Synthesis, Characterization and Polymerization Behavior of {(1*R*,*S*)-2-(η^5-9-Fluorenyl)-1-[η^5-(1*R*,*S*)-indenyl]-1-phenylethane}zirconium Dichloride and {(1*R*,*S*)-Cyclohexyl-2-(η^5-octahydro-9-fluorenyl)-1-[η^5-tetrahydro-(1*R*,*S*)-indenyl]ethane}zirconium Dichloride

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Epoxystyrene (**1a**) and oxirane (**1b**) were converted into their corresponding alcohols, **2a**–**c**, by treatment with either fluorenyl- or indenyllithium. These alcohols were then further converted into their trifluoromethanesulfonate derivatives, **3a**–**c**. Subsequent reaction of the triflates with fluorenyl-, indolyl-, or tetraphenylcyclopentadienyllithium resulted in formation of 2-(9-fluorenyl)-1-(1-indenyl)-1-phenylethane (**4a**), 1-(9-fluorenyl)-2-(1-indolyl)-1-phenylethane (**4b**) and 1-(9-fluorenyl)-2-(5-tetraphenylcyclopentadienyl)ethane (**4c**). The *ansa*-metallocene {1(*R*,*S*)-2-(η^5-9-fluorenyl)-1-[η^5-1(*R*,*S*)-indenyl]-1-phenylethane}ZrCl$_2$ (**5a**) was prepared from the dilithio salt of **4a**. Hydrogenation of **5a** with H$_2$/PtO$_2$ leads to {1(*R*,*S*)-cyclohexyl-2-(η^5-octahydro-9-fluorenyl)-1-[η^5-tetrahydro-1(*R*,*S*)-indenyl]ethane}zZrCl$_2$ (**6a**). The complexes **5a** and **6a** were activated with methylalumoxane (MAO) and used for propene polymerization. The solid state structures of **4b**, **4c**, and **5a** are reported.

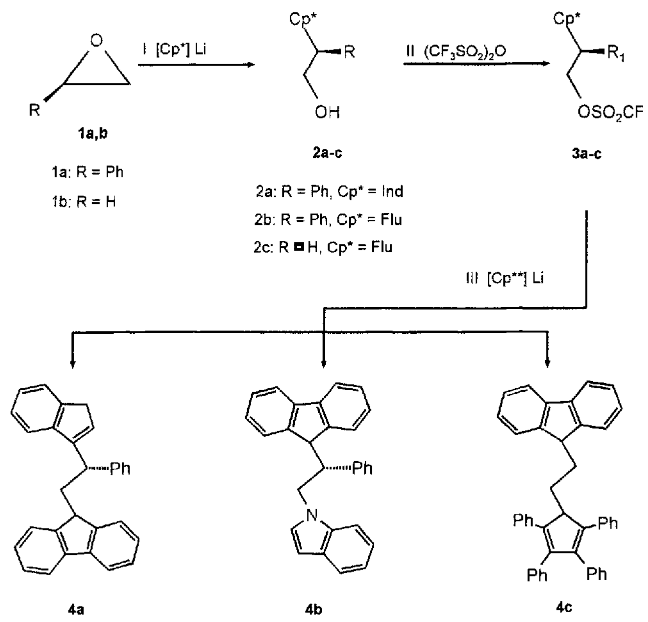
For more than a decade, chiral group-IV metallocenes have been the subject of considerable interest as catalysts in the stereospecific polymerization of α-olefins, opening up the possibility of tailoring the polyolefinic properties over a wide range[2]. Homologous lanthanide complexes have recently been found suitable for the polymerization of even polar monomers such as methyl methacrylate[3]. Enantiomerically pure metallocenes[4] have also attracted interest as catalysts in enantioselective hydrogenation of prochiral olefins[5] and imines[6], asymmetric oligomerization[7] and cyclopolymerization[8], and in metal-assisted Diels-Alder reactions[9].

We have earlier established a synthetic route based on ring-opening reactions of epoxides for the preparation of non-symmetric ethylene-bridged *ansa*-metallocenes bearing two different cyclopentadienyl fragments[10]. In this paper we report the synthesis of new metallocene dichlorides for the further investigation of the influence of the ligand environment on the polymerization behavior of the catalytically active metal center.

Complex Synthesis

The ligand precursors 2-(9-fluorenyl)-1-(1-indenyl)-1-phenylethane (**4a**), 1-(9-fluorenyl)-1-phenyl-2-(1-indolyl)-ethane (**4b**) and 1-(9-fluorenyl)-2-(5-tetraphenylcyclopentadienyl)ethane (**4c**) were synthesized starting from a nucleophilic ring-opening reaction of the epoxides **1a**, **b** with indenyl or fluorenyl anions. Their corresponding alcohols **2a**–**c** can be further functionalized with trifluoromethane sulfonic acid anhydride (**3a**–**c**) by the introduction of a second cyclopentadienyl moiety in the ethylene bridge, as depicted in Scheme 1.

Scheme 1



Deprotonation of the bis(cyclopentadiene) **4a** with two equivalents of *n*-butyllithium and subsequent reaction of its

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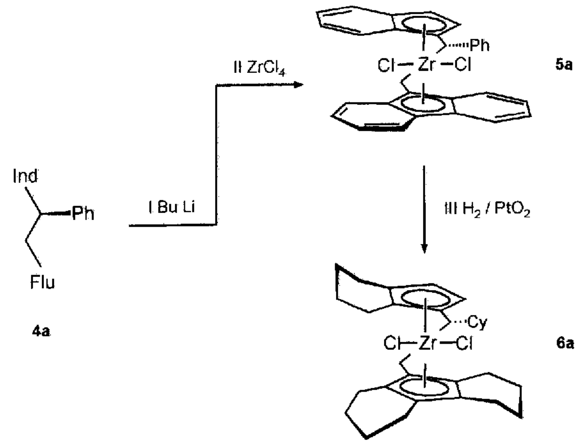
dilithio salt with $ZrCl_4$ afforded the *ansa*-zirconocene complex {1(*R*,*S*)-2-(η^5-9-fluorenyl)-1-[η^5-1(*R*,*S*)-indenyl]-1-phenylethane}$ZrCl_2$ (**5a**, Scheme 2), which was purified by crystallization from hot toluene. Using PtO_2 as a catalyst, **5a** was further hydrogenated at 125 bar in a high-pressure autoclave giving {1(*R*,*S*)-cyclohexyl-2-(η^5-octahydro-9-fluorenyl)-1-[η^5-tetrahydro-1(*R*,*S*)-indenyl]ethane}$ZrCl_2$ (**6a**).

Scheme 2



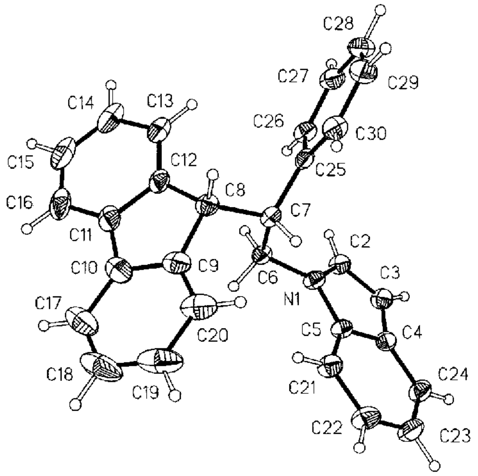
Due to the fact that substitution of the triflate group of **3b** was performed exclusively via the nitrogen atom in the five-membered ring of the indolyl anion, **4b** could be used neither for common bis-η^5-coordination nor as an amido-mono-η^5 ligand in a manner similar to that reported recently by Okuda et al.[11].

All attempts to connect the dilithio salt of **4c** to zirconium failed and no complex formation was observed. One explanation might be given by the polymerization behavior of *rac*-[1-(η^5-cyclopentadienyl)-1-phenyl-2-(tetraphenyl-η^5-cyclopentadienyl)ethane]$ZrCl_2$[12]. This complex was found to be almost inactive for propene polymerization since its phenyl groups rotate in an almost unhindered fashion above 0°C, blocking the active catalytic center (see ref.[10a]). We assume that in the case of **4c** a complexation is inhibited because of a similar kind of steric interference between the rotating phenyl substituents and the condensed aromatic rings of the fluorenyl fragment. Figure 2 gives an impression of the high steric demand of the tetraphenylcyclopentadienyl unit in **4c**.

Crystal Structures

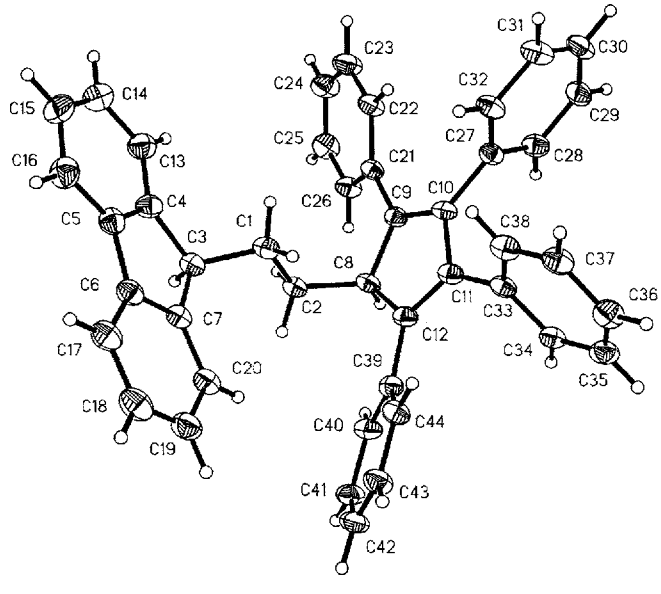
Figures 1 and 2 show the molecular structures of the non-symmetric ligand precursors **4b**, **c**, in which two different cyclopentadienyl fragments are connected via an ethylene bridge. In the case of **4b**, the tertiary amine inhibits the possibility for a deprotonation at the indolyl moiety to form an aromatic cp system (Figure 1). **4b** crystallizes in the same space group as a similar type of bis(cyclopentadiene), 1-(9-fluorenyl)-2-(1-indenyl)-1-phenylethane (see ref.[10c]), showing a slightly shortened ethylene bridge [0.066(3) Å], as expected. In **4b** and **4c** almost similar values for bond lengths and angles can be found for the fluorenyl ethyl fragments. Differences occur with the second cp ring since the tetraphenylcyclopentadienyl unit is bonded via a tertiary carbon atom to the ethylene bridge (Figure 2).

Figure 1. Solid-state structure of **4b**[a]



[a] Selected bond lengths [Å] and angles [°] for **4b**: N1–C2 1.378(3), N1–C5 1.378(3), N1–C6 1.455(3), C2–C3 1.353(3), C6–C7 1.525(3), C7–C8 1.562(3); C5–N1–C2 107.9(2), N1–C2–C3 110.3(2), C2–N1–C6 126.2(2), N1–C6–C7 114.4(2), C6–C7–C8 109.9(2), C7–C8–C9 112.4(2), C7–C8–C12 116.1, C9–C8–C12 101.9(2).

Figure 2. Solid-state structure of **4c**[a]

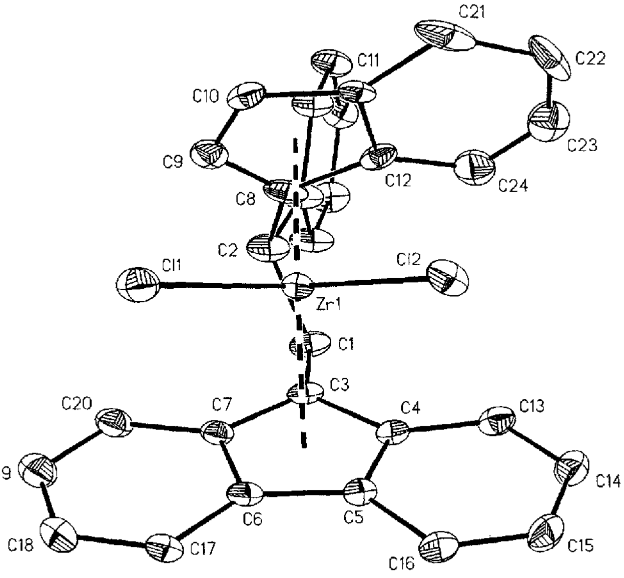


[a] Selected bond lengths [Å] and angles [°] for **4c**: C1–C2 1.528(5), C1–C3 1.552(5), C2–C8 1.527(4), C3–C4 1.508(5), C8–C9 1.510(4); C2–C1–C3 112.7(3), C1–C2–C8 112.7(3), C1–C3–C4 114.8(3), C4–C3–C7 102.1(3),C2–C8–C9 115.3(3), C9–C8–C12 103.7(3), C2–C8–C12 113.8(3).

The non-symmetric *ansa*-zirconocene complex **5a** exist in two different conformations, depending on the enantiofacial orientations of its indenyl fragment. In both cases, the phenyl substituent in the ethylene bridge occupies the energetically favored equatorial position of the metallacycle (see ref.[10b]). However, only one diastereomer with either a

(*R,S*) or (*S,R*) configuration of the backbone substituent and the indenyl fragment could be isolated, although the ^{1}H-NMR spectra of the crude product proved the formation of the predicted (*R,R*)/(*S,S*)-configured second diastereomer[13]. Figure 3 shows the structure of the isolated conformer in the solid state.

Figure 3. Solid-state structure of **5a**. Hydrogen atoms, toluene solvate molecules and another, similar **5a** molecule in the asymmetric unit have been omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°] for **5a**: Zr1–Cl1 2.420(2), Zr1–Cl2 2.403(2), Zr1–Flu(centr) 2.272, Zr1–Ind(centr) 2.212, C1–C2 1.498(8), C1–C3 1.515(7), C2–C8 1.517(8); Cl1–Zr1–Cl2 97.62(7), Flu(centr)–Zr1–Ind(centr) 127.9, C2–C1–C3 114.1(5), C1–C2–C8 109.6(5), C1–C3–C4 124.7(5), C4–C3–C7 106.8(5), C2–C8–C9 123.6(6), C9–C8–C12 106.6(5).

Polymerization Experiments

Propene polymerization was performed in toluene using complexes **5a** and **6a** after activation with methylalumoxane (MAO, Al/Zr = 2000:1). Table 1 summarizes the results at 50, 70 and 85°C and constant monomer concentration. All polymers produced by **5a**/MAO are partly crystalline materials with a nearly equal amount of [mmmm] pentads ranking between 35.2 and 44.1% (see ref.[10b]) and show the typical activity increase with rising polymerization temperature. **6a**/MAO was found to be relatively inactive at 70 and 85°C, only producing atactic oils in low yields. One reason for the severe decline in activity of **6a**/MAO, in contrast to *rac*-[1,2-bis(η^5-tetrahydro-1-indenyl)ethane]ZrCl$_2$[14], can be found in the high steric demand of the octahydrofluorenyl fragment which presumably blocks both sides of the former Cl–Zr–Cl plane, resulting in a lack of coordination sphere for the monomer and polymer chain around the catalytically active center.

In Table 2, polymerization data at variable monomer concentrations and constant polymerization temperature are summarized. While **5a**/MAO at [C$_3$] = 1.75 mol l^{-1} showed a considerable increase in activity and decline in stereoselectivity (see ref.[10b]), **6a**/MAO gave polypropene with an unexpectedly high [mmmm] pentad content of 54.7%.

Table 1. Polymerization data for **5a** and **6a** at different temperatures and constant monomer concentration (0.71 mol l^{-1})

entry	compd.	T_P[a] °C	t_P[b] s	[Zr][c] µmol	yield[d] g	activity[e]	[mmmm][f] %
1	**5a**	50	6196	10	1.4	117	44.1
2		70	4268	10	18.2	2160	41.0
3		85	5070	10	28.2	2821	35.2
4	**6a**	50	2812	20	0.0	0	-
5		70	6234	20	5.6	227	12.4
6		85	5810	20	10.8	469	11.6

[a] Polymerization temperature. – [b] Polymerization time. – [c] Metallocene concentration. – [d] Obtained polymer. – [e] kg (PP) ([Zr] [C$_3$] h)$^{-1}$.

Table 2. Polymerization data for **5a** and **6a** at different monomer concentrations and constant temperature (50°C)

entry	compd.	[C$_3$][a] mol l^{-1}	t_P[b] s	[Zr][c] µmol	yield[d] g	activity[e]	[mmmm][f] %
1	**5a**	0.71	6196	10	1.4	84	44.1
2		1.16	6106	10	3.2	189	41.0
3		1.75	4715	10	8.2	626	26.9
4	**6a**	0.71	2812	20	0.0	0	-
5		1.16	2415	20	0.0	0	-
6		1.75	5935	20	4.5	136	54.7

[a] Monomer concentration. – [b] Polymerization time. – [c] Metallocene concentration. – [d] Obtained polymer. – [e] kg (PP) ([Zr] h)$^{-1}$.

Currently, we are investigating in more detail why complexes bearing octahydrofluorenyl ligands seem to be more stereoselective in propene polymerization at high monomer concentrations than their non-hydrogenated analogs.

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Experimental Section

General: All preparative reactions were carried out under dry argon using standard Schlenk techniques. Diisopropyl ether was purified by distillation from LiAlH$_4$. Dichloromethane and pyridine were distilled from CaH$_2$, dioxane and toluene from sodium. (CF$_3$SO$_2$)$_2$O[15], **2a–c** and **3a–c** were prepared according to literature procedures (see ref.[10]). – ^{1}H-NMR spectra were recorded with Bruker AC 250, Bruker AMX 400 and Varian Gemini 2000 spectrometers; chemical shifts are referenced with respect to TMS. – Mass spectra were acquired with a Finnigan MAT-711A instrument modified by AMD Intectra (FD, FAB) and on a JEOL JMS-SX102 mass spectrometer (EI). – Elemental analyses were determined using a Carlo Erba, Model 1106 and Heraeus VT-CHN-Rapid.

Preparation of the Ligand Precursors **4a–c**: 30 mmol of the alcohols **2a–c** were converted into their corresponding triflates **3a–c**, dissolved in 50 ml of dioxane and added at room temp. to a suspension of 36 mmol of either fluorenyl- (**3a**), indolyl- (**3b**) or tetraphenylcyclopentadienyllithium (**3c**) in 250 ml of dioxane. After stirring overnight the reaction mixtures were heated for 1 h at 70°C and the dioxane was distilled off. The solid residues were suspended in an aqueous solution of NH_4Cl and extracted thoroughly with Et_2O. After evaporation of the organic layer, the crude products were chromatographed on silica gel (eluent: toluene/hexane, 2:3) leading to (a) 4.7 g of brownish amorphous **4a** (40.8%): ^1H NMR (250 MHz, $CDCl_3$): δ = 2.36 [ddd, *J* = 6.3/2.0/6.3 Hz, 1H, CH_2], 2.55 [ddd, *J* = 7.2/6.8/7.1 Hz, 1H, CH_2], 3.29 [s, 2H, Ind CH_2], 3.90 [dd, *J* = 6.6/6.8 Hz, 1H, C*H*Ph], 4.39 [dd, *J* = 7.1/7.2 Hz, 1H, Flu CH], 6.39 [s, 1H, Ind CH], 7.1–7.8 [m, 17H, aromatic H]. – FD MS; *m*/*z* (%): 384.1 (100). – $C_{30}H_{24}$ (384.1): calcd. C 93.71, H 6.29; found C 93.56, H 6.39; (b) 7.4 g of colorless crystalline **4b** (64.3%): ^1H NMR (250 MHz, $CDCl_3$): δ = 4.03 [ddd, *J* = 5.0/4.3 Hz, 1H, C*H*Ph], 4.28–4.48 [m, 3H, CH_2, Flu CH], 6.26 [d, *J* = 2.5 Hz, 1H, Indol CH], 6.74 [d, *J* = 3.1 Hz, 1H, Indol CH], 7.0–7.7 [m, 17H, aromatic H]. – FD MS; *m*/*z* (%): 385.3 (100), and (c) 4.1 g of colorless crystalline **4c** (24.5%): ^1H NMR (200 MHz, $CDCl_3$): δ = 1.37–1.57 [m, 2H, CH_2], 1.78 [m, 2H, CH_2], 3.74 [t, *J* = 5.2/4.8 Hz, 1H, TPhCp CH], 4.14 (t, *J* = 4.4 Hz, 1H, Flu CH], 6.8–7.7 [m, 28H, aromatic H]. – $C_{44}H_{34}$ (562.7): calcd. C 93.91, H 6.09; found C 93.43, H 6.27.

Preparation of the ansa-Zirconocene Dichloride **5a**: 10 mmol of the ligand precursor **4a** was dissolved in 50 ml of Et_2O and treated dropwise with 12.5 ml of *n*-butyllithium (1.6 M in hexane) at 0°C. After stirring for 30 min, the ether was evaporated. The dry dilithio salt was cooled down to – 78°C and suspended in 200 ml of precooled (–80°C) toluene. 10 mmol of $ZrCl_4$ was added and the reaction mixture was stirred overnight and allowed to come to room temp. The suspension was filtered through a 1-in. pad of Celite and the remaining solid extracted several times with hot toluene. Crystallization from toluene at 4°C yielded 2.6 g of orange crystalline **5a** (47%). – ^1H NMR (400 MHz, $CDCl_3$): δ = 4.42 [dd, *J* = 7.4/7.1 Hz, 1H, CH_2], 4.94 [dd, *J* = 13.9/13.8 Hz, 1H, C*H*Ph], 5.80 [dd, *J* = 7.3/5.9 Hz, 1H, CH_2], 6.07 [d, *J* = 3.2 Hz, 1H, Ind CH], 6.22 [d, *J* = 3.4 Hz, 1H, Ind CH], 6.9–8.1 [m, 17H, aromatic H]. – FAB MS; *m*/*z* (%): 545.0 (100). – $C_{30}H_{22}ZrCl_2$ (545.0): calcd. C 66.61, H 4.07, Cl 13.01; found C 65.18, H 3.98, Cl 12.45.

Preparation of **6a**: In a 250-ml high-pressure autoclave 1.1 g of complex **5a** (2 mmol) and 100 mg of $PtO_2 \times H_2O$ were suspended in 150 ml of CH_2Cl_2. The autoclave was filled with hydrogen (125 bar) and the suspension was stirred for 48 h. The resulting slightly green slurry was filtered through a 1-in. pad of Celite and the solvent was evaporated. The solid residue was crystallized from hexane resulting in 0.9 g of colorless crystalline **6a** (79%). – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.6–3.3 [m, 38H, alkyl H], 5.33 [d, *J* = 2.9 Hz, 1H, Ind CH], 6.02 [d, *J* = 2.8 Hz, 1H, Ind CH]. – FD MS; *m*/*z* (%): 562.4 (100). – $C_{30}H_{40}ZrCl_2$ (562.9): calcd. C 64.03, H 7.16, Cl 12.59; found C 67.71, H 8.55, Cl 10.45[16].

Polymerizations: In a 1-l Büchi glass autoclave, 300 ml of toluene was mixed with the desired amount of MAO (10% solution in toluene) and thermostated. The system was charged with propene up to the desired concentration and the polymerization was started by the addition of 20 ml of calibrated complex/toluene solution. Monomer pressure (±50 mbar) and temperature (±0.5°C) were kept constant during each polymerization experiment. Monomer consumption, inside temperature, and pressure were controlled by real-time monitoring, one data set being taken every 2 s. The polymerizations were stopped and the polymers precipitated quantitatively by pouring the solution into 600 ml of methanol, acidified with aqueous hydrochloric acid. After thorough washing with methanol and water, the polymers were dried overnight at 70°C. ^{13}C-NMR spectra of the product samples were measured in $C_2D_2Cl_4$ with respect to TMS and recorded on a Bruker AC 250 spectrometer.

X-ray Crystallographic Studies: Crystal data of compounds **4b**, **4c**, and **5a** were collected with a Rigaku AFC-7S single-crystal diffractometer at 193(2) K using Mo-K_α radiation (graphite monochromator), 0.71073 Å (**4b**, **5a**: scan type $\omega/2\Theta$; **4c**: scan type ω). Intensities were corrected for Lorenz and polarization effects. An absorption correction was performed for compound **4b**. Solution: Direct methods combined with subsequent Fourier analysis. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were on calculated positions (riding model). In compound **5a** one toluene solvent molecule has two orientations and it was refined without hydrogen atoms. Calculations were performed with the SHELXLTL/PC and SHELXL-92 program systems[17].

Crystal Data for **4b**: Suitable crystals were obtained from toluene/hexane (2:3 mixture) at ambient temperature. Crystal dimensions 0.4 × 0.4 × 0.2 mm; a = 11.274(6), b = 12.024(6), c = 9.333(4) Å, α = 94.23(4), β = 112.15(3), γ = 63.06(4)°, V = 1037.4(9) Å^3, crystal system triclinic, space group *P*1bar (No. 2), Z = 2, mol. mass 385.48, *d*(calcd.) = 1.234 g/cm^3, λ = 0.71073 Å, measured reflections 4533, independent reflections 4307, observed reflections 2870, refined parameters 295, $R1$ = 0.0668 and $wR2$ = 0.1743 (observed data), $R1$ = 0.1037 and $wR2$ = 0.2071 (all data)[18].

Crystal Data for **4c**: Suitable crystals were obtained from acetone at ambient temperature. Crystal dimensions 0.3 × 0.2 × 0.1 mm; a = 12.271(0), b = 6.125(7), c = 40.531(18) Å, α = 90, β = 90.94(8), γ = 90°, V = 3046(4) Å^3, crystal system monoclinic, space group *P*2(1)/*c* (No. 14), Z = 4, mol. mass 562.71, *d*(calcd.) = 1.227 g/cm^3, λ = 0.71073 Å, measured reflections 4154, independent reflections 3959, observed reflections 2693, refined parameters 432, $R1$ = 0.0624 and $wR2$ = 0.1303 (observed data), $R1$ = 0.1033 and $wR2$ = 0.1598 (all data)[18].

Crystal Data for **5a**: Suitable crystals were obtained from toluene at 4°C. Crystal dimensions 0.45 × 0.33 × 0.2 mm; a = 11.797(2), b = 15.401(3), c = 17.549(4) Å, α = 77.51(3), β = 80.61(3), γ = 88.03(3)°, V = 3071.2(11) Å^3, crystal system triclinic, space group *P*1bar (No. 2), Z = 4, mol. mass 659.76, *d*(calcd.) = 1.427 g/cm^3, λ = 0.71073 Å, measured reflections 9712, independent reflections 9712, observed reflections 7898, refined parameters 766, $R1$ = 0.0626 and $wR2$ = 0.1330 (observed data), $R1$ = 0.0802 and $wR2$ = 0.1410 (all data)[18].

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[13] The (*R*,*S*)/(*S*,*R*) and (*R*,*R*)/(*S*,*S*) diastereomers of **5a** were obtained in a 3:1 ratio, from which the (*R*,*S*)/(*S*,*R*) conformer was isolated and purified by crystallization from toluene. All attempts to separate the corresponding (*R*,*R*)/(*S*,*S*) diastereomer out of the remaining 1:1 mixture failed. ^{1}H-NMR data of the (*R*,*R*)/(*S*,*S*) diastereomer (400 MHz, $CDCl_3$): δ = 4.19–4.33 (m, 2 H, C*H*Ph, CH_2), 5.90 (dd, *J* = 7.2/5.6 Hz, 1 H, CH_2), 6.50 (d, *J* = 3.5 Hz, 1 H. Ind CH), 6.59 (d, *J* = 3.6 Hz, 1 H, Ind CH), 6.9–8.1 (m, 17 H, aromatic H). For a more detailed discussion of the configuration and conformation of metallacycles in ehtylene-bridged complexes see ref.[10b] and the literature cited there.

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[18] Further details of the structure determinations are available on request from Fachinformationszentrum Karlsruhe, D-76334 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406018 (**4b**), -406019 (**4c**), and -406020 (**5a**), the names of the authors and the journal citation.

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