A Cholestenyl-Substituted Bis(indenyl)zirconocene-Derived Homogeneous Ziegler Catalyst for Stereoselective Propene Polymerization

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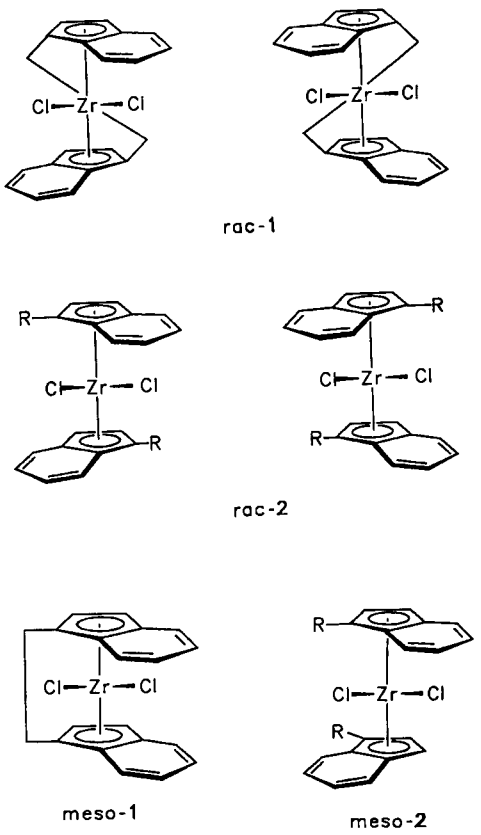
(−)-5-Cholesten-3β-yl tosylate (**6**) undergoes S_N2 substitution with indenyllithium to give (−)-3-(5-cholesten-3α-yl)indene (**7**), which is subsequently deprotonated by methyllithium to give the cholestenyl-substituted indenyllithium reagent **8**. Its reaction with 0.5 molar equivalents of $ZrCl_4(THF)_2$ furnished the three bis[3-(5-cholesten-3α-yl)indenyl]$ZrCl_2$ diastereoisomers in a ratio of **9a**:**9b**:**9c** = 60:16:24. The major organometallic reaction product **9a** was recovered isomerically pure and used for the generation of an active homogeneous metallocene/alumoxane Ziegler-type catalyst for stereoselective propene polymerization. The catalyst derived from the non-bridged chirally substituted bis(indenyl)zirconocene complex **9a** produces partially isotactic polypropylene almost completely by enantiomorphic site control in the temperature range from −50 to +15°C.

The advent of the homogeneous bent metallocene/methylalumoxane-type Ziegler catalysts marks a major contribution to the development of catalytic α-olefin polymerization and related reactions[1]. The use of chiral ansa-metallocenes of the group 4 transition elements, especially their hydrocarbyl-bridged ("ansa") bis(indenyl)MX_2 derivatives, has allowed the generation of a variety of very reactive catalyst systems for the stereoselective polymerization of α-olefins (mostly of propene) at very high reaction rates[2].

We have recently shown that chiral non-bridged bis(indenyl)zirconium dichloride/methylalumoxane catalyst systems can produce isotactic polypropylene under enantiomorphic site control conditions as well. The examples successfully used for stereoselective polypropylene formation all bear a set of 1-substituted indenyl ligands[3]. With regard to their *configurational* characteristics these complexes are thus not fundamentally different from their respective ansa-metallocene counterparts (see Scheme 1)[4]; they may, however, exhibit different *conformational* properties.

When homochiral substituents are introduced into the 1-positions of the pair of indenyl ligands a stereochemical situation arises which allows for the formation of three diastereomeric complexes. The combination of two planarly chiral ligand/metal entities with the attached homochiral side chains may lead to the occurrence of two "*racem*-like" diastereoisomers (with relative configurations *R**,p-*R**, p-*R**,*R** and *R**,p-*S**,p-*S**,*R**, with R* denoting the configuration of the leading substituent chirality in the closest possible position to the indenyl π ligand framework) in addition to one "*meso*-like" congener (*R**,p-*R**,p-*S**,*R**-configurated), all of which are of course chiral and should be produced with an enantiomeric excess mainly determined by the optical purity of the synthetic precursor used to introduce the chiral substituent at the 1-indenyl position.

Scheme 1



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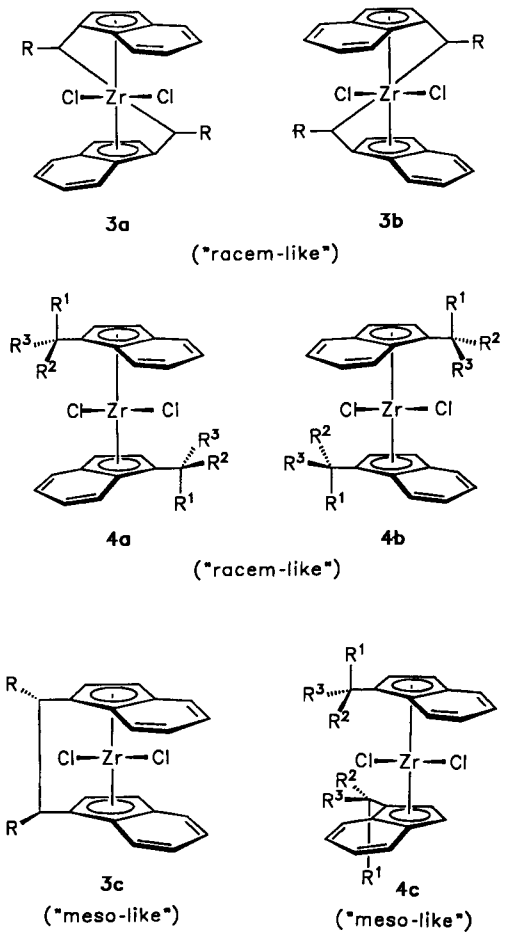
Scheme 2



A small number of (1-*R**)-indenyl systems have been used so far to successfully generate chiral non-bridged bent metallocene-derived active catalyst systems for the stereoselective formation of isotactic polypropylene[3,5]. In this account we describe an interesting new example where a steroidal substituent from the chiral pool, namely cholestenyl, effectively controls the metallocene stereochemistry for the stereoselective carbon-carbon coupling reaction.

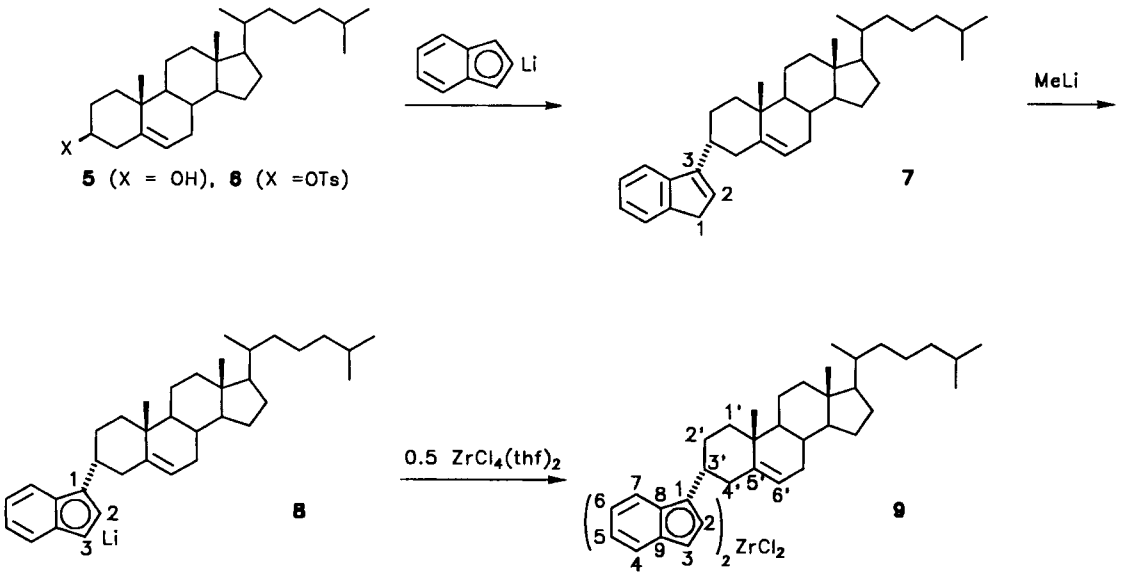
Results and Discussion

The starting material of our synthesis was β-cholestenol (**5**) which was converted to (−)-(5-cholesten-3β-yl) *p*-toluenesulfonate (**6**)[6]. This was subjected to a S_N2 substitution reaction with indenyllithium[7]. The expected primary product would be 1-(5-cholesten-3α-yl)indene. However, under the reaction conditions applied rearrangement involving hydrogen migration is fast enough to yield exclusively the (−)-3-(5-cholesten-3α-yl)indene isomer (**7**) (61% isolated)[8].

The structure assignment of the regioisomer **7** follows from the NMR spectra of the indene moiety and from an X-ray crystal structure analysis. Product **7** exhibits ^{1}H-NMR signals of the 1-H/1-H′ protons at δ = 3.26 and of 2-H at 6.28. In the ^{13}C-NMR spectrum the resonance for C-1 appears at δ = 38.1, the resonances for C-2 and C-3 are observed at δ = 129.7 and 147.5 and those of C-4 to C-7 at δ = 119.0, 125.8, 124.2, and 123.7, respectively. The quaternary carbon centers of the aromatic ring systems are observed at δ = 144.2 and 145.7 (C-8, C-9).

The X-ray crystal structure analysis of **7** (Figure 1) confirms that the cholestenyl system is 3α-substituted. The indenyl substituent, therefore, occupies an axial position at the chair-shaped A ring of the cholestenyl framework. The pertinent bond lengths inside the five-membered ring of the indenyl system are as expected for the 3-substitution: the C1 − C2 bond length is typical of a $C(sp^2)-C(sp^3)$ σ bond[9] at 1.496(5) Å whereas the adjacent C2 − C3 linkage is a C = C double bond [1.318(4) Å]. The connecting bond to the cholestenyl group is 1.519(4) Å, i.e. nearly as long as the C1 − C8 linkage [1.522(4) Å] inside the indene five-membered ring. The indene C3 − C9 bond length is 1.491(4) Å.

Scheme 3



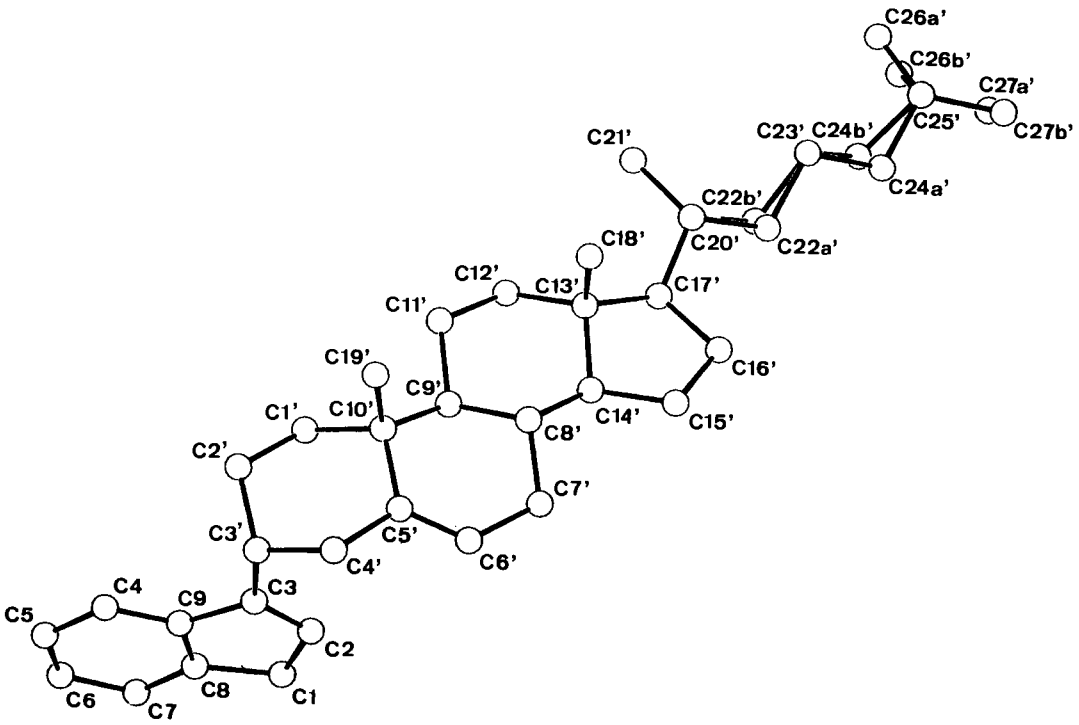


Figure 1. Molecular geometry of **7** with atom numbering scheme. Bond lengths [Å]: C(1)–C(2) 1.496(5), C(1)–C(8) 1.522(4), C(2)–C(3) 1.318(4), C(3)–C(3′) 1.519(4), C(3)–C(9) 1.491(4), C(4)–C(9) 1.378(4), C(5)–C(6) 1.340(6), C(8)–C(9) 1.384(4). Bond angles [°]: C(3)–C(2)–C(1) 113.0(3), C(9)–C(3)–C(3′) 121.5(2), C(9)–C(3)–C(2) 107.7(3), C(3′)–C(3)–C(2) 130.7(3), C(4′)–C(3′)–C(3) 116.1(3), C(4′)–C(3′)–C(2′) 108.5(2), C(3)–C(3′)–C(2′) 108.7(2), C(6)–C(5)–C(4) 120.9(3), C(8)–C(9)–C(3) 109.0(2), C(4)–C(9)–C(3) 130.5(3)

The hydrocarbon **7** was treated with methyllithium in ether to give the corresponding 1-(5-cholesten-3α-yl)-substituted indenyllithium reagent **8** (isolated in >90% yield). The lithium compound **8** was characterized spectroscopically. The ^{1}H-NMR spectrum in [D$_6$]benzene/[D$_8$]tetrahydrofuran (≈10:1) shows the 2-H/3-H protons at δ = 7.01/6.16 with a vicinal coupling constant of ^3J = 3.2 Hz. The 4-H/5-H hydrogens appear at 7.69, the 5-H/6-H system is centered at δ = 6.91. Their relative assignment is substantiated by the observation of a ^5J coupling (0.4 Hz) between hydrogen atoms 3-H and 7-H which is thought to be characteristic of such indenyllithium systems[10]. The cholestenyl 3-H resonance is located at δ = 3.78. The corresponding ^{13}C-NMR signals of **8** are observed at δ = 111.9 (C-1), 115.5 (C-2), 88.2 (C-3), 120.2/114.5 (C-4/C-7), and 118.4/116.0 (C-5/C-6)[11].

The cholestenyl-substituted indenyllithium reagent **8** was treated with bis(tetrahydrofuran)zirconium tetrachloride in a 2:1 stoichiometry. Attachment of two such chirally substituted indenyl ligands should give rise to the formation of three different diastereomeric bis[(*R**)-indenyl)]zirconium dichloride products, as outlined above[12]. The "*racem*-like" and "*meso*-like" diastereomers should be easily distinguished from one another because of their difference in the overall molecular symmetry. Each "*racem*-like" isomer is of averaged C_2 symmetry in solution and should therefore only give rise to one ^{1}H-NMR AX pattern of the 2-H/3-H hydrogens at the indene five-membered ring. The "*meso*-like" isomer is of lower symmetry and should therefore give rise to two such ^{1}H-NMR AX systems of the 2-H/3-H hydrogens at the then non-equivalent (*R**)-indenyl moieties (see Scheme 2)[3].

These characteristic ^{1}H-NMR features were helpful for the determination of the ratio of diastereoisomers initially formed in the reaction of **8** with $ZrCl_4(THF)_2$. We observed the formation of three diastereoisomeric bis[1-(5-cholesten-3α-yl)indenyl]zirconium dichlorides in a ratio of **9a** : **9b** : **9c** = 60:16:24. Complexes **9a** and **9b** exhibited only one 2-H/3-H ^{1}H-NMR AX pattern each at δ = 6.38, 5.71 and 6.03, 5.61, respectively. Thus, we conclude that these two complexes belong to the "*racem*-like" series. Complex **9c** shows four 2-H/3-H resonances at δ = 6.78, 6.42, 5.48, and 5.12. The (*R**)-indenyl inequivalence reveals that this complex must then be the "*meso*-like" diastereoisomer **9c**.

The major isomer **9a** could be separated from its congeners and isolated in a reasonable yield (36%). The pure "*racem*-like" diastereoisomer **9a** was used to generate an active homogeneous propene polymerization catalyst. In an orientating series of experiments the selectivity features and the relative polymerization activities of the **9a**/methylalumoxane catalyst were monitored in a temperature range between −50 and +15°C.

The active polymerization catalyst was generated by the reaction of **9a** with a large excess of methylalumoxane (Al:Zr ≈ 1000) in toluene containing ca. 30% of propene. The polymerization reaction was then allowed to take place for some time to yield a sufficient quantity of polypropylene. The reaction was then quenched and the polymer isolated. The molecular mass of the obtained polymer was determined by viscosimetry ($\bar{M}_\eta$). The stereochemical analysis of

the polymer was carried out by NMR spectroscopy (^{13}C-NMR methyl pentade analysis)[13].

As expected the polymerization activity of the **9a**/$(MeAlO)_x$ catalyst system was temperature-dependent. It was rather low at -50°C (a = 23 g polypropylene/g Zr · h), then rapidly increased with increasing temperature (see Table 1). Propene polymerization activity passed a broad maximum located in the temperature range between -30 and 0°C. At higher temperatures a markedly decreased activity was observed. This relation between temperature and activity indicates a rather complex kinetic behavior of the overall carbon-carbon coupling reaction[14], whose detailed mechanistic description must be based on a larger body of exact kinetic data, which is beyond what was intended with this orientating series of qualitative experiments.

Table 1. Selected data of the propene polymerization reactions carried out with the bis[1-(5-cholesten-3α-yl)indenyl]zirconium dichloride/methylalumoxane catalyst system [**9a**/$(MeAlO)_x$]

Polypropylene	PP 1	PP 2	PP 3	PP 4	PP 5	PP 6
Temp. [°C]	−50	−30	−8	0	+10	+15
Al/Zr[a]	1100	1070	1060	890	990	1140
activity[b]	23	226	257	225	138	52
$\bar{M}_n$	[f]	110000	51000	33000	11000	[f]
Analysis[c]						
ω	0.98	0.96	0.94	0.98	0.98	0.99
α	0.92	0.89	0.90	0.88	0.87	0.86
$\langle m \rangle_n$ α[d]	11.6	8.2	9.1	7.5	6.8	6.3
σ	[g]	0.74	0.85	[g]	[g]	[g]
ee*[e]	0.82	0.75	0.75	0.74	0.73	0.71

[a] Al/Zr = mmol [MeAlO]/mmol [Zr] (**9a**). — [b] g polymer/g Zr · h. — [c] Based on the ^{13}C-NMR methyl pentade distribution. — [d] Calculated average lengths of isotactic sequences (in monomer units). — [e] $(2\alpha - 1)\omega$. — [f] Not determined. — [g] Insignificant.

The ^{13}C-NMR methyl signals of each polymer obtained (polypropylenes PP 1–6) were monitored at the pentade resolution level and the respective signals integrated. The resulting methyl pentade signal ratios were then fitted by computational iteration with a simple statistical model[15] by using the parameters ω [giving the fraction of effective overall enantiomorphic site control of the polymerization process: $(1 - \omega)$ then denotes the part of the polymer whose stereochemistry is being determined by chain-end control in this double stereodifferentiation situation] and α. The latter parameter is a statistical descriptor for the degree of isotacticity achieved under enantiomorphic site control: it characterizes the probability by which an *R*-controlling catalytic center actually produces an *R*-configurated stereogenic center at the product chain. The quality of the transfer of the chirality information inherently present at the active catalytic site is thus represented by a combination of both denominators ω and α. We have proposed to express the quality of chirality transfer by the numerical value $(2\alpha - 1)\omega$ = ee*, with ee* being equivalent to a "relative enantiomeric excess"[5b].

The ^{13}C-NMR methyl pentade analysis (i.e. combined with the statistical treatment as outlined above) has revealed

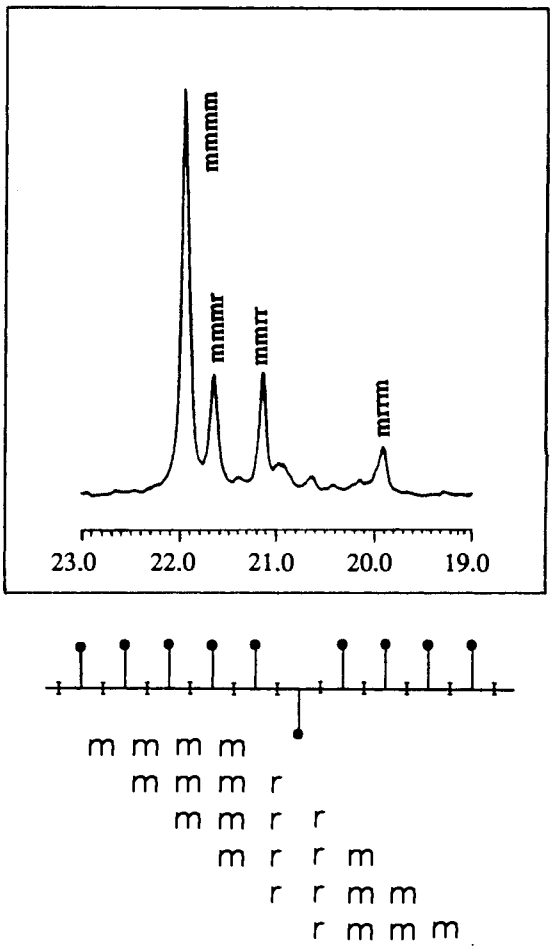


Figure 2. ^{13}C-NMR methyl resonances of the polypropylene sample PP 4 formed at 0°C at the **9a**/$(MeAlO)_x$ catalyst system (δ scale)

that the stereochemistry of the polymer formed is almost completely controlled by the enantiomorphic site. The expanded methyl resonance region of polypropylene PP 4 formed at 0°C as shown in Figure 2 may serve as an example of what is typically observed here. The spectrum shows a very prominent ^{13}C-NMR methyl resonance at δ = 22.0 which is due to the mmmm pentade representing the dominating portion of the isotactic polypropylene formed. In addition, there are three sharp signals to be seen (in a 2:2:1 relative ratio) which correspond to the mmmr, mmrr, and mrrm pentades. Their presence indicates that the polymer contains singular stereochemical "mistakes" along the chain, i.e. that the stereochemical control is mainly due to the persistent chirality of the enantiomorphic active site and not to the non-persistent chirality of the polymer chain end. The ratio of the peaks due to the singular mistakes (i.e. 1/2 [mmmr], 1/2 [mmrr], or [mrrm]) to [mmmm] is reflected by the magnitude of α, which for this specific example is 0.88. The spectrum of PP 4 (as well as those of the other polymers formed) shows small features resulting from the additional five resolved ^{13}C-NMR methyl pentades. Their presence indicates a small fraction of higher configurational disorder having occurred during carbon-carbon bond formation in the course of the polymerization process. For-

mally, this leads to a reduction of both numerical descriptors ω and α in our statistical evaluation process. For the specific polymer looked at (PP 4) the effectiveness of transfer of stereochemical information from the chiral catalytically active metal complex to the growing polymer chain is 74% (= ee*).

The values listed in Table 1 show that both the percentage of enantiomorphic site control and the ee* value are not very much temperature-dependent. The ω fraction seems to be almost the same within the limits of experimental accuracy in the temperature range between −50 and +15°C. The ee* value decreases by about 10% (absolute; from 82% at −50°C to ca. 71% at +15°C). Our analysis shows that this is mainly due to the formation of a slightly higher number of "singular stereochemical mistakes" along the polypropylene chain.

In conclusion, our study has shown that planarly chiral non-bridged bent metallocene complexes, such as bis[1-(5-cholestenyl-3α-yl)indenyl]$ZrCl_2$ (**9a**) can effectively be used for the generation of homogeneous Ziegler catalysts for stereoselective propene polymerization. In principle, they can transfer their inherent chirality information to the growing isotactic polypropylene chain by means of enantiomorphic site control similar to the chiral ansa-metallocenes which have been frequently used for this purpose. The chiral non-bridged metallocenes still have several shortcomings as compared to their ansa-metallocene analogues with regard to activity, selectivity, and catalyst stability. However, there are probably no fundamental differences between these related catalyst types; the observed deviations are probably only gradual in nature. The performance of the **9a**-derived catalyst system makes us feel optimistic about the future development of such chiral non-bridged metallocene complexes for stereoselective catalysis, especially as many such complexes are very easily available optically pure by starting from readily available precursors from the natural chiral pool.

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Experimental

All reactions with organometallic reagents were carried out in an inert atmosphere (argon) by using Schlenk-type glassware. Solvents were dried and distilled under argon prior to use. — NMR: Bruker WP 200 SY NMR spectrometer (200 MHz ^1H; 50 MHz ^{13}C). — IR: Nicolet 5 DXC FT IR spectrometer. — Optical rotations: Perkin-Elmer Polarimeter model 241 MC, sodium vapor lamp (λ = 589 nm), ambient temperature, concentration *c* in g/100 ml. — Melting points: Büchi SMP 20, melting points are uncorrected. — Elemental analyses: Perkin-Elmer model 240. — Methylalumoxane was prepared according to a literature procedure[16]. The propene polymerization reactions were carried out as was previously described[3,5]. The ^{13}C-NMR methyl pentade analysis of the polypropylenes PP 1–6 and the statistical analysis were performed analogously as described by us previously[5].

(−)-(5-Cholesten-3β-yl) p-Toluenesulfonate (**6**): The reaction was carried out according to a literature procedure[6]. Treatment of 72.0 g (186 mmol) of β-cholestenol (**5**) with 71.0 g (372 mmol) of *p*-toluenesulfonyl chloride in pyridine for 24 h yielded 52.1 g (52%) of **6**, $[\alpha]_D = -32$ (*c* = 0.14, toluene). — ^1H NMR ($CDCl_3$): δ = 7.77, 7.30 (AA'XX', ^3J = 8 Hz, 2H each, tolyl), 5.29 (m, 1H, 6-H, cholestenyl), 4.30 (m, 1H, 3-H, cholestenyl), 2.42 (s, 3H, tosyl-CH_3), 2.35–0.62 (m, 39H, remaining cholestenyl hydrogens).

(−)-3-(5-Cholesten-3α-yl)indene (**7**): A solution containing 18.3 g (150 mmol) of indenyllithium in 150 ml of tetrahydrofuran/110 ml of *n*-hexane was prepared according to a literature procedure[11] from indene and *n*-butyllithium. To this solution was added dropwise at 0°C a solution of the cholestenyl tosylate **6** in 100 ml of THF. The mixture was stirred at room temp. for 1 h, then refluxed for 72 h, and hydrolyzed with water (100 ml). Diethyl ether (150 ml) was added and the organic phase separated and washed with 3 portions (50 ml each) of water. The aqueous phase was extracted twice with ether (50 ml each). The combined organic layers were dried with sodium sulfate and the solvent was removed in vacuo. Recrystallization of the residue from pentane gave 28.2 g (61%) of **7**, m.p. 155°C, $[\alpha]_D = -89$ (*c* = 0.46, toluene). — ^1H NMR ($CDCl_3$): δ = 7.48–7.10 (m, 4H, 4- to 7-H), 6.42 (m, 1H, 2-H), 5.41 (m, 1H, 6'-H), 3.30 (m, 2H, 1-H), 3.12 (m, 1H), 2.78 (m,

Table 2. Atomic coordinates of **7**

Atom	x	y	z
C(1)	1.1923(6)	0.7586(3)	0.9197(1)
C(1')	0.9722(4)	0.3811(2)	0.8359(1)
C(2)	0.9975(6)	0.6800(3)	0.8987(1)
C(2')	0.9423(4)	0.3676(3)	0.9013(1)
C(3)	0.9854(5)	0.5831(3)	0.9317(1)
C(3')	0.8245(4)	0.4773(3)	0.9252(1)
C(4)	1.2298(5)	0.5111(3)	1.0275(1)
C(4')	0.6035(4)	0.4985(3)	0.8853(1)
C(5)	1.4210(6)	0.5391(4)	1.0673(1)
C(5')	0.6221(4)	0.5031	0.8199(1)
C(6)	1.5435(6)	0.6372(4)	1.0593(2)
C(6')	0.5221(5)	0.5888(3)	0.7866(1)
C(7)	1.4802(6)	0.7165(3)	1.0128(2)
C(7')	0.5134(5)	0.5987(3)	0.7211(1)
C(8)	1.2974(5)	0.6912(3)	0.9742(1)
C(8')	0.6010(4)	0.4869(3)	0.6935(1)
C(9)	1.1717(5)	0.5889(3)	0.9810(1)
C(9')	0.8027(4)	0.4365(2)	0.7323(1)
C(10')	0.7488(4)	0.4007(2)	0.7948(1)
C(11')	0.9137(4)	0.3329(2)	0.7011(1)
C(12')	0.9564(4)	0.3618(3)	0.6379(1)
C(13')	0.7417(4)	0.4038(2)	0.6001(1)
C(14')	0.6586(4)	0.5123(2)	0.6317(1)
C(15')	0.4806(5)	0.5684(3)	0.5866(1)
C(16')	0.5690(5)	0.5496(2)	0.5284(1)
C(17')	0.7713(4)	0.4626(2)	0.5388(1)
C(18')	0.5749(4)	0.3008(3)	0.5929(1)
C(19')	0.6075(4)	0.2864(3)	0.7933(1)
C(20')	0.7895(4)	0.3825(2)	0.4852(1)
C(21')	0.9715(4)	0.2881(2)	0.4949(1)
C(22a')	0.7978(9)	0.4671(5)	0.4313(3)
C(22b')	0.863(1)	0.4612(7)	0.4326(3)
C(23')	0.8215(5)	0.4007(3)	0.3726(1)
C(24a')	0.8260(8)	0.4890(5)	0.3219(2)
C(24b')	0.932(2)	0.4747(8)	0.3268(4)
C(25')	0.8627(8)	0.4278(3)	0.2643(2)
C(26a')	1.011(1)	0.3376(8)	0.2645(3)
C(26b')	1.118(2)	0.434(1)	0.2529(7)
C(27a')	0.884(1)	0.5145(8)	0.2169(3)
C(27b')	0.757(2)	0.503(1)	0.2164(6)

1 H), 2.35 (m, 1 H), 2.10–0.80 (m, 30 H, cholestenyl hydrogens), 1.08 (s, 3 H, 19′-H), 0.90 (d, ^3J = 7.7 Hz, 3 H, 21′-H), 0.86 and 0.85 (each d, ^3J = 6.6 Hz, 26′- and 27′-H), 0.68 (s, 3 H, 18′-H). – ^{13}C NMR ($CDCl_3$, assignment by APT): δ = 147.5, 145.7, 144.2, 142.0 (C-3, -8, -9, -5′), 129.7 ($^1J_{CH}$ = 168, $^2J_{CH}$ = 6 Hz), 125.8 (159, 7), 124.2, (160, 7), 123.7 (158, 7), 120.7 (148), 119.0 (157, 8), C-2, -4, -7, and -6′), 56.9, 56.3, 50.1, 35.9, 32.6, 31.9, 28.0 (C-3′, -8′, -9′, -14′, -17′, -20′, -25′), 42.4, 37.3 (C-10′, -13′), 39.9, 39.5, 38.1, 36.3, 36.2, 33.8, 32.1, 28.3, 24.8, 24.3, 23.9, 20.7 (C-1, -1′, -2′, -4′, -7′, -11′, -12′, -15′, -16′, -22′, -23′, 24′), 22.8, 22.6, 19.5, 18.7, 11.9 (C-18′, -19′, -21′, -26′, -27′). – IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3043, 2947, 1605, 1466, 1381, 1373, 960, 772, 720.

$C_{36}H_{52}$ (484.5) Calcd. C 89.18 H 10.82
Found C 88.83 H 10.88

X-ray Crystal Structure Analysis of **7** *(Data Collection and Structure Solution):* Molecular formula $C_{36}H_{52}$, molecular mass 484.8 g · mol^{-1}, crystal color light brown, crystal size 0.43 × 0.61 × 0.40 mm, a = 6.061(1), b = 11.064(1), c = 22.840(2) Å, β = 97.32(1)°, V = 1519.0 Å^3, d_{cal} = 1.06 g · cm^{-3}, μ = 4.03 cm^{-1}, Cu-K_α radiation, λ = 1.54179 Å, F(000) = 536 e, Z = 2, crystal system monoclinic, space group $P2_1$ (No. 4), Enraf Nonius CAD4 diffractometer, scan mode ω–2θ, $[\sin\theta/\lambda]_{max}$ = 0.63 $Å^{-1}$, 13707 measured reflections ($\pm h, \pm k, +l$), 6010 independent reflections, 5354 observed reflections [$I > 2\sigma(I)$] for 321 refined parameters, structure solved by direct methods, H atom positions calculated and kept fixed in the final refinement stages, disorder of the aliphatic chain C22–C27 included in the refinement with partial occupancies, R = 0.062, R_w = 0.043 [$w = 1/\sigma^2(F_o)$], residual electron density 0.51 $eÅ^{-3}$. Atomic coordinates see Table 2. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 56632, the names of the authors, and the journal citation.

1-(5-Cholesten-3α-yl)indenyllithium (**8**): To a solution of **7** (2.08 g, 4.29 mmol) in 60 ml of ether was added dropwise at room temp. a 2.2 M ethereal methyllithium solution (1.95 ml, 4.30 mmol). A dark-colored solution was obtained. The solvent was removed in vacuo and the remaining almost black crystalline precipitate vigorously stirred with 50 ml of pentane. The colorless precipitate was filtered from the black pentane phase and dried to give 2.02 g (96%) of **8** that was characterized only by NMR spectroscopy. – ^{1}H NMR ([D_6]benzene/[D_8]tetrahydrofuran, 10:1): δ = 7.74–7.64 (m, 2 H, 4-, 7-H), 7.01 (A part of AX, ^3J = 3.2 Hz, 1 H, 2-H), 6.93–6.88 (m, 2 H, 5-, 6-H), 6.16 [m, ^3J(2-H,3-H) = 3.2, ^5J(3-H,7-H) = 0.4 Hz, 1 H, 3-H], 5.49 (m, 1 H, 6′-H), 3.78 (m, 1 H, 3′-H), 3.10 (m, 1 H), 2.49 (m, 1 H), 2.20–0.92 (m, 29 H, cholestenyl), 1.21 (s, 3 H, 19′-H), 0.97 (d, ^3J = 6.4 Hz, 3 H, 21′-H), 0.88 (d, ^3J = 6.6 Hz, 6 H, 26- and 27′-H), 0.70 (s, 3 H, 18′-H). – ^{13}C NMR ([D_6]benzene/[D_8]tetrahydrofuran, 10:1): δ = 144.2 (C-5′), 125.7 (C-8 or -9, the other signal is hidden under the solvent), 111.9 (C-1), 120.2 ($^1J_{CH}$ = 149 Hz), 118.4 (146), 116 (157), 114.5 (154, C-4 to -7), 119.8 (150, C-6′), 115.5 (154, C-2), 88.2 (167, C-3), 57.4, 56.8, 50.6, 36.3, 33.6, 32.4, 28.4 (C-3′, -8′, -9′, -14′, -17′, -20′, -25′), 42.7, 37.9, C-10′, -13′), 40.4, 39.9, 39.5, 36.7, 34.6, 32.7, 29.2, 28.7, 24.7, 24.4, 21.2 (C-1′, -2′, -4′, -7′, -11′, 12′, -15′, -16′, -22′, -23′, -24′), 22.9, 22.7, 20.0, 19.0, 12.1, (C-18′, -19′, -21′, -26′, -27′).

Bis[1-(5-cholesten-3α-yl)indenyl]zirconium Dichloride (**9a**): To a suspension of 1.61 g (4.28 mmol) of $ZrCl_4(THF)_2$ in 80 ml of toluene was added with stirring at –78 °C a precooled solution of 4.20 g (8.56 mmol) of **8** in 250 ml of tetrahydrofuran. The mixture was allowed to warm to room temp. during 6 h and then stirred for 12 h. The solvent was removed in vacuo and the resulting yellow powder extracted with 100 ml of dichloromethane. Filtration removed the lithium chloride formed during the reaction. The clear filtrate was evaporated to dryness in vacuo. The residue was thoroughly washed twice with pentane (40 ml each) to remove some organic contaminants and the minor isomers (**9b**, **9c**). The remaining solid consisted of near to isomerically pure (>98%) **9a**; yield 1.74 g (36%), m.p. 280 °C (dec.), $[\alpha]_D$ = –35 (c = 0.21, toluene). – ^{1}H NMR ($CDCl_3$): δ = 7.68 (d, 1 H, 7-H), 7.49 (d, 1 H, 4-H), 7.32–7.10 (m, 2 H, 5-, 6-H), 6.38 and 5.71 (AX, ^3J = 3.2 Hz, 2 H, 2-, 3-H), 5.46 (m, 1 H, 6′-H), 3.75 (m, 1 H, 3′-H), 2.68 (m, 1 H), 2.42 (m, 1 H), 2.10–0.90 (m, 29 H, cholestenyl hydrogens), 1.00 (s, 3 H) and 0.64 (s, 3 H, 18′- and 19′-H), 0.86 (d, ^3J = 6.1 Hz, 3 H, 21′-H), 0.84 (d, ^3J = 6.4 Hz, 6 H, 26′-, 27′-H). – ^{13}C NMR ($CDCl_3$): δ = 141.8 (s, C-5′), 129.7, 126.1, 124.8 (C-1, -8, -9), 126.3 ($^1J_{CH}$ = 165 Hz), 126.0 (160), 125.2 (163), 124.4 (164, C-4 to -7), 122.9 (174,

Table 3. Stereochemical analysis of polypropylenes formed at the **9a**/$(MeAlO)_x$ catalyst: ^{13}C-NMR methyl pentade signal intensities observed (upper line)[a] and calculated with the statistical parameters given (lower line)

PP(T)[b]	ω	α	σ	mmmm	mmmr	rmmr	mmrr	rmrr	mmrm rmrm	rrrr	mrrr	mrrm
1 (-50)				0.67	0.12	0.00	0.13	0.00	0.00	0.02	0.02	0.04
	0.98	0.92	[c]	0.67	0.11	0.01	0.11	0.02	0.01	0.01	0.01	0.06
2 (-30)				0.55	0.17	0.01	0.15	0.04	0.02	0.01	0.02	0.05
	0.96	0.89	0.74	0.55	0.14	0.01	0.14	0.05	0.02	0.01	0.02	0.07
3 (-8)				0.59	0.15	0.01	0.13	0.04	0.01	0.00	0.02	0.05
	0.94	0.90	0.85	0.59	0.14	0.01	0.13	0.04	0.02	0.01	0.02	0.07
4 (0)				0.54	0.14	0.02	0.17	0.04	0.01	0.01	0.02	0.06
	0.98	0.88	[c]	0.54	0.14	0.01	0.14	0.04	0.02	0.01	0.02	0.07
5 (+10)				0.49	0.17	0.02	0.17	0.05	0.03	0.00	0.02	0.05
	0.98	0.87	[c]	0.49	0.15	0.01	0.15	0.05	0.03	0.01	0.03	0.07
6 (+15)				0.47	0.20	0.01	0.16	0.04	0.03	0.02	0.02	0.07
	0.99	0.86	[c]	0.47	0.15	0.02	0.15	0.06	0.03	0.01	0.03	0.08

[a] Measured in 1,2,4-trichlorobenzene at 90 °C. – [b] Polymerization temperature [°C]. – [c] Insignificant.

C-6′), 121.8 (167, C-2), 96.9 (168, C-3), 56.9 (119), 56.2 (121), 50.1 (120), 35.8, 32.7, 31.7, 28.0 (C-8′, -9′, -14′, -17′, -20′, -25′), 42.3, 37.1, (C-10′, -13′), 39.8, 39.5, 36.2, 34.1, 33.9, 32.0, 28.3, 27.0, 24.2, 23.9, 20.7 (C-1′, -2′, -4′, -7′, -11′, -12′, -15′, -16′, -22′, -23′, -24′), 22.8 (128), 22.6 (128), 19.5 (125), 18.7 (122), 11.9 (123, C-18′, -19′, -21′, -26′, -27′). – IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3040, 2951, 2933, 2867, 1653, 1560, 1457, 1436, 799, 743.

$C_{72}H_{102}Cl_2Zr$ (1129.7) Calcd. C 76.55 H 9.10
Found C 74.45 H 9.29

Propene Polymerization Reactions were carried out as described previously in detail[5b]. The stereochemical assignment (^{13}C-NMR methyl pentade analysis) and the statistical analysis were performed according to procedures described[3,5,15]. In Table 3 are listed the observed ^{13}C-NMR methyl intensities and those calculated by using a three-parameter statistical model system as described by us previously[5] [for the definitions of ω and α see text; σ denotes the probability of forming a *meso* (m) dyad under chain-end control conditions]. For details concerning the stereochemical polymer analysis applied here, the reader is referred to the detailed descriptions which can be found in the literature cited above.

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