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ansa-METALLOCENE DERIVATIVES

IV. * SYNTHESIS AND MOLECULAR STRUCTURES OF CHIRAL *ansa*-TITANOCENE DERIVATIVES WITH BRIDGED TETRAHYDROINDENYL LIGANDS

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Summary

A synthesis for racemic ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride is described. The molecular structures of this compound, of its *meso*-isomer and of a binaphtholate complex of the (*S*,*S*)-enantiomer have been determined. Cleavage of this binaphtholate complex gives the pure (*S*,*S*)-enantiomer.

Introduction

ansa-Metallocene derivatives with suitably substituted covalently-bridged ring ligands represent a class of particularly stereorigid, chiral organometallic compounds [2]. For a practical utilization of compounds of this type as chiral hydride- or alkyl-transfer agents, easily accessible synthetic routes would be a prerequisite. We have found that *ansa*-metallocenes with ethylene-bridged tetrahydroindenyl ligands are advantageous in this regard, since in their synthesis, by way of ethylene-bridged bis(indenyl) precursors, the formation of otherwise rather troublesome substitutional isomers [2] is completely suppressed by the almost total discrimination of the indenyl anion against alkylation in position 2. The synthesis still involves a stereochemical ambiguity with respect to the ligation at the titanium center which can lead either to the desired chiral complex with both substituents on opposite sides or to a *meso*-isomer with both substituents on the same side of the titanocene framework. It was

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* For part III, see ref. 1.

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found that this problem could be resolved, however, in a rather unexpected manner.

Results

1. Synthesis of racemic ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (1)

When 1,2-bis(3-indenyl)ethane, prepared essentially as described by Maréchal and Lepert [3], is transformed into its dilithium salt and then treated with $TiCl_4$ in tetrahydrofuran (THF), one obtains, after quenching with HCl and suitable workup (see Experimental part), a product mixture containing two distinct bis(indenyl)titanium complexes, characterized by one narrow and one widely separated pair of cyclopentadienyl-α,β-proton signals at 6.49 and 6.91 ppm and at 6.07 and 6.74 ppm, respectively. Both of these products are quite stable towards degradation (in contrast to the previously reported instability of unbridged bis(indenyl)titanium dichloride [4—6]). This product mixture could be partially separated by chromatography on silanated silica gel at —20°C with toluene/petroleum ether. The product with the wide α,β-proton splitting was eluted, free from other compounds, in a slow-moving, intensely green band; it forms a dark green, microcrystalline residue upon removal of solvent. However the other product, which migrates on the column in a faster-moving olive-brown zone, was invariably found to be contaminated by some of the material with the wide α,β-proton splitting.

In order to circumvent this difficulty, the original product mixture was subjected to hydrogenation either with Adam's catalyst in CH_2Cl_2 or with palladium on charcoal in glyme solution [4]. Instead of the aromatic proton signals of their bis(indenyl) precursors the ^1H NMR spectra of the hydrogenation products in $CDCl_3$ showed the expected tetramethylene multiplet at 1.3—2.8 ppm. The cyclopentadienyl-α,β-proton pattern observed after hydrogenation indicates that two distinct products are still present. Column chromatography on silanized silica gel at —20°C with toluene/petroleum ether now gave complete separation of these two products. The product with the wide α,β-proton NMR splitting (6.58 and 5.55 ppm in $CDCl_3$) was first eluted from the column; it crystallized as dark red needles. X-ray structure analysis (see below) showed that this compound is the desired racemic ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (1). The other product, with α,β ^1H NMR signals at 6.44 and 6.29 ppm (in $CDCl_3$), was eluted in a second zone from the chromatographic column; it formed similar dark red crystals upon removal of solvent. X-ray structure analysis identified this product as the meso-ligated ethylene-bis-(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (2), in which both tetramethylene substituents are situated on the same side of the *ansa*-titanocene framework. While this reaction sequence can in principle give the chiral compound in sufficiently pure form, the need for chromatographic separations and the loss of a major product portion in form of the achiral *meso*-isomer are impediments to synthesis of the desired chiral *ansa*-titanocene.

In search of a better route we studied the ratios of *meso*- and *rac*-isomers arising in each reaction step. The reaction of the ethylene-bridged bis(indenyl) dianion with $TiCl_4$ yields a *meso* : *rac* ratio of about (2—10) : 1, with higher reaction temperatures favoring formation of racemic product *. During hydrogenation of the resulting product mixtures with palladium on charcoal, the *meso* isomer is transformed into the tetrahydro product significantly faster than the *rac*-isomer (hydrogenation with Adam's catalyst (PtO_2) did not show such differentiation). Surprisingly, however, a gradual conversion of the *meso*- into the *rac*-isomer is observed when a solution of the tetrahydroindenyl complexes in glyme at room temperature is exposed to sunlight for a period of 8—10 days. This transformation is complete within 3—4 h if the solution is irradiated with a high-pressure mercury lamp. That this reaction is truly a conversion of the *meso*-ligated complex to its racemic counterpart, rather than merely a selective destruction of the *meso*-component of the hydrogenation product mixture, is evident from an analogous reaction of chromatographically purified *meso*-compound **2**, from which the racemate **1** is obtained in almost quantitative yield. Since the racemate separates (as rhombus-shaped crystals) much more easily from most solvents than its *meso*-isomer, pure crystalline **1** can thus be obtained from this reaction sequence without the need for chromatographic separation from stereoisomers.

2. *Separation of enantiomers*

Pure (*S*,*S*)-**1** ** was obtained by enantio-selective reaction with (*S*)-(—)-1,1'-bi-2-naphthol. A mixture of racemic **1** with 0.5 equivalents of (*S*)-binaphthol [7] was stirred in toluene solution at 70°C with an excess of sodium metal; the product was chromatographed after removal of most of the solvent and of excess sodium on a silica gel column at —10°C with a toluene/petroleum ether eluent. The first colored zone contained, as judged from NMR and mass spectral analysis, the desired ethylene-bridged bis(tetrahydroindenyl)titanium binaphtholate derivative. This compound could be isolated, from toluene or CH_2Cl_2 as dark red crystals. By X-ray structural analysis (see below) the product was identified as ethylene-bis(4,5,6,7-tetrahydro-(*S*)-1-indenyl)titanium(IV)-(*S*)-1'-1''-bi-2-naphtholate ((*S*,*S*)-**1**:(*S*)-1'-**3**). The ^1H NMR spectrum shows that the reaction of the *ansa*-titanocene racemate with *S*-binaphthol yields pure (*S*,*S*)-**1**:(*S*)-1'-**3** without any detectable (*R*,*R*)-**1**:(*S*)-1' diastereomer. There is no indication, even in the clearly separated and structurally sensitive cyclopentadienyl proton region, of any signal assignable to such a diastereomer. Apparently, the complex formation between the chiral titanocene and the binaphtholate ligand is sterically so demanding that it can proceed only if both moieties have the same sense of chirality. The optical rotation of this product, measured in $CHCl_3$ solution, was found to be $[\alpha]^{25}_{578} = 3100°$ (1 cm, 40 mg/100 ml).

The (*R*,*R*)-enantiomer of **1**, left over after reaction of the racemate with (*S*)-binaphthol, can be recovered in partly purified form by eluting the silica gel column after elution of the binaphtholate complex with CH_2Cl_2 saturated with gaseous HCl ***.

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* The dark green ethylene bis(indenyl) complex with the wide α,β-proton splitting is directly transformed by hydrogenation over PtO_2/H_2 into the (*R*,*S*)-tetrahydroindenyl complex, and is thus, probably the *rac*-stereoisomer.

** Notation of stereoisomers according to the Cahn-Ingold-Prelog notation (extended to chiral metallocenes as outlined by Schlögl [7] refers to configuration of bridgehead C atoms 1 and $\bar{1}$.

** The product thus obtained has a specific rotation, in $CHCl_3$ solution, of $[\alpha]^{25}_{435} = +2440°$ (1 cm, 23.2 mg/100 ml), indicating approximately 75% optical purity.

The binaphtholate complex 3 is cleaved to (*S*,*S*)-1 and free (*S*)-binaphthol by treatment with gaseous HCl in dry toluene at 0°C. An attempted chromatographic separation of (*S*,*S*)-1 from free (*S*)-binaphthol on silica gel with toluene as eluent was unsuccessful. The two components can be cleanly separated, however, by treating the reaction mixture in petroleum ether suspension with an excess of methyllithium *. The titanocene dimethyl derivative formed in this manner is readily soluble in petroleum ether and is thus easily separated from the insoluble dilithium binaphtholate side-products. By treatment of a solution of the dimethyl derivative in toluene/petroleum ether with gaseous HCl, (*S*,*S*)-1 is regenerated and separates as NMR-spectrally pure microcrystalline material. The specific rotation of this product in $CHCl_3$ was $[\alpha]^{25}_{435} = -3300°$ (1 cm, 50 mg/100 ml).

3. *Crystal and molecular structures of compounds 1, 2 and 3*

Space groups, cell parameters and X-ray diffraction intensities were determined on a Syntex-P3 four-circle diffractometer at 228 K (Mo-K_α, λ 0.71069 Å, graphite monochromator, ω-scan with $1.8 < \omega < 29.3°$ min^{-1} for 1, $1.4 < \dot{\omega} < 29.3°$ min^{-1} for 2 and $2.3 < \dot{\omega} < 29.3°$ min^{-1} for 3, and $2 < 2\theta < 44°$ for all three compounds. One standard reflection was measured for every 100 reflections during data collection as a check on crystal and instrumental stability.

The crystals of compound 1 are monoclinic, space group *Cc*; *a* 1621.2(17), *b* 1004.6(8), *c* 1235.7(9) pm, α 90°, β 122.59(7)°, γ 90°; 4 crystallographically equivalent molecules per unit cell (2 each of opposite chirality); $V = 1696 \times 10^6$ pm^3; $d_{calcd.} = 1.49$ g/cm^3; absorption coefficient μ 8.3 cm^{-1}. Compound 2 forms rhombic crystals, space group *Pbca*; *a* 1495.2(17), *b* 1363.3(15), *c* 1735.2(17) pm, $\alpha = \beta = \gamma = 90°$; 8 crystallographically equivalent molecules per unit cell; $V = 3537 \times 10^6$ pm^3; $d_{calcd.} = 1.41$ g/cm^3; absorption coefficient μ 8 cm^{-1}. Compound 3 was found to be monoclinic, space group $P2_1$; *a* 937.5(4), *b* 1420(1), *c* 1186.9(6) pm, $\alpha = 90°$, $\beta = 108.37(4)°$, $\gamma = 90°$; 2 crystallographically equivalent molecules with identical chirality per unit cell; $V = 1499 \times 10^6$ pm^3; $d_{calcd.} = 1.32$ g/cm^3; absorption coefficient μ 3.4 cm^{-1}.

Independent reflections with $F_0 > 4\sigma$ used for resolving and refining the structures: 862 for 1, 1912 for 2, and 1707 for 3. Empirical absorption corrections were applied for all data sets. The structures were solved by direct methods (SHELXTL program [8]). The structures were refined using partially anisotropic models. A weighting scheme based on counting statistics was used throughout. The refinement converged at $R_1 = 0.0575$ and $R_2 = 0.0648$ for 1 **, $R_1 = 0.0555$ and $R_2 = 0.0862$ for 2, and $R_1 = 0.0631$ and $R_2 = 0.0746$ for 3, where $R_1 = (\Sigma||F_0| - |F_c||)/\Sigma|F_0|$ and $R_2 = [\Sigma\omega(|F_0| - |F_c|)^2]^{1/2}/[\Sigma\omega|F_0|^2]^{1/2}$.

Structural data as well as pertinent bond lengths and bond angles of 1, 2 and 3 are listed in Tables 1, 2 and 3. The molecular structures obtained for these compounds are represented in Figs. 1, 2 and 3. Inspection of the individual structures reveals the following features:

For the chiral *ansa*-titanocene derivative 1, the expected symmetry axis

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* Alternatively, the binaphtholate complex can be transformed directly to the soluble dimethyl derivative of (S)-1 by reaction with excess $LiCH_3$ in petroleum ether/diethyl ether.

** Minimal values were obtained for a fixed cyclopentadienyl geometry with identical C—C distances of 142 pm and C—C—C angles of 108° within the five-membered ring.

TABLE 1

STRUCTURAL PARAMETERS FOR RACEMIC ETHYLENE-BIS(4,5,6,7-TETRAHYDRO-1-INDENYL)-TITANIUM DICHLORIDE (1) [a]

Fractional coordinates (with e.s.d.'s) and isotropic thermal parameters

Atom	x/a	y/b	z/c	U^2
Ti	0.8823(0)	0.2381(2)	0.3108(0)	—
Cl(1)	0.7535(6)	0.0831(7)	0.2287(9)	—
Cl(2)	1.0099(6)	0.0796(8)	0.3890(9)	—
C(1)	0.874(1)	0.432(2)	0.412(2)	2.0(6)
C(2)	0.967(1)	0.373(2)	0.494(3)	3.2(7)
C(3)	0.954(1)	0.252(2)	0.542(2)	2.9(8)
C(3a)	0.852(1)	0.236(2)	0.490(2)	2.0(7)
C(4)	0.803(1)	0.143(2)	0.526(2)	1.1(5)
C(5)	0.704(2)	0.200(3)	0.502(2)	2.7(7)
C(6)	0.640(2)	0.257(2)	0.366(2)	2.7(6)
C(7)	0.698(2)	0.379(3)	0.357(2)	3.4(7)
C(7a)	0.803(1)	0.347(2)	0.409(2)	0.6(5)
C(8)	0.849(2)	0.554(3)	0.333(3)	2.5(9)
C($\bar{1}$)	0.892(1)	0.435(1)	0.208(2)	2.0(6)
C(2)	0.800(1)	0.371(1)	0.133(2)	1.2(6)
C($\bar{3}$)	0.814(1)	0.250(1)	0.086(2)	1.6(6)
C($\bar{3}$a)	0.915(1)	0.239(1)	0.131(2)	1.5(5)
C($\bar{4}$)	0.970(2)	0.123(2)	0.106(2)	3.2(7)
C($\bar{5}$)	1.057(2)	0.195(2)	0.116(2)	2.4(7)
C($\bar{6}$)	1.121(2)	0.265(3)	0.248(2)	1.6(7)
C($\bar{7}$)	1.073(1)	0.375(2)	0.275(2)	1.1(5)
C($\bar{7}$a)	0.963(1)	0.354(1)	0.207(2)	2.6(6)
C($\bar{8}$)	0.908(1)	0.569(2)	0.271(2)	1.6(5)

Anisotropic thermal parameters [b]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	1.5(1)	1.4(1)	1.7(1)	−0.2(3)	1.08(8)	−0.5(3)
Cl(1)	4.8(4)	3.2(4)	4.3(4)	−2.5(3)	3.5(4)	−2.2(3)
Cl(2)	4.9(5)	3.8(4)	4.3(4)	1.9(3)	3.8(4)	3.3(4)

Interatomic distances and bond angles

Ti—Cl(1)	235.2(9)	Cl(1)—Ti—Cl(2)	96.2(3)
Ti—Cl(2)	236.6(9)		
Ti—C(1)	236(2)	Ti—C($\bar{1}$)	241(2)
Ti—C(2)	234(2)	Ti—C($\bar{2}$)	229(2)
Ti—C(3)	244(2)	Ti—C($\bar{3}$)	238(2)
Ti—C(3a)	251(2)	Ti—C(3$\bar{\text{a}}$)	254(3)
Ti—C(7a)	246(2)	Ti—C($\bar{7}$a)	256(2)

[a] Interatomic distances in pm, bond angles in degrees, structural refinement for fixed cyclopentadienyl geometry with identical C—C distances of 142 pm and C—C—C angles of 108° within the five-membered ring; hydrogen atoms in calculated positions 100 pm from corresponding C atom. [b] U_{ij} in units of 10^2 pm^2 refer to $T = \exp(-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*))$.

bisecting the Cl—Ti—Cl angle is almost perfectly maintained, although the molecule is not situated on a crystallographic C_2 axis. Both coordination sites, in particular, are clearly framed by the tetramethylene substituents in an equivalent fashion; the resulting steric encumbrance of both sites is in accord with the requirements for an equivalent enantiofacial coordination of prochiral olefin or carbonyl substrates at both coordination sites.

The *ansa*-titanocene ligand framework of 1 is almost congruent with that of

(Continued on p. 240)

TABLE 2

STRUCTURAL PARAMETER FOR *meso*-ETHYLENE-BIS(4,5,6,7-TETRAHYDRO-1-INDENYL)TITANIUM DICHLORIDE (2) [a]

Fractional coordinates (with e.s.d.'s) and anisotropic thermal parameters

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ti	0,2844(1)	0,2929(1)	0,09142(8)	2,9(1)	2,0(1)	2,2(1)	0,1(1)	0,0(1)	−0,4(1)
Cl(1)	0,3455(2)	0,4507(1)	0,0880(1)	4,4(1)	1,9(1)	2,9(1)	0,1(1)	−0,7(1)	−0,3(1)
Cl(2)	0,1396(2)	0,3525(2)	0,1145(1)	3,1(1)	5,9(2)	4,6(1)	−0,5(1)	0,3(1)	0,2(1)
C(1)	0,3868(7)	0,1875(6)	0,1540(5)	6,2(7)	2,4(5)	2,2(5)	1,1(4)	−0,9(5)	0,2(5)
C(2)	0,2971(7)	0,1534(6)	0,1676(5)	6,8(7)	2,6(5)	3,0(5)	1,5(4)	−1,0(5)	−1,4(5)
C(3)	0,2516(7)	0,2218(7)	0,2151(5)	5,3(6)	4,3(6)	2,6(5)	1,3(4)	0,3(5)	−1,4(5)
C(3a)	0,3127(6)	0,2998(6)	0,2319(4)	4,5(6)	3,7(5)	1,8(5)	0,7(4)	−0,1(4)	−0,9(5)
C(4)	0,2994(7)	0,3873(7)	0,2833(5)	5,8(7)	4,1(6)	2,6(5)	−0,6(4)	1,0(5)	−0,3(5)
C(5)	0,3946(9)	0,4140(9)	0,3172(6)	8,6(9)	6,7(8)	4,7(7)	−1,7(6)	0,1(6)	−2,8(7)
C(6)	0,4635(7)	0,4265(8)	0,2571(6)	5,0(6)	5,2(6)	5,0(6)	−1,0(6)	−1,2(5)	−1,4(5)
C(7)	0,4791(6)	0,3385(7)	0,2077(5)	3,0(5)	4,7(6)	3,5(5)	0,8(5)	−0,8(4)	−0,4(5)
C(7a)	0,3961(6)	0,2784(6)	0,1952(4)	4,2(5)	3,2(5)	1,6(4)	1,0(4)	−0,3(4)	0,4(4)
C(8)	0,4565(7)	0,1397(7)	0,1039(6)	6,5(7)	3,3(5)	4,8(6)	0,5(5)	−0,0(6)	2,5(5)
C($\bar{1}$)	0,3437(7)	0,1785(6)	0,0017(5)	6,9(7)	2,0(5)	1,8(4)	−0,5(4)	0,0(5)	0,6(5)
C($\bar{2}$)	0,2484(7)	0,1742(7)	0,0011(5)	5,5(6)	3,5(6)	2,4(5)	−0,6(4)	0,3(5)	−2,1(5)
C($\bar{3}$)	0,2149(6)	0,2621(7)	−0,0315(5)	4,3(5)	3,8(5)	2,4(5)	−0,4(4)	−0,2(4)	−1,0(5)
C($\bar{3}$a)	0,2880(6)	0,3222(6)	−0,0499(4)	3,7(5)	2,8(5)	1,9(4)	−0,3(4)	0,1(4)	−0,2(4)
C($\bar{4}$)	0,2878(7)	0,4172(6)	−0,0934(5)	5,9(6)	2,6(5)	3,0(5)	0,6(4)	−0,7(5)	0,2(5)
C($\bar{5}$)	0,3834(8)	0,4572(7)	−0,1069(6)	7,7(8)	3,4(6)	4,7(6)	1,5(5)	1,1(6)	−1,1(6)
C($\bar{6}$)	0,4534(7)	0,3792(8)	−0,1176(6)	5,6(7)	5,4(7)	4,7(6)	−0,1(5)	1,5(6)	−1,9(6)
C($\bar{7}$)	0,4601(6)	0,3127(7)	−0,0464(5)	3,2(5)	4,3(6)	4,3(6)	−0,5(5)	0,9(5)	−0,3(5)
C($\bar{7}$a)	0,3689(6)	0,2724(6)	−0,0286(5)	3,9(5)	2,2(5)	2,1(4)	−0,6(4)	0,2(4)	0,2(4)
C($\bar{8}$)	0,4102(8)	0,1023(7)	0,0305(6)	9,1(9)	2,6(5)	4,4(6)	−0,2(5)	0,0(6)	2,2(6)

Interatomic distances and bond angles

Ti—Cl(1)	234(1)	Cl(1)—Ti—Cl(2)	92,7(4)
Ti—Cl(2)	235(2)		
Ti—C(1)	236(2)	Ti—C($\bar{1}$)	238(2)
Ti—C(2)	232(2)	Ti—C($\bar{2}$)	232(2)
Ti—C(3)	241(2)	Ti—C($\bar{3}$)	241(2)
Ti—C(3a)	248(2)	Ti—C($\bar{3}$a)	249(2)
Ti—C(7a)	246(2)	Ti—C($\bar{7}$a)	245(2)

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[a] Interatomic distances in pm, bond angles in degrees; hydrogen atoms in calculated positions 100 pm from corresponding C atom.

TABLE 3

STRUCTURAL PARAMETERS FOR ETHYLENE-BIS(4,5,6,7-TETRAHYDRO-(*S*)-1-INDENYL)-TITANIUM-(*S*)-1′,1″-BI-2-NAPHTHOLATE (3)

Fractional coordinates (with e.s.d.'s) and isotropic thermal parameters [a]

Atom	*x/a*	*y/b*	*z/c*	*B*
Ti	0.7554(2)	0.2740(0)	0.8271(1)	—
O(1)	0.7746(7)	0.3548(5)	0.7017(6)	—
O(2)	0.7225(8)	0.1609(5)	0.7312(6)	—
C(1)	0.616(1)	0.310(1)	0.962(1)	3.6(3)
C(2)	0.581(1)	0.377(1)	0.868(1)	4.1(3)
H(2)	0.607	0.442	0.875	8.0
C(3)	0.500(1)	0.330(1)	0.761(1)	3.4(3)
H(3)	0.462	0.358	0.684	8.0
C(3a)	0.484(1)	0.234(1)	0.788(1)	2.8(0)
C(4)	0.404(1)	0.154(1)	0.709(1)	4.2(3)
H(4-1)	0.461	0.138	0.657	8.0
H(4-2)	0.306	0.175	0.662	8.0
C(5)	0.388(2)	0.069(1)	0.777(1)	6.1(4)
H(5-1)	0.368	0.015	0.724	8.0
H(5-2)	0.304	0.078	0.806	8.0
C(6)	0.523(2)	0.048(1)	0.879(1)	6.0(4)
H(6-1)	0.506	−0.009	0.917	8.0
H(6-2)	0.607	0.039	0.850	8.0
C(7)	0.563(1)	0.127(1)	0.973(1)	4.6(3)
H(7-1)	0.661	0.117	1.028	8.0
H(7-2)	0.490	0.128	1.015	8.0
C(7a)	0.559(1)	0.218(1)	0.914(1)	3.7(3)
C(8)	0.704(1)	0.329(1)	1.091(1)	4.5(3)
H(8-1)	0.646	0.368	1.126	8.0
H(8-2)	0.728	0.271	1.134	8.0
C($\bar{1}$)	0.924(1)	0.328(1)	1.013(1)	3.5(3)
C($\bar{2}$)	0.926(1)	0.226(1)	1.009(1)	3.3(3)
H($\bar{2}$)	0.888	0.183	1.055	8.0
C($\bar{3}$)	0.998(1)	0.203(1)	0.921(1)	3.4(3)
H($\bar{3}$)	1.017	0.140	0.898	8.0
C($\bar{3}$a)	1.034(1)	0.285(1)	0.875(1)	3.2(2)
C($\bar{4}$)	1.120(1)	0.298(1)	0.786(1)	4.4(3)
H($\bar{4}$-1)	1.078	0.257	0.719	8.0
H($\bar{4}$-2)	1.223	0.282	0.824	8.0
C($\bar{5}$)	1.115(2)	0.398(1)	0.739(1)	6.6(4)
H($\bar{5}$-1)	1.018	0.409	0.681	8.0
H($\bar{5}$-2)	1.192	0.406	0.703	8.0
C($\bar{6}$)	1.137(2)	0.468(1)	0.839(1)	6.2(4)
H($\bar{6}$-1)	1.232	0.455	0.897	8.0
H($\bar{6}$-2)	1.138	0.530	0.807	8.0
C($\bar{7}$)	1.013(1)	0.465(1)	0.902(1)	5.0(3)
H($\bar{7}$-1)	0.921	0.491	0.850	8.0
H($\bar{7}$-2)	1.046	0.502	0.974	8.0
C($\bar{7}$a)	0.988(1)	0.364(1)	0.932(1)	3.1(3)
C($\bar{8}$)	0.852(1)	0.381(1)	1.094(1)	4.5(3)
H($\bar{8}$-1)	0.920	0.383	1.173	8.0
H($\bar{8}$-2)	0.829	0.445	1.065	8.0
C(1′)	0.683(1)	0.270(1)	0.519(1)	2.9(2)
C(2′)	0.681(1)	0.349(1)	0.587(1)	2.7(2)
C(3′)	0.585(1)	0.427(1)	0.542(1)	3.1(2)
H(3′)	0.593	0.483	0.590	8.0
C(4′)	0.482(1)	0.422(1)	0.430(1)	3.8(3)
H(4′)	0.418	0.475	0.399	8.0
C(4a′)	0.469(1)	0.339(1)	0.361(1)	3.6(3)
C(5′)	0.355(1)	0.332(1)	0.249(1)	4.2(3)

TABLE 3 (continued)

Atom	x/a	y/b	z/c	B
H(5')	0.289	0.384	0.218	8.0
C(6')	0.340(1)	0.249(1)	0.186(1)	4.7(3)
H(6')	0.264	0.244	0.110	8.0
C(7')	0.433(1)	0.172(1)	0.229(1)	4.8(3)
H(7')	0.419	0.114	0.184	8.0
C(8')	0.546(1)	0.117(1)	0.337(1)	4.0(3)
H(8')	0.610	0.124	0.367	8.0
C(8a')	0.569(1)	0.263(1)	0.406(1)	2.7(2)
C($\bar{1}$')	0.794(1)	0.193(1)	0.562(1)	2.5(2)
C($\bar{2}$')	0.806(1)	0.139(1)	0.659(1)	2.3(2)
C($\bar{3}$')	0.895(1)	0.056(1)	0.686(1)	3.2(3)
H($\bar{3}$')	0.892	0.017	0.751	8.0
C($\bar{4}$')	0.985(1)	0.033(1)	0.618(1)	3.4(3)
H($\bar{4}$')	1.043	—0.024	0.634	8.0
C($\bar{4}$a')	0.993(1)	0.092(1)	0.528(1)	3.0(3)
C($\bar{5}$')	1.103(1)	0.075(1)	0.465(1)	3.8(3)
H($\bar{5}$')	1.168	0.021	0.484	8.0
C($\bar{6}$')	1.114(1)	0.135(1)	0.382(1)	5.0(3)
H($\bar{6}$')	1.186	0.122	0.341	8.0
C($\bar{7}$')	1.025(1)	0.215(1)	0.351(1)	4.8(3)
H($\bar{7}$')	1.039	0.258	0.292	8.0
C($\bar{8}$')	0.916(1)	0.234(1)	0.407(1)	4.0(3)
H($\bar{8}$')	0.852	0.289	0.385	8.0
C($\bar{8}$a')	0.900(1)	0.172(1)	0.496(1)	2.8(2)

Anisotropic thermal parameters [b]

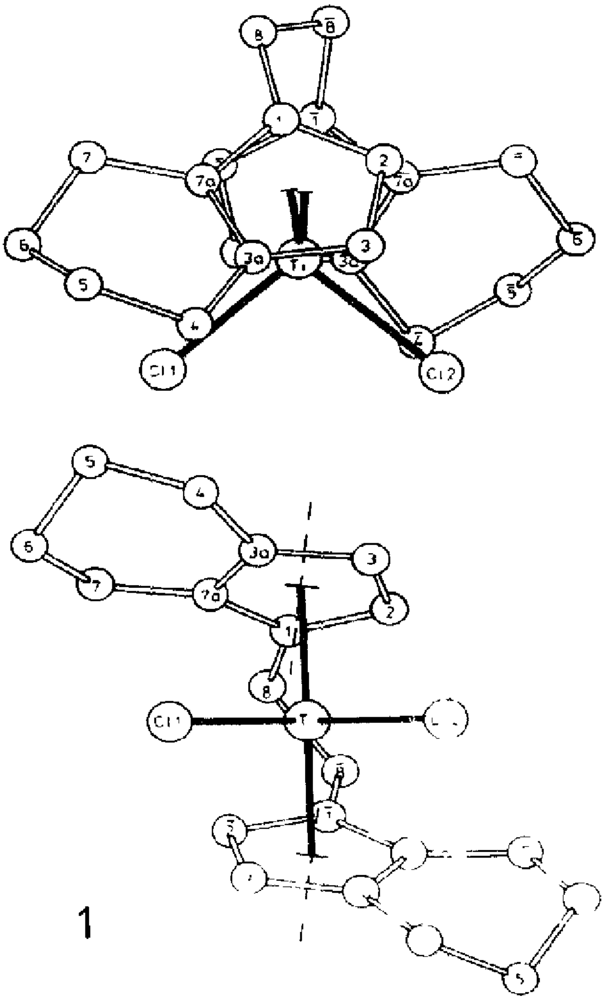
Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ti	2.35(8)	2.56(9)	2.13(8)	0.0(1)	0.0(1)	0.1(1)
O(1)	2.6(4)	2.9(4)	2.2(4)	0.1(3)	—0.2(3)	—0.4(3)
O(2)	3.0(4)	3.1(4)	2.2(4)	0.1(3)	0.0(3)	—0.1(3)

Interatomic distances and bond angles

Ti—O(1)	193.2(7)	O(1)—Ti—O(2)	94.4(3)
Ti—O(2)	193.5(7)	Ti—O(1)—C(2')	122.8(6)
		Ti—O(2)—C($\bar{2}$')	122.9(6)
Ti—C(1)	242(1)	Ti—C($\bar{1}$)	240(1)
Ti—C(2)	235(1)	Ti—C($\bar{2}$)	235(1)
Ti—C(3)	241(1)	Ti—C($\bar{3}$)	242(1)
Ti—C(3a)	251(1)	Ti—C($\bar{3}$a)	250(1)
Ti—C(7a)	250(1)	Ti—C($\bar{7}$a)	249(1)

[a] Hydrogen atoms bonded to carbon atoms with d(C—H) = 96 pm and normal angles. [b] U, U_{ij} in 10^2 pm^2 refer to $T = \exp(-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*))$.

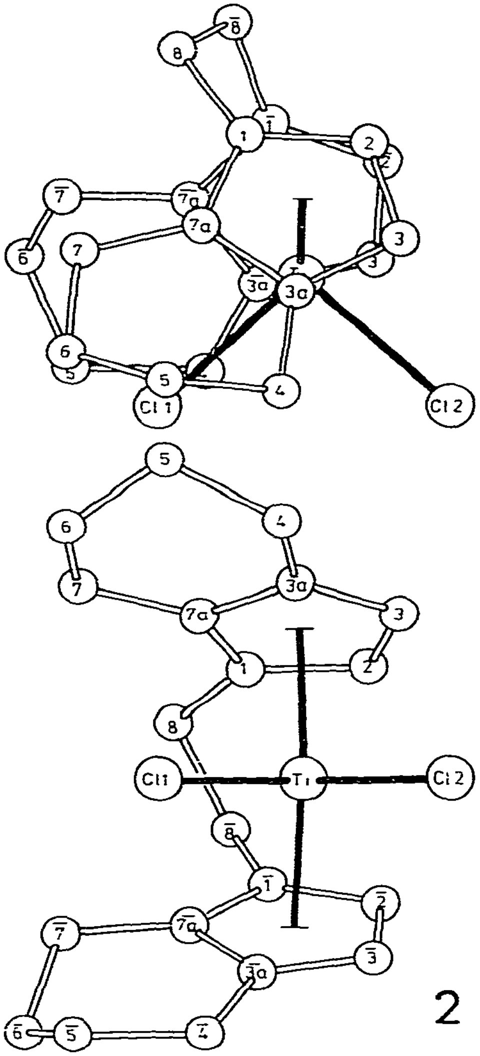
the unsubstituted *ansa*-titanocene $(CH_2)_2(C_5H_4)_2TiCl_2$ [9]. The tetramethylene substituents attached to the *ansa*-titanocene framework adopt a cyclohexene-like conformation; all the CH_2 groups bonded to the C_5-rings remain in the plane of the respective ring ligand within deviations of less than 1°. With four of their six C atoms confined to the cyclopentadienyl plane, each tetramethylene unit has one methylene group (C atoms 5 and $\bar{5}$) folded away from the $TiCl_2$ plane.



1

Fig 1 Molecular structure of racemic ethylene-bis(4,5 6 7 tetrahydro-1 indenyl titanium dichloride (1)

In a small but highly significant deviation from the unsubstituted *ansa*-titanocene analogue, both cyclopentadienyl ring ligands are twisted in such a way that their tetramethylene-substituted edges are farther removed from the $TiCl_2$ plane than their unsubstituted counterparts This distortion is obviously caused by repulsive interactions between the chloride ligand atoms and the methylene groups (C atoms 4 and $\bar{4}$) situated immediately above and below these atoms at a distance of about 315 pm. The severity of these interactions can be gauged by the angle by which the normal on each cyclopentadienyl plane deviates from the plane bisecting the Cl—Ti—Cl angle While this twist angle is nil within error limits for the unsubstituted *ansa*-titanocene analogue, it is 7 5 ± 1 5° in com-

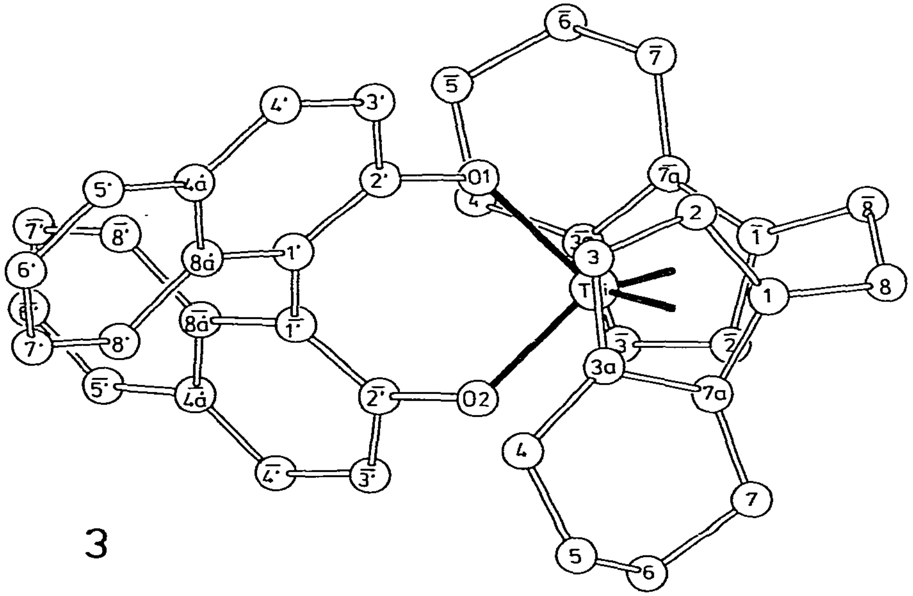


2

Fig. 2. Molecular structure of *meso*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (2).

pound 1, indicating a firm contact of the chiral ligand framework with both in-plane ligands.

In view of this close contact, it is somewhat surprising that of the two equivalent torsional conformations of an unsubstituted *ansa*-titanocene framework [9], compound 1 adopts the one in which both β-substituents are in a "forward" position, i.e. closer to the adjacent TiCl group. Apparently, a crowding of the α-methylene substituents (C atoms 7 and $\bar{7}$) on the backside of the titanocene framework would give rise to even greater repulsions. At any rate, the presence of the tetramethylene ring (instead of just a single alkyl substituent in the β position) appears to lock the ligand framework into a conformation with enhanced steric interactions at both ligand sites.



3

Fig. 3. Molecular structure of ethylene-bis(4,5,6,7-tetrahydro-(*S*)-1-indenyl)titanium-(*S*)-1′,1″-bi-2-naphtholate (3).

The molecular structure of compound **2** identifies it as the *meso*-isomer of **1**. In this compound, the two chloride ligands are clearly inequivalent, one of them being sterically hindered by tetramethylene units from both top and bottom, while the other is essentially unencumbered.

In **2**, the ethylene bridge is no longer situated on the rear extension of the axis bisecting the Cl—Ti—Cl angle; instead it is severely twisted to that side of the ligand framework which carries both tetramethylene substituents. This distortion allows one of the β-methylene substituents (C atom 4) to reside above the $TiCl_2$ group, almost midway between the two Cl ligands. A rather similar conformation, which appears to relieve some of the repulsive strain, is adopted, e.g. by bis(methylcyclopentadienyl)titanium dichloride [10]. The constraints of the bridged ligand framework of **2** keep the other tetrahydroindenyl moiety in a distinctly less favorable arrangement.

Although the constitutive symmetry plane of this *meso*-structure is clearly spoiled by conformational distortions of the molecule, it is apparent that the two halves of the molecule would become equivalent by a relatively minor torsion of the *ansa*-ligand framework and by an interchange of the tetrahydro-six-ring conformations by a twisting mode.

The structure of compound **3**, the *S*-binaphtholate derivative of compound **1**, retains the essential elements of structure **1**. Thus, the *ansa*-titanocene moiety of **3** is again locked in a torsional conformation which puts both β-methylene substituents in a "forward" position, thereby increasing interactions with the binaphthol moiety. The binaphthol ligand, with a torsional angle of 70° between its two naphthol planes, fits the coordination geometry of the Ti center without any noticeable strains *.

The *ansa*-titanocene and the binaphtholate parts of the molecule, each closely approaching axial symmetry, are kinked relative to each other by about 9° at the Ti center. This distortion, probably caused by packing effects, results in slightly inequivalent dispositions of the two O-ligand atoms relative to the substituted titanocene framework. Nevertheless, it is clearly apparent from structure 3 that a diastereomeric adduct between an (*R*,*R*)-enantiomer of the substituted *ansa*-titanocene and an (*S*)-(—)-binaphthol ligand would (even if both moieties were coaxially arranged) place the CH_2 groups (C atoms 4 and $\bar{4}$) at the front side of the titanocene within a distance of less than 2 Å from the CH groups in position 3 and $\bar{3}$ of the naphthol rings. Such an (*R*,*R*)-1:(*S*)-1′ diastereomer of 3 would thus involve practically unsurmountable repulsive interactions, in accord with our observation that the reaction between racemic 1 and (*S*)-binaphtholate yields exclusively the (*S*,*S*)-1:(*S*)-1′ diastereomer 3, in which the two interpenetrating parts of the molecule have the same sense of chirality.

Conclusions

Ethylene-bridged bis(tetrahydroindenyl)titanium derivatives are now accessible through a reaction sequence largely uncomplicated by formation of stereoisomeric side-products: The meso component of the initial product mixture is readily converted to the desired racemate by exposure to light. The mechanism of this synthetically useful reaction probably involves a reversible homolytic metal—ring separation similar to that involved in other photolytic reactions of titanocene derivatives [13]. Because of this photolability of the metal—ring linkage, solutions of the pure enantiomers of 1 must be shielded from light to prevent their racemization.

On the other hand, the chiral *ansa*-titanocene framework of 1 appears to be quite resistant towards racemisation during exchange of Ti-bound ligands. Repeated exchanges, e.g. of Cl for CH_3 ligands by methyllithium and reconversion of the dimethyl to the dichloro derivative by HCl, leaves the specific rotation of the product unchanged. This is in accord with the expectation that the chirality centers of 1, which are located at the cyclopentadienyl carbon atoms rather than at the central Ti atom, should not suffer configurational changes upon substitution of ligands in the $TiCl_2$ plane.

We are at present exploring the limits of configurational stability of these chiral *ansa*-titanocenes and of similarly accessible zirconium analogues in more highly reactive (e.g. hydride-transferring) reaction systems, as well as the stereoselectivity of their interactions with prochiral olefin and carbonyl substrates.

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* The absolute configuration of 3 as represented in Fig. 3 is based on the configurational assignment of (—)-1,1′-bi-2-naphthol as the (*S*)-enantiomer by Akimoto et al. [11]. In accord with this assignment, we find that the R_1 and R_2 values are slightly increased to 0.0637 and 0.0748, due to anomalous dispersion effects, if structure 3 is refined with the opposite absolute configuration.

Experimental

All solvents were thoroughly dried and stored under N_2. Silanized silica gel was prepared from Merck Grade A60/Silica Gel by reaction with $(CH_3)_3SiCl$ in refluxing toluene.

1. *Dilithio-1,2-bis(indenyl)ethane*

To a suspension of 10 g (38 mmol) of bisindenylethane [3] in 50 ml of THF, at —78°C under N_2, 77 mmol of n-butyllithium in hexane were added with a syringe. Upon warming to room temperature, the solution turned dark red. It was used directly for the following reaction step.

2. *Racemic and meso-ethylene-bis(indenyl)titanium dichloride*

In a three-neck flask equipped with a dropping funnel, a reflux condenser and a magnetic stirring bar, 100 ml of THF were cooled to —78°C and 4.2 ml (ca. 39 mmol) of $TiCl_4$ were added. The yellow suspension was heated to reflux under N_2, and to the refluxing, well-stirred suspension the solution of 38 mmol of dilithio-1,2-bis(indenyl)ethane (obtained as described above) was added all at once through the dropping funnel, whereupon the reaction mixture turned dark brown-green. The heating was stopped and the mixture stirred for about 15 min until it had cooled to room temperature. Gaseous HCl was then bubbled through for about half a minute, and the solvent was then removed in vacuo. The subsequent purification steps were conducted without inert gas protection.

The residue obtained after removal of solvent was washed on a Büchner funnel with several portions of diethyl ether until the filtrate was essentially colourless. The solid was then washed with 10% aqueous HCl, water, ethanol and diethyl ether. After drying in vacuo, 3.3 g (8.7 mmol; 22% of theoretical yield) of a dark greenish brown powder were obtained, and this consisted of a mixture of racemic and of *meso*-ethylene-bis(1-indenyl)titanium dichloride.

In the mass spectrum, parent ions of composition $C_{20}H_{16}TiCl_2^+$ were observed at m/e = 378—374 in the appropriate isotope ratios; the base peak, however, as with the unsubstituted *ansa*-titanocene previously described [1], corresponds to the benzofulvene complex $C_{10}H_8TiCl_2^+$, at m/e = 250—246. ^1H NMR spectral data for the racemic and *meso*-components of this product mixture are discussed above. The *rac*-isomer which could be purified by chromatography on silanized silica gel at —20°C with toluene/petroleum ether (1/2), gave the following ^1H NMR data (in $CDCl_3$): 7.61—7.21 ppm (8, m), protons in indenyl positions 4—7, 6.74 (2, d) and 6.07 ppm (2, d), protons at indenyl positions 2 and 3 (α and β-protons); 3.91—3.72 ppm (4, m), ethylene bridge.

3. *Racemic and meso-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride*

In the hydrogenation flask of a Parr pressure hydrogenator, were suspended 1 g of the crude mixture of racemic and *meso*-ethylene-bis(indenyl)titanium dichloride, obtained as described above, together with 75 mg of a 10%-palladium-on-charcoal catalyst (Merck No. 807104), in 30 ml of dry dimethoxyethane. Hydrogenation was carried out at a starting pressure of 30 psi of H_2. After 8 hours, the catalyst was removed by filtration and the red solution was

TABLE 4

^{1}H NMR DATA FOR COMPOUNDS 1 AND 2

rac-1		*meso*-2		Assignment
Chemical shift (δ, ppm)	Relative intensity (splitting)	Chemical shift (δ, ppm)	Relative intensity (splitting)	
6.58	(d, 3 Hz) 2	6.44	(d, 3 Hz) 2	H(2)
5.55	(d, 3 Hz) 2	6.29	(d, 3 Hz) 2	H(3)
3.2—3.0	(m) 6	3.2—3.0	(m) 6	CH_2
2.6—2.5	(m) 4	2.7—2.5	(m) 2	CH_2
2.4—2.3	(m) 2	2.5—2.2	(m) 4	CH_2
2.0—1.8	(m) 4	2.2—1.9	(m) 4	CH_2
1.6—1.4	(m) 4	1.65—1.45	(m) 4	CH_2

evaporated to give 0.72 g (70%) of a red powder, consiting of a mixture of the two stereoisomers. Alternatively, the hydrogenation was performed under 100 bar of H_2 with PtO_2 (Degussa) as catalyst. In this case, yields were around 90%.

For the chromatographic separation, 0.28 g of this product mixture, dissolved in ca. 4—5 ml of toluene, was put onto a 30 cm column containing ca. 60 ml of silanized silica gel in petroleum ether at −20°C. Elution with toluene/petroleum ether (1/2) gave two well-separated red fractions. Evaporation of solvent led to the spontaneous crystallisation of the racemate **1** from the first and of the *meso*-compound **2** from the second of these fractions. Both products have identical mass spectra, with parent ions at *m/e* = 386—382 showing appropriate isotope ratios and fragment ions corresponding to loss of one or two Cl and HCl particles, as well as a substituted fulvene species $C_{10}H_{12}TiCl$. Elemental analysis: Found C, 63.16, H 6.41, Cl 19.04. Calcd.: C 62.82, H 6.28, Cl 18.58%. The products are further characterized by the ^{1}H NMR data given in Table 4.

For the conversion of *meso*-**2** to the racemate **1**, the crude reaction mixture was exposed to sunlight for 1—2 weeks or irradiated for 4 h with a Hanovia 125W mercury irradiation set with quartz vessel and dichromate solution as light filter (cf. ref. 13) partial evaporation and decantation of the supernatant liquid gave well-shaped rectangular crystals of **1**.

4. *Ethylene-bis(4,5,6,7-tetrahydro-(S)-1-indenyl)titanium-(S)-1′,1″-bi-2-naphtholate (3)*

To a suspension of 0.45 g (1.57 mmol) of (*S*)-(—)-binaphthol and 1.2 g (3.15 mmol of *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)titanium dichloride in 150 ml of toluene was added a piece of (ca. 0.5 g) sodium. After stirring under N_2 for 4 hours at 80°C and 1 hour at room temperature, the sodium was removed from the dark red solution. The solution was evaporated in vacuo to about one quarter of its volume, and the mixture was transferred to a chromatographic column containing about 60 ml of silica gel in petroleum ether. With toluene/petroleum ether (1/2) at −20°C, a spread-out red zone was slowly eluted, leaving behind an almost black starting zone.

The red fraction containing the binaphtholate derivative was concentrated to yield 710 mg (1.12 mmol, 77% of theoretical yield for one enantiomer) of **3** as a red powder Mass spectrum Parent ion of composition $C_{42}H_{36}O_2Ti$ at *m e* = 540; elemental analysis. Found C, 80 31, H 6 78 Calc C 80.66, H 6 08% NMR data. 7 79—7 72 (m, 4), 7 2—6 85 (m, 8), naphthol protons, 5 54 (d, 4), cyclopentadienyl protons, 3.4—3.0 (m, 4), 2.57—2.47 (m, 4), 1.86—1.48 (m, 10), 1.23—1.14 (m, 2) ethylene bridge and tetrahydro indenyl CH_2 groups.

After elution of a yellow substance from the chromatographic column with toluene/petroleum ether (3/2), the dark starting zone was eluted with methylene chloride saturated with HCl to give, after removal of solvent, 430 mg (0 81 mmol, 70% of theoretical yield for one enantiomer) of ^{1}H NMR spectrally pure **1** with a specific optical rotation, in $CHCl_3$ of $[\alpha]^{20}_{436}$ = 2440° (1 cm, 23.2 mg/100 ml), indicating the presence of (*R*,*R*)-**1** in an optical purity of ca. 75%.

5 *Cleavage of the binaphtholate adduct 3*

About 20 ml of petroleum ether, containing 78 mg of the binaphtholate adduct **3** in suspension, were cooled to —78°C, 1.6 mmol of methyl lithium in diethyl ether were added with a syringe and the mixture was allowed to warm to room temperature. After stirring for about 4 hours, the yellow solution of the dimethyl derivative was filtered. Exposure of the filtrate to gaseous HCl led to precipitation of a red solid, which was filtered off, washed with pentane and dried in vacuo The material thus obtained was identified by ^{1}H NMR spectroscopy as pure **1** Its optical rotation in $CHCl_3$ (1 cm, 50 mg/100 ml) was $[\alpha]^{25}_{436}$ = —3300° Repeated conversion to the dimethyl derivative with CH_3Li and reconversion to **1** with HCl did not change the specific optical rotation of this material, which can thus be regarded as being pure (*S*,*S*)-**1**

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