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ansa-METALLOCENE DERIVATIVES

XII *. DIASTEREOMERIC DERIVATISATION AND ENANTIOMER SEPARATION OF ETHYLENEBIS(TETRAHYDROINDENYL)-TITANIUM AND -ZIRCONIUM DICHLORIDES **

ANDREA SCHÄFER, EBERHARD KARL, LASZLO ZSOLNAI, GOTTFRIED HUTTNER and HANS-HERBERT BRINTZINGER ***

Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz (F.R.G.)

Summary

Derivatisation of racemic ethylene-bridged bis(4,5,6,7tetrahydro-1-indenyl)-titanium and -zirconium dichlorides with *O*-acetyl-R-mandelic acid affords diastereomers which can be separately crystallised. Crystal and molecular structures of these diastereomers reveal different chelate ring conformations in the crystalline state. The separated diastereomers have been converted, via their dimethyl derivatives, into the corresponding titanocene and zirconocene dichloride enantiomers, the optical purity of these enantiomers has been demonstrated by their reconversion into the acetyl-R-mandelate derivatives.

Introduction

The study of chiral titanocene derivatives goes back to pioneering studies by Tirouflet and collaborators [1–7]. We recently showed that chiral *ansa*-metallocenes can be made from substituted cyclopentadienyl ligands which are interconnected by e.g. an ethylene bridge [9,10]. The racemic zirconium compound C_2H_4(4,5,6,7-tetrahydro-1-indenyl)$_2ZrCl_2$ [10] was found to act in the presence of a methylalumoxan cocatalyst as a highly active and stereoselective catalyst for the isotactic polymerisation of α-olefins [11]. Such an isotactic polymerisation requires a chiral catalyst, but a racemic mixture of the catalyst enantiomers is sufficient for this type of stereoselective catalysis since the tacticity of the polymer, rather than separate formation of *S*- and *R*-products, is the relevant selectivity criterion. For synthetic applications

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* For Part XI see ref. 8.

** Dedicated to Professor Jean Tirouflet on the occasion of his retirement.

*** To whom correspondence should be addressed.

of chiral *ansa*-metallocene catalysts, on the other hand, e.g. for hydrogen or alkyl transfer to prochiral unsaturated molecules, use of an isolated enantiomer of the organometallic catalyst is essential.

We previously described separation of the enantiomers of the chiral *ansa*-metallocene, $C_2H_4(4,5,6,7\text{-tetrahydro-1-indenyl})_2TiCl_2$, by way of its complexation with *S*-binaphthol [9]. In this complexation only the *S*-enantiomer of the chiral *ansa*-metallocene is converted into the *S*-binaphthol derivative when a half-equivalent amount of *S*-binaphthol is treated with the racemic complex mixture. Although isolation of this binaphthol diasteromer and its subsequent cleavage yields one of the dichloride enantiomers in high optical purity, the practical utility of this method is limited, since the enantiomer separation of the chiral auxiliary reagent, *S*-binaphthol, requires a rather involved, 4-step reaction sequence [12], and since its sodium-induced reaction with racemic *ansa*-metallocene dichlorides (especially with the zirconium compound) does not always yield reproducible results; possible side-reactions include a relatively rapid racemisation of the binaphthol monoanion and the replacement of ring ligands by an accidental local excess of the binaphtholate dianion.

In order to develop convenient enantiomer separation procedures for these chiral metallocenes we have investigated the formation of diastereomeric derivatives with a number of naturally-occurring chiral carboxylic acids, their separation by use of their differing solubilities and their reconversion into the enantiomeric dichloro derivatives.

Results and discussion

1. Diastereomer formation and fractional crystallisation

Transformation of the racemic *ansa*-metallocene dichlorides to the respective dicarboxylate derivatives was carried out in several ways:

(A) Conversion into the dimethyl derivative and subsequent reaction with 2 mol of the carboxylic acid in toluene *.

(B) Reaction with 2 mol of sodium carboxylate in ethanol solution.

(C) Reaction with 2 mol of carboxylic acid in the presence of a slight excess of triethylamine in ethanol or toluene.

After filtration followed by evaporation of solvent, the reaction products were taken up in benzene or toluene and characterised by their NMR spectra; their crystallisation behaviour was then studied.

Reactions with *N*-acetyl α-amino acids **, such as *N*-acetyl-L-leucine or -methionine by method C, yield in each case a yellow product mixture, the ^1H NMR spectrum of which indicates a clean formation of two diastereomers, with four cyclopentadienyl proton doublets at 5.8–6.1 ppm and two NH signals between 6

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* Because of the difficulty of separating the dimethyl-*ansa*-zirconocene derivative from excess methyl lithium, this otherwise rather convenient method was used only for *ansa*-titanocene derivatisation.

** Free α-amino acids did not react under conditions of method A, probably owing to insufficient solubility. Method C, gave only partial conversion into the corresponding amino acid derivatives; apparently hydrochloride formation occurs at the free amino group and causes reconversion to the dichloro derivative upon evaporation of the product mixture.

TABLE 1

^{1}H NMR DATA FOR DIASTEREOMERIC 1,2-ETHANEDIYLBIS(TETRAHYDRO-1-INDENYL)METAL(IV) DERIVATIVES IN $CDCl_3$ SOLUTION MEASURED AT 250 MHz.

	Diastereomer 1	Diastereomer 2	Assignment
$C_2H_4(C_{10}H_{10})_2$Ti(*N*-acetyl-L-leucine)$_2$	6.65 M (2H)	6.26 M (2H)	NH
	6.04 D [a] (2H)	6.05 D [a] (2H)	C_5H_2
	5.95 D [a] (2H)	5.85 D [a] (2H)	
$C_2H_4(C_{10}H_{10})_2$Ti(*N*-acetyl-L-methionine)$_2$	7.04 M (2H)	6.76 M (2H)	NH
	6.07 D [a] (2H)	6.05 D [a] (2H)	C_5H_2
	5.86 D [a] (2H)	5.96 D [a] (2H)	
$C_2H_4(C_{10}H_{10})_2$Ti((−)-camphanate)$_2$	6.44 D [a] (2H)	6.36 D [a] (2H)	C_5H_2
	6.08 D [a] (2H)	6.00 D [a] (2H)	
$C_2H_4(C_{10}H_{10})_2$Ti(*O*-acetyl-R-mandelate)$_2$	7.87 M (4H)	7.80 M (4H)	C_6H_5
	7.30 M (6H)	7.25 M (6H)	
	6.17 S (2H)	6.24 S (2H)	CH–COOTi
	5.96 D [a] (2H)	6.60 D [a] (2H)	C_5H_2
	5.43 D [a] (2H)	6.00 D [a] (2H)	
	2.7–2.5 M (6H)		CH_2
	2.2–1.9 M (10H)		CH_2
	1.95 S (6H)		CO-CH_3
	1.42 M (4H)		CH_2
$C_2H_4(C_{10}H_{10})_2$Zr(*O*-acetyl-R-mandelate)$_2$	7.54 M (4H)		C_6H_5
	7.35 M (6H)		
	5.82 S (2H)	5.78 S (2H)	CH–COOZr
	5.70 D [a] (2H)	5.60 D [a] (2H)	C_5H_2
	5.18 D [a] (2H)	5.36 D [a] (2H)	
	3.1–3.0 M (4H)		CH_2
	2.9–1.1 M (16H)		CH_2
	2.23 S (6H)		CO–CH_3

[a] Doublet with J(H–H) 3.0 Hz due to vinylic cyclopentadienyl protons.

and 7 ppm (see Table 1). However, attempted crystallisation yielded only oily products. Although allowing a partial diastereomer separation sufficient for an assignment of their separate ^{1}H NMR signals, these derivatives were clearly unsuitable for a practical separation procedure.

Amino acid derivatives with t-butoxycarbonyl- or benzoxy-carbonyl-protected amino groups yielded, by all three methods, reaction mixtures with ^{1}H NMR spectra which indicated the presence of substantial amounts of several side-products. Similar results were obtained in attempts to make derivatives of α-hydroxy-carboxylic acids, such as lactic acid or mandelic acid. Derivatisation, by method C, with *O*-acetyl lactic acid and with (−)-menthyloxy-acetic acid led to ^{1}H NMR evidence for a clean formation of diastereomer pairs, but these could not be crystallised separately.

Derivatisation with *O*-acetyl-R-mandelic acid by methods A, B or C finally resulted in a clean conversion to a diastereomer pair with solubility properties sufficiently different to allow their separate crystallisation, e.g. from a toluene/pentane mixture *.

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* A similar but somewhat less efficient separation was achieved with the diastereomeric *ansa*-titanocene derivatives of camphanic acid.

TABLE 2

SPECIFIC OPTICAL ROTATIONS [α] (in °) FOR THE *ansa*-TITANOCENE DIASTEREOMERS **1a** AND **2a**, AND THE *ansa*-ZIRCONOCENE DIASTEREOMERS **1b** AND **2b** (in CH_2Cl_2 solution, concentrations *c* in g/100 ml)

Wavelength (nm)	**1a** *c* 1.36; *l* 0.01 dm	**2a** *c* 1.88; *l* 0.01 dm	**1b** *c* 0.65; *l* 1 dm	**2b** *c* 3.1; *l* 0.1 dm
435	−246	+21	−25	−47
546	[a]	[a]	−29	−6.7
578	−148	+271	−22	−57

[a] Absorption too high for reliable measurements.

The less soluble *ansa*-titanocene diastereomer (**1a**), which was identified as C_2H_4(tetrahydro-1*S*-indenyl)$_2$Ti(*O*-acetyl-R-mandelate)$_2$ by an X-ray determination of its molecular structure and by its conversion into the *S*-enantiomer of the *ansa*-titanocene dichloride (see sections 2 and 3), shows in its ^1H NMR spectrum two characteristic cyclopentadienyl proton doublets at 5.96 and 5.43 ppm and a mandelate α-proton signal at 6.17 ppm. For the other diastereomer, C_2H_4(tetrahydro-1*R*-indenyl)$_2$Ti(*O*-acetyl-R-mandelate)$_2$ (**2a**), these resonances appear at 6.60 and 6.00 and 6.24 ppm, respectively (see Table 1). The corresponding resonances of the analogous zirconium diastereomers **1b** and **2b** are also given in Table 1. Of these zirconium diastereomers, **1b** was readily crystallised in pure form; because of the higher solubilities of the zirconium derivatives, **2b** was only obtained in an admixture with residual **1b**. Specific rotations for the separate diastereomers at several wavelengths are shown in Table 2.

2. *Crystal and molecular structures*

For a structural characterisation of the diastereomeric *ansa*-metallocene acetylmandelate derivatives **1a**, **1b** and **2a**, space groups, cell parameters and X-ray diffraction intensities of were determined on a Syntex-P3 four-circle diffractometer, (Mo-K_α,λ 71.069 pm, graphite monochromator, ω-scan), at the following settings: Compounds **1a**: *T* 248 K; $\Delta\omega$ 1°; $1.8 \leq \dot{\omega} \leq 29.3°$ min^{-1}; $2 \leq 2\theta \leq 44°$. Compound **1b**: *T* 243 K; $\Delta\omega$ 1°; $2.0 \leq \dot{\omega} \leq 29.3°$; $2 \leq 2\theta < 48°$. Compound **2a**: *T* 238 K; $\Delta\omega$ 1°; $1.8 \leq \dot{\omega} \leq 29.3°$ min^{-1}; $1 \leq 2\theta \leq 46°$.

The crystals of compound **1a** were orthorhombic, space group $P2_12_12_1$ with *a* 987.2(1.7), *b* 1753(3), *c* 1841 (2) pm; 4 crystallographically equivalent molecules per unit cell, *V* 3184×10^6 pm^3; $d_{\text{calcd.}}$ 1.46 g/cm^3; absorption coefficient μ 3.4 cm^{-1}. The crystals of compound **1b** are isostructural with **1a** with *a* 1005.1(.7), *b* 1776(1), *c* 1880.4(1.2) pm; *V* 3359×10^6 pm^3; $d_{\text{calcd.}}$ 1.47 g/cm^3; absorption coefficient μ 3.8 cm^{-1}. The crystals of compound **2a** are triclinic, space group *P*1, with *a* 931.8(.5), *b* 1000.2(.4), *c* 1087.8(.6) pm; α 108.54(.04), β 104.95(.04), γ 105.89(.04)°; *V* 885.7×10^6 pm^3; 1 molecule per unit cell; $d_{\text{calcd.}}$ 1.36 g/cm^3; absorption coefficient μ 3.2 cm^{-1}.

For resolution and refinement of these structures, 1701 independent reflections with $I > 2\sigma(I)$ were used for compound **1a**, 2782 for compound **1b** and 2362 for compound **2a**. The structures of **1a** and **1b** were solved by the Patterson method. Refinement with a partially anisotropic model (H atoms in calculated positions 100 pm from the corresponding C atom) converged at $R_1 = 0.0741$ and $R_2 = 0.0822$ * for **1a** and at $R_1 = 0.0671$ and $R_2 = 0.0745$ for **1b**. The structure of **2a** was solved by direct methods (SHELXTL); refinement, again with a partially anisotropic model and H atoms in calculated positions, converged at $R_1 = 0.0525$ and $R_2 = 0.0535$.

In all three cases, refinement with mirror-image configurations gave significantly higher R_1 and R_2 values, in agreement with the known R configuration of the mandelic acid α-C atom. Structural data as well as bond lengths and bond angles at the metal atoms are listed in Table 3, 4, 5 and 6 **.

The molecular structures of the *ansa*-titanocene diastereomers **1a** and **2a** are represented in Fig. 1. Comparison of gross coordination geometries around the metal centre does not reveal significant differences between **1a** and **2a**: Ti–Cp distances of 205–206 pm, Cp–Ti–Cp angles close to 129° and Ti–O distances of 185–196 pm are all within the range normally observed for tetracoordinate compounds of this type. The variations in Ti–O bond distances of 185–196 pm correlate with Ti–O–C(O)R bond angles of 159–132°. As noted in related cases [13–16] larger Ti–O–C angles appear to be associated with shorter Ti–O bond lengths, probably because of increased oxygen-to-titanium π donation.

Somewhat unusual is the rather large O(1)–Ti–O(2) angle of 99° in diastereomer **1a**; normally O–Ti–O (like other X–Ti–X) angles in tetracoordinate titanocene derivatives are in the range of 91–97° ***. Apparently, slight distortions of O–Ti–O and Ti–O–C angles are tolerated in the crystals of **1a** in order to achieve an increased packing density. Indeed the calculated crystal density for diastereomer **1a** is 1.46 g/cm^3, whereas that of diastereomer **2a** is only 1.36 g/cm^3. The density difference of about 7% in favour of diastereomer **1a** is undoubtedly associated with an increased lattice stability, which apparently overcompensates for the observed distortions of O–Ti–O and Ti–O–C bond angles.

In addition, the structures of **1a** and **2a** show a remarkable difference with respect to the conformation of their ligand frameworks: In the crystals of diastereomer **1a** the ethylene-bridged metallocene adopts the conformation which places the ring substituents in their "forward" position, i.e. with the β-CH_2 groups directly above and below the oxygen ligand atoms. For diastereomer **1a**, with *S*-configuration at its bridge-head ring atoms (C(2) and C(13) in Fig. 1), the five-membered chelate ring $\overline{\text{TiC(2)C(10)C(11)C(13)}}$ is thus in its λ conformation. A preference for such an *S*(λ) geometry (or the equivalent *R*(δ) geometry) has also been observed for the dichloro and the binaphtholate derivatives of these chirally substituted *ansa*-metallocenes [9,10]. Crystalline diastereomer **2a**, on the other hand, adopts an *R*(λ) geometry, which places the cyclopentadienyl substituents in their "backward" position, i.e. toward the narrow region of the wedged metallocene.

The crystal structure of diastereomer **2a** is the first example of this conformation. The fact that this conformation is normally avoided appears to be the result of

(Continued on p. 95)

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* $R_1 = (\Sigma || F_o| - |F_c||)/\Sigma|F_o|$ and $R_2 = [\Sigma\omega(|F_o| - |F_c|)^2]^{1/2}/[\Sigma\omega|F_o|^2]^{1/2}$.

** Detailed structural data are available on request from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldszentrum 2, upon citation of deposit No. CSD 52106, the names of the authors and the journal reference for this article.

*** See e.g. ref. 13–18 and literature cited therein.

TABLE 3

STRUCTURAL PARAMETERS FOR C_2H_4(4,5,6,7-tetrahydro-1*S*-indenyl)$_2$Ti(*O*-acetyl-R-mandelate)$_2$ (**1a**), FRACTIONAL COORDINATES (with e.s.d.'s) AND ISOTROPIC THERMAL PARAMETERS [a]

Atom	*x*	*y*	*z*	*U*
Ti	1.0023(3)	0.3101(1)	0.6820(1)	
C(1)	0.972(1)	0.2257(7)	0.5894(6)	0.036(3)
C(2)	0.970(1)	0.2988(7)	0.5561(6)	0.034(3)
C(3)	0.850(1)	0.3322(7)	0.5791(7)	0.035(3)
C(4)	0.782(1)	0.2822(7)	0.6250(7)	0.031(3)
C(5)	0.856(1)	0.2170(7)	0.6323(7)	0.033(3)
C(6)	0.797(1)	0.4085(7)	0.5566(7)	0.038(3)
C(7)	0.666(1)	0.4292(8)	0.5959(8)	0.050(4)
C(8)	0.578(1)	0.3623(8)	0.6089(7)	0.041(4)
C(9)	0.649(1)	0.3026(8)	0.6587(7)	0.044(4)
C(10)	1.076(1)	0.3291(8)	0.5068(7)	0.043(4)
C(11)	1.213(1)	0.3128(8)	0.5409(7)	0.036(3)
C(12)	1.160(1)	0.3990(7)	0.6515(7)	0.036(3)
C(13)	1.205(1)	0.3304(7)	0.6188(3)	0.035(3)
C(14)	1.240(1)	0.2793(7)	0.6747(7)	0.034(3)
C(15)	1.223(1)	0.3207(7)	0.7419(6)	0.028(3)
C(16)	1.174(1)	0.3927(7)	0.7269(7)	0.032(3)
C(17)	1.300(1)	0.2032(7)	0.6696(7)	0.037(3)
C(18)	1.313(2)	0.1672(8)	0.7445(8)	0.049(4)
C(19)	1.361(1)	0.2237(8)	0.7994(7)	0.041(4)
C(2))	1.265(1)	0.2912(7)	0.8119(7)	0.035(3)
C(21)	0.892(1)	0.2093(8)	0.7985(7)	0.039(4)
C(22)	0.921(1)	0.1362(7)	0.8345(7)	0.031(3)
C(23)	0.716(1)	0.0788(7)	0.8021(7)	0.033(3)
C(24)	0.592(1)	0.0439(8)	0.8315(7)	0.042(4)
C(25)	0.996(2)	0.1480(7)	0.9039(6)	0.034(3)
C(26)	1.125(1)	0.1197(8)	0.9132(8)	0.046(4)
C(27)	1.191(2)	0.1321(8)	0.9776(8)	0.055(4)
C(28)	1.132(1)	0.1728(8)	1.0316(8)	0.050(4)
C(29)	1.008(2)	0.2010(8)	1.0230(7)	0.051(4)
C(30)	0.940(1)	0.1898(8)	0.9588(7)	0.045(4)
C(31)	0.866(1)	0.4463(8)	0.7564(7)	0.033(3)
C(32)	0.833(1)	0.4318(7)	0.8369(6)	0.027(3)
C(33)	0.610(2)	0.4703(8)	0.8366(8)	0.050(4)
C(34)	0.507(2)	0.5193(8)	0.8750(8)	0.057(4)
C(35)	0.955(1)	0.4412(7)	0.8836(7)	0.035(3)
C(36)	1.003(2)	0.3818(7)	0.9207(7)	0.042(3)
C(37)	1.114(2)	0.3918(8)	0.9648(8)	0.050(4)
C(38)	1.180(2)	0.4596(8)	0.9688(8)	0.053(4)
C(39)	1.133(2)	0.5192(9)	0.9276(8)	0.054(4)
C(40)	1.020(2)	0.5112(8)	0.8850(8)	0.051(4)
O(1)	0.993(1)	0.2348(5)	0.7604(4)	
O(2)	0.8963(8)	0.3862(5)	0.7724(4)	
O(3)	0.7868(9)	0.2448(5)	0.8094(5)	
O(4)	0.7986(8)	0.0990(5)	0.8558(4)	
O(5)	0.747(1)	0.0848(5)	0.7402(5)	
O(6)	0.865(1)	0.5093(5)	0.7332(5)	
O(7)	0.7328(9)	0.4829(5)	0.8633(5)	
O(8)	0.585(1)	0.4270(6)	0.7909(6)	

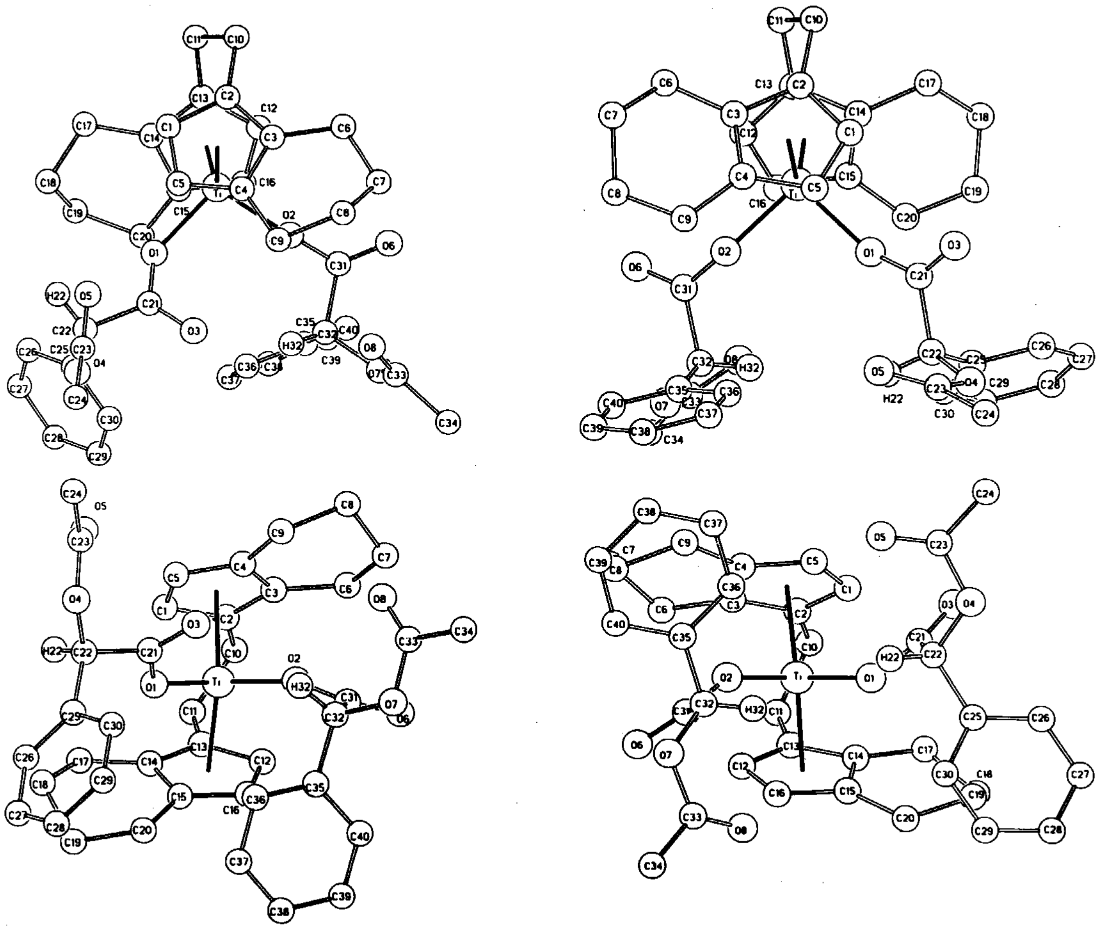

Fig. 1. Molecular structure of C_2H_4(tetrahydro-1*S*-indenyl)$_2$ Ti(*O*-acetyl-*R*-mandelate)$_2$ (**1a**, left) and of its 1*R*-indenyl diastereomer (**2a**, right). Projections perpendicular to TiO(1)O(2) plane (top) and parallel to the C(10)–Ti–C(11) bisector (bottom).

TABLE 4

STRUCTURAL PARAMETERS FOR C_2H_4(4,5,6,7-tetrahydro-1*R*-indenyl)$_2$Ti(O-Acetyl-R-mandelate)$_2$ (**2a**) FRACTIONAL COORDINATES (with e.s.d.'s) AND ISOTROPIC THERMAL PARAMETERS

Atom	*x*	*y*	*z*	*U*
Ti	0.00000	0.00000	0.00000	
C(1)	0.2204(9)	0.0164(8)	0.1673(8)	0.044(2)
C(2)	0.1593(9)	−0.1332(8)	0.0606(8)	0.039(2)
C(3)	0.1812(8)	−0.1183(7)	−0.0582(7)	0.032(2)
C(4)	0.2617(9)	0.0368(8)	−0.0242(7)	0.034(2)
C(5)	0.2810(9)	0.1199(8)	0.1150(8)	0.039(2)
C(6)	0.1480(9)	−0.2419(8)	−0.1967(8)	0.041(2)
C(7)	0.254(1)	−0.1802(9)	−0.2657(8)	0.048(2)
C(8)	0.244(1)	−0.0321(9)	−0.2700(8)	0.051(2)
C(9)	0.314(1)	0.0941(8)	−0.1215(8)	0.040(2)
C(10)	0.084(1)	−0.280(1)	0.0692(9)	0.057(2)
C(11)	−0.087(1)	−0.363(1)	−0.0423(9)	0.055(2)
C(12)	−0.2192(9)	−0.2166(8)	−0.1614(8)	0.038(2)
C(13)	−0.1634(9)	−0.2513(8)	−0.0483(8)	0.039(2)
C(14)	−0.1870(9)	−0.1572(8)	0.0641(7)	0.035(2)
C(15)	−0.2669(9)	−0.0730(8)	0.0166(7)	0.032(2)
C(16)	−0.2815(9)	−0.1070(8)	−0.1214(7)	0.037(2)
C(17)	−0.159(1)	−0.1550(9)	0.2069(8)	0.047(2)
C(18)	−0.261(1)	−0.088(1)	0.272(1)	0.081(3)
C(19)	−0.268(1)	0.046(1)	0.254(1)	0.070(3)
C(20)	−0.326(1)	0.0276(9)	0.1039(8)	0.048(2)
C(21)	0.0997(9)	0.3040(8)	0.2504(7)	0.033(2)
C(22)	0.0697(8)	0.4479(7)	0.2581(7)	0.032(2)
C(23)	0.3408(9)	0.6158(9)	0.3467(8)	0.042(2)
C(24)	0.469(1)	0.746(1)	0.470(1)	0.072(3)
C(25)	−0.0768(8)	0.4481(7)	0.2896(7)	0.030(2)
C(26)	−0.0731(9)	0.4670(8)	0.4218(7)	0.037(2)
C(27)	−0.205(1)	0.4690(9)	0.4548(9)	0.049(2)
C(28)	−0.341(1)	0.4515(9)	0.3564(9)	0.054(2)
C(29)	−0.346(1)	0.4349(9)	0.2263(9)	0.049(2)
C(30)	−0.2144(9)	0.4304(8)	0.1918(8)	0.041(2)
C(31)	−0.0941(8)	0.0846(8)	−0.2487(7)	0.032(2)
C(32)	−0.0714(8)	0.2479(8)	−0.2183(7)	0.033(2)
C(33)	−0.342(1)	0.205(1)	−0.3218(9)	0.053(2)
C(34)	−0.465(1)	0.203(1)	−0.439(1)	0.067(3)
C(35)	0.0879(8)	0.3382(7)	−0.2139(7)	0.030(2)
C(36)	0.2141(8)	0.4268(7)	−0.0854(7)	0.033(2)
C(37)	0.3633(9)	0.5071(8)	−0.0789(8)	0.042(2)
C(38)	0.388(1)	0.5004(9)	−0.1973(8)	0.047(2)
C(39)	0.2653(9)	0.4122(9)	−0.3246(8)	0.046(2)
C(40)	0.1133(9)	0.3289(8)	−0.3345(8)	0.037(2)
O(1)	0.0074(6)	0.1887(5)	0.1332(5)	
O(2)	−0.0064(5)	0.0756(5)	−0.1412(5)	
O(3)	0.1932(8)	0.3044(6)	0.3476(5)	
O(4)	0.2011(6)	0.5802(5)	0.3656(5)	
O(5)	0.3508(7)	0.5442(7)	0.2406(5)	
O(6)	−0.1755(7)	−0.0204(6)	−0.3608(5)	
O(7)	−0.1942(6)	0.2550(6)	−0.3243(5)	
O(8)	−0.3661(7)	0.1674(9)	−0.2321(7)	

TABLE 5

STRUCTURE PARAMETERS FOR C_2H_4(4,5,6,7-Tetrahydro-1*R*-indenyl)$_2$Zr(O-acetyl-R-mandelate)$_2$ (**1b**) FRACTIONAL COORDINATES (with e.s.d.'s) AND ISOTROPIC THERMAL PARAMETERS

Atom	*x*	*y*	*z*	*U*
Zr	0.9999(1)	0.31070(4)	0.68547(4)	
C(1)	0.9682(9)	0.2245(5)	0.5869(5)	0.023(2)
C(2)	0.9679(9)	0.2974(5)	0.5550(5)	0.023(2)
C(3)	0.850(1)	0.3336(5)	0.5782(5)	0.024(2)
C(4)	0.780(1)	0.2850(6)	0.6225(5)	0.027(2)
C(5)	0.852(1)	0.2172(6)	0.6278(5)	0.028(2)
C(6)	0.800(1)	0.4110(6)	0.5549(6)	0.034(3)
C(7)	0.668(1)	0.4306(6)	0.5941(6)	0.040(3)
C(8)	0.580(1)	0.3632(7)	0.6074(7)	0.045(3)
C(9)	0.648(1)	0.3041(6)	0.6537(6)	0.034(2)
C(10)	1.076(1)	0.3291(6)	0.5096(5)	0.032(2)
C(11)	1.210(1)	0.3136(6)	0.5419(5)	0.032(2)
C(12)	1.169(1)	0.4010(6)	0.6499(6)	0.033(2)
C(13)	1.210(1)	0.3326(5)	0.6189(5)	0.025(2)
C(14)	1.2480(9)	0.2826(5)	0.6752(5)	0.024(2)
C(15)	1.2342(9)	0.3243(5)	0.7401(5)	0.024(2)
C(16)	1.186(1)	0.3948(6)	0.7256(6)	0.030(2)
C(17)	1.305(1)	0.2064(5)	0.6704(5)	0.029(2)
C(18)	1.329(1)	0.1745(7)	0.7428(6)	0.051(3)
C(19)	1.377(1)	0.2297(7)	0.7961(7)	0.048(3)
C(20)	1.277(1)	0.2921(6)	0.8102(6)	0.035(2)
C(21)	0.897(1)	0.2101(7)	0.7988(6)	0.042(3)
C(22)	0.9163(9)	0.1374(5)	0.8391(5)	0.029(2)
C(23)	0.715(1)	0.0796(6)	0.8022(6)	0.033(2)
C(24)	0.590(1)	0.0492(7)	0.8310(6)	0.045(3)
C(25)	0.998(1)	0.1461(5)	0.9043(5)	0.028(2)
C(26)	1.126(1)	0.1199(6)	0.9125(6)	0.039(3)
C(27)	1.194(1)	0.1337(7)	0.9741(7)	0.052(3)
C(28)	1.134(1)	0.1721(7)	1.0281(7)	0.048(3)
C(29)	1.008(1)	0.1976(6)	1.0217(6)	0.045(3)
C(30)	0.940(1)	0.1845(6)	0.9591(5)	0.035(2)
C(31)	0.854(1)	0.4546(5)	0.7599(5)	0.023(2)
C(32)	0.8253(8)	0.4371(5)	0.8379(4)	0.025(2)
C(33)	0.599(1)	0.4706(6)	0.8400(6)	0.038(3)
C(34)	0.500(2)	0.5161(6)	0.8779(6)	0.050(3)
C(35)	0.947(1)	0.4424(5)	0.8837(5)	0.023(2)
C(36)	0.997(1)	0.3805(5)	0.9185(5)	0.036(2)
C(37)	1.109(1)	0.3895(7)	0.9603(6)	0.043(3)
C(38)	1.169(1)	0.4562(7)	0.9673(7)	0.049(3)
C(39)	1.121(1)	0.5183(8)	0.9312(7)	0.052(3)
C(40)	1.011(1)	0.5107(6)	0.8892(6)	0.045(3)
O(1)	0.998(1)	0.2307(6)	0.7638(4)	
O(2)	0.8952(7)	0.3972(4)	0.7243(3)	
O(3)	0.794(1)	0.2443(5)	0.8066(6)	
O(4)	0.7957(7)	0.1016(4)	0.8567(4)	
O(5)	0.7470(8)	0.0858(4)	0.7417(4)	
O(6)	0.8435(9)	0.5166(4)	0.7389(4)	
O(7)	0.7229(7)	0.4814(4)	0.8671(3)	
O(8)	0.5786(8)	0.4275(5)	0.7925(4)	

TABLE 6

BOND LENGTHS (pm) AND BOND ANGLES (°) AT THE METAL CENTRES OF THE DIASTEREOMERIC *ansa*-TITANOCENE DERIVATIVES **1a** AND **2a**, AND OF THE *ansa*-ZIRCONOCENE DERIVATIVE **1b** (CP = CENTROID OF CYCLOPENTADIENYL RING)

Compound **1a** (C_2H_4(4,5,6,7-tetrahydro-1*S*-indenyl)$_2$Ti(*O*-acetyl-R-mandelate)$_2$)			
Ti–O(1)	195.8(.9)	TiO(1)–C(21)	131.9(.9)
Ti–O(2)	185.1(.9)	Ti–O(2)–C(31)	159.1(.9)
Ti–CP(1)	206.5	O(1)–Ti–O(2)	99.3(.4)
Ti–CP(2)	204.6	CP(1)–Ti–CP(2)	129.4
Compound **2a** (C_2H_4(4,5,6,7-tetrahydro-1*R*-indenyl)$_2$Ti(*O*-acetyl-R-mandelate)$_2$)			
Ti–O(1)	195.0(.5)	Ti–O(1)–C(21)	142.0(.6)
Ti–O(2)	191.1(.6)	Ti–O(2)–C(31)	147.2(.5)
Ti–Cp(1)	205.1	O(1)–Ti–O(2)	92.5(.2)
Ti–Cp(2)	206.2	CP(1)–Ti–CP(2)	129.1
Compound **1b** (C_2H_4(4,5,6,7-tetrahydro-1*R*-indenyl)$_2$Zr(*O*-acetyl-R-mandelate)$_2$)			
Zr–O(1)	204.6(.9)	Zr–O(1)–C(21)	125.8(.9)
Zr–O(2)	200.0(.7)	Zr–O(2)–C(31)	165.2(.6)
Zr–CP(1)	219.1	O(1)–Zr–O(2)	105.4(.3)
Zr–CP(2)	220.4	CP(1)–Zr–CP(2)	125.4

relatively short non-bonding contacts between the β-CH_2 substituents and the equatorial ligand atoms, in this case O(1) and O(2). For the $S(\lambda)$ conformation of **1a**, the non-bonded distances O(1) $\cdots$ C(20) and O(2) $\cdots$ C(9) (301 and 308 pm) are just at the limit of normal Van der Waals contacts; for the $R(\lambda)$ conformation of **2a**, on the other hand, the relevant distances (296 and 289 pm) are slightly below this Van der Waals limit. The reduced distances in **2a**, which are not immediately apparent from Fig. 1, arise from a decreased deviation of the β-CH_2 substituents from the TiO(1)O(2) plane in the $R(\lambda)$ conformer *. The unfavourable $R(\lambda)$ conformation is apparently forced upon the ligand framework by crystal packing effects. It is apparent from the structure of **2a** (Fig. 1) that the normally preferred $R(\delta)$ conformation, with its β-CH_2 substituents in their "forward" position, would lead to unacceptably short non-bonding contacts of CH_2 groups 9 and 19 with phenyl C atoms 37 and 29, respectively. This means that even the lower packing density of diastereomer **2a** can be attained only at the expense of an energetically unfavourable conformation of the *ansa*-metallocene framework.

3. Conversion of bis(acetylmandelate) diastereomers to dichloride enantiomers

The *ansa*-metallocene bis(acetyl mandelate) derivatives, like other carboxylate derivatives, are easily and cleanly converted into the dichloro derivatives by reaction with HCl, e.g. in diethyl ether solution. The pure dichloride enantiomers, however, have relatively high solubilities (considerably higher than the corresponding race-

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* That the tetramethylene ring in **2a** is twisted in the opposite sense to that in **1a** places the hydrogen atoms at C(9) and C(20) further away from the adjacent O atoms, and so could be connected to the decreased ligand-framework distances in **2a**.

TABLE 7

SPECIFIC OPTICAL ROTATIONS [α] (in °) FOR THE *ansa*-METALLOCENE ENANTIOMERS C_2H_4(4,5,6,7-tetrahydro-1*S*-indenyl)$_2$MCl_2 (M = Ti, Zr) (in CH_2Cl_2 solution, concentrations *c* in g/100 ml CH_2Cl_2)

M = Ti		M = Zr	
Wavelength (nm)	*c* 1.2 (*l* 0.01)	Wavelength (nm)	*c* 0.48 (*l* 0.01)
578	208	435	+416
546	500	393	+1510
435	−2986	366	−501

mates) in all solvents, such as toluene or toluene/pentane mixtures, which would dissolve the acetyl mandelic acid co-product, and this makes separate crystallisation of the dichlorides rather inefficient. For this reason the bis(acetyl mandelate) derivatives were first converted into the respective *ansa*-metallocene dimethyl derivatives, which were obtained free of any co-products by extraction into n-hexane solution. Treatment of these solutions with ethereal HCl leads to precipitation of dichloride products which are pure as judged from their ^{1}H NMR spectra. Specific optical rotations of the enantiomeric dichlorides thus obtained are listed in Table 7. The [α]-values obtained for the titanocene derivative are in close agreement with those reported earlier [9].

4. *Determination of enantiomer purity by reconversion into bis(acetyl mandelate) diastereomers*

The reconversion of the isolated *ansa*-metallocene dichloride enantiomers to their acetyl mandelate derivatives provides a convenient and reliable check on their optical purities. To this end, 3–4 mg portions of the dichloride enantiomer in question were treated with a slight excess of acetyl-R-mandelate and triethylamine in $CDCl_3$ solution directly in an NMR tube. (see Experimental). The presence of the unwanted enantiomer (arising e.g. from incomplete separation or from subsequent racemisation) is easily detected from the integrals of the cyclopentadienyl and α-mandelate CH signals associated with the minor and major diastereomers. Products obtained in the manner described above contained no detectable amounts of the minor diastereomer, the optical purity of the products would thus amount to 0.98 or more. When, however, the dichloride enantiomers were produced by reaction with HCl at room temperature, 5–10% of racemisation was apparent from the acetyl mandelate diastereomer ratios determined in this manner. This method also proved useful for the determination of the enantiomeric purity of chiral *ansa*-metallocene dichlorides recovered from catalytic reaction systems [19].

Experimental

The racemic dichlorides, C_2H_4(tetrahydro-1-indenyl)$_2$MCl_2 (M = Ti, Zr) were prepared according to ref. 9 and 10. All solvents used were thoroughly dried and stored under nitrogen.

1. *C_2H_4(tetrahydro-1S-indenyl)Ti(acetyl-R-mandelate)$_2$ (1a)*

A solution of 0.16 ml (1.16 mmol) triethylamine in 15 ml ethanol was added under N_2 during 30 min to a well-stirred suspension of 192 mg (0.5 mmol) racemic C_2H_4(tetrahydro-1-indenyl)$_2$TiCl$_2$ and 194 mg (1.0 mmol) acetyl-R-mandelic acid in 15 ml of ethanol at 70 ° C. After 2 h stirring at 70 ° C, the mixture was cooled to room temperature and evaporated in vacuo to dryness. The orange residue was repeatedly extracted with small portions of dry toluene until it was practically colourless. The combined toluene extracts were evaporated to dryness in vacuo and the residue extracted again with five 1-ml portions of toluene. The combined toluene extracts were filtered, and the filtrate was transferred to a 20 ml sample vial which was then placed into a 100 ml round-bottom flask containing 10 ml of n-pentane. A partial vacuum was applied and the flask was placed in a cold room at 4 ° C; the diffusion-induced crystallisation was allowed to proceed for 3–4 days during which diastereomer **1a** separated as dark orange platelets at the bottom of the sample vial. After decantation of the supernatant solution, the product was washed with a little n-pentane and dried in vacuo. Yield: 154 mg **1a** (88%).

Occasionally, the second diastereomer, **2a**, began to crystallise in the upper (more pentane-rich) region of the inner crystallisation vial. It was easily recognized by its crystal form (bundles of light orange needles) and could be mechanically separated from product **1a**. Complete evaporation of the supernatant mother liquor yielded another crop of **2a**, which was, however, contaminated by about 6% of residual **1a**.

2. *C_2H_4(tetrahydro-1S-indenyl)$_2$Zr(acetyl-R-mandelate)$_2$ (1b)*

In a procedure similar to that described in 1, but with dry toluene as the solvent instead of ethanol the reaction of 213 mg (0.5 mmol) of racemic C_2H_4(tetrahydro-1-indenyl)$_2$ZrCl$_2$ and 194 mg (1.0 mmol) of acetyl-R-mandelic acid with 1 mmol of triethylamine was allowed to proceed for 3–4 h at 70 ° C. The reaction mixture was filtered, the solution evaporated in vacuo, and the solid residue was taken up in 4 × 1 ml portions of toluene. The combined extract was filtered and placed in the inner sample vial of a diffusion system containing 10 ml of n-pentane in the outer flask. After 3–4 days of diffusion-induced crystallisation, decantation of the supernatant solution, and washing and drying of the precipitate gave 143 g (77%) of diastereomer **1b** as small plate-like crystals. Evaporation of the mother liquor yielded diastereomer **2b** contaminated by about 10% of **1b**.

3. *C_2H_4(tetrahydro-1S-indenyl)$_2$TiCl$_2$*

To a solution of 208 mg (0.3 mmol) of **1a** in 10 ml of THF, stirred under N_2 at 0 ° C, were added 2 ml of 1.5 *M* solution (3 mmol) of CH_3MgCl in THF. After overnight stirring, the mixture was evaporated in vacuo to leave a thick slurry, to which 30 ml n-pentane were added. After 1–2 h stirring, the suspension was filtered under N_2. To the clear yellow solution of the dimethyl titanocene derivative, 1.3 ml of a 2.4 *M* solution (3.1 mmol) of HCl gas in diethyl ether were added at 0 ° C. After 1 min stirring, the mixture, still at 0 ° C, was evaporated to dryness in vacuo to yield 90 mg (79%) of ^{1}H NMR spectroscopically pure C_2H_4(tetrahydro-1*S*-indenyl)$_2$TiCl$_2$.

4. *C_2H_4(tetrahydro-1S-indenyl)$_2$ZrCl$_2$*

A procedure similar to that described in 3, above, but involving treatment of 200 mg (0.27 mmol) of **1b** with 2.6 mmol of CH_3MgCl in THF, extraction of the dimethyl derivative into pentane solution, and treatment with ethereal HCl, gave 63 mg (52%) of ^{1}H NMR spectroscopically pure C_2H_4(tetrahydro-1*S*-indenyl)$_2ZrCl_2$.

5. Reconversion to bis(acetylmandelate) derivatives

A 3–4 mg sample of the appropriate dichloride enantiomer and 4–5 mg of acetyl-R-mandelic acid were dissolved in 0.25 ml of $CDCl_3$ in an NMR tube, and treated with 0.15 ml of a 0.15 *M* $CDCl_3$ solution of triethylamine. The reaction mixture was kept, with occasional shaking, at 50 ° C for 3 h. The ^{1}H NMR spectrum was recorded to reveal the amounts of diastereomers **1** and **2** present.

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