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Stereoselective propene polymerization at a metallocene/alumoxane catalyst derived from the chirally-substituted "*meso*-like" (*p-R,p-S*)-bis[1-(neoisopinocamphyl)-4,5,6,7-tetrahydroindenyl]-zirconium dichloride

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Abstract

Isopinocamphyl-tosylate (**2**) was treated with indenyllithium to yield 3-(neoisopinocamphyl)-indene (**3**). Treatment of **3** with methyllithium gave 1-(neoisopinocamphyl)indenyllithium (**4**) which was then treated with 0.5 molar equivalents of $ZrCl_4(thf)_2$ to give a 52:48 mixture of one of the "*racemic*-like" isomers of bis[1-(neoisopinocamphyl)indenyl]$ZrCl_2$ (**5A**) and its "*meso*-like" diastereomer **5C**. Hydrogenation of the **5A/5C** mixture (50 bar H_2, Pt) furnished a mixture of the corresponding tetrahydroindenylzirconium complexes **6A** and **6C**, from which the "*meso*-like" bis[1-(neoisopinocamphyl)-4,5,6,7-tetrahydroindenyl]zirconium dichloride diastereoisomer (**6C**) was isolated. Treatment of **6C** with an excess of methylalumoxane in toluene/propene generated an active α-olefin polymerization catalyst. At −30°C partly isotactic polypropylene ($\overline{M}_\eta = 39000$) was obtained. The catalyst derived from the chirally-substituted "*meso*-like"metallocene complex **6C** produced polypropylene predominantly under enantiomorphic site control.

1. Introduction

1-Substituted indenyl and -4,5,6,7-tetrahydroindenyl ligands are prochiral. When attached to a metal centre through the π-system of the five-membered ring planarly chiral metal/ligand arrangements are obtained. The combination of two such ligands at, for example, an early transition metal centre thus leads to the formation of two diastereoisomers, namely a *meso*- and a *racemic*-form [1*]. The situation becomes slightly more complicated when chiral substituents at the 1-positions of these ligands are involved. Attachment of homochiral substituents now results in the formation of three diastereoisomers, two of which resemble the *racemic*-diastereomer as mentioned above, and hence will be termed the two "*racemic*-like" isomers (**1A, 1B**). The third isomer (**1a**) involves a combination of planar-chirality elements of *p-R,p-S*-configuration at the bent metallocene unit just as in the *meso*-compound mentioned above, and will thus be termed "*meso*-like".

We previously prepared a number of examples of the general complex types **1A, 1B**, and **1C**. In several cases the pure "*racemic*-like" diastereomers were employed to generate homogeneous metallocene/alumoxane α-olefin polymerization catalysts. Some of these compounds (*e.g.* with [R*] 3α- or 3β-cholestanyl, 3α-cholestenyl, neomenthyl, neoisomenthyl, or 8-phenylneomenthyl) were used successfully for generating active catalysts to produce highly isotactic polypropylene [2]. In a few cases isotacticities matching those ob-

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* Reference number with an asterisk denotes a note in the list of references.

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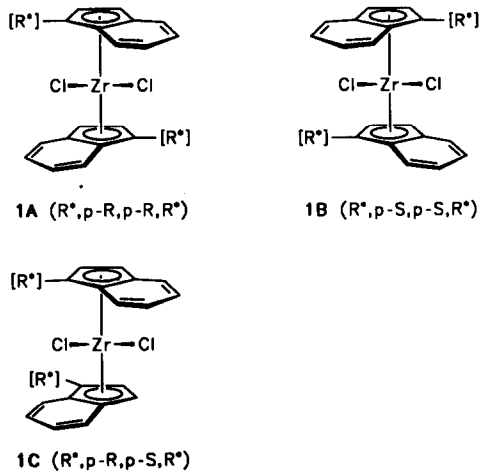


Scheme 1. The three diastereomeric chiral bis(η^5-1-[R^*]-4,5,6,7-tetrahydroindenyl)zirconocenedichlorides ([R^*] denotes a pair of homochiral substituents per bent metallocene unit; relative configurations of the diastereomers are given in parentheses).

tained with commonly used *ansa*-metallocene/methylalumoxane catalysts were achieved with these chiral non-bridged metallocene-derived systems.

In all these cases we employed chiral metallocene systems from the "*racemic*-like" series. It should be noted, however, that their respective diastereomeric congeners, the "*meso*-like" complexes **1C**, are also chiral molecules. Their persistent chirality (R^*, *p*-R^*, *p*-S^*, R^*-configuration) could in principle also become transferable to a growing polymer chain at an active catalyst using the **1C** derived chirally substituted bent metallocene backbone as an enantiomorphic site. We have now been able to synthesize and isolate such an example of a chirally substituted "*meso*-like" bis(tetrahydroindenyl)zirconium dichloride derivative, and have investigated its ability to give rise to chirality transfer in isotactic polypropylene formation under enantiomorphic site control [3].

2. Results and discussion

Our synthesis started from optically pure (+)1*S*,2*S*,3*S*,5*R*-isopinocampheol (**1**) which was first converted into its tosylate. The 1*S*,2*S*,3*S*,5*R*-pinan-3-yl *p*-toluene-

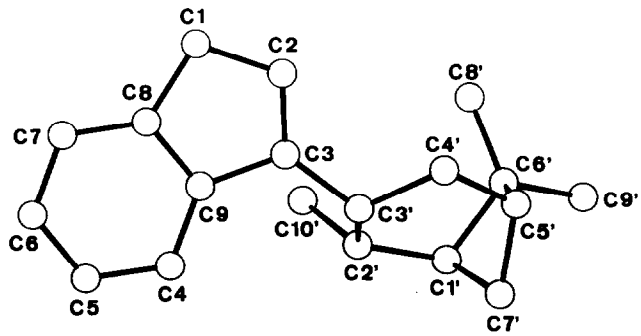
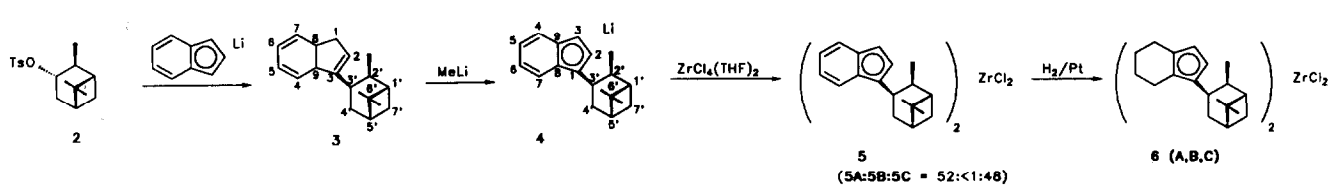


Fig. 1. A view of the molecular structure of 3-neoisopinocamphylindene (**3**) with atom numbering scheme.

sulfonate(**2**) was then subjected to S_N2 substitution by treatment with indenyllithium (*ca.* 30% excess) in tetrahydrofuran at the reflux temperature. Initially, formation of the 1-substituted indene derivative is expected. However, under the reaction conditions used rapid rearrangement, such as is often observed [4], took place to give the thermodynamically more stable 3-substituted indene product. After recrystallization, (−)3-(1′*S*,2′*S*,3′*R*,5′*R*-pinan-3′-yl)indene (**3**) was isolated in 58% yield.

The regio- and stereo-isomeric assignment of **3** is based on the spectroscopic data and the result of an X-ray crystal structure analysis of the product obtained. Product **3** shows ^{1}H NMR signals at δ 3.39 (2H, indene 1-H) and 6.39 (1H, indene 2-H) from the protons attached to the indene five-membered ring. In the ^{13}C NMR spectrum the aromatic carbon resonances are at δ 146.2, 144.3 (C8, C9), 123.6, 124.4, 126.0, 119.2 (C7–C4). The C3 resonance appears at δ 146.8, the signals found at δ 127.6 and 27.8 coming from carbon atoms C2 and C1, respectively.

Recrystallization from pentane gave crystals of **3** suitable for an X-ray crystal structure determination. The indene framework of the hydrocarbon **3** is planar; the mean bond length within the aromatic ring system is 1.389(7) Å, and the corresponding angles vary between 121.4° and 118.2°, with a mean of 120(1)°. The pinan-3′-yl substituent is clearly bonded to the sp^2-carbon atom C3, which is part of the indene C=C double bond [C2–C3: 1.343(2) Å] of the five-membered



Scheme 2.

ring [C1–C2: 1.494(2), C1–C8: 1.510(3), C3–C9: 1.471(2) Å] [5].

The X-ray crystal structure analysis confirmed that the **2** → **3** substitution reaction proceeds strictly with overall inversion. Starting from the isopinocamphyltosylate (**2**) we have thus obtained the 3-(neoisopinocamphyl)indene product (**3**) in which the methyl substituent at C2 of the terpene framework and the bulky indenyl group at C3′ are oriented *cis* to each other. The length of the C2′–C10′ bond is 1.524(2) Å, and that of the C3–C3′ bond connecting the two hydrocarbyl frameworks is 1.504(2) Å. This indicates that the *cis*-arrangement of groups at the C1′–C6′ terpene six-membered ring does not result in significant strain. The system is sufficiently flexible to allow the substituents to be arranged in such a way as to avoid marked repulsive steric interaction. The C10′–C2′–C3′–C3 torsional angle is $\theta = 20.4°$ and the corresponding C2–C3–C3′–C2′ angle is 113.6°. It should be noted that in this case three carbon-containing substituents can be nicely accommodated, oriented *cis* to each other at the bicyclo[3.1.1]heptane framework, namely the indenyl group at C3′, and the CH_3 groups at C2′ (*i.e.* the C10′ methyl group) and C6′ (*i.e.* the C8′ methyl group).

The hydrocarbon **3** was then treated with methyllithium to give the neoisopinocamphyl-substituted indenyllithium reagent **4** (94% isolated), which was char-

TABLE 1. Bond distances (Å) and angles (°) in **3**

C(1)–C(2)	1.494(2)	C(1)–C(8)	1.510(3)
C(2)–C(3)	1.343(2)	C(3)–C(9)	1.471(2)
C(3)–C(3′)	1.504(2)	C(4)–C(5)	1.390(3)
C(4)–C(9)	1.402(2)	C(5)–C(6)	1.379(3)
C(6)–C(7)	1.393(3)	C(7)–C(8)	1.385(2)
C(8)–C(9)	1.385(2)	C(1′)–C(2′)	1.529(2)
C(1′)–C(6′)	1.564(2)	C(1′)–C(7′)	1.552(3)
C(2′)–C(3′)	1.579(2)	C(2′)–C(10′)	1.524(2)
C(3′)–C(4′)	1.554(2)	C(4′)–C(5′)	1.513(2)
C(5′)–C(6′)	1.559(2)	C(5′)–C(7′)	1.545(3)
C(6′)–C(8′)	1.523(3)	C(6′)–C(9′)	1.531(3)
C(1)–H(1a)	1.01(2)	C(1)–H(1b)	0.94(2)
C(2)–H(2)	1.06(2)	C(4)–H(4)	1.01(1)
C(5)–H(5)	1.03(2)	C(6)–H(6)	1.07(2)
C(7)–H(7)	0.99(2)	C(1′)–H(1′)	1.02(2)
C(2′)–H(2′)	1.06(2)	C(3′)–H(3′)	1.07(2)
C(4′)–H(4a′)	1.09(2)	C(4′)–H(4b′)	1.05(2)
C(5′)–H(5′)	1.04(2)	C(7′)–H(7a′)	1.10(2)
C(7′)–H(7b′)	1.06(2)	C(8′)–H(8a′)	1.05(2)
C(8′)–H(8b′)	1.02(2)	C(8′)–H(8c′)	1.03(2)
C(9′)–H(9a′)	0.99(2)	C(9′)–H(9b′)	0.98(3)
C(9′)–H(9c′)	1.03(3)	C(10′)–H(10a′)	1.04(2)
C(10′)–H(10b′)	1.02(2)	C(10′)–H(10c′)	1.06(2)
C(8)–C(1)–C(2)	102.6(1)	C(3)–C(2)–C(1)	111.9(2)
C(3′)–C(3)–C(9)	123.2(1)	C(3′)–C(3)–C(2)	129.2(1)
C(9)–C(3)–C(2)	107.7(1)	C(9)–C(4)–C(5)	118.2(2)
C(6)–C(5)–C(4)	121.4(2)	C(7)–C(6)–C(5)	120.4(2)
C(8)–C(7)–C(6)	118.7(2)	C(9)–C(8)–C(7)	121.2(2)
C(9)–C(8)–C(1)	108.2(1)	C(7)–C(8)–C(1)	130.6(2)
C(8)–C(9)–C(4)	120.2(1)	C(8)–C(9)–C(3)	109.6(1)
C(4)–C(9)–C(3)	130.2(1)	C(7′)–C(1′)–C(6′)	87.5(1)
C(7′)–C(1′)–C(2′)	109.1(1)	C(6′)–C(1′)–C(2′)	114.8(1)
C(10′)–C(2′)–C(3′)	116.7(1)	C(10′)–C(2′)–C(1′)	113.3(1)
C(3′)–C(2′)–C(1′)	109.9(1)	C(4′)–C(3′)–C(2′)	113.8(1)
C(4′)–C(3′)–C(3)	113.8(1)	C(2′)–C(3′)–C(3)	113.2(1)
C(5′)–C(4′)–C(3′)	112.6(1)	C(7′)–C(5′)–C(6′)	87.9(1)
C(7′)–C(5′)–C(4′)	110.0(1)	C(6′)–C(5′)–C(4′)	110.5(1)
C(9′)–C(6′)–C(8′)	107.9(2)	C(9′)–C(6′)–C(5′)	112.7(2)
C(9′)–C(6′)–C(1′)	111.0(2)	C(8′)–C(6)′–C(5′)	118.0(1)
C(8′)–C(6′)–C(1′)	121.1(1)	C(5′)–C(6′)–C(1′)	84.8(1)
C(5′)–C(7′)–C(1′)	85.7(1)		

TABLE 2. Atomic coordinates for 3

Atom	x	y	z
C(1)	0.0379(3)	0.5581(2)	0.4144(1)
C(2)	0.0014(3)	0.6884(2)	0.4338(1)
C(3)	0.1366(2)	0.7634(1)	0.4097(1)
C(4)	0.4459(2)	0.7212(2)	0.3402(1)
C(5)	0.5555(3)	0.6294(2)	0.3105(1)
C(6)	0.5015(3)	0.5083(2)	0.3135(1)
C(7)	0.3329(3)	0.4752(2)	0.3457(1)
C(8)	0.2223(2)	0.5661(1)	0.3752(1)
C(9)	0.2769(2)	0.6878(1)	0.3730(1)
C(1')	0.0545(2)	1.0982(1)	0.3577(1)
C(2')	0.1349(2)	0.9702(1)	0.3452(1)
C(3')	0.1538(2)	0.8999(1)	0.4171(1)
C(4')	0.0307(2)	0.9545(2)	0.4767(1)
C(5')	−0.0192(2)	1.0873(1)	0.4642(1)
C(6')	−0.1397(2)	1.1009(1)	0.3964(1)
C(7')	0.1431(3)	1.1523(2)	0.4252(1)
C(8')	−0.2898(3)	1.0046(2)	0.3819(1)
C(9')	−0.2323(4)	1.2269(2)	0.3901(1)
C(10')	0.0381(3)	0.9020(2)	0.2856(1)

acterized spectroscopically (see Experimental section). Its reaction with $ZrCl_4(thf)_2$ gave a mixture of bis(neoisopinocamphylindenyl)$ZrCl_2$ complexes (**5**). As was outlined in the Introduction, attachment of two planarly prochiral 1-(neoisopinocamphyl)indenyl anion equivalents at a zirconium centre could result in the formation of three diastereoisomers. Each of the two "*racemic*-like" diastereoisomers (**5A, 5B**) should contain a pair of symmetry equivalent ligand systems. Thus, a single "*racemic*-like" isomer (*e.g.* **5A**) would exhibit only a single set of ligand NMR signals. In contrast, the R*-indenyl ligands in the "*meso*-like" isomer (*e.g.* **5C**) are non-equivalent, and should give rise to two distinct sets of NMR resonances in a 1:1 ratio [2].

These very characteristic NMR features provided a simple and reliable method for analysis of the product mixture obtained from the reaction of the neoisopinocamphyllithium reagent **4** with $ZrCl_4(thf)_2$. This reaction gave only a mixture of two diastereoisomers, namely one "*racemic*-like" isomer [which we denote by **5A** although its relative configuration distinguishing it from **5B** (see above) has not been established during the course of this study] and the "*meso*-like" bis(neoisopinocamphylindenyl)$ZrCl_2$ system **5C**. The complexes **5A** and **5C** were formed in a 52:48 ratio. The "*racemic*-like" isomer showed only one set of signals from the indene methine protons 2-H and 3-H at δ 6.45 and 5.57 (AX, $^3J = 3.3$ Hz), representing two hydrogen atoms each, whereas the "*meso*-like" diastereomer **5C** exhibited four separate signals from these ligand hydrogens at δ 6.35, 6.21, 5.93 and 5.83 (2 AX systems, $^3J = 3.2$ Hz each).

The **5A/5C** mixture of isomers was isolated only in *ca.* 20% yield. We have not so far been able to separate the diastereomeric bis(neoisopinocamphylindenyl)$ZrCl_2$ complexes. Therefore, the **5A/5C** (52:48) mixture was subjected to catalytic hydrogenation (Pt, H_2) [6]. This cleanly produced the corresponding mixture of the bis(neoisopinocamphyl-4,5,6,7-tetrahydroindenyl)zirconocene dichloride isomers (**6A, 6C**). At this point fractional crystallization from methylene chloride furnished a sample (27% isolated) of the isomerically pure "*meso*-like" (*p-R, p-S*)bis(1-neoisopinocamphyl-4,5,6,7-tetrahydroindenyl)$ZrCl_2$ diastereoisomer (**6C**). The "meso-like" compound **6C** is, of course, chiral. In this synthesis its optical activity ($[\alpha]_D = -21°$ ($c = 0.19$, toluene)) is determined solely by the optical purity of the chiral starting material (in this case the isopinocampheol). As expected, complex **6C** contains a pair of inequivalent substituted tetrahydroindenyl ligands. This gives rise to the observation of, *e.g.*, two sets of 2-H/3-H ^{1}H NMR resonances at δ 6.37, 6.16, 5.68 and 5.11, and four ^{13}C NMR signals from the corresponding carbon atoms C2 and C3 of the five-membered rings at δ 115.8, 107.5, 107.1 and 103.7.

Complex **6C** was used to generate a homogeneous Ziegler-type catalyst for α-olefin polymerization [7]. For that purpose we treated a sample of **6C** with a large excess of methylalumoxane (Al/Zr-ratio:570) in toluene. Propene polymerization was carried out at −30°C, at a rather low value of 19 for activity a [g polymer formed/g [Zr] · h]. The produced polypropylene was isolated and its average molecular weight $\bar{M}_\eta$ found to be 39000.

The stereochemical analysis of the polypropylene obtained was carried out by ^{13}C NMR methyl pentade analysis [8], including a statistical evaluation of the observed intensities as previously described [9]. The ^{13}C NMR methyl resonance intensity distribution for the polymer obtained with the catalyst "meso-like" derived from bis(neoisopinocamphyltetrahydroindenyl)$ZrCl_2$ deviates markedly from that expected for an atactic species. As can be seen from the methyl section of the ^{13}C NMR spectrum shown in Fig. 2 there is a prominent mmmm resonance present. In addition the mmmr and mmrr signal intensities are also clearly above the statistical values. Detailed analysis revealed that about 60% of the stereocontrol during this polymer formation is by the enantiomorphic site ($\omega = 0.61$) with a value of α (denoting the probability that an *R*-controlling centre is producing an *R*-configurated stereogenic centre under enantiomorphic site control [3]) of 0.83. This value corresponds to the average presence of isotactic sequences containing *ca.* 5 monomeric units ($\langle m \rangle_n \alpha = 5.1$) terminated by singular stereochemical mistakes along the formed polymer

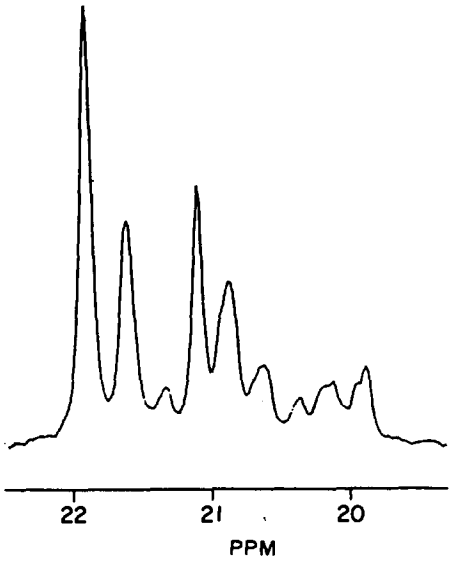


Fig. 2. ^{13}C NMR methyl pentade signals of the polypropylene obtained at the **6C**/methylalumoxane catalyst at −30°C.

chain. In view of this analysis the remainder of the polymer is seen to be almost atactic [$(1-\omega)=0.39$, $\sigma=0.56$ (where σ is the probability of finding a *meso*-like (m) dyad under chain end control)].

The effective transfer of chirality from the chiral metal complex unit in the active catalyst to the growing polymer chain can be expressed by the numerical value of ee*, $(2\alpha-1)\omega$, which can be termed as the "relative enantioselectivity" [9]. From the analysis described above we have calculated ee* to be 0.40. We thus conclude that the "*meso*-like" **6C**-derived catalyst can transfer chirality information during a carbon–carbon coupling process to a substantial extent despite the fact that the configuration of the planarly chiral bent metallocene backbone is (*p-R,p-S*). We assume that the chiral neoisopinocamphyl substituents can induce formation of a chiral rotameric species as the global minimum on the bent metallocene backbone conformational hypersurface, thereby allowing for the transfer of the inherent chirality information introduced by the pair of homochiral substituents through the bent metallocene unit on to the growing polymer chain during carbon-carbon coupling at the active **6C**-derived catalyst system.

3. Experimental section

Reactions involving organometallic compounds were carried out under argon by use of Schlenk-type glassware or in a drybox. Solvents were dried and distilled under argon prior to use. The NMR spectra were obtained with a Bruker WP 200 SY spectrometer (^1H: 200 MHz, ^{13}C: 50 MHz) and IR spectra with a Nicolet 5DXC FT IR instrument. Optical rotations were determined with a Perkin Elmer polarimeter model 241 M (sodium vapour lamp, $\lambda=589$ nm, room temperature; concentration given in g/100 ml). Melting points (uncorrected) were determined with a Büchi SM P 20 apparatus. C,H elemental analyses were carried out at the microanalytical laboratory of the Organisch-Chemisches Institut der Universität Münster with a Perkin Elmer C,H analyzer model 240. (+)1*S*,2*S*,3*S*,5*R*-Isopinocampheol was used as purchased. Methylalumoxane was prepared by treating trimethylaluminium dimer with copper sulphate pentahydrate [10]. The propene polymerization reaction was carried out as previously described in detail for a related example [9]. The ^{13}C NMR methyl pentade analysis and the statistical treatment of the obtained intensity data were carried out as previously described [9].

3.1. Isopinocamphyl tosylate (2)

The preparation of the tosylate **2** was carried out in the way previously described for a similar compound [11]. Reaction of 25.0 g (0.16 mol) of isopinocampheol with 34.0 g (0.18 mol) of tosyl chloride in pyridine (24 h) gave 34.6 g (69%) of the isopinocamphyl tosylate **2**, ^1H NMR ($CDCl_3$): δ 7.78, 7.30 (AA'XX, 4H, arom. H), 4.72 (m, 1H, 3-H), 2.41 (s, 3H, tosyl–CH_3), 2.40–1.70 (m, 6H, 1-H, 2-H, 4-H, 4-H', 5-H, 7-H), 1.15 (s, 3H, CH_3), 1.07 (m, 1H, 7-H'), 0.87 (d, 3H, CH_3), 0.82 (s, 3H, CH_3).

3.2. (−)3-(1'S,2'S,3'S,5'R-Pinan-3'-yl)indene (3)

A solution containing 24.4 g (200 mmol) of indenyllithium in a mixture of 200 ml of tetrahydrofuran and 150 ml of n-hexane was prepared from indene and n-butyllithium as previously described [12]. To this was added dropwise at 0°C a solution of 48.8 g (158 mmol) of the isopinocamphyltosylate **2** in 150 ml of THF. The mixture was stirred for 1 h at ambient temperature, refluxed for 72 h, then cooled to room temperature and hydrolyzed (150 ml of water). Diethyl ether (200 ml) was added and the organic layer separated and washed three times with water (70 ml each), with the aqueous layers extracted twice with ether. The combined organic phases were dried (sodium sulphate). Solvent was removed *in vacuo* and the remaining solid recrystallized from petrol to give neoisopinocamphylindene **3**, 22.9 g (58%), m.p. = 119°C. Crystals suitable for an X-ray crystal structure determination of **3** were obtained from pentane. For details of data collection and structure solution see Table 3. Anal. Found: C, 90.21; H, 9.45. $C_{19}H_{24}$ (252.4) calcd.: C, 90.41; H, 9.59%. $[\alpha]_D=-75°$ ($c=0.32$, toluene). ^1H NMR ($CDCl_3$): δ 7.48–7.10 (m, 4H, 4-H–7-H), 6.39 (m, 1H,

TABLE 3. X-ray crystal structure analysis of 3 [a]: details of data collection and structure solution

Formula	$C_{19}H_{24}$
Molecular weight	252.4
Crystal size (mm)	0.35×0.63×0.18
Crystal colour	yellow-brown
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a (Å)	7.093(1)
b (Å)	10.927(1)
c (Å)	19.098(2)
V (Å^3)	1480.2
Z	4
Calculated density (g cm^{-3})	1.13
μ (cm^{-1})	4.36
Cu Kα radiation (Å)	1.54179
$F(000)$ (e)	552
Temperature (K)	100
Diffractometer	Enraf-Nonius CAD4
Scan mode	ω–2θ
$[(\sin\theta)/\lambda]_{max}$(Å^{-1})	0.62
Total number of reflections ($\pm h$, $\pm k$, $\pm l$)	10710
Independent reflections	2929
R_{av}	0.02
Observed reflections [$I > 2\sigma(I)$]	2706
Refined parameters	269
R	0.039
$R_w[w = 1/\sigma^2(F_o)]$	0.017
Error of fit	2.09
Residual electron density (eÅ^{-3})	0.19
Method of structure solution	direct methods
H-atom positions located and refined isotropically	

[a] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (Germany), on quoting the depository number CSD-57106, the names of the authors, and the journal citation.

2-H), 3.68 (m, 1H, 3'-H), 3.39 (m, 2H, 1-H), 2.82 (m, 1H), 2.40–2.22 (m, 2H), 2.12–1.99 (m, 3H), 1.63 (m, 1H, neoisopinocamphyl-hydrogens), 1.23 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.70 (d, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 146.8, 146.2, 144.3 (C3, C8, C9), 127.6 (^1J(CH) = 164 Hz, ^2J(CH) = 5 Hz), 126.0 (159, 7), 124.4 (158, 7), 123.6 (158, 7), 119.2 (157, 8; C2, C4–C7), 48.9 (^1J(CH) = 142 Hz), 40.8 (135), 37.1 (129), 29.5 (121; C1', C2', C3', C5'), 39.6 (C6'), 37.8 (129), 29.8 (127), 27.8 (125; C1, C4', C7'), 28.2 (125), 23.1 (124), 17.0 (125; CH_3-groups). IR (KBr): ν = 3068 cm^{-1}, 2918, 2892, 2884, 1604, 1462, 973, 769, 719.

3.3. *1-(Neoisopinocamphyl)indenyllithium (4)*

(−)3-(Neoisopinocamphyl)indene (**3**) (15.8 g, 62.7 mmol) was dissolved in 300 ml of ether. At 0°C 26.1 ml of a 2.4 molar ethereal solution of methyllithium (62.7 mmol) was added dropwise with stirring. The mixture was stirred for 2 h at room temperature. Solvent was removed *in vacuo* and the dark oily residue vigorously stirred with pentane (100 ml). The white precipitate formed was filtered off, washed twice with 50 ml of pentane, and dried *in vacuo* to yield 15.2 g (94%) of **4**. ^{1}H NMR (tetrahydrofuran-d_8 benzene-d_6, 1:10): δ 7.72–7.58 (m, 2H, 4-H, 7-H), 6.90–6.77 (m, 3H, 2-H, 5-H, 7-H), 6.17 (X-part of an AX-system, ^3J(2-H, 3-H) = 3.3 Hz, 1H, 3-H), 4.35 (m, 1H, 3'-H), 2.91 (m, 1H), 2.66 (m, 1H), 2.40–2.11 (m, 4H), 1.92 (m, 1H, neoisopinocamphyl-hydrogens), 1.31 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 0.70 (d, ^3J = 7.7 Hz, 3H, CH_3). ^{13}C NMR (tetrahydrofuran-d_8/benzene-d_6 1:10): δ 126.9 (C8/C9, one signal under solvent), 120.2 (^1J(CH) = 154 Hz, ^2J(CH) = 6 Hz), 118.5 (149, 4), 115.5 (153, 8), 114.6 (154, 9; C4–C7), 114.3 (154, 6; C2), 108.9 (C1), 88.4 (162; C3), 49.7 (140), 42.2 (136), 40.0 (124), 29.8 (140; C1', C2', C3', C5'), 33.6 (127), 28.3 (132; C4', C7'), 28.8 (124), 23.6 (123), 17.9 (125; CH_3 groups).

3.4. *Bis[1-(neoisopinocamphyl)indenyl]zirconiumdichloride (5)*

To a suspension of 4.93 g (13.1 mmol) of $ZrCl_4(thf)_2$ in 100 ml of toluene was added dropwise at −78°C a precooled solution of 6.75 g (26.1 mmol) of **4** in 100 ml of tetrahydrofuran. The mixture was allowed to warm to room temperature during 6 h and then stirred for an additional 12 h. Solvent was removed *in vacuo* and the remaining solid extracted with 300 ml of methylene chloride. The filtrate was evaporated to dryness and the residue washed with pentane (100 ml) to give a 52:48 mixture of **5A** and **5C** (1.80 g, 21%). This mixture was not separated. After spectroscopic characterization it was subjected directly to catalytic hydrogenation. ^{1}H NMR ($CDCl_3$): δ 8.0–7.1 (several m, 16 H, 4-H–7-H, both isomers), 6.45 and 5.57 (AX, ^3J = 3.3 Hz, 4H, 2-H, 3-H of **5A**), 6.35, 6.21, 5.93 and 5.83 (two AX, both ^3J = 3.2 Hz, 4H, 2-H, 3-H of **5C**), 4.25, 4.11, 3.99, 2.75–0.80 (several m, 24H, neoisopinocamphyl-hydrogens of both isomers), 1.24, 1.21, 1.20, 1.13, 1.11, 0.98 (each s, CH_3), 0.77, 0.62, 0.25 (each d, CH_3).

3.5. *(p-R,p-S)-Bis[1-(neoisopinocamphyl)-4,5,6,7-tetrahydroindenyl]zirconiumdichloride (6C)*

A sample of the **5A/5C** mixture of isomers (1.00 g, 1.50 mmol), prepared as described above, was dissolved in 60 ml of methylenechloride. The PtO_2-catalyst (80 mg) was added and the mixture kept under H_2 (50 bar) for 12 h at ambient temperature. The catalyst was filtered off and the solvent removed *in vacuo* to yield the corresponding **6A/6C** mixture (0.93 g, 92%). Fractional crystallization from CH_2Cl_2 gave as the first crop the pure "*meso*-like" isomer **6C** (0.27 g, 27%), mp = 319°C, $[\alpha]_D$ = −21° (c = 0.19, toluene) Anal.

calcd. for $C_{38}H_{54}Cl_2Zr$ (673.0): C, 67.82; H, 8.08; found: C, 68.02; H, 8.00 %. IR (KBr): $\nu = 2932$ cm^{-1}, 2904, 2894, 1463, 1382, 822, 801. ^{1}H NMR ($CDCl_3$): δ 6.34, 6.16, 5.68, 5.11 (two AX, each $^3J = 3.3$ Hz, 4H, 2-H, 3-H), 3.93 (m, 1H), 3.50 (m, 1H), 3.21–1.40 (m, 30H), 1.18 (s, 6H, CH_3), 1.05 and 1.02 (s, each 3H, CH_3), 0.72 (d, $^3J = 7.7$ Hz, 3H, CH_3), 0.58 (d, $^3J = 7.7$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 136.2, 134.0, 132.9, 130.7, 129.8, 129.0 (C1, C8, C9 of the diastereotopic ligand systems), 115.8, 107.5, 107.1, 103.7 (C2, C3), 48.9, 48.5, 42.2, 40.9, 40.6, 37.2, 34.6, 30.0 (C1′, C2′, C3′, C5′), 39.9, 39.3 (C6′), 29.8, 27.4, 27.3, 26.5, 25.8, 25.7, 25.0, 23.5, 23.0, 22.6, 22.3, 22.2 (C4-C7, C4′, C7′), 28.6, 28.1, 23.6, 23.3, 17.6, 17.3 (CH_3-groups). Complex **6A** could not be recovered sufficiently pure.

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