Bis-Chelated Imine-Alkoxytitanium Complexes: Novel Chiral Dopants with High Helical Twisting Power in Liquid Crystals

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Dedicated to Professor Günter Wulff on the occasion of his 70th birthday

Abstract: Enantiomerically and diastereomerically pure bis-chelated imine-alkoxytitanium complexes **6** and **7** have been synthesized and used as chiral dopants for converting nematic into cholesteric phases. The dopants were tested in mainly commercially available nematic liquid crystalline compounds or mixtures: LC1 (BASF), ZLI-1695 and ZLI-1840 (Merck), as well as *N*-(4-methoxybenzylidene)-4′-butylaniline (MBBA). The values of the helical twisting power (HTP) were determined by the Grandjean–Cano method. Exceptionally high helical twisting powers were obtained. Thus, the titanium complex **6h** displayed a HTP value of 740 μm^{-1} in MBBA, the highest HTP value reported. The helical twisting power has been found to depend strongly on the structure of the nematic phase and the substitution pattern of the chiral ligand in the titanium complexes **6** and **7**. Crystal structure analysis of **6f** confirmed the *A*,*R*,*R* configuration of the metal complex. The chiral imine ligands **4** and **5** were derived from the regioisomeric amino alcohols **1** and **2**.

Keywords: chirality · crystal structure · liquid crystals · N,O ligands · titanium

Introduction

Chiral liquid crystalline compounds are considered as "smart materials", being highly important in technical applications, for example, in displays, polarizers, certain polymers and paints, or as coloring-effect materials.[1] A particularly efficient and elegant route to chiral mesophases is based on the addition of small amounts of an enantiomerically pure dopant to a nematic phase so that the latter is converted into a cholesteric phase.[2] This phenomenon was observed as long ago as the 1920s by Friedel.[3] Fifty years later, systematic studies by Buckingham, Stegemeyer, and Baessler, and their co-workers have led to a deeper insight into this phenomenon.[4] Stegemeyer and Mainusch showed[4c] that even those enantiomerically pure compounds that do not form a mesophase are able to function as dopants, thus inducing a helical arrangement in a nematic phase (Figure 1).[1d]

The efficiency of a chiral dopant is quantified by the "helical twisting power" (HTP), which is defined by Equation (1) for small concentrations of the dopant, where p is the pitch of the induced helix and x is the mole fraction of the

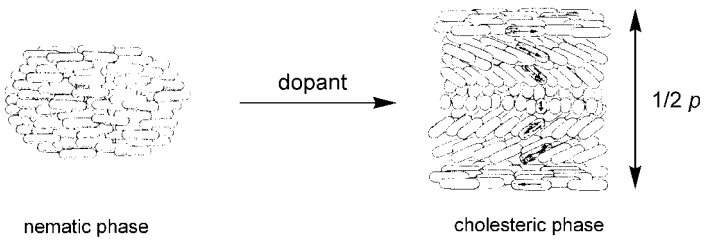

Figure 1. Conversion of a nematic phase into a cholesteric phase by addition of a dopant.[1d]

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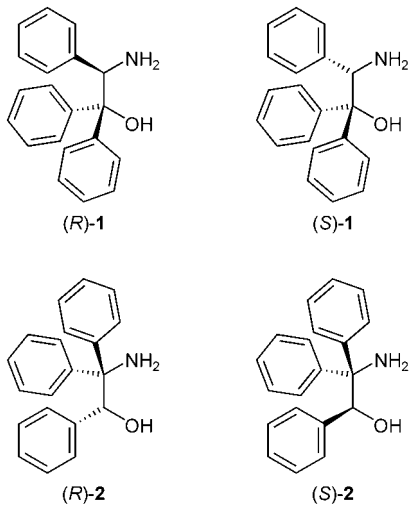
dopant.[2] As a goal, high HTP values are desirable so that as small as possible a mole fraction x of the dopant induces maximum helicity. The degree of helicity is given by the quantity of the pitch p of the helix, a value that can be in the range of the wavelength of visible light. Of the different physical procedures that are available to determine the HTP value,[5] the method of Grandjean and Cano is most frequently applied.[5a,b] Historically, the first substances used as chiral dopants were readily available natural products, mainly terpenes and steroids, and simple derivatives thereof.[4c] Among the synthetic dopants available are binaphthol-derived esters,[6a] biphenyls,[6b] and, in particular, some TADDOL derivatives,[7] which have the highest HTP value (534 μm^{-1}) measured so far.[7b]

$$\mathrm{HTP} = \lim_{x \to 0} \frac{1}{px} \qquad (1)$$

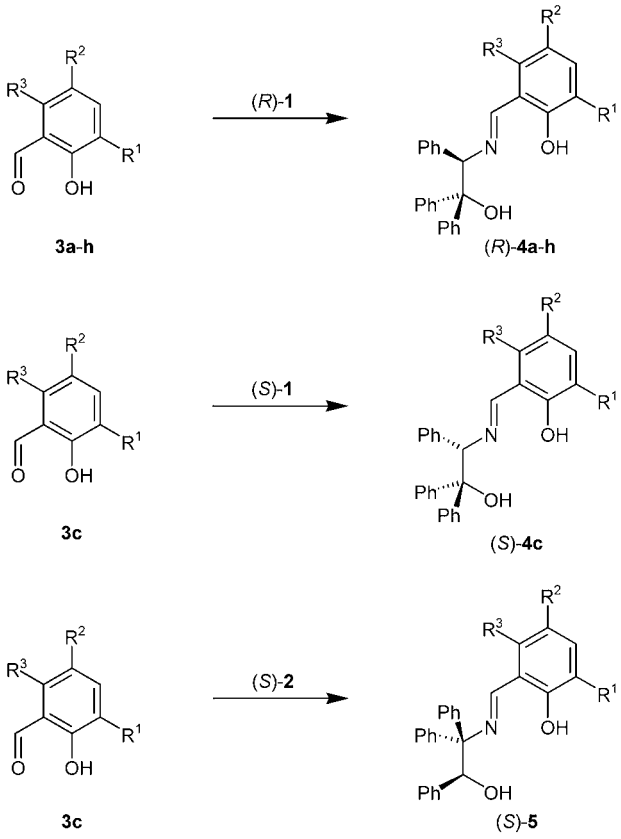
Chiral metal complexes seem predestined to serve as chiral dopants owing to the large number of possible structures that result from the diversity of metals that may serve as stereogenic centers on the one hand and the plethora of ligands, which may be chiral or achiral, on the other. Surprisingly however, only a very limited number and kind of metal complexes have found application as chiral dopants. Tris(dionato)metal(III) complexes with chromium, cobalt, rhodium, and ruthenium as the metal have been reported to display HTP values in the order of 100 μm^{-1}.[8] In addition, the use of binaphthol-derived titanates as chiral dopants has been mentioned.[9] Recently, we synthesized and characterized several bis-chelated imine-alkoxytitanium(IV) complexes,[10] which served us as precatalysts in various enantioselective conversions.[11] Here, we report for the first time the use of this novel type of titanium complex, derived from the regioisomeric triphenyl(amino)ethanols **1** and **2** (Scheme 1), as chiral dopants for nematic mesophases. They turned out to display very high HTP values, and their application as chiral dopants seems to meet commercial interest.[12]



Scheme 1. The regioisomeric triphenyl(amino)ethanols **1** and **2**.

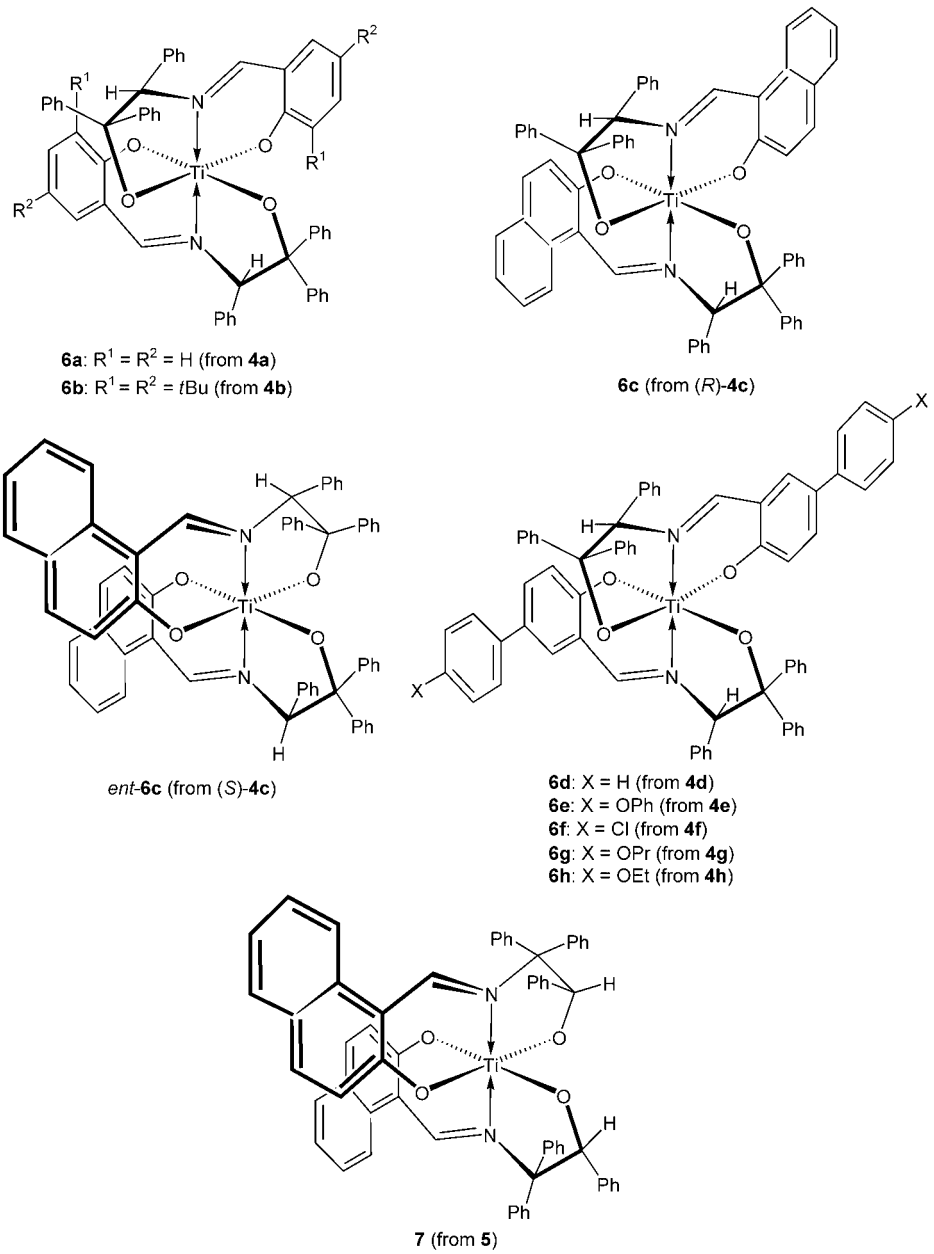
Results and Discussion

To convert the different isomers of triphenyl(amino)ethanol **1** and **2** into compounds that could serve as tridentate ligands, they were condensed with various *ortho*-hydroxy substituted aromatic aldehydes **3a–h** to give the corresponding imines **4a–h** and **5** (Scheme 2). Whereas the preparation of enantiomeric phenylglycine-derived amino alcohols (*R*)- and (*S*)-**1** was first described in the first part of the last century by McKenzie and Wills,[13] the regioisomers (*R*)- and (*S*)-**2** became accessible only recently from the corresponding enantiomer of methyl mandelate.[11a,b] The aldehydes **3a–d** were either commercially available or prepared according to known procedures.[14] The aldehydes **3e–h**, which contain the 4′-substituted biphenyl moiety, were obtained by Suzuki-



		R^1	R^2	R^3
3a	(*R*)-**4a**	H	H	H
3b	(*R*)-**4b**	*t*Bu	*t*Bu	H
3c	(*R*)-**4c**, (*S*)-**4c**, (*S*)-**5**	H	C_4H_4	
3d	(*R*)-**4d**	H	Ph	H
3e	(*R*)-**4e**	H	4-PhO-C_6H_4	H
3f	(*R*)-**4f**	H	4-Cl-C_6H_4	H
3g	(*R*)-**4g**	H	4-PrO-C_6H_4	H
3h	(*R*)-**4h**	H	4-EtO-C_6H_4	H

Scheme 2. Condensation of aldehydes **3** with triphenyl(amino)ethanols **1** and **2**.



Scheme 3. Bis-chelated titanium(IV) complexes **6a–h**, *ent*-**6c**, and **7**, prepared from imines **4** and **5** and used as dopants.

type coupling reactions of 4-bromo-2-formylphenol with 4-phenoxy-, 4-chloro-, 4-propoxy-, and 4-ethoxyphenylboronic acids, respectively (see Experimental Section).

The imines **4** and **5** were generated by condensation of the aldehydes **3** with triphenylethanols **1** and **2**, the different combinations being outlined in Scheme 2. Procedures for the generation of **4a–c** have been elaborated previously.[10] The imines **4d–h** and **5** were prepared by following analogous protocols.

Titanium(IV) complexes that contain various chiral ligands have proved extremely fruitful in their applications in asymmetric catalysis. In particular, complexes derived from carbohydrates, axially chiral biaryls, tartaric acid, as well as di- and oligopeptides and amino alcohol-derived imines, have been widely used in various enantioselective conversions.[7b,15] We have previously shown that imines like **4a–c** readily form bis-chelated titanium(IV) complexes of the TiL_2-type[16] when treated with titanium tetraisopropoxide in a 2:1 molar ratio.[10] This protocol was applied to all of the imines **4** and **5** shown in Scheme 2. It turned out that one diastereomer of the corresponding bis-chelated titanium complex was formed predominantly or exclusively. In all the cases studied so far, the major diastereomer was isolated by column chromatography and/or recrystallization as a diastereomerically and enantiomerically pure compound. Thus, the titanium complexes **6a–h**, *ent*-**6c**, and **7** were isolated and characterized from their analytical and spectroscopic data (see Scheme 3).[17] In view of the exceptionally high HTP obtained with biphenyl-substituted titanium complexes **6d–h**, the X-ray crystal structure of one of them, compound **6f**, was determined. The structure shown in Figure 2 clearly reveals that the ligands are arranged in a meridional position around the central metal atom, which becomes a stereogenic center as a result of the complexation. It turns out that complex **6f** has the *A* configuration. The assignment of this configuration to complexes **6a–e** and **6g**,**h** and the opposite configuration *C* to compounds *ent*-**6c** and **7** is not only based on analogy but also on comparison of their CD spectra. The chemical yields of the imines **4** and **5** as well as the yields and the optical rotations of the bis-chelated titanium complexes **6** and **7** are shown in Table 1.

The induction of chirality, a feature of dopants, obviously relies on noncovalent interactions between the dopant and the nematic phase. As a consequence, the helical twisting power is expected to depend not only on the structure of the dopant but also on the nematic "host" compound. Therefore, the HTP values of the titanium complexes **6** and

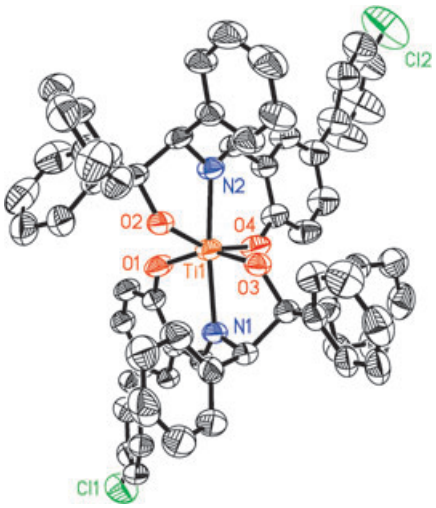


Figure 2. Structure of the titanium complex **6f** in the hexane/ethyl acetate solvate, **6f**·0.5 C_6H_{14}·0.5 $C_4H_8O_2$ (ORTEP diagram; displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms and labels of carbon atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Ti1–O1 1.903(3), Ti1–O2 1.859(2), Ti1–O3 1.902(3), Ti1–O4 1.861(2), Ti1–N1 2.195(3), Ti1–N2 2.164(3); O1-Ti1-O2 92.15(11), O1-Ti1-O3 89.48(12), O1-Ti1-O4 154.60(10), O2-Ti1-O3 155.26(12), O2-Ti1-O4 94.04(11), O3-Ti1-O4 95.00(12), O1-Ti1-N1 80.53(11), O1-Ti1-N2 99.66(11), O2-Ti1-N1 113.71(10), O2-Ti1-N2 74.13(11), O3-Ti1-N1 90.91(10), O3-Ti1-N2 81.26(11), O4-Ti1-N1 74.42(11), O4-Ti1-N2 105.73(11), N1-Ti1-N2 172.16(11).

Table 1. Yields of imines **4** and **5** and yields and optical rotations of titanium complexes **6** and **7**.

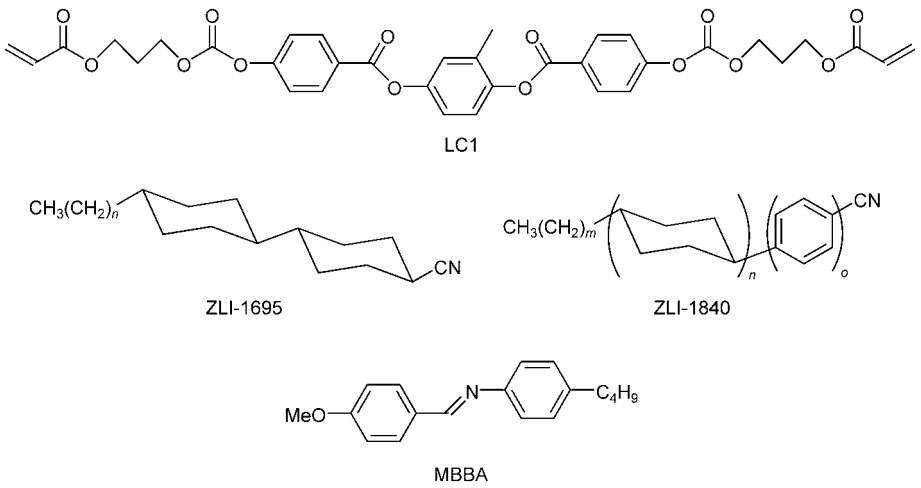
Imines **4**, **5**	Yield [%]	Titanium complexes **6**, **7**	$[\alpha]_D^{20}$[a]	Yield [%][b]
(*R*)-**4a**[c]	81	**6a**	+929	68
(*R*)-**4b**[c]	88	**6b**	+287	49
(*R*)-**4c**[c]	93	**6c**	+1021	78
(*R*)-**4d**	68	**6d**	+814	48
(*R*)-**4e**	43	**6e**	+693	18
(*R*)-**4f**	51	**6f**	+792	53
(*R*)-**4g**	83	**6g**	+799	51
(*R*)-**4h**	91	**6h**	+820	49
(*S*)-**4c**	79	*ent*-**6c**	−1024	53
(*S*)-**5**	75	**7**	+205	80

[a] $c = 1$, in chloroform. [b] Isolated yield of diastereomerically pure product. [c] See ref. [10].

7 were measured in various nematic phases that differ significantly in their geometry and functional groups. As the dopants developed here might be useful for end-applications, mainly commercially available nematic phases were selected. To be specific, the liquid crystalline compound LC1 (made available by BASF) and the commercial nematic compounds ZLI-1840 and ZLI-1695, both available from Merck (Darmstadt), were used. In addition, the helical twisting power in the achiral mesophase formed by MBBA was also studied. Whereas LC1 and MBBA are pure compounds, the commercial products ZLI-1840 and ZLI-1695 are mixtures (see Scheme 4); ZLI-1695 is a mixture of four alkyl-substituted bicyclohexylcarbonitriles, whereas the nematic liquid crystalline product ZLI-1840 contains eight alkyl-substituted cyclohexylphenyl and cyclohexylbiphenyl nitriles. Both liquid crystalline mixtures are suitable mesogenic materials for LC displays.

The titanium complexes **6** and **7** were dissolved in the nematic compounds (Scheme 4) at different concentrations in the range of 10^{-3} to 10^{-4} mole fraction of the respective dopant. The HTP values were determined by the Grandjean–Cano wedge method.[5a,b] The chiral nematic mixture was sandwiched between a glass-plate surface and a plane-convex lens of known radius ($R = 3.618$ mm). The samples under the crossed polarizers of an optical microscope showed concentric disclination rings the radii r of which are directly correlated to the helical pitch p of the sample: $p = \Delta r^2/R$, where Δr^2 is the difference between the squared radii of neighboring disclination rings. The $1/p$ values were measured at different dopant concentrations and the HTP values were determined by the gradient of the plot of $1/p$ versus molar fraction. The sign of the helicity was determined by observing the change in the disclination ring size under the polarization microscope when monochromatic light was used and the analyzer rotated clockwise against the polarizer direction.[5n] The HTP values and the signs of the helicity are shown in Table 2. The right- and left-handed systems are characterized by positive (*P*) or negative (*M*) HTP values, respectively.

As expected, the HTP values depend both on the structure of the ligand in the particular titanium complex and on the nematic host (Table 2). Those ligands that contain a mononucleic aromatic moiety in the salene moiety (Table 2, entry 1) exhibit only moderate helical twisting power. Extension of the aromatic skeleton by replacing the phenyl group in the salene unit with a naphthyl group clearly enhances the helical twisting power, as shown by comparison of the HTP values of **6c** and *ent*-**6c** with that of **6a** (Table 2, entries 2 and 3 versus 1). It was also expected that regioisomerism would influence the helical twisting power. Thus, the HTP of the titanium complex **7** derived from the novel amino alcohol (*S*)-**2** was measured. Comparison of the HTP values of **7** and **6c**, both determined by using ZLI-1840 as the nematic host, revealed the regioisomer **7** to display a higher HTP value (Table 2, entries 2 and 4, respectively). This tendency was even more obvious when the HTP values of the titanium complexes were measured in the nematic phase LC1. Here again, substantially higher HTP values were obtained when the dopant **6c** (Table 2, entry 5) was replaced with **7** (Table 2, entry 6). The latter complex is derived from the regioisomeric amino alcohol **2** whereas the former was generated from **1**. This same tendency, the better performance of the regioisomer-derived titanium complex **7**, is also shown in the nematic mixture ZLI-1695 by comparison of the HTP values of *ent*-**6c** and **7** (Table 2, entries 7 and 8). This effect, however, is clearly exceeded by the influence of the substitution pattern of the aromatic rings in the salene moiety. Thus, changing the naphthyl group to a *para*-biphenyl ring system in the titanium complexes substantially improved the HTP values measured in ZLI-1695 (Table 2, entries 7 and 8 versus 9). Rather unex-



Scheme 4. Nematic phases used as host compounds for the chiral dopants **6** and **7**.

Table 2. HTP values of bis-chelated imine alkoxytitanium complexes **6** and **7** in different nematic phases.

Entry	Titanium complex	Nematic phase	HTP [μm^{-1}]	Helicity
1	**6a**	ZLI-1840	20	(P)
2	**6c**	ZLI-1840	39	(P)
3	*ent*-**6c**	ZLI-1840	43	(M)
4	**7**	ZLI-1840	49	[a]
5	**6c**	LC1	15	(P)
6	**7**	LC1	48	[a]
7	*ent*-**6c**	ZLI-1695	200	[a]
8	**7**	ZLI-1695	250	[a]
9	**6d**	ZLI-1695	311	(M)
10	**6b**	MBBA	480	(P)
11	**6d**	MBBA	400	(M)
12	**6e**	MBBA	500	(M)
13	**6f**	MBBA	560	(M)
14	**6g**	MBBA	450	(M)
15	**6h**	MBBA	740	(M)

[a] Not determined.

pectedly, complex **6b** with ligands with a mononucleic aromatic moiety provided a relatively high HTP value in MBBA, presumably due to the *tert*-butyl substitution pattern (Table 2, entry 10). As a general trend, the HTP was enhanced when measured in the nematic phase MBBA (Table 2, entries 10–15). In view of the positive influence of the *para*-biphenyl moiety on the helical twisting power, it was an obvious idea to improve it even further by introducing substituents onto the biphenyl system. This has been realized through the 4,4′-disubstituted derivatives **6e–h** (Table 2, entries 12–15): Indeed, exceptionally high HTP values ranging from 450 to 740 μm^{-1} were obtained.

Aside from the chiral dopant, the nematic phase strongly influences the helical twisting power. The mesophases ZLI-1840 and LC1 clearly tend to give lower HTP values than ZLI-1695 and particularly MBBA. It seems that twisting is accomplished more easily as the size of the nematic molecule decreases. There might also be an additional effect based on the similarities of the structures of the dopant and the nematic phase. As a result, MBBA, which contains an imine moiety, is most strongly twisted by a dopant that bears the same functional group. A phenolic ether moiety present in the dopants **6e**, **6g**, and **6h**, as well as in the nematic phase, MBBA, also seems to have a favorable effect. In conclusion, bis-chelated titanium complexes display the highest HTP values reported so far, including a "record" 740 μm^{-1} obtained with the derivative **6h**.

Experimental Section

General: Melting points (uncorrected) were determined with a Büchi 540 melting point apparatus. Optical rotations were measured with a Perkin-Elmer 341 polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg $cm^2 g^{-1}$. NMR spectra were recorded in $CDCl_3$ solution (internal standard) with a Varian VXR 200 or 300 or a Bruker DRX 500 spectrometer. IR spectra were recorded with a Bruker Vector 22 spectrometer. Mass spectra were measured with a Varian MAT 311 spectrometer. UV spectra were recorded with a Perkin-Elmer Lambda 19 spectrophotometer.

Silica gel 60 F_{254} TLC plates (Merck) were used to separate the products. Column chromatography was performed using Macherey-Nagel Kieselgel 60 or Merck Kieselgel 60, mesh size 0.04–0.063. The GC–MS spectra were measured with a Hewlett-Packard apparatus 5890/5790 using a HP OV-1-FS capillary column or with a Varian GC 1700 using an Optima 1 capillary column. Elemental analyses were carried out with a Perkin-Elmer CHN-Analysator 263. Elemental analyses were carried out at the Institut für Pharmazeutische Chemie (Universität Düsseldorf) or by Mikroanalytisches Laboratorium Beller (Göttingen). All reactions involving organometallic compounds or metal complexes were carried out under anhydrous nitrogen. Reactions at temperatures below 0 °C were monitored by a thermocouple connected to a resistance thermometer (Ebro). [1,1′-Bis(diphenylphosphino)ferrocene]palladium(II) chloride–dichloromethane complex, [Pd(dppf)Cl_2] was purchased from Alfa Aesar.

2-Hydroxy-5-(4-phenoxyphenyl)benzaldehyde (3e): A 100-mL two-necked round-bottomed flask was equipped with a magnetic stirrer and a reflux condenser, which was connected to the combined nitrogen/vacuum line. The flask was charged with 4-phenoxyphenylboronic acid (5.00 g, 23.36 mmol), 5-bromo-2-hydroxybenzaldehyde (4.27 g, 21.24 mmol), [Pd(dppf)Cl_2] (0.05 equiv, 0.866 g, 1.06 mmol), and dry sodium carbonate (3.377 g, 31.86 mmol) and closed with a septum. The air in the flask was replaced with nitrogen and a degassed mixture of 1,2-dimethoxyethane and water (30 mL and 10 mL, respectively) was added by syringe. The septum was replaced by a stopper and the mixture was heated to 100 °C for 5 h. After cooling to room temperature, the mixture was filtered and the filtrate was poured into deionized water (150 mL). The mixture was extracted with three 200 mL portions of dichloromethane and the combined organic layers were dried with sodium sulfate and concentrated in a rotary evaporator. The residue was purified by column chromatography to give solid **3e** (0.824 g, 13 %); m.p. 109.5–111.0 °C; $R_f = 0.25$ (*n*-hexane/chloroform, 1:2); ^{1}H NMR (500 MHz): $\delta = 7.04$–7.09 (m, 5H), 7.11–7.14 (m, 1H), 7.33–7.37 (m, 2H), 7.48–7.51 (m, 2H) and 7.71–7.74 (m, 2H) (aromatic H), 9.95 (s, 1H, CHO), 10.98 ppm (s, 1H, OH); ^{13}C NMR (125 MHz): $\delta = 118.13$–135.49 (aromatic C), 156.93 (C-O-C), 156.95 (C-O-C), 160.75 [C(OH)], 196.62 ppm (CHO); MS (70 eV): *m*/*z* (%): 291 (21) $[M+1]^+$, 290 (100) $[M]^+$, 279 (4), 261 (2), 213 (5), 185 (4), 167 (6), 97 (8), 69 (14), 43 (21).

5-(4-Chlorophenyl)-2-hydroxybenzaldehyde (3f): Compound **3f** was prepared according to an analogous procedure starting from 4-chlorophenylboronic acid (4.739 g, 30.30 mmol), 5-bromo-2-hydroxybenzaldehyde (5.538 g, 27.55 mmol), [Pd(dppf)Cl_2] (0.06 equiv, 1.348 g, 1.65 mmol), and dry sodium carbonate (1.5 equiv, 4.380 g, 41.32 mmol). Heating was maintained at 100 °C for 15 h. The aldehyde **3f** was obtained as a solid in 51 % yield (3.248 g): m.p. 86.0–87.5 °C; R_f = 0.4 (*n*-hexane/chloroform, 1:1); ^{1}H NMR (200 MHz): δ = 7.04–7.08 (m, 1H), 7.36–7.49 (m, 4H) and 7.68–7.74 (m, 2H) (aromatic H), 9.95 (s, 1H, CHO), 11.00 ppm (s, 1H, OH); ^{13}C NMR (125 MHz): δ = 118.73–138.20 (aromatic C), 161.58 [C(OH)], 196.95 ppm (CHO); MS (70 eV): *m*/*z* (%): 232 (100) $[M]^+$, 198 (13), 186 (7), 168 (8), 139 (15), 84 (6), 63 (5), 53 (4), 40 (7); elemental analysis calcd (%) for $C_{13}H_9O_2Cl$: C 67.11, H 3.90; found: C 67.09, H 4.05.

2-Hydroxy-5-(4-propoxyphenyl)benzaldehyde (3g): Compound **3g** was prepared according to an analogous procedure starting from 4-propoxyphenylboronic acid (5.105 g, 28.36 mmol), 5-bromo-2-hydroxybenzaldehyde (15.182 g, 25.78 mmol), [Pd(dppf)Cl_2] (0.05 equiv, 1.053 g, 1.29 mmol), and dry sodium carbonate (4.099 g, 38.67 mmol). Heating was maintained at 100 °C for 7 h. The crude product was purified by two-fold column chromatography (1: chloroform, R_f = 0.3; 2: *n*-hexane/chloroform, 1:3, R_f = 0.2) to give **3g** (0.736 g, 11 %) as a solid; ^{1}H NMR (500 MHz): δ = 1.04 (t, J = 7.4 Hz, 3H, CH_3), 1.82 (m, 2H, $CH_2CH_2CH_3$), 3.95 (t, J = 6.6 Hz, 2H, $CH_2CH_2CH_3$), 6.95–7.04 (m, 3H, aromatic H), 7.43–7.46 (m, 2H, aromatic H), 7.68–7.73 (m, 2H, aromatic H), 9.94 (s, 1H, CHO), 10.94 ppm (s, 1H, OH).

5-(4-Ethoxyphenyl)-2-hydroxybenzaldehyde (3h): Compound **3h** was prepared according to an analogous procedure starting from 4-ethoxyphenylboronic acid (5.000 g, 30.12 mmol), 5-bromo-2-hydroxybenzaldehyde (5.504 g, 27.38 mmol), [Pd(dppf)Cl_2] (0.06 equiv, 1.339 g, 1.64 mmol), and dry sodium carbonate (4.353 g, 41.07 mmol). Heating was maintained at 100 °C for 7 h. After two-fold chromatographic purification, the aldehyde **3h** was obtained as a solid product in 10 % yield (0.683 g): m.p. 89.0–91.0 °C; R_f = 0.2 (*n*-hexane/chloroform, 1:3); ^{1}H NMR (200 MHz): δ = 1.43 (t, J = 7.0 Hz, 3H, CH_3), 4.06 (q, J = 6.9 Hz, 2H, CH_2), 6.92–7.05 (m, 3H, aromatic H), 7.41–7.49 (m, 2H, aromatic H), 7.68–7.74 (m, 2H, aromatic H), 9.94 (s, 1H, CHO), 10.94 ppm (s, 1H, OH); MS (70 eV): *m*/*z* (%): 243 (17) $[M+1]^+$, 242 (100) $[M]^+$, 214 (81), 213 (55), 185 (18), 168 (7); elemental analysis calcd (%) for $C_{15}H_{14}O_3$: C 74.37, H 5.82; found: C 74.40, H 5.87.

Imines **4a–c** and titanium complexes **6a–c** were prepared according to procedures described in reference [10].

[OC-6-22′-(C,*S*,*S*)]-Bis{1-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}-2-naphtholato(2−)-*N*,*O*,*O*′}titanium (*ent*-6c): Prepared analogously, from (*S*)-**4c** (0.155 g, 0.35 mmol) and Ti(O*i*-Pr)$_4$ (0.050 g, 0.175 mmol). The reaction mixture was refluxed for 4 h. Yield: 0.086 g (53 %). The NMR and MS data correspond to those of **6c**.[10] $[\alpha]_D^{20} = -1024$ (c = 1 in chloroform); elemental analysis calcd (%) for $C_{62}H_{46}N_2O_4Ti$: C 79.99, H 4.98, N 3.01; found: C 79.67, H 5.10, N 2.89.

General procedure for the preparation of imines 4d–h and 5: A 100-mL two-necked flask equipped with a magnetic stirrer and a connection to the combined nitrogen/vacuum line was charged with (*R*)-**1** (0.304 g, 1.05 mmol) and dry sodium sulfate (0.401 g, 2.82 mmol). The flask was closed with a septum, the air in the flask was replaced by nitrogen and dry methanol (15 mL) and dry dichloromethane (15 mL) were added by syringe. The suspension was cooled to −20 °C. With vigorous stirring, a solution of the corresponding aldehyde **3**, dissolved under nitrogen in 20 mL of dry methanol or mixtures of methanol and dichloromethane, was slowly injected at such a rate that the temperature, monitored by a resistance thermometer, did not exceed −20 °C. Stirring was continued at the same temperature for 48 h. Then, the solid was removed by filtration at 0 °C and the filtrate was concentrated in an oil pump vacuum at 0 °C to give the imines **4d–h**. The crude products obtained quantitatively were either used in the following step or purified by stirring in pentane and subsequent filtration. They were stored at −18 °C in a refrigerator.

(*R*)-2-{[(2-Hydroxy-1,2,2-triphenylethyl)imino]methyl}-4-phenylphenol [(*R*)-4d]: Prepared from (*R*)-**1** (0.507 g, 1.75 mmol) and **3d** (0.416 g, 2.10 mmol). Yield: 68 % (according to the NMR spectra); ^{1}H NMR (500 MHz): δ = 2.92 (br s, 1H, Ph_2COH), 5.53 [s, 1H, PhCH(N)], 6.96–7.75 (m, 23H, aromatic H), 8.38 (s, 1H, N=CH), 12.84 ppm (s, 1H, ArOH); MS (FAB, NBA): *m*/*z* (%): 470 (29) $[M]^+$, 287 (100), 286 (36), 273 (22), 272 (38), 183 (38), 167 (29), 106 (84), 105 (65), 77 (84).

(*R*)-2-{[(2-Hydroxy-1,2,2-triphenylethyl)imino]methyl}-4-(4-phenoxyphenyl)phenol [(*R*)-4e]: Prepared from (*R*)-**1** (0.735 g, 2.54 mmol) and **3e** (0.775 g, 2.67 mmol). Yield: 43 % (according to the NMR spectra); ^{1}H NMR (200 MHz): δ = 2.90 (s, 1H, Ph_2COH), 5.52 [s, 1H, PhCH(N)], 6.93–7.82 (m, 27H, aromatic H), 8.37 (s, 1H, N=CH), 12.82 ppm (s, 1H, ArOH); MS (FAB, NBA): *m*/*z* (%): 562 (22) $[M+1]^+$, 561 (4) $[M]^+$, 486 (9), 485 (6), 451 (3), 379 (100), 362 (5), 272 (29).

(*R*)-4-(4-Chlorophenyl)-2-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenol [(*R*)-4f]: Prepared from (*R*)-**1** (4.098 g, 14.16 mmol) and **3f** (3.138 g, 13.49 mmol). The crude product was stirred in *n*-pentane and then filtered. Yield: 3.458 g (51 %); m.p. 133.5–134.0 °C; $[\alpha]_D^{20} = +130$ (c = 1 in chloroform); ^{1}H NMR (200 MHz): δ = 2.86 (s, 1H, Ph_2COH), 5.52 [s, 1H, PhCH(N)], 6.93–7.62 (m, 22H, aromatic H), 8.36 (s, 1H, N=CH), 12.88 ppm (s, 1H, ArOH); ^{13}C NMR (125 MHz): δ = 79.11 [PhCH(N)], 81.01 [Ph_2C(OH)], 118.00–145.11 (aromatic C), 160.84 [aromatic C(OH)], 167.53 ppm (NCHAr); MS (FAB, NBA): *m*/*z* (%): 504 (15) $[M]^+$, 460 (3), 426 (2), 391 (2), 321 (45), 289 (15), 242 (5), 195 (7), 183 (23), 136 (83), 105 (46), 89 (63), 77 (76), 63 (47); elemental analysis calcd (%) for $C_{33}H_{26}O_2NCl$: C 78.64, H 5.20, N 2.78; found: C 77.74, H 5.23, N 2.67.

(*R*)-2-{[(2-Hydroxy-1,2,2-triphenylethyl)imino]methyl}-4-(4-propoxyphenyl)phenol [(*R*)-4g]: Prepared from (*R*)-**1** (0.810 g, 2.80 mmol) and **3g** (0.684 g, 2.67 mmol). The crude product was stirred in *n*-pentane and then filtered. Yield: 1.171 g (83 %); m.p. 136.5–138.0 °C; $[\alpha]_D^{20} = +134$ (c = 1 in chloroform); ^{1}H NMR (500 MHz): δ = 0.97 (t, J = 7.3 Hz, 3H, CH_3), 1.74 (m, 2H, $CH_2CH_2CH_3$), 2.84 (s, 1H, OH), 3.86 (t, J = 6.6 Hz, 2H, $CH_2CH_2CH_3$), 5.45 [s, 1H, PhCH(N)], 6.83–6.88 [m, 3H, aromatic H), 7.02–7.40 (m, 17H, aromatic H), 7.53–7.55 (m, 2H, aromatic H), 8.30 (s, 1H, N=CH), 12.68 ppm (s, 1H, ArOH); ^{13}C NMR (125 MHz): δ = 10.93 ($CH_2CH_2CH_3$), 23.00 ($CH_2CH_2CH_3$), 70.00 ($CH_2CH_2CH_3$), 79.15 [PhCH(N)], 81.00 [Ph_2C(OH)], 115.21–160.03 (aromatic C), 167.81 ppm (NCHAr); MS (MALDI): *m*/*z*: 528 $[M+1]^+$.

(*R*)-4-(4-Ethoxyphenyl)-2-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenol [(*R*)-4h]: Prepared from (*R*)-**1** (0.721 g, 2.49 mmol) and **3h** (0.574 g, 2.37 mmol). The crude product was stirred in *n*-pentane and then filtered. Yield: 1.103 g (91 %); m.p. 141.0–142.5 °C; $[\alpha]_D^{20} = +142$ (c = 1 in chloroform); ^{1}H NMR (200 MHz): δ = 1.41 (t, J = 7.0 Hz, 3H, CH_3), 2.87 (s, 1H, OH), 4.03 (q, J = 6.9 Hz, 2H, CH_2), 5.51 [s, 1H, PhCH(N)], 6.86–6.95 (m, 3H, aromatic H), 7.08–7.48 (m, 17H, aromatic H), 7.56–7.62 (m, 2H, aromatic H), 8.37 (s, 1H, N=CH), 12.74 ppm (s, 1H, ArOH); MS (MALDI): *m*/*z*: 514 $[M+1]^+$; elemental analysis calcd (%) for $C_{35}H_{31}NO_3$: C 81.85, H 6.08, N 2.73; found: C 81.93, H 5.89, N 2.59.

(*S*)-1-{[(2-Hydroxy-1,1,2-triphenylethyl)imino]methyl}-2-naphthol (5): Prepared from (*S*)-**2** (0.21 g, 1.51 mmol) and **3c** (0.128 g, 0.744 mmol). The reaction mixture was stirred at 60 °C for 20 h and the crude product was purified by column chromatography. Yield: 0.234 g (74.6 %); m.p. 133.2–134.4 °C; R_f = 0.6 (ethyl acetate/chloroform, 1:10); $[\alpha]_D^{20} = -129$ (c = 1 in chloroform); ^{1}H NMR (500 MHz): δ = 2.42 [br s 1H, PhCH(O*H*)], 5.79 [d, J = 2.5 Hz, 1H, PhC*H*(OH)], 6.79–7.80 (m, 21H, aromatic H), 8.77 (d, J = 8.0 Hz, 1H, N=CH), 15.48 ppm (d, J = 8.0 Hz, 1H, naphtholic OH); ^{13}C NMR (125 MHz): δ = 70.35 [Ph_2C(N)], 78.22 [Ph*C*H(OH)], 103.23 and 117.9–129.7 (aromatic C), 139.56–145.35 (aromatic *ipso*-C), 159.18 (N=CH), 163.78 ppm [naphtholic C(OH)]; MS (70 eV): m/z: 444 $[M+1]^+$, 336, 259, 169, 167, 154, 126, 106.

General procedure for the synthesis of titanium complexes 6d–h: A 100 mL two-necked flask was charged with an imine (**4d–h**) (0.50 mmol), equipped with a magnetic stirrer and a reflux condenser, connected to the combined nitrogen/vacuum line, and closed with a septum. The air in the flask was replaced by nitrogen, the solid was dissolved by adding dry dichloromethane (2 mL), and, thereafter, whilst stirring, titanium tetraisopropoxide (0.25 mmol) was injected at room temperature. The solution was refluxed for the time given below. The solvent was then removed in a rotary evaporator and the residue was purified by column chromatography.

[OC-6-22′-(*A*,*R*,*R*)]-Bis{2-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}-4-phenylphenolato(2−)-*N*,*O*,*O*}titanium (6d): Prepared from (*R*)-**4d** (0.272 g, 0.579 mmol) and Ti(O*i*-Pr)$_4$ (0.082 g, 0.29 mmol). The reaction mixture was refluxed for 7 h. Yield: 0.138 g (48 %), m.p. 205–206 °C (color changing from yellow to brown), 215 °C (decomposition); R_f = 0.7 (*n*-hexane/chloroform, 1:4); $[\alpha]_D^{20}$ = +814 (*c* = 1 in chloroform); ^{1}H NMR (500 MHz): δ = 5.56 (d, *J* = 8.8 Hz, 2H, *o*-phenolato-H), 6.43 [s, 2H, PhCH(N)], 6.92–7.14 (m, 18H) 7.23–7.37 (m, 12H), 7.43–7.49 (m, 10H) and 8.00–8.02 (m, 4H) (aromatic H), 8.74 ppm (s, 2H, N=CH); ^{13}C NMR (125 MHz): δ = 87.15 [PhCH(N)], 93.07 [Ph$_2$*C*(OTi)], 119.04 (C-6), 120.07 (C-2), 131.14 (C-4), 133.91 (C-5), 140.26, 141.73, 146.81, 146.83 [aromatic *ipso*-C (Ph)], 125.61–130.15 (remaining aromatic C), 163.98 (C-1), 166.57 ppm (N=CH) (carbon numbering refers to the phenolato ring); MS (FAB, NBA): *m*/*z* (%): 983 (18) [M]$^+$, 906 (3), 905 (3), 801 (39), 800 (57), 724 (14), 723 (18), 695 (6), 619 (60), 618 (100), 516 (16), 515 (31), 514 (26), 411 (32).

[OC-6-22′-(*A*,*R*,*R*)]-Bis{2-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}-4-(4-phenoxyphenyl)phenolato[2−]-*N*,*O*,*O*}titanium (6e): Prepared from **4e** (0.652 g, 1.16 mmol) and Ti(O*i*-Pr)$_4$ (0.165 g, 0.58 mmol). The reaction mixture was refluxed for 8 h. The crude product was first purified by two-fold column chromatography. The product was then dissolved in diethyl ether (100 mL) and extracted three times with a saturated solution of sodium hydrogen sulfite and another three times with water. The organic layer was dried with sodium sulfate and concentrated in vacuo. The residue was recrystallized from methanol to give 0.120 g (18 %) of **6e**; m.p. 177.5–179.0 °C; $[\alpha]_D^{20}$ = +693 (*c* = 1 in chloroform); ^{1}H NMR (500 MHz): δ = 5.54 (d, *J* = 8.8 Hz, 2H, *o*-phenolato-H), 6.42 [s, 2H, PhCH(N)], 6.91–7.49 (m, 48H, aromatic H), 8.00 (d, *J* = 6.95 Hz, 4H, aromatic H), 8.73 ppm (s, 2H, N=CH); ^{13}C NMR (125 MHz): δ = 87.54 [PhCH(N)], 93.45 [Ph$_2$C(OTi)], 119.2–147.2, 156.51 and 157.66 (aromatic C), 164.19 (COTi), 166.95 ppm (N=CH); MS (FAB, NBA): *m*/*z* (%): 1167 (14) [*M*+1]$^+$, 984 (54), 907 (12), 802 (97), 726 (12), 699 (17), 307 (100).

[OC-6-22′-(A,*R*,*R*)]-Bis{4-(4-chlorophenyl)-2-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-*N*,*O*,*O*}titanium (6f): Prepared from (*R*)-**4f** (3.002 g, 5.96 mmol) and Ti(O*i*-Pr)$_4$ (0.847 g, 2.98 mmol). The reaction mixture was refluxed for 7 h. Yield: 1.657 g (53 %); R_f = 0.6 (*n*-hexane/chloroform 1:4); m.p. 213.0 °C; $[\alpha]_D^{20}$ = +792 (*c* = 1 in chloroform); ^{1}H NMR (200 MHz): δ = 5.54 (d, *J* = 8.8 Hz, 2H, *o*-phenolato-H), 6.42 [s, 2H, PhCH(N)], 6.89–7.18 (m, 19H), 7.25–7.49 (m, 19H) and 7.97–8.02 (m, 4H) (aromatic H), 8.73 ppm (s, 2H, N=CH); ^{13}C NMR (125 MHz): δ = 87.61 [PhCH(N)], 93.57 [Ph$_2$(COTi)], 119.6–147.1 (aromatic C), 164.48 (COTi), 166.89 ppm (N=CH); MS (70 eV): *m*/*z* (%):1051 (13) [*M*+1]$^+$, 975 (5), 868 (65), 791 (21), 686 (100), 479 (43).

Crystal structure determination of complex 6f: Crystals of **6f** were obtained from a 4:1 mixture of hexane and ethyl acetate. A single crystal, suitable for X-ray study, was selected by using a polarization microscope and investigated on a Stoe Imaging Plate Diffraction System using graphite monochromatized Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). Unit cell parameters were determined by a least-squares refinement on the positions of 8000 strong reflections distributed equally in reciprocal space. An orthorhombic lattice was found and space group $P2_12_12_1$ was uniquely determined. Crystal data of **6f**·0.5 C_6H_{14}·0.5 $C_4H_8O_2$: M_r($C_{71}H_{59}Cl_2N_2O_5Ti$) = 1138.97, *a* = 13.2663(8), *b* = 19.8502(9), *c* = 23.4711(17) Å, *V* = 6180.9(6) Å^3, *Z* = 4, D_x = 1.224 g cm^{-3}, μ = 0.276 mm^{-1}, *T* = 291 K, orange prisms of dimensions 0.4 × 0.35 × 0.15 mm. 57012 intensity data (Θ_{min} = 2.05°, Θ_{max} = 26.04°) were collected and corrected for Lorentzian and polarization effects. The structure was solved by direct methods,[18] subsequent Fourier analysis, and a trial-and-error procedure for the inclusion of the highly mobile hole-filling solvent molecules with rigid idealized geometry. The 1:1 ratio of hexane and ethyl acetate was determined by NMR spectroscopic investigation after dissolving a sufficient number of crystals in $CDCl_3$. Approximate positions of all the hydrogen atoms of the titanium complex were found by difference Fourier analysis. Taking into account the 1:1 statistical occupation of one site by the solvent molecules, refinement (690 parameters, all 11677 unique reflections were used, 1 restraint) by full-matrix least-squares calculations on F^2[19] converged to the following final indicators: $R_1[F_o^2 > 2\sigma(F_o^2)]$ = 0.0495, wR_2 = 0.0966 (all data), $w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 1.0P]$, where $P = (F_o^2 + 2F_c^2)/3$, *S* = 0.993,[19] largest peak and hole in the final difference map are 0.351 e Å^{-2} and −0.153 e Å^{-3}, respectively. The absolute structure was determined by refinement of a Flack parameter [−0.02(3)].[20] Anisotropic displacement parameters were used for the refinement of all non-hydrogen atoms of the titanium complex. All the hydrogen atoms were treated as riding on their parent carbon atoms in idealized positions. Their isotropic displacement parameters were kept equal to 120 % of the isotropic or equivalent isotropic displacement parameters of the parent "aromatic", tertiary or secondary carbon atom and equal to 150 % of the parent primary carbon atom, respectively. Scattering factors, dispersion corrections, and absorption coefficients were taken from ref. [21]. CCDC-258177 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[OC-6-22′-(*A*,*R*,*R*)]-Bis{2-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}-4-(4-propoxyphenyl)phenolato(2−)-*N*,*O*,*O*]titanium (6g): Prepared from (*R*)-**4g** (1.131 g, 2.14 mmol) and Ti(O*i*-Pr)$_4$ (0.304 g, 1.07 mmol). The reaction mixture was stirred at room temperature for 72 h. The crude product was purified by column chromatography (chloroform, R_f = 0.4). Yield: 0.601 g (51 %); m.p. 191 °C (decomp); $[\alpha]_D^{20}$ = +799 (*c* = 1 in chloroform); ^{1}H NMR (500 MHz): δ = 1.03 (t, *J* = 7.45 Hz, 6H, CH_3), 1.80 (pseudosextet, *J* = 7.20 Hz, 4H, $CH_2CH_2CH_3$), 3.92 (t, *J* = 6.62 Hz, 4H, $CH_2CH_2CH_3$), 5.53 (d, *J* = 8.75 Hz, 2H, *o*-phenolato-H), 6.41 [s, 2H, PhCH(N)], 6.88–6.94 (m, 6H, aromatic H), 7.00–7.13 (m, 16H, aromatic H), 7.26–7.28 (m, 6H, aromatic H), 7.33–7.37 (m, 6H, aromatic H), 7.46–7.48 (m, 4H, aromatic H), 8.00 (d, *J* = 8.5 Hz, 4H, aromatic H), 8.72 ppm (s, 2H, N=CH); ^{13}C NMR (125 MHz): δ = 10.94 ($CH_2CH_2CH_3$), 23.01 ($CH_2CH_2CH_3$), 69.98 ($CH_2CH_2CH_3$), 87.50 [PhCH(N)], 93.36 [Ph$_2$C(OTi)], 115.1–158.5 and 164.0 (aromatic C), 167.0 ppm (N=CH); MS (MAlDI): *m*/*z*: 1099 [*M*]$^+$.

[OC-6-22′-(A,*R*,*R*)]-Bis{4-(4-ethoxyphenyl)-2-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-*N*,*O*,*O*}titanium (6h): Prepared from (*R*)-**4h** (1.058 g, 2.06 mmol) and Ti(O*i*-Pr)$_4$ (0.293 g, 1.03 mmol). The reaction mixture was refluxed for 6 h. The crude product was purified by column chromatography (chloroform, R_f = 0.2). Then it was stirred in *n*-pentane and filtered. Yield: 0.541 g (49 %); m.p. 192.5 °C (decomp.); $[\alpha]_D^{20}$ = +820 (*c* = 1 in chloroform); ^{1}H NMR (500 MHz): δ = 1.40 (t, *J* = 6.9 Hz, 6H, CH_3), 4.03 (q, *J* = 6.9 Hz, 4H, CH_2), 5.53 (d, *J* = 8.5 Hz, 2H, *o*-phenolato-H), 6.41 [s, 2H, PhCH(N)], 6.87–6.94 (m, 6H, aromatic H), 7.00–7.03 (m, 4H, aromatic H), 7.06–7.13 (m, 12H, aromatic H), 7.26–7.28 (m, 6H, aromatic H), 7.33–7.37 (m, 6H, aromatic H), 7.46–7.48 (m, 4H, aromatic H), 8.00 [d, *J* = 8.55 Hz, 4H, aromatic H), 8.72 ppm (s, 2H, N=CH); ^{13}C NMR (125 MHz): δ = 15.28 (CH_3), 63.89 (CH_2), 87.51 [Ph*C*H(N)], 93.37 [Ph$_2$*C*(OTi)], 115.1–158.3 and 164.0 (aromatic C), 166.97 ppm (N=CH); MS (MALDI): *m*/*z*: 1071 [*M*]$^+$.

[OC-6-22′-(C,*S*,*S*)]-Bis{1-{[(2-hydroxy-1,1,2-triphenylethyl)imino]methyl}-2-naphtholato(2−)-*N*,*O*,*O*}titanium (7): Prepared from **5** (0.155 g, 0.35 mmol) and Ti(O*i*-Pr)$_4$ (0.050 g, 0.175 mmol). The reaction mixture was refluxed for 7 h. The product obtained after column chromatography was recrystallized from *n*-hexane. Yield: 0.13 g (80 %); R_f = (chloroform/*n*-hexane, 1:1); m.p. 182.4–183.8 °C; $[\alpha]_D^{20}$ = +205 (*c* = 1 in chloroform); ^{1}H NMR (500 MHz): δ = 6.84 (s, 2H, *o*-naphtholato-H), 6.84–7.96 (m, 42H, aromatic H), 9.02 ppm (s, 2H, N=CH); ^{13}C NMR (125 MHz): δ = 71.55 [Ph$_2$*C*(N)], 79.36 [Ph*C*H(O)], 138.29–144.76 (aromatic *ipso* C), 106.95 [O*C*(naphthyl)], 165.48 ppm (N=CH); MS (FAB, NBA): *m*/*z* (%): 931 (17) [*M*]$^+$, 825 (73), 718 (100); elemental analysis calcd (%) for $C_{62}H_{46}N_2O_4Ti$; C 79.99, H 4.98, N 3.01; found C 79.01, H 5.66, N 2.53.

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