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Economic preparation of 1,3-diphenyl-1,3-bis(diphenylphosphino)propane: a versatile chiral diphosphine ligand for enantioselective hydrogenations

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Abstract—The enantioselective hydrogenation of 1,3-diarylpropane-1,3-diones with chiral Ru(II)-diphosphine catalyst has been studied. In a first approach it was found, that Tol-BINAP together with Ru(COD)methallyl$_2$ formed the most selective catalyst. One of the C_2-symmetric enantiopure 1,3-diols obtained in turn was transformed via its 1,3-di-*O*-mesylate into 1,3-bisdiarylphosphines. One of them, 1,3-diphenyl-1,3-bis(diphenylphosphino)propane, could be advantageously utilized as a ligand for the efficient enantioselective Ru-catalyzed hydrogenation of its own 1,3-diketone precursor. Thus, the condition for a 'cross self-breeding' catalytic system is fulfilled. A further reduction of the preparation costs could be achived by application of $RuCl_3 \cdot H_2O$ instead of other more expensive precatalyst precursors without compromosing the enantioselectivity. The ligand was used in the Rh(I)-catalyzed asymmetric hydrogenation of model substrates and β-amino acid precursors where up to 97% ee could be achieved.

1. Introduction

Chiral trivalent phosphorus compounds play an important role as ligands of late transition metals in homogeneous catalysis, e.g. asymmetric hydrogenation.[1] To date a great variety of ligands have been synthesized by different methodologies.[2] The overwhelming majority is accessible starting from enantiopure compounds which are preferentially derived from the chiral pool, e.g. carbohydrates,[3] amino acids,[4] amino alcohols,[5] terpenes[6] or other chiral material.[7] Another general approach is based on the kinetic resolution of racemic starting materials or intermediates.[8] Similarly effective are enantioselective syntheses with chiral auxiliaries in stoichiometric quantities.[9] However, it is quite strange to note that only rarely has enantioselective catalysis itself been employed for the synthesis of chiral phosphorus ligands.

From the economical point of view particularly interesting are enantioselective catalytic reactions giving rise to ligands that are able to generate their own precursors. For such a process the term 'self-breeding' system was introduced.[10] An example of a hydrogenation catalyst, which breeds its own chirality is the Rh-complex of the chiral diphosphine ProPHOS.[10a] Interestingly, a Ru-catalyst based on (*S*,*S*)-SkewPHOS afforded in the hydrogenation of 2,5-pentandione the precursor diol of the opposite enantiomer of the ligand.[10b] Therefore, Brunner and Terfort named this process 'cross breeding'. Similar approaches could be established at the basis of the ligands DuPHOS and *i*-Pr-BPE.[10c] Preconditions for the use of self-breeding chiral catalysts are either extremely high enantioselectivities (>99% ee) produced directly in the hydrogenation procedure or the opportunity to enrich chiral products of low enantioselectivity in a subsequent purification step.

Herein, we report on the highly enantioselective and economical preparation of C_2-symmetric 1,3-diols **2a–c** (Scheme 1) as a part of a cross self-breeding system. These diols have shown promise as chiral derivatising agents and important synthetic intermediates.[11] We will provide further evidence that such diols can also be

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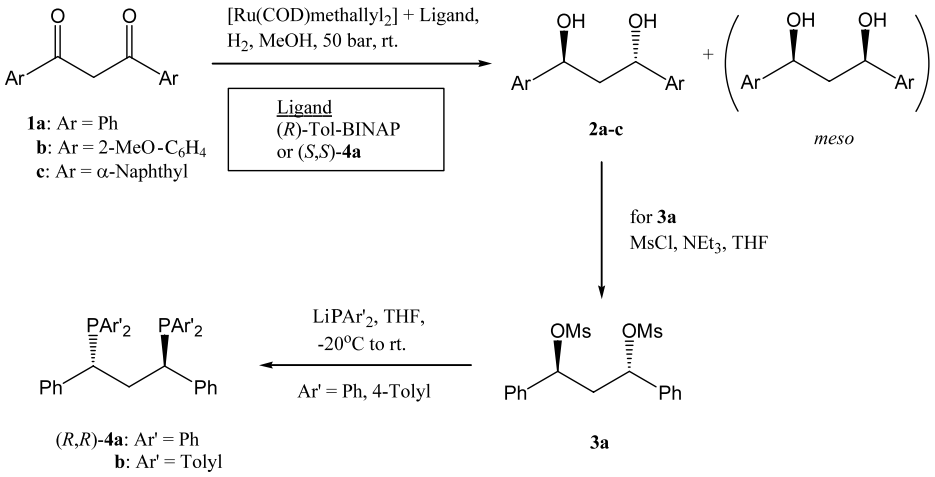


Scheme 1.

used for the preparation of chiral diphosphine ligands. One of these ligands could be conveniently employed for the asymmetric hydrogenation of its own synthetic precursor with opposite configuration. Moreover, the new ligand showed a good catalytic performance in different other asymmetric hydrogenations.

2. Results and discussion

2.1. Economic preparation of the new ligand

For the preparation of chiral 1,3-diarylpropane-1,3-diols, such as **2a** several methods have been reported in the literature. A crucial problem connected with their preparation consists in the high tendency for the elimination of water, affording unsaturated alcohols. Moreover, besides the formation of the desired chiral 1,3-diol, as a side product the corresponding *meso* compound is frequently observed.[12] Raney-nickel modified with tartaric acid,[13] chiral β-ketoiminato cobalt(II) complexes[14] and Ru(II) complexes based on BIPHEMP[15] or chiral ferrocenyl diphosphines[16] gave moderate to excellent des and ees in this reaction. However, these catalysts require special conditions for their preparation and are not easily available.

We prepared the first batch of the 1,3-diol **2a** by the Ru(II) catalyzed enantioselective hydrogenation of diketone **1a** with (*R*)-Tol-BINAP as the chiral ligand following the general procedure of precatalyst preparation suggested by Genêt et al.[17]

The diketone **1a** was reduced quantitatively under the conditions indicated in Table 1. Analysis of the hydrogenation solution by HPLC showed the formation of diol (*S*,*S*)-**2a** with 98% de. That means, the formation of the corresponding *meso*-diol was negligable. No elimination product was found. The enantioselectivity of the product in the solution was 70% ee. Interestingly, enantiomerically pure diol **2a** crystallized spontaneously from the solution as a white powder in 49% yield.

The diol in turn was converted via its dimesylate (*S*,*S*)-**3a** into the 1,3-diphosphines (*R*,*R*)-**4a** and (*R*,*R*)-**4b**. It should be noted that compound **3a** (quantitative yield) is only stable at low temperature. Remarkably, diphosphine (*R*,*R*)-**4a** could be advantageously used as the ligand in the Ru(II)-catalyzed hydrogenation of the diketone **1a** affording enantiomerically pure (*R*,*R*)-diol **2a** in 55% yield. After mesylation and introduction of the phosphino groups ligand (*S*,*S*)-**4a** was obtained.

Table 1. Enantioselective hydrogenation with chiral Ru(II)-diphosphine catalysts[a]

Diketone	Ligand	Time (min)	Diol	Crude product			After crystallization		
				Yield (%)[b]	de (%)	ee (%)	Yield (%)	de (%)	ee (%)
1a	(*R*)-Tol-BINAP	200	(*S*,*S*)-**2a**	>99	98[c]	70[c]	49	>99[c]	>99[c]
1a	(*S*,*S*)-**4a**	170	(*S*,*S*)-**2a**	>99	>98[c]	77[c]	55	>99[c]	>99[c]
1b	(*R*)-Tol-BINAP	170	(−)-**2b**	>99	92[d]	91[d]	62	>99[d]	>99[d]
1c	(*R*)-Tol-BINAP	700	(−)-**2c**	>99	98[e]	95[e]	68	>99[e]	>99[e]

[a] *Conditions*: In a typical run 2.5 mmol of the diketone was hydrogenated at 50 bar initial H_2-pressure, with 0.05 mmol of the precatalyst in MeOH at rt; the precatalyst was generated by mixing 0.05 mmol of [Ru(COD)methallyl$_2$], 0.06 mmol of ligand and 0.055 mmol of 2 M aq. HCl.
[b] Quantitative hydrogen consumption.
[c] Determined by HPLC (CHIRALCEL-OD-H (DAICEL), *n*-hexane/EtOH 95/5).
[d] Determined by HPLC (CHIRALPAK-AD (DAICEL), *n*-hexane/EtOH 95/5).
[e] Determined by HPLC (CHIRALCEL-OD-H (DAICEL), *n*-hexane/EtOH 90/10).

That means starting with 2.24 g (0.01 mol) of diketone **1a** in the initial run, already in the second run (self-breeding system) 85 g of enantiopure **4a** could be derived. Based on this amount of ligand in a third run ca. 4.54 kg of the diphosphine **4a** are accessible. Due to this cross self-breeding property any quantity of the chiral ligand can be now synthesized in a cheap and convenient manner being an important precondition for an industrial application.[18]

Surprisingly, application of the related diphosphine **4b** as ligand in the reduction of diketone **1a** afforded the diol **2a** in only 12% ee, which reveals the high sensitivity of the reaction towards small changes in the structure of the chiral ligand. Moreover, with Ru(II)-complexes of 1,3-diphosphines **4a** and **4b**, respectively, considerable amounts of elimination product and low ee were found, when 1,3-diketones **1b** and **1c** were employed as substrates. For these ketones the application of Tol-BINAP as ligand revealed to be superior. Excellent stereoselectivities were achieved. With the exception of **2b**, which had to be crystallized from benzene/hexane, **2a** and **2c** could be directly derived from the hydrogenation solution. As Table 1 indicates after crystallization all diols were obtained in >99% de and >99% ee. Unfortunately, relevant bis-sulfonates of diols **2b**,**c** decomposed immediately and could not be used for former transformations.

Since the cost of a catalyst is also strongly influenced by the price of the metal, we next investigated the applicability of different Ru-precatalyst precursors for the hydrogenation of diketone **1a**. As ligands (*R*)-BINAP, (*R*)-Tol-BINAP and ligand (*R*,*R*)-**4a** were employed for these studies. Besides the method of Genêt used above for the cross self-breeding system, we also generated the Ru-catalyst by mixing the ligands $[Ru(C_6H_6)Cl_2]$ according to the procedure of Noyori.[19] Another method consisted of the reaction of $[Ru(COD)Cl_2]$ with one equivalent of the ligand prior to the hydrogenation. Finally, as the cheapest method we generated the catalyst by treatment of the diphosphine with $RuCl_3 \cdot H_2O$. Results of the hydrogenation are listed in Table 2.

In general ees observed are only slightly dependent on the catalyst preparation. The catalyst derived from Tol-BINAP is superior to that of BINAP in terms of activity and ee. As clearly to be seen, our new ligand **4a** formed a catalyst with the highest activity and stereodiscriminating ability. Interestingly, complexes formed from the ligand and $RuCl_3 \cdot H_2O$ are also able to reduce the diketone. Although relevant catalysts are less active in comparison to other Ru-precursors some synthetic steps are saved.

In conclusion the principle of the cross self-breeding system combined with the employment of a cheap Ru-catalyst precursors provides the basis for an economically advantageous synthesis of our new chiral ligand.

2.2. Enantioselective hydrogenations

In order to evaluate the full hydrogenation capabilities of ligand **4a** we incorporated it also in other hydrogenation catalysts. First we synthesized a cationic Rh(I)-precatalyst by reaction of ligand **4a** with [Rh(COD)acac] and subsequent addition of HBF_4 and tested it in the reduction of the standard substrates methyl α-Z-*N*-acetylaminocinnamate, methyl α-*N*-acetylamino acrylate, itaconic acid and its dimethylester. As related and industrially important substrates also the β-amino acid precursors methyl *E*- and *Z*-β-*N*-acetylaminobutenoate were tested.

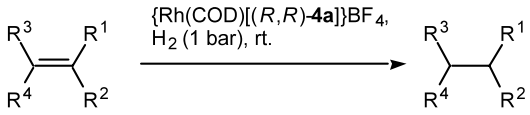
As seen in Table 3 the new catalyst shows a varying enantiodiscriminating ability for different functionalized olefins. Low ees were observed in the hydrogenation of α-amino acid precursors (runs 1 and 2), whereas depending on the solvent used, good to excellent results were achieved in the reduction of the other benchmark substrates itaconic acid (runs 3–5) and its dimethyl ester (runs 6–8). Particularly striking are differences in the hydrogenation of α- and β-amino acid precursors (compare runs 1, 2 and 9–24). Thus with the latter promising ees were achieved. This holds also for *E*-/*Z*-substrate mixtures (runs 15 and 16). As reported several times in the recent literature, *Z*-substrates give significantly lower ees (runs 12–14 and 20–22) than their *E*-counterparts (runs 9–11 and 17–19).[20] A small improvement of the ee could be achieved by application of the benzyl esters (runs 17–24) instead of methyl esters (runs 9–16). Noteworthy is that in most cases CF_3CH_2OH was superior as solvent. This result correlates with our recent observation that polar solvents have a beneficial effect on the hydrogenation of unsaturated β-amino acid precursors.[20a]

Table 2. Hydrogenation of diketone **1a** in dependency on the ligand and the nature of catalyst preparation[a]

	ee (%)/time (h)			
Ligand	L+$[Ru(COD)(methallyl)_2]$	L+$[Ru(C_6H_6)Cl_2]$	L+$[Ru(COD)Cl_2]$	L+$RuCl_3$
(*R*)-BINAP	39/20	42/26	–	40/30
(*R*)-Tol-BINAP	70/3.5	66/6	–	66/20
(*R*,*R*)-**4a**	77/3	–	73/8	76/16

[a] *Conditions*: In a typical run 2.5 mmol of the diketone was hydrogenated at 50 bar H_2-pressure, with 0.05 mmol of the catalyst in 10 ml of MeOH at rt until consumption of H_2 had finished.

Table 3. Enantioselective hydrogenations with {Rh(COD)[(*R*,*R*)-**4a**]}BF_4[a]



Run	R^1	R^2	R^3	R^4	Solvent	ee (%)[b]
1	COOMe	NHAc	H	Ph	MeOH	20 (*S*)[c]
2	COOMe	NHAc	H	H	MeOH	25 (*S*)[d]
3	COOH	CH_2COOH	H	H	CH_2Cl_2	87 (*R*)[e]
4	COOH	CH_2COOH	H	H	MeOH	88 (*R*)[e]
5	COOH	CH_2COOH	H	H	THF	94 (*R*)[e]
6	COOMe	CH_2COOMe	H	H	CH_2Cl_2	96 (*R*)[f]
7	COOMe	CH_2COOMe	H	H	MeOH	75 (*R*)[f]
8	COOMe	CH_2COOMe	H	H	THF	79 (*R*)[f]
9	H	COOMe	NHAc	Me	CF_3CH_2OH	97 (*S*)[g]
10	H	COOMe	NHAc	Me	CH_2Cl_2	94 (*S*)[g]
11	H	COOMe	NHAc	Me	MeOH	86 (*S*)[g]
12	H	COOMe	Me	NHAc	CF_3CH_2OH	71 (*S*)[g]
13	H	COOMe	Me	NHAc	CH_2Cl_2	75 (*S*)[g]
14	H	COOMe	Me	NHAc	MeOH	65 (*S*)[g]
15	H	COOMe	Me/NHAc[h]	NHAc/Me[h]	CF_3CH_2OH	84 (*S*)[g]
16	H	COOMe	Me/NHAc[h]	NHAc/Me[h]	CH_2Cl_2	88 (*S*)[g]
17	H	COOBn	NHAc	Me	CF_3CH_2OH	96 (*S*)[i]
18	H	COOBn	NHAc	Me	CH_2Cl_2	97 (*S*)[i]
19	H	COOBn	NHAc	Me	MeOH	92 (*S*)[i]
20	H	COOBn	Me	NHAc	CF_3CH_2OH	76 (*S*)[i]
21	H	COOBn	Me	NHAc	CH_2Cl_2	82 (*S*)[i]
22	H	COOBn	Me	NHAc	MeOH	81 (*S*)[i]
23	H	COOBn	Me/NHAc[h]	NHAc/Me[h]	CF_3CH_2OH	87 (*S*)[i]
24	H	COOBn	Me/NHAc[h]	NHAc/Me[h]	CH_2Cl_2	92 (*S*)[i]

[a] *Conditions*: 0.01 mmol precatalyst, 1.0 mmol of prochiral olefin in 15.0 ml solvent at 25.0°C, 1.0 atm overall pressure over the solution.
[b] Measured after consumption of the calculate amount of H_2.
[c] Determined by GC, 25 m Chirasil-val (Alltech), 150°C.
[d] Determined by GC, 25 m Chirasil-val (Alltech), 120°C.
[e] After esterification with diazomethane as dimethyl methylsuccinate.
[f] Determined by GC, 25 m cyclodextrine, Lipodex E (Machery and Nagel), fused silica, 85°C.
[g] Determined by GC, 50 m, Chiraldex β-PH, 130°C.
[h] 1:1-mixture was applied.
[i] Determined by HPLC, Chiralcel OD-H (DAICEL), *n*-hexane/EtOH 95:5.

3. Summary and conclusion

As a new chiral ligand for asymmetric hydrogenation 1,3-diphenyl-1,3-bis(diphenylphosphino)propane **4a** was prepared starting from 1,3-diphenylpropane-1,3-dione. Crucial for the preparation of the new ligand, synthesized for the first time in enantiopure form, is the Ru-catalyzed asymmetric hydrogenation of the diketone. In the first trial this was achieved by application of (*R*)-Tol-BINAP as ancillary ligand. After conversion of the enantiopure diol obtained into the diphosphine **4a** the latter could be advantageously employed for the diketone hydrogenation step, which represents one of a rare example of a cross self-breeding system. The new ligand could be also successfully applied for the enantioselective Rh(I)-catalyzed hydrogenation of functionalized olefins. Particularly noteworthy are the good ees achived in the reduction of β-amino acid precursors. Our results give evidence that asymmetric catalysis has also a great potential for the synthesis of enantiopure phosphorus ligands and we hope, that they will stimulate the search for other self-breeding catalytic systems.

4. Experimental

4.1. General

All reagents except otherwise mentioned were purchased from commercial sources and were used without additional purification. Solvents were dried and freshly distilled under argon before use. 1,3-Diketones were prepared according to known methods (for completeness of known data, herein only relevant ^1H and ^{13}C NMR spectra are detailed). The syntheses of methyl *E*- and *Z*-β-*N*-acetylaminobutenoate used as substrates were carried out following known protocols.[21] All reactions involving phosphines were performed under an argon atmosphere by using standard Schlenk techniques. Thin-layer chromatography was performed on precoated TLC plates (silica gel). Melting points are corrected. The optical rotations were measured on a 'gyromat-HP' instrument (Fa. Dr. Kernchen). NMR spectra were recorded at the following frequencies: 400.13 MHz (^1H), 100.63 MHz (^{13}C), 161.98 MHz (^{31}P). Chemical shifts of ^1H and ^{13}C NMR spectra are

reported in ppm downfield from TMS as an internal standard. Chemical shifts of ^{31}P NMR spectra are referred to H_3PO_4 as an external standard. Elemental analyses were performed with a LEGO CHNS-932. Mass spectra were recorded on an AMD 402 spektrometer.

4.2. Synthesis of 1,3-diketones 1b,c

To a mixture of the corresponding methyl ester (0.054 mol) and NaH (6.24 g, 0.13 mol, 50% suspension in paraffin) in THF (150 ml) was slowly added a solution of the corresponding ketone (0.043 mol) in THF (20 ml). The mixture was refluxed under stirring for 14 h. After cooling to room temperature, the mixture was filtered. The residue was washed with ethanol (3×50 ml) and carefully added to a vigorously stirred mixture of ice/hydrochloric acid. The product was extracted with diethyl ether, washed with water and dried over Na_2SO_4. The ether solution was evaporated and the residue was recrystallized from ethanol.

4.2.1. 1,3-Bis(*o*-methoxyphenyl)propane-1,3-dione 1b. Yield: 9.17 g (75%); ^1H NMR ($CDCl_3$) δ 3.52 (3H, s, OCH_3, ketoform), 3.72 (3H, s, OCH_3, enol), 4.49 (2H, CH_2, ketoform), 6.78 (5H, CH=C(OH), arom. H), 7.31–7.39 (2 H, m), 7.77 (2H, dd, ketoform), 7.83 (2H, dd), 11.5 (1H, s, OH); ^{13}C NMR ($CDCl_3$) δ 55.7 (OCH_3, ketoform), 56.1 (OCH_3, enol), 59.8 (CH_2, ketoform), 104.7 (CH=C(OH)), 112.1, 121.1, 130.7, 131.3 (ketoform), 133.4, 134.7 (ketoform), 158.9, 159.3 (ketoform), 189.7 (C=O).

4.2.2. 1,3-Di(1-naphthyl)propane-1,3-dione 1c. Yield: 11.44 g (82%); ^1H NMR ($CDCl_3$) δ 6.43 (1H, s, CH=C(OH)), 7.31–7.48 (6 H, m), 7.66 (2H, d), 7.73 (2H, d), 7.81 (2H, d), 8.48 (2H, d), 12.5 (1H, s, OH); ^{13}C NMR ($CDCl_3$) δ 103.5 (CH=C(OH)), 125.3–132.5, 189.7 (C=O).

4.3. Reduction of 1,3-diketones 1a–c

4.3.1. Reduction of dibenzoylmethane 1a using [Ru(COD)methallyl$_2$] and diphosphine 4a. The precatalyst was prepared from Ru(COD)methallyl$_2$ (0.016 g, 0.05 mmol), (*R*,*R*)-diphosphine **4a** (0.034 g, 0.06 mmol) and 2 M HCl (0.055 ml) in acetone according to Ref. 17. This red–brown solid was dissolved in methanol (10 ml). The clear reddish brown solution was directly added to the autoclave containing dibenzoylmethane (2.24 g, 0.01 mol). The hydrogenation was performed at 50 bar initial H_2-pressure. When the hydrogen consumption ceased (ca. 20 h) the enantiopure diol was filtered off and dried. Yield: 1.25 g (55%); $[\alpha]_D^{23}=+66.5$ (*c* 0.6, EtOH): ref.[11a] $[\alpha]_D=+67.5$ (*c* 0.3, EtOH).

4.3.2. Reduction of dibenzoylmethane 1a using [Ru(COD)Cl$_2$] and diphosphine 4a. The suspension of [Ru(COD)Cl_2] (0.014 g, 0.05 mmol) and (*R*,*R*)-diphosphine **4a** (0.034 g, 0.06 mmol) in DMF (2 ml) was stirred at 100°C for 3 h. The mixture was cooled to 50°C and the solvent removed under vacuum to give the precatalyst as an red–brown solid. This precatalyst was dissolved in methanol (10 ml). This solution was directly added to the autoclave containing dibenzoylmethane (0.56 g, 2.5 mmol). The hydrogenation was performed at 50 bar initial H_2-pressure.

4.3.3. Reduction of dibenzoylmethane 1a using $RuCl_3 \cdot H_2O$. The mixture of $RuCl_3 \cdot H_2O$ (0.010 g, 0.05 mmol) and 0.06 mmol of ligand (BINAP, Tol-BINAP or **4a**) in CH_2Cl_2 (3 ml) and methanol (10 ml) was stirred 1.5 at room temperature to give a green–brown solution. This solution was used for hydrogenation as described above.

4.4. (−)-Bis(2-methoxyphenyl)propane-1,3-diol 2b

The precatalyst was prepared from Ru(COD)methallyl$_2$ (0.016 g, 0.05 mmol), (*R*)-Tol-BINAP (0.034 g, 0.06 mmol) and 2 M HCl (0.055 ml) in acetone according to Ref. 17. This red–brown solid was dissolved in methanol (10 ml). The clear reddish brown solution was directly added to the autoclave containing 1,3-bis(2-methoxyphenyl)propane-1,3-dione **1b** (0.71 g, 2.5 mmol). The hydrogenation was performed at 50 bar initial H_2-pressure for 3 h. 1,3-Diol **2b** (91% ee, 92% de) was recrystallized from benzene/*n*-hexane to give the enantiomerically pure product as white crystals. Yield: 0.45 g (62%); mp 103–104°C, $[\alpha]_D=-133°$ (*c* 0.6, EtOH); ^1H NMR ($CDCl_3$) δ 2.25 (2H, t, CH_2), 3.70 (6H, s, OCH_3), 3.80 (2H, s, OH, exchangeable with D_2O), 5.18 (2H, m, CH), 6.83 (2H, d), 6.95 (2H, m), 7.22 (2H, m), 7.40 (2H, dd); ^{13}C NMR ($CDCl_3$) δ 42.0 (CH_2), 55.2 (OCH_3), 68.2 (CH), 110.3, 120.7, 126.7, 128.1, 132.6, 156.7; MS (70 eV) *m*/*z* (%) 288 $[M]^+$ (2), 270 $[M-H_2O]^+$ (45), 151 (30), 134 (100). $C_{17}H_{20}O_4$ (M = 288.35) calcd: C, 70.81; H, 6.99; found: C, 70.76; H, 6.90.

4.5. (−)-1,3-Di(1-naphthyl)propane-1,3-diol 2c

The precatalyst was prepared from Ru(COD)methallyl$_2$ (0.016 g, 0.05 mmol), (*R*)-Tol-BINAP (0.034 g, 0.06 mmol) and 2 M HCl (0.055 ml) in acetone according to Ref. 17. This red–brown solid was dissolved in methanol (10 ml). The clear reddish brown solution was directly added to the autoclave containing 1,3-di(1-naphthyl)propane-1,3-dione **1c** (0.81 g, 2.5 mmol). The hydrogenation was performed at 50 bar initial H_2-pressure for 12 h. 1,3-Diol (95% ee, 98% de) was recrystallized from MeOH to give the enantiomerically pure product as white crystals. Yield: 0.56 g (68%); mp 168–169°C, $[\alpha]_D=-373$ (*c* 0.6, EtOH); ^1H NMR ($CDCl_3$) δ 2.44 (2H, t, CH_2), 3.10 (2H, s, OH, exchangeable with D_2O), 5.82 (2H, t, CH), 7.20–7.86 (14 H, m); ^{13}C NMR ($CDCl_3$) δ 45.1 (CH_2), 69.2 (CH), 123.0, 123.1, 125.8, 125.9, 126.4, 128.3, 129.2, 130.1, 134.1, 140.1; MS (70 eV) *m*/*z* (%) 328 $[M]^+$ (18), 310 $[M-H_2O]^+$ (44), 154 (100). $C_{23}H_{20}O_2$ (M = 328.42) calcd: C, 84.11; H, 6.13; found: C, 84.08; H, 6.26.

4.6. (*S*,*S*)-Methansulfonyloxy-1,3-diphenylpropane-1,3-diol 3a

(*S*,*S*)-1,3-Di-*O*-(methylsulfonyl)-1,3-diphenylpropane-1,3-diol **3a** was prepared according to the protocol given for the racemic compound in Ref. 12. quantitative yield; decomp. 62–63°C, $[\alpha]_D = -112°$ (*c* 0.8, $CHCl_3$).

4.7. Synthesis of 1,3-diphosphines 4a,b: general procedure

A solution of $LiPAr_2$ (prepared from 17.6 mmol of chlorodiphenylphosphine or chlorobis(*p*-tolyl)phosphine and 106 mmol of Li) was added under stirring to a solution of 1,3-dimesylate **3a** (1.69 g, 4.4 mmol) in THF (30 ml) at −20°C. The resulted solution was allowed to warm to room temperature (5 h) and then the solvent was removed under reduced pressure. The residue was washed with MeOH (30 ml) and recrystallized from MeOH–CH_2Cl_2 (4:1) mixture to afford the product as white crystals.

4.7.1. (*R*,*R*)-Bis(diphenylphosphino)-1,3-diphenylpropane 4a. Yield: 1.34 g (54%); mp 142–143°C, $[\alpha]_D = 190$ (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.07 (2H, m, CH_2), 3.08 (2H, m, CH), 6.61–7.42 (30 H, m, arom. H); ^{13}C NMR ($CDCl_3$) δ 36.3 (CH_2), 43.2 (CH), 126.7–128.5 (m), 130.2, 131.1, 131.7, 135.5, 137.2; ^{31}P NMR ($CDCl_3$) δ −0.48 (s); MS (70 eV) *m*/*z* (%) 564 $[M]^+$ (39), 487 $[M-C_6H_5]^+$ (24), 379 $[M-HPPh_2]^+$ (80), 275 $[M-PPh_2-C_6H_5CH{=}CH_2]^+$ (100). $C_{39}H_{34}P_2$ (M = 564.65) calcd: P, 10.97; found: P, 10.74.

4.7.2. (*R*,*R*)-Bis[(di-*p*-tolyl)phosphino]-1,3-diphenylpropane 4b. Yield: 1.78 g (65%); mp 183–184°C, $[\alpha]_D = 207$ (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.00 (2H, m, CH_2), 2.07 (6H, s, CH_3), 2.33 (6H, s, CH_3), 3.07 (2H, m, CH), 6.56 (4H, m), 6.68 (4H, m), 6.82 (4H, m), 7.02–7.17 (14 H, m); ^{13}C NMR ($CDCl_3$) δ 20.0 (CH_3), 20.4 (CH_3), 34.7 (CH_2), 41.8 (CH), 125.2–133.4 (m), 136.9, 138.4, 143.2; ^{31}P NMR ($CDCl_3$) δ −1.8 (s); MS (70 eV) *m*/*z* (%) 620 $[M]^+$ (34), 529 $[M-CH_3C_6H_5]^+$ (19), 407 $[M-HP(p\text{-Tol})_2]^+$ (81), 303 $[M-P(p\text{-Tol})_2-C_6H_5CH{=}CH_2]^+$ (100). $C_{43}H_{42}P_2$ (M = 620.75) calcd: P, 9.97; found: P, 9.95.

4.8. Preparation of [Rh(COD)4a]BF_4

Diphosphine **4a** (1.34 g, 2.37 mmol) was dissolved in THF (30 ml) and slowly added to a solution of Rh(COD)acac (0.74 g, 2.37 mmol) in THF (30 ml). The solution was stirred for 15 min. Then a stoichiometric amount of aq. 40% HBF_4 was added and stirring was continued for another 15 min. The complex was precipitated with ether. Yield: 1.43 g (72%); ^{13}C NMR ($CDCl_3$) δ 29.4, 32.0 (CH_2, COD), 36.0 (CH_2), 40.6 (CH), 99.5, 102.3 (=CH, COD), 126.3–128.5, 130.2, 131.1, 131.7, 135.5, 137.2; ^{31}P NMR ($CDCl_3$) δ 25.1 (d, J(P,Rh) = 141.5 Hz); FAB MS *m*/*z* (%) 775 $[M-BF_4]^+$, 667 $[M-BF_4-COD]^+$. $C_{47}H_{46}BF_4P_2Rh$ (M = 862.53) calcd: C, 65.44; H 5.37; P 7.18; Rh 11.98; found: C, 64.79; H 4.87; P 6.41; Rh 10.93 (found P:Rh is 1.95:1).

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References

1. (a) McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809; (b) Ohkuma, T.; Kitamura, M.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed. Asymmetric Hydrogenation; Wiley-VCH: New York, 2000; (c) Lagasse, F.; Kagan, H. B. *Chem. Pharm. Bull.* **2000**, *48*, 315; (d) Brunner, H.; Zettlmeier, W. In *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, *Ligands*; VCH: Weinheim, 1993; Vol. 2; (e) Seyden-Penne, J. *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*; John Wiley & Sons: New York, 1995; Chapter 7, p. 367.
2. (a) Tang, W; Zhang, X. *Chem. Rev.* **2003**, *203*, in press; (b) Laurenti, D.; Santelli, M. *Org. Prep. Proc. Int.* **1999**, *31*, 245; (c) Ohff, M.; Holz, J.; Quirmbach, M.; Börner, A. *Synthesis* **1998**, 1391; (d) Holz, J.; Quirmbach, M.; Börner, A. *Synthesis* **1997**, 983; (e) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375.
3. For some recent examples, see: (a) Ohe, K.; Morioka, K.; Yonehara, K.; Uemura, S. *Tetrahedron: Asymmetry* **2002**, *13*, 2155; (b) Suárez, A.; Pizzano, A.; Fernández, I.; Khiar, N. *Tetrahedron: Asymmetry* **2001**, *12*, 633; (c) Faltin, F.; Fehring, V.; Kadyrov, R.; Arrieta, A.; Schareina, T.; Selke, R.; Miethchen, R. *Synthesis* **2001**, 638; (d) Diéguez, M.; Pàmies, O.; Ruiz, A.; Castillón, S.; Claver, C. *Tetrahedron: Asymmetry* **2000**, *11*, 4701; (e) Li, W.; Zhang, X. *J. Org. Chem.* **2000**, *65*, 5871; (f) Yan, Y.-Y.; RajanBabu, T. V. *J. Org. Chem.* **2000**, *65*, 900; (g) Holz, J.; Heller, D.; Stürmer, R.; Börner, A. *Tetrahedron Lett.* **1999**, *40*, 7059.
4. For some recent examples, see: (a) Brauer, D. J.; Kottsieper, K. W.; Schenk, S.; Stelzer, O. *Z. Anorg. Allgem. Chem.* **2001**, *627*, 1151; (b) Quirmbach, M.; Holz, J.; Tararov, V. I.; Börner, A. *Tetrahedron* **2000**, *56*, 775; (c) Saitoh, A.; Misawa, M.; Morimoto, T. *Tetrahedron: Asymmetry* **1999**, *10*, 1025.
5. For a recent example, see: Moulin, D.; Darcel, C.; Jugé, S. *Tetrahedron: Asymmetry* **1999**, *10*, 4729.
6. For some recent examples, see: (a) Komarov, I. V.; Monsees, A.; Spannenberg, A.; Baumann, W.; Schmidt, U.; Fischer, C.; Börner, A. *Eur. J. Org. Chem.* **2003**, 138; (b) Komarov, I. V.; Monsees, A.; Kadyrov, R.; Fischer, C.; Schmidt, U.; Börner, A. *Tetrahedron: Asymmetry* **2002**, *13*, 1615; (c) Robertson, A.; Bradaric, C.; Frampton, C. S.; McNulty, J.; Capretta, A. *Tetrahedron Lett.* **2001**, *42*, 2609; (d) Ogasawara, M.; Yoshido, K.; Hayashi, T. *Organometallics* **2001**, *20*, 1014; (e) Li, X.; Lou, R.; Yeung, C.-H.; Chan, A. S. C.; Wong, W. K. *Tetrahedron: Asymmetry* **2000**, *11*, 2077.
7. Enev, V.; Harre, M.; Nickisch, K.; Schneider, M.; Mohr, J. T. *Tetrahedron: Asymmetry* **2000**, *11*, 1767.

8. For some recent examples, see: (a) Duprat de Paule, S.; Jeulin, S.; Ratovelomanana-Vidal, V.; Genêt, J.-P.; Champion, N.; Dellis, P. *Tetrahedron Lett*. **2003**, *44*, 823; (b) Demay, S.; Volant, F.; Knochel, P. *Angew. Chem*. **2001**, *113*, 1272; *Angew. Chem., Int. Ed*. **2001**, *40*, 1235; (c) Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T, Sayo, N.; Miura, T.; Kumobayashi, H. *Adv. Synth. Catal*. **2001**, *343*, 264; (d) Tissot, O.; Gouygou, M.; Dallemer, F.; Daran, J.-C.; Balavoine, G. G. A. *Angew. Chem*. **2001**, *113*, 1110; *Angew. Chem., Int. Ed*. **2001**, *40*, 1076; (e) Bienewald, F.; Ricard, L.; Mercier, F.; Mathey, F. *Tetrahedron: Asymmetry* **1999**, *10*, 4701; (f) Miura, T.; Imamoto, T. *Tetrahedron Lett*. **1999**, *40*, 4833; (g) Reetz, M. T.; Beuttenmüller, E. W.; Goddard, R.; Pastó, M. *Tetrahedron Lett*. **1999**, *40*, 4977.
9. For some recent examples, see: (a) Ohashi, A.; Imamoto, T. *Tetrahedron Lett*. **2001**, *42*, 1099; (b) Guillen, F.; Fiaud, J.-C. *Tetrahedron Lett*. **1999**, *40*, 2939.
10. (a) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc*. **1978**, *100*, 5491; (b) Brunner, H.; Terfort, A. *Tetrahedron: Asymmetry* **1995**, *6*, 919; (c) Burk, M. J.; Harper, T. G. P.; Kalberg, C. S. *J. Am. Chem. Soc*. **1995**, *117*, 4423.
11. (a) Roos, G. H. P.; Donovan, A. R. *Tetrahedron: Asymmetry* **1999**, *10*, 991; (b) Sugimura, T.; Katagiri, T.; Tai, A. *Tetrahedron Lett*. **1992**, *33*, 367; (c) Prasad, K. R. K.; Joshi, N. N. *Tetrahedron: Asymmetry* **1996**, *7*, 1957; (d) Alexakis, A.; Mangeney, P. *Tetrahedron: Asymmetry* **1990**, *1*, 477; (e) Sugimura, T.; Futagawa, T.; Yoshikawa, M.; Tai, A. *Tetrahedon Lett*. **1989**, *30*, 3807.
12. Brown, J. M.; Murrer, B. A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 489.
13. (a) Ito, K.; Harada, T.; Tai, A. *Bull. Chem. Soc. Jpn*. **1980**, *53*, 3367; (b) Bakos, J.; Tóth, I.; Heil, B. *Tetrahedron Lett*. **1984**, *25*, 4965.
14. Ohtsuka, Y.; Kubota, T.; Ikeno, T.; Nagata, T.; Yamada, T. *Synlett* **2000**, 535.
15. Pini, D.; Mandoli, A.; Iuliano, A.; Salvadori, P. *Tetrahedron: Asymmetry* **1995**, *6*, 1031.
16. Ireland, T.; Großheimann, G.; Wieser-Jeunesse, C.; Knochel, P. *Angew. Chem*. **1999**, *111*, 3397; *Angew. Chem., Int. Ed*. **1999**, *38*, 3212.
17. Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Caño de Andrade, M. C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 665.
18. Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. *Adv. Synth. Catal*. **2003**, *345*, 103.
19. Kitamura, M.; Tokunaga, M.; Ohkuma, T.; Noyori, R. *Tetrahedron Lett*. **1991**, *32*, 4163.
20. (a) Heller, D.; Holz, J.; Drexler, H.-J.; Lang, J.; Krimmer, H.-P.; Drauz, K.; Börner, A. *J. Org. Chem*. **2001**, *66*, 6816; (b) Heller, D.; Drexler, H.-J.; You, J.; Drauz, K.; Krimmer, H.-P.; Börner, A. *Chem. Eur. J*. **2002**, *8*, 5196; (c) Heller, D.; Holz, J.; Komarov, I.; Drexler, H.-J.; You, J.; Drauz, K.; Börner, A. *Tetrahedron: Asymmetry* **2002**, *13*, 2735; (d) Lee, S.-g.; Zhang, Y. J. *Org. Lett*. **2002**, *4*, 2429; (e) Tang, W.; Zhang, X. *Org. Lett*. **2002**, *4*, 4159; (f) Peña, D.; Minnaard, A. J.; de Vries, J. G.; Feringa, B. L. *J. Am. Chem. Soc*. **2002**, *124*, 14552; (g) Drexler, H.-J.; You, J.; Zhang, S.; Fischer, C.; Baumann, W.; Spannenberg, A.; Heller, D. *Org. Proc. Res. Dev*. **2003**, *7*, 355.
21. (a) Lubell, W. D.; Kitamura, M.; Noyori, R. *Tetrahedron: Asymmetry* **1991**, *2*, 543; (b) Zhu, G.; Chen, Z.; Zhang, X. *J. Org. Chem*. **1999**, *64*, 6907; (c) Holz, J.; Monsees, A.; Jiao, H.; Komarov, I. V.; Fischer, C.; Drauz, K.; Börner, A. *J. Org. Chem*. **2003**, *68*, 1701.