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# Cooperative attractive interactions in asymmetric hydrogenations with dihydroxydiphosphine Rh(I) catalysts — a competition study

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**Abstract**

Studies for controlling rate and enantioselectivity of the asymmetric hydrogenation with Rh–diphosphine catalysts by cooperative attractive interactions within the framework of catalyst–substrate complexes are represented. In strong contrast to a Rh(I)[*threo*-1,4-bis(diphenylphosphino)butane-2,3-diol] catalyst an extremely fast reaction took place applying the complex of the analogue *erythro* ligand. This is likely due to a strong intramolecular hydrogen bond between the vicinal HO groups impeding the hemilabile coordination of one of the hydroxy groups on the metal center during the hydrogenation. When a substrate with strong hydrogen bond acceptor properties such as (*E*)-methyl 3-dimethoxyphosphorylbut-2-enoate was hydrogenated even the *threo* catalyst exhibited a fast reaction. The product was obtained in 83% ee. In contrast, when in the ligand both HO groups were replaced by MeO groups only poor conversion and 24% ee were achieved. While with the complex bearing HO groups in methanolic solution the corresponding diastereomeric catalyst substrate complexes were dominant, analogue MeO groups bearing catalyst substrate complexes could not be detected by NMR. For the latter, only the Rh(I)–solvent complex was found revealing the high importance of the additional functional groups on this equilibrium. 

*Keywords:* Asymmetric synthesis; Cooperative effect; Hydrogenation; Phosphines; Rhodium

## 1. Introduction

One of the most fascinating features in homogeneously metal catalyzed asymmetric synthesis is the transfer of the chiral information residing in the backbone of the chiral catalyst to the prochiral substrate. The understanding of this mechanism is essential for a rational design of new ligands and catalysts. Several rationalizations have been suggested to explain results with selected catalytic systems accumulated over the years in terms of product configuration and degree of stereoselection. Besides electronic effects [1] and kinetic features [2], rigid or restrained conformations of the ligand have been identified to be of pivotal importance [3]. Inspired by these 'steric' models for the construction of new ligands, main attention is usually given to the incorporation of bulky groups in order to increase repulsive interactions between parts of the catalyst and the prochiral substrate. By these interactions a difference in the thermodynamic stabilities and reactivities of diastereomeric intermediates yields being the precondition for the achievement of enantioselectivity in the product. It is interesting to note that additional attractive interactions e.g. electrostatic interactions or hydrogen bonds within the framework of the catalyst–substrate assembly have been seldom employed to control conformational fluxionality [4]. One crucial problem of this type of recognition widely distributed in enzymes consists is the large number and variety of competing binding sites in relevant polyfunctionalized catalyst–substrate complexes. Therefore, modeling of individual interactions, studies of equilibria and evaluation of their effect on rate and enantioselectivity represent a great challenge.

Since some years we elaborate the effect of hydroxy groups incorporated in different positions of conventional chiral Rh(I) diphosphine catalysts on rate and enantioselectivity of the asymmetric hydrogenation. We and others showed that the introduction of one or more hydroxy groups into a conventional catalyst changes its

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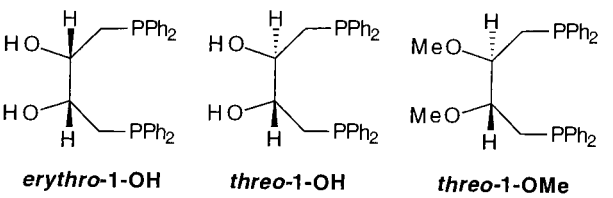
enantiodifferentiating ability [5]. In several cases the intrinsic enantioselectivity of the parent catalyst could be improved [6]. A similar effect was observed when a properly situated methoxy group in the catalyst was replaced by a hydroxy group [7]. Unfortunately, the additional functionality in the diphosphine Rh(I) catalyst caused in most examples a lowering of the reaction rate [8,9]. Particularly pronounced effects were observed in the hydrogenation of *N*-acetylaminocinnamic acid and itaconic acid derivatives with a conformationally-flexible Rh(I) catalyst based on (*R*,*R*)-1,4-bis(-diphenylphosphino)butane-2,3-diol (***threo*-1-OH**) as ligand serving therefore as a model [10]. Spectroscopic studies, X-ray analysis and DFT calculations gave evidence that one of the hydroxy groups can interact with the metal center forming a coordinatively saturated $\eta^3$-coordinated 18 $e^-$ Rh complex (Scheme 1, **A**) [11,12]. Complexes of this type are catalytically inactive. Only the dissociation of the hydroxy group from the metal center affording a $\eta^2$-coordinated species allows the oxidative addition of hydrogen (**C**). In other words, the concentration of complex **A** and the rate of decomplexation, respectively, can influence the rate of the hydrogenation process decisively.

In our model system the formation of the $\eta^3$-coordinated species is forced by the *threo* arrangement of the hydroxy groups. In the analogous mono-hydroxy complex no interactions between the HO group and metal center could be observed both in solution and in the solid state [7]. Nevertheless, unique catalytic effects attributed to the HO group were found. The interaction in the dihydroxy catalyst is dependent on the solvent [11]. Thus, by changing from methanol to methylene chloride, the second (non-coordinated) hydroxy group competed with the metal for the (metal)coordinated hydroxy group by formation of an intramolecular hydrogen bond. By $^{31}P\{^1H\}$-NMR and IR spectroscopy in $CD_2Cl_2$ the coordinatively unsaturated $\eta^2$-complex **B** was found to be dominant (Scheme 1). Interestingly, when the hydrogenation was performed in methylene chloride the consumption rate of hydrogen increased. Based on these results we anticipated that by a change of the geometry of the *threo* 2,3-diol moiety to *erythro* the tendency for the formation of the intramolecular hydrogen bond should be forced. As a result the rate limiting interaction between hydroxy group and the metal center should be weakened. A strong hydrogen bond acceptor in a suitable position of the prochiral substrate could result in the same effect.

In order to prove these hypotheses herein we report on the synthesis of the requisite (achiral) (2*R*,3*S*)-1,4-bis(diphenylphosphino)butane-2,3-diol (***erythro*-1-OH**) and its application in the Rh-catalyzed hydrogenation of several standard olefins. For comparison results observed with the chiral (*R*,*R*)-configurated counterpart ***threo*-1-OH** and its corresponding dimethylether ***threo*-1-OMe** will be also detailed [10]. As a chelating substrate with strong hydrogen bond acceptor properties a prochiral bifunctional α,β-unsaturated phosphonate was chosen for the subsequent asymmetric hydrogenation with chiral Rh(I) complexes of ***threo*-1-OH** and ***threo*-1-OMe**, respectively.

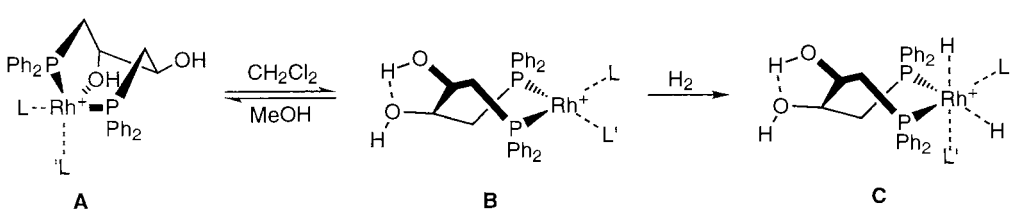



## 2. Results and discussion

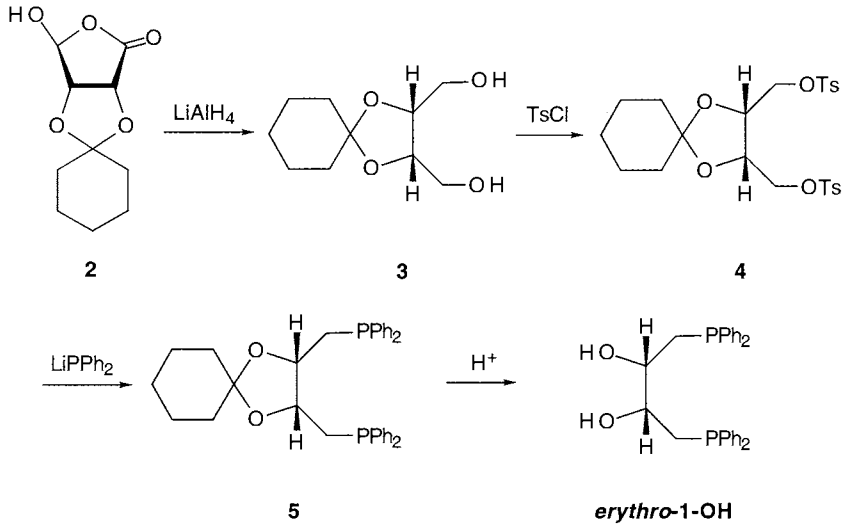
### 2.1. Cooperative effects on the rate of the hydrogenation

#### 2.1.1. Synthesis of the new ligand

The synthesis of (2*R*,3*S*)-1,4-bis(diphenylphosphino)butane-2,3-diol (***erythro*-1-OH**) was accomplished as detailed in Scheme 2. In general, protected erythritol **3** being a key compound in the whole synthesis can be prepared from commercially available *meso* tartaric acid [13]. But due to the high price of the starting material this approach is quite expensive. An alternative pathway starting with maleate, however, requires several synthetic steps [14]. Therefore, we based our approach on commercially available (+)-2,3-*O*-cyclohexylidene-L-erythruronic acid (**2**) which was reduced with $LiAlH_4$ to give **3**. Esterification of the HO groups with tosyl chloride afforded the ditosylate **4**. Replacement of both tosyl groups by lithium phos-




Scheme 1. HO–Rh interactions of ***threo*-1-OH** complexes and their influence on the reactivity towards $H_2$ (L,L′ = diolefin, MeOH, bidentate substrate).




Scheme 2. Synthesis of (2*R*,3*S*)-1,4-bis(diphenylphosphino)butane-2,3-diol (***erythro*-1-OH**).

phide gave rise to the diphosphine **5**, which represents an achiral analogue of DIOP [15]. In the $^{31}P\{^1H\}$-NMR spectrum in $CDCl_3$ this phosphine was characterized by a singlet at $\delta$ −20.6. Cleavage of the cyclohexylidene acetal was performed with methanesulfonic acid in aqueous methanol affording ***erythro*-1-OH** in 56% yield. As a result of the liberation of the HO groups a highfield shift took place in the $^{31}P\{^1H\}$-NMR. The phosphorus resonance was observed at $\delta$ −23.0.

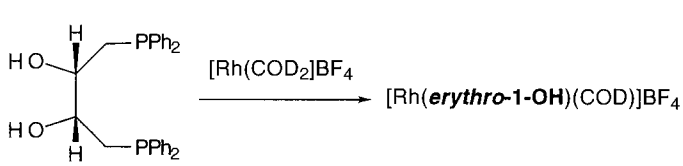
The functionalized diphosphine ***erythro*-1-OH** was reacted with $[Rh(COD)_2]BF_4$ (COD = 1,5-cyclooctadiene) to give the rhodium(I) complex as a yellow powder (Scheme 3).

### 2.1.2. Spectroscopic investigations

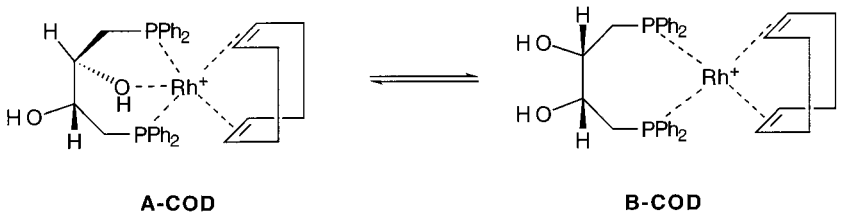
In the IR solid state spectrum the HO valence band was found at 3443 $cm^{-1}$. This is only a small difference compared to the *threo* complex, where the corresponding band was observed at 3441 $cm^{-1}$ [10]. This indicates that also in the *erythro* precatalyst the interaction between one of the hydroxy groups and the rhodium center takes place, giving rise to a $\eta^3$-coordinated complex.

The $^{31}P\{^1H\}$-NMR spectrum of [Rh(***erythro*-1-OH**)(COD)]$BF_4$ in $CD_3OD$ was characterized by a doublet at $\delta$ 18.2. When the solution was cooled the signal became broader. At 225 K two new resonances appeared. Finally at 185 K two doublets of doublets at $\delta$ 29.1 ($J_{Rh,P}$ = 146.1 Hz, $J_{P,P}$ = 36.4 Hz) and 7.2 ($J_{Rh,P}$ = 143.4 Hz) were observed. Following the analysis of the low temperature spectrum of [Rh(***threo*-1-OH**)(COD)]$BF_4$ detailed in a recent publication [11] the doublet at low field can be attributed to a phosphorus atom which is involved in a five-membered chelate ring being formed by the coordination of one of the hydroxy groups on the rhodium center. The resonance at high field characterizes the second phosphorus, which is part of the fused six-membered chelate. The small difference in the chemical shift of $\Delta\tilde{\nu}$ 21.9 ppm is in remarkable contrast to the value observed for [Rh(***threo*-1-OH**)(COD)]$BF_4$ ($\Delta\tilde{\nu}$ = 46.7 ppm), but corresponds to the difference found with [Rh(***threo*-1-OMe**)(COD)]$BF_4$ ($\Delta\tilde{\nu}$ = 16.1 ppm) [10]. For the latter a higher dominance of the bidentate coordination mode was found in deuterated methanol. Obviously, also with [Rh(***erythro*-1-OH**)(COD)]$BF_4$ besides $\eta^3$-coordinated species **A-COD** (Scheme 4) considerable amounts of $\eta^2$-coordinated conformations **B-COD** are present at ambient temperature.

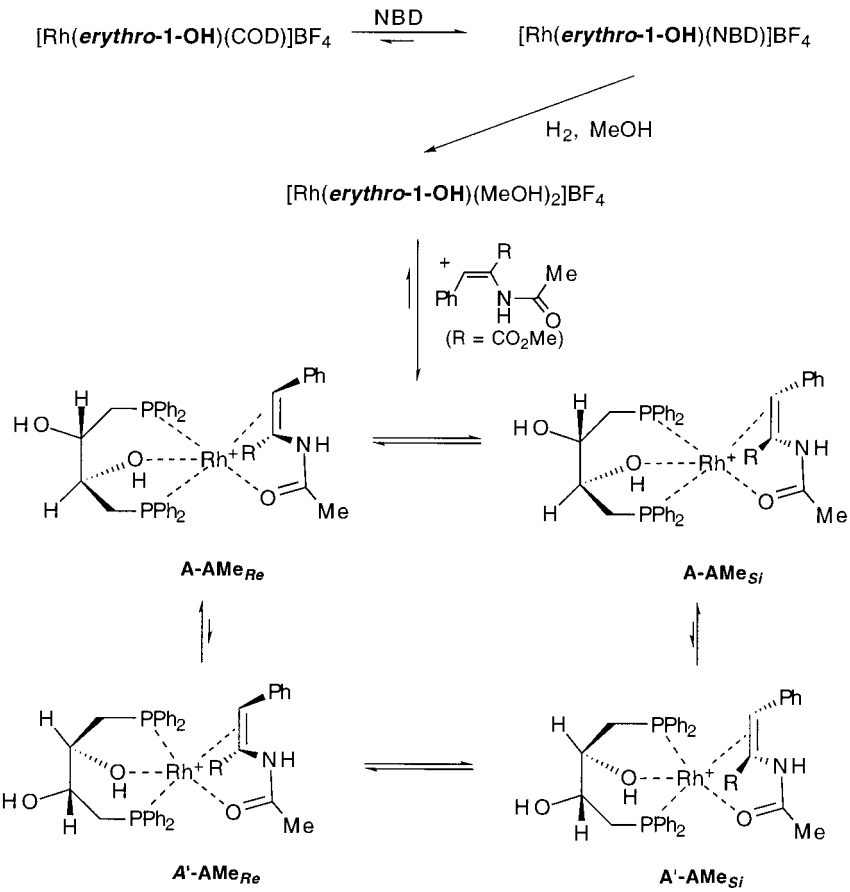
Since the COD complex could not be cleanly reduced to the desired bis-methanol complex (catalytically active species) it was converted into [Rh(***erythro*-1-OH**)(NBD)]$BF_4$ (NBD = norbornadiene) by treatment with an excess of norbornadiene (Scheme 5). Subsequently, this complex was exposed for 30 min to 0.1 MPa of hydrogen in order to remove norbornadiene by hydrogenation and to generate [Rh(***erythro*-1-OH**)$(MeOH)_2]BF_4$. To this complex a five-fold molar excess of methyl (*Z*)-*N*-acetylaminocinnamate (AMe) was added. Due to the $^{31}P\{^1H\}$-NMR spectrum the bis-methanol complex was fully converted into substrate–catalyst complexes (**A-AMe**). At 297 K an ABX pattern with different line width for the A and B part became visible. The signals broadened as the temperature was lowered further. Finally, two well separated




Scheme 3. Synthesis of [Rh(***erythro*-1-OH**)(COD)]$BF_4$.




Scheme 4. Alternate interactions of HO groups in [Rh(*erythro*-**1-OH**)(COD)]$BF_4$ in $CD_3OD$.



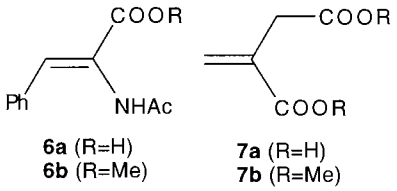

Scheme 5. Formation of diastereomic catalyst–substrate complexes via NBD- and bis-methanol complex.

ABX spectra could be observed characterizing four phosphorus nuclei of two diastereomeric substrate complexes in a ratio of approximately 1:1. The close chemical shift of all resonances in the range between $\delta$ 25.6 and 20.1, as well as two small $^{103}Rh$–$^{31}P$ coupling constants of 136.5 and 136.0 Hz [11], indicate the tripodal coordination of the hydroxyphosphine ligand. In principle, due to the stereofacial coordination of prochiral AMe on rhodium the alternate coordination of both hemilabile HO ligands should produce a spectrum characterizing four diastereomeric substrate complexes (**A-AMe**$_{Re}$, **A-AMe**$_{Si}$, **A′-AMe**$_{Re}$, **A′-AMe**$_{Si}$). Only two of them are observed. In agreement with earlier investigations [11] we suggest that the phosphine *trans* to the carbonyl oxygen is involved in the six-membered O–P–Rh chelate (**A-AMe**$_{Re}$, **A-AMe**$_{Si}$). The line-shape analysis indicated that high-field signals exchange with high-field and the low-field with low-field signals, respectively, and gives proof for the proposed ***Re*/*Si***-interconversion.

### *2.1.3. Hydrogenations*

Hydrogenation experiments with achiral [Rh(***erythro*-1-OH**)(COD)]$BF_4$ were performed with a substrate–catalyst ratio of 100:1 in methanol with a hydrogen pressure over the solution of 0.1 MPa. As test substrates (*Z*)-*N*-acetylaminocinnamic acid (**6a**), itaconic acid (**7a**) and their methyl esters (**6b** = AMe, **7b**) were employed. The times measured for the consumption of 50% of hydrogen are summarized in Table 1. Values measured with the chiral *threo* catalysts and its dimethylether are given for comparison. Since the enan-

Table 1
Time (in min) required for 50% consumption of hydrogen with [Rh(ligand)(COD)]$BF_4$ [a]




**6a** (R=H) **6b** (R=Me) **7a** (R=H) **7b** (R=Me)

| Ligand | Substrate | | | |
|---|---|---|---|---|
| | **6a** | **6b** | **7a** | **7b** |
| ***erythro*-1-OH** | <2 | <2 | <2 | <2 |
| ***threo*-1-OH** | 190 [b] | 960 | 6.0 [b] | – [c] |
| ***threo*-1-OMe** | 145 [b] | 240 | 3.7 [b] | 40 |

[a] Conditions: 0.01 mmol of precatalyst, 1.0 mmol of substrate in 15 ml of MeOH at 25°C and 0.1 MPa $H_2$ pressure. Times indicated were measured with an automatically registrating hydrogen consumption device.

[b] Times are derived from Ref. [10]. In this reference also the % ee values are detailed.

[c] Hydrogenation proceeded only under elevated pressure.

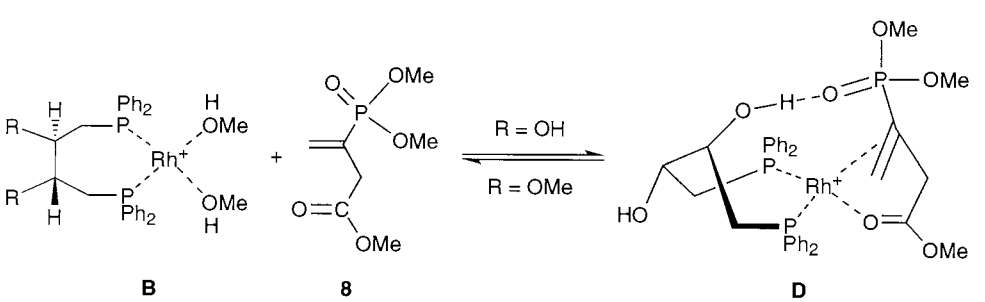
tioselectivities achieved with the latter are not relevant for the discussion herein, they are omitted from the table. Browsing the values listed clearly shows that hydrogenations with the ***erythro*-1-OH** complex proceeded superior. Conversions with this catalyst occured so fast that the time required for the hydrogenation of COD has to be taken into consideration [9]. Therefore, exact specifications of times are not given. It is noteworthy that hydrogenation times noted with the ***erythro*-1-OH** catalyst were even shorter than with the catalyst bearing only a single hydroxy group [7].

Although in the $^{31}P\{^1H\}$-NMR spectra no differences between catalyst–substrate complexes of ***erythro*-1-OH** and ***threo*-1-OH** at low temperature could be found, which is in contrast to results obtained with precatalysts strikingly different consumption rates of hydrogen were observed. Clearly, only the identification of individual stable catalyst–substrate complexes does not allow a reliable conclusion on macroscopically observed overall rates. Rate constants of preequilibria and rate determining steps are required in order to enlighten the special role of the catalytically non-reactive $\eta^3$-coordinated catalyst–substrate complexes (**A-AMe**) on the catalytic cycle. Unfortunately, up to now due to the great complexity of our model systems chosen the complete set of data under hydrogenation conditions were not accessible.

### *2.2. Cooperative effects on the asymmetric hydrogenation*

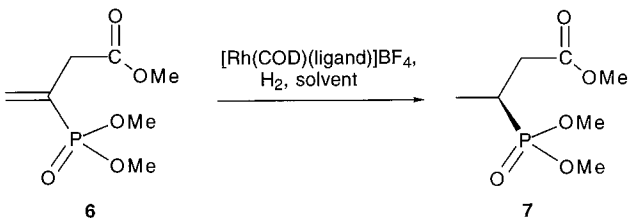
As mentioned in the introduction an accelerating effect on the hydrogenation of dehydroamino acid derivatives has been already achieved, when the ***threo*-1-OH** catalyst operated in a nonpolar solvent [11]. In comparison to the reaction in methanol the asymmetric hydrogenation proceeded approximately five-fold faster in methylene chloride without affecting the enantioselectivity. The change from methanol to the nonpolar solvent shifted in the precatalyst the equilibrium from the $\eta^3$- to the $\eta^2$-coordination mode and simultaneously an intramolecular hydrogen bond between both HO groups was formed (Scheme 1, **B**).

We found that addition of triphenylphosphine oxide to the solution of the precatalyst [Rh(***threo*-1-OH**)(COD)]$BF_4$ in $CD_2Cl_2$ led to the cleavage of the intramolecular hydrogen bond in the backbone of the chiral complex and the concomitant construction of an intermolecular hydrogen bond between phosphine oxide and one of the HO groups. The other hydroxy group coordinated on the rhodium. Inspired by this experiment we anticipated that the P=O fragment incorporated in an appropriate prochiral substrate could provide for the same effect by formation of an intramolecular hydrogen bond. For this reason, we have chosen 3-dimethylphosphono-butenoate (**8**, Scheme 6) [16] representing a phosphonate analogue of dimethyl itaconate.




Scheme 6. Shift of the equilibrium between solvent complex and catalyst–substrate complex in dependence on the substituent R in $CD_3OD$ as solvent.

Table 2
Asymmetric hydrogenation of (*E*)-methyl 3-dimethoxyphosphorylbut-2-enoate [a]




| Run | Ligand | Solvent | $t/2$ [b] (min) | ee [c] (%) |
|---|---|---|---|---|
| 1 | [Rh(***threo*-1-OMe**)(COD)]$BF_4$ | Methanol | >1000 | 24 (*S*) |
| 2 | [Rh(***threo*-1-OH**)(COD)]$BF_4$ | Methanol | 220 | 83 (*S*) |
| 3 | [Rh(***threo*-1-OH**)(COD)]$BF_4$ | $CH_2Cl_2$ | No conversion | – |

[a] For conditions of the hydrogenation compare with Table 1.
[b] Time required for 50% consumption of hydrogen.
[c] For the analysis of the hydrogenation product, see Ref. [16].

### 2.2.1. Spectroscopic studies

In order to study interactions in relevant catalytic intermediates $^{31}P\{^1H\}$-NMR spectra in deuterated methanol were recorded. When [Rh(***threo*-1-OMe**)-$(MeOH)_2]BF_4$ generated by prehydrogenation of the NBD complex was treated with an five-fold excess of (*E*)-methyl 3-dimethoxyphosphorylbut-2-enoate the bis-solvent complex was found exclusively which is characterized by a doublet at $\delta$ 45.4 ($J_{Rh,P} = 199.8$ Hz) (Scheme 6, **B**). In this complex no intramolecular interaction between MeO groups and rhodium occurred [11]. The observation of the bis-solvent complex gives proof for the low stability of the diastereomeric catalyst–substrate complexes belonging to it and fits well to our results obtained with [Rh((*R*,*R*)-DIOP)-$(MeOH)_2]BF_4$ and methyl 3-dimethylphosphonobutenoate as substrate in hand where the relevant bis-methanol complex was also dominant.

In contrast, by addition of (*E*)-methyl 3-dimethoxyphosphorylbut-2-enoate to [Rh(***threo*-1-OH**)-$(MeOH)_2]^+$ the resonances of catalyst–substrate complexes were observed revealing their high thermodynamic stability. In deuterated methanol a variety of complexes were formed. The major complex present in a concentration of more than 70% was characterized by three sets of signals at $\delta$ −6.3 ($PPh_2$, ddd, $J_{Rh,P} = 121.0$ Hz, $J_{P,P} = 31.6$ Hz, $J_{P,P=O} = 14.0$ Hz), $\delta$ 58.4 ($PPh_2$, dd, $J_{P,Rh} = 159.5$ Hz, $J_{P,P} = 31.6$ Hz) and $\delta$ 34.6 (P=O, dd, $J_{P,P} = 14.0$, $J_{P,Rh} = 2.8$ Hz). In principle, (*E*)-methyl 3-dimethoxyphosphorylbut-2-enoate affords the possibility of competitive or cooperative binding by the α- and β-functional groups. However, due to the small $^{103}Rh$–$^{31}P(O)$ coupling of 2.8 Hz the coordination of the P=O group in the major complex could be excluded. The $^{31}P$–$^{31}P$ coupling constant of 14.0 Hz gave proof for the *trans* arrangement of the vinylphosphonate moiety and the concerned phosphine. The large shift differences of the observed signals indicate that no interaction between HO groups and metal center takes place. We suggest that the Rh–O interaction is suspended due to a intramolecular hydrogen bond between HO group and P=O functionality (**D**). Unfortunately, this feature could not be verified by spectroscopy because a clear differentiation between hydrogen bonds between P=O and HO groups of the ligand (intramolecular) or between P=O and HO groups of the solvent (intermolecular) was not possible.

Besides the pattern of the major catalyst–substrate complex discussed in detail a second complex with similar chemical shifts and coupling constants was observed in very low concentration [$\delta$ 3.0, ($PPh_2$, ddd), $\delta$ 57.5 ($PPh_2$, dd)]. Apparently, in two other minor catalyst–substrate complexes also detected coordination of the P=O group on the metal took place which was indicated by rather large $^{103}Rh$–$^{31}P$ and $^{31}P$–$^{31}P$ couplings of 19.0 and 6.6 Hz, respectively.

### 2.2.2. Asymmetric hydrogenations

Results of the hydrogenation are listed in Table 2. As can be clearly seen with [Rh(***threo*-1-OMe**)(COD)]$BF_4$ very poor conversion took place (run 1). The hydrogenation product was obtained in 24% ee. In striking contrast [Rh(***threo*-1-OH**)(COD)]$BF_4$ reduced the prochiral substrate much faster (run 2). (*S*)-Methyl 3-dimethoxyphosphoryl-butyrate was obtained in 83% ee. It is remarkable that by application of the latter in methylene chloride as solvent no conversion was observed (run 3). We assume that in both solvents an intramolecular hydrogen bond between one of the HO groups and the P=O group of the substrate is established. While in MeOH the other HO group is engaged by the solvent allowing the oxidative addition of hydrogen to proceed; in methylene chloride this HO group couples on the rhodium center. The $\eta^3$-coordinated complexes formed are catalytically inactive and therefore interrupt the hydrogenation. This assumption explains the dramatic reversal of the hydrogenation activity by changing from *N*-acetylaminocinnamate to 3-dimethoxyphosphorylbut-2-enoate as substrate in MeOH and methylene chloride, respectively. With the former the catalytically inactive $\eta^3$-complex is dominant in MeOH, whereas in the latter this $\eta^3$-complex dominates in methylene chloride.

In conclusion we have shown that the decelerating effect frequently observed in the asymmetric hydrogenation with Rh(I) complexes bearing hydroxyphosphines as ligands can be fully suspended by the cooperative effect of a properly placed second hydroxy

group. Obviously, the latter competes with the metal for the hydroxy functionality by formation of an intramolecular hydrogen bond. The Rh–OH dissociation step seems to be essentially for the oxidative addition of hydrogen on the rhodium center. Surprisingly, a strong hydrogen bond accepting group like P=O incorporated in the substrate may also induce the acceleration of the hydrogenation. Simultaneously, a dramatic increase of the enantioselectivity was observed. Thus, with (*E*)-methyl 3-dimethoxyphosphorylbut-2-enoate as prochiral olefin 83% ee could be achieved with the Rh(I) catalysts based on the conformationally flexible *threo*-1,4-bis(diphenylphosphino)butane-2,3-diol as ligand. This represents an increase of ca. 60% compared to the result obtained with the analogous dimethoxy catalysts. It has to be verified if the superior enantioselectivities noted several times in the asymmetric hydrogenation of difunctionalized olefins like (*Z*)-*N*-acetylaminocinnamic acid, itaconic acid and their methyl esters is also caused by an intramolecular hydrogen bond between hydroxy groups of the ligand and the carboxylic group of the substrate. In principle, our results clearly demonstrate the high potential of hydroxy groups in chiral metal catalysts for tuning of reactivity and enantioselectivity of asymmetric transformations. It opens entirely new perspectives for the enantioselective discrimination of prochiral substrates.

## 3. Experimental

### 3.1. (2R,3S)-2,3-O-Cyclohexylidene-butan-1,2,3,4-tetrol (3)

(+)-2,3-*O*-Cyclohexylidene-L-erythruronic acid **2** (6.00 g, 28.0 mmol) was dissolved in THF (50 ml). The solution was slowly dropped to a stirred suspension of $LiAlH_4$ (2.13 g, 56.0 mmol) in THF (100 ml). Then the reaction mixture was stirred under reflux for 1 h. The excess of hydride was carefully destroyed with water (2.2 ml), 15% aqueous NaOH (2.2 ml) and water (6.6 ml). After filtration the precipitated hydroxide was extracted with boiling methylene chloride overnight. The combined extracts were dried with anhydrous $Na_2SO_4$ and the solution was concentrated. The residue was purified by column chromatography (*n*-hexane–AcOEt = 1:1) to give the crystalline tetrol **3**.

Yield: 4.90 g (86%); m.p. 43–45°C; $^1$H-NMR ($CDCl_3$) $\delta$ 4.20 (m, 2H, CHO), 3.68 (m, 4H, $CH_2O$), 3.60 (s, 2H, OH, exchangeable with $D_2O$), 1.52–1.32 (m, 10H, $(CH_2)_5$); $^{13}$C-NMR ($CDCl_3$) $\delta$ 108.8 (OCO), 76.4 (CHO), 60.6 ($CH_2OH$), 37.3 ($CH_2O$), 34.4 ($CH_2O$), 24.9 ($CH_2$), 23.8 ($CH_2$), 23.4 ($CH_2$); IR (KBr) $\tilde{\nu}_{OH}$ 3232; MS (EI, $m/z$) 202 ($M^+$, 22), 171 ($M^+ - CH_2OH$, 13), 159 ($M^+ - C_3H_7$, 100); $C_{10}H_{18}O_4$ (202.25) calc.: C, 59.39; H, 8.97; found: C, 59.47; H, 8.81.

### 3.2. (2R,3S)-2,3-O-Cyclohexylidene-1,4-di-O-p-toluenesulfonyl-butan-1,2,3,4-tetrol (4)

To a stirred solution of the diol **3** (4.60 g, 22.7 mmol) in pyridine (20 ml) was added *p*-toluenesulfonyl chloride (10.0 g, 52.3 mmol) in small portions at 0°C. The reaction mixture was stirred overnight at room temperature before it was poured on ice. The product was extracted with methylene chloride (3 × 100 ml) and the organic layers were washed with 5% aqueous sulfuric acid until the water phase stayed acidic. After washing with water and drying with $Na_2SO_4$ the solvent was removed and the residue was recrystallized with ethanol to give **4** as white needles.

Yield: 8.15 g (70%); m.p. 108–110°C; $^1$H-NMR ($CDCl_3$) $\delta$ 7.76 (m, 4H, arom. H), 7.34 (m, 4H, arom. H), 4.29 (m, 2H, CHO), 4.02 (m, 4H, $CH_2O$), 2.44 (s, 6H, $CH_3$), 1.55–1.30 (m, 10H, $(CH_2)_5$); $^{13}$C-NMR ($CDCl_3$) $\delta$ 145.2 (arom. C), 132.6 (arom. C), 130.0 (arom. C), 128.0 (arom. C), 110.6 (OCO), 73.6 (CHO), 67.1 ($CH_2OTs$), 37.2 ($CH_2O$), 34.5 ($CH_2O$), 24.9 ($CH_2$), 23.8 ($CH_2$), 23.5 ($CH_2$), 21.6 ($CH_3$); MS (EI, $m/z$) 481 ($M^+ - C_2H_5$, 27), 467 ($M^+ - C_3H_7$, 95), 91 ($C_7H_7^+$, 100); $C_{24}H_{30}O_8S_2$ (510.62) calc.: C, 56.45; H, 5.92; S, 12.56; found: C, 56.44; H, 6.00; S, 12.69.

### 3.3. (2R,3S)-2,3-O-Cyclohexylidene-1,4-bis-(diphenylphosphino)-butan-2,3-diol (5)

A freshly prepared solution of $LiPPh_2$ [from $ClPPh_2$ (4.3 ml, 23.5 mmol) and Li (0.50 g, 71 mmol in THF (15 ml)] was added slowly to a solution of the ditosylate **4** (3 g, 5.88 mmol) in THF (15 ml). The addition was stopped when the red color remained. After an additional 2 h the THF was removed under vacuum and the residue was treated with water (10 ml) and methylene chloride (50 ml). The organic phase was dried with $Na_2SO_4$. After evaporation of the solvent the crude product was purified by column chromatography (*n*-hexane–AcOEt = 19:1, $R_f = 0.5$) to give the phosphine **5** as a colorless syrup.

Yield: 2.10 g (66%); $^{31}$P-NMR ($CDCl_3$) $\delta$ −20.6; $^1$H-NMR ($CDCl_3$) $\delta$ 7.50–7.22 (m, 20H, arom. H), 4.12 (m, 2H, CHO), 2.42 (m, 2H, $CH_2P$), 2.32 (m, 2H, $CH_2P$), 1.61–1.31 (m, 10H, $(CH_2)_5$); $^{13}$C-NMR ($CDCl_3$) $\delta$ 138.6 (d, arom. C–P), 138.1 (d, arom. C–P), 133.1–128.3 (arom. C), 108.8 (OCO), 75.4 (m, CHO), 38.3 ($CH_2O$), 35.1 ($CH_2O$), 30.1 (d, $^1J_{C,P} = 13.1$ Hz, $CH_2P$), 25.1 ($CH_2$), 24.0 ($CH_2$), 23.8 ($CH_2$); MS (EI, $m/z$) 538 ($M^+$, 31), 461 ($M^+ - C_6H_5$, 100), 185 ($PPh_2^+$, 29); $C_{34}H_{36}O_2P_2$ (538.61) calc.: C, 75.82; H, 6.74; P, 11.50; found: C, 76.04; H, 6.50; P, 11.29.

### 3.4. (2R,3S)-1,4-Bis(diphenylphosphino)-butan-2,3-diol (*erythro*-1-OH)

Diphosphine **5** (1.80 g, 3.34 mmol) was stirred in a anaerobic mixture of methanol (50 ml), water (8 ml) and methanesulfonic acid (100 μl) under reflux. The reaction was followed by TLC ($CH_2Cl_2$–AcOEt = 20:1, $R_f = 0.3$). After completion of the reaction the solvents were evaporated and the residue was purified by column chromatography.

Yield: 0.86 g (56%); m.p. 114–116°C; $^{31}$P-NMR ($CDCl_3$) $\delta$ −23.0; $^1$H-NMR ($CDCl_3$) $\delta$ 7.50–7.26 (m, 20H, arom. H), 3.76 (m, 2H, CHO), 2.48–2.32 (m, 6H, $CH_2P$, OH); $^{13}$C-NMR ($CDCl_3$) $\delta$ 138.2 (d, arom. C–P), 137.5 (d, arom. C–P), 133.2–128.5 (arom. C), 72.3 (m, CHO), 30.1 (d, $^1J_{C,P} = 12.1$ Hz, $CH_2P$); IR (KBr) $\tilde{\nu}_{OH}$ 3475; MS (EI, $m/z$) 458 ($M^+$, 11), 381 ($M^+ - C_6H_5$, 29), 273 ($M^+ - PPh_2$, 100), 185 ($PPh_2^+$, 69); $C_{28}H_{28}O_2P_2$ (458.48) calc.: C, 73.35; H, 6.16; P, 13.51; found: C, 73.01; H, 6.47; P, 13.19.

### 3.5. [Rhodium(*erythro*-1-OH)(cyclooctadiene)]-tetrafluoroborate complex

Diphosphine ***erythro*-1-OH** (0.47 g, 1.03 mmol) and $[Rh(COD)_2]BF_4$ (418 mg, 1.03 mmol) were stirred in THF (8 ml) at r.t. for 1 h. Then the solution was filtrated and the desired complex was precipitated by addition of diethylether. Filtration and washing of the orange powder with diethylether (2 × 4 ml) yielded the pure complex.

Yield: 0.49 g (63%); $^{31}$P-NMR ($CDCl_3$) $\delta$ 16.5 (d, $^1J_{Rh,P} = 144$ Hz); $^1$H-NMR ($CDCl_3$) $\delta$ 7.72–7.33 (m, 20H, arom. H), 4.59 (m, 4H, H–COD), 4.07 (m, 2H, CHO), 3.60 (s, 2H, OH), 2.75–2.10 (m, 12H, $CH_2P$, $CH_2$); $^{13}$C-NMR (DMSO-$d_6$) $\delta$ 135.7–129.2 (arom. C), 99.2 (m, =CH), 70.9 (m, CHO), 31.9 (d, $^1J_{C,P} = 20.0$ Hz, $CH_2P$), 30.9 ($CH_2$); IR (KBr) $\tilde{\nu}_{OH}$ 3443; $C_{36}H_{40}BF_4O_2P_2Rh$ (756.38) calc.: C, 57.17; H, 5.33; P, 8.19; Rh, 13.61; found: C, 57.59; H, 5.85; P, 8.43; Rh, 12.99.

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