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Chiral 1,4-bis-diphosphine ligands from optically active (*Z*)-olefines

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Abstract—The catalytic asymmetric hydrogenation of prochiral ketones was carried out with Ru(II) complexes prepared from new chiral diphosphine ligands, *cis*-(*R*,*R*)-2,5-bis[(diarylphosphino)]-3-hexenes. These new ligands were prepared from enantiomerically pure (*R*,*R*) or (*S*,*S*)-(*Z*)-3-hexene-2,5 diol and enantiomeric excesses up to 85% were obtained in the reduction of 2-benzamidomethyl-3-oxobutanoate, starting material for the synthesis of 4-acetoxy-2-azetidinone.

1. Introduction

Transition metals, which are known to be excellent catalysts for asymmetric synthesis, have optically active diphosphine ligands as source of chirality. Usually chirality is based upon one or more stereogenic atoms such as those in DIOP, the breakthrough in the field of chiral phosphorus ligands.[1] DIOP has a C_2-axis with two stereogenic sp^3 carbons, whose chirality depends on starting material, the tartaric acid.

DIPAMP, the first example of a successful industrial application of metal-catalyzed asymmetric hydrogenation has two asymmetric phosphorus atoms.[2] Thousands of ligands based on stereogenic sp^3 atoms derived from the systematic exploitation of the chiral pool are currently available and some of the corresponding Rh–phosphine complexes have smoothed the way to natural and unnatural amino acids by asymmetric hydrogenation of the corresponding enamides.[3]

Unlike the reduction of C=C double bonds, the successful catalytic reduction of prochiral C=X bonds (X = O, N) was achieved only when di-aryl or di-heteroaryl ligands with a C_2 axial chirality such as BINAP,[4] BIPHEMP[5] or BITIOP[6] became available; these ligands gave the corresponding Ru–phosphine complexes catalysts able to reduce C=O and C=N double bonds often with ees higher than 99%; no doubt that while the family of chelating diphosphines based on sterogenic carbon atoms is very large, diphosphines based on axial chirality are a rather more limited class of ligands.

R. Nojori, Nobel Prize for Chemistry in 2001, recently wrote "..... *Despite the tremendous effort made to discover useful asymmetric hydrogenation catalyst, there still remains much potential for the continued development of these reactions, only a limited number of truly efficient catalysts have been found. Furthermore, because of the structural and functional diversity of unsaturated organic compounds, no universal catalysts exist.....*" [7]

As is epitomized in these words, in the area of asymmetric catalysis there is still much potential research with regards to the development of new catalysts with satisfactory enantioselectivity, productivity and process robustness to find applications on an industrial scale which is closely connected to the availability of new chiral ligands.

Herein, we report a new class of chiral chelating diphosphines that should combine the easiness of synthesis of ligands based on stereogenic sp^3 carbon atoms with a tendency to chelate to the metal in an octahedral geometry, typical of the aromatic di-aryl or di-heteroaryl diphosphines with C_2 axial chirality.

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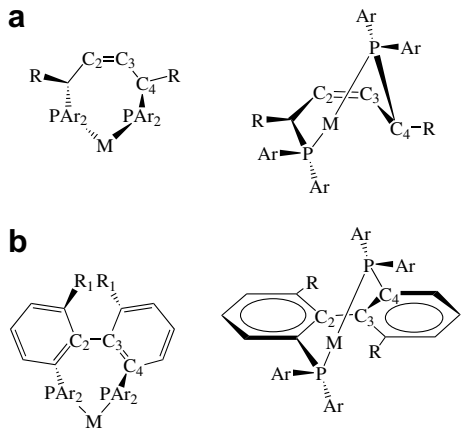


Figure 1.

Figure 1a shows a top and side view (upper and lower, respectively) of these new ligands in comparison with the general formula of an atropisomeric diphosphine (Fig. 1b). A general feature of these ligands is that the double bond between C2 and C3 and, consequently the C1–C4 atoms, defines the molecular plane; upon coordination to a metal if the R group on the backbone assume the typical equatorial disposition, the phosphorus can lie over and below this plane according to the chirality of the two stereogenic atoms C1 and C4; furthermore upon coordination, the aryl groups on the phosphorus are forced into the axial/equatorial disposition that generates the usual C_2 chiral environment of chelating diphosphines around a metal.[8]

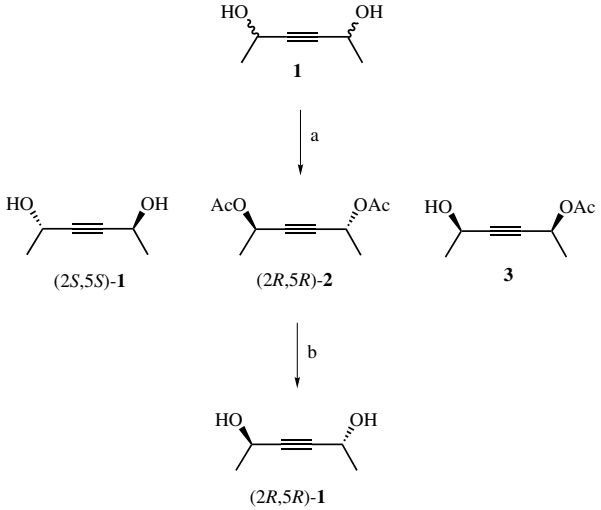
This is a scaffold similar to that generated by the coordination of an atropisomeric diphosphine, (Fig. 1b); now the molecular plane is defined by the metal and carbon atoms C2 and C3 while the phosphorus atoms lie over and below this plane according to the axial chirality of the ligand.

The great difference of this new class with respect to atropisomeric diphosphines is that the R substituents on the stereogenic carbons C1 and C4 (Fig. 1a) can be easily changed depending only on the chiral *cis* diols used as starting materials.

2. Results and discussion

Scheme 1 depicts the reactions for the synthesis of the chiral diphosphines hereafter defined as ZEDPHOS. Treatment of a commercially available mixture of 50/50 *meso* and racemic (2,5)-3-hexyne-diol **1** with Lypase AK in the presence of vinylacetate[9] led to the diacetylated stereoisomer (2*R*,5*R*)-**2** while the meso stereoisomer (2,5)-3-hexyne-diol **1** was selectively monoacylated. The unreacted enantiomerically pure (2*S*,5*S*)-**1** and the diacetylester (2*R*,5*R*)-**2** were easy isolated quantitatively by flash chromatography; the diol (2*R*,5*R*)-**1** was obtained from (2*R*,5*R*)-**2** by acid hydrolysis.

(2*S*,5*S*)-3-Hexyne-2,5-diol-**1** was selectively reduced to (*Z*)-(2*S*,5*S*)-3-hexene-2,5-diol-**4** with $Pd/CaCO_3$. (2*S*,5*S*)-3-Hexene-2,5-diol di-*p*-tosylate-**5** was reacted with $LiPPh_2$



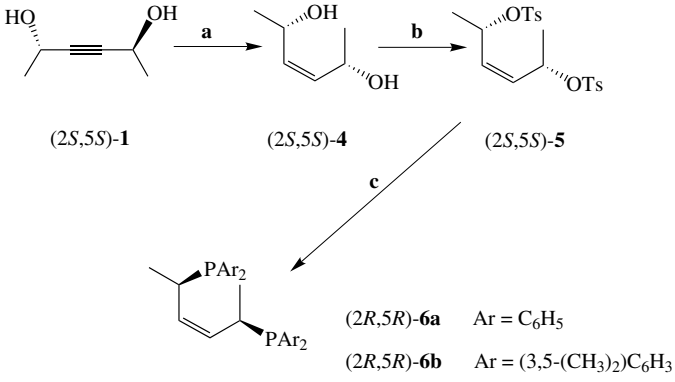
Scheme 1. Resolution of diols. Reaction conditions: (a) **1** = 1.4 M in vinylacetate, Lipase AK (24,600 unit/g, Amano) 77 mg/ml, temperature 32 °C, reaction time 16 h; (b) flash chromatography hexane/ethylacetate = 1/1.

or $LiP(3,5\text{-}CH_3)_2C_6H_3$) to give the corresponding diphosphines (*Z*)-(2*R*,5*R*)-diarylphosphino-3-hexene-(*R*,*R*)-ZEDPHOS-**6a** and -(*R*,*R*)-ZEDPHOS-**6b** (Scheme 2).

The Rh(I) and Ru(II) complexes of the ligands (*R*,*R*)-ZEDPHOS-**6a** and (*R*,*R*)-ZEDPHOS-**6b** were prepared by following the literature procedures and applied to the catalytic hydrogenation of β-ketoesters and prochiral olefins described in Figure 2.

The results are summarized in Tables 1 and 2.

Before discussing the catalytic activities of Rh(I) and Ru(II) complexes with (*R*,*R*)-ZEDPHOS ligand, it is worth mentioning that the double bond in the 3-hexene scaffold of the ligand was not reduced even under the most severe conditions described in Table 1. [Ru((*R*,*R*)-ZEDPHOS-**6a**)$Cl_2(DMF)_n$] was dissolved in MeOH and stirred at



Scheme 2. Synthesis of the (*Z*)-diarylphosphines. Reaction conditions: (a) [sub] = 1.7 M, solvent: ethylacetate, $Pd/CaCO_3$ (5 wt.%) 0.033 equiv, quinoline 0.087 equiv, H_2 pressure = 1 atm, temperature = 25 °C; (b) [sub] = 0.35 M, tosyl chloride = 1.25 equiv, NaOH = 4.5 equiv solvent: anhydrous THF, temperature = −20 °C, reaction time = 4 h; (c) [sub] = 0.094 M, $LiPAr_2$ = 0.26 M, solvent: anhydrous THF, temperature = −78 °C, under inert atmosphere.

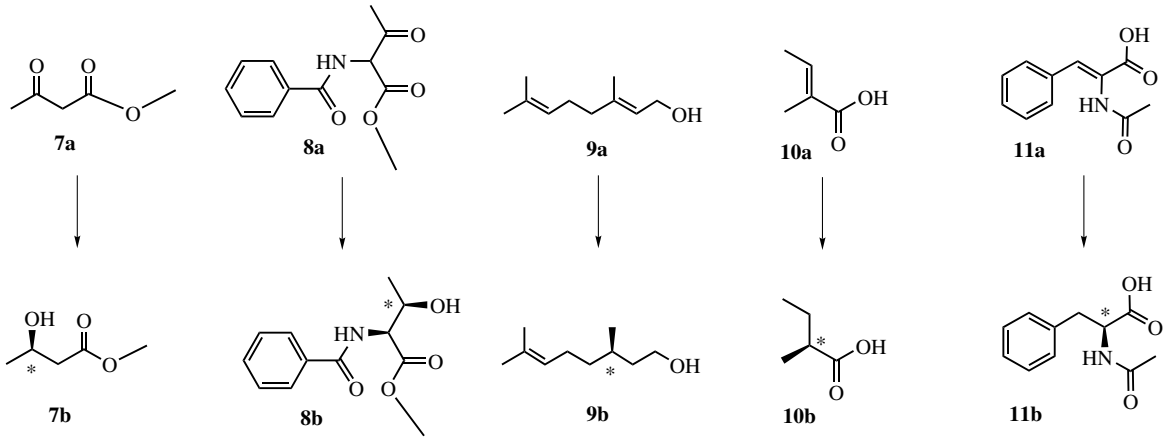


Figure 2.

Table 1. Asymmetric hydrogenation of β-ketoesters catalyzed by RuL*Cl_2 $(DMF)_n$ or [RuL*(*p*-cymene)I]I[a]

Entry	Ligand	[Ru] catalyst	Substrate	Product	ee %	de %[d]
1	**6a**	[Ru(*p*-cymene)I]I	**7a**	(*R*)-**7b**	4[b]	—
2	**6a**	[Ru(*p*-cymene)I]I	**7a**	(*R*)-**7b**	58[b]	—
3	**6b**	[Ru(*p*-cymene)I]I	**7a**	(*R*)-**7b**	63[b]	—
4	**6b**	$RuCl_2(DMF)_n$	**7a**	(*R*)-**7b**	39[b]	—
5	**6a**	$RuCl_2(DMF)_n$	**7a**	(*R*)-**7b**	66[b]	—
6	**6a**	[Ru(*p*-cymene)I]I	**8a**	(2*S*,3*R*)-**8b**	70[c]	43
7	**6a**	$RuCl_2(DMF)_n$	**8a**	(2*S*,3*R*)-**8b**	71[c]	55
8	**6b**	$RuCl_2(DMF)_n$	**8a**	(2*S*,3*R*)-**8b**	70[c]	63
9	**6b**	[Ru(*p*-cymene)I]I	**8a**	(2*S*,3*R*)-**8b**	85[c]	55

[a] Reaction conditions: Solvent: CH_2Cl_2/MeOH = 7:3, except entry 1 (MeOH 100%); Reaction time 24 h; Conversion > 99%; Substrate/[Ru] = 50:1; substrate concentration = 0.025 mmol/ml; $T = 60$ °C; $P = 50$ atm H_2.
[b] The ee values were determined by chiral GC DANI GC86.10 equipped with a capillary column with a chiral stationary phase MEGA DAcTButSilBETA (25 m, internal diameter 0.35 mm).
[c] The ee values were determined by chiral HPLC with a Daicel Chiralcel OD colum or Chiralpak AD.
[d] The de values were determined by ^{1}H NMR.

Table 2. Asymmetric hydrogenation of C=C double bonds catalyzed by $RuCl_2(DMF)_n$, [Ru(*p*-cymene)I]I or [Ru(COD)(η^3-C_3H_5)$_2$][a]

Entry	Ligand	[Ru] catalyst	Substrate	Product	ee %[h]
1[b]	**6b**	$RuCl_2(DMF)_n$	**9a**	(*R*)-**9b**	15
2[d]	**6b**	$RuCl_2(DMF)_n$	**10a**	(*R*)-**10b**	34
3[c,e]	**6a**	[Ru(*p*-cymene)I]I	**9a**	**9b**	0
4[d]	**6a**	[Ru(*p*-cymene)I]I	**10a**	(*R*)-**10b**	35
5[c,f]	**6a**	[Ru(*p*-cymene)I]I	**9a**	**9b**	0
6[b]	**6a**	$RuCl_2(DMF)_n$	**9a**	(*S*)-**9b**	10
7	**6a**	$RuCl_2(DMF)_n$	**10a**	(*R*)-**10b**	48
8[d]	**6a**	[Ru(COD)(η^3-C_3H_5)$_2$]	**10a**	(*R*)-**10b**	30
9[g]	**6b**	$RuCl_2(DMF)_n$	**9a**	**9b**	5
10[g]	**6b**	$RuCl_2(DMF)_n$	**10a**	(*R*)-**10b**	10

[a] Reaction conditions: Solvent: MeOH; Reaction time 24 h; Conversion > 99%; Substrate/[Ru] = 100:1; substrate concentration = 0.025 mmol/ml; $T = 20$°C; $P = 70$ atm H_2 if not otherwise stated.
[b] Substrate/[Ru] = 150:1.
[c] Substrate/[Ru] = 300:1.
[d] P = 10 atm H_2.
[e] P = 50 atm H_2.
[f] Solvent: CH_2Cl_2/MeOH = 7:3.
[g] Solvent: toluene.
[h] The ee values were determined by chiral GC DANI GC86.10 equipped with a capillary column with a chiral stationary phase MEGA DAcTButSilBETA (25 m, internal diameter 0.35 mm).

60 °C for 24 h under 70 atm H_2; after evaporation of the solvent the ^{1}H, ^{31}P NMR, MS-FAB$^+$ spectra and elemental analysis of the brown residue were almost super imposable to those of the complex before the treatment.

In a second test [Pd((*R*,*R*)-ZEDPHOS-**6a**)Cl_2], (vide infra) was dissolved in MeOH and stirred at 60 °C for 72 h under 70 atm H_2 in the presence of 5% [Ru((*R*,*R*)-ZEDPHOS-**6a**)$Cl_2(DMF)_n$]. After the usual work-up, the Pd(II) complex was recovered almost unchanged from the reaction mixture.

Stereoselective reduction of β-ketosters provides a direct approach to optically active β-hydroxyesters, which are building blocks in the synthesis of bioactive products; particularly interesting is the reduction of substrate 2-benzamidomethyl-3-oxobutanoate **8a** as **8b** is the starting material for the synthesis of 4-acetoxy-2-azetidinone **8c**, which is a key intermediate in the preparation of Carbapenem and other β-lactam antibiotics (Fig. 3).

Stereodifferentiation appeared to be dependent on the solvent and, to a lesser extent, on the catalyst precursor. The highest enantiomeric excess (85%) was obtained in the reduction of **8a** with (*R*,*R*)-ZEDPHOS-**6b** and [Ru(*p*-cymene)I]I (Table 1, entry 9). Methyl acetoacetate **7a** was reduced with 66% ee with $RuCl_2(DMF)_n$ and (*R*,*R*)-ZEDPHOS-**6a** (Table 1, entry 5). MeOH alone gave a disappointing 4% ee but a 7:3 mixture CH_2Cl_2/MeOH raised the ee to 58% (Table 1, compare entries 1 and 2). Both ligands (*R*,*R*)-ZEDPHOS-**6a** and (R,R)-ZEDPHOS-**6b** gave comparable results with [Ru(*p*-cymene)I]I in the reduction of **7a** (Table 1, compare entries 2 and 3) while $RuCl_2(DMF)_n$ gave comparable results in the reduction of **8a** (Table 1, compare entries 7 and 8) although different enantioselectivities were obtained in the reduction of **7a** (Table 1, compare entries 4 and 5).

Less satisfactory results were obtained in the reduction of prochiral olefins. Cationic complexes [Rh(COD)((*R*,*R*)-ZEDPHOS-**6a**)]$^+$ and [Rh(COD)((*R*,*R*)-ZEDPHOS-**6b**)]$^+$ gave almost racemic *N*-acetyl-phenylalanine **11b**; slightly better results were obtained with $RuCl_2(DMF)_n$ in the reduction of tiglic acid (Table 2, entry 7). Again stereodifferentiation was strongly dependent on the nature of the catalyst precursor (Table 2, entries 4, 7 and 8) and on the solvent (Table 2, entries 7 and 10).

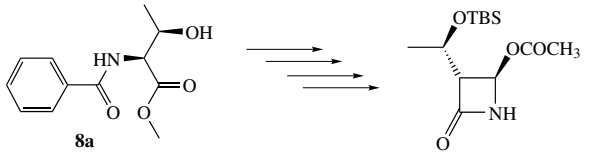


Figure 3.

Neither Ru(II) nor Rh(I) gave crystals suitable for an X-ray investigation; a detailed structure of the ligand (*R*,*R*)-ZEDPHOS-**6a** was possible by its palladium dichloride complex.

[Pd((*R*,*R*)-ZEDPHOS-**6a**)Cl_2] was prepared by exchange from [Pd(C_6H_5CN)$_2Cl_2$] and (*R*,*R*)-ZEDPHOS-**6a**; crystals for X-ray diffraction structural determination were obtained by slow diffusion of diethyl ether in a CH_2Cl_2 solution. The molecular structure is reported in Figure 4a (front view) and 4b (top view).

[Pd((*R*,*R*)-ZEDPHOS)-**6a**)Cl_2] is a slightly distorted square planar complex; atoms Pd, Cl1, C1 and C2 lie in the molecular plane; only chlorine Cl2 is 0.061 Å out of the least square plane. The most relevant feature of the ligand in the solid state is that the four phenyl rings are symmetrically arranged above and below the molecular plane, as shown in Figure 4a (front view) with the methyl group close to the P2 atom in an almost perfect equatorial disposition in the molecular plane. In asymmetric hydrogenation, the aryl groups on the phosphorus atoms are the chirality transmitters assuming, upon the coordination, a local C_2 symmetry as determined by their axial/equatorial disposition which in its turn is determined by the chirality of the backbone. The X-ray structure of the square planar Pd(II) complex shows that the phenyl groups assume a disposition more close to C_s than C_2 symmetry. This arrangement should be typical of all the transition metals in a square planar geometry, similar to those of Rh(I); if such a disposition is maintained in solution, it should explain why [Rh((2*R*,5*R*)-**6a**)(COD)]$^+$ and [Rh((2*R*,5*R*)-**6b**)(COD)]$^+$ are very efficient catalysts in the hydrogenation of *N*-acetyl-dehydrophenylalanine and *N*-benzoyl-dehydrophenylalanine methyl ester but with very

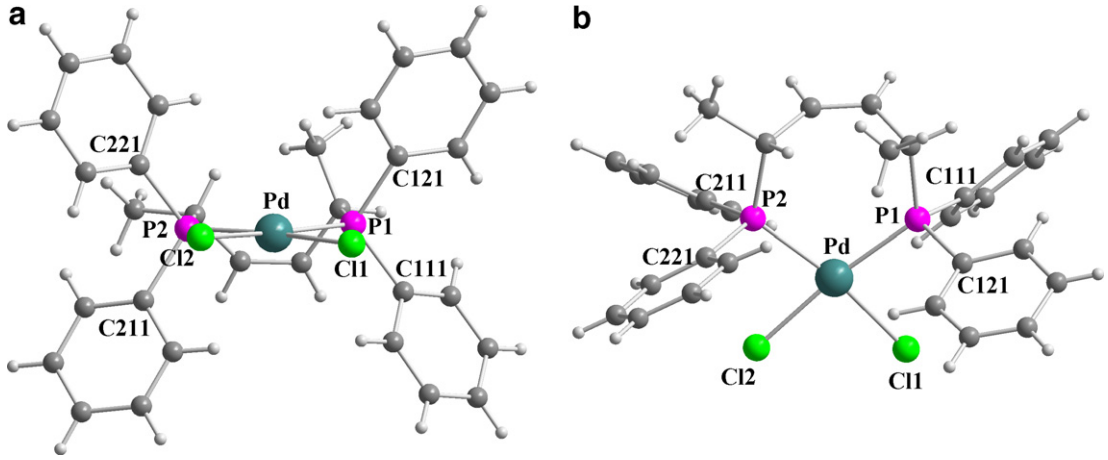


Figure 4. (a) and (b) views of $PdCl_2$(*R*,*R*)-ZEDPHOS-**6a**.

poor enantioselectivities. The tendency of ligands **6a** and **6b** to chelate to the metal in an octahedral geometry, typical of Ru(II) complexes should keep away the metal from C_s towards a more pronounced C_2 symmetry. Whatever would be the origin of the stereodifferentiation there is no doubt that the Ru(II)-ZEDPHOS complexes are efficient enantioselective hydrogenation catalysts, at least for ketones. The steric control of a catalytic hydrogenation is the result of several factors amongst which geometric parameters and bulkiness of the substituents on the ligand exert a central role.

Efforts are currently being carried out in order to verify if the introduction of bulkier groups on the C1 and/or C4 atoms will effect to a great extent the enantioselectivity of the reaction.

3. Experimental

Catalytic reactions were performed in a 200 ml stainless steel autoclave equipped with temperature control and magnetic stirrer. Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. The rhodium and ruthenium catalysts were prepared according to the well established literature procedure.[10]

^{31}P NMR and ^{1}H NMR spectra were recorded on a Bruker DRX Avance 300 MHz equipped with a non-reverse probe and also or on a Bruker DRX Avance 400 MHz. GC–MS spectra were recorded on Thermo Finningan MD 800 equipped with GC Trace (SE 52 column: length 25 mt, ϕ int. 0.32 mm, film 0.4–0.45 μm). GC analysis: DANI GC86.10 equipped with a capillary column with a chiral stationary phase MEGA DAcTButSilBETA (25 m, internal diameter 0.35 mm). HPLC analysis: Merck–Hitachi L-7100 equipped with Detector UV6000LP and Diacel Chiralcel OD or Chiralpak AD.

3.1. Preparation of the diol (*S*,*S*)-4

The diol was prepared according to the literature.[11]

3.2. Preparation of (*S*,*S*)-bis-*p*-toluensulfonate (*S*,*S*)-5

A 10% solution of 3.50 g (18.30 mmol) tosyl chloride in either THF or diethyl ether was added to a solution of 0.85 g (7.32 mmol) diol (*S*,*S*)-**4** in THF, and the reaction mixture cooled to −20 °C. Thereafter a large excess of finely powdered sodium hydroxide was added in small portions to the vigorously stirred solution. The temperature was kept below −5 °C during the sodium hydroxide addition. To complete the reaction, the solution was stirred for another 3 h at 0 °C and then poured into ice water. The aqueous phase was extracted several times with dichloromethane. After the collected organic extracts were dried on sodium sulfate, the solvent was removed in vacuum and the crude product recrystallized from diethyl ether. The colourless crystals can be stored at −18 °C for several months without decomposition.

(*S*,*S*)-**5** was obtained in 70% yield after crystallization from diethyl ether and characterized with a melting point = 70 °C with decomposition.

Elemental analysis calculated for $C_{20}H_{24}O_6S_2$: C, 56.59; H, 5.70; found: C, 56.94; H, 5.66. $[\alpha]_D^{25} = +35.4$ (c $2.1 \cdot 10^{-3}$ M; C_3H_6O) ^{1}H NMR (300 MHz; $CDCl_3$): (ppm) 1.26 (6H; d), 2.48 (6H; s), 5.29–5.33 (2H; m), 5.41–5.46 (2H; m), 7.34–7.36 (4H; d), 7.76–7.78 (4H; d).

3.3. Preparation of (*R*,*R*)-ZEDPHOS-6a

A solution of $LiPPh_2$ (0.98 mmol; 0.26 M in THF) was dropped into a solution of (*S*,*S*)-**5** in THF at −78 °C, under argon. After the addition the temperature was allowed to rise to room temperature and stirred for an additional 30 min. The excess of $LiPPh_2$ was neutralized by $Na_2SO_4{\cdot}10H_2O$ and the mixture was filtered under argon. Evaporation of the solvent followed by methanol afforded the chiral diphosphine (*R*,*R*)-ZEDPHOS-**6a** enantiomerically and chemically pure.

Yield % = 95%; $[\alpha]_D^{25} = -50.3$ (c 0.001 M; C_3H_6O); ^{31}P NMR (300 MHz; C_3D_6O): (ppm) −1.525 (s); ^{1}H NMR (300 MHz; C_3D_6O): (ppm) 0.54 (6H; d), 2.25–3.30 (2H; m), 5.13–5.22 (2H; m), 7.32–7.64 (20H; m); ^{13}C NMR (300 MHz; C_3D_6O): (ppm) 17.75 (CH_3), 29.63 (CH), 129.15 (=CH), 134.31 (C-aromatic).

3.4. Preparation of (*R*,*R*)-ZEDPHOS-6b

The ligand was prepared as (*S*,*S*)-ZEDPHOS-**6a**. Yield % = 95%; ^{31}P NMR (300 MHz) (C_3D_6O) (ppm): −2.703 (s); ^{1}H NMR (300 MHz; C_3D_6O): (ppm) 0.46–0.53 (6H; m), 2.28–2.32 (24H; d), 3.21 (2H; m), 5.08 (2H; m), 7.2–7.67 (12H; m).

3.5. Preparation of $PdCl_2$ (*R*,*R*)-ZEDPHOS-6a

A mixture of (*R*,*R*)-ZEDPHOS-**6a** (PM = 452.2; 0.21 mmol) and $(C_6H_5CN)_2PdCl_2$ (PM = 383.4; 0.21 mmol) in argon-degassed acetone (5 ml) was stirred at rt for 30 min, under an argon atmosphere; the solvent was removed by filtration to give a $PdCl_2$(*R*,*R*)-ZEDPHOS-**6a** complex as a yellow solid. Recrystallization of the crude product by slow diffusion of ether into a CH_2Cl_2-saturated solution afforded crystals suitable for X-ray structure analysis.

Yield % = 91%; Elemental analysis calculated for $C_{30}H_{30}P_2PdCl_2$: C, 57.21; H, 4.80; found C, 56.26; H, 4.86. ^{31}P NMR (300 MHz) ($CDCl_3$) (ppm): 24.20 (s).

3.6. Preparation of [Ru(*p*-cymene)I(*R*,*R*)-ZEDPHOS-6a]$^{+}$I^{-}

This complex was prepared according to the literature procedure.[10,12] ^{31}P NMR (300 MHz) ($CDCl_3$) (ppm): 31.89 (d, $J_{P-P} = 45.78$ Hz), 27.14 (d, $J_{P-P} = 49.59$ Hz), ($J_{Ru-P} = 576.02$, $J_{Ru-P} = 579.83$).

3.7. Preparation of [Rh(COD)(*R*,*R*)-ZEDPHOS-6a]

The complex was prepared according to the literature procedure.[10,12] ^{31}P NMR (300 MHz) ($CDCl_3$) (ppm): 24.56 (d, $J_{P-P} = 144$ Hz).

3.8. Preparation of [Ru(η^3-C_3H_5)$_2$(*R*,*R*)-ZEDPHOS-6a] and of [$RuCl_2(DMF)_n$(*R*,*R*)-ZEDPHOS-6a]

The complexes were prepared according to the literature procedure.[10,12]

3.9. General procedure of the asymmetric hydrogenation

In a Schlenk tube sealed under argon, the substrate was added to the precatalyst followed by 20 ml of a choice solvent. The solution was stirred for 30 min and then transferred to an autoclave with a cannula.

The stainless steel autoclave (200 ml), equipped with temperature control and magnetic stirrer, was purged 5 times with hydrogen. After the transfer of the reaction mixture, the autoclave was pressurized. At the end, the autoclave was vented and the mixture was analyzed by GC–MS, NMR spectra and HPLC.

3.10. X-ray crystal structure determination of $PdCl_2$ (*R*,*R*)-ZEDPHOS-6a

Crystal data. $C_{30}H_{30}P_2PdCl_2$, $M = 629.78$, monoclinic, $a = 9.3915(10)$, $b = 14.3912(15)$, $c = 20.5625(22)$ Å, $\beta = 97.86(1)°$, $U = 2753.0(5)$ Å^3, $T = 294(2)$ K, space group $P2_1/c$ (No. 14), $Z = 4$, μ = (Mo Kα) 1.002 mm^{-1}. 24,080 reflections (5413 unique, $R_{int} = 0.049$) were collected at room temperature in the range $2.00 \leqslant 2\theta \leqslant 52.06°$, employing a partly twinned $0.14 \times 0.05 \times 0.03$ mm crystal mounted on a Siemens SMART CCD area-detector diffractometer. Graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) was used with the generator working at 45 kV and 40 mA.

Intensities were corrected for Lorentz-polarization effects and empirical absorption correction (SADABS.[13] The structure was solved by direct methods (SIR-97[14]) and refined on F_o^2 with the SHELXL-97[15] programme (WinGX suite[16]). All non-hydrogen atoms were refined with anisotropic thermal parameters, while hydrogen atoms, located on the ΔF maps, were allowed to rìde on their carbon atom. Final $R1$ [$wR2$] values of 0.0928 [0.1347] on 3607 reflections with $I > 2\sigma(I)$ [all data] and 318 parameters. The maximum and minimum residual electron density on the final ΔF map are 1.59 and −1.58 e Å^3, respectively.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-640071. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.

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