), 5.3 (d, J = 2.1 Hz, 2H, CH(Ind)), 5.8 (d, J = 2.1 Hz, 2H, CH(Ind)). MS (FD): m/z 402.6 (M^+, 100%). Anal. Calcd for $C_{30}H_{42}$: C, 89.48; H, 10.52. Found: C, 88.79; H, 10.33.

Crystal Structure Determination of [1-(η^5-9-Fluorenyl)-1-(*R*)-phenyl-2-(η^5-1-(*S*)-indenyl)ethane]zirconium Dichloride (7b), [1-(*R*)-Cyclohexyl-1,2-bis(η^5-octahydro-9-fluorenyl)ethane]zirconium Dichloride (8c), and (μ-Oxo)bis{[1-(*R*)-cyclohexyl-1-(η^5-octahydro-9-fluorenyl)-2-(η^5-tetrahydro-1-(*S*)-indenyl)ethane]zirconium hydroxide} (12b). Crystallographic and experimental details of the X-ray structure determination are given in Table 1. Conditions: Siemens P4 diffractometer, Mo Kα radiation (0.710 73 Å), graphite monochromator. Intensities were corrected for Lorenz and polarization effects. Absorption corrections were made for **7b** and **8c**. Solution: direct methods combined with Fourier analysis (**7b**, **12b**) and Patterson method combined with direct methods and Fourier analysis (**8c**) (program SHELXL 93). Absolute configuration were determined for **7b**, **8c**, and **12b**. All non-hydrogen atoms were refined anisotropically. Empirical absorption corrections (ψ Scans) were performed on **7b** and **8c** (maximum and minimum transmissions: **7b**, 0.569, 0.564; **8c**, 0.535, 0.488).

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Supporting Information Available: Tables giving structure determination summaries, atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients for **7b**, **8c**, and **12b** (24 pages). Ordering information is given on any current masthead page.

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