β-Alkoxy- and β-Hydroxyalkylphosphanes as Ligands in the Stereoselective Hydrogenation – A Comparison

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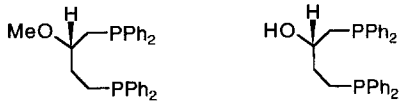
Optically pure 1,4-bis(diphenylphosphanyl)-2-hydroxy-butane (**2**) and its methyl ether **1** can be conveniently prepared by starting from chiral pool substances such as malic or L-ascorbic acid. Different pathways to these compounds were elucidated. In one case an interesting migration of an acetalic OH-protective group was observed. The reaction of the bisphosphanes with Rh^{I} or Pd^{II} gave uniform metal complexes. On the basis of X-ray structural analysis, NMR and IR data it was concluded that in the investigated precatalysts of the type [Rh(COD)(bisphosphane)]BF_4 a coordination of the alkoxy or hydroxy oxygen to the metal does not take place. Nevertheless, significant differences in enantioselectivity and activity could be observed when several prochiral substrates were hydrogenated.

Among the vast number of enantiomerically pure bisphosphanes used in the rhodium-mediated stereoselective hydrogenation ether bisphosphanes have been revealed to be very effective. Knowles and co-workers made the initial breakthrough with the synthesis of DiPAMP, which contains two anisyl groups[1]. Several other chiral aryl or alkyl ether phosphanes have been reported to be similarly useful[2]. It was suggested that the high efficiency of such ether phosphane complexes derives from the lability of the rhodium-oxygen bond. In a widely accepted model the alkoxy group is regarded as an intramolecular solvent molecule, which makes empty coordination sites available for a stronger coordinating substrate ("windshield wiper effect")[3]. On the other hand, the superior stereoselectivity of such "hemilabile" O–P ligands is explained by the mentioned partially chelating nature of the metal oxygen interaction, that may, if properly directed, advantageously support the stereodiscriminating ability of the catalyst. From this point of view, it is interesting to note some sporadic observations published in the literature in which replacement of an alkoxy group by the hydroxy group lowers the reactivity of the catalyst[4]. Therefore, it seemed to us desirable to get a more detailed understanding of how a hydroxy group influences the catalysis in terms of activity and enantioselectivity in comparison with the related alkoxy group. Recently, we could provide first evidence that the spatial arrangement of the hydroxy group may be decisive for the observed inhibition of the reaction[5,6]. Based on these synthetic studies we concluded that close contact of the hydroxy group to the metal should be avoided by steric hindrance in order to create a highly active catalyst[7].

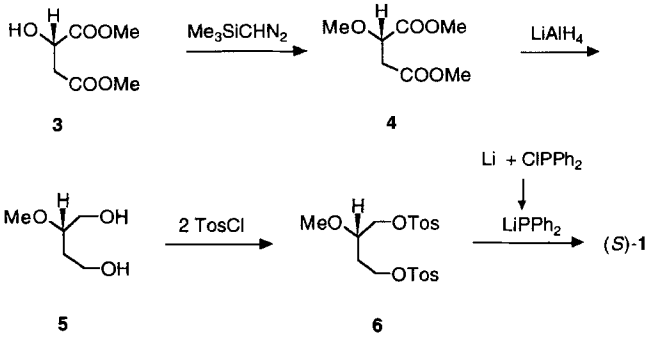
In this paper we report on our results obtained by a comparison of the spectroscopic and catalytic properties of metal complexes of (*S*)-1,4-bis(diphenylphosphanyl)-2-methoxybutane [(*S*)-**1**] and its hydroxy analog (*S*)-**2**.



(*S*)-**1** (*S*)-**2**

Synthesis of the Ligands

A convenient access to these ligands is gained by starting from the dimethyl ester of enantiomerically pure (*S*)-malic acid (**3**). Thus, acid-catalyzed methylation of the hydroxy group with (trimethylsilyl)diazomethane yielded the methyl ether **4**. This procedure gave higher yields than the reaction with iodomethane in the presence of a base, considerable amounts of olefinic esters being formed as by-products. Reduction of both ester groups with $LiAlH_4$ furnished the partially methylated triol **5**. This compound was converted into the 1,4-ditosylate **6** by the reaction with tosyl chloride. Replacement of the tosyl groups by $LiPPh_2$ yielded the desired (methoxyalkyl)phosphane (*S*)-**1**.



The hydroxy analog **2** was obtained by a similar approach. In the first step the hydroxy group of dimethyl malate (**3**) was protected by treatment with 3,4-dihydro-2*H*-py-

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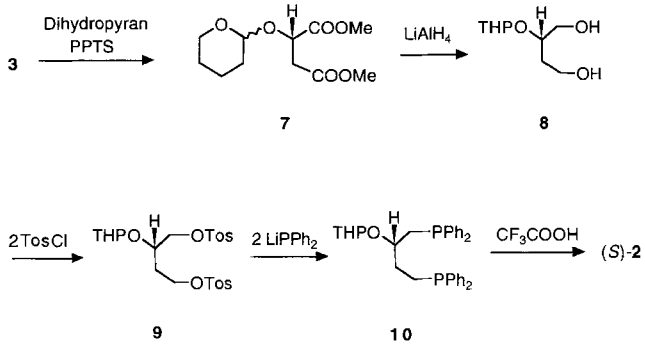
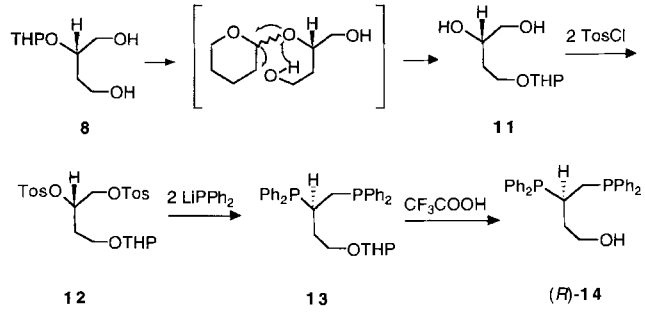
ran in the presence of a catalytic amount of pyridinium *p*-toluenesulfonate to yield a 1:1 mixture of the diastereomeric acetals **7**. Reduction of the ester groups with $LiAlH_4$ afforded the partially protected triol **8**. The crude product was allowed to react with tosyl chloride to give the 1,4-ditosylate **9** in 70% yield. Replacement of the tosyl groups by $LiPPh_2$ and hydrolysis of the acetal **10** with methanolic CF_3COOH[8] furnished the desired (hydroxyalkyl)phosphane (*S*)-**2**. One interesting feature of this relatively air-stable compound is its low optical rotation measured at 589 nm ($[\alpha]_D^{23} = +1.0$, $c = 1$, $CHCl_3$).

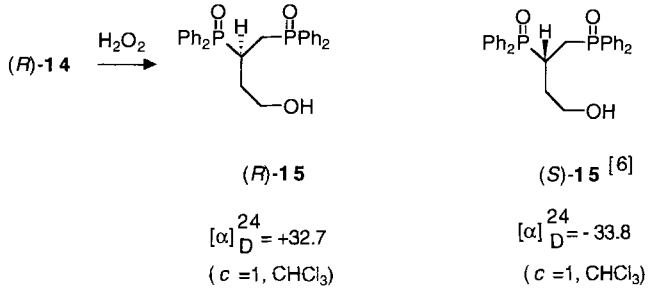


It should be mentioned, that only the crude alcohol **8** could be successfully converted to the 1,4-ditosylate **9**. All attempts to purify the THP ether **8** by distillation under reduced pressure or by flash chromatography caused a migration or total loss of the THP moiety. By application of these procedures, 4-*O*-THP-1,2,4-butanetriol (**11**) was isolated as the main product[9]. Detailed investigations showed that migration of the protective group is initiated by traces of acids and accelerated by heating at elevated temperatures in different solvents (THF, benzene, $CHCl_3$). It is important to note that the migration does not occur under the conditions applied to the tosylation of the crude diol **8**. In order to infer the position of the THP group in the main product, the diol **11** was esterified with tosyl chloride to give the 1,2-ditosylate **12**. Replacement of the tosyl groups by phosphide furnished the bisphosphane **13**.



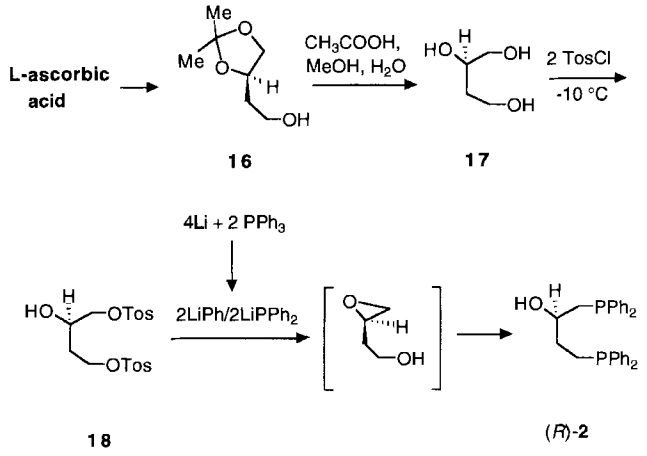
The structure of **13** could be unambiguously deduced from the ^{13}C- and ^{31}P-NMR spectra. Especially the remarkable phosphane-induced shift of the signals of C-4 and C-3 to higher field allowed the assignment of the positions of the two phosphanyl groups. As conjectured, the shift of the signal of C-1 remains rather constant. Another important feature is the occurrence of two sets of widely separated phosphanyl signals in the ^{31}P-NMR spectrum ($\delta = -1.4/-1.7$ and $-20.1/-20.4$). The shift of one set of signals to lower field indicates that the concerned diphenylphosphanyl group is attached to a secondary carbon atom. The large ^{31}P-^{31}P coupling constants for the two diastereomers of 27.8 and 27.3 Hz, respectively, furnish an additional proof of the assumption of a vicinal bisphosphane. The cleavage of the THP-protective group in **13** afforded (*R*)-3,4-bis(diphenylphosphanyl)-1-butanol [(*R*)-**14**].

We have previously described the synthesis of the corresponding (*S*)-configurated enantiomer of **14** as well as its bisphosphane oxide (*S*)-**15** starting from L-ascorbic acid[6]. In order to demonstrate the configurational relationship of both highly air-sensitive (hydroxyalkyl)phosphanes, (*R*)-**14** was oxidized with H_2O_2. As expected the optical rotation of the obtained phosphane oxide (*R*)-**15** is in close agreement with the value reported for (*S*)-**15**, but is opposite in sign. This result gives clear evidence that during the migration of the THP group the chiral center was not affected.

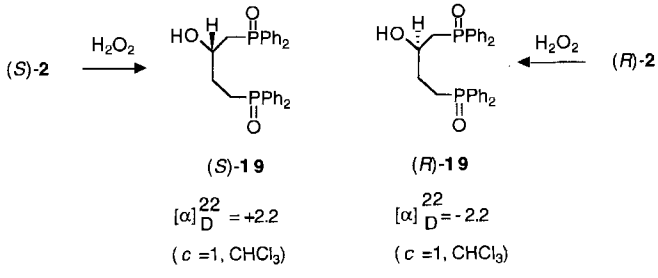


To verify the optical purity of (*S*)-1,4-bis(diphenylphosphanyl)-2-butanol [(*S*)-**2**] the corresponding (*R*) enantiomer was prepared by a different pathway. For this synthesis we envisaged the introduction of the phosphanyl groups into a corresponding triol without protection of the hydroxy group at C-2. The required enantiomerically pure (*R*)-1,2,4-butanetriol **17** was readily available from L-ascorbic acid by hydrolysis of the acetonide **16**[10–12]. Upon treatment with two equivalents of tosyl chloride at $-10\,°C$, only the primary hydroxy groups were selectively esterified to yield the ditosylate **18**. It is remarkable that the secondary hydroxy group was not attacked when the reaction was performed below $0\,°C$. Finally, replacement of the tosyl groups by $LiPPh_2$ afforded the desired (*R*)-**2**. In contrast to the procedures demonstrated above, for this approach the metal phosphide was generated by reaction of lithium with PPh_3[13]. This method simultaneously furnishes LiPh, that reacts with the hydroxy group to afford the corresponding lithium alkoxide. Under the conditions applied the formation of an epoxide as intermediate which is concomitantly opened by the attacking phosphide cannot be excluded. However, as observed by Zhang et al. the opening of chiral terminal epoxides by phosphide always proceeds regio- and stereoselectively[14]. In general, this approach avoids the ap-

plication of an excess of phosphide, sometimes difficult to remove during the workup.



The comparison of the values of the optical rotation of the corresponding phosphane oxides (*S*)-**19** and (*R*)-**19** illustrates the agreement with the supposed configurational correlation and indicates that the two pathways proved furnished optically pure products[15].



Synthesis and Characterization of Metal Complexes of (*S*)-1 and (*S*)-2

Rh complexes were synthesized by reaction of [Rh(COD)acac] with the bisphosphanes (*S*)-**1** and (*S*)-**2** in THF and subsequent addition of HBF_4. Both complexes were precipitated with ether and could be isolated as orange solids in good yields.

In order to demonstrate the behavior of the complexes in solution some characteristic analytical data are listed in Table 1. They are briefly discussed here and compared to values recently published by us[16].

Table 1. NMR and IR data of Rh complexes of the type [Rh(COD)(L*)]BF_4

Ligand (L*)	NMR					IR
	^{31}P		^{103}Rh	^{13}C COD		
	$^4CH_2P$	$^1CH_2P$				ν̃(OH)
(*S*)-**1**						
δ (ppm)	29.5 dd	12.8 dd	- 249	103.2 m	98.5 m	-
$^1J_{PRh}$ [Hz]	145.8	144.2				
J_{PP} [Hz]	38.1	38.1				
(*S*)-**2**						
δ (ppm)	20.2 dd	15.6 dd	- 156	98.3 m	96.7 m	3511
$^1J_{PRh}$ [Hz]	142.6	139.3				
J_{PP} [Hz]	38.1	38.1				

The complexes of (*S*)-**1** and (*S*)-**2** are characterized in the ^{31}P-NMR spectrum by two sets of double doublets between δ = 29.5 and 12.8. In general, such chemical shifts are observed for 1,4-bisdiphenylphosphanyl-Rh^I complexes. Since (O–P)Rh^I chelates of 1,2-hydroxyphosphanes show a significant shift to lower field due to the ring strain, it can be deduced from these values as well as from the relatively small ^{103}Rh-^{31}P coupling constants that chelation of oxygen to the metal in these complexes does not take place. The inspection of the ^{13}C-NMR spectra supports this reasoning. All methine carbon atoms from the COD can be observed between δ = 104 and 96, which indicates the *trans* relationship to the π-accepting phosphorus. Oxygen in the *trans* position would cause a significant shift to higher field of the carbon atom signals considered. Therefore, besides O–P chelates, also O-bridging dimers can be excluded. This assumption is confirmed by the IR spectrum where the OH band of [Rh(COD){(*S*)-**2**}]BF_4 is observed at 3511 cm^{-1}. In the ^1H-NMR spectrum the hydroxy proton can be found as a broadened singlet at δ = 4.35. In a similar case Hitchcock et al. reported on a coupling of a hydroxy proton with rhodium (δ = 3.02, J_{HRh} = 2.7 Hz)[17]. From this finding as well as according to an X-ray structural analysis they presumed a close rhodium-oxygen contact (Rh–OH: 3.8 Å), which is maintained even in solution. Apparently, this relation does not account for the rhodium complex of the (hydroxyalkyl)phosphane (*S*)-**2**.

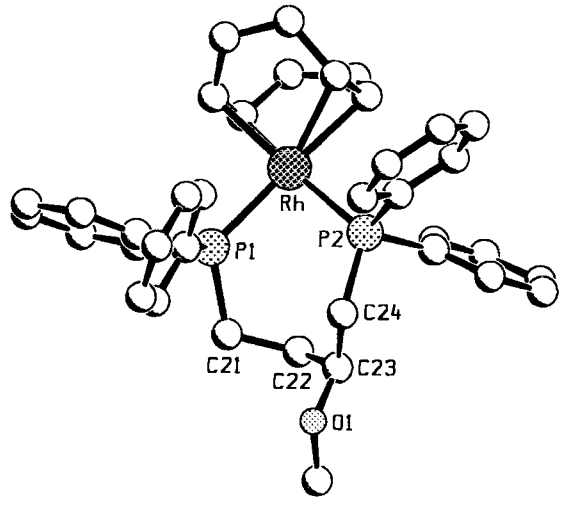
The corresponding Pd^{II} complexes of the structure [Pd(bisphosphane)]I_2 were prepared by reaction of [Pd(COD)]Cl_2 with the corresponding bisphosphane and subsequent addition of NaI or by direct complexation with PdI_2 in CH_2Cl_2[18]. The crude Pd complexes were purified by flash chromatography on silica gel.

X-Ray Structural Analyses

Crystals of [Rh(COD){(*S*)-**1**}]BF_4, [Rh(COD){(*S*)-**2**}]BF_4, and [Pd{(*S*)-**2**}]I_2 suitable for X-ray analysis could be obtained from EtOH/water or CH_2Cl_2/*n*-hexane, respectively. A single-crystal X-ray structural analysis of [Rh(COD){(*S*)-**1**}]$(BF_4)(CH_2Cl_2)_{0.6}$ established the structure of the cation as shown in Figure 1 along with the selected bond lengths and interbond angles.

The coordination of the 1,4-bisphosphane (*S*)-**1** is in accordance with similar rhodium complexes that form seven-membered rings and contain COD as an ancillary ligand[19]. A Flack parameter of −0.05(8) verified the expected (*S*) configuration of [Rh(COD){(*S*)-**1**}]BF_4[20]. Neither intermolecular nor intramolecular interactions between rhodium and alkoxy oxygen were observed. The distance through space between Rh and the oxygen is greater than 5 Å. A successful refinement of [Rh(COD){(*S*)-**2**}]BF_4 as well as of the complex [Pd{(*S*)-**2**}]I_2 could not be accomplished because of disordered hydroxy oxygen. Despite this fact we could not detect an intermolecular or intramolecular interaction between rhodium and oxygen in the solid state. Relations almost identical to that in [Rh(COD){(*S*)-**1**}]BF_4 were found.

Figure 1. Molecular structure of the cation of [Rh(COD){(*S*)-**1**}]BF_4 in the crystal as determined by X-ray structural analysis. Selected bond lengths [Å] and angles [°]: P(1)–Rh 2.325(2), P(2)–Rh 2.319(3), P(2)–C(24) 1.83(1), P(1)–C(21) 1.85(1); P(2)–Rh–P(1) 91.66(9), O(1)–C(23)–C(22) 112(1), O(1)–C(23)–C(24) 105(1)



Hydrogenation Properties

As already mentioned in the introduction, the catalytic properties of the complexes derived from (*S*)-**1** and (*S*)-**2** were proven in the hydrogenation of selected substrates. If not stated otherwise, in all hydrogenation experiments a standard set of reaction conditions was applied. The results are given in Table 2.

Table 2. Results of the hydrogenation of selected substrates with [Rh(COD)(L*)]BF_4[a]

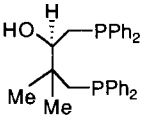
Ligand (L*)	AMe[b]		AH[c]		ItMe$_2$[d]		ItH$_2$[e]	
	time/ min[f]	%*ee*[g]	time/ min[f]	%*ee*[g]	time/ min[f]	%*ee*[g]	time/ min[f]	%*ee*[g]
(*S*)-**1**	13	5.3 (*S*)	6	4.6 (*S*)	15	2.6 (*R*)	1.5[h]	8.3 (*R*)
(*S*)-**2**	35	25.6 (*S*)	15	41.7 (*S*)	20	24.8 (*R*)	2.5	45.2 (*R*)

[a] Catalyst/substrate = 1/100, 1 atm total pressure above the reaction mixture, 25 °C; 1 mmol substrate in 15 ml of methanol. – [b] Methyl (*Z*)-acetamidocinnamate. – [c] (*Z*)-Acetamidocinnamic acid. – [d] Dimethyl itaconate. – [e] Itaconic acid. – [f] Determined after 100% conversion. – [g] Measured on the crude product, GC with a chiral column: for *N*-acetylphenylalanine and methylsuccinic acid after esterification with diazomethane and for methyl ester of *N*-acetylphenylalanine and dimethyl methylsuccinate, respectively, with XE 60-L-valine *tert*-butylamide, 150 °C. – [h] 0.005 mmol of catalyst was applied.

Several features are worth mentioning. In general, the methoxy group-bearing catalyst induces only poor enantioselectivities for all prochiral olefins, whereas the application of the (hydroxyalkyl)phosphane (*S*)-**2** as ligand leads to improved selectivities. Of particular interest is the fact that the carboxylic acids are reduced with considerably higher enantioselectivities than the corresponding esters when the (*S*)-**2**-catalyst is applied. It is suggestive to attribute these results to additional hydrogen bonds between the hydroxy ligand (*S*)-**2** and the substrate. Simultaneously with the increase of the enantioselectivity observed with the (hydroxyalkyl)phosphane, a serious decrease of the activity has to be stated. This result may also account for an additional bonding interaction between catalyst and substrate hence influencing the rate of the reaction.

It should be noted by a comparison of the two catalysts considered, that no change in the sense of the induced asymmetry takes place. However, it seems that the enantiodiscriminating ability of the hydroxy catalyst is strongly sensitive to the change of substituents in the backbone of the ligand. Thus, Brunner et al. obtained 17% *ee* (*S*) product in the hydrogenation of AH when an in situ prepared catalyst bearing the ligand (*R*)-**20** was applied[21].

(*R*)-**20**



The origin of the distinct behavior of hydroxy phosphanes has not been clarified yet. However, the foregoing results clearly demonstrate the enantioselectivity-increasing role of hydroxy groups in selected catalytic hydrogenations. The work also manifests the intriguing hitherto still unexplored effect responsible for the lowering of the rate of this reaction. At least for precatalysts of the ligands **1** and **2** interactions of the oxygen with the metal atom can be excluded. Studies of the scope and mechanistic aspects of the catalytic hydrogenation with chiral (hydroxyalkyl)phosphanes, also by ab initio methods, are continuing.

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Experimental

All dry solvents were distilled under argon. Reactions involving phosphanes and organometallic compounds were conducted under argon by using standard Schlenk techniques. – Thin-layer chromatography: precoated TLC plates (silica gel 60 F_{254}, Merck). – Flash chromatography: Silica gel 60 (0.040–0.063 mm, Merck). – Melting points are corrected. – Optical rotations: Gyromat-HP (Firma Dr. Kernchen). – IR: Nicolet Magna – IR 550 instrument. – NMR: Bruker AC 250, at 303 K [250.13 MHz (^{1}H), 62.90 MHz (^{13}C), 101.26 MHz (^{31}P) with TMS as internal or with H_3PO_4 as external standard] and Bruker ARX 400 [^{103}Rh (12.64 MHz)][22]. – MS: AMD 402 (Firma Intectra), at an ionization voltage 70 eV. – X-ray structural analyses: CAD4 MACH3 diffractometer (Firma Enraf Nonius). – CH analyses: LECO CHNS-932.

(S)-Dimethyl O-Methylmalate (**4**): To a solution of 1.62 g (10 mmol) of (*S*)-dimethyl malate and 1.72 ml of aqueous 40% HBF_4 in 20 ml of CH_2Cl_2 5 ml of a 2 M solution of (trimethylsilyl)diazomethane ($TMSCHN_2$) in *n*-hexane was added with stirring at 0 °C. Evolution of nitrogen was observed. After stirring for 20 min at this temp. once again 2.50 ml of $TMSCHN_2$ was added. This procedure was repeated at intervals of 20 min with 2 × 1.30 ml of the alkylating agent. Finally, after the yellow color of the solution had disappeared it was poured into ice/water and extracted with

CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4) and the solvent evaporated in vacuo. The crude methyl ether was subjected to flash chromatography (*n*-hexane/EtOAc, 7:3) which afforded **4** as a colorless oil; yield 0.82 g (46%), $[\alpha]_D^{23} = -44.1$ (c = 1, $CHCl_3$). – ^1H NMR ($CDCl_3$): δ = 4.08 (m, 1H, OCH), 3.62 (s, 3H, CH_3), 3.58 (s, 3H, CH_3), 3.35 (s, 3H, CH_3), 2.64 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.5 (C=O), 170.2 (C=O), 76.2 (C-2), 58.5 (CH_3), 51.9 (CH_3), 51.7 (CH_3), 37.3 (C-3). – IR (KBr): $\tilde{\nu}$ = 1747 cm^{-1} [ν(C=O)]. – MS, *m/z* (%): 176 (0.01) [$M^{\cdot+}$], 161 (0.02) [$M^+ - CH_3$], 146 (6) [$M^+ - 2 \times CH_3$], 117 (70) [146 – CHO], 75 (100) [$C_3H_7O_2$]. – $C_7H_{12}O_5$ (176.2): calcd. C 47.73, H 6.87; found C 47.64, H 6.84.

(S)-2-O-Methyl-1,2,4-butanetriol (**5**): To a suspension of 1.68 g (44.2 mmol) of $LiAlH_4$ in 30 ml of THF a solution of 2.3 g (13.0 mmol) of dimethyl ester **4** in 10 ml of THF was dropped with stirring. When the addition was completed stirring was continued for a further 1 h. Then the mixture was heated at reflux for 1 h. After cooling to room temp. excess $LiAlH_4$ was carefully decomposed by addition of 1.6 ml of water, 1.6 ml of a 15% aqueous solution of NaOH, and 4.8 ml of water. After filtration the solution was dried (Na_2SO_4) and concentrated to give the diol **5** as a pale yellow oil, which could be employed for the reaction with tosyl chloride without further purification; yield 1.0 g (64%), $[\alpha]_D^{25} = -2.0$ (c = 1, $CHCl_3$). – ^1H NMR ($CDCl_3$): δ = 3.72–3.30 (m, 10H, OCH, OCH_2, and CH_3, 2 × OH exchangeable with D_2O), 1.75 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 79.9 (C-2), 63.3 (C-1), 59.2 (C-4), 57.1 (OCH_3), 33.6 (C-3). – IR (KBr): $\tilde{\nu}$ = 3448 cm^{-1} [ν(OH)]. – $C_5H_{12}O_3$ (120.1): calcd. C 49.98, H 10.07; found C 49.79, H 10.20.

(S)-2-O-Methyl-1,4-di-O-tosyl-1,2,4-butanetriol (**6**): To a solution of 0.95 g (7.9 mmol) of diol **5** in 10 ml of dry pyridine at 0°C was added 3.78 g (19.8 mmol) of *p*-toluenesulfonyl chloride. The mixture was stirred at 0°C for 15 min and then allowed to warm to room temp. Stirring was continued for 6 h. The reaction mixture was poured onto excess ice/water and extracted several times with CH_2Cl_2. The extracts were washed with 5% aqueous H_2SO_4, a 5% $NaHCO_3$ solution, and water, dried (Na_2SO_4) and concentrated. The resultant colorless oil was purified by flash chromatography (*n*-hexane/AcOEt, 7:3) to give **6** as a colorless oil; yield 2.64 g (78%), $[\alpha]_D^{23} = -2.5$ (c = 1, $CHCl_3$). – ^1H NMR ($CDCl_3$): δ = 7.75–7.24 (8H, aromat), 4.06–3.83 (m, 4H, OCH_2), 3.42 (m, 1H, OCH), 3.18 (s, 3H, OCH_3), 2.42 (s, 6H, CH_3), 2.77 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 144.6–127.8 (aromat), 74.4 (C-2), 69.9 (C-1), 66.4 (C-4), 57.8 (CH_3), 30.9 (C-3), 21.5 (CH_3). – $C_{19}H_{24}O_7S_2$ (428.1): calcd. C 53.26, H 5.65; found C 53.54, H 5.33.

(S)-1,4-Bis(diphenylphosphanyl)-2-methoxybutane [(*S*)-**1**]: A solution of lithium diphenylphosphide was generated from 0.114 g (16.38 mmol) of lithium strips and 0.85 ml (4.68 mmol) of freshly distilled chlorodiphenylphosphane in 5 ml of THF. The resultant deep red solution was added at 0°C to a solution of 0.50 g (1.17 mmol) of ditosylate **6** in 5 ml of THF over a period of 15 min. The solution was stirred for 2 h at room temp. Then 3 ml of water was added. After the removal of the solvent the residue was dissolved in 50 ml of CH_2Cl_2. The solution was dried (Na_2SO_4) and the solvent evaporated. The remaining crude phosphane was subjected to flash chromatography (*n*-hexane/EtOAc, 9:1) to give the bisphosphane (*S*)-**1** as a colorless oil; yield 0.34 g (64%), $[\alpha]_D^{23} = -29.6$ (c = 2.8, $CHCl_3$). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –14.8 (s), –21.2 (s). – ^1H NMR ($CDCl_3$): δ = 7.38–7.12 (20H, aromat), 3.18 (m, 1H, OCH), 3.04 (s, 3H, CH_3), 2.45 (dd, 1H, J = 13.7, 6.4 Hz, PCH_{2a}), 2.27–2.00 (m, 3H, PCH_2), 1.75 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 138.9–128.3 (aromat.), 79.3 (t, J_{PC} = 13.2 Hz, C-2), 56.4 (CH_3), 33.5 (d, $^1J_{PC}$ = 14.8 Hz, C-1), 30.7 (dd, $^2J_{PC}$ = 8.6, $^3J_{PC}$ = 7.6 Hz, C-3), 22.8 (d, $^1J_{PC}$ = 11.6 Hz, C-4). – $C_{29}H_{30}OP_2$ (456.5): calcd. C 76.30, H 6.62; found C 76.59, H 6.46.

(2S,2'RS)-Dimethyl 2-O-(Tetrahydro-2'-pyranyl)malate (**7**): To a solution of 12.40 g (76 mmol) of (*S*)-dimethyl malate in 250 ml of CH_2Cl_2 were added 9.59 g (114 mmol) of 3,4-dihydro-2*H*-pyran and 1.90 g (7.6 mmol) of pyridinium *p*-tosylate (PPTS). The mixture was stirred for 3 h at room temp. The solution was diluted with 200 ml of ether, the ethereal phase was separated and washed twice with half-saturated brine and water, then dried (Na_2SO_4) and concentrated in vacuo to give the protected dimethyl ester **7** as a colorless oil; yield 12.25 g (70%). – ^1H NMR ($CDCl_3$): δ = 4.81/4.65 (m, 1H, OCHO), 4.60/4.45 (m, 1H, OCH), 3.65–3.60 (m, 8H, 2 × CH_3, OCH_2), 2.78 (m, 2H, CH_2), 1.95–1.43 (m, 6H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.9/171.8 (C=O), 170.4/170.4 (C=O), 97.5/97.3 (C-2'), 73.1/70.4 (C-2), 62.3/61.9 (C–6'), 52.0 (CH_3), 51.7 (CH_3), 37.8/37.4 (C-3), 30.2/30.0 (C–3'), 25.2/25.1 (C-5'), 18.9/18.6 (C-4'). – $C_{11}H_{18}O_5$ (230.3): calcd. C 57.38, H 7.88; found C 57.27, H 7.60.

(2S,2'RS)-2-O-(Tetrahydro-2'-pyranyl)-1,2,4-butanetriol (**8**): Analogously as described for **5**, but using 16.56 g (71.9 mmol) of dimethyl ester **7** and 9.26 g (244 mmol) of $LiAlH_4$ as starting materials. In the workup procedure the lithium salts were extracted for 24 h with CH_2Cl_2 (Soxhlet). The combined extracts were dried (Na_2SO_4), and the solvent was evaporated in vacuo to give the crude diol **8** as a pale yellow oil; yield 9.30 g (68%). – ^1H NMR ($CDCl_3$): δ = 4.56 (m, 1H, OCHO), 4.05–3.20 (m, 7H, OCH and OCH_2), 2.78 (br, 2 × OH, exchangeable with D_2O), 1.95–1.32 (m, 8H, 4 × CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 100.9/99.5 (C-2'), 79.6/75.7 (C-2), 66.1/64.1 (C-1), 64.9/63.9 (C-6'), 59.2/58.8 (C-4), 35.3/35.2 (C-3), 31.6/31.5 (C-3'), 25.5/25.4 (C-5'), 20.8/20.8 (C-4').

(2S,2'RS)-2-O-(Tetrahydro-2'-pyranyl)-1,4-di-O-tosyl-1,2,4-butanetriol (**9**): Analogously as described for **6**, but using 1.35 g (7.1 mmol) of diol **8** and 3.41 g (17.9 mmol) of *p*-toluenesulfonyl chloride as starting materials; colorless oil, yield 2.48 g (70%). – ^1H NMR ($CDCl_3$): δ = 7.75–7.25 (m, 8H, aromat), 4.41/4.38 (m, 1H, OCHO), 4.18–3.42 (m, 7H, OCH and OCH_2), 2.27 (s, 6H, CH_3), 1.80–1.20 (m, 8H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 129.9–127.8 (aromat), 100.3/97.9 (C-2'), 72.1/71.4 (C-2), 70.3/69.6 (C-1), 66.7/66.3 (C-4), 63.0/62.6 (C-6'), 31.9/31.4 (C-3), 30.9/30.5 (C-3'), 25.0 (C-5'), 21.5 (CH_3), 19.6/19.4 (C-4'). – MS, *m/z* (%): 414 (3) [$M^+ - C_5H_8O$], 173 (75), 155 (70) [Tos], 91 (100) [C_7H_7]. – $C_{23}H_{30}O_8S_2$ (498.6): calcd. C 55.41, H 6.06; found C 55.49, H 6.23.

(2S,2'RS)-1,4-Bis(diphenylphosphanyl)-2-O-(tetrahydro-2'-pyranyl]-2-butanol (**10**): Analogously as described for (*S*)-**1**, but using 2.0 g (4 mmol) of ditosylate **9** as starting material; colorless oil, yield 0.9 g (43%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –14.5/–14.9 (s), –21.0/–21.5 (s). – ^1H NMR ($CDCl_3$): δ = 8.52–7.45 (20H, aromat), 5.83/5.65 (m, 1H, OHCO), 4.00–3.42 (m, 3H, HCO and OCH_2), 2.80–1.40 (m, 12H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 139.3–128.0 (aromat), 97.9/97.5 (s, C-2'), 75.5 (m, C-2), 62.4/62.3 (C-6'), 34.5 (d, $^1J_{PC}$ = 14.6 Hz, C-1)/33.9 (d, $^1J_{PC}$ = 15.4 Hz, C-1), 32.6 (d, $^2J_{PC}$ = 8.6 Hz, C-3)/32.4 (d, $^2J_{PC}$ = 8.6 Hz, C-3), 30.7/30.5 (C-3'), 25.3 (C-5'), 23.0 (d, $^1J_{PC}$ = 11.5 Hz, C-4)/22.3 (d, $^1J_{PC}$ = 12.1 Hz, C-4), 19.6/19.4 (C-4'). – $C_{33}H_{36}O_2P_2$ (526.6): calcd. C 75.27, H 6.89; found C 75.19, H 6.95.

(S)-1,4-Bis(diphenylphosphanyl)-2-butanol [(*S*)-**2**]: A solution of the diastereomeric mixture of 0.68 g (1.3 mmol) of THP ether **10** in 30 ml of methanol, 3 ml of water, and 40 ml of trifluoroacetic acid was heated at reflux for 3 h. The solution was cooled to room temp., and the solvents were removed under reduced pressure. The residue was purified by flash chromatography (*n*-hexane/EtOAc,

4:1) to yield the hydroxy bisphosphane (*S*)-**2**; yield 0.49 g (85%), m.p. 107–112°C, $[\alpha]_D^{23} = +1.0$ ($c = 1$, $CHCl_3$). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −14.9 (s), −22.7 (s). – ^1H NMR ($CDCl_3$): δ = 7.40–7.15 (20H, aromat), 3.76 (m, 1H, OCH), 2.38–1.80 (m, 5H, OH exchangeable with D_2O, 2 × PCH_2), 1.63 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 138.2–128.2 (aromat), 70.1 (t, J_{PC} = 13.7 Hz, C-2), 37.4 (d, $^1J_{PC}$ = 13.2 Hz, C-1), 34.6 (dd, $^2J_{PC}$ = 15.6, $^3J_{PC}$ = 7.6 Hz, C-3), 23.7 (d, $^1J_{PC}$ = 11.6 Hz, C-4). – IR (KBr): $\tilde{\nu}$ = 3556 cm^{-1} [ν(OH)], 1431 [ν(P–Ph)]. – $C_{28}H_{28}OP_2$ (442.5): calcd. C 76.01, H 6.38; found C 75.79, H 6.33.

(2S,2'RS)-4-O-(Tetrahydro-2'-pyranyl)-1,2,4-butanetriol (**11**): The crude oil obtained by the preparation of **8** was distilled in vacuo. The fraction obtained at 0.12 Torr with b.p. 103–110°C was subjected to flash chromatography (toluene/acetone, 7:3). The fraction with R_f = 0.25 [yield 15–50% after various attempts; ^1H NMR ($CDCl_3$): δ = 4.52 (m, 1H, OCHO), 4.40–3.20 (m, 9H, OH exchangeable with D_2O, OCH and OCH_2), 2.10–1.10 (m, 8H, CH_2)] was directly employed for the esterification with tosyl chloride.

(2S,2'RS)-4-O-(Tetrahydro-2'-pyranyl)-1,2-di-O-tosyl-1,2,4-butanetriol (**12**): Analogously as described for the preparation of **6**, but using 1.01 g (5.3 mmol) of diol **8** and 2.55 g (13.4 mmol) of *p*-toluenesulfonyl chloride as starting materials; colorless solid, yield 1.98 g (75%), m.p. 61.5–65.0°C. – ^1H NMR ($CDCl_3$): δ = 7.82–7.25 (8H, aromat), 4.82 (m, 1H, OCH), 4.42/4.28 (m, 1H, OCHO), 3.73 (m, 2H, OCH_2), 3.40 (m, 3.5H, OCH_2), 3.21 (m, 0.5H, OCH_2), 2.41 (s, 6H, CH_3), 1.92 (m, 2H, CH_2), 1.80–1.35 (m, 6H, CH_2). – ^{31}C NMR ($CDCl_3$): δ = 145.0–127.9 (aromat), 99.0/98.7 (C-2'), 76.6/76.3 (C-2), 70.0/69.8 (C-1), 62.4/62.3 (C-4), 62.2/62.0 (C-6'), 31.5 (C-3), 30.5/30.4 (C-3'), 25.3 (C-5'), 19.5/19.4 (C-4'), 21.6 (CH_3). – MS, *m/z* (%): 415 (68) [$M^+ - C_5H_8 + 1$], 155 (100) [Tos]. – $C_{23}H_{30}O_8S_2$ (498.6): calcd. C 55.40, H 6.06, S 12.86; found C 55.04, H 6.10, S 12.88.

(2'RS,3R)-3,4-Bis(diphenylphosphanyl)-O-(tetrahydro-2'-pyranyl)-1-butanol (**13**): Analogously as described for (*S*)-**1**, but using 0.8 g (1.6 mmol) of ditosylate **12** as starting material. The resulting oil was purified by repeated flash chromatography (1st run: CH_2Cl_2/EtOAc, 20:1; 2nd run: *n*-hexane/EtOAc, 7:3); colorless oil, yield 0.228 g (27%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −1.4 (d, $^3J_{PP}$ = 27.8 Hz, $^4CH_2P$)/−1.7 (d, $^3J_{PP}$ = 27.3 Hz, $^4CH_2P$), −20.1 (d, $^3J_{PP}$ = 27.8 Hz, ^3CHP)/−20.4 (d, $^3J_{PP}$ = 27.3 Hz, ^3CHP). – ^1H NMR ($CDCl_3$): δ = 7.41–7.10 (20H, aromat), 4.41 (m, 1H, OCHO), 3.73 (m, 1H, OCH), 3.40 (m, 2H, OCH_2), 2.38/2.15 (m, 2H, OCH_2), 1.92–1.34 (m, 10H, PCH, PCH_2, CH_2). – ^{31}C NMR ($CDCl_3$): δ = 139.1–128.1 (aromat), 98.4/98.3 (C-2'), 65.2 (dd, $^3J_{PC}$ = 7.6, $^4J_{PC}$ = 2.2 Hz, C-1)/65.2 (dd, $^3J_{PC}$ = 7.3, $^4J_{PC}$ = 2.5 Hz, C-1), 61.8/61.6 (C-6'), 31.5 (m, C-2), 31.2 (m, C-3), 30.5 (C-3'), 28.9 (m, C-4), 25.4 (C-5'), 19.2 (C-4'). – $C_{33}H_{36}O_2P_2$ (526.6): calcd. C 75.27, H 6.89; found C 75.50, H 7.05.

(R)-4-Hydroxy-1,2-butanediylbis(diphenylphosphane oxide) [(*R*)-**15**]: The corresponding hydroxy bisphosphane (*R*)-**14** was prepared analogously as described for the preparation of (*S*)-**2** by using 0.153 g (0.3 mmol) of THP-ether **13** as starting material to give the phosphane as a colorless, highly air-sensitive oil. Attempts to purify the phosphane by flash chromatography (*n*-hexane/EtOAc, 4:1) caused partial oxidation of the product. For the determination of the optical rotation the phosphane was immediately converted into the phosphane oxide (*R*)-**15** by treatment with aqueous 30% H_2O_2; $[\alpha]_D^{24} = +32.7$ ($c = 1$, $CHCl_3$); the analytical data are in agreement with those reported for the (*S*) enantiomer[6].

(R)-1,2,4-Butanetriol (**17**): A solution of 3.0 g (20.5 mmol) of (*R*)-1,2-*O*-isopropylidene-1,2,4-butanetriol **16**[10] in 15 ml of glacial acetic acid, 5 ml of H_2O, and 5 ml of THF was heated 4 h at 40°C. Then a mixture of toluene/EtOH (1:1) was codistilled several times. The residue was dried in vacuo to give the triol **17** as a colorless oil in quantitative yield (2.17 g). $[\alpha]_D^{24} = +26.6$ ($c = 3.3$, MeOH), {reported for the (*S*) enantiomer (ref.[12]): $[\alpha]_D^{22} = -24.6$ ($c = 3.32$, MeOH)}. – ^1H NMR (DMSO): δ = 4.28 (b, 3H, OH exchangeable with D_2O), 3.48 (m, 3H, OCH and OCH_2), 3.26 (m, 2H, OCH_2), 1.52 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR (D_2O): δ = 71.7 (C-2), 68.5 (C-1), 61.3 (C-4), 37.7 (C-3). – $C_4H_{10}O_3$ (106.1): calcd. C 45.27, H 9.50; found C 45.10, H 9.52.

(R)-1,4-Di-O-tosyl-1,2,4-butanetriol (**18**): A solution of 0.65 g (6.12 mmol) of the triol **17** in 5 ml of dry pyridine was treated with stirring with 2.57 g (13.5 mmol) of *p*-toluenesulfonyl chloride at −10°C. The mixture was stirred at this temp. for 2 h, then allowed to warm to room temp. Stirring was continued for 2 h. The reaction mixture was poured onto excess ice/water and extracted several times with CH_2Cl_2. The extracts were washed with 5% aqueous HCl, a 5% $NaHCO_3$ solution and water, dried (Na_2SO_4) and concentrated. The resultant colorless oil was then purified by flash chromatography (*n*-hexane/AcOEt, 7:3) to give **18** as colorless solid; yield 1.65 g (65%), m.p. 56–58°C, $[\alpha]_D^{21} = +5.0$ ($c = 1$, $CHCl_3$). – ^1H NMR ($CDCl_3$): δ = 7.80–7.27 (8H, aromat), 4.13 (m, 3H, OCH and OCH_2), 3.92 (m, 2H, OCH_2), 2.42 (s, 6H, CH_3), 2.15 (s, 1H, exchangeable with D_2O), 1.73 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 148.7–127.9 (aromat), 73.3 (C-2), 66.6 (C-1), 65.2 (C-4), 32.1 (C-3), 21.6 (CH_3). – MS, *m/z* (%): 414 [$M^{\cdot+}$] (0.6), 396 [$M^+ - 18$] (0.1), 327 (0.1), 262 (0.1), 243 [$M^+ -$ OTos] (2), 229 [$CH(OH)CH_2CH_2OTos$] (25), 155 [OTos] (60), 91 [$C_6H_4CH_3$] (100). – IR (neat): $\tilde{\nu}$ = 3531 cm^{-1} [ν(OH)]. – $C_{18}H_{22}O_7S_2$ (414.5): calcd. C 52.16, H 5.35, S 15.47; found C 52.16, H 5.35, S 15.43.

(R)-1,4-Bis(diphenylphosphanyl)-2-butanol [(*R*)-**2**]: In an ice bath 10 ml of THF was slowly added to a stirred suspension of 0.083 g (12 mmol) of lithium and 0.63 g (2.4 mmol) of triphenylphosphane. Stirring was continued for 2 h at room temp., then to the resultant red solution 0.5 g (1.2 mmol) of tosylate **18** in 5 ml of THF was added at −10°C. After stirring for 2 h at room temp. water was added and the solvent evaporated. The residue was subjected to flash chromatography (*n*-hexane/EtOAc, 4:1) to give (*R*)-**2** as a colorless oil; yield 0.292 g (55%), m.p. 105–109°C, $[\alpha]_D^{23} = -0.5$ ($c = 1$, $CHCl_3$). The spectroscopical data are in full agreement with those given above for (*S*)-**2**. – $C_{28}H_{28}OP_2$ (442.5): calcd. C 76.01, H 6.38; found C 75.85, H 6.12.

[Rh(COD){(*S*)-**1**}]BF_4: To a stirred solution of 312 mg (0.684 mmol) of (alkoxyalkyl)phosphane (*S*)-**1** in 10 ml of THF 212 mg (0.684 mmol) of [Rh(COD)]acac was added. After stirring for 10 min 150 mg (0.684 mmol) of 40% aqueous HBF_4 was dropwise added to the solution. After a few min the complex began to precipitate. To complete the precipitation 10 ml of ether was added. After further stirring for 1 h the complex was isolated by filtration, recrystallized from EtOH/CH_2Cl_2 (1:1) and dried in vacuo; yield 0.34 g (65%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 29.5 (dd, $^1J_{RhP}$ = 145.8, J_{PP} = 38.1 Hz), 12.8 (dd, $^1J_{RhP}$ = 144.2, J_{PP} = 38.1 Hz). – ^{103}Rh NMR ($CDCl_3$): δ = −249. – ^1H NMR ($CDCl_3$): δ = 7.95–7.14 (20H, aromat), 4.72 (m, 2H, COD), 4.26 (m, 2H, COD), 3.10 (m, 1H, OCH), 3.06 (s, 3H, CH_3), 2.65–1.82 (m, 14H, 2 × CH_2P, CH_2, COD). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 135.2–128.9 (aromat), 103.2 (m, CH, COD), 98.5 (m, CH, COD), 76.0 (d, $^2J_{PC}$ = 5.9 Hz, C-2), 56.2 (CH_3), 34.6 (d, $^1J_{PC}$ = 21.4 Hz, C-1), 30.4 (C-3), 30.2 (COD), 28.9 (COD), 24.5 (d, $^1J_{PC}$ = 25.7 Hz, C-4). – $C_{37}H_{42}BF_4OP_2Rh(CH_2Cl_2)_{0.6}$ (805.3): calcd. C 56.03, H 5.36, P 7.69, Rh 12.78; found C 55.84, H 5.81, P 7.99, Rh 11.80.

X-Ray Structural Analysis of [Rh(COD){(*S*)-**1**}]BF_4: Empirical formula $C_{37.6}H_{43.20}OBCl_{1.2}F_4P_2Rh$, molecular mass 805.3 $gmol^{-1}$,

orthorhombic, space group $Pca2_1$, a = 20.003(3), b = 9.4488(7), c = 19.988(2) Å, Z = 4, d_{calc} = 1.42 g cm^{-1}; single crystal: 0.4 × 0.3 × 0.2 mm, orange prism; data collection: CAD4 MACH3 diffractometer, graphite-monochromated Mo-K_α radiation, ω-2Θ scan, Θ_{min} = 2.6°, Θ_{max} = 25.0°, h from −23 to 0, k from −11 to 0, l from −23 to 0, 3422 reflections measured, 3422 reflections unique, 2802 reflections observed (criterion: $I > 2\sigma(I)$), absorption coefficient = 0.67 mm^{-1}, absorption correction with psi-scan (transmission: min/max = 92.1, 100%). – Structure analysis and refinement: Solution by direct methods using SHELXS-86 (G. M. Sheldrick, *Acta Crystallogr., Sect. A*, **1990**, *46*, 467–473), refinement against $F2$ using SHELXL-93 (G. M. Sheldrick, SHELXL-93, University of Göttingen, **1993**), rigid groups for hydrogen positions and BF_4 constrained, I_o/parameter ratio = 8.7, final R_1 = 0.052 [$I > 2\sigma(I)$] wR_2 = 0.163 (all data). – Molecular graphics: SCHAKAL-92 (E. Keller, SCHAKAL-92, University of Freiburg, **1992**). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58941, the names of the authors, and the journal citation.

[Rh(COD){(*S*)-**2**}]BF_4: Analogously as described for the preparation of {Rh(COD)[(*S*)-**1**]}BF_4, but using 312 mg (0.684 mmol) of (*S*)-**2** in 10 ml THF, 212 mg (0.684 mmol) of [Rh(COD)]acac, and 150 mg (0.684 mmol) of 40% aqueous HBF_4. The resulting complex was recrystallized from ethanol/H_2O; yield 0.39 g (78%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.2 (dd, $^1J_{RhP}$ = 142.6, J_{PP} = 38.1 Hz), 15.6 (dd, $^1J_{RhP}$ = 139.3, J_{PP} = 38.1 Hz). – ^{103}Rh NMR ($CDCl_3$): δ = −156. – ^1H NMR ($CDCl_3$): δ = 7.81–7.32 (20H, aromat), 4.62 (m, 2H, COD), 4.35 (b, OH, exchangeable with D_2O), 4.30 (m, 2H, COD), 3.53 (m, 1H, OCH), 2.95–2.70 (m, 2H, CH_2), 2.59–1.73 (m, 12H, PCH_2, COD). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 133.4–128.9 (aromat), 97.9 (m, CH, COD), 96.8 (m, CH, COD), 67.8 (d, $^2J_{PC}$ = 18.5 Hz, C-2), 37.1 (d, $^1J_{PC}$ = 22.0 Hz, C-1), 31.8 (C-3), 31.7 (COD), 29.4 (COD), 23.8 (d, $^1J_{PC}$ = 24.7 Hz, C-4). – IR (KBr): $\tilde{\nu}$ = 3511 cm^{-1} [ν(OH)]. – $C_{36}H_{40}BF_4OP_2Rh$ (740.4): calcd. C 58.40, H 5.45, Rh 13.90, P 8.37; found C 57.50, H 5.37, Rh 12.70, P 8.02.

[Pd{(*S*)-**1**}]I_2: To a stirred solution of 560 mg (1.23 mmol) of (alkoxyalkyl)phosphane (*S*)-**1** in 5 ml of CH_2Cl_2 442 mg (1.23 mmol) of PdI_2 was added. The resulting orange suspension was stirred with the exclusion of light overnight. After 5 ml of CH_2Cl_2 had been added to the suspension it was warmed a short time to obtain a clear solution. After filtration to the warm solution 5 ml of *n*-hexane was added. The resulting crystals were collected and dried; yield: 751 mg (92%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 28.3 (d, J = 14.7 Hz), 8.49 (d, J = 14.7 Hz). – ^1H NMR ($CDCl_3$): δ = 8.05–7.15 (20H, aromat), 3.10 (m, 1H, OCH), 2.98 (s, 3H, CH_3), 2.58 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 2.03 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 133.2–125.9 (aromat), 73.2 (d, $^2J_{PC}$ = 6.8 Hz, C-2), 53.9 (CH_3), 31.7 (d, $^1J_{PC}$ = 22.5 Hz, C-1), 29.5 (C-3), 22.1 (d, $^1J_{PC}$ = 23.8 Hz, C-4). – $C_{29}H_{30}I_2OP_2Pd$ (816.7): calcd. C 42.65, H 3.70, P 7.58, Pd 13.03; found C 41.50, H 3.85, P 7.86, Pd 12.71.

[Pd{(*S*)-**2**}]I_2: To a stirred solution of 221 mg (0.5 mmol) of (hydroxyalkyl)phosphane (*S*)-**2** in 5 ml of CH_2Cl_2 143 mg (0.5 mmol) of Pd(COD)Cl_2 was added. After stirring of the mixture for 30 min 223 mg (1.5 mmol) of NaI was added. The resulting orange solution was stirred with the exclusion of light overnight. Then the solvent was evaporated in vacuo. The residue was purified by flash chromatography with CH_2Cl_2/AcOEt (95:5) as the eluent to furnish the desired complex as a red powder. It was recrystallized from CH_2Cl_2/*n*-hexane (2:1) to give [Pd{(*S*)-**2**}]I_2 as orange-red crystals; yield: 217 mg (55%). – $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO): δ = 28.5 (d, J = 12.0 Hz), 13.8 (d, J = 12.0 Hz). – ^1H NMR ([D$_6$]DMSO): δ = 7.97–7.11 (20H, aromat), 3.53 (m, 1H, OCH), 3.42 (s, 1H, OH, exchangeable with D_2O), 2.92–2.26 (m, 4H, PCH_2), 1.79–1.45 (m, 2H, CH_2). – $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 136.1–128.8 (aromat), 65.8 (C-2), 36.3 (d, $^1J_{PC}$ = 22.4 Hz, C-1), 31.1 (C-3), 24.0 (d, $^1J_{PC}$ = 29.5 Hz, C-4). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3598 cm^{-1} [ν(OH)]. – $C_{28}H_{28}I_2OP_2Pd$ (802.7): calcd. C 41.90, H 3.52, P 7.72, Pd 13.26; found C 42.63, H 3.64, P 7.86, Pd 12.64.

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