Unsymmetric *ansa*-Zirconocene Complexes with Chiral Ethylene Bridges: Influence of Bridge Conformation and Monomer Concentration on the Stereoselectivity of the Propene Polymerization Reaction

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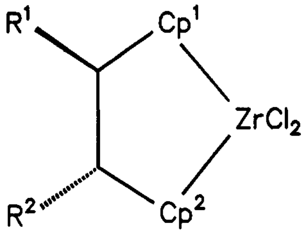
Two general synthetic routes for the preparation of ethylene-bridged *ansa*-zirconocene dichlorides *rac*-[1-(η^5-Cp^1)-1-R^1-2-(η^5-Cp^2)-2-R^2-C_2H_2]$ZrCl_2$ (**6a-c**) bearing different cyclopentadienyl fragments [Cp^1,Cp^2 = Cp (cyclopentadienyl), Ind (indenyl), Flu (fluorenyl)] and a variable bridge substitution pattern (R^1, R^2 = H, Ph) are described, using chiral epoxides as starting materials. Diastereomeric complexes were separated by crystallization. The solid-state structures of two representative examples are reported. In combination with methylalumoxane (MAO), *rac*-[1-(η^5-9-fluorenyl)-2-(η^5-1-indenyl)ethane]$ZrCl_2$ (**6a**), carrying no bulky bridge substituent, and the diastereomeric systems *rac*-[1-(η^5-9-fluorenyl)-1(*R*,*S*)-phenyl-2-(η^5-1(*R*,*S*)-indenyl)ethane]$ZrCl_2$ (**6b1** = *RR*,*SS*; **6b2** = *RS*,*SR*), showing different bridge conformations, were used for propene polymerization. The stereoselectivity depends on monomer concentration for all three unsymmetric catalysts. Under comparable conditions **6a** and **6b1,2** produce polypropenes with significantly different stereoregularities. This demonstrates the importance of a defined bridge conformation for the design of highly stereoselective catalysts.

Introduction

The discovery of *ansa*-zirconocene dichloride/MAO systems as polymerization catalysts has stimulated intensive research on C_2- or C_s-symmetric[1] as well as on unsymmetric[2] complex species. Some of the polymerization properties of these catalysts, especially the temperature dependence of stereoselectivity of ethylene-bridged complexes, have led to the question whether an equilibrium between λ- and δ-chelate ring conformers could be responsible for the decrease of polymer stereoregularity with increasing polymerization temperature.[2e,3] This hypothesis is supported by polymerization experiments with mono-atom-bridged complexes where the effect of temperature on stereoregularity is much less pronounced.[4] Our interest therefore is focused on the synthesis of ethylene-bridged *ansa*-metallocenes with bulky bridge substituents, since increased stereorigid chelate ring conformers are to be expected from complexes of this kind.[5]

Chart 1



6a–c

	Cp^1	Cp^2	R^1	R^2
a:	Flu	Ind	H	H
b:	Flu	Ind	Ph	H
c:	Ind	Cp	H	Ph

We recently showed that chiral epoxides can serve as excellent starting materials for the preparation of ethylene-bridged complexes with two different cyclopentadienyl fragments.[6] Here we report that this highly versatile strategy can also be applied in the synthesis of the zirconocenes **6a–c** (Chart 1) with a variable bridge substitution pattern. Diastereomeric complexes having stereorigid λ- and δ-chelate ring conformations were isolated, characterized by X-ray structure analysis, and used separately for propene polymerization experiments.

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[1] (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *102*, 339. (d) Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Organometallics* **1991**, *10*, 2061. (e) Erker, G.; Nolte, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *101*, 628. (f) Spalek, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem.* **1992**, *104*, 1373. (g) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (h) Razavi, A.; Ferrara, J. *J. Organomet. Chem.* **1992**, *435*, 299.

[2] (a) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *12*, 2030. (b) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, G. Y.; Winter, H. H. *J. Am. Chem. Soc.* **1991**, *113*, 8569. (c) Spalek, W.; Antberg, M.; Dolle, V.; Klein, R.; Rohrmann, J.; Winter, A. *New J. Chem.* **1990**, *14*, 499. (d) Miya, S.; Mise, T.; Yamazaki, H. *Stud. Surf. Sci. Catal.* **1990**, *56*, 531. (e) Chien, J. C. W.; Rieger, B.; Sugimoto, R.; Mallin, D. T.; Rausch, M. D. *Stud. Surf. Sci. Catal.* **1990**, *56*, 535. (f) Erker, G.; Temme, B. *J. Am. Chem. Soc.* **1992**, *114*, 4004. (g) Giardello, M. A.; Eisen, M. S.; Stern, Ch. L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3326.

[3] Rieger, B.; Mu, X.; Mallin, D. T.; Rausch, M. D.; Chien, J. C. W. *Macromolecules* **1990**, *23*, 3559.

[4] Rieger, B.; Reinmuth, A.; Röll, W.; Brintzinger, H. H. *J. Mol. Catal.* **1993**, *82*, 67.

[5] For different approaches concerning the synthesis of bridge-substituted C_2-symmetric complexes, cf: (a) Rieger, B. *J. Organomet. Chem.* **1992**, *428*, C33. (b) Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 1869. (c) Sutton, S. C.; Nantz, M. H.; Parkin, S. R. *Organometallics* **1993**, *12*, 2248.

[6] Rieger, B.; Fawzi, R.; Steimann, M. *Chem. Ber.* **1992**, *125*, 2373.

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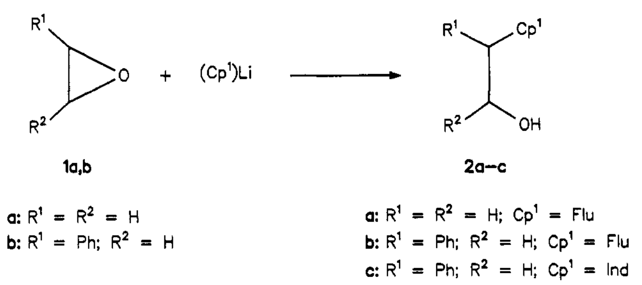
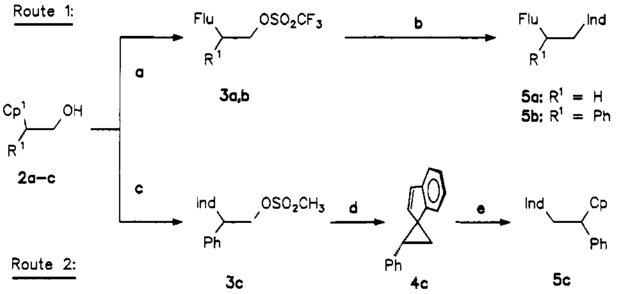
Scheme 1



Scheme 2



[a] **Legend**: (a) $(CF_3SO_2)_2O$ (1 equiv), pyridine (1 equiv), CH_2Cl_2, 0 °C, ~90 %. (b) [Ind]Li (1.2 equiv), dioxane, ~70%. (c) CH_3SO_2Cl (1 equiv), NEt_3 (1 equiv), CH_2Cl_2, 0 °C, 84%. (d) LDA (1.2 equiv), THF, 20 °C, 87%. (e) [Cp]Na (1.2 equiv), DMF, -15 °C, 3 d, 49%.

Results and Discussion

Ligand Systems. The epoxides **1a,b** react quantitatively with 1 equiv of indenyllithium or fluorenyllithium to give high yields of the alcohols **2a–c**, as depicted in Scheme 1.[7] For epoxystyrene the reaction has to be performed in diisopropyl ether. In diethyl ether or in tetrahydrofuran (THF) polymerization occurs, probably due to the high solubility of the lithium alkoxide intermediate.

The alcohols **2a–c** can be converted into dicyclopentadiene ligand precursor compounds according to two different synthetic strategies which allow control of the backbone substitution pattern. Route 1 in Scheme 2 uses the trifluoromethanesulfonate derivatives **3a,b** to introduce the indenyl fragment by direct substitution. The relative position of the phenyl group remains unchanged. Following route 2, deprotonation of the methanesulfonate **3c** gives the spiro compound **4c** first, which then undergoes a clean reaction by treatment with 1 equiv of cyclopentadienylsodium in dimethylformamide (DMF).[8] The ring opening of **4c** is highly regiospecific and leads exclusively and in good yield to the ligand precursor **5c**, where the bridge substituent is located in the position α to the incoming Cp group.

Complex Formation, Separation of Diastereomers, and Solid-State Structures. Preparation of the zirconocene dichlorides **6a–c** (Chart 1) was accomplished by reaction of the dilithio salts of **5a–c** in CH_2Cl_2 solution at −78 °C with $ZrCl_4$ in isolated yields up to 64%. All fluorenyl-group-containing ligand precursors gave no products if the reaction was performed in THF.

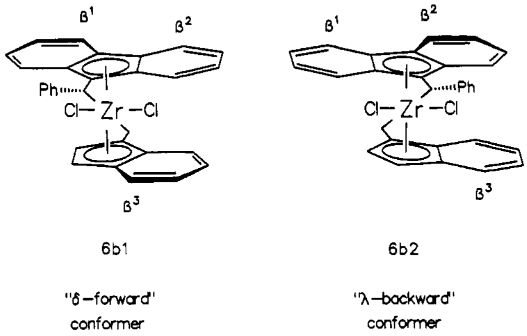


Figure 1. Bridge conformation and arrangement of the β-CH substituents of the unsymmetric diastereomeric complexes **6b1** and **6b2**.

Whereas **6a** exists as a racemic mixture of enantiomers, each of the complexes **6b,c** can be isolated in two diastereomeric forms. For example, the two conformers of **6b**, [1-(η^5-9-fluorenyl)-1(*R*)-phenyl-2-(η^5-1(*R*)-indenyl)ethane]$ZrCl_2$ (**6b1**) and [1-(η^5-9-fluorenyl)-1(*S*)-phenyl-2-(η^5-1(*R*)-indenyl)ethane]$ZrCl_2$ (**6b2**),[9] are shown in Figure 1. In both complexes the bulky phenyl groups occupy the energetically favored equatorial positions of the metallacycles.[10] This leads to preferred conformations of the chelate rings, depending on the nature of the stereogenic backbone center. An *R*-configuration causes a δ-conformation[11] (**6b1**), whereas the *S*-stereocenter gives rise to the λ-conformer (**6b2**), while the stereochemistry of the indenyl fragments remains unchanged (*R*-configuration in Figure 1). The different bridge twists result in staggered arrangements of the fluorenyl (Flu) and indenyl (Ind) units within **6b1** and **6b2**. This allows control of the relative positions of the β-CH substituents[12] (Figure 1) to each other, which are assumed to play a major role in the enantiofacial discrimination of the inserting propene monomer.[4,13] According to a notation first introduced by Brintzinger et al.,[14a,b] the δ-conformation places the opposite-standing substituents β^1 and β^3 in a "forward" position, minimizing the distance between both groups. Consequently a "backward" arrangement is expected for the λ-conformation with a maximal distance of β^1 and β^3.

In these unsymmetric complexes the ethylene backbone substituent, which originates from the epoxide starting material, creates a stereogenic carbon center. In combination with the stereocenter of the indenyl group, **6b1,2** and **6c1,2** exist as diastereomers and can be separated by crystallization.[15] **6b1** and **6c1** were obtained from toluene solution at −30 °C in pure form. Extraction of the residue with 1,2-dimethoxyethane left **6b2** and **6c2** in roughly 80% excess. Recrystallization from toluene again resulted in precipitation of the pure diastereomers **6b2** and **6c2**. For the formation of **6c1,2** a remarkable dependence of the diastereoselectivity on solvent and temperature was ob-

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[7] For ring-opening reactions of epoxides with [Cp]Na or [Flu]Li, cf. also: (a) Ohta, H.; Kobori, T.; Fujisawa, T. *J. Org. Chem.* **1977**, *42*, 1231. (b) Rieger, B. *J. Organomet. Chem.* **1991**, *420*, C17.

[8] Ring-opening reactions of spiro[4.2]hepta-1,3-diene and spiro[cyclopropane-1,1′-indene] with other nucleophiles have been reported previously: (a) Kauffmann, Th.; Olbrich, A.; Varenhort, J. *Chem. Ber.* **1982**, *115*, 467. (b) Kauffmann, Th.; Bisling, M.; Köning, R.; Rensing, A.; Steinseifer, F. *Chem. Ber.* **1985**, *118*, 4517.

[9] Each diastereomer exists in two enantiomeric forms (e.g., **6b1** = *RR,SS*; **6b2** = *SR,RS*) since the synthesis started from a racemic mixture of epoxystyrene. The text refers only to one enantiomer for clarity.

[10] Buckingham, D. A.; Sargeson, A. M. *Top. Stereochem.* **1971**, 219.

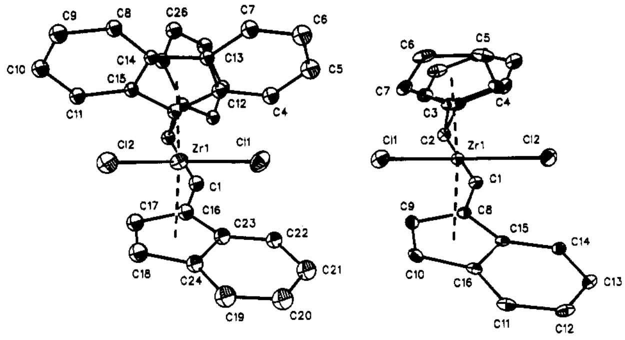
[11] For the notation of chiral metallacycles, cf.: Corey, E. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 2620.

[12] The term "β" refers to the position of the Cp substituents relative to the bridge connection; see also ref 13.

[13] Hortmann, K.; Brintzinger, H. H. *New J. Chem.* **1992**, *16*, 51.

[14] Cf. also: (a) Schäfer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1987**, *328*, 87. (b) Brintzinger, H. H. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H.-J., Eds.; Springer Verlag: Berlin, 1988; p 249. (c) Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695.

[15] The isolated molar ratio of **6b,c** is roughly 3:2 (conformer 1: conformer 2) independent of the ligand structure.



6b1 6c1

Figure 2. Molecular structure of the ethylene-bridged complexes **6b1** and **6c1** at −100 °C with 20% probability thermal ellipsoids depicted and H atoms removed for clarity.

Table 1. Crystallographic Data for Complexes 6b1 and 6c1[a]

	6b1	6c1
formula	$C_{30}H_{22}Cl_2Zr$	$C_{22}H_{18}Cl_2Zr$
fw	544.6	444.5
cryst color, form	red, near-cubic prism	yellow, needle
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, pm	1103.1(2)	837.0(2)
b, pm	1187.9(2)	985.8(2)
c, pm	1245.5(2)	1110.2(3)
α, deg	87.08(3)	102.43(2)
β, deg	84.00(3)	100.01(2)
γ, deg	70.16(3)	97.92(2)
V, 10^6 pm^3	1526.7(5)	903.5(3)
d_{calcd}, g/cm^3	1.185	1.63
Z	2	2
cryst dimens, mm	0.10 × 0.15 × 0.20	0.30 × 0.30 × 0.40
abs coeff (μ), mm^{-1}	0.548	0.905
T, K	173	173
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$	$w^{-1} = \sigma^2(F) + 0.0008F^2$
scan mode	Wyckoff	Wyckoff
scan range, deg	2.0	1.5
2θ range, deg	4–40	4–50
scan speed, deg/min	7.32–29.30	6.51–29.30
no. of data collected	5783	6397
no. of indep data	2848	3202
no. of unique data	2233	2756
obsd criterion	$F > 4\sigma(F)$	$F > 4\sigma(F)$
no. of params	298	226
R^b	0.098	0.023
$R_w{}^c$	0.097	0.023
residual density, 10^{-6}e pm^{-3}	2.44[d]	0.36

[a] Conditions: Siemens P4 four-cycle diffractometer, Mo Kα radiation, 71.073 pm, graphite monochromator. Solution: Direct methods; all non-hydrogen atoms were refined anisotropically. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \sum||F_o|-|F_c||(w)^{1/2}/\sum|F_c||(w)^{1/2}/\sum|F_o|(w)^{1/2}$. [d] High residual density due to two disordered toluene molecules which could not be resolved.

served. Preparation of the complexes according to the above mentioned procedure in CH_2Cl_2 gives a 3:2 mixture of **6c1** and **6c2**, respectively. Reaction of the dilithio salt of **5c** with $ZrCl_4(THF)_2$ in THF under reflux afforded **6c1** in 89% diastereomeric excess. Analogous solvent influences were reported recently by Chien and Rausch for the preparation of unsymmetric diastereomers with a single carbon bridge.[16]

The solid-state structures of **6b1** and **6c1** were determined (Figure 2, Tables 1–4). Both diastereomers show a δ-conformation of the metallacycle with the phenyl substituents located in the equatorial position of the chelate rings and the β-CH groups (C8, C19 in **6b1**; C11 in **6c1**) in a foward arrangement. The bond distances and angles (Table 2) of both *ansa*-zirconocene dichlorides are largely in accord with expectations. The conformations found for the solid-state structures are expected to be also preferred in solution, due to the steric demand of the bulky bridge substituents. If there is any flip between δ- and λ-conformations, it has to be fast, since variable temperature ^{1}H NMR experiments performed on the backbone ABX-spin system of **6b1** showed no line broadening at temperatures down to −100 °C, which could be indicative of such a process.

Table 2. Selected Distances (pm), Angles (deg), and Torsion Angles (deg) for Complexes 6b1 and 6c1

6b1		6c1	
Zr–Cl(1)	239.8(6)	Zr–Cl(1)	245.4(1)
Zr–Cl(2)	242.6(6)	Zr–Cl(2)	242.3(1)
Zr–Flu(centr)	225.9	Zr–Cp(centr)	219.5
Zr–Ind(centr)	222.6	Zr–Ind(centr)	223.2
Cl(1)–Zr–Cl(2)	96.1(2)	Cl(1)–Zr–Cl(2)	99.8(1)
Flu(centr)–Zr–Ind(centr)	127.3	Cp(centr)–Zr–Ind(centr)	125.0
C(3)–C(2)–C(1)–C(16)	45(2)	C(3)–C(2)–C(1)–C(8)	49.0(2)

No crystals suitable for X-ray diffraction could be obtained either for **6b2** or for **6c2**. However, the structure we proposed for **6b2** (Figure 1) is confirmed by comparison with [bis[4,5,6,7-tetrahydro-1(*R*)-indenyl]ethane]bis[*O*-acetyl-(*R*)-mandelato]titanium. The crystal structure of this complex was reported recently[14a,b] by Brintzinger et al. In the solid state the ethylene bridge of the titanocene adopts a λ-conformation (*R*-configuration of the indenyl stereogenic carbon center) with both indenyl fragments in their "backward" arrangement, as we suggested it for **6b2**.

A further comparison of the gross coordination geometry of the above 1(*R*)-indenyl Ti complex with its 1(*S*)-indenyl Ti diastereomer[14a,b] revealed no significant differences of bond lengths and bond angles which could be indicative of general structural distortions of λ-backward conformers.

Propene Polymerization at Different Temperatures. In a first series of experiments the catalysts **6a**, **6b1**, and **6b2**/MAO (MAO, methylalumoxane) were used for propane polymerization in toluene at 50, 70, and 85 °C and constant monomer concentration.[17] A comparison of the polymerization data in Table 5 shows the typical activity increase with polymerization temperature (T_p) for all three complexes. At 50 and 70 °C the propene consumption is constant over the entire polymerization period (see Experimental Section). Although the activity is highest at 85 °C, **6a**, **6b1**, and **6b2** undergo a slow decomposition reaction at this temperature and above, which results in a steady decline of monomer consumption with time.

The unsubstituted **6a**/MAO is the highest activity system in the present series of catalysts. The activities of the diastereomeric complexes **6b1** and **6b2** are comparable. Interestingly the higher selectivity **6b1** shows also a tendency toward higher polymerization activity compared to **6b2**. The molecular weights decrease with increasing T_p, as expected. Within the error limits of the GPC mea-

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(16) Llinas, G. H.; Day, R. O.; Rausch, M. D.; Chien, J. C. W. *Organometallics* **1993**, *12*, 1283.

(17) Propene concentrations were measured by the use of a calibrated gas flow meter (Bronkhurst F-111-C-HD-33-V). The experimental results were checked by comparison with calculated data. For an appropriate equation of state for the system propene/toluene, see: (a) Plöcker, U.; Knapp, H.; Prausnitz, J. *Ind. Eng. Chem. Process Des. Rev.* **1978**, *17*(3), 324. (b) Tyvina, T. N.; Efremova, G. D.; Pryanikova, R. O. *Russ. J. Phys. Chem.* **1973**, *47*(10), 1513.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$) for Complex 6b1

atom	*x*	*y*	*z*	U_{eq}
Zr(1)	1869(2)	776(2)	2531(2)	33(1)
Cl(1)	2532(5)	158(5)	4302(4)	51(2)
Cl(2)	1549(5)	−1068(4)	2108(4)	49(2)
C(1)	2309(19)	3308(16)	1393(15)	42(9)
C(2)	905(17)	3541(16)	1329(15)	31(8)
C(3)	442(17)	2762(15)	2129(14)	28(8)
C(4)	851(20)	3416(17)	3976(17)	47(10)
C(5)	600(23)	3247(20)	5114(19)	61(11)
C(6)	−90(22)	2466(19)	5542(17)	50(10)
C(7)	−527(19)	1837(18)	4860(17)	43(9)
C(8)	−1407(18)	767(16)	2826(17)	37(9)
C(9)	−1715(20)	488(18)	1826(19)	45(10)
C(10)	−1320(19)	944(18)	877(17)	40(9)
C(11)	−572(19)	1678(17)	887(16)	40(9)
C(12)	366(18)	2772(16)	3253(16)	35(9)
C(13)	−323(17)	1955(15)	3727(15)	26(8)
C(14)	−719(16)	1505(14)	2882(13)	19(7)
C(15)	−290(17)	1999(15)	1880(15)	29(8)
C(16)	3031(19)	1971(19)	1442(16)	42(9)
C(17)	2933(20)	1102(18)	722(16)	41(9)
C(18)	3698(21)	−27(21)	1054(17)	52(10)
C(19)	5217(20)	−772(22)	2605(20)	60(11)
C(20)	5680(21)	−314(23)	3414(21)	59(11)
C(21)	5268(22)	911(24)	3615(20)	60(12)
C(22)	4395(18)	1725(18)	3012(16)	36(9)
C(23)	3902(19)	1349(19)	2209(17)	42(10)
C(24)	4344(19)	87(18)	1965(17)	41(10)
C(25)	−1254(21)	5092(17)	1494(16)	43(10)
C(26)	−2139(22)	6253(19)	1654(17)	53(11)
C(27)	−1644(23)	7196(19)	1774(16)	50(10)
C(28)	−341(22)	6955(18)	1731(14)	38(10)
C(29)	483(19)	5797(18)	1591(14)	36(9)
C(30)	38(18)	4826(16)	1468(14)	30(9)

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$) for Complex 6c1

atom	*x*	*y*	*z*	U_{eq}
Zr(1)	1476(1)	4362(1)	2520(1)	19(1)
Cl(1)	−1394(1)	3734(1)	1704(1)	34(1)
Cl(2)	1659(1)	3544(1)	4439(1)	39(1)
C(1)	5015(3)	5228(2)	1704(2)	25(1)
C(2)	4340(3)	6578(3)	1665(2)	26(1)
C(3)	3098(3)	6642(2)	2477(2)	25(1)
C(4)	3271(3)	6576(3)	3746(2)	30(1)
C(5)	1799(3)	6691(3)	4103(3)	38(1)
C(6)	718(3)	6765(3)	3049(3)	39(1)
C(7)	1497(3)	6714(2)	2030(3)	31(1)
C(8)	3695(3)	3977(2)	1440(2)	23(1)
C(9)	2273(3)	3668(3)	495(2)	26(1)
C(10)	1325(3)	2428(3)	580(2)	29(1)
C(11)	1812(3)	686(3)	2017(2)	31(1)
C(12)	2916(3)	442(3)	2934(3)	33(1)
C(13)	4397(3)	1367(3)	3426(2)	31(1)
C(14)	4764(3)	2560(2)	3024(2)	25(1)
C(15)	3646(3)	2862(2)	2069(2)	21(1)
C(16)	2159(3)	1899(2)	1545(2)	25(1)
C(17)	5815(3)	8731(3)	1212(3)	38(1)
C(18)	6990(4)	9931(3)	1553(3)	47(1)
C(19)	7965(3)	10321(3)	2728(3)	47(1)
C(20)	7798(3)	9510(3)	3575(3)	45(1)
C(21)	6631(3)	8299(3)	3244(3)	36(1)
C(22)	5622(3)	7900(2)	2057(2)	27(1)

surements the products of all three catalysts have equivalent molecular weight. No regio-misinsertions, like head-to-head combinations or 1,3-insertions, could be detected for all three catalysts, neither in the total polymers nor in the fractions.[18]

However, the most interesting results arise from a comparison of the product stereoregularities. The δ-forward conformer **6b1** gives by far the most selective catalyst. The polymers produced with **6b1**/MAO are crystalline materials with defined melting transitions at all polymerization temperatures applied. One of the major implications of the stabilizing bridge substituents is demonstrated by an increase of T_p from 50 to 70 °C. In contrast to *rac*-ethylenebis(indenyl)zirconium dichloride[3] there is no significant effect on polymer stereoregularity. The polypropenes prepared at these temperatures have mmmm-pentad contents ([mmmm]) of 70.5% and 69.8%, respectively. Only a further increase of T_p to 85 °C reduces [mmmm] to 64.4%.

Inversion of the backbone twist to the λ-backward conformer results in a nearly complete loss of stereoselectivity. **6b2** produces atactic oils or waxes with [mmmm] values ranking between 26.5% (T_p = 85 °C) and 36.0% (T_p = 50 °C).

The stereoregularities of polypropenes resulting from the unsubstituted derivative **6a** lie between those of **6b1** and **6b2**. Here the lack of the stabilizing phenyl group leads to a rapid decline of [mmmm] from 63.9% (T_p = 50 °C) to 39.2% (T_p = 85 °C).

For recently described sets of diastereomeric catalysts, the reported differences in stereoselectivity can be explained, since in most of the cases they consist of a racemic C_2-symmetric complex mixture giving isotactic polypropene and an unsymmetric diastereomer with reduced stereoselectivity. Well-known examples are the racemic and meso derivatives of the ethylenebis(indenyl) system[1a] or their alkyl-substituted counterparts.[1d] In the present series of catalysts both diastereomers are unsymmetric with comparatively small differences (forward and backward conformers) of their ligand arrangements. At the moment, we have no genuine explanation for the unexpected high selectivity difference of **6b1** and **6b2**. However, **6b1** is expected to provide a tight chiral coordination cage, due to the forward position of the β-substituents (see Figures 1 and 2). To account for the stereoregularity of polypropenes prepared with **6b1**, one could assume that the stereorigidity of this template accommodates one particular geometry of the chain and the propene monomer preferentially. It would then be easy to visualize that the opened cage in **6b2** allows for a less rigid arrangement with more than one possible olefin-insertion transition state. Our argumentation is supported by the polymerization results of **6a** (cf. Tables 5 and 6), which carries no bulky bridge substituent and should therefore be free to adopt a sterically "optimal" geometry during chain propagation, somewhere in between the two extremes **6b1** and **6b2**. This results in the highest activity in the series of the complexes **6a**, **6b1**, and **6b2** but also in a significantly reduced stereoselectivity compared to the δ-forward conformer **6b1**. The importance of an optimal coordination gap geometry for the design of highly selective catalysts was recently pointed out by Brintzinger et al.[13]

Propene Polymerization at Variable Monomer Concentration. In most of the metallocene catalysts used for propene polymerization, both coordination sites are related to each other by C_2 symmetry. This leads to the same enantiofacial preference for each inserting olefin and hence to the formation of isotactic polymers. Unsymmetric catalysts have two different coordination sites with different selectivities. If the particular substitution pattern on either site also influences the rate of the selectivity-determining step, the stereoselectivity of those complexes should depend on monomer concentration.[19]

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[18] Selected polymer samples were fractionated according to Pasquon's method; cf. ref 3 and literature cited there.

Table 5. Polymerization Data of 6a, 6b1, and 6b2 at Different Temperatures and Constant Monomer Concentration[a]

entry	metallocene	T_p,[b] °C	t_p,[c] s	[Zr], 10^{-5} mol/L	yield, g	activity[d]	[mmmm], %	T_m,[e] °C	M_w, 10^3 g/mol	M_w/M_N
1	**6a**	50	1230	1.1	7.1	2660	63.9	110	27.8	1.8
2		70	1020	1.1	11.4	5150	59.3	104	19.3	1.4
3		85	1070	1.1	13.2	5690	39.2	wax	8.6	1.9
4	**6b1**	50	2360	1.1	5.1	990	70.5	121	26.6	1.4
5		70	2650	1.1	26.2	4560	69.8	119	20.8	1.6
6		85	1690	1.1	19.8	5400	64.4	98	8.9	2.1
7	**6b2**	50	2740	1.7	8.3	900	36.0	wax	27.9	1.8
8		70	2330	1.7	22.1	2830	29.7	wax	21.9	2.0
9		85	1670	1.1	18.3	5050	26.5	oil	9.3	1.7

[a] Monomer concentration: $[C_3] = 0.71$ mol/L.[17] [b] T_p: polymerization temperature. [c] t_p: polymerization time. [d] Activity in (10^3 g of pp)[(mol L^{-1} of C_3)(mol L^{-1} of Zr)h]$^{-1}$. [e] T_m: maximum of polymer melting transition.

Table 6. Polymerization Data of 6a, 6b1,2, and 6c1,2 at Variable Monomer Concentrations and Constant Temperature[a]

entry	metallocene	$[C_3]$,[b] mol/L	t_p,[c] s	[Zr], 10^{-5} mol/L	yield, g	activity[d]	[mmmm], %	M_w, 10^3 g/mol	M_w/M_N
1	**6a**	0.45	1480	1.1	5.7	1260	68.1	nd[e]	nd
2		1.16	1430	1.1	9.6	2200	52.4	nd	nd
3		1.76	1340	1.1	16.6	4060	42.8	nd	nd
4		3.38	1620	1.1	20.3	4100	37.5	nd	nd
5	**6b1**	0.45	1790	1.5	8.0	1070	80.4	11.5	1.6
6		1.16	2010	1.5	16.1	1920	63.2	25.1	1.8
7		1.76	1640	1.1	14.4	2870	53.1	36.7	1.4
8		3.38	1470	1.1	16.4	3660	46.5	49.0	2.0
9	**6b2**	0.45	1930	1.5	7.0	870	28.3	13.7	1.8
10		1.16	1910	1.5	12.1	1520	21.3	27.0	1.5
11		1.76	1920	1.5	14.5	1810	17.7	47.5	2.1
12		3.38	1570	1.1	14.2	2960	15.5	62.9	1.4
13	**6c1**	0.45	3020	3.1	1.3	50	40.6	0.5	1.8
14		1.16	3170	3.1	12.0	440	39.9	1.4	2.1
15		1.76	2120	3.1	15.5	850	40.1	4.2	1.7
16		3.38	2720	1.5	21.5	1900	39.3	11.0	1.5
17	**6c2**	0.45	3070	1.5	0.7	60	35.4	0.8	2.0
18		1.16	2850	1.5	2.3	190	35.0	1.8	1.8
19		1.76	2770	1.5	6.6	570	35.7	4.5	1.7
20		3.38	2630	1.5	13.0	1190	34.4	10.8	1.7

[a] Polymerization temperature $T_p = 50$ °C. [b] $[C_3]$: monomer concentration.[17] [c] t_p: polymerization time. [d] Activity in (10^3 g of pp)[(mol L^{-1} of Zr)h]$^{-1}$. [e] Not determined.

To test this hypothesis **6a**, **6b1,2**, and **6c1,2**/MAO were used for propene polymerization at various monomer concentrations (T_p = constant = 50 °C). The polymerization data in Table 6 show that the highly substituted catalysts **6a**, **6b1**, and **6b2**/MAO produce polypropenes with reduced stereoregularities at increasing concentration.[20] **6b1** is the most selective species, but its stereoselectivity declines from [mmmm] = 80.4% (0.45 mol of C_3/L) to 46.5% (3.38 mol of C_3/L) with increasing propene concentration. An analogous dependence was found for the less selective derivative **6a** and for the unselective λ-backward conformer **6b2**.[21] The [mmmm]-pentad content of the polymers prepared with **6c1,2**/MAO remains unchanged with variations of monomer concentration (see Figure 3).

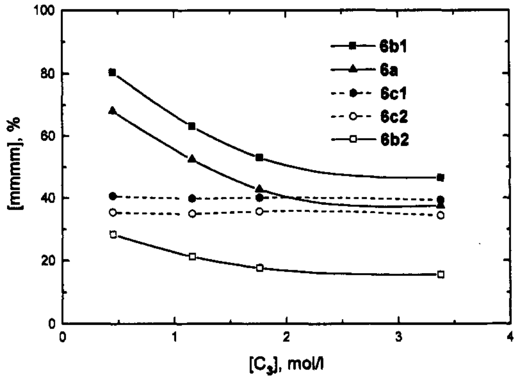

Figure 3. Plot of the polypropene stereoregularity ([mmmm] pentads) versus monomer concentration [(C_3]) for **6a**, **6b1,2**, and **6c1,2** at constant polymerization temperature (T_p = 50 °C).

We would like to discuss this dependence on the basis of a coordination equilibrium (Scheme 3) which encompasses four differently ligated species. The catalytically active cation can exist in two states (**I** and **III**) depending on the coordination of the growing chain. The left side of **I** resembles the structure of the ethylenebis(indenyl)zirconium system. Monomer coordination and insertion should be fast and highly selective (state **II**), leading to state **III** after a stereoregular insertion.[22]

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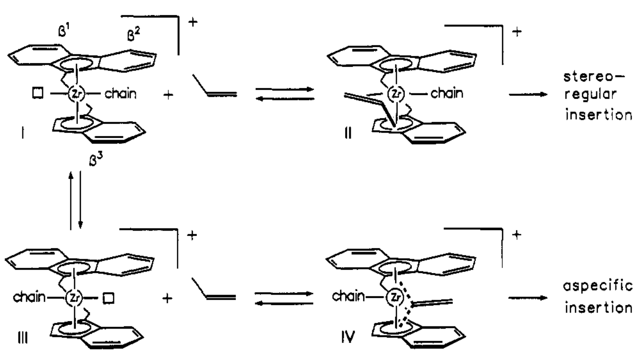
[19] An increase of polymer stereoregularity with monomer concentration was found for C_s-symmetric isopropylidene[(9-fluorenyl)cyclopentadienyl]zirconium dichloride. With the same system a decrease of the rrmr pentad at higher monomer concentration was reported. This finding was attributed to a facile chain migration at low C_3-concentration between two successive insertions (skipped insertion) as a consequence of the coordinately unsaturated zirconium cation. Cf.: (a) Ewen, J. A. *Stud. Surf. Sci. Catal.* **1990**, *56*, 439. (b) Herferth, N.; Fink, G. *Makromol. Chem., Makromol. Symp.* **1993**, *66*, 157.

[20] Polymerization experiments with C_2-symmetric *rac*-ethylenebis(indenyl)zirconium dichloride did not show any influence of monomer concentration on the polymer stereoregularity.

[21] The polypropene products of **6b2** show a slight increase of the syndiotactic rrr pentad (up to 10%; C_3 = 3.38 mol/L) at increased monomer concentrations. This could be attributed to a structural relation of this complex to the known, highly syndioselective isopropylidene[(9-fluorenyl)cyclopentadienyl]zirconium dichloride.

[22] It is interesting to extrapolate the curves for **6b1** and **6b2** to $[C_3]$ = 0. The limiting values ([mmmm] = 93% for **6b1**; 33% for **6b2**) should provide a measure for the selectivity of the left, "ethylenebis(indenyl)-like" catalyst side at a given temperature and a defined bridge conformation, since insertion from state **II** is expected to be preferred at reduced monomer concentration, according to the discussed coordination equilibrium (Scheme 3).

Scheme 3



In state **III** the chain occupies the free segment between β^1 and β^3, and **III** is therefore expected to be preferred over **I**. Monomer coordination to state **IV** should be hindered, due to the sterically shielding influence of the fluorenyl and indenyl groups on the right complex moiety. On the basis of polymerization results reported recently for the syndiospecific system isopropylidene[(η^5-9-fluorenyl)cyclopentadienyl]zirconium dichloride/MAO, one can assume a fast chain migration between **I** and **III**,[19] which should allow for isospecific propagation via state **II** at low monomer concentration. With increasing propene pressure, complexation to state **III** becomes more important. At high C_3 concentrations, chain migration to state **I** is obviously too slow to overcompensate the high population of state **III**. Both states equally take part in chain propagation. Presumably the adjacent positions of β^2 and β^3 allow no efficient enantiofacial discrimination of a prochiral monomer unit (state **IV**). Insertion of a coordinated propene molecule from state **IV** leads to a stereoerror in the chain and hence to the observed decrease of polymer stereoregularity with increasing monomer pressure. A plot of [mmmm] versus [C_3] is shown in Figure 3 for **6a**, **6b1,2**, and **6c1,2**.

Complexes **6c1** and **6c2** are provided with only one sterically demanding β-CH substituent (e.g., C11, **6c1**, Figure 2). Facile monomer coordination is allowed at each catalyst site. Consequently no influence of propene concentration on polymer stereoregularity can be observed (Figure 3). On the other hand, one β-substituent defines no chiral cage tight enough to favor a single transition-state geometry. Hence the polymer stereoregularities are low. However, even here the δ-forward conformer shows a tendency toward formation of higher stereoregularity polypropene.

We are currently studying variations of the synthetic strategy presented here to provide C_2-symmetric metallocene systems with defined bridge conformations. It will be interesting to find out if the concept of conformational rigidity can be useful for the design of catalysts with improved stereoselectivity.

Experimental Section

All preparative reactions were carried out under an atmosphere of dry argon using standard Schlenk tube techniques. The hydrocarbon and ether solvents were purified by distillation from $LiAlH_4$. CH_2Cl_2 was distilled from CaH_2. $ZrCl_4(THF)_2$,[23] NaCp(dioxane),[24] $(CF_3SO_2)_2O$,[25] **2b**, and **3b**[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. ^{13}C NMR spectra of the polymer products were measured in $C_2D_2Cl_4$ at 120 °C and analyzed by known methods.[1a,4,26] Mass spectra were acquired with Finnigan instruments (MAT-711A, modified by AMD Intectra (FD, FAB); Finnigan TSQ70 (EI, FAB), 70 eV). Molecular weights and molecular weight distributions of the polymers were determined by gel-permeation chromatography (GPC, Waters 150 chromatograph, 140 °C in 1,2,4-trichlorobenzene). Melting points (T_m) as well as melting enthalpies were measured by differential scanning calorimetry (Perkin-Elmer DSC 4). Elemental analyses were determined in the microanalytical laboratory of the Institute (Carlo Erba, Model 1106).

Preparation of 2-(9-Fluorenyl)ethanol (2a). A solution of fluorene (30.0 g, 180 mmol) in 200 mL of diisopropyl ether was treated with *n*-butyllithium in hexane (1.6 M, 112.5 mL, 180 mmol) at 0 °C. Frozen ethylene oxide (8 g, 182 mmol) in a Schlenk tube was fed continuously to the pale yellow solution by being warmed to room temperature. The color of the suspension turned to orange. After all of the epoxide was consumed, the reaction mixture was stirred for an additional 30 min at 0 °C and then neutralized with 150 mL of a saturated aqueous solution of NH_4Cl. The organic layer was separated and the water phase washed twice with diethyl ether. The combined and dried (Na_2SO_4) organic phases were concentrated in vacuo. **2a** crystallizes from toluene/hexane (2:3) (colorless needles) (32.1 g, 153 mmol, 84.8%), mp 107–108 °C. ^1H NMR ($CDCl_3$): δ 1.48 (s, 1H), 2.2–2.4 (m, 2H), 3.4–3.6 (m, 2H), 4.13 (t, J = 6.21 Hz, 1H), 7.1–7.9 (m, 8H). FDMS: 210 (M^+, 100). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.73; H, 6.68.

Preparation of 2-(1-Indenyl)-2-phenylethanol (2c). The synthesis of **2c** was carried out according to the route used for the preparation of **2a**. Starting from indene (14.2 mL, 121 mmol), we obtained **2c** (19.9 g, 84.2 mmol, 69.6%) as pale yellow crystals after column chromatography over silica (eluent: toluene/diethyl ether, 95:5), mp 85–87 °C. ^1H NMR ($CDCl_3$): δ 7.1–7.5 (m, 9H), 6.3 (m, 1H), 4.94–4.99 (m, 1H), 3.3 (m, 2H), 2.91–2.94 (m, 2H). EIMS (70 eV, 120 °C): 236 (M^+). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.47; H, 6.75.

Preparation of 2-(1-Indenyl)-2-phenylethyl Methanesulfonate (3c). A solution of **2c** (20 g, 83.9 mmol) and triethylamine (11.6 mL, 83.9 mmol) in 200 mL of CH_2Cl_2 was treated dropwise with methanesulfonyl chloride (6.5 mL, 83.9 mmol) in 40 mL of CH_2Cl_2 at 0 °C. The reaction mixture was stirred for 30 min at this temperature and then extracted three times with water. The CH_2Cl_2 layer was dried (Na_2SO_4) and the solvent distilled off, leaving crude **3c** as a yellow oil. Crystallization of the colorless product was performed by stirring a suspension of the oil in ethanol overnight. Colorless **3c** was isolated by filtration (22.2 g, 70.6 mmol, 84%), mp 88 °C dec. ^1H NMR ($CDCl_3$): δ 2.7 (s, 3H), 3.38–4.44 (m, 1H), 3.30 (m, 2H), 3.46–3.63 (m, 1H), 3.91–3.98 (m, 1H), 4.29 (d, J = 5.5 Hz, 1H), 6.31 (m, 1H), 6.94–7.71 (m, 9H). FDMS: 314 (M^+, 75), 219 ($M^+ - CH_3SO_3$, 100). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77. Found: C, 68.81; H, 5.61.

Preparation of Spiro[(2-phenylcyclopropane)-1,1′-indene] (4a). To a solution of diisopropylamine (8.0 mL, 56.9 mmol) and *n*-butyllithium (1.6 M, 35.6 mL, 56.9 mmol) in 150 mL of THF at 0 °C was added (20 g, 54.9 mmol) in 100 mL of THF over a period of 15 min. The mixture was stirred overnight at ambient temperature, and then the solvents were evaporated and the dark oily residue was suspended in a saturated aqueous solution of NH_4Cl. The mixture was extracted with diethyl ether (6 × 50 mL). 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** (10.48 g, 48.0 mmol, 87%) (pale yellow oil; 1:3 mixture of the two possible isomers). ^1H NMR ($CDCl_3$): δ, for one isomer, 2.3 (d, J = 7.8 Hz, 2H), 3.2 (t, J = 7.8 Hz, 1H), 3.31 (m, 2H), 6.32 (m, 1H), 6.5–7.6 (m, 9H); for the other isomer, 2.7 (d, J = 6.8 Hz, 2H), 3.5 (t, J

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= 6.8 Hz, 1H), 3.38 (m, 2H), 6.36 (m, 1H), 6.4–7.7 (m, 9H). FDMS: 218 (M^+, 100). Anal. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.38; H, 6.32.

Preparation of 1-(9-Fluorenyl)-2-(1-indenyl)ethane (5a) via 2-(9-Fluorenyl)ethyl Trifluoromethanesulfonate (3a). Trifluoromethanesulfonic acid anhydride (7.8 mL, 47.6 mmol) was added to a solution of alcohol **2a** (10 g, 47.6 mmol) and pyridine (3.84 mL, 47.6 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The reaction mixture was stirred for 15 min. The organic layer was washed with ice water and dried (Na_2SO_4). Evaporation of the solvent at 0 °C gave **3a** as a colorless solid,[27] which was dissolved in 75 mL of precooled dioxane (~10 °C). The clear solution was added at room temperature to a colorless suspension of indenyllithium in dioxane (200 mL), which was prepared by the reaction of indene (6.7 mL, 57.1 mmol) and *n*-butyl lithium (1.6 M, 35.7 mL, 57.1 mmol). The mixture was stirred overnight, and then the solvent was distilled off and the solid residue was suspended in 200 mL of a saturated aqueous solution of NH_4Cl. The mixture was extracted thoroughly with diethyl ether (4 × 200 mL). From the dried ether phase (Na_2SO_4) the solvent was evaporated. After column chromatography over silica (eluent: toluene/hexane, 2:7), **5a** (10.3 g, 33.4 mmol, 70%) was obtained as a crystalline colorless solid, mp 99–100 °C. ^1H NMR ($CDCl_3$): δ 2.15–2.45 (m, 4H), 4.05 (t, J = 5.1 Hz, 1H), 6.08 (s, 1H), 6.3 (s, 2H), 7.1–7.8 (m, 12H). FDMS: 308 (M^+, 100). Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.39; H, 6.62.

Preparation of 1-(9-Fluorenyl)-1-phenyl-2-(1-indenyl)ethane (5b) via 2-(9-Fluorenyl)ethyl Trifluoromethanesulfonate (3b). **2b** (10 g, 34.9 mmol) was treated in a manner similar to that of **2a** to yield **5b** (8.5 g, 22.1 mmol, 63%) as a slightly yellow crystalline material, mp 118–119 °C. ^1H NMR ($CDCl_3$): δ 2.61–2.94 (m, 2H), 3.16 (d, J = 1.9 Hz, 2H), 4.07–4.14 (m, 1H), 4.39 (d, J = 3.8 Hz, 1H), 5.99 (t, J = 1.9 Hz, 1H), 7.1–7.7 (m, 17H). FDMS: 384 (M^+, 100). Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.74; H, 6.30.

Preparation of 1-Cyclopentadienyl-1-phenyl-2-(1-indenyl)ethane (5c). NaCp(dioxane) (12.1 g, 68.8 mmol) was added to a solution of **4a** (10 g, 45.8 mmol) in DMF (100 mL) at −15 °C. The dark red mixture was stirred at this temperature for 3 days. The solvent was distilled off at reduced pressure, and the dark brown residue was worked up in a manner similar to that described for **5a,b**, leaving **5c** (6.4 g, 22.5 mmol, 49%) as a pale yellow oil. The ^1H NMR spectrum of **6a** gives 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: 284 (M^+, 100). Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.58; H, 6.78.

Preparation of the Zirconocene Dichlorides 6a–c. To a solution of one of the ligand precursors **5a–c** (22 mmol) in 50 mL of diethyl ether was added *n*-butyllithium (1.6 M in hexane, 27.5 mL, 44 mmol) 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 of CH_2Cl_2 which was precooled to −80 °C. The suspension was warmed to room temperature and stirred overnight. The mixture was passed through a 1-in. pad of Celite, with CH_2Cl_2 washing. 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.

Compound 6a: 2.8 g, 6.0 mmol, 27%. ^{1}NMR ($CDCl_3$): δ 6.9–7.9 (m, 12H), 6.28 (d, J = 2.1 Hz, 1H), 6.14 (d, J = 3.3 Hz, 1H), 3.8–4.4 (m, 4H). FABMS: 469 (M^+, 30), 433 (M^+ − Cl, 100). Anal. Calcd for $C_{24}H_{18}Cl_2Zr$: C, 61.52; H, 3.87. Found: C, 61.63; H, 4.02.

Compound 6b1,2: 7.7 g, 14.1 mmol, 64%. ^1H NMR ($CDCl_3$): δ, **6b1**, 6.9–7.9 (m, 17H), 6.51 (d, J = 3.4 Hz, 1H), 6.44 (d, J = 3.4 Hz, 1H), 5.80 (dd, J = 6.9, 13.4 Hz), 2 diastereotopic protons 4.69 (dd, J = 13.4, 14.1 Hz, 1H), 4.09 (dd, J = 6.9, 14.1 Hz, 1H); **6b2**, 7.1–8.0 (m, 17H), 6.31 (m, 1H), 6.20 (d, J = 3.28 Hz, 1H), 5.94 (d, J = 3.25, 1H), 4.4–4.5 (m, 2H). FABMS: 545 (M^+, 40), 509 (M^+, −Cl, 100). The complexes crystallize with variable amounts of toluene. Elemental analysis was performed on powdered crystals which had been dried in vacuo overnight. Anal. Calcd for $C_{30}H_{22}Cl_2Zr$: C, 66.16; H, 4.07. Found: 66.19; H, 4.10.

Compound 6c1,2: 3.9 g, 8.8 mmol, 40%. ^1H NMR ($CDCl_3$): δ, **6c1**, 7.2–7.6 (m, 9H), 7.0 (d, J = 3.43 Hz, 1H), 6.34–6.37 (m, 1H), 6.64–6.67 (m, 2H), 5.95–6.03 (m, 2H), 4.97–5.05 (m, 1H), 3.67–3.70 (m, 2H); **6c2**, 7.1–7.7 (m, 9H), 7.1 (m, 1H), 6.61–6.68 (m, 1H), 6.47–6.49 (m, 2H), 5.83–5.92 (m, 2H), 5.01–5.13 (m, 1H), 2 diastereomeric protons 3.97 (dd, J = 16.0, 17.2 Hz, 1H), 3.69 (dd, J = 7.1, 4.1 Hz, 1H). FABMS: 445 (M^+, 60), 409 (M^+ −Cl, 100). Anal. Calcd for $C_{22}H_{18}Cl_2Zr$: C, 59.44; H, 4.08. Found: C, 59.64; H, 4.21.

Separation of the Diastereomeric Complexes 6b1,2 and 6c1,2. **6b1** (3.2 g, 5.9 mmol) and **6c1** (2.2 g, 4.9 mmol) crystallized from a toluene solution (saturated at room temperature) at −30 °C as pure isomers. From the mother liquors the solvents were removed and the residues were extracted with boiling ethylene glycol dimethyl ether (4 × 20 mL), leaving **6b2** and **6c2** in excess (**6b2**, 85%; **6c2**, 79%). Recrystallization from toluene gave pure **6b2** (1.3 g, 2.4 mmol) and **6c2** (0.9 g, 2.0 mmol).

6c was also prepared in THF. The solution was refluxed for 3 h after the addition of $ZrCl_4(THF)_2$ to the dilitho salt. The solvent was then removed and the residue crystallized from toluene solution at −30 °C as described above. This procedure afforded the formation of the diastereomers (**6c1**:**6c2**) in a 17:1 ratio. Recrystallization from toluene at −30 °C gave pure **6c1**.

Polymerizations. Toluene (300 mL) was mixed with the desired amount of MAO (solution in toluene; 4.7 wt % Al; M_w = 900 g mol^{-1}) in a 1-L Büchi glass autoclave, thermostated at 50, 70 or 85 °C, respectively. The system was charged with propene up to the desired concentration.[17] The polymerization reaction was started by addition of a calibrated metallocene/toluene solution. Monomer pressure (±50 mbar) and temperature (±0.5 °C) were kept constant. Monomer consumption, pressure, and inside temperature were controlled by real time monitoring, one data set being taken every 2 s. After 1 h the polymerization was quenched by addition of 10 mL of methanol. The polymer was quantitatively precipitated by pouring the solution into excess acidified methanol. After thorough washing with methanol/HCl and methanol the product was dried overnight at 70 °C.

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Supplementary Material Available: Structure determination summaries and tables of atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and hydrogen atom coordinates (15 pages). Ordering information is given on any current masthead page.

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(27) The trifluorosulfonates decompose above 0 °C. No satisfying analytical results could be obtained. **3a,b** were used for the preparation of **5a,b** without isolation.