Synthesis and Structure Determination of Novel Chiral Imine-Alkoxytitanium Complexes

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The imines **4** containing a diphenylcarbinol moiety serve as chiral ligands in novel enantiomerically pure imine-alkoxytitanium(IV) complexes. Depending on the molar ratio of the starting materials, imines **4** and titanium tetraisopropoxide, mono-chelated complexes **5** or bis-chelated complexes **6/7** result. The latter are formed diastereoselectively and the isomers **6** are main or exclusive products. Their (*A*) configuration is determined by a crystal-structure analysis of **6b**. The bis-ligand complexes **6** or mixtures of **6/7**, which are found to be remarkably stable, are used as precursors not only for the reactive dihalo complexes **8a/8b** but also for the preparation of the mixed chloroisopropoxytitanium complex **8c**.

Tuned reactivity and improved selectivity are the outstanding features of titanium reagents compared to their polar organometallic counterparts, mainly lithium and magnesium compounds. Although discovered less than two decades ago,[1] these advantages led to a plethora of novel titanium compounds which are used either in a stoichiometric way or catalytically and brought about enormous success in chemo-, diastereo-, and enantioselective transformations.[2] The latter rely mainly on various chiral ligands which enable complexation of the titanium. Especially titanates derived from carbohydrates,[3] tartaric acid,[4] and axially chiral biaryls[5] as well as di- and oligopeptides[6] found wide application in the enantioselective addition of nucleophiles to carbonyl compounds.[7] More recently, imine-alkoxytitanium catalysts were used for enantioselective trimethylsilylcyanations[8] and diketene additions[8b][9] to aldehydes. The corresponding Schiff bases were usually prepared by condensation of salicylaldehyde derivatives with amino alcohols, preferably valinol, *tert*-leucinol,[8b] and 2-amino-1,2-diphenylethanol.[8c] Despite of the success of imine-alkoxytitanium complexes with respect to chemical and optical yields, only a few details are known about the structure of these catalysts.[8a][10]

In this paper, we report for the first time on the synthesis, the isolation and the structure determination of imine-alkoxytitanium complexes which are derived from (*R*)-2-amino-1,1,2-triphenylethanol (**2**), both in the crystalline state and in solution. This chiral auxiliary which is readily available from (*R*)-phenylglycine methyl ester hydrochloride (**1**) contains the diarylhydroxymethyl group discovered to be crucial in many chiral reagents used by us and others.[11]

Results and Discussion

When methyl ester hydrochloride **1**, accessible from (*R*)-phenylglycine,[12] was treated with an excess of phenylmagnesium bromide, the amino alcohol (*R*)-**2** resulted in 66% yield.[13][14] The slow addition of salicylaldehyde (**3a**), 3-*tert*-butyl-2-hydroxybenzaldehyde (**3b**) or the di-*tert*-butyl-substituted homologue **3c** to a cooled solution of **2** resulted in the formation of the imines **4a**, **4b**, and **4c**, respectively. In an analogous way 2-hydroxy-1-naphthaldehyde (**3d**) was converted into the Schiff base **4d**. The condensation of aldehydes with 2-amino alcohols is known to lead in several cases to 1,3-oxazolidines besides imines.[15] The former were, however, not found as side products in the preparation of the Schiff bases **4a**−**d**.

In most cases, chiral titanates used in asymmetric syntheses are generated in situ from achiral titanium precursors by ligand-exchange reactions.[7] The aim of this work, however, was the isolation and structure elucidation or at least the spectroscopic characterization of titanium complexes derived from the imines **4a**−**d**. It was found that the type of titanium compound formed thereby depended strongly on the stoichiometric ratio of the titanate used as achiral precursor and the chiral ligands. Thus, the treatment of titanium tetraisopropoxide in deuteriochloroform with the imines **4a**−**d** in a molar ratio of 1:1 gave solutions of the unstable chelate complexes **5a**−**d** besides two equivalents of 2-propanol, as shown by NMR spectroscopy. The titanium complex **5c** could also be obtained free of solvent and 2-propanol, though in this case it decomposed rapidly even when stored under an inert atmosphere.

When, on the other hand, the starting materials titanium tetraisopropoxide and imines **4a**−**d** were mixed in a molar ratio of 1:2 and stirred in dichloromethane for several hours, TiL_2-type complexes **6/7** resulted and were isolated. One diastereomer was formed predominantly in the cases **4a**, **4b**, and **4d**, and a single isomer arose from the reaction of **4c** with titanium tetraisopropoxide. The diastereomeric

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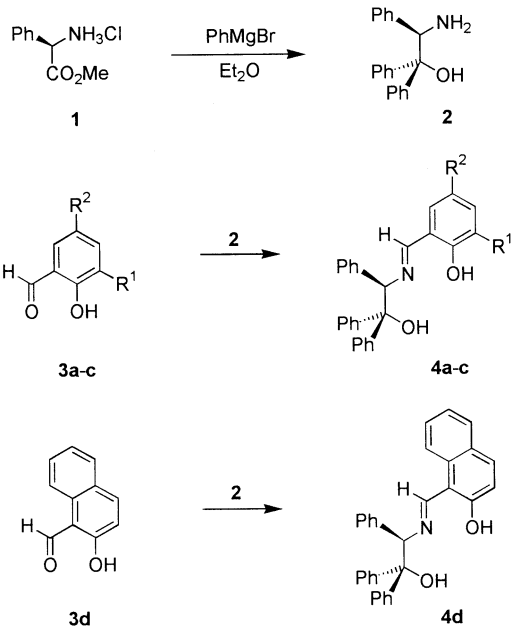
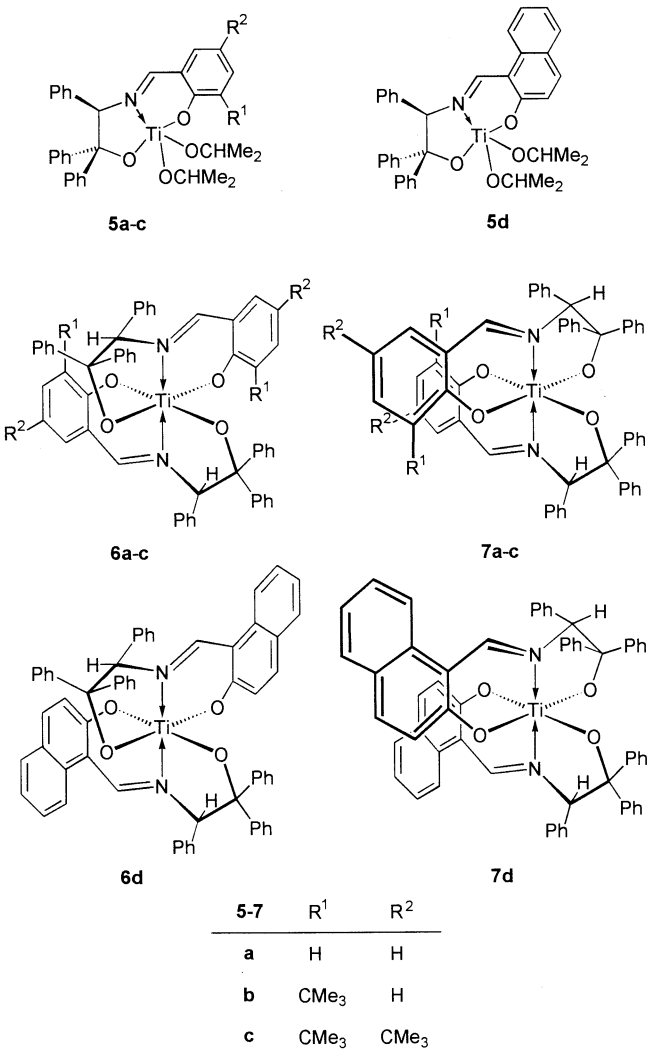


3,4	R^1	R^2
a	H	H
b	CMe_3	H
c	CMe_3	CMe_3



5-7	R^1	R^2
a	H	H
b	CMe_3	H
c	CMe_3	CMe_3

ratio of **6/7** in the crude product mixture could be determined by NMR spectroscopy since the isomers differ significantly in their ^1H and ^{13}C spectra. In addition, the ^1H-NMR spectra of the main products **6a−d** display a characteristic upfield shift of 0.8−1.4 ppm of either the aromatic proton signal or the *tert*-butyl group signal in the *ortho* position of the phenol moiety, compared with the imines **4a−d**, as shown in Table 1. The diastereomers **6a−d** were easily isolated as enantiomerically pure isomers by column chromatography or by crystallization. These complexes exhibited exceptionally high amounts of optical rotation, especially the non-alkyl substituted derivatives **6a** and **6d**. In the case of the isomeric mixture **6b/7b** the minor diastereomer **7b** could also be obtained as pure compound. The bis-chelated complexes **6** and **7** were found to be stable at room temperature in the air.

On the other hand, the decision which geometric arrangement of the ligand atoms had to be assigned to the main product **6** could not be made based on the NMR data. Therefore, the structure of the predominant isomer **6b** was determined by a crystal-structure analysis, the result of which is shown in Figure 1. In a distorted octahedron, the central titanium atom is covalently bound to the phenolic oxygen atom and to the oxygen atom at the tertiary carbon atom of each ligand. In addition, the nitrogen atoms of both imino groups form coordinative bonds to the titanium atom with bond lengths of 214.9(5) and 216.0(5) pm, respectively. For clarity, only the core of the complex **6b**, as determined by the X-ray structure analysis, is shown in Figure 2. Obviously, the terdendate ligand **4b** is bound to the central atom in a meridional manner. Due to this arrangement of the two ligands, octahedral chirality results and the (*A*) configuration has to be assigned to the complex **6b** according to the literature.[16] The obtuse, relatively large Ti−O−C angles, which range from 128.5(4) in a five-membered to 137.7(4)° in a six-membered chelate, indicate a substantial π-donation effect of the oxygen lone pairs. As a consequence, the Ti−O bonds are shortened to average values of 185.9(4) within the five-membered and of 192.5(4)

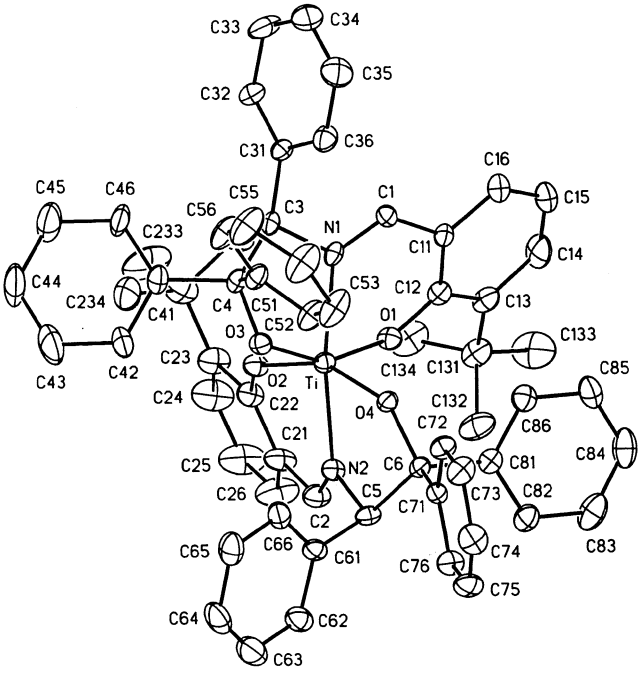
Table 1. Yield and selected proton shift in the imines **4**; diastereomeric ratio of **6/7**; yield, selected proton shift and optical rotation of the titanium complexes **6**

	4			**6/7**	**6**			
	yield [%]	δ_H [ppm] [a]	[b]	d.r.	yield [%]	δ_H [ppm] [a]	[b]	$[\alpha]_D^{20}$[c]
a	81	6.89		83:17	68	5.45		929
b	91		1.38	91:9	75		0.55	296[d]
c	88		1.39	[e]	49		0.55	287[f]
d	93	6.90		87:13	78	5.52		1021

[a] Aromatic proton in the *ortho* position to the phenol moiety. − [b] Protons of the *tert*-butyl group in the *ortho* position to the phenol moiety. − [c] $c = 1$ in chloroform. − [d] Optical rotation of the minor diastereomer **7b**: $[\alpha]_D^{20} = +170$ ($c = 1$ in chloroform). − [e] Only a single isomer was detected. − [f] $T = 25°C$, $c = 0.74$.

within the six-membered rings compared to the calculated value of 210 pm.[17] The two six-membered rings display small but nevertheless remarkable torsions in the conjugated system, and the titanium atom projects out of these chelate planes (e. g. torsion angles N1−Ti−O1−C12 30.7, N2−Ti−O2−C22 −41.2°). The titanium complex **6b** is distinctly monomeric. Both the thermal and the chemical stability of **6b** are easily understood if one takes into account that the metal atom obtains the favoured hexacoordination,[10][18] that the periphery is largely shielded by bulky substituents (aryl and *tert*-butyl), and that neither bond lengths nor angles are extraordinary. The structural properties of **6b** are in accordance with the NMR data so that any dissociation in solution can be excluded. The structures of the complex **6b** as well as of **6a**, **6c**, and **6d** were also confirmed by the CI mass spectra which showed the characteristic titanium isotope pattern of the protonated molecular ion in each case. The configurations of **6a**, **6c**, and **6d** are assigned based on the NMR spectra and by analogy with the complex **6b**.

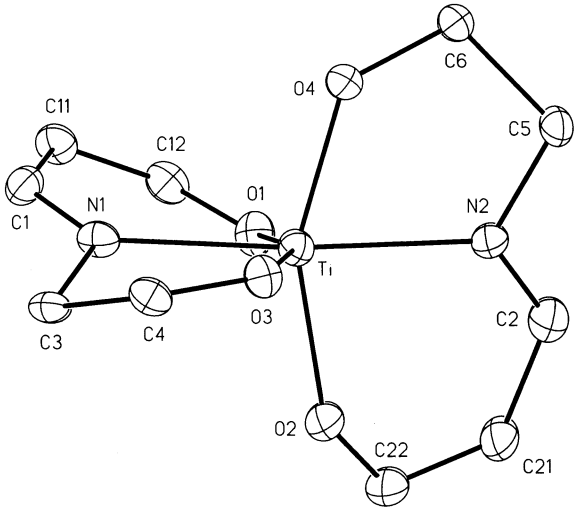
Figure 1. Crystal structure of the compound **6b**·2 $CHCl_3$ (SHELXTL-PLUS[19]; 25% probability displacement ellipsoids; hydrogen atoms and chloroform molecules omitted for clarity)



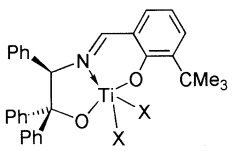
In consequence of theoretical reflections, nine facial diastereomers besides two *mer*-isomers are conceivable by chelation of two homochiral terdentate ligands, each of them possessing three different functional groups.[20] Due to the rigid arrangement in the ligands **4a**−**d** the formation of one or more of the *fac*-isomers seems to be strongly disfavoured. Presumably, the minor diastereomers **7** are formed as meridional isomers with a (*C*) configuration.

The stable bis-chelated complex **6b** and/or its diastereomer **7b** turned out to be suitable, storage-type precursors of the reactive halo complexes **8a**−**c**. Thus, the addition of titanium tetrachloride to a solution of **6b/7b** gave

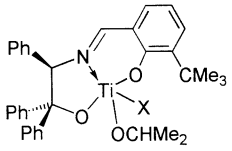
Figure 2. Inner skeleton of the complex **6b**[a]



[a] Selected bond lengths [pm] and angles [°]: Ti−O1 193.8(4), Ti−O2 191.2(4), Ti−N1 214.9(5), Ti−N2 216.0(5), Ti−O3 183.5(4), Ti−O4 188.2(4), N1−C1 128.6(7), N2−C2 128.5(7); O1−Ti−N1 80.7(2), O2−Ti−N2 80.7(2), N1−Ti−O3 74.7(2), N2−Ti−O4 74.7(2), N1−Ti−N2 169.5(2), O1−Ti−O2 87.8(2), O3−Ti−O4 93.9(2), Ti−O1−C12 137.7(4), Ti−O2−C22 135.0(4), Ti−O3−C4 132.2(3), Ti−O4−C6 128.5(4).



8a: X = Cl
8b: X = F



8c

the dichlorotitanate **8a** in quantitative yield. This showed itself to be a highly air- and moisture-sensitive solid but, nevertheless, was characterized by its NMR and CI mass spectra. In an analogous way, the difluoro complex **8b** was accessible from **6b** by treatment with titanium tetrafluoride. Remarkably, *two* fluorine resonances were displayed at δ = 140.0 and 201.2 in the ^{19}F-NMR spectrum at room temperature. When the isomeric mixture of **6b/7b** was allowed to react with dichlorotitanium diisopropoxide, the monochlorotitanate **8c** resulted diastereoselectively, and only a single isomer could be detected by NMR spectroscopy. In addition, the complex **8c** showed the characteristic intensity pattern of $[MNH_4]^+$ in its CI mass spectrum. Thus, the highly reactive, Lewis acidic halo complexes **8a**−**c** are readily available from the novel stable bis-chelated titanates **6/7**. The titanium complexes **8** are expected to be useful catalysts for asymmetric transformations. The corresponding work, the results of which will be published in future communications, is in progress in our laboratory.

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Matthiesen, who detected the protonated molecular ions of several titanium complexes.

Experimental Section

General: All reactions were carried out under dry, purified argon. The solvents were dried according to established procedures and distilled under argon. Diethyl ether and dichloromethane were withdrawn from the receiving flask, which was closed by a septum, with syringes or cannulas. Deuteriochloroform was dried with molecular sieves (4 Å) and kept over beaten silver. 3-*tert*-Butyl-2-hydroxybenzaldehyde (**3b**)[21] and dichlorotitanium diisopropoxide[22] were prepared according to literature procedures. Of the commercially available reagents, solids were employed without further purification and liquids were distilled prior to use. For general remarks concerning reactions under inert atmosphere, see ref.[23] − M.p. (uncorrected): Büchi B-510 and B-540; Reichert Thermovar. − Specific rotations: Perkin-Elmer 341. − IR: Bruker Vector 22 and Perkin-Elmer 1420. − NMR: Bruker DRX 500 and Varian VXR 300; unless stated otherwise, $CDCl_3$ solutions and TMS as internal standard. − EI-MS: Varian MAT 311A. − FAB-MS: Varian MAT 8200. − CI-MS: Finnigan MAT Incos 50. − TLC: Precoated silica gel 60 F_{254} aluminium plates (Merck). − CC: Silica gel 60, mesh size 0.04−0.063 mm (Merck). − Elemental analyses: Mikroanalytisches Laboratorium Beller (Göttingen) and Institut für Pharmazeutische Chemie (Universität Düsseldorf).

Methyl (R)-2-Aminophenylacetate Hydrochloride (**1**): A three-necked flask was equipped with a reflux condenser, a stopper, and a fritted gas-dispersion tube, which allowed the introduction of hydrochloric acid gas via a three-way stopcock. The gas was passed through two gas-washing bottles and the reflux condenser was closed with a three-way cock, which was not only connected to a combined argon/vacuum line but also to a bubble gage filled with silicon oil. The flask was charged with (*R*)-2-aminophenylacetic acid (phenylglycine) (50.2 g, 0.33 mol), and the air in the flask was replaced by argon. Absolute methanol (250 ml) was poured into the flask while a vigorous stream of argon was maintained. The suspension thus formed was cooled to 0°C and subsequently saturated with gaseous hydrogen chloride. In the course of this, the mixture was allowed to reach room temp. and a clear colourless solution formed. The solution was refluxed for 3 h and kept at room temp. overnight. Thereby, a white precipitate formed which was washed with diethyl ether and recrystallized from methanol/diethyl ether (1:1). The crystals were subsequently washed with diethyl ether and dried at 50°C in vacuo (oil pump). Concentration of the mother liquors in the recrystallization described above gave another crop of **1** which was treated in the same way. Total yield: 58.0 g (87%) (ref.[12c] 33%, ref.[12b] 70−85%); m.p. 220.5−221°C (ref.[12c] 222−223°C); $[\alpha]_D^{20} = -115$ (c = 1 in water) {ref.[12c]: $[\alpha]_D^{24} = -119$ (c = 1.09 in water)}. − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2940, 1735, 1560, 1500, 1420, 1380, 1240, 1050, 710. − ^1H NMR (300 MHz, D_2O, [D_4]sodium trimethylsilylpropionate): δ = 3.82 (s, 3 H, CH_3), 5.34 (s, 1 H, 2-H), 7.49−7.57 (m, 5 H, aromatic H).

(R)-2-Amino-1,1,2-triphenylethanol (**2**): A four-necked flask was equipped with an overhead stirrer, a jacketed coil condenser connected to the combined argon/vacuum line, a pressure-equalizing dropping funnel closed by a septum, and a stopper. The flask was charged with magnesium cuttings (63.7 g, 2.62 mol), and the air was replaced by argon. Absolute diethyl ether (100 ml) was added through the dropping funnel and the stopper was removed for the addition of crystalline iodine (approx. 0.05 g). The flask was closed immediately and the mixture was stirred until the brownish color disappeared. Thereafter, neat bromobenzene (7.9 ml, 0.075 mol) was added and the mixture was warmed with a heat gun without stirring. After the start of the reaction, a solution of bromobenzene (273 ml, 2.61 mol) in 500 ml of diethyl ether was added through the dropping funnel within 3 h, in course of that the mixture boiled gently without external heating. After stirring for an additional 3 h at room temp., the mixture was cooled to 0°C and (*R*)-**1** (58.0 g, 0.29 mol) was added in small portions at such a rate that the temp. did not exceed 5°C. After stirring for 6 h at room temp., the reaction mixture was slowly poured into a steel beaker containing 2 kg of ice. The mixture was treated with 6 N hydrochloric acid (500 ml) and stirred vigorously. The hydrochloride of (*R*)-**2** formed thereby as a white precipitate was collected in a suction filter, washed with diethyl ether and dissolved in a 2 N solution of sodium hydroxide in methanol. The solution was concentrated in a rotary evaporator and the oily residue was distributed between dichloromethane (2 l) and water (1 l). The aqueous phase was removed and the organic layer was washed three times with water (500 ml), dried with $MgSO_4$, and concentrated. The white solid residue thus obtained was recrystallized from toluene (75 ml) to give 54.9 g (66%) of (*R*)-**2** (ref.[13] 49%); m.p. 130.5−132°C (ref.[14] 131−133°C); R_f = 0.15 (*n*-hexane/ethyl acetate, 5:1); $[\alpha]_D^{20} = +235$ (c = 1 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 3100, 3080, 3040, 1600, 1580, 1500, 1450, 1180, 920, 750, 740, 705. − ^1H NMR (300 MHz): δ = 1.56 (br. s, 2 H, NH_2), 4.70 (br. s, 1 H, OH), 4.97 (s, 1 H, 2-H), 6.97−7.40 (m, 13 H, aromatic H), 7.71−7.74 (m, 2 H, aromatic H).

General Procedure for the Synthesis of the Imines **4a**−**d**: A two-necked pear-shaped flask was charged with 15.75 mmol of the aldehyde **3**, connected to the combined argon/vacuum line and closed with a septum. The air in the flask was replaced by argon, and absolute methanol (50 ml) was added by syringe. In a second, round-bottom three-necked flask, equipped with a magnetic stirrer, a connection to the combined argon/vacuum line, and two septa, a mixture of (*R*)-**2** (4.34 g, 15.0 mmol), Na_2SO_4 (4.30 g, 30.3 mmol), absolute methanol (40 ml) and dichloromethane (40 ml) was stirred under argon and cooled to −20°C. The solution of the aldehyde **3** was added slowly through a cannula whereby the flask containing the amino alcohol **2** was slightly evacuated. Immediately, the mixture turned bright yellow. During the addition, the temp. as monitored by a thermocouple, introduced through the septum, was not allowed to exceed −18°C. After treating the mixture under the reaction conditions given below, the mixture was filtered at 0°C. (In the case of **4d**, the mixture was diluted with 100 ml of dichloromethane prior to filtration.) Thereupon, the filtrate was concentrated in vacuo at 0°C. In the cases of **4a**, **4b**, and **4d** the solid residue was treated with *n*-pentane (40 ml) and stirred vigorously for 30 min. The solid thus formed was filtered in a sintered glass frit, washed with 40 ml of *n*-pentane and dried at 40°C for 5 h in vacuo (oil pump). Crude **4c** was submitted to CC.

According to this procedure, the following were obtained:

(R)-2-{[(2-Hydroxy-1,2,2-triphenylethyl)imino]methyl}phenol (**4a**): Light yellow solid, prepared in 81% yield by stirring at −18°C for 18 h; m.p. 125−126°C; R_f = 0.4 (*n*-hexane/ethyl acetate, 5:1); $[\alpha]_D^{25} = +207$ (c = 1 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3580 cm^{-1}, 3100, 3080, 1635, 1590, 1500, 1455, 1280, 1060, 765, 705. − ^1H NMR (300 MHz): δ = 2.93 [s, 1 H, $Ph_2C(OH)$], 5.49 [s, 1 H, PhCH(N)], 6.81 (t, $J_{3\text{-H},4\text{-H}} = J_{4\text{-H},5\text{-H}}$ = 7.6 Hz, 1 H, 4-H), 6.89 (d, $J_{5\text{-H},6\text{-H}}$ = 8.2 Hz, 1 H, 6-H), 7.06−7.35 (m, 15 H, aromatic H), 7.58−7.61 (m, 2 H, aromatic H), 8.32 (s, 1 H, NCHAr), 12.82 (s, 1 H, ArOH). − ^{13}C NMR (75 MHz): δ = 78.8 [PhCH(N)], 80.5 [$Ph_2C(OH)$], 116.9 (C-6), 118.7 (C-4), 118.8 (C-2), 126.4−129.7 [aromatic C (Ph)], 131.8, 132.7 (C-3, C-5), 138.2, 143.7, 144.7 [aromatic *ipso*-C (Ph)], 160.6 (C-1), 167.3 (NCHAr). − EI-MS (70 eV);

m/z (%): 393 (1) [M^+], 212 (16), 211 (100) [$M^+ - Ph_2CO$], 210 (27) [$M^+ - Ph_2C(OH)$], 194 (4) [211 − OH], 183 (21), 182 (25) [Ph_2CO], 107 (8) [hydroxytropylium cation], 106 (26), 105 (53) [PhCO and/or $PhC(NH_2)$], 91 (27) [C_7H_7], 77 (27), 51 (9). − $C_{27}H_{23}NO_2$ (393.5): calcd. C 82.42, H 5.89, N 3.56; found C 82.24, H 5.98, N 3.55.

(R)-2-(1,1-Dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)-imino]methyl}phenol (**4b**): Light yellow solid, prepared in 91% yield by stirring at −18 to 0°C for 18 h; m.p. 124.5−126.5°C; R_f = 0.6 (*n*-hexane/ethyl acetate, 6:1); $[\alpha]_D^{25}$ = +193 (*c* = 1 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1}, 3060, 3040, 2960, 1615, 1600, 1495, 1450, 1435, 1265, 1145, 750, 700. − ^1H NMR (300 MHz): δ = 1.38 [s, 9 H, $C(CH_3)_3$], 3.04 [s, 1 H, $Ph_2C(OH)$], 5.44 [s, 1 H, PhCH(N)], 6.74 (t, $J_{3\text{-H},4\text{-H}} = J_{4\text{-H},5\text{-H}}$ = 7.7 Hz, 1 H, 4-H), 6.97 (dd, *J* = 7.7 Hz, $J_{3\text{-H},5\text{-H}}$ = 1.6 Hz, 1 H, 3-H or 5-H), 7.08−7.33 (m, 14 H, aromatic H), 7.59−7.61 (m, 2 H, aromatic H), 8.35 (s, 1 H, NCHAr), 13.24 (s, 1 H, ArOH). − ^{13}C NMR (75 MHz): δ = 29.2 [$C(CH_3)_3$], 34.8 [$C(CH_3)_3$], 79.2 [PhCH(N)], 80.4 [$Ph_2C(OH)$], 117.9 (C-4), 118.6 (C-6), 126.4−130.1 [aromatic C (Ph), C-3, C-5], 137.2, 138.5, 143.7, 144.7 [aromatic *ipso* C (Ph), C-2], 160.0 (C-1), 167.9 (NCHAr). − EI-MS (70 eV); *m/z* (%): 450 (1) [M^+ + 1], 268 (20), 267 (100) [$M^+ - Ph_2CO$], 266 (23) [$M^+ - Ph_2C(OH)$], 183 (26), 182 (12) [Ph_2CO], 163 (2) [(C_4H_9)-hydroxytropylium cation], 107 (12) [hydroxytropylium cation], 106 (63), 105 (46) [PhCO and/or $PhC(NH_2)$], 91 (25) [C_7H_7], 77 (27), 57 (16) [C_4H_9], 51 (7). − $C_{31}H_{31}NO_2$ (449.6): calcd. C 82.82, H 6.95, N 3.12; found C 82.69, H 6.89, N 3.07.

(R)-2,4-Bis-(1,1-dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenol (**4c**): Yellow solid, prepared by stirring at −18°C for 72 h and isolated by CC in 88% yield (*n*-hexane/ethyl acetate, 10:1); m.p. 129.5−130.5°C; R_f = 0.5; $[\alpha]_D^{20}$ = +187 (*c* = 0.5 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1}, 3060, 3040, 2960, 1625, 1600, 1480, 1450, 1390, 1360, 1250, 1170, 750, 700. − ^1H NMR (300 MHz): δ = 1.25 [s, 9 H, $C(CH_3)_3$ bound to C-4], 1.39 [s, 9 H, $C(CH_3)_3$ bound to C-2], 3.06 [s, 1 H, $Ph_2C(OH)$], 5.46 [s, 1 H, PhCH(N)], 6.96 (d, $J_{3\text{-H},5\text{-H}}$ = 2.4 Hz, 1 H, 3-H or 5-H), 7.06−7.35 (m, 14 H, aromatic H), 7.58−7.61 (m, 2 H, aromatic H), 8.40 (s, 1 H, NCHAr), 13.00 (s, 1 H, ArOH). − ^{13}C NMR (75 MHz): δ = 29.4, 31.4 [$C(CH_3)_3$], 34.1, 35.0 [$C(CH_3)_3$], 79.0 [PhCH(N)], 80.4 [$Ph_2C(OH)$], 117.9 (C-6), 126.4−129.6 [aromatic C (Ph), C-3, C-5], 136.6, 138.8, 140.2, 143.9, 145.0 [aromatic *ipso*-C (Ph), C-2, C-4], 157.7 (C-1), 168.5 (NCHAr). − FAB-MS (NBA); *m/z* (%): 506 (6) [M^+ + 1], 324 (24), 323 (100) [$M^+ - Ph_2CO$], 322 (55) [$M^+ - Ph_2C(OH)$], 266 (6) [323 − C_4H_9], 203 (11), 183 (22) [$Ph_2C(OH)$], 167 (12) [Ph_2CH], 106 (17), 105 (41) [PhCO and/or $PhC(NH_2)$], 91 (26) [C_7H_7], 77 (19), 57 (42) [C_4H_9], 51 (5), 41 (20) [C_3H_5]. − $C_{35}H_{39}NO_2$ (505.7): calcd. C 82.72, H 7.96, N 2.84; found C 83.05, H 7.74, N 2.72.

(R)-1-{[(2-Hydroxy-1,2,2-triphenylethyl)imino]methyl}-2-naphthol (**4d**): Yellowish brown solid, prepared in 93% yield by stirring at −18 to 0°C for 18 h; m.p. 124−126°C; R_f = 0.1 (*n*-hexane/ethyl acetate, 5:1); $[\alpha]_D^{25}$ = + 203 (*c* = 1 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1}, 3060, 3035, 1625, 1545, 1495, 1450, 1355, 750, 700. − ^1H NMR (500 MHz): δ = 3.38 [s, 1 H, $Ph_2C(OH)$], 5.57 [s, 1 H, PhCH(N)], 6.90 (d, $J_{3\text{-H},4\text{-H}}$ = 9.5 Hz, 1 H, 3-H), 7.10−7.35 (m, 15 H, aromatic H), 7.58 (d, $J_{5\text{-H},6\text{-H}}$ = 7.6 Hz, 1 H, 5-H), 7.63−7.67 (m, 4 H, aromatic H), 8.80 (s, 1 H, NCHAr), 14.81 (s, 1 H, ArOH). − ^{13}C NMR (75 MHz): δ = 75.4 [PhCH(N)], 80.6 [$Ph_2C(OH)$], 107.6 (C-1), 118.3, 122.9 (C-6, C-8), 123.1 (C-3), 126.4 [aromatic C (Ph)], 126.6 (C-10), 126.8−129.5 [aromatic C (Ph), C-7], 129.1 (C-5), 133.3 (C-9), 136.5 (C-4), 137.5, 143.6, 144.0 [aromatic *ipso*-C (Ph)], 159.6 (NCHAr), 171.9 (C-2).[24] − FAB-MS (NBA); *m/z* (%): 444 (26) [M^+ + 1], 262 (35), 261 (100) [$M^+ - Ph_2CO$], 260 (70) [$M^+ - Ph_2C(OH)$], 244 (11) [261 − OH], 183 (28), 182 (15) [Ph_2CO], 167 (24) [Ph_2CH], 165 (21) fluorenyl cation], 157 (20) [$C_{10}H_6(CH_2)(OH)$], 136 (21), 115 (17), 107 (21) [hydroxytropylium cation], 106 (41), 105 (80) [PhCO and/or $PhC(NH_2)$], 91 (34) [C_7H_7], 77 (75), 51 (18). − $C_{31}H_{25}NO_2$ (443.5): calcd. C 83.94, H 5.69, N 3.16; found C 83.58, H 5.83, N 3.23.

General Procedure for the Preparation of NMR Samples of **5a−d**: Under argon, the corresponding imine **4** (0.34 mmol) was dissolved in 2.5 ml of deuteriochloroform in a 10-ml flask. *Freshly distilled* titanium tetraisopropoxide (0.1 ml, 0.34 mmol) was added by syringe, and the mixture was stirred for 12 h at room temp. A part of this solution (0.7 ml) was transferred into an argon-filled NMR tube. In all cases no signals arising from the corresponding imine **4** could be detected and the diastereomeric mixture of **6/7** was only obtained as byproduct in small amounts besides unreacted titanium tetraisopropoxide (usually < 4%; in the case of **5d** 39%). After the removal of the solvent under reduced pressure (oil pump), **5c** was kept in vacuo for 1 h, after which the complex was free of solvent and 2-propanol and could also be characterized spectroscopically.

The following NMR data were obtained:

(R)-{2-{[(2-Hydroxy-1,2,2-triphenylethyl)imino]methyl}-phenolato(2−)-N,O,O′}titanium Bis-1-methylethoxide (**5a**·2 *i*PrOH): ^1H NMR (500 MHz): δ = 1.13 [d, *J* = 6.0 Hz, 6 H, $OCH(CH_3)_2$], 1.20 [d, *J* = 6.0 Hz, 12 H, $HOCH(CH_3)_2$], 1.30 [d, *J* = 6.0 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.34 [d, *J* = 6.0 Hz, 3 H, $OCH(CH_3)(CH_3)$], 4.01 [m, 2 H, $HOCH(CH_3)_2$], 4.68 [sept, *J* = 6.0 Hz, 1 H, $OCH(CH_3)_2$], 4.89 [sept, *J* = 6.0 Hz, 1 H, $OCH(CH_3)_2$], 5.98 [s, 1 H, PhCH(N)], 6.75−7.40 (m, 17 H, aromatic H), 7.73−7.75 (m, 2 H, aromatic H), 8.48 (s, 1 H, NCHAr). − ^{13}C NMR (125 MHz): δ = 25.4 [$HOCH(CH_3)_2$], 25.8, 25.9 [$OCH(CH_3)_2$], 64.4 [$HOCH(CH_3)_2$], 78.6, 79.2 [$OCH(CH_3)_2$], 87.5 [PhCH(N)], 90.6 [$Ph_2C(OTi)$], 118.1, 119.0 (C-4, C-6), 121.0 (C-2), 125.7−129.3 [aromatic C (Ph)], 133.2, 135.7 (C-3, C-5), 140.2, 146.0, 148.3 [aromatic *ipso*-C (Ph)], 164.3 (C-1), 166.3 (NCHAr).

(R)-{2-(1,1-Dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-N,O,O′}titanium Bis-1-methylethoxide (**5b**·2 *i*PrOH): ^1H NMR (500 MHz): δ = 1.06 [d, *J* = 6.0 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.20 [d, *J* = 6.0 Hz, 12 H, $HOCH(CH_3)_2$], 1.23 [d, *J* = 6.0 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.31−1.32 [m, 6 H, $OCH(CH_3)_2$], 1.45 [s, 9 H, $C(CH_3)_3$], 4.01 [m, 2 H, $HOCH(CH_3)_2$], 4.72 [m, 1 H, $OCH(CH_3)_2$], 4.88 [m, 1 H, $OCH(CH_3)_2$], 5.95 [s, 1 H, PhCH(N)], 6.69−7.42 (m, 16 H, aromatic H), 7.67−7.68 (m, 2 H, aromatic H), 8.46 (s, 1 H, NCHAr). − ^{13}C NMR (125 MHz): δ = 25.4 [$HOCH(CH_3)_2$], 25.0, 26.0, 26.06, 26.12 [$OCH(CH_3)_2$], 29.5 [$C(CH_3)_3$], 35.0 [$C(CH_3)_3$], 64.4 [$HOCH(CH_3)_2$], 78.1, 78.9 [$OCH(CH_3)_2$], 86.8 [PhCH(N)], 90.7 [$Ph_2C(OTi)$], 117.4 (C-4), 121.4 (C-6), 125.6−129.4 [aromatic C (Ph)], 131.6, 132.4 (C-3, C-5), 139.0, 140.4, 146.6, 149.0 [aromatic *ipso*-C (Ph), C-2], 163.7 (C-1), 166.8 (NCHAr).

(R)-{2,4-Bis-(1,1-dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-N,O,O′}titanium Bis-1-methylethoxide (**5c**): ^1H NMR (300 MHz): δ = 1.07 [d, *J* = 6.1 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.22 [d, *J* = 6.1 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.26 [s, 9 H, $C(CH_3)_3$ bound to C-4], 1.32 [d, *J* = 6.1 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.33 [d, *J* = 6.1 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.47 [s, 9 H, $C(CH_3)_3$ bound to C-2], 4.74 [sept, *J* = 6.1 Hz, 1 H, $OCH(CH_3)_2$], 4.90 [sept, *J* = 6.1 Hz, 1 H, $OCH(CH_3)_2$], 5.96 [s, 1 H, PhCH(N)], 6.90−7.51 (m, 15 H, aromatic H), 7.68−7.70 (m, 2 H, aromatic H), 8.50 (s, 1 H, NCHAr). − ^{13}C NMR (75 MHz): δ = 26.0 [$OCH(CH_3)(CH_3)$], 26.1 [$OCH(CH_3)_2$], 26.2 [$OCH(CH_3)(CH_3)$], 29.6, 31.3 [$C(CH_3)_3$], 34.1,

35.2 [$C(CH_3)_3$], 77.9, 78.7 [$OCH(CH_3)_2$], 86.9 [PhCH(N)], 90.6 [$Ph_2C(OTi)$], 120.5 (C-6), 125.6−130.6 [aromatic C (Ph), C-3, C-5], 138.2, 139.6, 140.6, 146.7, 149.1 [aromatic *ipso*-C (Ph), C-2, C-4], 161.9 (C-1), 167.2 (NCHAr).

(R)-{1-{[(2-Hydroxy-1,2,2-triphenylethyl)imino]methyl}-2-naphtholato(2−)-N,O,O'}titanium Bis-1-methylethoxide (**5d**·2 *i*PrOH): − ^{1}H NMR (500 MHz): δ = 1.06 [m, 6 H, $OCH(CH_3)_2$], 1.19 [d, *J* = 5.7 Hz, 12 H, $HOCH(CH_3)_2$], 1.36 [d, *J* = 5.7 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.40 [d, *J* = 5.7 Hz, 3 H, $OCH(CH_3)(CH_3)$], 3.99 [sept, *J* = 5.7 Hz, 2 H, $HOCH(CH_3)_2$], 4.55 [m, *J* = 5.7 Hz, 1 H, $OCH(CH_3)_2$], 4.95 [m, *J* = 5.7 Hz, 1 H, $OCH(CH_3)_2$], 6.13 [s, 1 H, PhCH(N)], 6.90−7.98 (m, 21 H, aromatic H), 9.36 (s, 1 H, NCHAr).

General Procedure for the Synthesis of the Bis-Chelated Complexes **6a**−**d**: A two-necked flask, equipped with a magnetic stirrer, a reflux condenser with a connection to the combined argon/vacuum line, and a septum, was charged with 2.05 mmol of the corresponding imine **4**. The air in the flask was replaced by argon, and absolute dichloromethane (6 ml) was added. *Freshly distilled* titanium tetraisopropoxide (0.3 ml, 1.02 mmol) was injected, and the solution was treated according to the reaction conditions given below. The solvent was removed in a rotary evaporator and the solid residue was either submitted to crystallization (**6c**) or to CC (**6a**, **6b**, and **6d**), both methods resulting in the isolation of the enantiomerically pure main products **6**. For the isolation of the pure diastereomeric mixtures of **6**/**7**, an alternative procedure to CC can be followed: The residue was suspended in 10 ml of methanol (**6b**, **6d**) or *n*-hexane (**6a**) and stirred vigorously for 30 min. Thereupon, the solid was collected in a glass frit, washed with 10 ml of the suspension agent used before and dried at 40°C in vacuo for 6 h.

According to this procedure, the following were obtained:

[OC-6-22'-(A),(R),(R)]-Bis-{2-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-N,O,O'}titanium (**6a**): Bright yellow solid, prepared in 68% yield by stirring 12 h at room temp.; m.p. 239−241°C; R_f = 0.6 (chloroform/*n*-hexane, 3.5:1); $[\alpha]_D^{20}$= +929 (*c* = 1 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3035, 1620, 1545, 1445, 1390, 1310, 1260, 1040, 910, 805, 755, 700. − ^{1}H NMR (500 MHz): δ = 5.45 (d, $J_{5\text{-H},6\text{-H}}$ = 8.8 Hz, 2 H, 6-H), 6.38 [s, 2 H, PhCH(N)], 6.59 (t, $J_{3\text{-H},4\text{-H}} = J_{4\text{-H},5\text{-H}}$ = 7.6 Hz, 2 H, 4-H), 6.92−7.10 (m, 20 H, aromatic H), 7.16 (d, $J_{3\text{-H},4\text{-H}}$ = 7.6 Hz, 2 H, 3-H), 7.19−7.46 (m, 4 H, aromatic H), 7.98−7.99 (m, 4 H, aromatic H), 8.64 (s, 2 H, NCHAr). − ^{13}C NMR (75 MHz): δ = 87.0 [PhCH(N)], 92.9 [$Ph_2C(OTi)$], 117.0 (C-4), 118.5 (C-6), 120.0 (C-2), 125.5−129.6 [aromatic C (Ph)], 133.0 (C-3), 134.8 (C-5), 141.7, 146.8, 146.9 [aromatic *ipso*-C (Ph)], 164.3 (C-1), 166.3 (NCHAr). − CI-MS (NH_3); *m*/z (%): 831 (100) [M^+ + 1], 217 (51) [$Ph_2CO(NH_3)(NH_4)$], 200 (43) [$Ph_2CO(NH_4)$], 183 (5) [$Ph_2C(OH)$], 123 (14) [$PhCO(NH_4)$]. − EI-MS (70 eV); *m*/*z* (%): 648 (47) [M^+ − Ph_2CO], 466 (69) [M^+ − 2 (Ph_2CO)], 375 (23) [466 − C_7H_7], 324 (11) [M^+ − Ph_2CO; *z* = 2], 256 (40), 183 (10), 182 (39) [Ph_2CO], 165 (15) fluorenyl cation], 106 (9), 105 (63) [PhCO and/or $PhC(NH_2)$], 91 (11) [C_7H_7], 77 (29), 57 (98) [C_4H_9], 51 (12), 44 (83), 43 (100) [C_3H_7]. − $C_{54}H_{42}N_2O_4Ti$ (830.8): calcd. C 78.05, H 5.10, N 3.37; found C 77.78, H 5.23, N 3.63. − Intensity pattern of [M^+ + 1]; *m*/*z* (calcd., found [%]): 835 (2.3, 3), 834 (9.5, 10), 833 (29.5, 30), 832 (66.2, 68), 831 (100.0, 100), 830 (15.9, 17), 829 (10.0, 11).

[OC-6-22'-(A),(R),(R)]-Bis-{2-(1,1-dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-N,O,O'}titanium (**6b**): Bright yellow solid, prepared in 75% yield by stirring 12 h at room temp. In order to obtain a crystalline product, a sample was dissolved in the minimum amount of methanol and chloroform (1:1). When half of the solvent had evaporated at room temp., yellow crystals formed which were suitable for a crystal-structure analysis. M.p. 283−284°C; R_f = 0.8 (chloroform/*n*-hexane, 2:1); $[\alpha]_D^{20}$ = +296 (*c* = 1 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 2955, 2865, 1615, 1550, 1420, 1390, 1300, 1200, 1045, 910, 875, 755, 705. − ^{1}H NMR (500 MHz): δ = 0.55 [s, 18 H, $C(CH_3)_3$], 6.48 [d, *J* = 1.3 Hz, 2 H, $PhCH(NCHAr)$], 6.63 (t, $J_{3\text{-H},4\text{-H}} = J_{4\text{-H},5\text{-H}}$ = 7.6 Hz, 2 H, 4-H), 6.95−7.13 (m, 22 H, aromatic H), 7.51−7.60 (m, 12 H, aromatic H), 8.42 [d, *J* = 1.3 Hz, 2 H, $PhCH(NCHAr)$]. − ^{13}C NMR (75 MHz): δ = 28.5 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$], 89.0 [PhCH(N)], 93.1 [$Ph_2C(OTi)$], 117.0 (C-4), 121.8 (C-6), 125.7−130.4 [aromatic C (Ph)], 131.8, 132.2 (C-3, C-5), 137.6, 140.4, 147.2, 148.2 [aromatic *ipso*-C (Ph), C-2], 164.4 (C-1), 164.6 (NCHAr). − CI-MS (NH_3); *m*/*z* (%): 943 (100) [M^+ + 1], 217 (38) [$Ph_2CO(NH_3)(NH_4)$], 200 (30) [$Ph_2CO(NH_4)$], 183 (4) [$Ph_2C(OH)$], 123 (6) [$PhCO(NH_4)$]. − EI-MS (70 eV); *m*/*z* (%): 760 (46) [M^+ − Ph_2CO], 578 (65) [M^+ − 2 (Ph_2CO)], 380 (21) [M^+ − Ph_2CO; *z* = 2], 183 (6), 182 (29) [Ph_2CO], 165 (10) fluorenyl cation], 106 (9), 105 (100) [PhCO and/or $PhC(NH_2)$], 91 (20) [C_7H_7], 77 (64), 64 (34), 57 (56) [C_4H_9], 51 (30), 43 (30) [C_3H_7]. − $C_{62}H_{58}N_2O_4Ti$ (943.0): calcd. C 78.95, H 6.20, N 2.97; found C 78.64, H 6.24, N 2.99. − Intensity pattern of [M^+ + 1]; *m*/*z* (calcd., found [%]): 947 (3.2, 4), 946 (12.2, 12), 945 (35.3, 34), 944 (74.3, 73), 943 (100.0, 100), 942 (16.5, 19), 941 (9.8, 11).

[OC-6-22'-(A),(R),(R)]-Bis-{2,4-bis-(1,1-dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-N,O,O'}titanium (**6c**): Bright yellow crystals, prepared in 49% yield by heating to reflux for 4 h and crystallization in methanol/chloroform (2:1); m.p. 279.5−281°C; $[\alpha]_D^{25}$= +287 (*c* = 0.74 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3025, 2960, 2870, 1620, 1540, 1310, 1255, 1175, 1030, 850, 760, 700. − ^{1}H NMR (500 MHz): δ = 0.55 [s, 18 H, $C(CH_3)_3$ bound to C-2], 1.24 [s, 18 H , $C(CH_3)_3$ bound to C-4], 6.45 [s, 2 H, PhCH(N)], 6.94−6.99 (m, 12 H, aromatic H), 7.05 [d, $J_{3\text{-H},5\text{-H}}$ = 2.5 Hz, 2 H, 3-H or 5-H), 7.10−7.12 (m, 6 H, aromatic H), 7.22 (d, $J_{3\text{-H},5\text{-H}}$ = 2.5 Hz, 2 H, 3-H or 5-H), 7.50−7.60 (m, 12 H, aromatic H), 8.42 (s, 2 H, NCHAr). − ^{13}C NMR (125 MHz): δ = 28.7, 31.4 [$C(CH_3)_3$], 34.0, 34.4 [$C(CH_3)_3$], 88.9 [PhCH(N)], 93.0 [$Ph_2C(OTi)$], 121.1 (C-6), 125.6−127.1 [aromatic C (Ph)], 127.4 (C-3 or C-5), 127.9−128.1 [aromatic C (Ph)], 130.3 (C-3 or C-5), 130.5 [aromatic C (Ph)], 136.8, 139.1, 140.6, 147.4, 148.4 [aromatic *ipso*-C (Ph), C-2, C-4], 162.7 (C-1), 164.8 (NCHAr). − CI-MS (NH_3); *m*/*z* (%): 1055 (48) [M^+ + 1], 217 (32) [$Ph_2CO(NH_3)(NH_4)$], 200 (100) [$Ph_2CO(NH_4)$], 183 (23) [$Ph_2C(OH)$], 123 (17) [$PhCO(NH_4)$], 106 (20) [PhCHO]. − EI-MS (70 eV); *m*/*z* (%): 873 (100) [MH^+ − Ph_2CO], 691 (71) [MH^+ − 2 (Ph_2CO)], 436.5 (38) [MH^+ − Ph_2CO; *z* = 2], 182 (12) [Ph_2CO], 105 (39) [PhCO and/or $PhC(NH_2)$], 83 (62), 77 (21), 57 (30) [C_4H_9]. − $C_{70}H_{74}N_2O_4Ti$ (1055.2). − Intensity pattern of [M^+ + 1]; *m*/*z* (calcd., found [%]): 1059 (4.4, 4), 1058 (15.5, 13), 1057 (41.6, 37), 1056 (82.2, 75), 1055 (100.0, 100), 1054 (17.2, 15), 1053 (9.7, 9).

[OC-6-22'-(A),(R),(R)]-Bis-{1-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}-2-naphtholato(2−)-N,O,O'}titanium (**6d**): Bright yellow solid, prepared in 78% yield by heating to reflux for 4 h; m.p. 200.5−202°C; R_f = 0.6 (chloroform/*n*-hexane, 2:1), $[\alpha]_D^{20}$ = 1021 (*c* = 1 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3030, 1620, 1605, 1540, 1455, 1400, 1360, 1340, 1195, 1045, 825, 750, 700. − ^{1}H NMR (300 MHz): δ = 5.52 (d, $J_{3\text{-H},4\text{-H}}$ = 9.1 Hz, 2 H, 3-H), 6.44 [s, 2 H, PhCH(N)], 6.84−7.49 (m, 36 H, aromatic H), 7.96−8.00 (m, 4 H, aromatic H), 9.48 (s, 2 H, NCHAr). − ^{13}C NMR (75 MHz): δ = 88.0 [PhCH(N)], 93.2 [$Ph_2C(OTi)$], 110.6 (C-1), 119.0 (C-6 or C-8), 121.9 (C-3), 122.9 (C-6 or C-8), 125.6−129.6

[aromatic C (Ph), C-5, C-7], 127.3 (C-10), 133.2 (C-9), 135.7 (C-4), 142.0, 146.9, 147.0 [aromatic *ipso*-C (Ph)], 160.8 (NCHAr), 165.9 (C-2).[24] − CI-MS (NH_3); *m/z* (%): 931 (100) [$M^+ + 1$], 217 (41) [$Ph_2CO(NH_3)(NH_4)$], 200 (91) [$Ph_2CO(NH_4)$], 183 (19) [$Ph_2C(OH)$], 123 (26) [$PhCO(NH_4)$]. − FAB-MS (NBA); *m/z* (%): 931 (7) [$M^+ + 1$], 853 (2) [$M^+ - Ph$], 748 (29) [$M^+ - Ph_2CO$], 671 (13) [$M^+ - Ph_3CO$], 566 (65) [$M^+ - 2\,(Ph_2CO)$], 492 (14), 462 (15) [566 − PhCNH], 359 (29), 207 (50), 157 (49) [$C_{10}H_6(CH_2)(OH)$], 106 (26), 105 (33) [PhCO and/or $PhC(NH_2)$], 91 (56) [C_7H_7], 77 (100), 51 (45). − $C_{62}H_{46}N_2O_4Ti$ (930.9). − Intensity pattern of [$M^+ + 1$]; *m/z* (calcd., found [%]): 935 (3.2, 5), 934 (12.1, 17), 933 (35.2, 38), 932 (74.2, 72), 931 (100.0, 100), 930 (16.5, 18), 929 (9.8, 10).

Minor Diastereomer [OC-6-22'-(C),(R),(R)]-Bis-{2-(1,1-dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}-phenolato(2−)-N,O,O'}titanium (**7b**): Dec.p. 272−273°C; R_f = 0.4 (chloroform/*n*-hexane, 2:1); $[\alpha]_D^{20}$ = +170 (*c* = 1 in chloroform). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 2955, 2865, 1620, 1555, 1420, 1390, 1300, 1200, 1005, 875, 755, 705. − ^1H NMR (500 MHz): δ = 1.14 [s, 18 H, $C(CH_3)_3$], 6.67 [d, *J* = 1.9 Hz, 2 H, PhC*H*(NCHAr)], 6.68 (t, $J_{3\text{-H},4\text{-H}} = J_{4\text{-H},5\text{-H}}$ = 7.6 Hz, 2 H, 4-H), 6.70−6.74 (m, 4 H, aromatic H), 7.00−7.23 (m, 24 H, aromatic H), 7.33−7.34 (m, 4 H, aromatic H), 7.37 (dd, *J* = 7.6 Hz, $J_{3\text{-H},5\text{-H}}$ = 1.9 Hz, 2 H, 3-H or 5-H), 8.00 [d, *J* = 1.9 Hz, 2 H, PhCH(NC*H*Ar)]. − ^{13}C NMR (75 MHz): δ = 29.8 [$C(CH_3)_3$], 35.0 [$C(CH_3)_3$], 85.8 [PhCH(N)], 94.8 [$Ph_2C(OTi)$], 117.3 (C-4), 121.7 (C-6), 126.4−132.1 [aromatic C (Ph)], 132.2, 132.3 (C-3, C-5), 136.1, 137.8, 145.6, 147.9 [aromatic *ipso*-C (Ph), C-2], 161.7 (NCHAr), 164.0 (C-1).

(R)-Dichloro-{2-(1,1-dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-N,O,O'}titanium (**8a**): A solution of the titanium complex **6b** and/or **7b** (107.5 mg, 0.114 mmol) in 3 ml of absolute dichloromethane was stirred under argon at −78°C. A 0.23 M solution of titanium tetrachloride (0.5 ml, 0.114 mmol) in dichloromethane, also prepared under argon, was added slowly by syringe at such a rate that the temp. did not exceed −70°C. The deeply orange-coloured mixture formed immediately was allowed to reach room temp. within 2 h. Subsequently, the solvent was removed in vacuo and the residue was exposed to oil-pump vacuum for 30 min to give quantitatively 122 mg solid, orange **8a** which had to be stored under argon. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3055, 3015, 2955, 1600, 1555, 1445, 1420, 1391, 1000, 885, 755, 710, 700. − ^1H NMR (500 MHz): δ = 1.54 [s, 9 H, $C(CH_3)_3$], 6.49 [s, 1 H, PhCH(N)], 6.98−7.38 (m, 15 H, aromatic H), 7.65 (d, *J* = 7.6 Hz, 1 H, 3-H or 5-H), 7.76−7.77 (m, 2 H, aromatic H), 8.70 (s, 1 H, NCHAr). − ^{13}C NMR (125 MHz): δ = 29.8 [$C(CH_3)_3$], 35.2 [$C(CH_3)_3$], 90.3 [PhCH(N)], 97.8 [$Ph_2C(OTi)$], 122.0 (C-4), 122.7 (C-6), 126.4−129.3 [aromatic C (Ph)], 132.2, 135.0 (C-3, C-5), 138.4, 138.6, 143.2, 145.6 [aromatic *ipso*-C (Ph), C-2], 163.3 (C-1), 167.4 (NCHAr). − CI-MS (NH_3); *m/z* (%): 583 (8) [$M^+ + NH_4$], 566 (2) [$M^+ + 1$], 432 (9), 274 (17), 256 (5), 217 (52) [$Ph_2CO(NH_3)(NH_4)$], 200 (100) [$Ph_2CO(NH_4)$], 183 (45) [$Ph_2C(OH)$], 123 (5) [$PhCO(NH_4)$], 111 (23). − $C_{31}H_{29}Cl_2NO_2Ti$ (566.4). − Intensity pattern of [$M^+ + NH_4$]; *m/z* (calcd., found [%]): 588 (6.5, 7), 587 (20.0, 20), 586 (30.6, 30), 585 (76.7, 78), 584 (48.0, 51), 583 (100.0, 100), 582 (13.0, 14), 581 (9.7, 12).

(R)-Difluoro-{2-(1,1-dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-N,O,O'}titanium (**8b**): A 10-ml flask, equipped with a magnetic stirrer and a connection to the combined argon/vacuum line, was charged with **6b** (94.3 mg, 0.1 mmol) and closed with a septum. The air in the flask was replaced by argon, and absolute dichloromethane (3 ml) was injected by syringe. In a second flask, titanium tetrafluoride (13.6 mg, 0.11 mmol) was dissolved in absolute acetonitrile (1 ml) under argon.[25] The latter solution was added dropwise by syringe to the solution of **6b** at room temp. After stirring for 12 h, the solvent was removed under reduced pressure and the solid, yellow residue was exposed to oil pump vacuum for 1 h at room temp. Yield: 105 mg (99%). − ^1H NMR {500 MHz, [D_3]acetonitrile}: δ = 1.34 [s, 9 H, $C(CH_3)_3$], 6.54 [s, 1 H, PhCH(N)], 6.84−7.20 (m, 10 H, aromatic H), 7.31−7.37 (m, 3 H, aromatic H), 7.47 (dd, *J* = 7.5 Hz, $J_{3\text{-H},5\text{-H}}$ = 1.7 Hz, 1 H, 3-H or 5-H), 7.57−7.69 (m, 4 H, aromatic H), 8.82 (s, 1 H, NCHAr). − ^{13}C NMR {125 MHz, [D_3]acetonitrile}: δ = 29.6 [$C(CH_3)_3$], 35.4 [$C(CH_3)_3$], 85.8 [PhCH(N)], 94.0 [$Ph_2C(OTi)$], 120.2 (C-4), 123.1 (C-6), 126.5−130.8 [aromatic C (Ph)], 133.4, 133.8 (C-3, C-5), 138.0, 140.9, 147.0, 148.2 [aromatic *ipso*-C (Ph), C-2], 162.4 (C-1), 167.8 (NCHAr). − ^{19}F NMR {470 MHz, [D_3]acetonitrile}: δ = 140.0 (s, 1 F), 201.2 (s, 1 F). − CI-MS (NH_3); *m/z* (%): 568 (82) [$M^+ + NH_3 + NH_4$], 551 (70) [$M^+ + NH_4$], 534 (20) [$M^+ + 1$], 462 (17), 274 (4), 259 (8), 217 (95) [$Ph_2CO(NH_3)(NH_4)$], 200 (100) [$Ph_2CO(NH_4)$], 183 (14) [$Ph_2C(OH)$], 136 (14), 123 (9) [$PhCO(NH_4)$], 111 (48). − $C_{31}H_{29}F_2NO_2Ti$ (533.5). − Intensity pattern of [$M^+ + NH_4$]; *m/z* (calcd., found [%]): 554 (3.8, 3), 553 (15.8, 12), 552 (42.3, 57), 551 (100.0, 100), 550 (13.8, 14), 549 (10.4, 13).

(R)-Chloro-{2-(1,1-dimethylethyl)-6-{[(2-hydroxy-1,2,2-triphenylethyl)imino]methyl}phenolato(2−)-N,O,O'}titanium 1-Methylethoxide (**8c**): The synthesis was effected by analogy with the preparation of the dichlorotitanium complex **8a**. In place of titanium tetrachloride, the diastereomeric mixture of **6b/7b** (94.3 mg, 0.1 mmol) was treated with a 0.1 M solution of dichlorotitanium diisopropoxide (1.1 ml, 0.11 mmol) in dichloromethane. Thereafter, the light-orange-coloured mixture was allowed to reach room temp. within 6 h. After the removal of the solvent, the residue was dried in vacuo for 1 h to give solid, orange **8c** in 67% yield (byproducts: 25% dichlorotitanium complex **8a**, unreacted **6b/7b**). − ^1H NMR (500 MHz): δ = 1.10 [d, *J* = 5.7 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.20 [d, *J* = 5.7 Hz, 3 H, $OCH(CH_3)(CH_3)$], 1.46 [s, 9 H, $C(CH_3)_3$], 4.86 [sept, *J* = 5.7 Hz, 1 H, $OCH(CH_3)_2$], 6.10 [s, 1 H, PhCH(N)], 6.85−7.83 (m, 18 H, aromatic H), 8.58 (s, 1 H, NCHAr). − CI-MS (NH_3); *m/z* (%): 607 (3) [$M^+ + NH_4$], 590 (12) [$M^+ + 1$], 274 (9), 257 (4), 217 (48) [$Ph_2CO(NH_3)(NH_4)$], 200 (100) [$Ph_2CO(NH_4)$], 183 (36) [$Ph_2C(OH)$], 123 (8) [$PhCO(NH_4)$], 111 (56), 105 (12) [PhCO]. − $C_{34}H_{36}ClNO_3Ti$ (590.0). − Intensity pattern of [$M^+ + 1$]; *m/z* (calcd., found [%]): 595 (1.5, 2), 594 (6.2, 6), 593 (18.4, 16), 592 (48.3, 43), 591 (48.2, 42), 590 (100.0, 100), 589 (13.6, 10), 588 (10.0, 9).

Crystal-Structure Analysis of **6b**·*2 CHCl*$_3$:[26] − Crystal data: $C_{64}H_{60}Cl_6N_2O_4Ti$ (1181.7), *F*(000) = 1228, lattice parameters from 32 reflections (20° < 2Θ < 24°): *a* = 1316.7(4), *b* = 1863.0(4), *c* = 1358.1(3) pm, β = 115.78(4)°, *V* = 2.9999(13) nm^3, *Z* = 2, $d_{calcd.}$ = 1.308, d_{found} = 1.311 gcm^{-3}, monoclinic, $P2_1$ (no. 4). − Data collection: Siemens $P2_1$/P3 diffractometer, Mo-K_α (λ = 71.073 pm), graphite monochromator, crystal size 0.60 × 0.40 × 0.30 mm, $T \approx$ 300 K, ω/2Θ scan, 4° ≤ 2Θ ≤ 53°, indices $0 \le h \le 16$; $0 \le k \le 23$; $-17 \le l \le 15$, reflections: 6663 collected, 6405 independent (R_{int} = 0.04), 3510 observed ($I > 2\sigma_I$), μ = 0.46 mm^{-1}, absorption correction not applied. − Structural analysis and refinement: The measured density (by flotation) pointed to the addition of two molecules of $CHCl_3$ per complex, which was confirmed by the crystal structure. However, the strong decrease of the intensities in dependence of Θ together with the low percentage of observed reflections indicated a disorder within the structure mainly caused by the solvent. The structure was solved by automatic interpretation of the Patterson function[19] localizing the central octahedron. The com-

plex was completed in the usual way and at a later stage the two molecules of the solvent had to be added. During the final refinement by full-matrix least squares on F^2,[27] using anisotropic displacement parameters and fixed H atoms, a twofold disorder of the Cl atoms with restraints to their geometry had to be introduced. The refinement of 751 parameters converged at $wR2 = 0.128$ (6400 reflections) and $R1 = 0.055$ (3510 observed reflections). The description of the disorder by split positions (one chloroform molecule 0.64:0.36, the other 0.50:0.50) remains unsatisfactory with respect to values of U_{eq} up to 0.28 ($pm^2 \times 10^{-4}$). The residual electron density ranged from -0.39 to $0.45 \cdot 10^{-6}$ epm^{-3}.

[1] M. T. Reetz in *Topics in Current Chemistry* (Ed.: F. L. Boschke), Springer, Berlin, **1982**, vol. 106, pp. 1−54; B. Weidmann, D. Seebach, *Angew. Chem.* **1983**, *95*, 12−26; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 31−45.

[2] D. Seebach, B. Weidmann, L. Widler in *Modern Synthetic Methods* (Ed.: R. Scheffold), Salle, Frankfurt, **1983**, vol. 3, pp. 217−353; D. Seebach, A. K. Beck, M. Schiess, L. Widler, A. Wonnacott, *Pure Appl. Chem.* **1983**, *55*, 1807−1822; M. T. Reetz, *ibid.* **1985**, *57*, 1781−1788; M. T. Reetz, *Organotitanium Reagents in Organic Synthesis*, Springer, Berlin, **1986**; D. Hoppe in *Methoden Org. Chem. (Houben-Weyl) 4th ed.* **1952** −, vol. E 21b, pp. 1551−1583.

[3] M. Riediker, R. O. Duthaler, *Angew. Chem.* **1989**, *101*, 488−490; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 494−495; M. Riediker, A. Hafner, U. Piantini, G. Rihs, A. Togni, *Angew. Chem.* **1989**, *101*, 493−495; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 499−500; A. Hafner, R. O. Duthaler in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), Wiley, Chichester, **1995**, pp. 1104−1106 and references given therein.

[4] R. Dahinden, A. K. Beck, D. Seebach in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), Wiley, Chichester, **1995**, pp. 2167−2170; A. Hafner, R. O. Duthaler, *ibid.* **1995**, pp. 1106−1108.

[5] K. Mikami, S. Matsukawa, *J. Am. Chem. Soc.* **1994**, *116*, 4077−4080; K. Mikami in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), Wiley, Chichester **1995**, pp. 403−406; R. A. Singer, E. M. Carreira, *Tetrahedron Lett.* **1997**, *38*, 927−930.

[6] A. Mori, H. Nitta, M. Kudo, S. Inoue, *Tetrahedron Lett.* **1991**, *32*, 4333−4336; H. Nitta, D. Yu, M. Kudo, A. Mori, S. Inoue, *J. Am. Chem. Soc.* **1992**, *114*, 7969−7975; B. M. Cole, K. D. Shimizu, C. A. Krueger, J. P. A. Harrity, M. L. Snapper, A. H. Hoveyda, *Angew. Chem.* **1996**, *108*, 1776−1779; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1668−1671.

[7] R. O. Duthaler, A. Hafner, *Chem. Rev.* **1992**, *92*, 807−832.

[8] [8a] M. Hayashi, Y. Miyamoto, T. Inoue, N. Oguni, *J. Org. Chem.* **1993**, *58*, 1515−1522. − [8b] M. Hayashi, T. Inoue, Y. Miyamoto, N. Oguni, *Tetrahedron* **1994**, *50*, 4385−4398. − [8c] Y. Jiang, X. Zhou, W. Hu, Z. Li, A. Mi, *Tetrahedron: Asymmetry* **1995**, *6*, 2915−2916.

[9] M. Hayashi, T. Inoue, N. Oguni, *J. Chem. Soc., Chem. Commun.* **1994**, 341−342; E. J. Corey, D. Barnes-Seeman, T. W. Lee, *Tetrahedron Lett.* **1997**, *38*, 4351−4354.

[10] T. Aoyama, S. Ohba, Y. Saito, C. Sasaki, M. Kojima, J. Fujita, K. Nakajima, *Acta Crystallogr.* **1988**, *C44*, 1309−1311; C. Sasaki, K. Nakajima, M. Kojima, J. Fujita, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1318−1324.

[11] M. Braun, *Angew. Chem.* **1996**, *108*, 565−568; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 519−522.

[12] [12a] A. Kossel, *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 4145−4156. − [12b] H. Reihlen, L. Knöpfle, *Justus Liebigs Ann. Chem.* **1936**, *523*, 199−210. − [12c] W. Klyne, P. M. Scopes, R. N. Thomas, H. Dahn, *Helv. Chim. Acta* **1975**, *54*, 2420−2430.

[13] A. McKenzie, A. C. Richardson, *J. Chem. Soc.* **1923**, *123*, 79−91.

[14] For efficient asymmetric reductions of ketones and α,β-unsaturated ketones catalyzed by the *B*-methyl-oxazaborolidine derived from (*R*)-**2**, see: R. Berenguer, J. Garcia, J. Vilarrasa, *Tetrahedron: Asymmetry* **1994**, *5*, 165−168; J. Bach, R. Berenguer, J. Farràs, J. Garcia, J. Meseguer, J. Vilarrasa, *ibid.* **1995**, *6*, 2683−2686.

[15] K. Higashiyama, H. Inoue, H. Takahashi, *Tetrahedron Lett.* **1992**, *33*, 235−238; A. D. Gupta, B. Singh, V. K. Singh, *Ind. J. Chem.* **1994**, *33B*, 931−933.

[16] M. F. Brown, B. R. Cook, T. E. Sloan, *Inorg. Chem.* **1975**, *14*, 1273−1278; G. J. Leigh, *Nomenclature of Inorganic Chemistry: Recommendations 1990*, 1st ed., Blackwell, Oxford, **1990**.

[17] J. C. Huffman, K. G. Moloy, J. A. Marsella, K. G. Caulton, *J. Am. Chem. Soc.* **1980**, *102*, 3009−3014.

[18] F. E. Hahn, S. Rupprecht, K. H. Moock, *J. Chem. Soc., Chem. Commun.* **1991**, 224−225; B. A. Borgias, S. R. Cooper, Y. B. Koh, K. N. Raymond, *Inorg. Chem.* **1984**, *23*, 1009−1016; G. D. Smith, C. N. Caughlan, J. A. Campbell, *idid.* **1972**, *11*, 2989−2993.

[19] *SHELXTL-PLUS* Release 4.21/V, Siemens Analytical X-ray Instruments Inc., Madison, WI, U.S.A., **1990**.

[20] Four out of five geometric *fac*-isomers are chiral octahedrons thus forming pairs of diastereomers.

[21] M. Hayashi, H. Kaneda, N. Oguni, *Tetrahedron: Asymmetry* **1995**, *6*, 2511−2516.

[22] K. Narasaka, I. Yamamoto, *Tetrahedron* **1992**, *48*, 5743−5754.

[23] R. Devant, U. Mahler, M. Braun, *Chem. Ber.* **1988**, *121*, 397−406.

[24] Assignments of the carbon atoms C-1 to C-10 are based on the calcd. increments for 2-hydroxy-1-naphthaldehyde (**3d**), see: H. O. Kalinowski, S. Berger, S. Braun, *13*C-NMR-Spektroskopie, 1st ed., Thieme, Stuttgart, **1984**.

[25] Titanium tetrafluoride is insoluble in common aprotic solvents; however, its solubility is moderate in acetonitrile, see: D. R. Gauthier, E. M. Carreira, *Angew. Chem.* **1996**, *108*, 2521−2522; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2363−2365.

[26] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100872. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)/336−033, e-mail: deposit@ccdc.cam.ac.uk].

[27] G. M. Sheldrick, *SHELXL-93*, University of Göttingen, Germany, **1993**.

[97296]