

ansa-Metallocene derivatives XXXIX¹

Biphenyl-bridged metallocene complexes of titanium, zirconium, and vanadium: syntheses, crystal structures and enantioseparation²

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Abstract

Chiral, biphenyl-bridged metallocene complexes of general type $\text{biph}(3,4\text{-R}_2\text{C}_5\text{H}_2)_2\text{MCl}_2$ (biph = 1,1'-biphenyldiyl) were synthesized and characterized. For the dimethyl-substituted titanocenes and zirconocenes ($\text{R} = \text{CH}_3$; $\text{M} = \text{Ti, Zr}$), preparations with increased overall yields and an optical resolution method were developed. The bis(2-tetrahydroindenyl) complexes ($\text{R,R} = (\text{CH}_2)_4$; $\text{M} = \text{Ti, Zr}$) were obtained by an alternative synthetic route and characterized with regard to their crystal structures. Syntheses of the phenyl-substituted derivatives ($\text{R} = \text{C}_6\text{H}_5$; $\text{M} = \text{Ti, Zr}$) and of a chiral, methyl-substituted vanadocene complex ($\text{R} = \text{CH}_3$; $\text{M} = \text{V}$) are also reported. © 1997 Elsevier Science S.A.

Keywords: Titanium; Zirconium; Vanadium; Metallocene; Enantioseparation

1. Introduction

Ever since meso and racemic *ansa*-titanocene isomers were first characterized by Huttner and coworkers [1], the formation of these diastereomers and their separation has been a continuing challenge in metallocene chemistry (for a review see Ref. [3]). Increasing interest in chiral *ansa*-metallocenes, especially of Group 4 metals, as catalysts for stereoselective reactions [3,4] has been associated with substantial efforts to develop strategies which yield the pure racemic diastereomer [5–16].

Several attempts have been made to achieve higher rac/meso ratios in metallation reactions of ethylene- or dimethylsilyl-linked bis(cyclopentadienyl) ligand salts [6,7]. Substituents in α -position to the bridge favor the formation of rac compounds by steric interactions [8,9]. By incorporation of α -trimethylsilyl substituents Bercaw and coworkers obtained exclusively the racemic

$\text{Me}_2\text{Si}(2\text{-SiMe}_3\text{4-}^t\text{BuC}_5\text{H}_2)_2$ -metallocenes of Y, Sc, Ti, and Zr [10]. Jordan and coworkers recently developed a powerful method for the syntheses of *rac*- $\text{C}_2\text{H}_4(1\text{-indenyl})_2\text{Zr}(\text{NMe}_2)_2$ and *rac*- $\text{SiMe}_2(1\text{-indenyl})_2\text{Zr}(\text{NMe}_2)_2$ in high yields, which is based on equilibration of rac and meso products by the amine eliminated in the reaction of the bis(indenes) with $\text{Zr}(\text{NMe}_2)_4$ [11]. A different approach is the incorporation of a second linker to prevent the bis(cyclopentadienyl) ligands from isomerization [12]. Chiral, doubly bridged [13] or spiro-bridged [14] substituted ligand systems have recently been designed which give solely the racemic metallocenes.

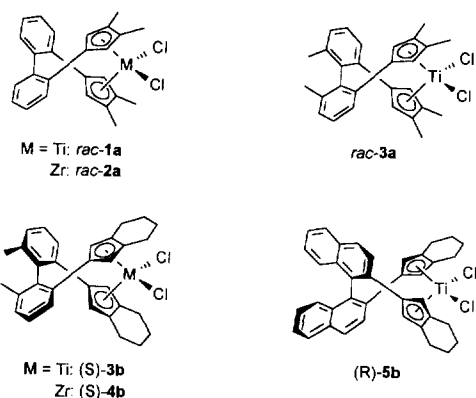
Exchange of the Me_2Si - and C_2H_4 -backbones of bis(1-indenyls) or related prochiral bis(cyclopentadienyl) ligand systems with stereogenic linkers gives either complexes which are not C_2 -symmetric [15] and/or diastereomers [16]. This problem can be resolved by introduction of a chiral bridge together with a symmetric substitution pattern at the cyclopentadienyl rings. As we have shown recently, biphenyl- and *o*-bitolyl-linked bis(3,4-dimethylcyclopentadienyl) ligands are chiral, even though the cyclopentadienyl rings are not prochiral, and form the racemic titanium and zirconium

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¹ For part XXXVIII see Ref. [2].

² Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

nium complexes **1–3a** that are free of diastereomers [17].



Starting from optically active *o*-bitolyl and binaphthyl precursors Bosnich and coworkers [18] and Halterman and Ramsey [19] have subsequently synthesized related biaryl-bridged bis(2-tetrahydroindenyl) metallocenes **3–5b** in enantiopure form. The direct synthesis of only one enantiomer is undoubtedly of great advantage, since difficult separations are avoided. However, resolution of the biaryl precursors still must be accomplished. Considering the fact that the major part of the enantiopure biaryls is wasted in the ligand synthesis and metallation reaction, we have chosen a strategy where the enantiomers of a racemic metallocene complex are separated by kinetic resolution [1,20–25]. This ‘classical’ enantioseparation method affords also optically active metallocenes containing a simple biphenyl bridge, which cannot be obtained by direct stereoselective synthesis.

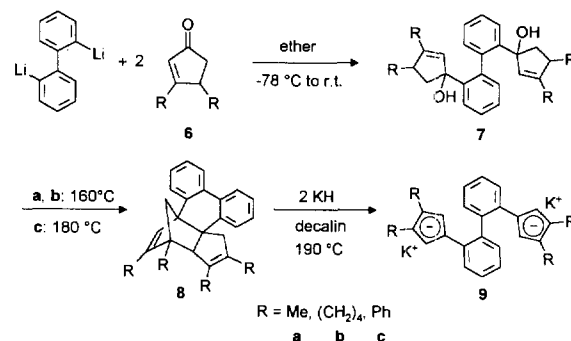
In the present report we describe improved syntheses for chiral biphenyl-bridged dimethyl titanocene and zirconocene dichlorides and a method for their optical resolution, an alternative preparation method for biphenyl-bridged bis(2-tetrahydroindenyl) complexes ³ and their crystal structures, a synthesis for novel phenyl-substituted metallocenes and for a biphenyl-bridged vanadocene.

2. Results and discussion

2.1. Syntheses of the biphenyl-bridged ligand systems

For the syntheses of the biphenyl-bridged ligands we used the procedure already established for **9a** (R = Me)

³ A different procedure was used to synthesize 2,2'-biphenyldiylbis(2-tetrahydroindenyl)-titanium dichloride **1b** and zirconium dichloride **2b** by B. Bosnich and coworkers [18].



Scheme 1.

outlined in Scheme 1 [17]. By this method, substituents are introduced to the ligand system via the appropriate 3,4-disubstituted cyclopent-2-en-1-one species **6** [26]. Reaction of 3,4-dimethylcyclopentenone **6a** [27], 2-hexahydroindenone **6b** [28], or 3,4-diphenylcyclopentenone **6c** [29] with 0.5 equiv. of 2,2'-dilithiobiphenyl ⁴ proceeded in diethyl ether at low temperature to give the respective bis(cyclopentenols) **7a–c** as mixtures of diastereomers. These product mixtures were subjected to thermal dehydration without further purification [32]. ⁵

The bis(cyclopentadienes) arising from this dehydration react immediately to intramolecular cycloadducts **8**, despite their bulky substituents. These substituents are crucial, however, in that they facilitate the *retro*-Diels–Alder reaction. While the unsubstituted cycloadduct (R = H) fails to crack at 190 °C [17], the substituted derivatives **8a–c** re-open at this temperature and are trapped by deprotonation with potassium hydride [33].

2.2. Syntheses of biphenyl-bridged titanocene dichlorides

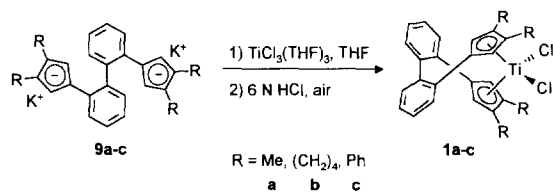
Reaction of the dipotassium ligand salts **K–9a–c** with TiCl₃(THF)₃ in THF and subsequent oxidation with HCl/O₂ afforded the biphenyl-bridged titanocenes **1a–c** (Scheme 2).

The crude product mixture of the tetrahydroindenyl derivative **1b** ⁶ was contaminated with unbridged complex **10b** (**1b**/**10b** ca. 4.4:1). This is due to an impurity formed in the ligand synthesis by reaction of 2,2'-dilithiobiphenyl with only 1 equiv. of cyclopentenone **6b**. Mono(cyclopentadienyl) biphenyls are also by-products in the syntheses of **7a** and **7c**, but no unbridged ti-

⁴ 2,2'-Dilithiobiphenyl was prepared in situ from 2,2'-diiodobiphenyl and *n*-butyllithium [30]. Freshly prepared TMEDA complex of 2,2'-dilithiobiphenyl can also be used [31].

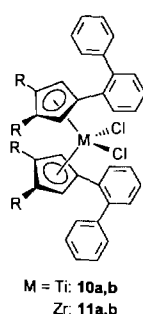
⁵ Dehydration of the bis(cyclopentenols) **7a–c** takes place also in CHCl₃ solutions and on silica gel columns.

⁶ See footnote 3.



Scheme 2.

tanocene **10c** and very little **10a** were detected by ^1H NMR spectra of the crude product mixtures.⁷



Pure biphenyl-bridged titanocenes **1a–c** were isolated in 11–21% yield (based on 2,2'-diiodobiphenyl); they precipitate as dark red crystals when diethyl ether is added to concentrated product solutions. Recrystallization of the bis(2-tetrahydroindenyl) complex **1b** from $\text{CH}_2\text{Cl}_2\text{--Et}_2\text{O}$ (1:3) gave single crystals appropriate for an X-ray diffraction determination (Fig. 1).

The structure of the bis(2-tetrahydroindenyl) complex **1b** is similar to that of the dimethyl derivative **1a** which we reported earlier [17]. A significant difference concerns only the deviation angle of the TiCl_2 fragment from the C_2 axis of the ligand framework, which is about twice as large in **1b** (10.70°) as in **1a** (5.1°). Bond lengths and angles are comparable to those of other titanocenes (Table 1) [1,34–36]. The cyclopentadienyl centroid–titanium–centroid angle of 133.5° is larger than normally found in *ansa*-titanocenes and closer to values observed in unbridged titanocenes [37]. Remarkable is the conformation of the cyclopentadienyl rings in **1b**. As in **1a**, the biphenyl bridge in **1b** forces the

⁷ Unbridged titanocenes **10a** and **10b** could not be isolated from these mixtures; they were identified by comparison of the ^1H NMR spectra of the crude product mixtures with those of pure **10a** and **10b** prepared by a different procedure [17]. **10a**: ^1H NMR (CDCl_3 , 250 MHz): δ 1.93 (s, 12 H), 5.61 (s, 4 H), 6.98–7.43 (m, 18 H). MS (EI): m/z 608 (8%, $\text{M}^+ - \text{Cl}$), 363 (100%, $\text{M}^+ - \text{C}_{19}\text{H}_{17}$). Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{Cl}_2\text{Ti}$: C, 74.89; H, 5.62%. Found: C, 74.47; H, 5.83%. **10b**: ^1H NMR (CDCl_3 , 250 MHz): δ 1.47 (m, 4 H), 7.2 (m, 10 H). MS (FAB): m/z 660 (14%, M^+), 625 (100%, $\text{M}^+ - \text{Cl}$), 389 (80%, $\text{M}^+ - \text{C}_{21}\text{H}_{19}$).

cyclopentadienyl rings to a conformation in which the bridge-head atoms differ from being eclipsed by an angle of 57.6° . One β -substituent of each C_5 ring therefore comes near to the plane bisecting the Cl–Ti–Cl angle. A similar arrangement of substituents is found in doubly bridged metallocenes [38].

2.3. Synthesis of a biphenyl-bridged vanadocene dichloride

For the synthesis and isolation of paramagnetic *ansa*-vanadocene dichlorides the formation of diastereomers is particularly cumbersome, since a determination of *rac*/*meso* ratios by standard NMR methods is not possible here. Further reaction steps are necessary to convert the vanadocene dichlorides to diamagnetic compounds, e.g. to the corresponding di(*tert*-butylisocyanide) complexes [39]. A ligand system which forms exclusively the chiral vanadocene is therefore of special interest.

Vanadium tetrachloride is partially reduced when reacted with cyclopentadienyl ligand salts. Higher yields of *ansa*-vanadocene chlorides are obtained by reaction of vanadium(III)chloride or acetylacetonato vanadium(III) compounds with MgCl -ligand salts. Potassium–ligand salts give unidentified reduction products even with these vanadium(III) starting compounds [40].

The potassium salt of the biphenyl-bridged ligand **K–9a** was therefore converted to the corresponding MgCl -salt **MgCl–9a** by treatment with MgCl_2 in THF (Scheme 3). Reaction with $\text{V}(\text{acac})_3$ or $\text{VCl}_3(\text{THF})_3$ in THF afforded the green biphenyl-bridged vanadocene chloride. Oxidation with PCl_3 or AgCl in ether gave the yellow dichloride **12a** in yields of 50% and 32% respectively (based on 2,2'-diiodobiphenyl). **12a** was charac-

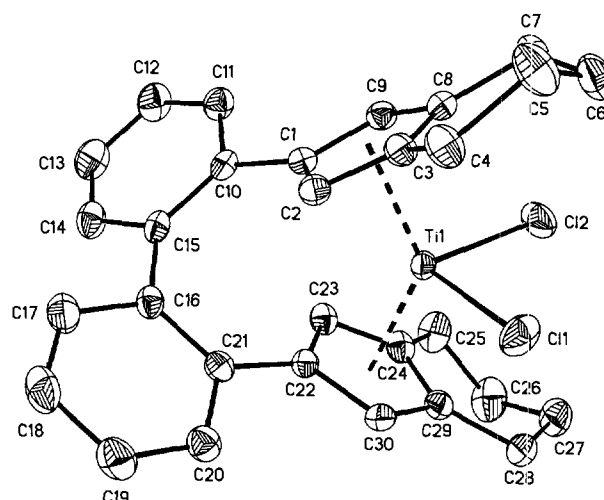


Fig. 1. ORTEP drawing of one enantiomer of biphenyl-bridged titanocene dichloride *rac*-**1b** with 50% probability ellipsoids.

Table 1
Selected distances (ppm) and angles (deg) for complexes **1b**, **2b**, **12a**, and *rac*-**16a**

1b		2b		12a		16a	(1)	(2) ^e
Ti(1)–Cl(1)	234.6(1)	Zr(1)–Cl(1)	244.7(2)	V(1)–Cl(1)	237.8(1)	Ti(1)–O(1)	191.6(7)	191.6(6)
Ti(1)–Cl(2)	234.5(1)	Zr(1)–Cl(2)	243.8(2)	V(1)–Cl(2)	238.8(1)	Ti(2)–O(2)	191.4(6)	190.9(6)
Ti(1)–C(1)	240.0(3)	Zr(1)–C(1)	250.3(3)	V(1)–C(1)	231.8(2)	Ti(1)–C(1)	245.1(10)	235.4(9)
Ti(1)–C(2)	239.3(3)	Zr(1)–C(2)	251.2(4)	V(1)–C(2)	229.6(3)	Ti(1)–C(2)	239.0(10)	238.3(8)
Ti(1)–C(3)	251.9(3)	Zr(1)–C(3)	257.8(4)	V(1)–C(3)	238.5(3)	Ti(1)–C(3)	247.5(10)	251.3(9)
Ti(1)–C(8)	248.9(3)	Zr(1)–C(4)	259.0(4)	V(1)–C(4)	243.5(3)	Ti(1)–C(4)	251.9(11)	253.8(9)
Ti(1)–C(9)	238.0(3)	Zr(1)–C(5)	248.5(3)	V(1)–C(5)	231.8(2)	Ti(1)–C(5)	244.7(9)	243.2(9)
Ti(1)–C(22)	236.8(3)	Zr(1)–C(6)	249.3(4)	V(1)–C(6)	232.9(2)	Ti(1)–C(6)	236.5(8)	241.8(9)
Ti(1)–C(23)	238.3(3)	Zr(1)–C(7)	248.8(4)	V(1)–C(7)	233.3(3)	Ti(1)–C(7)	241.5(9)	244.2(9)
Ti(1)–C(24)	250.4(3)	Zr(1)–C(8)	259.7(4)	V(1)–C(8)	241.5(3)	Ti(1)–C(8)	252.6(9)	251.8(10)
Ti(1)–C(29)	248.0(3)	Zr(1)–C(9)	257.6(4)	V(1)–C(9)	236.7(3)	Ti(1)–C(9)	250.8(10)	250.8(8)
Ti(1)–C(30)	238.9(3)	Zr(1)–C(10)	250.7(4)	V(1)–C(10)	230.3(3)	Ti(1)–C(10)	242.2(9)	238.9(9)
Ti(1)–CR(1) ^a	211.7	Zr(1)–CR(1) ^a	222.9	V(1)–CR(1) ^a	202.0	Ti(1)–CR(1) ^a	214.6	212.9
Ti(1)–CR(2)	210.4	Zr(1)–CR(2)	222.6	V(1)–CR(2)	201.7	Ti(1)–CR(2)	212.6	214.0
Cl(1)–Ti(1)–Cl(2)	94.9(1)	Cl(1)–Zr(1)–Cl(2)	96.8(1)	Cl(1)–V(1)–Cl(2)	87.9(1)	O(1)–Ti(1)–O(2)	91.8(3)	92.5(2)
CR(1)–Ti(1)–CR(2)	133.5	CR(1)–Zr(1)–CR(2)	130.2	CR(1)–V(1)–CR(2)	134.1	CR(1)–Ti(1)–CR(2)	130.7	132.3
CP(1)–CP(2) ^b	53.4	CP(1)–CP(2) ^b	55.8	CP(1)–CP(2)	49.9	CP(1)–CP(2) ^b	54.7	54.6
PH(1)–PH(2) ^c	51.8	PH(1)–PH(2) ^c	61.8	PH(1)–PH(2)	53.9	PH(1)–PH(2) ^c	59.9	54.4
PH(1)–CP(1)	26.8	PH(1)–CP(1)	17.4	PH(1)–CP(1)	25.6	PH(1)–CP(1)	24.6	18.2
PH(2)–CP(2)	18.9	PH(2)–CP(2)	18.1	PH(2)–CP(2)	17.9	PH(2)–CP(2)	11.6	25.9
						BNP(1)–BNP(2) ^d	63.5	65.0

^a CR(1), CR(2) denote the centroids of C₅-rings.

^b CP(1), CP(2) denote the respective C₅-ring mean planes.

^c PH(1), PH(2) denote the mean planes of C₆-rings.

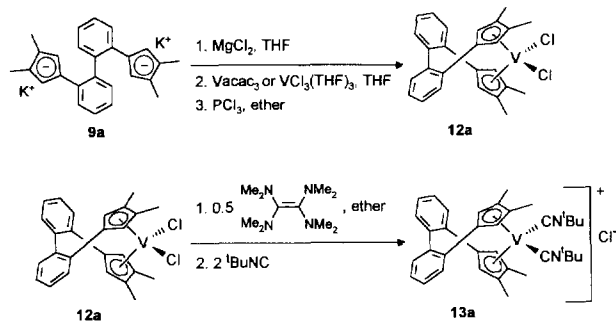
^d BNP(1), BNP(2) denote the mean planes of the binaphthyl-rings.

^e Molecule (2) = molecule (1) with C(*n* + 100) and X(*n* + 1) for X = Ti, O, CP, CR, PH, BNP.

terized by IR- and mass-spectra and by its crystal structure (Fig. 2).

Dihedral angles within the biphenyl bridge and between the phenyl and cyclopentadienyl rings in **12a** are comparable to those of biphenyl-bridged titanocenes **1a** [17] and **1b** (Table 1). Bond lengths and angles are similar to those found in Me₄C₂(C₅H₄)₂VCl₂ [41], but cyclopentadienyl centroid–vanadium distances are about 5 ppm longer in **12a**. Notable is the small deviation of the VCl₂ bisector from the C₂ axis of the ligand framework of 3.3° in **12a** compared to 16.3° in the Me₄C₂-bridged vanadocene.

The brown diamagnetic *ansa*-vanadocene di(iso-nitrile) cation **13a** was obtained by reducing the dichloride **12a** with tetrakis(dimethyldiamino) ethylene and



Scheme 3.

addition of *tert*-butylisocyanide (Scheme 3). As in analogous Group 4 metallocene dichlorides, the inequivalence of α - and β -positions of the C₅-rings in biphenyl-bridged vanadocene **13a** gives rise to two separate signals for the cyclopentadienyl as well as for the methyl protons. The chemical shift difference between the two doublets of the cyclopentadienyl protons is generally found to be larger in biphenyl-bridged complexes than in other *ansa*-metallocenes (Table 2)

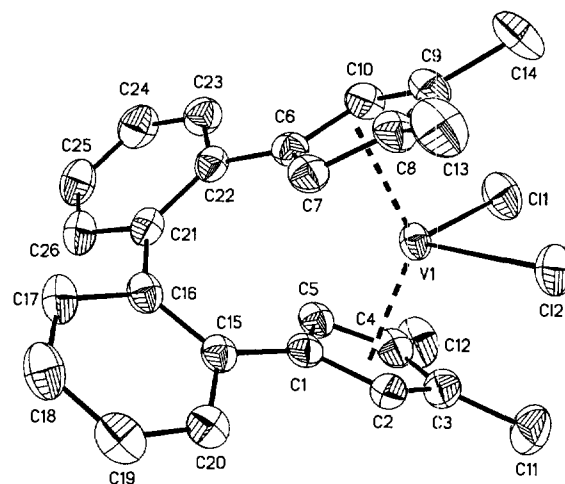


Fig. 2. ORTEP drawing of one enantiomer of biphenyl-bridged vanadocene dichloride *rac*-**12a** with 50% probability ellipsoids.

Table 2

Chemical shifts of the cyclopentadienyl ring protons in biphenyl-bridged metallocenes (CDCl_3)

	M	R	X	H(a) (ppm)	H(b) (ppm)
1a	Ti	Me	Cl	6.30	4.95
13a	V	Me	CN ^t Bu	5.72	3.67
2a	Zr	Me	Cl	6.39	4.86
1b	Ti	C ₂ H ₈	Cl	6.34	4.88
2b	Zr	C ₂ H ₈	Cl	6.39	4.79
1c	Ti	Ph	Cl	7.24	5.55
2c	Zr	Ph	Cl	7.25	5.36

[1,8,21,34,35,42]. ROESY-experiments of **1a** and **13a** indicate that the cyclopentadienyl protons H(b), which are oriented toward the aromatic bridge, are shifted to higher fields, while protons H(a) remain unaffected (Fig. 3).

2.4. Syntheses of biphenyl-bridged zirconocene dichlorides

From the reaction of dipotassium salt **K-9a** with $\text{ZrCl}_4(\text{THF})_2$ in THF, the biphenyl-bridged zirconocene dichloride $\text{biph}(3,4\text{-Me}_2\text{C}_5\text{H}_2)_2\text{ZrCl}_2$ (**2a**) had previously been obtained in only 3% yield [17]. Further experiments showed that the zirconation step depends strongly on the counter ions of the ligand salts used [6,43]. When **K-9a** was transmetalated to the corresponding MgCl^+ , MgBr^+ - or Li^+ -salts, reaction with ZrCl_4 gave the biphenyl-bridged zirconocene **2a** in isolated yields of up to 44% (Scheme 4, Table 3).⁸ Formation of unbridged complex **11a** is completely avoided by this reaction protocol. Complex **2a** is now available in yields about three times as high as those of alternative procedures leading to related complexes [18].

When bromide was present in the reaction solution, the zirconocene **2a** was obtained as a mixture of species with different halides coordinated to the zirconium center (entries 1 and 3 in Table 3). By stirring these mixtures with magnesium bromide in THF solution, a clean conversion to the dibromide $\text{ZrBr}_2\text{-2a}$ was achieved.

Reactions of the potassium salt **K-9b** with $\text{ZrCl}_4(\text{THF})_2$ in THF led to formation of the biphenyl-bridged bis(2-tetrahydroindenyl) zirconocene dichloride **2b**. Here, however, the main product was the unbridged complex **11b** (**2b/11b** = 1:1.8). Bridged zirconocene **2b** was formed together with unbridged complex **11b** in a ratio of 5:2 by treatment of the ligand lithium salt **Li-9b** with ZrCl_4 in toluene.⁹ While we could not isolate preparative yields of **2b**—which makes this

⁸ Yields of 19% were obtained, when titanocene **1a** was prepared from the MgCl^- or Li^- ligand salts **MgCl-9a** or **Li-9a**.

⁹ This result could not be improved by using ligand magnesium salts.

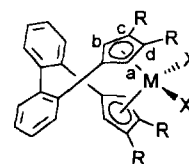


Fig. 3.

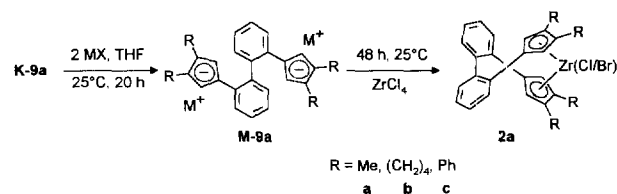
procedure less attractive than that described by Bosnich and coworkers [18]—a few crystals of the biphenyl-bridged zirconocene dichloride **2b** separated upon recrystallization from THF–ether (1:10) at -30°C , such that we were able to determine the structure of **2b** by X-ray diffraction (Fig. 4). Bond lengths and angles of **2b** are unexceptional (Table 1). Notable again is the unusual conformation and the cyclopentadienyl centroid–zirconium–centroid angle of 131.5° , which is wider than normally found in C_2 - and Me_2Si -bridged zirconocenes [8,35,42]. The angle between the phenyl rings of the biphenyl bridge in **2b** (61.8°) is larger and the angles between the C_5 and C_6 rings (17.4 and 18.1°) are smaller than in the dimethyl-substituted complex **2a** (57.9° ; 22.4 and 24.2° respectively) [17].

The diphenyl-substituted zirconocene dichloride **2c** was obtained as a reddish-brown solid in 14% yield (based on 2,2'-diiodobiphenyl) by the reaction of **MgCl-9c** with $\text{ZrCl}_4(\text{THF})_2$ in THF. Once precipitated, complex **2c** is practically insoluble in normal solvents such as toluene or ether, whereas decomposition of **2c** was observed in CH_2Cl_2 or CHCl_3 . Further purification of **2c** by recrystallization was thus not feasible.

The biphenyl-bridged zirconocene dichlorides **2a-c** are relatively stable to moisture and air. In pure form, as solids or dissolved in toluene, they can be stored for several days in the presence of air. Solutions of **2a-c** in dry ether, however, become green even under rigorous exclusion of air and should not be handled longer than a few hours in this solvent. These colored impurities are not detectable in ^1H NMR spectra; nevertheless, such ether solutions of **2a-c** were purified by filtration over silanized silica gel with toluene as eluent.

2.5. Enantioseparation of biphenyl-bridged metallocenes

For the kinetic resolution of racemic titanocene and zirconocene dichlorides, one of two enantiopure reagents



Scheme 4. (For counter ions M^+ and reaction conditions see Table 3.)

Table 3

Entry	M ⁺	Conditions	ZrCl ₂ -2a	ZrClBr-2a	ZrBr ₂ -2a	2a:11a	Yield (%)
1	MgBr ⁺	ZrCl ₄ (THF) ₂ /THF	1	2.6	2.3	1	17
2	MgCl ⁺	ZrCl ₄ (THF) ₂ /THF	1	—	—	1	20
3	Li ⁺	ZrCl ₄ /toluene	10	6.3	1	1	44
4	K ⁺	ZrCl ₄ (THF) ₂ /THF	1	—	—	5:1	9

is generally used: *O*-acetyl-mandelic acid [25] or, more frequently, 2,2'-binaphthol [1,20–24]. While reaction of biph(3,4-Me₂C₅H₂)₂TiCl₂ (**1a**) with *O*-acetyl-(*R*)-mandelic acid and NEt₃ in refluxing ethanol did not give the corresponding bis(*O*-acetyl-(*R*)-mandelates) **14a**, titanocene dimethyl **15a** (readily obtained from **1a** and methyl lithium) reacted smoothly with *O*-acetyl-(*R*)-mandelic acid under evolution of methane (Scheme 5).

From this reaction a 1:1 mixture of the diastereomers (*S,R,R*)-**14a** and (*R,R,R*)-**14a** was obtained in near-quantitative yield. Unfortunately, all attempts to separate these diastereomers failed; neither were we able to synthesize the bis(*O*-acetyl-(*R*)-mandelates) of the titanium complexes **1b** and **1c** or of the zirconocene analog **2a**.

Problems arising from formation of diastereomeric mixtures are not expected when 2,2'-binaphthol is used for kinetic resolution. Only one enantiomer of a racemic metallocene dichloride is generally found to react to the appropriate binaphtholate complex [1,20–24]. Preliminary studies with racemic 2,2'-binaphthol revealed substantial difficulties, however. Syntheses of biphenyl-bridged titanium and zirconium binaphtholates, **16a** and **17a**, by methods described for related complexes in the literature [1,6,20–24] failed or were found to be incomplete.

The following procedure, finally, gave satisfactory

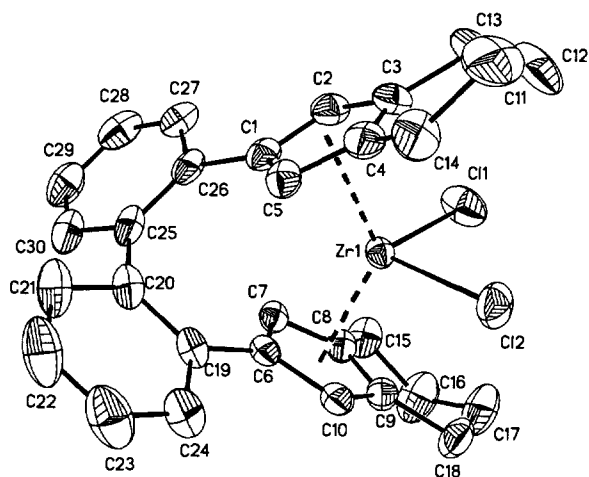


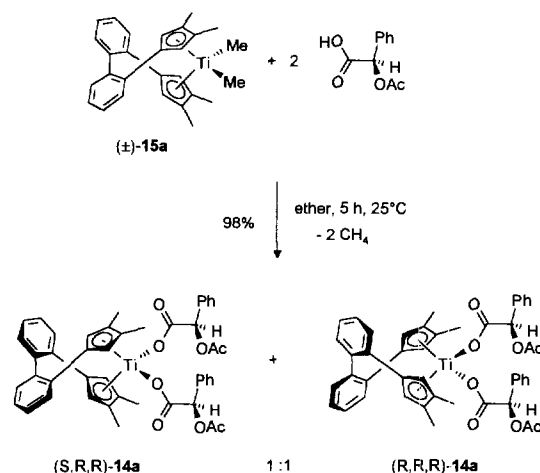
Fig. 4. ORTEP drawing of one enantiomer of biphenyl-bridged zirconocene *rac*-**2b** with 50% probability ellipsoids.

results: 2 equiv. of *n*-butyllithium were added at –50 °C to a THF solution containing equimolar amounts of titanocene dichloride **1a** and *rac*-binaphthol. Upon warming to room temperature, the reaction was complete and a single diastereomer of titanocene binaphtholate **16a** was isolated as a red, air-stable powder in 96% yield. Preparation of the bis(2-tetrahydroindenyl) derivative proceeded similarly to give **16b** in 90% yield. Synthesis of the diphenyl-substituted binaphthol derivative **16c** failed, however. In this case, ligand exchange is presumably hindered by the bulky phenyl groups.

Crystals of **16a**, suitable for an X-ray structure determination, were obtained from a concentrated solution in ether–THF (10:1) at 4 °C. For racemic **16a** two independent molecules were found in the unit cell (Fig. 5). Their structural parameters are similar to those reported in the literature for other metallocene binaphtholate complexes (Table 1) [1,6,20,24].

Optical resolution of the biphenyl-bridged titanocenes was achieved by this procedure when 0.5 equiv. of (*R*)-binaphthol and 1 equiv. of *n*-butyllithium were reacted with the titanocene dichlorides **1a** or **1b** (Scheme 6). Here, longer reaction times (18 h at room temperature) were necessary to let the reactions come to completion. The resulting reaction mixtures contained comparable amounts of enantiopure (*R,R*)-titanocene binaphtholates (*R,R*)-**16a,b** and of the dichloro complexes (*S*)-**1a,b**.

The binaphtholate complexes **16a,b** are more soluble



Scheme 5.

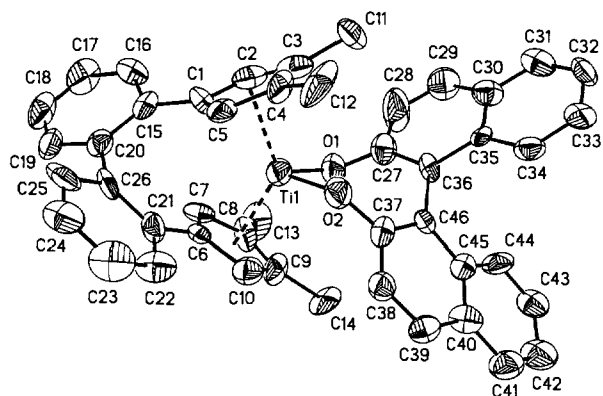
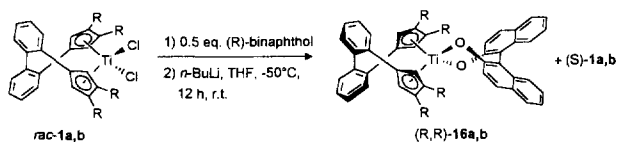


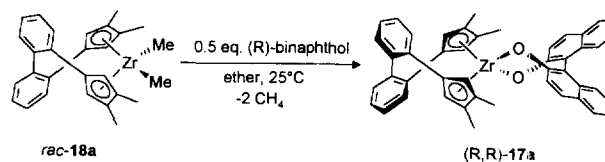
Fig. 5. ORTEP drawing of one enantiomer of titanocene binaphtholate complex *rac*-**16a** with 50% probability ellipsoids (one of two independent molecules found in the unit cell).

than the corresponding titanocene dichlorides **1a,b**. While racemic titanocene dichlorides *rac*-**1a,b** crystallize readily from ether solutions, the enantiopure compounds remained dissolved even in pentane [1,24]. The pure binaphtholate complexes (*R,R*)-**16a,b** were thus isolated by chromatography. The dimethyl-substituted derivative (*R,R*)-**15a** was obtained in 95% yield by filtration over neutral alumoxide with hexane–ether (10:1) as eluent. The titanocene dichloride **1a** decomposed under these conditions to give the intramolecular cycloadduct **8a**. On silica gel, conversely, the binaphtholate (*R,R*)-**16a** decomposed, while the dichloride (*S*)-**1a** remained intact. The bis(2-tetrahydroindenyl) compounds (*R,R*)-**16b** and (*S*)-**1b**, on the other hand, both elute from alumoxide or silica gel. Better separation was achieved on silica gel, but even here bands were rather broad and two subsequent columns were necessary to obtain pure (*R,R*)-**16b** in 46% yield.

Cleavage of titanocene binaphtholate (*R,R*)-**16a** with methylolithium and treatment of the resulting dimethyl complex (*R*)-**15a** with anhydrous HCl in ether solution gave the dichloro compound (*R*)-**1a** in 85% yield. The enantiomeric purity of this complex was checked by its conversion to the *O*-acetyl-(*R*)-mandelate complex **14a** by the procedure discussed above (Scheme 5) [25]. Only one of the two possible diastereomers of the bis(*O*-acetyl-(*R*)-mandelate) (*R,R,R*)-**14a** was obtained. This documents that kinetic resolution was stereoselective and that cleavage of titanocene binaphtholate (*R,R*)-**16a** by methylolithium and conversion to the dichloride (*R*)-**1a** proceeded without racemization.



Scheme 6.



Scheme 7.

A similarly efficient enantioseparation as for the biphenyl-bridged titanocene complex **1a** has not been achieved, so far, for its zirconocene analog **2a**. While the binaphtholate complex **17a**, synthesized from the dimethyl derivative **18a** and 0.5 equiv. of binaphthol (Scheme 7), gave a ¹H NMR spectrum almost identical to that of its titanium analog **16a**, control of its enantiomeric purity was not feasible in a manner analogous to that employed for the titanium complex **16a**. Optical resolution of the biphenyl-bridged zirconocene complex **2a** thus requires further elaboration.

3. Experimental

Moisture- and air-sensitive compounds were handled under an argon atmosphere using Schlenk techniques. Toluene, THF, and diethyl ether were distilled from sodium benzophenone ketyl, decalin from sodium and pentane from CaH₂. Standard NMR spectra were recorded on Bruker WM-250 and AC-250 spectrometers with TMS as internal standard.

3.1. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)] dipotassium salt (**K-9a**)

To a suspension of 5.86 g 2,2'-diiodobiphenyl (14.4 mmol) in 60 ml ether, cooled to -78°C , was added 18 ml (28.9 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The resulting yellow solution was stirred for 15 min at -78°C and for 1 h at room temperature. Then it was cooled again to -78°C and a solution of 3.17 g (28.9 mmol) 3,4-dimethylcyclopent-2-en-1-one (**6a**) in 20 ml ether was added dropwise. The reaction mixture was stirred overnight, while slowly warming to room temperature. The turbid solution or suspension thus obtained was hydrolyzed with 50 ml of saturated aqueous NH₄Cl solution. The organic layer was separated and the water layer extracted with two 100 ml portions of ether. The combined organic layers were dried over MgSO₄, filtered and evaporated to dryness, giving a light yellow oil containing the diastereomeric bis(cyclopentenols) **7a**, contaminated with mono(cyclopentenol), biphenyl, and cyclopentenone **6a**. For thermal dehydration, this product mixture was transferred into a 300 ml Schlenk vessel. The vessel was evacuated and heated to 100°C . The temperature was then increased to 160°C under static vacuum and kept there for 1 h. To remove the eliminated water, the

resulting light brown oil was evacuated while still hot until it reached room temperature. The product was immediately dissolved in 60 ml of decalin and treated with 1.16 g (28.9 mmol) of KH. The Schlenk tube was fitted with a condenser and the suspension was heated to reflux. After 6–10 h, the initially formed black, tarry product turned into a suspension, which was stirred for another hour at 190 °C. Then it was cooled to room temperature, diluted with 80 ml of pentane, and filtered. The solid residue was washed with two 50 ml portions of pentane and dried in vacuo to give the biphenyl-bridged ligand salt **K-9a**, contaminated with unbridged material, as a beige powder.

When bis(cyclopentenolate) of **7a** was obtained as a separable suspension from the synthesis described above, it was possible to purify it further. The solid was then collected by filtration, washed with pentane and suspended in ether. After hydrolysis with saturated NH₄Cl solution and the usual work-up, a colorless oil was obtained, which was dissolved in hot methanol. From this solution **7a** precipitated as a white solid upon cooling to room temperature. MS (EI): *m/z* 356 (100%, M⁺ – H₂O). ¹H NMR spectrum (250 MHz, CDCl₃) and **7a** was complicated; four doublets at δ 0.68–1.05 indicate the presence of at least four diastereomers. **7a** was further identified by dehydration giving the intramolecular cycloadduct **8a**.

NMR-studies of **8a** indicate the presence of one single isomer. ¹H NMR (250 MHz, CDCl₃): δ 1.33 (s, 3 H), 1.37 (d, 1 H), 1.49 (s, 3 H), 1.74 (d, 3 H), 1.78 (d, 1 H), 1.81 (s, 3 H), 1.89 (broad d, 1 H), 2.3 (broad d, 1 H), 3.26 (broad s, 1 H), 5.86 (broad s, 1 H), 7.22–7.31 (m, 5 H), 7.47–7.50 (m, 1 H), 7.81–7.86 (m, 2 H). ¹³C NMR (CDCl₃, 77 MHz): δ 13.77, 14.16, 14.71, 17.41, 49.81, 55.23, 56.27, 56.78, 62.07, 78.02, 122.94, 123.52, 125.88, 126.80, 127.54, 127.82, 128.09, 128.18, 130.10, 130.48, 131.69, 132.75, 133.14, 138.45, 147.68, 149.26. Anal. Calcd for C₂₆H₂₆: C, 92.26; H, 7.74%. Found: C, 91.82; H, 7.72%.

Since the isolated yield of **7a**, resulting from this separation procedure, was only 11%, further reaction steps were conducted with the crude product mixtures, which gave rise to substantially higher yields of the final metallocene products. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]titanium dichloride (**1a**) was prepared in 21% yield as previously described [17].

3.2. [2,2'-Biphenyldiylbis(2-tetrahydroindenyl)]titanium dichloride (**1b**)

The potassium salt **K-9b**, obtained analogously to the procedure described above, starting from 2.98 g (7.35 mmol) of 2,2'-diiodobiphenyl and 2 g (14.7 mmol) of 2-hexahydroindenone (**6b**), was dissolved in 100 ml THF. The resulting mixture was frozen in liquid nitro-

gen and 2.72 g (7.35 mmol) of TiCl₃(THF)₃ was added in one portion. The reaction mixture was allowed to reach room temperature and was then refluxed for 3 h. The resulting black solution was treated, at room temperature, with 50 ml of 6 N HCl in small portions and then opened to the air. The dark red solution was extracted with ether until the organic layer remained colorless. The red solution, containing bridged titanocene **1b** and unbridged complex **10b** in a ratio of 4.4:1, was dried over MgSO₄ and filtered. Addition of 30 ml of ether to the concentrated solution gave 420 mg of **1b** as dark red, fine crystals upon filtration (11% based on 2,2'-diiodobiphenyl). Crystals suitable for X-ray structure determination were obtained at 4 °C from a concentrated CH₂Cl₂-ether solution (3:1). ¹H NMR (250 MHz, CDCl₃): δ 1.56 (m, 4 H), 2.05 (m, 4 H), 2.33 (m, 2 H), 2.73 (m, 4 H), 3.20 (m, 2 H), 4.88 (d, *J* = 2.6 Hz, 2 H), 6.34 (δ, *J* = 2.6 Hz, 2 H), 7.34–7.49 (m, 8 H). ¹³C NMR (63 MHz, CDCl₃): δ 21.62, 21.86, 25.18, 25.69, 111.76, 118.77, 126.38, 127.33, 128.65, 129.18, 131.96, 132.33, 133.81, 137.99, 144.07. MS (EI): *m/z* 506 (7%, M⁺), 471 (29%, M⁺ – Cl), 434 (100%, M⁺ – 2HCl). Anal. Calcd for C₃₀H₂₈Cl₂Ti (507.34 g mol⁻¹): C, 71.02; H, 5.56%. Found: C, 70.69; H, 5.57%.

3.3. [2,2'-Biphenyldiylbis(3,4-diphenyl-1-cyclopentadienyl)]titanium dichloride (**1c**)

The same procedure and the same molar ratios as in the synthesis of **1b** were used for the preparation of **1c**, starting from 2.94 g (7.24 mmol) 2,2'-diiodobiphenyl and 3.39 g (14.48 mmol) 3,4-diphenylcyclopentenone **6c**. Dehydration, however, was carried out at 180 °C. In the crude titanation product the biphenyl-bridged titanocene **1c** (free of unbridged complex **10c**) was detected by its ¹H NMR spectrum. The solvent was removed to a volume of ca. 10 ml. Upon addition of 20 ml ether, 613 mg feathery, shiny black crystals precipitated and were isolated by filtration. Another crop of 202 mg was isolated as a dark red powder from the concentrated solution after standing overnight at 4 °C, to give a total yield of 815 mg **1c** (16% based on 2,2'-diiodobiphenyl). ¹H NMR (250 MHz, CDCl₃): δ 5.55 (d, *J* = 3.0 Hz, 2 H), 7.04 (m, 4 H), 7.17 (m, 8 H), 7.24 (m, 6 H), 7.42 (m, 2 H), 7.52 (m, 4 H), 7.64 (m, 4 H), 7.78 (m, 2 H). ¹³C NMR (63 MHz, CDCl₃): δ 116.13, 119.87, 126.26, 127.00, 127.65, 127.70, 127.89, 128.08, 128.93, 129.92, 130.29, 131.53, 132.34, 132.64, 133.91, 134.00, 138.23, 141.19. MS (EI): *m/z* 702 (100%, M⁺), 667 (85%, M⁺ – Cl), 666 (59%, M⁺ – HCl), 315 (85%, ((M – 2HCl)²⁺)). Anal. Calcd for C₄₆H₃₂Cl₂Ti (703.55 g mol⁻¹): C, 78.53; H, 4.58%. Found: C, 78.79; H, 4.72%.

3.4. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]vanadium(IV) dichloride (**12a**)

Ligand salt **K-9a** was prepared from 2.03 g (5 mmol) of 2,2'-diiodobiphenyl and 1.1 g (10 mmol) of 3,4-dimethylcyclopentenone **6a** by the procedure described above. For the transmetallation, **K-9a** was stirred with 2.4 g (10 mmol) of $\text{MgCl}_2(\text{THF})_2$ in 100 ml of THF at room temperature for 1 h. The resulting mixture was added during 1 h to a suspension of 1.9 g (5 mmol) of $\text{VCl}_3(\text{THF})_3$ in 100 ml of THF at -78°C . After warming up to room temperature and stirring for 12 h, the solvent was removed in vacuo. The solid residue was suspended in 150 ml of ether and filtered. The filtrate, which contained the green vanadocene monochloride, was oxidized with 0.44 ml (5 mmol) of PCl_3 to the yellow dichloride **12a**, which precipitated and was collected by filtration to yield 733 mg of **12a** (32% based on 2,2'-diiodobiphenyl).

Alternatively, **12a** was prepared by slow addition of the THF-solution of **MgCl-9a** to 1.72 g (5 mmol) of $\text{V}(\text{acac})_3$ dissolved in 60 ml of THF. After stirring the mixture for 24 h, the solvent was removed in vacuo. The residue was taken up in 100 ml of ether and filtered. **12a** precipitated when the filtrate was treated with 0.44 ml (5 mmol) of PCl_3 . The solid was dissolved in 40 ml of CH_2Cl_2 , filtered, and the filtrate concentrated to a volume of ca. 2–3 ml. Addition of 50 ml of diethyl ether and cooling to -30°C afforded a solid, which was collected by filtration and dried in vacuo to yield 1.15 g of **12a** (50% based on 2,2'-diiodobiphenyl). Single crystals were obtained from a hot ether solution of **12a**. IR (KBr, Nujol, cm^{-1}): 3100 (w), 3061 (w), 3056 (w), 3019 (w), 1490 (m), 1482 (s), 1456 (s), 1102 (w), 1033 (w), 1016 (w), 866 (m), 768 (m), 761 (s). MS (EI): m/z 457 (35%, M^+), 422 (100%, $\text{M}^+ - \text{Cl}$), 386 (42%, $\text{M}^+ - \text{Cl} - \text{HCl}$), 315 (18%, $(\text{M} - \text{Cl} - \text{HCl})^{2+}$). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{Cl}_2\text{V}$ (458.23 g mol^{-1}): C, 68.14; H, 5.28%. Found: C, 67.89; H, 5.36%.

3.5. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]vanadium(IV) bis(tert-butylisonitrile) chloride (**13a**)

Vanadocene dichloride **12a** (390 mg, 0.85 mmol) was dissolved in 10 ml of THF and reduced with 0.1 ml (0.43 mmol) of $(\text{NCH}_3)_2\text{C}_2$, whereupon the color of the reaction mixture immediately changed from yellow to green. After addition of 50 ml of toluene, the suspension was filtered, and the filtrate was treated with 0.2 ml (1.7 mmol) of t-butylisonitrile. The solvent was removed in vacuo and the residue was recrystallized from CH_2Cl_2 -ether to yield, 410 mg of the diamagnetic **13a** (81%). IR (KBr, Nujol, cm^{-1}): 2127, 2104. ^1H NMR (250 MHz, CDCl_3): δ 1.58 (s, 18 H), 1.92 (s, 6 H), 1.94 (s, 6 H), 3.67 (d, 2 H), 5.27 (d, 2 H), 7.20–7.43 (m, 8

H). ^{13}C NMR (63 MHz, CDCl_3): 13.77, 14.04, 31.39, 58.84, 86.08, 99.60, 105.84, 108.40, 115.74, 125.97, 128.85, 130.03, 130.54, 132.49, 137.73.

3.6. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]zirconium dichloride (**2a**) from K-ligand salt **K-9a**

Ligand salt **K-9a**, prepared from 10.63 mmol 2,2'-diiodobiphenyl by the procedure described above, was dissolved in 100 ml of THF and added to a suspension of 4 g (10.63 mmol) of $\text{ZrCl}_4(\text{THF})_2$ in 40 ml of THF. After stirring the reaction mixture for 4 days at room temperature, the solvent was removed in vacuo. The residue was suspended in 100 ml of toluene and filtered. The filtrate, containing biphenyl-bridged zirconocene **2a** and unbridged complex **11a** in a ratio of 5:1, was evaporated to dryness. Addition of 80 ml of ether and filtration gave a yellow filtrate which was evaporated to dryness and then treated again with 15 ml of ether. The resulting suspension was stirred for 30 min. The yellow solid was collected by filtration, subsequently washed with 5 ml of ether and 10 ml of pentane, and dried in vacuo to yield 340 mg of **2a**. A second crop of 120 mg of **2a** was obtained after adding 10 ml of ether to the dried filtrate to give a total yield of 9% based on 2,2'-diiodobiphenyl. ^1H NMR (250 MHz, CDCl_3): δ 1.99 (s, 6 H), 2.19 (s, 6 H), 4.86 (d, $J = 3.1$ Hz, 2 H), 6.39 (d, $J = 3.1$ Hz, 2 H), 7.27–7.5 (m, 8 H). For further characterization and crystal structure see Ref. [17].

3.7. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]zirconium dichloride (**2a**) from MgCl-ligand salt **MgCl-9a**

A THF-solution of **K-9a**, prepared from 10.63 mmol 2,2'-diiodobiphenyl, was stirred with 5.1 g (21.26 mmol) of $\text{MgCl}_2(\text{THF})_2$ overnight, filtered and then reacted with 4 g (10.63 mmol) of $\text{ZrCl}_4(\text{THF})_2$. The resulting yellow suspension was stirred for 2 days. Work-up as described in Section 3.6 gave 1.08 g of **2a** (20% yield, based on 2,2'-diiodobiphenyl).

3.8. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]zirconium dichloride (**2a**) from MgBr-ligand salt **MgBr-9a**

K-ligand salt **K-9a**, prepared from 7.87 mmol 2,2'-diiodobiphenyl by the procedure above, was dissolved in 100 ml of THF and stirred with 4.33 g (16.78 mmol) $\text{MgBr}_2(\text{OEt}_2)$ overnight at room temperature. The resulting suspension was filtered and the filtrate transferred via cannula to a suspension of 2.97 g (7.87 mmol) $\text{ZrCl}_4(\text{THF})_2$ in 20 ml of THF. After stirring for 2 days at room temperature, the yellow reaction mixture, con-

taining **ZrCl₂-2a**, **ZrBrCl-2a**, and **ZrBr₂-2a** in a ratio of 1:4.5:4.9, was worked up by the procedure described in Section 3.6, to yield 740 mg of a light yellow powder. The isolated product contained the three zirconocenes **2a** in a ratio of 1:2.6:2.3, since **ZrCl₂-2a** is less soluble than the Br-containing zirconocenes (17% yield, based on 2,2'-diiodobiphenyl and an average molecular weight of 553 g mol⁻¹). ¹H NMR (250 MHz, CDCl₃) **ZrClBr-2a**: δ 1.97 (s, 3 H), 2.14 (s, 3 H), 2.20 (s, 3 H), 2.23 (s, 3 H), 4.74 (d, *J* = 2.9 Hz, 1 H), 4.95 (d, *J* = 2.9 Hz, 1 H), 6.36 (d, *J* = 2.9 Hz, 1 H), 6.56 (d, *J* = 2.9 Hz, 1 H), 7.26–7.5 (m, 8 H). **ZrBr₂-2a**: δ 2.12 (s, 6 H), 2.26 (s, 6 H), 4.82 (d, *J* = 2.9 Hz, 2 H), 6.52 (d, *J* = 2.9 Hz, 2 H), 7.26–7.5 (m, 8 H).

3.9. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]zirconium dichloride (**2a**) from Li-ligand salt **Li-9a**

K-ligand salt **K-9a**, prepared from 14.26 mmol 2,2'-diiodobiphenyl by the procedure above, was dissolved in 100 ml of THF and stirred with 2.48 g (28.52 mmol) LiBr overnight. The reaction mixture was filtered and the filtrate evaporated to dryness. The residue was washed with pentane, thoroughly dried in vacuo and mixed with 3.32 g (14.26 mmol) of ZrCl₄. Addition of 100 ml of toluene gave an orange suspension which became greenish while stirring for 2 days at room temperature. The reaction mixture was filtered and the filtrate, containing **ZrCl₂-2a**, **ZrClBr-2a**, and **ZrBr₂-2a** in a ratio of 7.8:4.3:1, was evaporated to dryness. Addition of 100 ml of ether gave a suspension which was stirred for 1 h. The greenish-yellow solid was collected by filtration, washed with 10 ml of pentane, and dried in vacuo to yield 2.52 g of a 10:6.3:1 mixture of **ZrCl₂-2a**, **ZrClBr-2a**, and **ZrBr₂-2a**. A further crop precipitated from the concentrated filtrate by addition of 30 ml THF-ether (1:3), to give a total yield of 3.29 g of **2a** (44% based on 2,2'-diiodobiphenyl and an average molecular weight of ca. 520 g mol⁻¹).

3.10. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]zirconium dibromide (**ZrBr₂-2a**) via halogen exchange

A solution of 54 mg (0.1 mmol) of the zirconocene bromide chloride mixture **2a**, obtained from Section 3.9, in 10 ml of THF was treated with 10 ml of a THF solution containing 210 mg (0.81 mmol) of MgBr₂(THF)₂ and stirred overnight at room temperature. To remove the resulting magnesium salts, the solution was evaporated to dryness and the solid residue taken up in 20 ml of toluene and filtered. When the filtrate was concentrated to a small volume, a greenish-yellow solid crystallized, to give 61 mg (96% yield) of **ZrBr₂-2a**. Traces of **ZrClBr-2a** (*m/z* 542, 8%) were

detected by a mass spectrum (EI) with peaks at *m/z* 586 (100%, M⁺), 506 (72%, M⁺ - Br), 423 (10%, M⁺ - 2HBr). **ZrClBr-2a** was not observed in the ¹H NMR spectrum; this indicates that **ZrBr₂-2a** was > 95% pure.

3.11. [2,2'-Biphenyldiylbis(2-tetrahydroindenyl)]zirconium dichloride (**2b**)

Ligand lithium salt **Li-9b** was prepared in a manner similar to that described above for **Li-9a**, starting from 7.39 mmol of 2,2'-diiodobiphenyl and 17.78 mmol of 2-hexahydroindenone **6b**. Reaction with 1.72 g (7.39 mmol) of ZrCl₄ in 100 ml of toluene gave a 5:2 mixture of biphenyl-bridged zirconocene **2b** and unbridged compound **11b**, which could not be purified by the procedure described for **2a**, nor by additional crystallization. The crude product was then dissolved in 10 ml of toluene and filtered over a small column of silanized silica gel. Evaporation of the eluate to a volume of 1–2 ml gave 30 mg of a yellow powder, enriched with **2b** (**2b:11b** 10:1), from which a few crystals of pure **2b** were obtained upon recrystallization from THF-ether (1:10). ¹H NMR (250 MHz, CDCl₃) of **2b**: δ 1.48–1.66 (m, 4 H), 1.85–2.06 (m, 4 H), 2.28–2.40 (m, 2 H), 2.54–2.74 (m, 4 H), 2.94–3.06 (m, 2 H), 4.79 (d, *J* = 2.7 Hz, 2 H), 6.39 (d, *J* = 2.7 Hz, 2 H), 7.26–7.52 (m, 8 H). **11b**: ¹H NMR (250 MHz, CDCl₃): δ 1.40–1.60 (m, 4 H), 1.82–1.95 (m, 4 H), 2.20–3.12 (m, 4 H), 3.43–3.59 (m, 4 H), 5.44 (s, 4 H), 6.92–7.0 (m, 4 H), 7.1–7.2 (m, 2 H), 7.2–7.36 (m, 12 H).

3.12. [2,2'-Biphenyldiylbis(3,4-diphenyl-1-cyclopentadienyl)]zirconium dichloride (**2c**)

A solution of MgCl-ligand salt **MgCl-9c** in 100 ml of THF, prepared from 3.62 mmol of 2,2'-diiodobiphenyl and 7.24 mmol of 3,4-diphenylcyclopentenone **6c**, analogous to the procedures described above, was transferred to a suspension of 1.36 g (3.62 mmol) of ZrCl₄(THF)₂ in 30 ml of THF and stirred for 24 h at room temperature. The dried crude product was suspended in 100 ml of toluene, stirred for 2 h, and filtered. The filtrate was evaporated to dryness and taken up in 100 ml of ether, giving a sticky mass. Repeated evaporation in vacuo and addition of ether finally gave a suspension, from which **2c** was collected by filtration. For further purification, **2c** was dissolved in toluene and filtered over silanized silica gel. Upon addition of 5 ml of ether to the concentrated eluate, **2c** precipitated to give 370 mg of a reddish brown powder (ca. 14% yield based on 2,2'-diiodobiphenyl). The product was slightly contaminated by toluene, which could not be removed, neither by evaporation nor by co-evaporation with hexane. Recrystallization experiments were unsuccessful, due to the low solubility of **2c** in common solvents. ¹H

NMR (250 MHz, CDCl_3): δ 5.36 (d, $J = 3.1$ Hz, 2 H), 6.96 (m, 4 H), 7.16 (m, 8 H), 7.25 (m, 6 H), 7.37 (m, 2 H), 7.52 (m, 4 H), 7.59 (m, 4 H), 7.85 (m, 2 H). MS (EI): m/z 746 (100%, M^+), 709 (9%, $\text{M}^+ - \text{HCl}$), 672 (20%, $\text{M}^+ - 2\text{HCl}$), 368 (30%, $\text{M}^+ - 4\text{C}_6\text{H}_5$), 336 (77%, $\text{M}^+ - \text{HCl}$)²⁺).

3.13. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]titanium dimethyl (**15a**)

To a suspension of 920 mg (2.02 mmol) of **1a** in 100 ml of ether 2.5 ml (4.04 mmol) of a 1.6 M methyl-lithium solution in ether was added dropwise at room temperature. The resulting yellow suspension was stirred for 1 h and the solvent was then removed in vacuo. The residue was taken up in 100 ml of pentane and filtered over a small plug of Celite. The filter cake was extracted with pentane until the pentane layer remained colorless. The filtrate was concentrated to a small volume, from which **15a** crystallized at -30°C . The yellow solid was isolated and dried in vacuo to yield 810 mg of **15a** (97%). ¹H NMR (250 MHz, CDCl_3): δ -0.57 (s, 6 H), 1.86 (s, 6 H), 2.42 (s, 6 H), 4.27 (d, $J = 2.7$ Hz, 2 H), 6.00 (d, $J = 2.7$ Hz, 2 H), 7.14–7.31 (m, 8 H). MS (EI): m/z 399 (18%, $\text{M}^+ - \text{CH}_3$), 384 (100%, $\text{M}^+ - 2\text{CH}_3$), 192 (35%, $(\text{M} - 2\text{CH}_3)^{2+}$).

3.14. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]titanium bis(*O*-acetyl-(*R*)-mandelate) (**14a**)

To a solution of 290 mg (0.7 mmol) **15a** in 50 ml ether was added 272 mg (1.4 mmol) of *O*-acetyl-(*R*)-mandelic acid at room temperature. Methane evolved and the reaction mixture slowly turned orange. After 5 h, the solvent was removed in vacuo to yield 510 mg of a light red powder, consisting of a 1:1 mixture of (*R,R,R*)-**14a** and (*S,R,R*)-**14a**, which was pure by ¹H NMR spectrum (95% yield). All attempts to separate the two diastereomers by fractional crystallization failed. Chromatography on silica gel, silanized silica gel or alumoxide led to decomposition of **14a**. ¹H NMR (250 MHz, CDCl_3) of (*R,R,R*)-**14a**: δ 1.17 (s, 6 H), 1.57 (s, 6 H), 2.26 (s, 6 H), 5.03 (d, $J = 2.8$ Hz, 2 H), 6.10 (s, 2 H), 6.95 (d, $J = 2.8$ Hz, 2 H), 7.33–7.65 (m, 18 H); (*S,R,R*)-**14a**: δ 1.10 (s, 6 H), 1.63 (s, 6 H), 2.16 (s, 6 H), 5.21 (d, $J = 2.8$ Hz, 2 H), 6.06 (s, 2 H), 6.65 (d, $J = 2.8$ Hz, 2 H), 7.33–7.65 (m, 18 H). MS (EI): m/z 770 (2%, M^+), 577 (26%, $\text{M}^+ - \text{C}_{10}\text{H}_9\text{O}_4$), 443 (100%, $\text{M}^+ - \text{C}_{10}\text{H}_9\text{O}_4 - \text{C}_8\text{H}_6\text{O}_2$).

3.15. Racemic [2,2'-biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]titanium binaphtholate (*rac*-**16a**)

A solution of 100 mg (0.22 mmol) of **1a** and 63 mg (0.22 mmol) of racemic binaphthol in 40 ml THF was treated at -50°C with 0.8 ml (0.44 mmol) of a 0.53 M

solution of *n*-butyllithium in hexane in one portion. When the cooling bath was removed and the solution allowed to warm to room temperature, the initially red solution turned almost black. After stirring for 30 min at ambient temperature, THF was removed in vacuo and the residue taken up in 40 ml of ether. The suspension was filtered and to the filtrate 10 ml of water were added. The layers were separated, the water layer was extracted with 20 ml of ether and the combined organic layers were dried over magnesium sulfate. Removal of the solvent yielded 142 mg (96%) of *rac*-**16a**. Crystals suitable for a structure determination were obtained by recrystallization from THF–ether (1:10) at 4°C . ¹H NMR (CDCl_3 , 250 MHz): δ 0.72 (s, 6 H), 1.60 (s, 6 H), 5.43 (d, $J = 2.8$ Hz, 2 H), 6.03 (d, $J = 2.8$ Hz, 2 H), 6.87–7.79 (m, 20 H). ¹³C NMR (75 MHz, CDCl_3): δ 11.58, 13.91, 111.68, 115.67, 121.87, 122.17, 125.08, 125.64, 127.15, 127.57, 127.96, 128.18, 128.39, 130.06, 132.43, 114.81, 128.87, 133.55, 135.16, 138.43, 141.59, 165.45. MS (EI, 70 eV, 230°C): m/z 668 (M^+ , 100%), 525 ($\text{M}^+ - \text{C}_{10}\text{H}_7\text{O}$, 20%), 382 ($\text{M}^+ - 2\text{C}_{10}\text{H}_7\text{O}$, 7%), 333 ($\text{M}^+ - \text{C}_{26}\text{H}_{24}$, 24%).

3.16. Racemic [2,2'-biphenyldiylbis(2-tetrahydroindenyl)]titanium binaphtholate (*rac*-**16b**)

The same procedure and the same molar ratios as for *rac*-**16a** were used to prepare *rac*-**16b** from a solution of 100 mg (0.2 mmol) titanocene dichloride **1b**. By removal of the solvent in vacuo, a dark red oil was isolated, which was taken up in 50 ml of hexane. After standing at room temperature for 1 h, the binaphtholate complex *rac*-**16b** began to crystallize in the form of light red needles, which were collected by filtration and washed with pentane to yield 130 mg (90%) of *rac*-**16b**. ¹H NMR (250 MHz, CDCl_3): δ 0.37–0.56 (m, 4 H), 0.61–0.8 (m, 2 H), 0.95–1.15 (m, 2 H), 1.29–1.55 (m, 2 H), 2.05–2.21 (m, 4 H), 2.37–2.53 (m, 2 H), 5.30 (d, $J = 2.5$ Hz, 2 H), 6.04 (d, $J = 2.5$ Hz, 2 H), 6.80–7.79 (m, 20 H). MS (EI, 70 eV, 280°C): m/z 720 (100%, M^+), 432 (63%, $\text{M}^+ - \text{C}_{20}\text{H}_{16}\text{O}_2$), 360 (21%, M^{2+}).

3.17. Optical resolution of [2,2'-biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]titanium dichloride (**1a**) via (*R,R*)-**16a**

A mixture of 728 mg (1.6 mmol) titanocene dichloride **1a** and 229 mg (0.8 mmol) (*R*)-binaphthol, dissolved in 50 ml of THF, was treated with 1 ml (1.6 mmol) of a 1.6 M solution of *n*-butyllithium in hexane at -50°C . After 18 h stirring at room temperature the solvent was removed in vacuo and the residue was taken up in ether and filtered. The filtrate, containing a 1:1 ratio of (*S*)-**1a** and (*R,R*)-**16a**, was concentrated to a small volume and the binaphtholate complex (*R,R*)-**16a** isolated by chromatography on neutral alumoxide

with hexane–ether (10:1) as eluent. The yellow band consisting of intramolecular cycloadduct **8a** was discarded. The following red zone ($r = 0.46$) was collected and evaporated to dryness, to yield 510 mg (95% based on (*R*)-binaphthol) of (*R,R*)-**16a**. $[\alpha]_{589} = -3240^\circ$ (1 mg in 12 ml CH_2Cl_2 , $d = 1$). Anal. Calcd for $\text{C}_{46}\text{H}_{36}\text{O}_2\text{Ti}$ (668.67): C, 82.62; H, 5.43%. Found: C, 81.99; H, 5.66%.

3.18. Optical resolution of [2,2'-biphenyldiylbis(2-tetrahydroindenyl)]titanium dichloride (**1b**) via (*R,R*)-**16b**

The synthesis of the enantiopure binaphtholate complex (*R,R*)-**16b** was carried out as described for (*R,R*)-**16a**, starting from 460 mg (0.9 mmol) of the titanocene dichloride **1b** and 130 mg (0.45 mmol) of (*R*)-binaphthol. The resulting ether filtrate was concentrated to a small volume and chromatographed over silica gel with hexane–ether (10:1). The first yellow zone was discarded. The red eluent was collected in small portions,

the purities of which were examined by TLC. The first few fractions contained pure binaphtholate complex (*R,R*)-**16b**. Further fractions consisted of mixtures of (*R,R*)-**16b** ($r_F = 0.33$) and titanocene dichloride (*S*)-**1b** ($r_F = 0.19$), which were combined and subjected to a second column to give a total yield of 150 mg of (*R,R*)-**16b** (46% based on (*R*)-binaphthol). $[\alpha]_{589} = -1820^\circ$ (1 mg in 10 ml CH_2Cl_2 , $d = 1$). Anal. Calcd for $\text{C}_{50}\text{H}_{40}\text{O}_2\text{Ti}$ (720.73): C, 83.32; H, 5.59%. Found: C, 82.96; H, 5.67%.

3.19. [2,2'-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]zirconium binaphtholate (*R,R*)-**17a**

To a suspension of 230 mg (0.46 mmol) zirconocene dichloride **2b** in 20 ml ether was added 1.3 ml (2.1 mmol) of a 1.6 M solution of methyllithium in ether at room temperature, whereupon **2a** dissolved completely. From the resulting colorless solution a white precipitate was formed, presumably LiCl. After stirring for 30 min, the

Table 4
Crystallographic data^a for compounds **1b**, **2b**, **12a**, and **16a**

	1b	2b	12a	16a
Formula	$\text{C}_{30}\text{H}_{28}\text{TiCl}_2$	$\text{C}_{30}\text{H}_{28}\text{ZrCl}_2$	$\text{C}_{26}\text{H}_{24}\text{VCl}_2$	$\text{C}_{46}\text{H}_{36}\text{O}_2\text{Ti}$
Formula weight (g mol^{-1})	507.34	550.6	458.32	668.67
Crystal color, form	red cubes	pale yellow rhombohedron	brown rhombohedron	red needles
Crystal size (mm^3)	$0.3 \times 0.3 \times 0.3$	$0.3 \times 0.3 \times 0.2$	$0.2 \times 0.2 \times 0.3$	$0.3 \times 0.2 \times 0.35$
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.537(4)	14.136(9)	14.826(4)	18.630(4)
b (Å)	14.197(7)	10.094(5)	8.981(3)	14.968(6)
c (Å)	14.813(6)	17.607(8)	16.345(5)	24.670(9)
β (deg)		90.04(4)	93.34(2)	92.65(2)
V (Å ³)	2426(2)	2512(2)	2172.6(11)	6872(4)
d_{calc} (g cm^{-3})	1.389	1.456	1.401	1.293
Z	4	4	4	8
Absorption coefficient μ (cm^{-1})	5.86	6.6	0.699	2.88
T (K)	273	245	243	263
Weighting scheme ^b	$s^2(F) + 0.0006F^2$	$s^2(F) + 0.0006F^2$	$s^2(F) + 0.0002F^2$	$1/\sigma^2F_o^2 + (0.0224P)^2$
Scan range (deg)	0.60	1.40	0.70	1.70
2θ range (deg)	4.0 to 54.0	4.0 to 45.0	4.0 to 50.0	3.18 to 40.0
Scan speed (deg min^{-1}) ^c	2.3 to 29.3	1.53 to 14.65	1.50 to 14.65	1.50 to 14.65
Reflections collected	5757	3363	4730	6670
Independent reflections	4816	2902	4258	6408
Observed reflections	4604 ($F > 4\sigma(F)$)	2581 ($F > 4\sigma(F)$)	3343 ($F > 4\sigma(F)$)	6403 ($F > 2\sigma(F)$)
Solution ^d	Patterson	Patterson	direct methods	direct methods
No. of parameters	298	295	262	883
R_F ^e	4.17	2.79	3.56	7.36
R_{wF} ^f	4.98	3.90	4.14	9.24
Goodness of fit	1.41	1.32	1.69	1.07
Residual density $\times 10^{-6}$ ($\text{e}^- \text{pm}^{-3}$)	0.43	0.34	0.26	0.286

^a Conditions: Siemens P3m/V four-circle diffractometer, Mo K α radiation (0.71073 Å), graphite monochromator.

^b $(F_o^2 + 2F_c^2)/3$.

^c Wyckoff scan.

^d **1b**, **2b**, **12a**: SHELXTL PLUS; **16a**: SHELXL 93.

^e $R_F = \sum(F_o - F_c)/F_c$.

^f $R_{wF} = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$.

reaction mixture was thoroughly dried in vacuo and the solid residue slurried in 20 ml of pentane. Filtration over a small plug of Celite gave 210 mg of the zirconocene dimethyl **18a** as a colorless solid. $^1\text{H NMR}$ (250 MHz, C_6D_6): δ -0.30 (s, 6 H), 1.75 (s, 6 H), 2.09 (s, 6 H), 4.64 (d, $J = 2.8$ Hz, 2 H), 6.12 (d, $J = 2.8$ Hz, 2 H) 7.05 (m, 6 H), 7.30 (m, 2 H). Compound **18a** was dissolved in 20 ml of ether and treated with a solution of 66 mg (0.23 mmol) (*R*)-binaphthol in 10 ml of ether at room temperature. Methane evolved and the reaction mixture became turbid. Stirring overnight gave a colorless suspension. The white solid was separated by filtration and discarded, since no signals were detected in the $^1\text{H NMR}$ spectrum of its solution in CDCl_3 . The filtrate, containing (*R,R*)-**17a** as the sole zirconocene compound, was dried in vacuo, to yield 125 mg of a light yellow solid, quite soluble even in hexanes. Further purification by crystallization was thus not feasible. $^1\text{H NMR}$ (250 MHz, C_6D_6): δ 0.88 (s, 6 H), 1.54 (s, 6 H), 5.50 (d, $J = 3.0$ Hz, 2 H), 6.09 (d, 3.0 Hz, 2 H), 6.86–7.78 (m, 20 H). $[\alpha]_{589} = -90^\circ$ and $[\alpha]_{436} = -400^\circ$ (1 mg in 10 ml CH_2Cl_2 , $d = 1$).

3.20. Enantiopure [2,2'-biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]titanium dichloride ((*R*)-**1a**)

A suspension of 375 mg (0.56 mmol) titanocene binaphtholate (*R,R*)-**16a** in 10 ml of ether was treated with 1 ml (1.6 mmol) of a 1.6 M solution of methyl-lithium in ether and stirred for 1 h at room temperature. The resulting yellow suspension was thoroughly dried in vacuo and the solid residue slurried in 10 ml of pentane. The solid was removed by filtration over a small plug of Celite and washed with two 10 ml portions of pentane. The filtrate was evaporated to dryness and dissolved in 10 ml of ether. Upon slow addition of a solution of HCl in ether (10 ml) at room temperature, (*R*)-**1a** precipitated under vigorous evolution of methane. The resulting red microcrystals were isolated by filtration and washed with ether to give 210 mg (83%) of enantiopure titanocene dichloride (*R*)-**1a**. $[\alpha]_{589} = 700^\circ$ (1.78 mg in 10 ml CHCl_3 , $d = 1$). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{Cl}_2\text{Ti}$ (455.26): C, 68.59; H, 5.31%. Found: C, 68.15; H, 5.42%.

3.21. Determination of enantiomeric purity

Titanocene dichloride (*R*)-**1a** (26 mg, 0.06 mmol) in 5 ml of ether was converted to the dimethyl compound (*R*)-**15a** with 0.1 ml (0.16 mmol) of a 1.6 M solution of methyl lithium in ether; **15a** was isolated by extraction with pentane and treated with 20 mg (0.12 mmol) of *O*-acetyl-(*R*)-mandelic acid as described above. The resulting light red solid consisted of diastereomeric pure (*R,R,R*)-**14a** as shown by its $^1\text{H NMR}$ spectrum, with signals at δ 1.17 (s, 6 H), 1.57 (s, 6 H), 2.26 (s, 6 H),

5.03 (d, $J = 2.8$ Hz, 2 H), 6.10 (s, 2 H), 6.95 (d, $J = 2.8$ Hz, 2 H), 7.33–7.65 (m, 18 H).

3.22. Crystal structure determinations

For crystals of complexes **1b**, **2b**, **12a** and **16a**, obtained as described above, space group determinations, diffraction data collection and solution and refinement of the structures were conducted as summarized in Table 4. Additional crystallographic data for compounds **1b**, **2b**, **12a** and **16a** are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen 2, upon quotation of depositary number CSD-406313-406317, the authors and the journal reference for this article.

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