The Effect of Internal Hydroxy Groups in Chiral Diphosphane Rhodium(I) Catalysts on the Asymmetric Hydrogenation of Functionalized Olefins

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Keywords: Asymmetric synthesis / Cooperative effects / Hydrogenation / Phosphanes / Rhodium

The unique effects of internal hydroxy groups in chiral rhodium(I) diphosphane catalysts on the asymmetric hydrogenation of functionalized olefins are summarized. In the first part, effects caused by the additional functional group on the rate and enantioselectivity of the catalytic reaction with Rh^I-diphosphane complexes are shown. For comparison, the results obtained with relevant parent catalysts or complexes bearing alkoxy groups are also considered. Subsequently, mechanistic studies which may explain the rate-reducing as well as the *ee*-enhancing effect of hydroxy groups are discussed in detail. Furthermore, the subtle competitive interplay between the hemilabile behaviour of hydroxy groups and their ability to establish hydrogen bonding within the framework of the ligand or between the ligand and the substrate is shown. Proof is given that conformationally flexible ligands bearing hydroxy groups can respond to varying electronic features of the catalytic centre and the substrate. Finally, the beneficial effect of hydroxy groups on the fine-tuning of diphosphane catalysts of low performance is demonstrated for some examples. This modification resulted in catalysts which afforded the chiral hydrogenation product in up to 99% *ee*.

Introduction

The effective control of stereoselective transformations is at the centre of modern organic chemistry research.[1] In stereodifferentiating catalysis employing transition metal complexes, two principal interactions between the catalyst and the prochiral substrate can be identified and these interactions enable chiral recognition: stereodiscriminating bond formation and diastereoselective repulsive interactions. These factors lead to diastereomeric intermediates with different thermodynamic stabilities and consequently in different concentration ratios. The diastereomeric intermediates in turn react to form the enantiomeric products. Owing to the energy differences of the intermediates, the rates are more or less different. For most catalytic reactions, the thermodynamic stabilities of the intermediates as well as the rate constants of the pre-equilibrium and the rate-determining steps are not available and cannot be predicted by theoretic methods. Consequently, the design of asymmetric catalysts is mainly based on trial and error.

To optimize chiral catalysts of low performance, several approaches have been envisaged. The most common way is to increase the bulkiness of selected parts of the ligand or to ensure rigid or restrained conformations of the catalyst.[2,3] Achiwa[4] and RajanBabu[5] showed that in some cases electronic effects can be advantageously employed for the fine-tuning of chiral catalysts. Most of these approaches consider the chiral catalyst as being static and focus on the construction of conformationally fixed molecules and do not take the varying steric and electronic features of catalytic intermediates or different substrates into consideration.[6]

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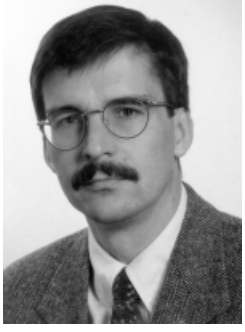

Armin Börner received his Ph.D. in 1984 from the University of Rostock (Germany) with Prof. H. Kristen, working in the field of carbohydrate chemistry. He moved to the Department of Complex Catalysis of the Academy of Sciences of the former GDR, at that time led by Prof. H. Pracejus. After some research stays in the pharmaceutical industry and abroad (1981, Debrecen, Hungary; 1987, Hyderabad, India), he joined the group of Prof. H. B. Kagan at the Laboratoire Synthèse Asymétrique at Orsay (France) in 1991 for a postdoctoral position. In 1992 he joined the "Asymmetric Catalysis" group at the Max-Planck-Gesellschaft (leader Prof. R. Selke), where he finished his habilitation in 1994. In 1993/94 he was a guest lecturer at the University of Würzburg. Currently, he is working as head of department at the Institut für Organische Katalyseforschung (IfOK). In 2000 he was appointed a C3-professor for "Asymmetric Catalysis" at the university of Rostock. His main research is focused on basic research in asymmetric catalysis with transition metals and its application in industry.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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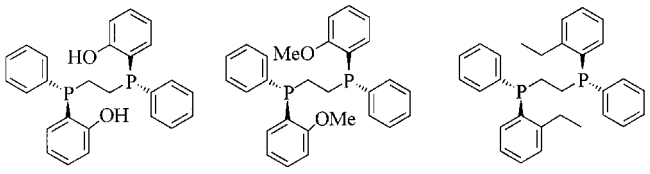
In 1992 Sawamura and Ito addressed the question of the benefit of secondary interactions in asymmetric metal catalysis.[7] Since that time, we and several other groups have elaborated the synthesis and application of chiral ligands containing additional functional groups. The aim was to control the conformational fluxionality within diastereomeric catalyst−substrate assemblies by electrostatic interactions,[8] π,π-interactions,[9] charge-transfer interactions,[10] hydrogen bonding,[11] Lewis acid/base interactions[12] or by inclusion in crown ethers.[13]

In particular, we were interested in investigating the influence of hydroxy groups in the backbone of conventional chiral diphosphane Rh^I-catalysts on the asymmetric hydrogenation. This reaction is of pivotal importance from an academic point of view[14] as well as for practical applications.[15] In the beginning of the research, we focused our attention on the synthesis of chiral hydroxy phosphanes and developed main strategies for their preparation. This work has recently been reviewed.[16] In this paper we will concentrate on the effects caused by hydroxy groups in diphosphane metal catalyst on the asymmetric hydrogenation. Simultaneously, reasons for these peculiar effects will be discussed. It should be noted that the effect of other "active" functional groups like amino or carboxylate groups are also worth being elaborated on, but are not considered here in detail.[7] Other typical features of phosphane ligands bearing hydroxy groups, such as the improvement of the solubility of the catalyst in water,[17] transformations into other functional groups[18] or the construction of heterobimetallic catalysts[12d,12e] have been discussed elsewhere.

In order to illustrate the distinct behaviour of the hydroxy group in the hydrogenation catalysts, comparison with closely related catalysts acting under the same conditions is necessary. From this point of view, valuable information can be derived particularly by comparison with analogous catalysts bearing alkoxy groups. The beneficial effect of alkoxy functionalities, especially that of the OMe group in asymmetric hydrogenation, has been more thoroughly investigated and employed in the past.[19] Principally, the OMe and the OH groups have some common features in catalysis, e.g. both can act as hemilabile ligands[20] and show a "windshield wiper effect" if properly placed,[21] but only the latter is able to serve as a hydrogen-bond donor. In this review, similarities between both are analyzed, but evidence will be also provided to show that the structural differences can have a significant influence on the course of the rhodium-catalyzed asymmetric hydrogenation.

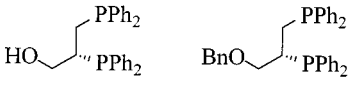
Effects and Preliminary Results

As far back as 1982, Knowles et al. briefly noted that by substitution of the methoxy groups in the industrially applied DiPAMP[22] ligand (**1-OMe)** by OH groups (**1-OH**), a hydrogenation catalyst was obtained which exhibited good enantioselectivity but rather poor reactivity.[23] This sporadic observation indicated for the first time that the hydroxy group may be used for enantiocontrol. Furthermore, a relationship between the additional functional group and the lowered rate of the asymmetric hydrogenation was found.



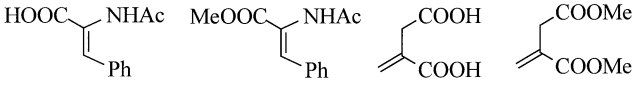
1-OH **1-OMe (DiPAMP)** **1-Et**

In the same year, Amma and Stille reported the synthesis of (*R*)-1,2-bis(diphenylphosphanyl)propan-3-ol (**2-OH**).[24]



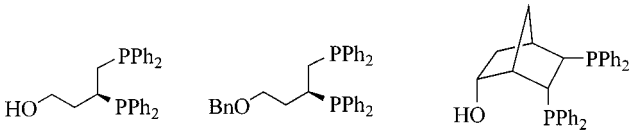
2-OH **2-OBn**

Attempts to utilize this ligand in the asymmetric hydrogenation of (*Z*)-*N*-acetylamino acrylic and (*Z*)-*N*-acetylamino cinnamic acid (AH), which are commonly used as standard substrates,[25] failed owing to the poor activity of the relevant Rh^I complex. Interestingly, by benzylation of the OH group (ligand **2-OBn**) an active catalyst was obtained.



AH **AMe** **ItH_2** **$ItMe_2$**

We explored the same catalytic reaction with the homologous ligand **3-OH**.[26] The corresponding Rh-catalyst hydrogenated AH and its methyl ester (AMe) very slowly. This negative effect could be overcome by protection of the OH-group as the benzyl ether (**3-OBn**).

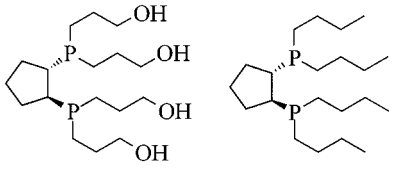


3-OH **3-OBn** **4 (HO-NorPHOS)**

At this time we concluded that an attractive interaction between the OH group and other parts of the catalyst−substrate complexes could be responsible for the observed decelerating effect. It is worth mentioning that the hydrogenations described above were performed in a large excess of methanol. In general, with parent catalysts no rate-reducing effects were observed in this solvent. That means that the effect of the hydroxy group could unambiguously be attributed to intramolecular and not to intermolecular interactions. In a ligand based on a rigid carbon skeleton such as **4**, this interaction should be disturbed. Indeed, **HO-NorpHOS** gave a hydrogenation catalyst with an activity similar to Brunner's **NorPHOS**, in spite of the fact that

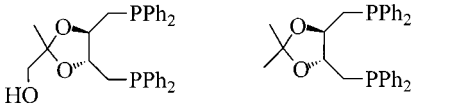
the former was also based on the 4-hydroxy-1,2-bis(diphenylphosphanyl)butane moiety like **3-OH**.[27]

In the meantime, other groups also reported interesting catalytic effects observed after functionalization of phosphane catalysts. Thus, Dahlenburg and Kurth found that by incorporation of hydroxy groups, bis-trialkylphosphanes such as **5-H** may get profit in the Rh^I-catalyzed asymmetric hydrogenation of AH.[28] **5-OH** showed a 12% higher enantioselectivity than was observed with the parent ligand.

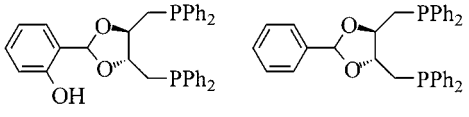


5-OH **5-H**

All the 1,2-diphosphanes described above form five-membered chelates with rhodium(I). Owing to the low conformational flexibility of this chelate size, attractive interactions of the additional functional group may be hindered or even overridden by steric effects. For example, Imamoto et al. found similarly high *ee*'s by application of a rhodium(I) complex with the DiPAMP analogous ligand **1-Et**.[29] Based on this result, they advocated the idea that the effect of the methoxy group in the DiPAMP−Rh-catalyst is based preferentially on steric reasons. A change of the reaction rate owing to the nonpolar ethyl group was not reported. Prompted by this result, we next turned our attention to the synthesis and application of conformationally flexible seven-membered chelates of the DIOP type like **6-OH** and **7-OH**.[30]



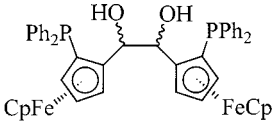
6-OH **6-H (DIOP)**



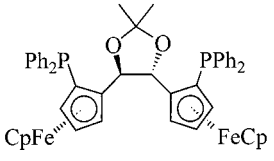
7-OH **7-H**

Surprisingly, under reduced H_2 pressure, Rh^I catalysts based upon these hydroxy phosphanes reduced the standard substrates more slowly than their parent catalysts derived from **DIOP** and **7-H**.[31] These results gave evidence that a remote OH group may also influence the rate and thus the mechanism of the asymmetric reaction. In several instances, improved enantioselectivities were also noted owing to the effect of the hydroxy group, but this correlation was not generally valid for all pairs of ligands tested. Interestingly, the X-ray structural analysis of the precatalyst [Rh(**6-OH**)(COD)]BF_4 gave no evidence that the OH group interfered with the rhodium centre. In contrast the hydroxy group was found to be situated far away from the metal. This fact indicated that the decisive interaction of the functional group with the catalytic centre is of low energy and may first come into play during the catalytic cycle or at least after coordination of the prochiral substrate.

Recently, Kagan et al. noted a striking enhancement of the enantioselectivity from 45% *ee* to more than 85% *ee* in the hydrogenation of AH, when the isopropylidene-protected bis-ferrocene ligand **8-Isoprop** was replaced by the corresponding diols **8-OH**.[32] It is noteworthy, that the increase in the *ee* found with these OH substituted nine-membered chelates was almost independent of the configurations at the 2,3-positions (**8(a-c)-OH**).



8a-OH (1*R*,2*R*)
8b-OH (1*S*,2*S*)
8c-OH (1*R*,2*S*)



8-Isoprop

Mechanistic Studies

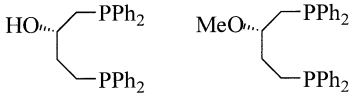
To better elaborate the dual effect of the OH group, we required a suitable model catalyst. As discussed above, conformers of 1,2-diphosphane chelates might be too rigid to permit a clear differentiation between attractive interactions within the catalyst−substrate assembly and sterically driven effects due to the 5-membered ring. Furthermore, because of the conformational rigidity, low hydrogenation rates are generally characteristic for these hydrogenation catalysts. Therefore, decelerating effects caused by additional functional groups may entirely block the catalytic reaction (vide supra). Conformationally flexible seven-membered chelates and therefore more active catalysts based on 1,4-bis(diphenylphosphanyl)butane ligands bearing one or two hydroxy groups in the carbon chain seemed to be much better suited. In addition, since other stabilizing groups are not present in these model complexes, catalytic effects can clearly be traced to the effect of the oxygen functionalities.

In a first study, we compared the Rh^I complexes of (*S*)-1,4-bis(diphenylphosphanyl)butan-2-ol (**9-OH**) and its methyl ether (**9-OMe**) in the asymmetric hydrogenation of AH, itaconic acid (ItH_2) and their corresponding methyl esters (AMe, $ItMe_2$).[33] The results are listed in Table 1. For comparison, results obtained with the Rh-complex of 1,4-bis(diphenylphosphanyl)butane (DPPB) are also included, representing a seven-membered chelate ring without any additional coordinating groups.[34a]

Table 1. Hydrogenations with [Rh(ligand)(COD)]BF_4

Ligand[a]	AH t [min][b]	*ee* [%]	AMe t [min][b]	*ee* [%]	ItH_2 t [min][b]	*ee* [%]	$ItMe_2$ t [min][b]	*ee* [%]
DPPB	<2	–	<2	–	<2	–	<2	–
9-OMe	6	4.6 (*S*)	13	5.3 (*S*)	1.5	8.3 (*R*)	15	2.6 (*R*)
9-OH	15	41.7 (*S*)	35	25.6 (*S*)	2.5	45.2 (*R*)	20	24.8 (*R*)
11-OMe	150[c]	0.6 (*S*)	420[d]	23.7 (*R*)[d]	6.0[c]	22.4 (*S*)	80[d]	7.6 (*S*)[d]
11-OH	420[c]	36.3 (*R*)	1920[d]	32.2 (*R*)[d]	15.0[c]	56.8 (*S*)	–[e]	–
13-OH	<2	–	<2	–	<2	–	<2	–

[a] Molar ratio catalyst/substrate = 1:100, 1 bar H_2 in methanol, room temp.; substrates: **AH**, **AMe**, **ItH_2**, **$ItMe_2$**. – [b] Corresponds to the time when 100% consumption of hydrogen was observed. – [c] In the original publication (ref.[34a]) times for 50% consumption of hydrogen were given. – [d] D. Heller, A. Börner, unpublished results. – [e] Hydrogenation proceeded only under elevated pressure.

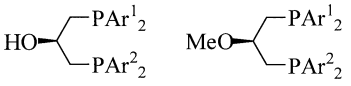


9-OH **9-OMe**

The latter is the most active catalyst in this series. It is remarkable that in comparison to the unfunctionalized catalyst, the incorporation of the methoxy as well as the hydroxy group diminished the rate of the reaction. This comparison nicely illustrates that the decelerating effect is not only restricted to the hydroxy but also to the methoxy group bearing catalysts.[35] In our opinion, this effect of the OMe group has been underestimated in the past.[36]

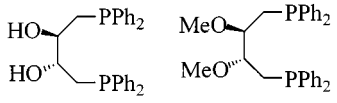
It is clear that the hydroxy group bearing catalyst gave generally superior enantioselectivities. In some cases, improvement of the selectivity by more than 35% *ee* was achieved relative to the catalyst based on **9-OMe**. In particular, the hydrogenation of substrate acids profits from this effect. Simultaneously with the enhancement of the enantioselectivity, a serious decrease in the activity was observed. In general, no change in the sense of the induced chirality was observed when **9-OH** was used instead of **9-OMe**. Interestingly, X-ray structural analysis and $^{31}P\{^1H\}$ NMR spectroscopic studies of the relevant precatalysts gave no evidence of a close proximity of the oxygen functional groups to the metal centre. This result again implicated that the decisive interaction takes place more in certain catalytic species rather than in the precatalyst.

Of relevance to this discussion are results by Huttner et al. with cationic Rh^I complexes based on chiral 1,3-bis(diarylphosphanyl)propan-2-ol (**10-OH**).[37] In the hydrogenation of standard substrates, no reduced rate was found relative to the corresponding OMe substituted catalyst (**10-OMe**). The OH group bearing catalyst was even more active than its OMe counterpart. No significant difference in the stereodiscriminating abilities of both ligands was observed. NMR spectroscopic investigations of the precatalysts in solution revealed that among different twist and chair conformations present in a dynamic equilibrium, no species was found with the oxygen group coordinated at the rhodium centre. Apparently, the absence of catalytic effects in this system commonly attributed to the OH group can be described as being a result of the high stability of the relevant conformations of the six-membered chelate which does not allow the OH group to play an active role in the chirality transfer.



10-OH **10-OMe**

In order to enhance the tendency of the hydroxy group to approach the catalytic centre, we incorporated in the butane chain of **9-OH** a second hydroxy group in a *threo* position in order to create **11-OH**.[34] For comparison, the corresponding dimethoxy ligand (**11-OMe**) was synthesized in a similar way.

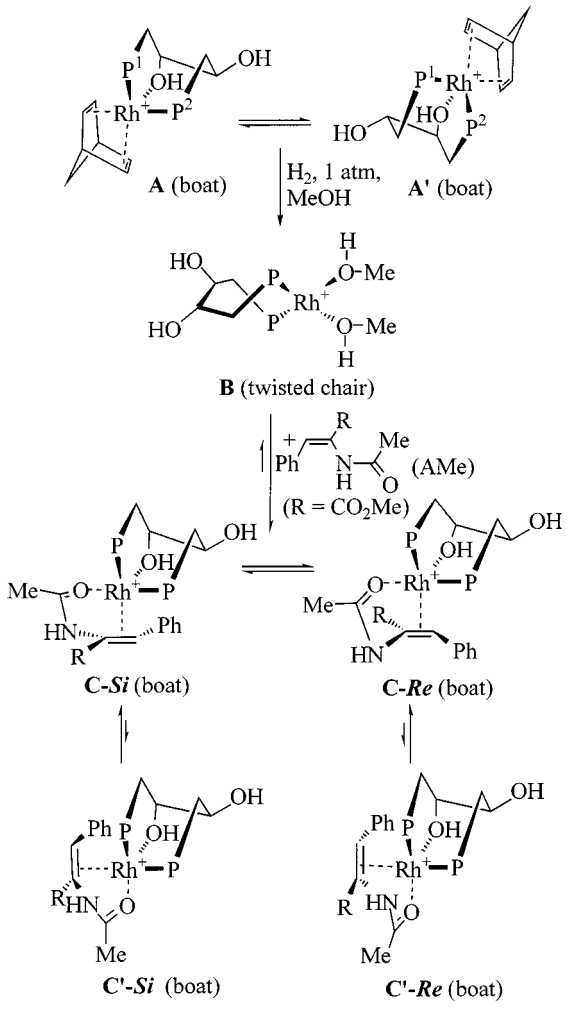


11-OH **11-OMe**

Rh^I complexes of these ligands were proofed for the asymmetric hydrogenation of standard substrates in methanol.[34a] Results are also shown in Table 1. In comparison to catalysts with only one oxygen group (**9-OMe**, **9-OH**) the incorporation of the second oxygen group further diminished the rate. As was also found with single oxygen-substituted ligands, exchange of the methoxy by hydroxy groups resulted in a significant increase in selectivity by up to 35% *ee*.

The X-ray structural analyses of the precatalysts based on **9-OH** and **9-OMe** showed some agreements but also striking differences. Neither structure was C_2 symmetric as the structures of the ligands imply. In the former, the phosphorus atoms are bonded to the rhodium with different interatomic distances (2.283 Å and 2.377 Å). Furthermore, one of the enantiotopic hydroxy groups interacts with the metal (2.396 Å) to a degree never before observed in related methoxyphosphane complexes derived from DiPAMP[38] or Nagel's PyrPHOS.[39] Owing to this interaction the seven-membered chelate is forced to adopt a boat conformation (see Scheme 1, **A**). As anticipated, one important driving force for the formation of the five-membered O–Rh–P

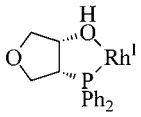
cycle is the pseudo-equatorial arrangement of the hydroxy group in the fused six-membered ring which is fixed in a distorted chair conformation.



Scheme 1. The counter-ligand-dependent O−Rh-interactions at different stages of the asymmetric hydrogenation of AMe (*P*−Ph groups are omitted)

For the structure of [Rh(COD)(**11-OMe**)]BF_4, different features were noted. Both phosphorus atoms are thus bonded at approximately equal distances to the metal. The most important difference in comparison to the hydroxy complex is the distance between rhodium and the oxygen of the neighbouring ether group (3.282 Å). This is a difference of more than 0.9 Å.

The occurrence of the five-membered O−Rh−P chelate should be also confirmed in solution. To have a model compound for this investigation, *cis*-3-diphenylphosphanyl-4-hydroxytetrahydrofuran[40] was synthesized and its cationic Rh^I complex **12** was spectroscopically characterized in solution.[41] Particularly valuable for this discussion was the observation in the $^{31}P\{^1H\}$ NMR spectrum of the downfield shift of the phosphorus signal at δ = 40.1 owing to the formation of the five-membered chelate.[42]



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With this result in hand, we analyzed the $^{31}P\{^1H\}$ NMR spectra of the precatalyst [Rh(NBD)(**11-OH**)]BF_4 in CD_3OD, since CH_3OH was the solvent of the hydrogenation. (Figure 1a). The complex was characterized at ambient temperature by a doublet at δ = 18.1 which showed a coalescence at 243 K when the temperature was lowered. The spectrum at 189 K displayed two sets of well-separated double doublets at δ = 44.0 (J_{Rh-P} = 141.5 Hz, J_{P-P} = 41.4 Hz) and δ = −2.7 (J_{Rh-P} = 129.1 Hz, J_{P-P} = 41.4 Hz) produced by two nonequivalent phosphorus atoms. Keeping the typical downfield resonance of the five-membered hydroxy phosphane rhodium chelate **12** in mind, the resonance at δ = 44.0 could be unambiguously assigned to this ring size. The coordination of the oxygen causes the seven-membered ring to adopt the boat conformation **A** (Scheme 1) as concluded from the X-ray structural analysis. The typical change of the band shapes with decreasing temperature gave clear evidence that the doublet observed at room temperature was characteristic of a rapid exchange of the phosphane signals. This interchange of upfield with downfield and downfield with upfield phosphorus resonances caused by the alternate coordination of the two hydroxy groups was not distinguishable on the NMR time scale at ambient temperatures. Due to the C_2-symmetry of the ligand boat structures **A** and **A′** are identical.

The methoxy complex [Rh(COD)(**11-OMe**)]BF_4 showed a different behaviour with decreasing temperature (Figure 1b). The coalescence temperature was 35 K lower than in the hydroxy complex. Even at 177 K the doublets of doublets were less separated. Additionally, at δ = 17.2 a doublet was observed which corresponds in shift and coupling to that of the cationic Rh(DPPB)-complex. The signal could therefore clearly be assigned to a C_2-symmetric complex and proved that at low temperatures this complex also existed in a conformation where the oxygen atoms did not interact with the metal (Scheme 2, twisted chair-conformation **B**). Owing to these measurements, considerable differences in the populations of the conformers **A** and **B** of the hydroxy and methoxy complexes were concluded. This difference was explained by repulsive interactions between the oxygen group and the phenyl rings of the phosphanyl moiety. Increasing size of the oxygen substituent prevented the ligand from binding in the η^3-coordination mode. Further proof for this assumption came from the comparison with the corresponding bis-*O*-Ph_3Si-substituted complex. No Rh−O interaction was found owing to the bulky silyl groups.

The precatalyst in turn was converted into the catalytically active species by hydrogenation of the stabilizing diolefin (Scheme 1).[34b] The $^{31}P\{^1H\}$ NMR spectrum of the bis-methanol complex **B** at room temperature showed a doublet at δ = 47.5. In comparison to the bis-olefin com-

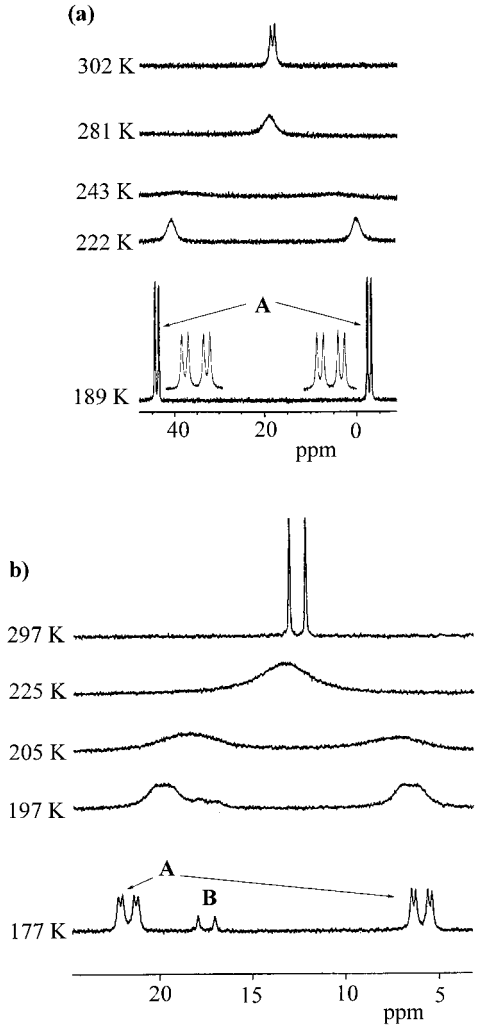
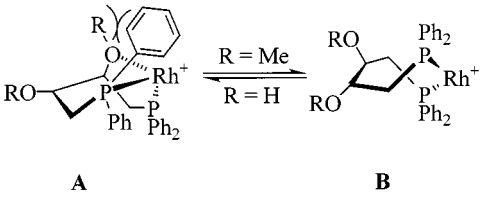


Figure 1. $^{31}P\{^1H\}$ NMR spectra of the complexes [Rh(NBD)(**11-OH**)]BF_4 (a) and [Rh(COD)(**11-OMe**)]BF_4 (b) in CD_3OD at different temperatures; the relevant equilibrium of the conformers is depicted in Scheme 1 (top) and Scheme 2, respectively



Scheme 2. Influence of the size of the *O*-substituent on the equilibrium of metal-coordinated and uncoordinated conformers

plex, the downfield shift was caused by the strong π-donor, but weak π-acceptor properties of the *O*-coordinated solvent.[43] However, no dynamic phenomenon was observed at all accessible temperatures. This was a clear indication that in contrast to the precatalyst in the catalytically active species, the interaction of the hydroxy groups with the metal was fully suspended. The complex existed exclusively in the relaxed C_2-symmetric twisted chair conformation **B**. This behaviour was rationalized by the decrease in the Lewis-acidity of rhodium(I) caused by the coordination of methanol, hence the interaction of the metal with the OH group (Lewis-base) is disfavoured.

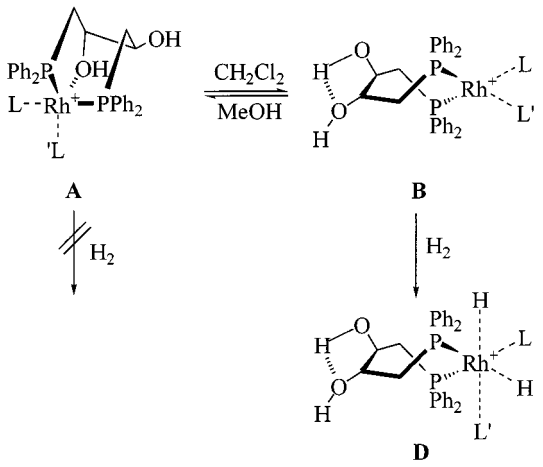
This finding clearly illustrated that in the precatalyst not only steric interactions assisted by the second hydroxy group forces the hydroxy group to approach the metal, but also attractive interactions come into play. This result was additionally confirmed by a combined ^{103}Rh NMR density-functional study.[44] It was calculated that the "pure electronic" effect of the coordinated OH group causes an upfield shift of more than 150 ppm in the ^{103}Rh NMR spectrum relative to the resonance of the same conformation of the non-functionalized complex.

By addition of a non-symmetric prochiral substrate such as AMe, catalyst−substrate complexes were formed from the solvent complex (Scheme 1, **C**).[34b] In contrast to corresponding complexes of related 1,4-diphosphanes like DPPB, the solvent−complex was fully consumed by the substrate. This result agrees well with the small Michaelis constant measured in the hydrogenation of AMe with [Rh(**11-OH**)$(MeOH)_2$]BF_4. The peculiar pattern of the spectrum was rationalized by the assumption of a tripodal coordination of the hydroxy phosphane ligand. In principle, because of the stereofacial coordination of prochiral AMe to rhodium, the alternate coordination of both hemilabile OH ligands should produce a spectrum characterising four diastereomeric substrate complexes (**C-*Si***, **C-*Re***, **C′-*Si***, **C′-*Re***). But the only complexes found were those where the phosphane *trans* to the carbonyl oxygen was involved in the six-membered O−P−Rh chelate (**C-*Si***, **C−R*e***). Up to now there is no rationale for this preference.

In general, these results showed that electronically different counter-ligands can significantly influence the "arm-off arm-on"-mechanism between the hydroxy group and the metal and consequently the conformation of the chiral catalyst. Furthermore, these results provided evidence that the coordination of the OH group takes place stereoselectively in catalyst−substrate complexes with electronically non-symmetric substrates.

Basically, the tripodal coordination mode of the ligand and the bidentate coordination of the prochiral dehydroamino acid produces 18-electron Rh^I complexes. For the subsequent oxidative addition of hydrogen, which is considered as the rate-determining step in the asymmetric hydrogenation,[45] prior decomplexation of the hemilabile ligand is necessary (Scheme 3, **A** → **B** → **D**). Obviously, this feature is responsible for the lowering of the hydrogenation rate observed in the presence of hemilabile OH and OMe ligands. In other words, the concentration of the inactive 18-electron complexes and the rate of decomplexation determines the rate of the hydrogenation.

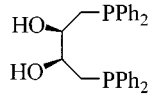
Unexpected proof for this assumption derived from the hydrogenation in a non-polar solvent.[34b] In contrast to the reaction in methanol in CH_2Cl_2 the hydrogenation proceeded approximately fivefold faster without affecting the enantioselectivity. The temperature-dependent $^{31}P\{^1H\}$ NMR spectra of the precatalyst in $CD_2Cl_2/CHCl_2F$ strikingly differed from those observed in CD_3OD. Thus at low temperature, a C_2-symmetric complex featuring no Rh−O interactions was preferentially found. The corresponding complex with tripodal coordination of the chiral ligand was



Scheme 3. HO/Rh- and HO/HO-interactions of **11-OH** complexes and their influence on the reactivity towards H_2 (L,L′ = diolefin, MeOH, bidentate substrate)

observed only in a small quantity. In the IR spectrum in solution the formation of intramolecular hydrogen bonding between the OH groups was observed (**B**, Scheme 3). Evidently, in a nonpolar solvent this strong intramolecular hydrogen bonding is more favoured than the (weak) interaction of one of the hydroxy groups with rhodium (**A**). When the Rh−O interaction is suspended, the hydrogenation can operate unhindered. In methanol the intramolecular hydrogen bonding is cleaved and the Rh−O interaction dominates. The complex is converted into an inactive state. Macroscopically, the decrease in the concentration of the active catalyst−substrate complex is expressed in the deceleration of the hydrogenation.

In the model system discussed above, the formation of the η^3-coordinated species was assisted by the *threo* arrangement of the hydroxy groups, which in the chelate cycle caused the pseudo-equatorial orientation of the uncoordinated OH group. We therefore anticipated that by changing the geometry of the *threo* 2,3-diol moiety to *erythro*, the Rh−O interaction should be disfavoured. Simultaneously, the tendency for the formation of the intramolecular hydrogen bonding should be improved.[46] In order to give evidence for this hypothesis, the required (achiral) (2*R*,3*S*)-1,4-bis(diphenylphosphanyl)butane-2,3-diol (**13-OH**) was synthesized.[47]



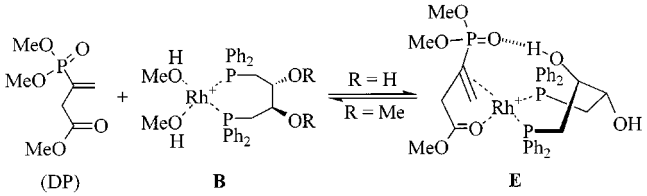
13-OH

IR solid state spectra and $^{31}P\{^1H\}$ NMR of [Rh(**13-OH**)(COD)]BF_4 in CD_3OD revealed also for this precatalyst an intramolecular interaction between the OH group and the Rh centre. However, the small difference in the chemical shift of $\delta = 21.9$ is in remarkable contrast to the value observed for the relevant *threo*-complex ($\Delta\nu = 46.7$ ppm), but corresponds to the difference found with [Rh(**11-OMe**)(COD)]BF_4 ($\Delta\nu = 16.1$ ppm). As discussed above for the latter, a higher dominance of the bidentate coordination mode in methanol was concluded. Obviously, in addition to η^3-coordinated species, the *erythro*-complex also showed considerable amounts of η^2-coordinated conformations at ambient temperature. Interestingly, in the $^{31}P\{^1H\}$ NMR spectra of relevant catalyst−substrate complexes, no significant differences between catalyst−substrate complexes of **11-OH** and **13-OH** at low temperature could be found, which is in contrast to observations made with precatalysts.

Results of hydrogenation experiments with (achiral) [Rh(**13-OH**)(COD)]BF_4 are also given in Table 1. Inspection of all the values clearly shows that hydrogenations with this complex were superior. The hydrogenation times measured with this catalyst were even shorter than with the catalyst bearing only a single hydroxy group (**9-OH**). Its activity was similar to that of the Rh(DPPB) catalyst. This result showed that the typical decelerating effect of the OH group can be fully suspended by a second OH group.

It should be reminded that an accelerating effect on the hydrogenation of dehydroamino acid derivatives has been already achieved with the **11-OH** catalyst when the reaction was carried out in a non-polar solvent. The change from methanol to CH_2Cl_2 facilitated the formation of an intramolecular hydrogen bond and shifted the equilibrium from η^3- to η^2-coordination.

Recently, it could be shown that this hydrogen bonding between the *threo* OH groups was easily disrupted by the addition of triphenylphosphane oxide owing to the favoured intermolecular hydrogen bonding between P=O and one of the OH groups.[47] The other hydroxy group coordinated to the rhodium. This cleavage reaction could be also initiated when the P=O fragment was incorporated in an appropriate prochiral substrate like 3-dimethylphosphono-butenoate (DP), a phosphonate analogue of dimethyl itaconate (Scheme 4). $^{31}P\{^1H\}$ NMR spectroscopic studies in deuterated methanol showed that in a mixture of [Rh(**11-OMe**)$(MeOH)_2$]BF_4 and a fivefold excess of the prochiral substrate, the bis-solvent complex (**B**) was exclusively present. The observation of this complex gave proof of the low stability of the diastereomeric catalyst−substrate complexes.



Scheme 4. Shift of the equilibrium between solvent complex and catalyst−substrate complex in dependence on the substituent R in CD_3OD as solvent

In contrast, by addition of DP to [Rh(**11-OH**)$(MeOH)_2$]$^+$ predominantly the resonances of a catalyst−substrate complex (**E**) were observed, revealing its high thermodynamic stability. The typical shift of the signals indicated that, surprisingly, no interaction between one of the OH groups and the metal centre took place. It was assumed that the Rh−O interaction is suspended owing to

an intramolecular hydrogen bonding between the OH group and the P=O functionality.

Results of the asymmetric hydrogenation are listed in Table 2. As can be clearly seen, with [Rh(**11-OMe**)(COD)]BF_4 very poor conversion occurred. The hydrogenation product was obtained in 24% *ee*. In striking contrast, the rhodium complex based on **11-OH** reduced the prochiral substrate much faster, to give the saturated product with 83% *ee*. This is an increase of approximately 60%.

Table 2. Asymmetric hydrogenation of (*E*)-methyl 3-dimethoxyphosphorylbut-2-enoate (DP) with [Rh(COD)(Ligand)]BF_4

Ligand[a]	Solvent	*t*/2[min][b]	*ee*[%]
11-OMe	methanol	>1000	24 (*S*)
11-OH	methanol	220	83 (*S*)
11-OH	CH_2Cl_2	no conversion	–

[a] For conditions of the hydrogenation compare Table 1. – [b] Time required for 50% consumption of hydrogen.

It is remarkable that by application of [Rh(**11-OH**)(COD)]BF_4 in dichloromethane as solvent, no conversion was observed. As discussed above, it can be concluded that an intramolecular hydrogen bonding between one of the OH groups and the P=O group of the substrate is established in both solvents. While in MeOH the remaining OH group is engaged by the solvent affording a 16-electron species and therefore allowing the oxidative addition of hydrogen to proceed, in dichloromethane this OH group couples to the rhodium centre. The η^3-coordinated complexes produced are catalytically inactive and therefore hinder the hydrogenation. This assumption also explains the dramatic reversal of the hydrogenation activity by changing from AMe which is a poor hydrogen-bond acceptor to the strong hydrogen-bond acceptor DP in MeOH and dichloromethane, respectively. With the former substrate, the catalytically inactive η^3-complexes are dominant in MeOH, whereas in case of the latter, η^3-complexes dominate in dichloromethane.

The previously reviewed studies illustrate the high mobility of the internal hydroxy groups in appropriate metal complexes and their decisive role in the establishment of pre-equilibria between catalyst and catalyst–substrate complexes. In some cases, relationships between structure and catalytic properties could be deduced. Simultaneously, gradual (size) and fundamental (H-bonding) differences in the behaviour of OH and OMe groups became obvious. Clearly, the characterization of precatalysts or individual stable catalyst–substrate complexes alone does not allow for a reliable conclusion on macroscopically observed overall rates and enantioselectivities. The rate constants of the pre-equilibrium steps and of the rate-determining steps are required in order to determine the special role of the catalytically unreactive η^3-coordinated catalyst–substrate complexes on the enantioselectivity. Unfortunately, up to now the complete set of data under hydrogenation conditions has not been accessible owing to the great complexity of relevant model systems. Several features remain speculative. For example, this holds for the stabilization of hydrido alkyl rhodium complexes by the OH group beyond the oxidative addition of H_2, as was found by Brown et al. in relevant DiPAMP substrate complexes.[48] Furthermore, the question of the effect of potential attractive interactions between the proton of the functional group and metal-bonded hydride[49] has up to now not been addressed at all.

In summary, results observed with tailored model catalysts and model substrates clearly illustrates that the negative effect on the rate, frequently observed with Rh^I hydrogenation catalysts bearing hydroxy phosphanes as ligands, can be entirely overcome by the co-operative effect of an appropriately placed second hydroxy group or a strong hydrogen-bond accepting group such as P=O incorporated in the substrate. As a result we can take full advantage of the positive effect on the enantioselectivity. It has to be verified that the superior enantioselectivities in the asymmetric hydrogenation of standard substrates such as AH and ItH_2 as outlined above can also be explained by a (weak) intramolecular hydrogen bonding between the hydroxy groups of the ligand and the carboxylic group of the substrate during the catalytic cycle.

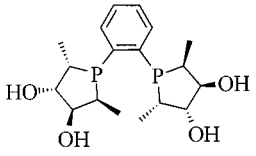
First Applications in Highly Enantioselective Asymmetric Hydrogenations

As seen above, the incorporation of hydroxy groups can dramatically improve the stereodiscriminating properties of

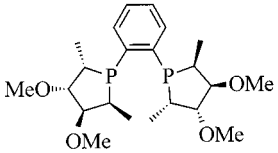
Table 3. Asymmetric hydrogenation with cationic Rh^I complexes based on RoPHOS-ligands

Ligand[a]	Substrate	*ee* [%]
14-OBn[b]	AH	93.6 (*S*)
14-OMe[b]	AH	97.0 (*S*)
14-OH[c]	AH	>99.0 (*S*)
14-OBn[b]	AMe	96.0 (*S*)
14-OMe[b]	AMe	98.3 (*S*)
14-OH[c]	AMe	>99.0 (*S*)

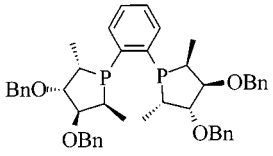
[a] 1–3 bar H_2 in methanol at room temp.; catalyst:substrate = 1:100. – [b] [Rh(Ligand)COD)]BF_4 was used. – [c] Precatalyst was prepared by mixing [Rh(COD)$_2$]PF_6 with **10-OH**.



14-OH



14-OMe



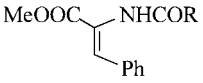
14-OBn

(RoPHOS)

chiral hydrogenation catalysts. Recently, we[50] and later, the groups of Zhang[51] and RajanBabu[52] found access to a new class of functionalized DuPHOS ligands derived from D-mannitol called RoPHOS (**14**). As shown in Table 3, benzyloxy,[50b] methoxy[53] and hydroxy groups[51] at the 3- and 4-positions of the phospholane moiety have a different effect on the enantioselectivity. Thus, with the OH bearing ligand **14-OH**, more than 99% *ee* could be achieved in the hydrogenation of AH and AMe. Although the increase is small, a significant gain in the enantioselectivity was achieved.

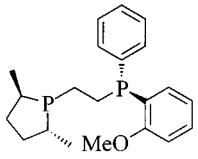
More dramatic effects were recently reported by Brown et al. in the hydrogenation of methyl *N*-acyl cinnamates with BPE-RoPHOS hybrid ligands.[54] The most striking results are listed in Table 4. Thus, by utilization of the ligand **15-H**, a hybrid of the well-known and individually efficient ligands BPE and DiPAMP, poor enantioselectivity was achieved. Incorporation of remote methoxy groups (**15-OMe**) in the phospholane increased the *ee*. The highest enhancement was obtained because of the assistance of the hydroxy groups (ligand **15-OH**). In some cases, in comparison to the parent ligand **15-H**, a difference of up to 90% resulted owing to the remote hydroxy groups.

Table 4. Asymmetric hydrogenation with cationic Rh^I complexes based on BPE/RoPHOS−DiPAMP hybrid ligands

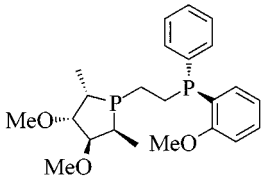


Ligand[a]	R (Substrate)	*ee* [%]
15-H	Me	38 (*S*)
15-OMe	Me	85 (*S*)
15-OH	Me	92 (*S*)
15-H	*tert*-Bu	5 (*R*)
15-OMe	*tert*-Bu	67 (*S*)
15-OH	*tert*-Bu	88 (*S*)
15-H	Ph	–
15-OMe	Ph	77 (*S*)
15-OH	Ph	90 (*S*)

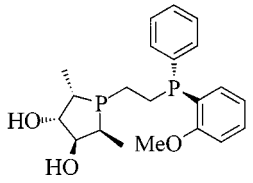
[a] 1.3 bar H_2 in methanol; catalyst:substrate = 1:100; the precatalyst was prepared by mixing $[Rh(COD)_2]PF_6$ with BH_3-ligand adducts in the presence of HBF_4−OMe_2.



15-H
(BPE-DiPAMP hybrid)



15-OMe



15-OH

(RoPHOS-DiPAMP hybrids)

Concluding Remarks

Results summarised herein show the great academic challenge, but also the high potential associated with the use of internal hydroxy groups in chiral rhodium diphosphane catalysts for tuning the reactivity and the enantioselectivity of asymmetric hydrogenations. The crucial issue lies in the large number and variety of competing binding sites in relevant polyfunctionalized catalyst−substrate complexes. These features are related to the action of enzymes. Modelling of individual interactions, studies of equilibria and evaluation of their effect on the rate and the enantioselectivity are therefore of great importance for the proper placement of additional functional groups within the catalyst. The effective control of such secondary interactions opens new perspectives for the enantiodiscrimination of prochiral substrates and gives access to a new generation of biomimetic catalysts.

There are an increasing number of reports in the literature indicating that hydroxy groups in phosphorus ligands may also influence other metal-catalyzed transformations, such as hydroformylations,[55] transfer hydrogenations[56]or Baylis−Hillman reactions.[51b] In some of these reports, the reduced rate of the catalytic reaction was problematic. The progress achieved over the last years in asymmetric hydrogenation with Rh^I hydroxy phosphane catalysts is an encouraging sign that the decelerating effect of the hydroxy group can also be overcome in these reactions by the employment of suitable substrates and/or appropriate reaction conditions.

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