Catalytic and Structural Features of Hydroxy and Methoxy Groups as Hemilabile Coordinating Ligands in Chiral (Diphosphane)rhodium(I) Hydrogenation Catalysts☆

Susanne Borns, Renat Kadyrov, Detlef Heller*, Wolfgang Baumann, Anke Spannenberg, Rhett Kempe, Jens Holz, and Armin Börner*

Institut für Organische Katalyseforschung an der Universität Rostock e.V.,
Buchbinderstr. 5/6, D-18055 Rostock, Germany
Fax: (internat.) + 49(0)381/4669324
E-mail: aboern@chemie1.uni-rostock.de

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The influence of two *threo*-arranged methoxy or hydroxy groups as hemilabile ligands in seven-membered (diphosphane)Rh^I chelates upon the asymmetric hydrogenation is studied. In comparison to the parent complex based on 1,4-bis(diphenylphosphanyl)butane (DPPB) a lowering of the reaction rate is caused by the hemilabile ligands. The catalyst bearing the hydroxy groups gives significantly higher enantioselectivities than the corresponding methoxy complex (by ca. 35 % ee). X-ray structural analysis reveals that the oxygen atom of the hydroxy group is by 0.9 Å closer to the metal center than that of the methyl ether. ^{31}P-NMR studies give evidence that the dihydroxy diphosphane ligand binds at low temperature exclusively in the η^3-coordination mode, whereas for the dimethoxy complex also an η^2-coordinated isomer can be found. These differences in complexation could be responsible for the superior enantioselectivities achieved with this and other hydroxy catalysts.

Introduction

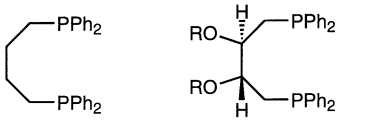
(Alkoxyaryl and -alkyl)phosphanes have seen broad application in asymmetric hydrogenations[1] as well as in numerous other metal-catalyzed stereodifferentiating reactions.[2] For example, (*R*,*R*)-DIPAMP [(*R*,*R*)-1,2-bis(*o*-anisylphenylphosphanyl)ethane] was the first industrially applied ligand.[3] The unique role of the alkoxy and preferentially that of the methoxy group is attributed to their property to act as hemilabile ligands[4] or intramolecular solvent,[5] which may temporarily coordinate to the metal center in the course of the catalytic cycle.[6][7]

Despite this, much less information is available on the influence of the related hydroxy group,[8] although it deserves particular attention due to its potential to create secondary interactions with a suitable substrate and to enhance the solubility of the catalyst in water.[9][10]

In recent investigations with a (diphosphane)rhodium complex bearing a single methoxy group we could show that the replacement of the latter by the hydroxy group increased the enantioselectivity of the hydrogenation in methanol.[11] Simultaneously, a conspicuous loss of reactivity was observed. To date there is no explanation for this unique behaviour of this and other catalysts bearing hydroxy groups.[12]

Herein, we report on a study concerning the synthesis, catalytic properties, and structure elaboration of cationic Rh^I complexes based on the ligands (*R*,*R*)-1,4-bis(diphenylphosphanyl)butane-2,3-diol (**1-OH**)[13a] and its bis(methyl ether) **1-OMe**[14] which may have important implications to the aspects discussed above. Both ligands are related to 1,4-bis(diphenylphosphanyl)butane (DPPB) which forms with metals seven-membered chelate rings.

Scheme 1



DPPB **1-OH** (R = H) **1-OMe** (R = Me) **1-OSiPh$_3$** (R = Ph_3Si)

In general, Rh catalysts based on such large and highly flexible chelates are more active in asymmetric hydrogenations than rigid five-membered chelates e.g. (DIPAMP)Rh^I, but require additional stabilization in order to provide for appreciable enantioselectivity. Due to the absence of any other stabilizing groups in our model complexes chosen catalytic effects can be clearly traced to the effect of the oxy functionalities.

Results and Discussion

The Rh^I complexes were synthesized by reaction of the C_2-symmetric diphosphanes with $[Rh(COD)_2]BF_4$ [COD = (*Z*,*Z*)-cycloocta-1,5-diene] (Scheme 2). The COD complex of **1-OH** was converted into the better crystallizing complex [Rh(NBD)(**1-OH**)]BF_4 by treatment with norbornadiene (NBD).[15]

The complexes obtained catalyze the hydrogenation of itaconic acid (ItH_2) and (*Z*)-2-*N*-acetylaminocinnamic acid (AH) in methanol (Table 1). The Rh complex of DPPB is

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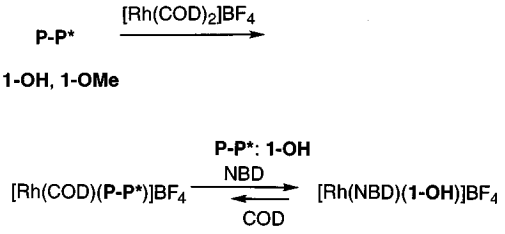
Scheme 2



the most active catalyst in the series. It is remarkable that the incorporation of the methoxy groups diminishes seriously the rate of the reaction, however, the selectivity observed is low. This gives a clear indication that the ether groups are not able to stabilize certain conformations of the highly flexible seven-membered chelate. The exchange of the methoxy by the hydroxy groups gives rise to a further loss of reactivity, however, affords a significant gain in selectivity by approximately 35% ee.

Table 1. Asymmetric hydrogenation of prochiral olefins in methanol[a]

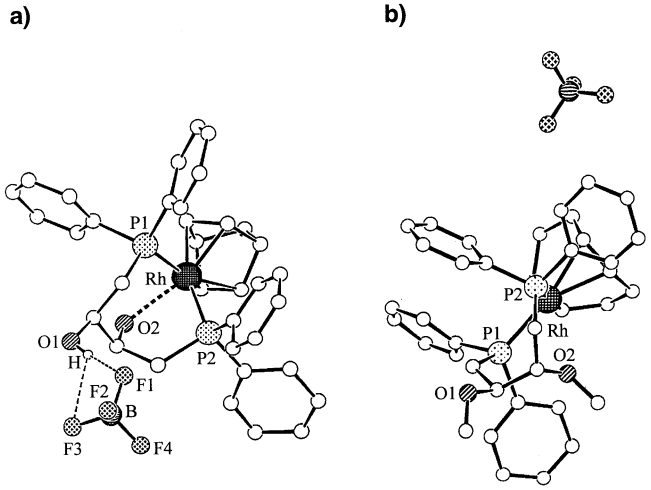
Precatalysts	Substrate	$t/2$ [min][b]	ee [%] (config.)
$[Rh(COD)(DPPB)]BF_4$	ItH_2	<2	–
$[Rh(COD)(\mathbf{1\text{-}OMe})]BF_4$	ItH_2	3.7	22.4 (*S*)
$[Rh(NBD)(\mathbf{1\text{-}OH})]BF_4$	ItH_2	6.0	56.8 (*S*)
$[Rh(COD)(DPPB)]BF_4$	AH	<2	–
$[Rh(COD)(\mathbf{1\text{-}OMe})]BF_4$	AH	145	0.6 (*S*)
$[Rh(NBD)(\mathbf{1\text{-}OH})]BF_4$	AH	190	36.3 (*R*)

[a] Conditions: 0.01 mmol of precatalysts, 1.0 mmol of substrate in 15 ml of MeOH at 25°C and at 0.1 MPa H_2 pressure. – [b] Corresponds to that time, when 50% of substrate is converted.

In order to explain these differences, X-ray structural analyses of the precatalysts were performed and their $^{31}P\{^1H\}$-NMR spectra recorded. Suitable crystals of $[Rh(NBD)(\mathbf{1\text{-}OH})]BF_4$ and $[Rh(COD)(\mathbf{1\text{-}OMe})]BF_4$ were obtained from methanol. The single-crystal X-ray structural analyses established the structures as shown in Figure 1a and 1b, respectively, along with selected bond lengths and interbond angles.[17] The inspection of the data shows some agreements but also striking differences.

In the complex $[Rh(NBD)(\mathbf{1\text{-}OH})]BF_4$[17a] both phosphorus atoms are differently bound to the rhodium center; the distances are 2.283 Å and 2.377 Å. One of the enantiotopic hydroxy groups interacts with the metal center (distance 2.396 Å) never before observed to such an extent in related (methyl phosphanylaryl ether)rhodium[6c] or -palladium complexes[1e]. The BF_4 anion binds via a hydrogen bond to the second hydroxy group. In the IR spectrum (KBr) appear two bands at 3508 and 3441 cm^{-1} also clearly indicating two different hydroxy groups.[18] One important force for the formation of the five-membered O–Rh–P ring is apparantly the pseudo-equatorial arrangement of the hydroxy group in the fused six-membered ring being fixed in a distorted chair conformation, since the interaction could not be found in the corresponding monohydroxy complex.[11] The dihedral angle formed by the two hydroxy groups is 157.3° which reveals a strong deviation from the *anti* arrangement.

Figure 1. Structures of $[Rh(NBD)(\mathbf{1\text{-}OH})]BF_4$ (Figure 1a) and $[Rh(COD)(\mathbf{1\text{-}OMe})]BF_4$ (Figure 1b) in the crystalline state; hydrogen atoms are omitted for clarity[a]



[a] Selected atomic distances [Å] and torsional angles [°]: $[Rh(NBD)(\mathbf{1\text{-}OH})]BF_4$: Rh(1)–P(1) 2.283(2), Rh(1)–P(2) 2.377(2), Rh(1)–O(2) 2.396, F(1)–O(1) 2.717; O(1)–C–C–O(2) 157.3; $[Rh(COD)(\mathbf{1\text{-}OMe})]BF_4$: Rh(1)–P(1) 2.320(2), Rh(1)–P(2) 2.333(2), Rh(1)–O(2) 3.282; O(1)–C–C–O(2) 169.1.

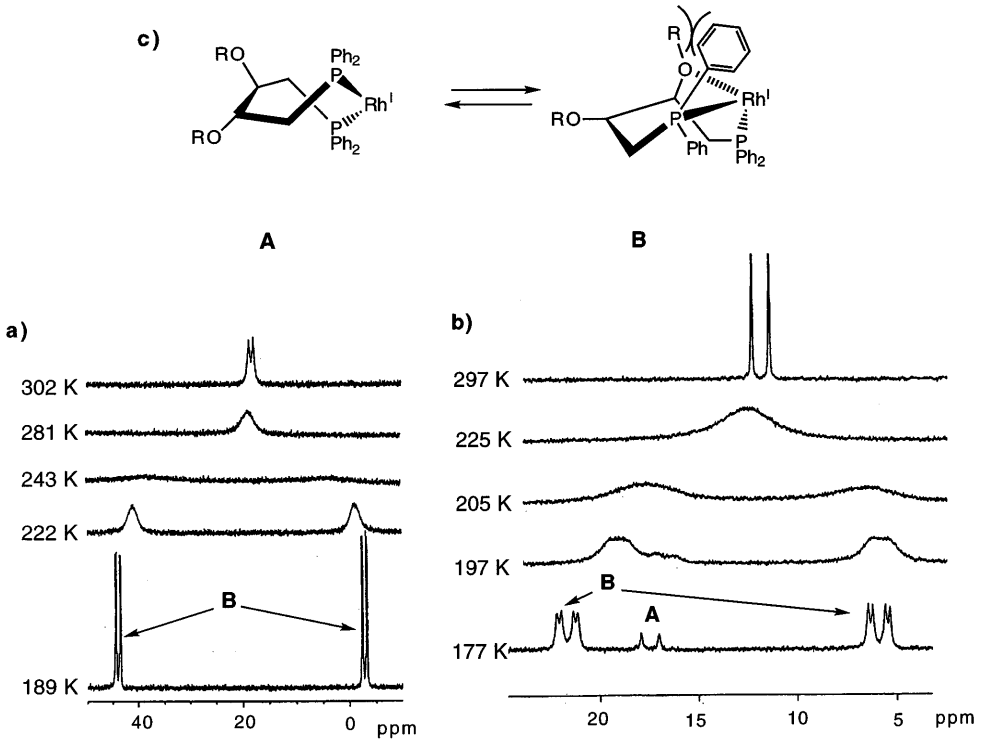
For the structure of $[Rh(COD)(\mathbf{1\text{-}OMe})]BF_4$ different features are noted.[17b] Thus, both phosphorus atoms are bound in approximately equal distances to the metal center. Due to the absence of a hydrogen-bond donor the BF_4 anion is located far away from the oxy groups. The most important difference in comparison to the hydroxy compound is the distance between the rhodium and the oxygen atom O(2) of the neighboured ether group (3.282 Å). This is a difference of more than 0.9 Å. The dihedral angle O(1)CCO(2) is widened to 169.1°.

In the $^{31}P\{^1H\}$-NMR spectra in CD_3OD also remarkable differences exist (Figure 2). $[Rh(NBD)(\mathbf{1\text{-}OH})]BF_4$ is characterized at 302 K by a doublet at $\delta = 18.1$. The decrease of the temperature caused the broadening of the signal. At 222 K the initial resonance had disappeared and two new signals could be observed at $\delta = 40$ and 0. Finally, the spectrum at 189 K displays two sets of well-separated double doublets at $\delta = 44.0$ ($J_{Rh\text{-}P} = 141.5$ Hz, $J_{P\text{-}P} = 41.4$ Hz) and $\delta = -2.7$ ($J_{Rh\text{-}P} = 129.1$ Hz, $J_{P\text{-}P} = 41.4$ Hz) produced by two nonequivalent phosphorus atoms. These results are consistent with one oxygen atom being attached to the metal center. The resonance at $\delta = 44.0$ has to be assigned to a phosphane which is involved in an O–P five-membered chelate.[19] Compared to related seven-membered chelate complexes {e.g. $[Rh(COD)(DPPB)]BF_4$} the downfield shift observed is caused by the increased ring strain in the newly formed five-membered ring. The fused O–P six-membered ring is characterized by a considerable shift of the concerned signal to higher field and the decrease of the ^{103}Rh-^{31}P coupling. The coordination of the oxygen atom causes the formation of the boat conformation (**B**) (Figure 2c). The typical change of the band shapes with

decreasing temperature gives clear evidence that the doublet observed at room temperature characterizes a rapid exchange of the phosphane signals. This exchange caused by the alternate coordination of the two oxygen atoms is not distinguishable on the NMR time scale at elevated temperatures.

ylsilyl ether) **1-OSiPh$_3$** (Scheme 1) recently published by Tamao.[20] In contrast to the complexes considered herein, [Rh(COD)(**1-OSiPh$_3$**)]SbF_6 is fixed in the C_2-symmetric conformation **A**.[21] This feature is explained by repulsive interactions between the bulky silyl groups and the phenyl rings of the phosphanyl moiety (Figure 2c). Clearly, these

Figure 2. $^{31}P\{^1H\}$-NMR spectra of the complexes [Rh(NBD)(**1-OH**)]BF_4 (Figure 2a; the small $J_{P\text{-}P}$ couplings of 41.4 Hz are not visible in the presentation) and [Rh(COD)(**1-OMe**)]BF_4 (Figure 2b) in CD_3OD at different temperatures; the relevant equilibrium of conformers is depicted in Figure 2c



The methoxy complex [Rh(COD)(**1-OMe**)]BF_4 shows a different behaviour with decreasing temperature. Thus, in comparison to the hydroxy complex the coalescence temperature is 35 K lower. Even at 177 K the doublets of doublets are less separated. Additionally, at $\delta = 17.2$ a doublet can be observed which corresponds in shift and coupling to that of the Rh(DPPB) complex. The signal can be unambigeously attributed to a C_2-symmetric complex and gives proof that at low temperatures [Rh(COD)(**1-OMe**)]BF_4 exists also in a conformation where the oxygen atoms do not interact with the metal center (twisted chair conformation **A**).

Due to the temperature dependency of the coupling constants and the inaccessibility of the data of the twisted chair conformation of Rh(NBD)(**1-OH**)]BF_4 we were not able to calculate the concentrations of the conformers at room temperature. However, taking the differences in the low-temperature spectra and the coalescence temperatures into account considerable differences in the populations of the conformers **A** and **B** of hydroxy und methoxy complex can be concluded.

The observation of these differences between hydroxy and methoxy complex provoked the comparison with the structure of a Rh complex based on the related bis(triphen-

interactions are also responsible for the fact that none of the oxygen atoms approaches the rhodium center, as found in [Rh(NBD)(**1-OH**)]BF_4 and [Rh(COD)(**1-OMe**)]BF_4. Taking our and the results of Tamao into consideration the preference for the shift of the boat (**B**) into the twisted chair conformation (**A**) is in the order $Ph_3Si > Me > H$. In other words, large groups at the oxygen atom prevent by interactions with the phenylphosphanyl groups the ligand to bind in the η^3-coodination mode. The η^2-coordination mode is responsible for a high hydrogenation activity as seen for the $(DPPB)Rh^I$ complex. Apparently, the tripodal coordination hinders the hydrogenation. However, only by this arrangement the highly flexible seven-membered chelate can be sufficiently stabilized which is the precondition to achieve conspicuous enantioselectivity.[22][23]

Conclusion

The conformation of chiral, highly flexible rhodium diphosphane chelates can be stabilized by the incorporation of hemilabile oxy groups. Due to the additional interaction of the ligand with the metal center a deceleration of the rate of the asymmetric hydrogenation results. With the hydroxy group significant higher enantioselectivities were achieved in comparison to the usually applied methoxy group. This

observation can be rationalized by the stronger preference of the hydroxy diphosphane ligand to bind in the η^3-coordination mode. In the precatalysts investigated herein the tripodal coordination is forced by the interplay of two *erythro*-arranged functional groups. The interaction between the hemilabile ligand and the rhodium center is counterbalanced by the repulsive interaction of the substituent at the oxygen atom with one phenylphosphanyl unit, which is stronger for the methyl group than for the proton of the hydroxy group.

In extension of these conclusions we suggest that in the catalytic cycle also other interactions between the hydroxy group and the metal center become operative,[24] since a significant gain of selectivity could be also noted in the hydrogenation with complexes bearing only one hydroxy group.[11][12] In general, these results and preliminary investigations with catalyst−substrate complexes clearly show that the main differences between hydroxy and methoxy group are preserved during the asymmetric hydrogenation. In combination with other conformation-stabilizing features selectivities of ≥ 90% ee can be achieved.[8][25] Therefore, the assistance of hemilabile hydroxy groups should be recommended also in other stereoselective reactions.

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Experimental Section

General: All reagents were obtained from Aldrich and Merck. Solvents were dried and freshly distilled under argon before use. Reactions were performed under argon by using standard Schlenk techniques. (*Z*,*Z*)-Cycloocta-1,5-diene (COD) and norborna-2,5-diene (NBD) were dried with CaH_2 and distilled under argon. (*R*,*R*)-1,4-bis(diphenylphosphanyl)butane-2,3-diol (**1-OH**) was synthesized by cleavage of the acetal group of (*R*,*R*)-3,4-bis(diphenylphosphanylmethylene)-2,3-dimethyl-1,3-dioxolane (DIOP) according to an already published procedure.[13a][13b] (*R*,*R*)-1,4-bis(diphenylphosphanyl)-2,3-dimethoxybutane (**1-OMe**) was prepared starting from (*R*,*R*)-tartaric acid as described in ref.[14]. Commercially available (*Z*)-2-(acetylamino)cinnamic acid (AH) and itaconic acid (ItH_2) were recrystallized under argon. − NMR: Bruker ARX 400 (400.13 MHz, 100.63 MHz, and 161.98 MHz for ^1H, ^{13}C and ^{31}P, respectively); for ^1H and ^{13}C NMR TMS as internal standard; for ^{31}P NMR H_3PO_4 as external standard. − X-ray: STOE-IPDS diffractometer. − IR: Nicolet Magna − IR 550 instrument. − MS: AMD 402 (Firma Intectra) − Elemental analysis: LECO CHNS-932. − The hydrogenation experiments were carried out under normal pressure and isobaric conditions with an automatically registrating gas-measuring device (1.0 atm overall pressure over the solution). The experiments were carried out under standard conditions with 0.01 mmol precatalyst, 1.0 mmol of prochiral olefin in 15 ml of solvent at 25°C. The conversion of the prochiral olefins was determined by GC. The acids were esterified with trimethylsilyldiazomethane before the GC measurements: GC 5890 Serie II; FID, carrier gas: argon: 1 ml/min. Methyl *N*-acetylphenylalaninate: fused silica; 10 m, XE-60-L-valin-*tert*-butylamide; ID 0.2 mm; oven temperature: 150°C. Dimethyl methylsuccinate: fused silica, Lipodex E (Machery and Nagel), 25 m, ID 0.25 mm; oven temperature: 85°C.

*[Rh(COD)(***1-OH***)]BF$_4$:* (*R*,*R*)-1,4-Bis(diphenylphosphanyl)butane-2,3-diol (120 mg, 0.262 mmol) and $[Rh(COD)_2]BF_4$ (106 mg, 0.262 mmol) were stirred in THF (2 ml) at ambient temperature for 1.5 h. After the addition of diethyl ether (8 ml), a precipitate formed which was filtered off and washed with a small quantity of diethyl ether to give 182 mg (92%) of the complex as a yellow-orange powder. − ^{31}P NMR ($CDCl_3$, 297 K): δ = 15.0 (d, *J* = 148.1 Hz). − ^{13}C NMR ($CDCl_3$, 297 K): δ = 133.9−128.5 (Ar), 95.9 (s, COD-*CH*), 95.5 (s, COD-*CH*), 71.7 (s, O*CH*), 33.0 (m, PCH_2), 28.7 (s, COD-CH_2). − ^1H NMR ($CDCl_3$, 297 K): δ = 7.70−7.34 (m, 20 H, Ar), 4.52 (m, 2 H, COD-*CH*), 4.17 (m, 2 H, COD-*CH*), 4.04 (m, 2 H, O*CH*), 2.84 (m, 2 H, H_b of PCH_2), 2.62−2.18 (m, 8 H, COD-CH_2), 2.01 (m, 2 H, H_a of PCH_2). − IR (KBr): $\tilde{\nu}$ = 3548, 3463, 3053, 2946, 2919, 2882, 2835, 2361, 1894, 1844, 1480 cm^{-1}. − FAB MS (3-nitrobenzyl alcohol matrix): *m*/*z* = 668.6 $[M - BF_4]^+$, 560.7 $[M - BF_4 - COD]^+$. − $C_{36}H_{40}BF_4O_2P_2Rh$ (756.37): C 57.17, H 5.33; found C 56.78, H 5.35.

*[Rh(NBD)(***1-OH***)]BF$_4$:* To a suspension of [Rh(COD)(**1-OH**)]BF_4 (151 mg, 0.2 mmol) in THF (45 ml) freshly distilled NBD (10 ml, 100 mmol) was added. Stirring over a period of 48 h yielded a dark orange solution. After the addition of diethyl ether (200 ml), an orange powder precipitated, which was filtered off and dried to give 133 mg (90%) of the desired NBD complex. − ^{31}P NMR (CD_2Cl_2, 297 K): δ = 18.1 (d, *J* = 146.2 Hz). − ^{13}C NMR (CD_2Cl_2, 297 K): δ = 134.3−129.2 (Ar), 72.2 (m, *CH*), 71.7 (m, *CH*), 70.6 (m, *CH*), 66.2 (s, *CH*), 31.9 [t, ^1J(P-C) = 12.3 Hz, PCH_2]. − ^1H NMR (CD_2Cl_2, 297 K): δ = 7.38−7.06 (m, 20 H, Ar), 3.97 (s, 2 H, *CH*), 3.85 (s, 2 H, *CH*), 3.76 (m, 2 H, *CH*), 3.62 (m, 2 H, *CH*), 2.65 (m, 2 H, H_a of PCH_2), 2.19 (m, 2 H, H_b of PCH_2), 1.23 (s, 2 H, NBD-CH_2). − IR (KBr): $\tilde{\nu}$ = 3508, 3441, 3056, 3003, 2952, 2920, 2848, 2681 cm^{-1}. − IR (CD_2Cl_2) $\tilde{\nu}$ = 3410, 3396 cm^{-1}. − FAB MS (3-nitrobenzyl alcohol matrix): *m*/*z* = 652.7 $[M - BF_4]^+$. − $C_{35}H_{36}BF_4O_2P_2Rh$ (740.33): C 56.78, H 4.90; found C 56.96, H 4.93.

*[Rh(COD)(***1-OMe***)]BF$_4$:* (*R*,*R*)-1,4-Bis(diphenylphosphanyl)-2,3-dimethoxybutane (290 mg, 0.6 mmol) and $[Rh(COD)_2]BF_4$ (243 mg, 0.6 mmol) were stirred in THF (2 ml) at ambient temperature for 2 h. After the addition of diethyl ether (8 ml), a precipitate formed which was filtered off and recrystallized from THF and diethyl ether to give 367 mg (78%) of the complex as a orange powder. − ^{31}P NMR ($CDCl_3$, 297 K): δ = 12.3 (d, *J* = 144.0 Hz). − ^{13}C NMR ($CDCl_3$, 297 K): δ = 134.5−128.9 (Ar), 99.4 (s, COD-*CH*), 95.0 (s, COD-*CH*), 78.0 (s, O*CH*), 58.5 (s, OCH_3), 31.8 [t, ^1J(P-C) = 13.2 Hz, PCH_2], 30.7 (s, COD-CH_2). − ^1H NMR ($CDCl_3$, 297 K): δ = 7.82−7.08 (m, 20 H, Ar), 4.38 (m, 2 H, *CH*), 4.25 (m, 2 H, *CH*), 3.46 (m, 2 H, *CH*), 3.27 (s, 6 H, OCH_3), 2.84−2.01 (m, 12 H, PCH_2 and COD-CH_2). − IR (KBr): $\tilde{\nu}$ = 3047, 2951, 2920, 2882, 2837, 1480, 1433 cm^{-1}. − FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z* = 696.6 $[M - BF_4]^+$, 588.6 $[(M - BF_4) - COD]^+$. − $C_{38}H_{44}BF_4O_2P_2Rh$ (784.42): C 58.19, H 5.65; found C 58.33, H 5.54.

☆ Dedicated to Professor *H. B. Kagan*.

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[17] General methods for X-ray structural analyses: STOE-IPDS diffractometer, graphite-monochromated Mo-K_α radiation, structure solution with direct methods (SHELXS-86: G.M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467), refinement against F^2 (SHELXL-93: G.M. Sheldrick, unpublished), structure representation: Schakal-92 (E. Keller, Universität Freiburg, **1992**). − [17a] Crystal data of [Rh(NBD)(**1-OH**)]BF_4: 0.3 × 0.2 × 0.1 mm, orange-red prism, space group $P2_12_12_1$, orthorhombic, a = 9.783(2), b = 17.870(3), c = 21.334(3) A, V = 3730(1) A^3, Z = 4, $\rho_{calcd.}$ = 1.381 g cm^{-3}, 11214 collected, 5864 unique reflections, observed 3658 [$I = 2\sigma(I)$], $R1$ = 0.054, wR^2 (all data) = 0.143, 397 parameters. − [17b] Crystal data of [Rh(COD)(**1-OMe**)]BF_4: 0.4 × 0.3 × 0.3 mm, orange prism, space group $P2_1$, monoclinic, a = 9.240(2), b = 13.878(3), c = 15.159(4) A, β = 94.74(1)°, V = 1937.2(8) A^3, Z = 2, $\rho_{calcd.}$ = 1.345 g cm^{-3}, 5862 collected, 5862 unique reflections, observed 5005 [$I = 2\sigma(I)$], $R1$ = 0.052, wR^2 (all data) = 0.149, 401 parameters. − Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC-100869. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

[18] In the related (monohydroxy diphosphane)$RhBF_4$ complex the noncoordinating hydroxy group was characterized in the solid-state IR by a band at 3511 cm^{-1}[11]. Therefore, we tentatively attribute the band observed at the longer wavelength to the Rh-coordinated hydroxy group.

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[21] The distance between the oxygen and the rhodium atom is larger than 3.5 A.

[22] In the related (DIOP)Rh complex[14] the stablization of the seven-membered chelate is provided by the rigid 1,3-dioxolane ring. Simultaneously, due to this construction both oxygen atoms are not available for the interaction with the metal center.

[23] In case of the HO-bearing complex attractive interactions between hydroxy and carboxylic group of the substrate may contribute to the improved stereoselection, however, up to now all attempts to obtain spectroscopical evidence for these interactions in methanol failed.

[24] Due to the change from Rh^I to Rh^{III} during the catalytic cycle[6a] electrostatic interactions may become more dominant at certain steps.

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