Asymmetric Thermal Transformation, a New Way to Enantiopure Biphenyl-Bridged Titanocene and Zirconocene Complexes: Efficient Catalysts for Asymmetric Imine Hydrogenation[1]

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Abstract: Enantiopure biphenyl-bridged titanocene and zirconocene complexes were obtained, by an asymmetric thermal transformation of the binaphthol complexes formed from the metallocene racemates and subsequent transformation to the corresponding dichlorides, in practically quantitative yields. Increased rates of this transformation in the presence of O₂ gas or TEMPO indicate a radical reaction mechanism. The biphenyl-bridged titanocene enantiomers give rise to an efficient asymmetric catalysis for the hydrogenation of cyclic and noncyclic imines.

Introduction

Asymmetric catalysis with chiral *ansa*-metallocene compounds has become a useful tool in chemical research.[2] This application is contingent, however, on efficient access to pure complex enantiomers. Presently, known methods are quite limited yet in this regard: While optical resolution of *ansa*-metallocene racemates[3−5] cannot yield more than 50% of a particular enantiomer, enantioselective *ansa*-metallocene synthesis[6] has proved chirally inefficient insofar as large parts of an enantiopure intermediate are wasted by subsequent low-yield reaction steps. An attractive alternative would be the complete asymmetric transformation of an *ansa*-metallocene racemate to one enantiomer. Whereas such asymmetric transformation can be achieved photochemically in a limited number of cases,[7] *ansa*-titanocene and -zirconocene complexes have generally

been considered to be configurationally too stable for thermal asymmetric transformations to be feasible; to the best of our knowledge, an equilibrating, dynamic resolution[8] of this class of complexes has not been achieved so far.

In an attempt to resolve the readily accessible racemate of a biphenyl-bridged zirconocene complex,[9] 2,2′-biphenyldiylbis-(3,4-dimethylcyclopentadienyl)zirconium dichloride (rac-**1-Cl₂**) by reaction of its dimethyl derivative, rac-**1-Me₂**, with (*R*)-1,1′-binaphthol (*R*-**binol**), we have recently found, however, that asymmetric transformations do occur in these reaction systems.[10] Here, we report on a new high-yield synthesis for enantiopure *ansa*-titanocene and -zirconocene complexes, which we have developed from these binaphthol-induced asymmetric transformations.
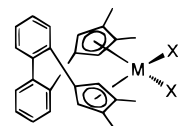
rac-**1** M = Zr
rac-**2** M = Ti

X,X = Cl₂, Me₂, (*R*)-binol

Results and Discussion

Reaction of rac-**1-Me₂** with 1 equiv of enantiopure (*R*)-**binol**, which is complete after 20 h at room temperature in toluene, yields the diastereomers (*R*)-**1**-(*R*)-**binol** and (*S*)-**1**-(*R*)-**binol**. Suprisingly, these diastereomers were found to arise in a ratio of about 2:1, rather than in the 1:1 ratio expected from the stoichiometry of the reactants. Obviously, a fraction of ca. 30% of the reactant (*S*)-**1-Me₂** was converted to the product (*R*)-**1**-(*R*)-**binol** during or after formation of the binaphthol complex.[11] When a mixture of the diastereomers (***R***)-**1**-(*R*)-**binol** and (*S*)-

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(11) The assignment of these diastereomers follows that of the corresponding Ti complexes reported in ref 9.

Scheme 1

Scheme 2

Scheme 3

Scheme 4
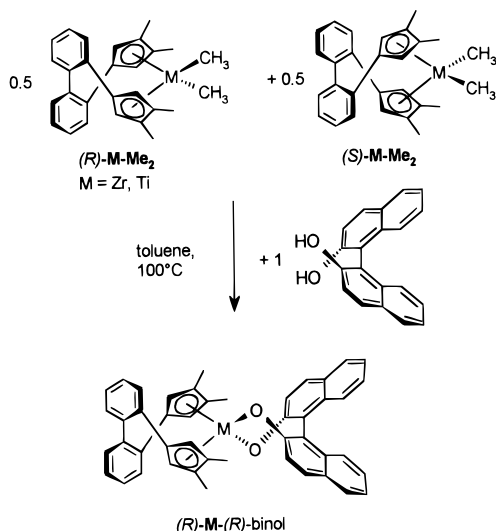
1-(*R*)-**binol** was kept in deuteriobenzene at 60−110 °C,[12] changes in the ^{1}H NMR-spectra indicate that the (*S*)-**1**-(*R*)-**binol** diastereomer is epimerized to the (*R*)-**1**-(*R*)-**binol** isomer. This epimerization goes to completion when the reaction mixture is kept in toluene at 100 °C for 2 days. This reaction sequence can be conducted as a one-pot reaction (Scheme 1).

We have further extended this new asymmetric transformation strategy to the corresponding titanium complex rac-**2-Me₂**. Previously, the binaphthol complex (*R*)-**2**-(*R*)-**binol** had been isolated in 48% yield by kinetic resolution with 0.5 equiv of (*R*)-binaphthol.[9] By reacting rac-**2-Me₂** with 1 equiv of (*R*)-binaphthol in toluene and heating the solution to 100 °C for 4 days, we obtained (*R*)-**2**-(*R*)-**binol** in 99% isolated yield.

To prepare the dichloride enantiomers (*R*)-**1-Cl₂** and (*R*)-**2-Cl₂**, the binaphthol complexes (*R*)-**1**-(*R*)-**binol** and (*R*)-**2**-(*R*)-**binol** were first converted to the dimethyl derivatives (*R*)-**1-Me₂** and (*R*)-**2-Me₂**, which were then transformed to (*R*)-**1-Cl₂** and (*R*)-**2-Cl₂**, respectively, with suitable chlorinating agents (vide infra).[13]

To determine the enantiomeric excess of complex **1-Me₂**, we used the commercially available enantiopure alcohol (*R*)-(+)-1-phenyl-1-propanol ((*R*)-**PP**).[14] Reaction of *rac*-**1-Me2** with 2 equiv of the alcohol in toluene yields, after 4 days,[15] the bis-alkoxy diastereomers (**R**)-**1**-((*R*)-**PP**)₂ and (*S*)-**1**-((*R*)-**PP**)₂, which are cleanly distinguished by their ^{1}H NMR spectra (Scheme 2, cf. Experimental Section).

When the optical purity of the dimethyl species **1-Me₂**, obtained from reaction of (*R*)-**1**-(*R*)-**binol** with methyllithium in ether at room temperature, was determined in this manner, racemization of the zirconocene complex was indicated by the formation of (*R*)-**1**-((*R*)**PP**)₂ and (*S*)-**1**-((*R*)**PP**)₂ in a ratio of 3:1

(50% ee). The same reaction at −20 °C gave a (*R*):(*S*) ratio of 97:3 (94% ee).[16] At still lower temperatures, the binaphthol complex does not react with methyllithium. With Grignard reagents the reaction was slow and led to the formation of more than one product species. With trimethylaluminum as methyl tranfer agent at −20 °C, finally, racemization was not detectable; in this case (*R*)-**1-Me₂** was isolated with 98% ee (Scheme 3).

While reaction of (*R*)-**2-Me₂** with dry HCl in ether at room temperature gives enantiopure (*R*)-**2-Cl₂**,[9] the analogous reaction with the zirconocene complex (*R*)-**1-Me₂** leads to partially racemized dichloride product **1-Cl₂** and to formation of an unknown byproduct, apparent in the ^{1}H NMR spectra.[17,18] When this reaction is conducted at −78 °C, racemization is suppressed, but the byproduct is still formed. Dry dichlorodimethylsilane was finally found to give a clean reaction, even at room temperature, according to Scheme 4.

When the rate of the asymmetric transformation was determined in C₆D₆ solution in closed NMR tubes at a temperature
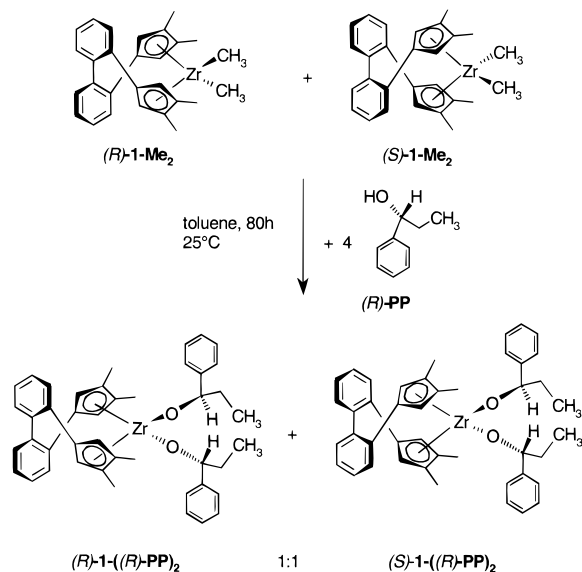
(12) ^{1}H NMR experiments were conducted with toluene or hexamethylbenzene as internal NMR standard, to ensure that the disappearance of one diastereomer is accompanied by an increase of the other one and not just by destruction of the complex.

(13) The titanium complex (*R*)-**2-Me₂** was found to be enantiopure by reaction with *O*-acetyl-(*R*)-mandelic acid, which yielded only a single diastereomer of [2,2′-biphenyldiylbis(3,4-dimethylcyclopentadienyl)]titanium-bis(*O*-acetyl-(*R*)-mandelate).[9]
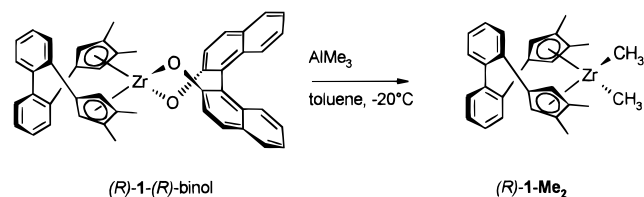
(14) *O*-Acetyl-(*R*)-mandelic acid proved unsuitable for this ee determination since it decomposes rac-**1-Me₂** under liberation of the biphenyl-bridged ligand. Reaction with Moshers reagent failed similarly.

(15) The monosubstituted complexes (*R*)-**1**-((*R*)-**PP**)-**Me** and (*S*)-**1**-((*R*)-**PP**)-**Me** arise from the reaction of rac-**1-Me₂** with 1 equiv of the alcohol in C₆D₆ after a reaction time of about 1 h. These monosubstituded complexes are equally suitable for the ee determination of **1-Me₂** as the disubstituted complexes (*S*)-**1**-((*R*)-**PP**)₂ and (*R*)-**1**-((*R*)-**PP**)₂ (see Experimental Section).
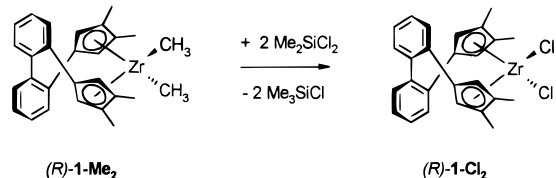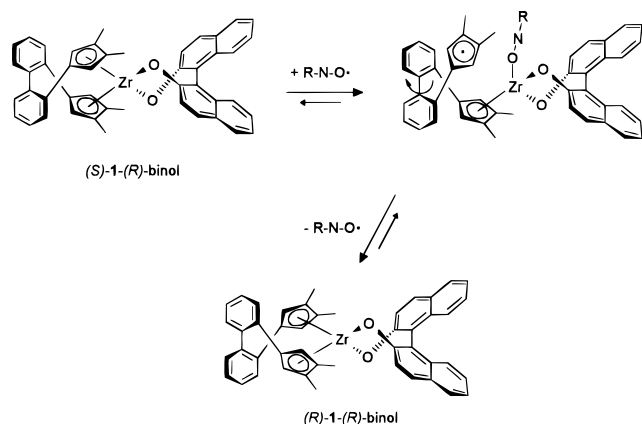
(16) Schäfer et al. also observed partial racemization in the reaction of (*R*)-ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)zirconium (*R*)-binaphthol with methyllithium in ether at temperatures above 0 °C.[4]

(17) A racemization in the chlorinating step was also observed by Schäfer in the reaction of (*R*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dimethyl with HCl at temperatures obove 0 °C.[4]

(18) For this ee determination, the dichloride product (*R*)-**1-Cl₂** is converted, with methyllithium in ether at −20 °C, to the dimethyl compound (*R*)-**1-Me₂**, which is then reacted with (*R*)-(+)-1-phenyl-1-propanol as described above.

Scheme 5

Scheme 6

obtained with (*R*)-**2-Cl₂**, although the catalyst:substrate ratio is smaller here by a factor of 20−100.

The biphenyl-bridged complex (*R*)-**2-Cl₂** in the presence of *n*-butyllithium thus yields a remarkably efficient imine hydrogenation catalyst, based on a metal which is inexpensive and environmentally safe. We are presently exploring possible extensions of the concept of asymmetric thermal transformation with the aim of providing efficient access to a wide range of enantiomerically pure metallocene catalysts.

Experimental Section

All reactions were carried out under an Ar or N₂ atmosphere using standard Schlenk and glovebox techniques. Solvents were dried and distilled from sodium benzophenone or CaH₂. NMR spectra were recorded on Bruker AC 250 MHz, Bruker DRX 600 MHz and JEOL FX 90Q spectrometers with residual C₆HD₅ (7.15 ppm), CHCl₃ (7.24 ppm), or C₆H₅CH₃ (2.09 ppm) as internal standards.

(*R*)-[2,2′-Biphenyldiylbis-(3,4-dimethylcyclopentadienyl)]zirconium (*R*)-1,1′-Bi-2-naphtholate ((*R*)-**1**-(*R*)-**binol**). A solution of 308 mg (1.08 mmol) *R*(+)-1,1′-bi-2-naphthol in 50 mL CH₂Cl₂ was added slowly to 490 mg (1.08 mmol) of biphenyl(3,4-Me₂-C₅H₃)₂ZrMe₂ (**1-Zr-Me₂**) in 150 mL of CH₂Cl₂. When the reaction mixture was stirred, both diastereomers (*R*)-**1**-(*R*)-**binol** and (*S*)-**1**-(*R*)-**binol** were obtained in ratios depending on the reaction time. Exchange of the solvent against 50 mL of toluene and heating the resulting solution for 2 days to 100 °C gave (*R*)-**1**-(*R*)-**binol** which was pure by ¹H NMR. (*R*)-**1**-(*R*)-**binol**: ¹H NMR(C₆D₆, 250 MHz, δ in ppm) 0.87 (s, 6H, C*H₃*), 1.53 (s, 6H, C*H₃*), 5.46 (d, 2H, *J* = 3 Hz, C₅*H*), 6.08 (d, 2H, *J* = 3 Hz, C₅*H*), 6.78−7.80 (m, 20H, C₆*H*); ¹³C NMR (CDCl₃, 600 MHz, δ in ppm) 11.02, 12.96, 109.56, 114.59, 115.82, 120.85, 122.04, 122.60, 125.27, 125.58, 126.54, 126.91, 127.60, 127.70, 128.40, 128.75, 128.82, 132.51, 132.74, 134.19, 135.37, 138.37, 160.48. (*S*)-**1**-(*R*)-**binol**: ¹H NMR (C₆D₆, 250 MHz, δ in ppm) 1.18 (s, 6H, C*H₃*), 1.66 (s, 6H, C*H₃*), 5.30 (d, 2H, *J* = 2 Hz, C₅*H*), 6.03 (d, 2H, *J* = 2 Hz, C₅*H*), 6.76−7.80 (m, 20H, C₆*H*); ¹³C NMR (CDCl₃, 600 MHz, δ in ppm) 11.22, 13.76, 108.99, 110.46, 114.22, 116.13, 117.76, 121.96, 123.20, 125.07, 125.80, 126.13, 126.86, 127.05, 127.24, 127.99, 128.22, 129.03, 130.09, 132.44, 135.61, 138.28, 159.45; [α]₅₈₉ = −163°, [α]₄₃₆ = −618° (1.20 mg/10 mL of toluene, *d* = 10) (lit.⁹ [α]₅₈₉ = −90°, [α]₄₃₆ = −400° (1 mg/10 mL of CH₂Cl₂, *d* = 10).

(*R*)-[2,2′-Biphenyldiylbis(3,4-dimethylcyclopentadienyl)]zirconium Dimethyl ((*R*)-1-Me₂). The (*R*)-**1**-(*R*)-**binol** (450 mg, 0.63 mmol) was dissolved in 80 mL toluene, cooled to −20 °C and reacted with 5 mL of a 2 M solution of trimethylaluminum in toluene. The solution was allowed to warm to room temperature. After 5 h, the reaction mixture was evaporated to dryness and the resulting residue was taken up in pentane; the salts were removed by filtration over Celite. The solvent was evaporated to give 230 mg (0.50 mmol, 80% yield) of

of 90 °C, we obtained a linear decrease of the logarithm of the ratio (*S*)-1-(*R*)-**binol**/((*R*)-**1**-(*R*)-**binol** + (*S*)-**1**-(*R*)-**binol**), indicating a first-order rate law. Suprisingly however, the apparent first-order rate constant measured at three different concentrations of diastereomeric mixtures of (*S*)-**1**-(*R*)-**binol** and (*R*)-**1**-(*R*)-**binol** decreased from *k* = 33.3 h⁻¹ at [Zr]ₜₒₜ = 4.3 mmol/L to *k* = 23.6 h⁻¹ at [Zr]ₜₒₜ = 8.6 mmol/L and to *k* = 17.5 h⁻¹ at [Zr]ₜₒₜ = 17.2 mmol/L. This apparent contradiction to a first-order rate law can be explained by the intervention of some impurities present in the reaction mixture, which is expected to be more pronounced at low zirconocene concentrations.
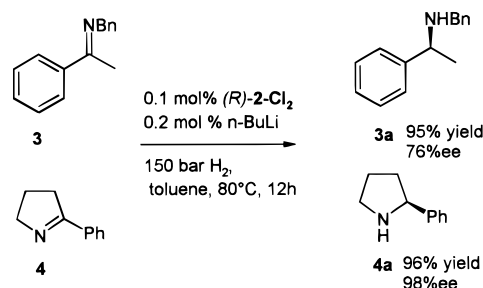
The reaction is indeed substantially accelerated by introducing dioxygen gas into the inert gas atmosphere above the reaction mixture (*k*= 127 h⁻¹ at [Zr]ₜₒₜ = 8.6 mmol/L). A similiar, but somewhat smaller, rate increase is caused by addition of 1 mg of tetramethylpiperidine *N*-oxide (TEMPO) (*k* = 45.6 h⁻¹ at [Zr]ₜₒₜ = 8.6 mmol/L). In Scheme 5 we present a possible reaction sequence for the catalytic action of TEMPO, where the radical TEMPO facilitates the release of a ligand radical similar to that discussed in photochemical ligand exchange reactions.[19]

At any rate, the configurational lability of the group IV metallocene complexes considered here appears to be intimately connected to the presence of a phenoxide ligand. The resolved enantiomers of the dichlorides (*R*)-**1-Cl₂** and (*R*)-**2-Cl₂** do not undergo any change in their specific optical rotation when kept in toluene solution at 50 °C for several days under exclusion of air and moisture.[20] These derivatives are thus sufficiently stable for use in enantioselective catalysis reactions.[21]

Imine Hydrogenation

Catalyst (*R*)-**2-Cl₂** in the presence of 2 equiv of *n*-butyllithium was used for the asymmetric hydrogenation of imines by dihydrogen at a pressure of 150 bar.[22] The results are represented in Scheme 6. While the selectivities of both catalytic hydrogenations are similar to those obtained by Willoughby and Buchwald with ethylenebis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride under comparable conditions,[22] higher yields are

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(20) While indefinitely stable as crystals in a nitrogen or argon atmosphere, the zirconocene complexes gradually decompose in the presence of air.

(21) The dimethyl derivative (*R*)-**1**-Me₂ was likewise found to be configurationally stable in toluene solution at 50 °C even in the presence of excess methylalumoxane.

(22) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562; Willoughby, C. A.; Buchwald, S. L. *J. Org. Chem.* **1993**, *58*, 7627. Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703. Recently, increased yields and enantioselectivities have been reported for imine hydrosilylations at catalyst:substrate ratios similar to those used here: Verdaguer, X.; Lange, U. E. W.; Reding, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 6784. Verdaguer, X.; Lange, U. E. W.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1103.

(*R*)-**1-Me₂** as a white solid: ¹H NMR (CDCl₃, 250 MHz, δ in ppm) −0.66 (s, 6H, Zr−C*H₃*), 1.88 (s, 6H, C*H₃*), 2.20 (s, 6H, C*H₃*), 4.39 (d, 2H, *J* = 2.8 Hz, C₅*H*), 6.21 (d, 2H, *J* = 2.8 Hz, C₅*H*), 7.11 (m, 2H, C₆*H*), 7.26 (m, 4H, C₆*H*), 7.41 (m, 2H, C₆*H*).

(*R*)-[2,2′-biphenyldiylbis(3,4-dimethylcyclopentadienyl)]zirconium Dichloride ((*R*)-1-Cl₂). The (*R*)-**1-Me₂** (230 mg, 0.50 mmol) was dissolved in 10 mL of toluene at room temperature and reacted with 10 mL of Me₂SiCl₂ for a period of 4 days. Evaporation gave 300 mg (0.48 mmol, 96% yield) of a yellow solid of enantiopure (*R*)-**1-Cl₂)** (ee ≥ 98%). The solid was stirred with ether for 15 min, filtered over a glass frit, and washed with ether. The overall yield was 76% based on rac-**1-Me₂**. A pure sample of the product was obtained by column chromatography over a small column of silanized silica gel with toluene as eluent: $[\alpha]_{589}$ = +201 (7.70 mg/10 mL toluene, *d* = 10). Anal. Calcd for C₂₆H₂₄ZrCl₂: C, 62.63; H, 4.85. Found: C, 62.73; H, 5.03.

(*R*)-[2,2′-Biphenyldiylbis(3,4-dimethylcyclopentadienyl)]--titanium (*R*)-1,1′-Bi-2-naphtholate ((*R*)-2-(*R*)-binol). To a solution of 260 mg (0.63 mmol) biphenyl(2,3-Me₂-C₅H₃)₂TiMe₂ (rac-**2-Me₂**) in 50 mL of toluene was added 180 mg (0.63 mmol) of (*R*)-(+)-1,1′-bi-2-naphthol. The solution was stirred for 4 days at 100 °C. After evaporation, 415 mg (0.62 mmol, 99% yield) of a deep red solid was isolated. A pure sample of the complex (*R*)-**2-(*R*)-binol** was isolated by filtration of a pentane solution over Celite. Anal. Calcd for C₄₆H₃₆O₂-Ti: C, 82.63; H, 5.43. Found, C, 82.73; H, 5.76.

(*R*)-[2,2′-Biphenyldiylbis(3,4-dimethylcyclopentadienyl)]-titanium Dimethyl ((*R*)-2-Me₂). Following a literature procedure,[9] 415 mg (0.62 mmol) (*R*),(*R*)-**2-binol** was dissolved in 60 mL of ether and reacted with 2.5 mL of 1.6 M methyllithium in ether. The color of the solution immediately changed to dark yellow. Extraction with pentane yielded 210 mg (0.51 mmol, 82% yield) of pure (*R*)-**2-Me₂** as a yellow powder: $[\alpha]_{589}$ = +333, $[\alpha]_{546}$ = +383 (1.20 mg/10 mL of toluene, *d* = 1). Anal. Calcd for C₂₈H₃₀Ti: C, 81.15; H, 7.30. Found: C, 80.98; H, 7.46.

(*R*)-[2,2′-Biphenyldiylbis(3,4-dimethylcyclopentadienyl)]-titanium Dichloride ((*R*)-2-Cl₂). To a solution of 210 mg (0.51 mmol) (*R*)-**2-Me₂** in 50 mL of ether was added a solution of 0.5 mL of 3.6 M HCl in ether at room temperature. The color of the solution changed to a dark red. After evaporation, 230 mg (0.51 mmol, 99% yield) of enantiopure (ee ≥ 98%) (*R*)-**2-Cl₂** was isolated. The overall yield was 81% based on the amount of rac-**2-Me₂** used for the reaction with (*R*)-**binol**: $[\alpha]_{589}$ = +786, $[\alpha]_{546}$ = −918 (0.49 mg/5 mL of CHCl₃, *d* = 1). (ref 9: $[\alpha]_{589}$ = +700 (1.78 mg/10 mL of CHCl₃, *d* = 1).

Reaction of rac-1-Me₂ with (*R*)(+)-1-Phenyl-1-propanol. rac-**1-Me₂)** in toluene (31.6 mg, 0.07 mmol) was treated in one portion with 20 mg (0.15 mmol) of (*R*)-(+)-1-phenyl-1-propanol. After a reaction time of 4 days, the solvent was removed to afford a yellow crystalline powder of the two diastereomers (*R*)-[2,2′-biphenyldiylbis(3,4-dimethylcyclopentadienyl)]zirconium bis((*R*)-1-phenyl-1-propanolate), (*R*)-**1-((*R*)-PP)₂**, and (*S*)-[2,2′-biphenyldiylbis(3,4-dimethylcyclopentadienyl)]-zirconium bis((*R*)-1-phenyl-1-propanolate), (*S*)-**1-((*R*)-PP)₂**. (*R*)-**1-((*R*)-PP)₂**: ¹H NMR (C₆D₆, 600 MHz, δ in ppm) 0.73 (t, 6H, *J* = 8 Hz, CH₂−C*H₃*), 1.52−1.87 (m, 4H, C*H₂*) 1.71 (s, 6H, C₅C*H₃*), 1.99 (s, 6H, C₅C*H₃*), 4.92 (t, 2H, *J* = 7 Hz, C*H*), 5.28 (d, 2H, *J* = 3 Hz, C₅*H*), 6.40 (d, 2H, *J* = 3 Hz, C₅*H*), 6.98−7.51 (m, 18H, C₆*H*). (*S*)-**1-((*R*)-

PP)₂**: 0.88 (t, 6H, *J* = 8 Hz, CH₂−C*H₃*), 1.52−1.87 (m, 4H, C*H₂*) 1.82 (s, 6H, C₅C*H₃*), 1.95 (s, 6H, C₅C*H₃*), 5.01 (t, 2H, *J* = 7 Hz, C*H*), 5.30 (d, 2H, *J* = 3 Hz, C₅*H*), 6.02 (d, 2H, *J* = 3 Hz, C₅*H*) 6.98−7.51 (m, 18H, C₆*H*); MS (EI): *m/z* 696 (M⁺, 16%)

Determination of the Enantiomeric Purity of (*R*)-1-Me₂. A 10-mg sample of a mixture of (*R*)-**1-Me₂** and (*S*)-**1-Me₂** was reacted in an NMR tube with a slight excess of (*R*)-(+)-1-phenyl-1-propanol ((*R*)-**PP**). After 2 h only the monosubstituted complexes (*R*)-[2,2′-biphenyldiylbis(3,4-dimethylcyclopentadienyl)]zirconium methyl((*R*)-1-phenyl-1-propanolate) (*R*)-**1-(Me)**−((*R*)-**PP**) and (*S*)-[2,2′-biphenyldiylbis-(3,4-dimethylcyclopentadienyl)]zirconium-methyl((*R*)-1-phenyl-1-propanolate) (*S*)-**1-(Me)**−((*R*)-**PP**) were detected. In the cyclopentadienyl region, eight doublets were observed. ¹H NMR (C₆D₆, 250 MHz, δ in ppm): (*R*)-**1-(Me)**−((*R*)-**PP**) 4.78, 5.19, 5.95, 6.17 and (*S*)-**1-(Me)**−((*R*)-**PP**) 4.81, 5.22, 5.92, 5.93.

Asymmetric Hydrogenation Reactions. In a dry Schlenk flask, 9.1 mg (20 μmol) of (*R*)-biphenyl(2,3-Me₂-C₅H₃)₂TiCl₂ ((*R*)-**2-Cl₂**) was dissolved in 20 mL of toluene under an argon atmosphere at room temperature. A solution of 40 μmol *n*-butyllithium (0.16 M in hexane) was added dropwise. The color changed rapidly to a dirty brown-green. After 5 min, 20 mmol (1000 equiv) of the imine in 10 mL of toluene were added. The resulting solution was transferred under argon to a Roth high-pressure autoclave, charged with 150 bar of hydrogen gas (99.999+%), and allowed to stir for 12 h at 80 °C. After cooling to room temperature, the vessel was carefully vented and opened. The amine product was freed from solvent in vacuo and purified by Kugelrohr distillation. The enantiomeric purity of the amines was determined by trifluoracetylation and subsequent gaschromatography on a BP-H-column (Astec)

(*R*)-(+)-*N*-Benzyl-1-phenylethylamine (3a). The general procedure with 0.1 mol % catalyst was used to hydrogenate 4.2 g (20 mmol) of a anti:syn (9:1) mixture of **(3)** *N*-(α-methylbenzylidene)benzylamine; 4.0 g (19 mmol) (*R*)-(+)-*N*-benzyl-1-phenylethylamine was isolated in 95% yield and 76% ee. The spectroscopic properties (¹H, ¹³C) of the amine match those from an authentic sample.

(*R*)-(+)-1-Phenylpyrrolidine (4a). The general procedure with 0.1 mol % catalyst was used to reduce 2.9 g (20 mmol) of 1-phenylpyrroline **(4)**. The resulting clear, yellow solution afforded, after purification, a colorless oil. 2.81 g (19.2 mmol) of (*R*)-(+)-1-phenylpyrrolidine was isolated in 96% yield and 98% ee: ¹H NMR (CDCl₃, 300 MHz, δ in ppm) 1.6−1.9 (m, 3H), 2.15 (m, 1H), 2.6 (br s, 1H), 2.9 (m, 1H), 3.2 (m, 1H), 4.1 (t, 1H, *J* = 6.9 Hz), 7.1−7.5 (m, 5H).

Supporting Information Available: NMR spectra of (*R*)- + (*S*)-**1**-(*R*)-binol, *R*-**1**-(*R*)-binol, (*R*)-**1-Cl₂**, (*R*)-**2-Me₂**, (*R*)-**2-Cl₂**, and (*R*)- + (*S*)-**1-((*R*)-PP)₂** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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