Synthesis of Chiral 2,5-Bis(oxymethyl)-Functionalized Bis(phospholanes) and Their Application in Rh- and Ru-Catalyzed Enantioselective Hydrogenations

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The synthesis of a series of chiral 2,5-bis(oxymethyl)-substituted bis(phospholanes) **13a–c** and **15a**,**b** (BASPHOS) is described, representing functionalized derivatives of the prominent DuPHOS or BPE ligands. D-Mannitol was used as the starting material for these ligands. New bisphospholanes were used as ligands in the enantioselective rhodium(I)-catalyzed hydrogenation of functionalized olefins like unsaturated α- and β-amino acid derivatives, itaconates, and an unsaturated phosphonate. A relevant ruthenium(II) catalyst was used for the reduction of prochiral β-oxo esters. The enantioselectivities, ranging from 8–99% *ee*, were strongly dependent on the type of the substituent on the oxymethyl group as well on the bridge connecting the phospholane units.

Introduction

Understanding the mechanism of chirality transfer in enantioselective transition metal catalyzed reactions is a challenging task in current synthetic chemistry.[1] However, in spite of literally thousands of chiral ligands that have been reported in the past,[2] there is no unique rationale for the efficiency of all catalysts not even for those that have been applied in the same reaction. Therefore, the design of new catalysts is mainly based on trial and error. Economic reasons, like the actual patent situation or easily available starting materials, as well as the aim of profiting from a certain synthetic methodology still dominate the disclosure of new ligands. Moreover, most ligands have been tested only for special reactions or selected substrates (standard substrates) and their suitability for other applications remains vague.

For some years we have been interested in elucidating the effect of additional functional groups like hydroxy and alkoxy groups in conventional diphosphane ligands on asymmetric hydrogenations with Rh^{I} catalysts.[3] In addition to their purely steric effect, such "hard" oxy functionalities can act as "hemilabile" ligands.[4,5] Moreover, a high potential exists for the establishment of hydrogen bonds between the ligand and parts of a suitably functionalized prochiral substrate.[6] In general, an alteration of the performance of the parent (nonfunctionalized) catalyst can be expected from these effects.[7,8]

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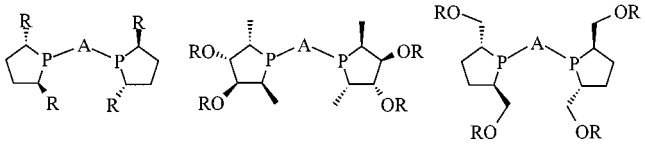
The electron-rich diphosphanes DuPHOS (A = 1,2-phenylene) and BPE (A = 1,2-ethylene) originally discovered by Burk belong to one of the most powerful family of ligands currently used in Rh^{I}- and Ru^{II}-catalyzed asymmetric hydrogenations.[9] There is some evidence that the high enantiofacial discriminating ability of these and other C_2-symmetric bis(phospholanes),[10a] as well as that of related bis(phosphetanes),[10b] originates from the nature of the alkyl groups in the 2,5-positions.[9c,11,12] Several pieces of evidence have been accumulated that show that for each class of substrates the appropriate alkyl groups have to be selected in order to achieve maximal enantioselectivity.[9c,9d]



DuPHOS/BPE **RoPHOS** **BASPHOS**

(A = 1,2-phenylene, 1,2-ethylene; R = H, Alkyl)

Interestingly, in a recent work Brunner et al. achieved some degree of enantioselection with a 3,4-dimethoxy-substituted bis(phospholane) ligand.[13] This report prompted us and the groups of Zhang and RajanBabu to utilize oxy groups in the 3,4-positions for the fine-tuning of 2,5-dimethyl-substituted phospholanes (RoPHOS).[14] Indeed, in the asymmetric hydrogenation, differences in the *ee* by up to 7% were observed, depending on the nature of the oxy substituent (BnO, MeO, HO).[14a,14b,15]

A closer proximity of the oxy groups to the catalytic center as in complexes of RoPHOS ligands should enhance their effect on the asymmetric reaction. In order to confirm this hypothesis we envisaged the synthesis of 2,5-bis(oxymethyl)-substituted bis(phospholanes) that we named BASPHOS.[16] In a preliminary note we gave evidence that

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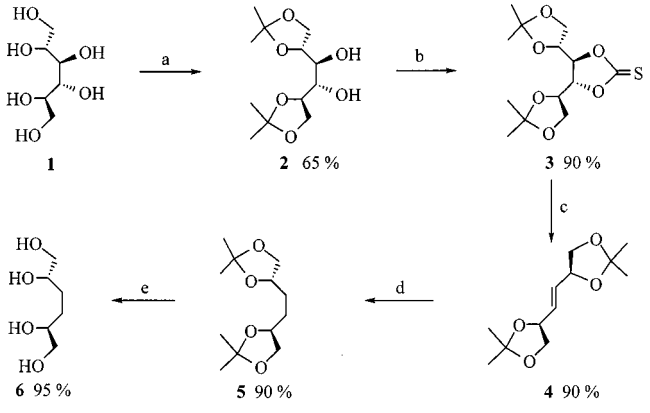
the relevant tetrahydroxy-substituted ligand can be advantageously used for the Rh-catalyzed hydrogenation in water, where excellent enantioselectivities could be achieved.[16]

In general, phospholanes with two oxymethyl groups in the 2,5-position combine structural motifs of alkyl and oxy groups and therefore the comparison with related DuPHOS and BPE ligands will give answers about the effect of the oxymethyl groups. As substrates for the hydrogenation with corresponding Rh^{I} and Ru^{II} catalysts we have tested standard substrates such as itaconic acid and α-(acetylamino)cinnamic acid derivatives, as well as an unsaturated β-amino acid precursor and β-oxo acid derivatives.

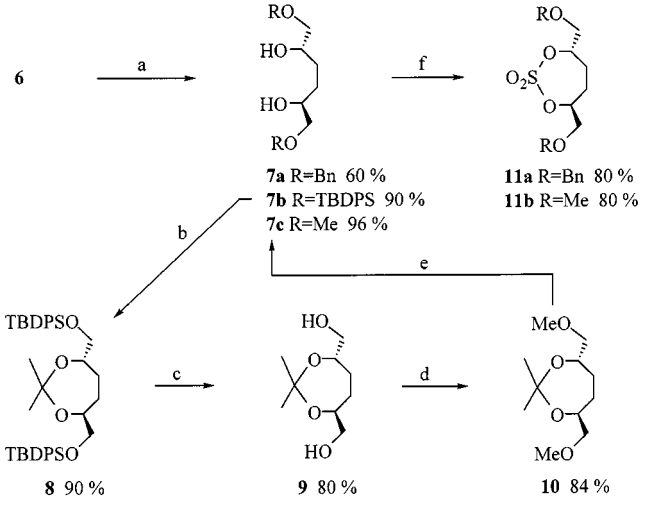
Synthesis of the Ligands

As already briefly described in the synthesis of the hydroxymethyl-substituted bis(phospholane),[16] our synthetic pathway starts from D-mannitol (**1**, Scheme 1) and follows general strategies for the synthesis of hydroxyphosphanes.[17] This approach is similar to the protocol giving access to RoPHOS-type ligands,[14] however, in contrast to the synthesis of the latter the hydroxy groups in 3,4-position of D-mannitol have to be reductively removed. The first step of this conversion could be conveniently achieved by selective protection of the hydroxy groups in 1,2;5,6-position as isopropylidene acetals, affording the diacetonide **2**.[18] Reaction of the remaining hydroxy groups with thiophosgene in turn gave the thiocarbonate **3**.[19] An elimination reaction with triethyl phosphite according to the procedure of Haines yielded the (*E*)-olefin **4** in 90% yield.[20] By hydrogenation of the double bond with heterogeneous Rh[21] or Pt catalyst at 1 bar of hydrogen pressure the protected tetrol **5** was obtained. It is necessary to mention that careful purification of **4** was important in order to obtain a sufficient yield in the subsequent hydrogenation of the olefin. Cleavage of the acetal groups with aq. HCl afforded the key compound **6** bearing four hydroxy groups.[21]l



Scheme 1. Reagents and conditions: a: acetone, $ZnCl_2$, 25 °C, 2 h; b: $S{=}CCl_2$, DMAP, 0 °C, 1 h; c: $P(OEt)_3$, 160 °C, 20 h; d: H_2, Rh/Al_2O_3, THF, room temp. or H_2, Pt/C, MeOH, room temp.; e: 2 N HCl, 80 °C, 2 h

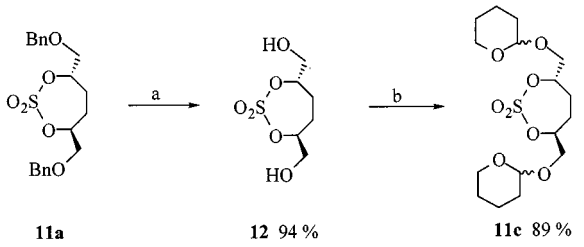
By regioselective reaction of the primary hydroxy groups, alkyl groups of different sizes could be incorporated in the 1,6-positions (Scheme 2). Among different alkylating reagents tried, we found that selective *O*-benzylation by employment of dibutyltin oxide and benzyl bromide was the most promising method.[22] The relevant 1,6-di-*O*-benzyl ether **7a** was obtained in 60% yield. Unfortunately, all attempts to achieve regioselective *O*-methylation only afforded mixtures of regioisomers. Therefore, the intermediate protection of the secondary hydroxy groups was necessary. This was possible by prior protection of the primary hydroxy groups with a bulky silylating agent such as TBDPS-Cl (*tert*-butyldiphenylsilyl chloride), affording the silylated compound **7b**.[22] In turn, the 2,5-dihydroxy groups were treated with 2-methoxypropene in the presence of toluenesulfonic acid to give 1,3-dioxepane **8**.[22] After liberation of the primary hydroxy groups with fluoride affording **9**,[22] and subsequent alkylation with methyl iodide, 1,6-di-*O*-methyl ether **10** was obtained. Cleavage of the acetal provided the desired selectively protected compound **7c**. Diols **7a** and **7c**, in turn, were treated with thionyl chloride according to the procedure of Burk et al.[9c] Subsequent in situ ruthenium-catalyzed oxidation of cyclic sulfites gave rise to the sulfates **11a** and **11b**.



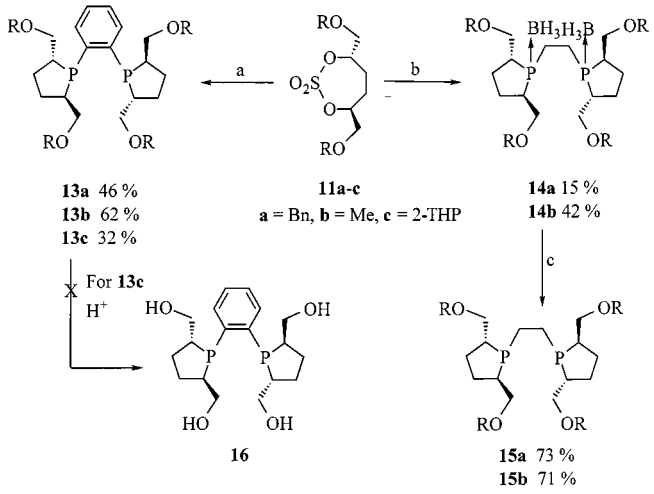
Scheme 2. Reagents and conditions: a: for **7a**: 1. $Bu_2Sn{=}O$, toluene, reflux, 4 h; 2. Bu_4NBr, BnBr, toluene, reflux, 16 h; for **7b**: TBDPS-Cl, imidazole, DMF, 0 °C to room temp., 24 h; b: 2-methoxy propene, TsOH, 0 °C, 1 h; c: TBAF, THF, room temp., 2 h; d: NaH, MeI, THF, room temp., 16 h; e: 1 N HCl, THF, room temp., 1 h; f: $SOCl_2$, CCl_4, reflux, 1.5 h; 2. $RuCl_3$, $NaIO_4$, CCl_4, CH_3CN, H_2O, 0 °C to room temp., 1 h

The dibenzyl ether **11a** could also be used for the synthesis of the 1,6-dihydroxy derivative **12** (Scheme 3). This compound can be advantageously employed for incorporation of other *O*-protective groups. As an example, the reaction to the THP-protected diol **11c** is given in the scheme. Due to the formation of a new stereogenic carbon atom in each THP ring three diastereomers were found in the reaction mixture.

Cyclic sulfates **11a**–**c** are direct precursors of the desired phospholanes (Scheme 4). Thus, treatment of 1,2-diphosphanylbenzene with *n*BuLi, followed by addition of the sul-



Scheme 3. Reagents and conditions: a: 1 bar H_2, Pd/C, MeOH, room temp.; b: 3,4-dihydro-2*H*-pyran, PPTS, CH_2Cl_2, room temp., 2 h



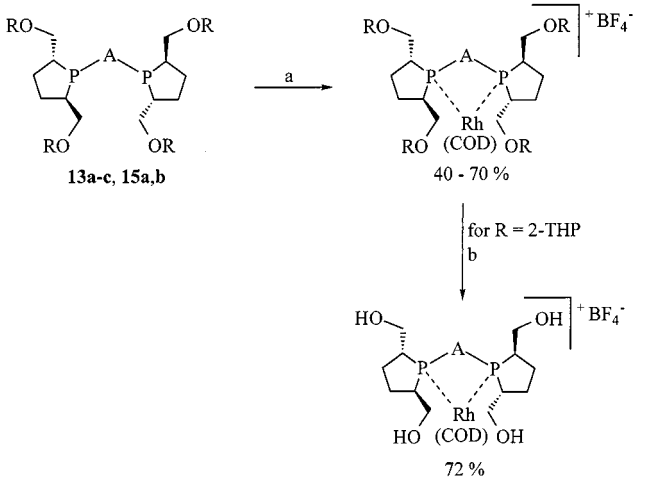
Scheme 4. Reagents and conditions: a: 1. BuLi, THF, −78 °C to room temp., 2 h; 2. 1,2-$(H_2P)_2C_6H_4$, −78 °C to room temp.; 3. BuLi, −78 °C to room temp., 12 h; b: 1. BuLi, THF, −78 °C to room temp., 2 h; 2. $H_2P-C_2H_4-PH_2$, −78 °C to room temp.; 3. BuLi, −78 °C to room temp., 12 h; 4. BH_3−THF, −10 °C to room temp., 2 h; c: DABCO, toluene, 40 °C

fates and a second portion of *n*BuLi gave, under complete inversion of the stereogenic carbon atoms, the C_2-symmetric phospholanes **13a**−**c** in 32−62% yield. The THP-protected sulfate **11c** was used as its diastereomeric mixture and gave rise to the expected mixture of diastereomeric bis(phospholanes) **13c**. Removal of the THP groups in this compound should give the interesting tetrakis(hydroxymethyl)-substituted bis(phospholane) **16**. However, owing to the high polarity and air sensibility of this compound, all attempts to isolate the polyhydroxyphosphane from the acidic reaction mixture failed.

Ethylene-bridged bis(phospholanes) **15a** and **15b** were obtained under the same reaction conditions employing 1,2-diphosphanylethane as a nucleophile. However, for the purification of the bis(phospholanes) prone to oxidation, prior conversion into their BH_3 adducts **14a** and **14b** was advantageous.[23] Final cleavage of the borane adducts with DABCO delivered the bis(phospholanes) **15a** and **15b**.

Synthesis of Precatalysts

Rhodium(I) precatalysts suitable for the enantioselective hydrogenation were produced by reaction of the bis(phospholanes) **13a**−**c** and **15a** and **15b** with $[Rh(COD)_2]BF_4$, affording cationic complexes of the type [Rh(COD){bis(phospholane)}]BF_4 (Scheme 5). In Table 1 the relevant ^{31}P NMR spectra of the ligands and their corresponding Rh complexes are detailed.



Scheme 5. Reagents and conditions: a: $[Rh(COD)_2]BF_4$, THF, 0 °C to room temp., 1 h; b: aq. HBF_4, MeOH, room temp., 24 h

Table 1. ^{31}P NMR spectra of functionalized bis(phospholanes) and their [Rh(COD){bis(phospholane)}]BF_4 complexes recorded in $CDCl_3$

Ligand	δ values of ligand	$\delta/J(^{103}Rh-^{31}P)$ [Hz] values of Rh complex
13a	−11.5	+64.3/149
13b	−11.7	+65.1/150
13c	−11.5 to −12.3[a]	+58.5 to +73.6[a]
16	−	+64.1/148
15a	−6.9	+67.3/147
15b	−7.0	+67.3/150

[a] Mixture of diastereomers.

As mentioned above, removal of the THP groups in the bis(phospholane) **13c** in order to obtain access to the tetrahydroxyphosphane **16** was not successful. A more advantageous route was revealed by the prior "protection" of the trivalent phosphorus atoms by complexation of **13c** to rhodium(I) by reaction with $[Rh(COD)_2]BF_4$ (Scheme 5).[16] In Figure 1 (a) the ^{31}P NMR spectrum of [Rh(COD)(**13c**)]BF_4 is depicted. The numerous resonances observed are due to the stereogenic THP groups in ligand **13c**. By treatment of this mixture with catalytic amounts of aqueous HBF_4 in methanol, all THP groups were removed by transacetalization, and the desired precatalyst [Rh(COD)(**16**)]BF_4 was obtained in 72% yield. In Figure 1 (b) the ^{31}P NMR spectrum of the product after hydrolysis is shown, which is characterized by a single doublet due to the $^{103}Rh-^{31}P$ coupling of 148 Hz.

Crystals of [Rh(COD)(**13b**)]BF_4 suitable for X-ray analysis could be obtained by slow diffusion of diethyl ether into a concentrated MeOH solution of the rhodium complex. A single-crystal X-ray structural analysis established

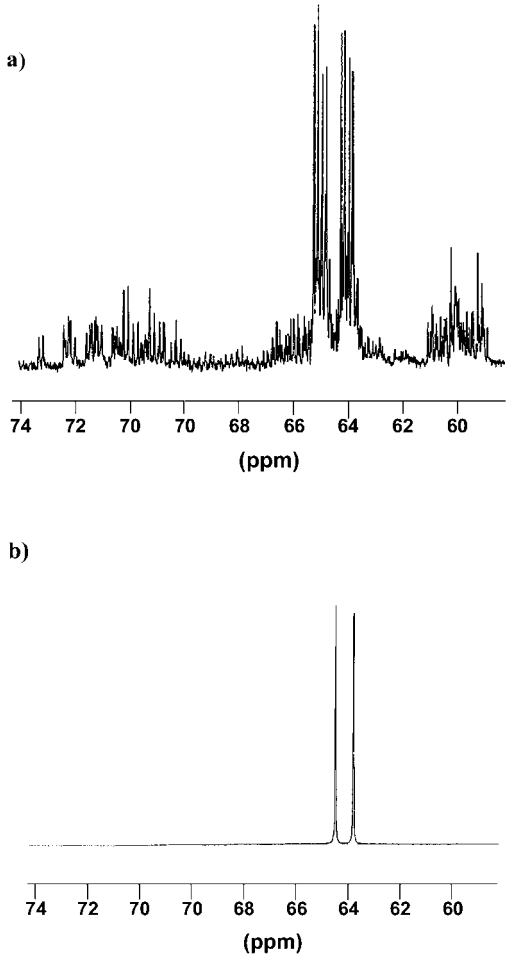


Figure 1. ^{31}P NMR spectra of [Rh(COD)(**13c**)]BF_4 (a) and [Rh(COD)(**16**)]BF_4 in $CDCl_3$ (b)

the structure of the cation as shown in Figure 2 (a), along with the selected bond lengths and intramolecular angles. All Rh−P and Rh−C bond lengths and angles of the examined complex are closely related to other bis(phospholanyl)-benzene precatalysts.[9c,24] The phospholane rings adopt a half-chair conformation wherein the substituents are adjusted in equatorial positions.

The C_2 symmetry is disturbed in the solid state by different conformations of the methoxymethyl groups. In general, however, no intramolecular interactions of ether groups with the rhodium center are visible [Figure 2 (b)]. As expected, only a very small dihedral angle (5.0 °) between the planar 1,2-phenylene unit and the P−Rh−P plane adopting λ configuration is observed. The dihedral angle between the planes P,Rh,P and X,Rh,X (X = centroid of the double bond) is 21.8° and matches well the value found with the corresponding Et-DuPHOS complex (21.1°).[24] The large deviation from the square-planar coordination geometry around the metal center observed with these (COD){bis(phospholane)}Rh complexes cannot be the result of steric interactions of the ligands as a space-filling model indicated. The reason for this deviation is not yet clear.

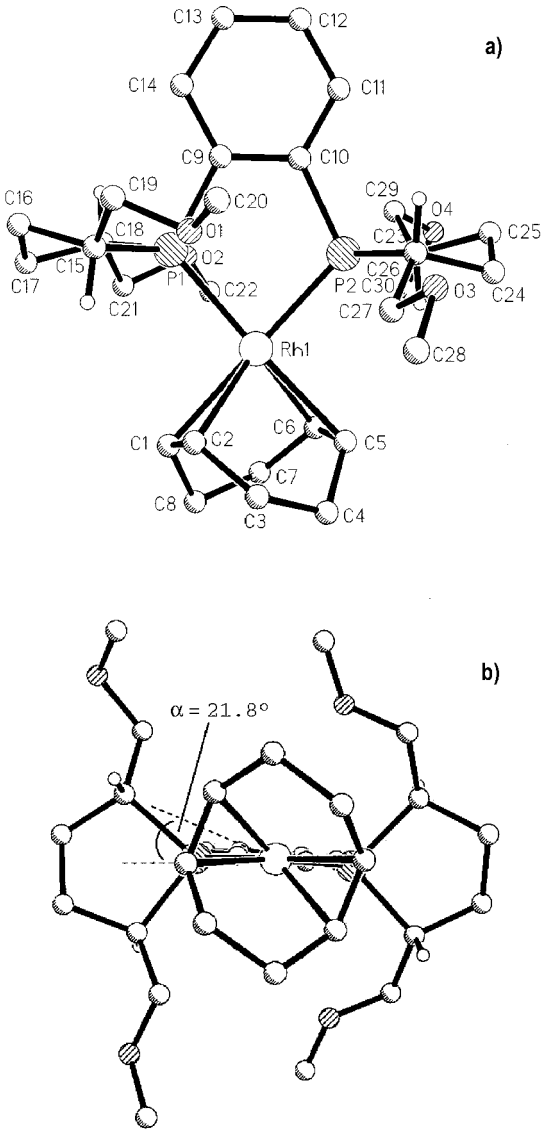
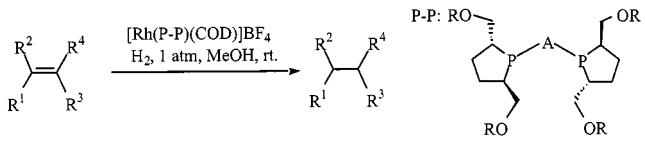


Figure 2. a: top view, showing the 1,2-phenylene unit and the orientation of the methyl oxymethylene group as well as the numbering scheme of [Rh(COD)(**13b**)]$^+$; all hydrogen atoms except those that are linked to stereogenic carbon atoms have been omitted for clarity; selected interatomic distances [Å]: Rh1−C1 2.283(4), Rh1−C2 2.207(5), Rh1−C5 2.250(4), Rh1−C6 2.211(4), Rh1−P1 2.285(1), Rh1−P2 2.265(1); selected intramolecular angles (°): P1−Rh1−P2 84.36(4), C1−Rh1−C2 35.5(3), C5−Rh1−C6 35.7(2); b: front view, showing phospholane rings and the dihedral angle between the P−Rh−P plane and the centroid−Rh−centroid plane

Enantioselective Hydrogenations

The catalytic properties of the complexes derived from the new functionalized bis(phospholanes) were first proven in the hydrogenation of standard substrates at 1 bar of H_2 pressure and at 25 °C in MeOH as solvent. Enantioselectivities achieved in the hydrogenation of (*Z*)-α-(acetylamino)-cinnamic acid and itaconic acid as well as their methyl esters are listed in Table 2. Also those results obtained in the

Table 2. Results of the hydrogenation of prochiral olefins with $[Rh(P\text{-}P)(COD)]BF_4$



Ligand No.	A	R	Substrate[a] R^1	R^2	R^3	R^4	*ee* [%][b]
13a	1,2-phenylene	Bn	Ph	H	NHAc	COOH	86.6 (*S*)
13b	1,2-phenylene	Me					94.8 (*S*)
16	1,2-phenylene	H					79.5 (*S*)
15a	1,2-ethylene	Bn					91.5 (*S*)
15b	1,2-ethylene	Me					81.1 (*S*)
13a	1,2-phenylene	Bn	Ph	H	NHAc	COOMe	95.7 (S)
13b	1,2-phenylene	Me					98.9 (*S*)
13c	1,2-phenylene	THP					96.6 (*S*)
16	1,2-phenylene	H					95.8 (*S*)
15a	1,2-ethylene	Bn					95.6 (*S*)
15b	1,2-ethylene	Me					87.3 (*S*)
13a	1,2-phenylene	Bn	H	H	CH_2COOH	COOH	95.9 (*R*)
13b	1,2-phenylene	Me					96.9 (*R*)
16	1,2-phenylene	H					37.1 (*R*)
13b	1,2-ethylene	Bn					81.5 (*R*)
13c	1,2-ethylene	Me					21.1 (*R*)
13a	1,2-phenylene	Bn	H	H	CH_2COOMe	COOMe	70.3 (*R*)
13b	1,2-phenylene	Me					97.9 (*R*)
16	1,2-phenylene	H					5.7 (*R*)
15a	1,2-ethylene	Bn					73.1 (*R*)
15b	1,2-ethylene	Me					8.1 (*R*)
13a	1,2-phenylene	Bn	Ph	H	NHBz	$P(O)(OMe)_2$	20.8 (*R*)
13b	1,2-phenylene	Me					78.8 (*R*)
16	1,2-phenylene	H					76.4 (*R*)
15a	1,2-ethylene	Bn					71.9 (*R*)
15b	1,2-ethylene	Me					56.2 (*R*)
13b	1,2-phenylene	Me	NHAc	Me	COOMe	H	68.2 (*S*)

[a] Catalyst/substrate (1:100), 1 atm total pressure above the reaction mixture, 25 °C; 1 mmol substrate in 15 mL of methanol. [b] Determined after 100% conversion. Measured on the crude product, GC with a chiral column: for *N*-acetylphenylalanine and dimethyl succinate after esterification with diazomethane and for the methyl ester of *N*-acetylphenylalanine and dimethyl succinate, respectively, with XE 60-L-valine *tert*-butylamide, 150 °C. The conversion into the saturated phosphonate and its *ee* were determined by HPLC: stationary phase Chiralcel OD-H, eluent *n*-hexane/ethanol. The conversion into methyl 3-acetylaminobutanoate and its *ee* were determined by GC: Chiraldex β-PM 50 m × 0.25 mm (astec), 130 °C.

hydrogenation of a pharmaceutically important α,β-unsaturated phosphonate and methyl (*Z*)-3-(acetylamino)butenoate are given. Measurements of the *ee* were performed after completion of the consumption of hydrogen. Times for conversion of the prochiral substrate are not detailed, due to individually varying periods necessary for the generation of the catalytically active species from the precatalysts.[24,25] This known feature did not allow a reliable differentiation and comparison between the time necessary for the prehydrogenation of the diolefin (1,5-cyclooctadiene) in the precatalyst and the time for the hydrogenation of the prochiral substrate proceeding in parallel. In general, no clear correlation in activity was found in dependency on the substituent R in the $ROCH_2$ groups, the type of the bridge A connecting the phospholane units and the substrate.

Table 2 clearly shows, that the nature of the bridge between both phospholanes (ethylene or phenylene) as well as the type of the oxy substituent exert a considerable, sometimes dramatic influence upon the stereo-discriminating ability of the catalyst. Several tendencies become obvious. In general, superior enantioselectivities were observed with the catalyst based on the ligand **13b** characterized by four methoxy groups and the phenylene bridge. When the methyl groups were replaced by the larger benzyl groups (**13a**) diminished *ee* values were obtained. Still more expressed is the decrease of the *ee* by application of the relevant tetrahydroxy-substituted bis(phospholane) **16** as ligand. It should be reminded that the relevant catalyst gave > 99% *ee* in the hydrogenation of α-(acetylamino)acrylic acid in water.[16] Noteworthy is the excellent enantioselectivity produced in the hydrogenation of methyl α-(acetylamino)cinnamate with the complex of THP-protected bis(phospholane) **13c**. Although the catalyst consists of a mixture of several diastereomers [see Figure 1 (a)] an enantioselectivity of 96.6% was reached. Either the configuration in the THP groups has no significant influence or only individual complexes

among the mixture of diastereomeric Rh complexes are active in the enantioselective hydrogenation. Since the isolation of single complexes failed, the answer remains speculative.

Seriously diminished enantioselectivities resulted from the replacement of the rigid 1,2-phenylene bridge by the conformationally more flexible ethylene bridge (ligands **15a** and **15b**). This tendency is in agreement with some observations of Burk with BPE catalysts in hand,[9c,26] but more expressed in the BASPHOS series (see in particular ligand **15b**). At least for the substrates considered herein, their is clear evidence that the oxy functionalization in the 2,5-position of the phospholane rings makes bis(phospholane) catalyst more sensitive to structural changes of the substrate. With all catalysts tried inferior *ee* values were observed in the hydrogenation of the α,β-unsaturated phosphonate in comparison with RoPHOS catalysts.[14a]

In order to broaden the scope of the substrates we also tested the precatalyst based on the MeO ligand (**13b**) in the enantioselective hydrogenation of methyl (*Z*)-3-(acetylamino)butenoate. In a parallel work we could show that highly enantioselective hydrogenation of this particular substrate is possible by application of an Rh-DuPHOS catalyst on condition that the reaction was run in a polar solvent like methanol under application of normal hydrogen pressures.[27] This protocol is contrary to the conditions usually recommended in the past for these type of (*Z*)-configured substrates. In Figure 3 the dependency of the enantioselectivity upon the H_2 pressure by application of [Rh(COD)(**13b**)]BF_4 is depicted. For comparison also relevant curves registered with the corresponding Me-BPE and Et-DuPHOS-Rh catalyst are shown. At elevated pressures the MeO catalyst is superior. However, surprisingly, the enantioselectivity is rather independent on the H_2 pressure, which is in contrast to the behaviour of DuPHOS catalysts. Thus, finally at 1 bar the Et-DuPHOS catalyst gave higher *ee* values. The BASPHOS complex provided the β-amino acid ester in only 68.2% *ee* (Table 2).

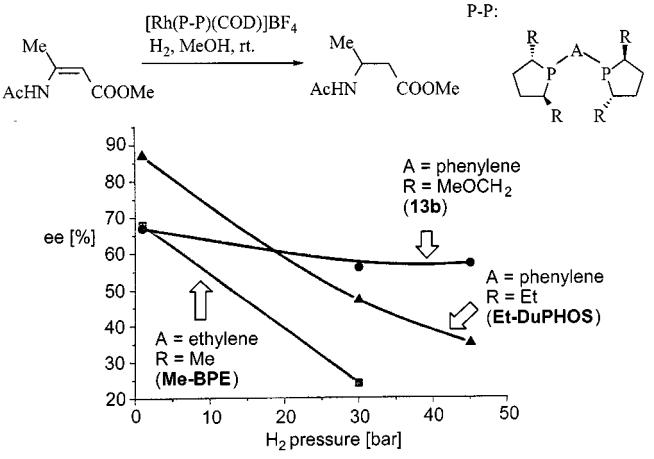
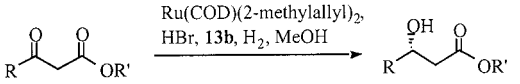


Figure 3. Dependency of the *ee* upon the H_2 pressure with [Rh(COD)(P-P)]BF_4 (P−P: **13b**, Et-DuPHOS, Me-DuPHOS) in the hydrogenation of methyl (*Z*)-3-(acetylamino)butenoate

The tetramethoxy ligand **13b** was also tested in the Ru-catalyzed hydrogenation of pharmaceutically important β-oxo esters (Table 3). The catalyst was prepared in situ according to the protocol of Genêt et al.[28] Hydrogenations were carried out at 30 or 90 bar of hydrogen pressure. Elevated temperature was required in order to obtain sufficient conversion. As Table 3 shows, (*S*)-configured β-hydroxycarboxylates were obtained with excellent enantioselectivities. Increasing of the reaction temperature only slightly influenced the *ee*. However, raising the hydrogen pressure from 30 to 90 bar decreased the *ee* significantly, although not to the extent reported for a BPE-Ru catalyst.[9e]

Table 3. Ruthenium-catalyzed hydrogenation of β-oxocarboxylates



R	R′	S/C	*T* [°C]	*p* [bar]	*t* [h]	Conversion [%]	*ee* [%]
$MeO_2C(CH_2)_2$	Me	200	35	30	24	70	98.8[a]
$MeO_2C(CH_2)_2$	Me	200	35	30	72	85	98.7[a]
$MeO_2C(CH_2)_2$	Me	300	25	90	72	15	90.8[a]
$MeO_2C(CH_2)_2$	Me	300	60	30	72	85	95.8[a]
Me	Me	300	25	30	24	11	96.2[b]
Me	Et	300	35	30	24	57	97.2[b]

[a] Determined after prior separation from nonconverted starting material by HPLC: Chiralcel OD-H, eluent *n*-hexane/ethanol (98:2). [b] Measured on the crude product, GC with a chiral column: 50 m Lipodex A, 50 °C.

Conclusion

The synthesis of a series of new 2,5-bis(oxymethyl)-functionalized bis(phospholanes) (BASPHOS) is described starting from D-mannitol. Key intermediates of the approach allow the incorporation of different *O*-alkyl groups. The new phosphanes represent functionalized ligands of the highly efficient DuPHOS/BPE-type established by Burk and co-workers. In the enantioselective hydrogenation of standard substrates like (*Z*)-α-(acetylamino)cinnamic acid or itaconic acid with cationic Rh^I complexes of the new diphosphanes, enantioselectivities ranging from 8 to 99% were observed. This means that in comparison to bis(phospholanes) of the DuPHOS/BPE-type the 2,5-dioxy functionalization affects more the enantiofacial discriminating properties of the catalyst than simple alkyl groups. In other words, the additional functional groups make the catalyst more sensible to changes in the structure of the prochiral substrate. The degree of the deviation from the catalytic performance of the DuPHOS/BPE ligands was dependent on the substrate used. Particularly large differences due to the type of the oxy groups and the bridge between both phospholane units were observed with itaconic acid and its dimethyl ester. Effects found are much stronger than those observed with corresponding RoPHOS catalysts bearing (remote) oxy groups in 3,4-position of the phospholane rings. In contrast, in the hydrogenation of an unsaturated

β-amino acid derivative the known pressure dependency of the *ee* with DUPHOS catalysts was less pronounced with an oxy-functionalized bis(phospholane) as ligand. In the hydrogenation of prochiral β-oxo esters up to 98.8% *ee* were achieved with the Ru^{II}(**13b**) catalyst, depending upon the pressure of hydrogen.

Experimental Section

General Remarks

All reagents were obtained from Aldrich and Merck. Solvents were dried and freshly distilled under argon before use. Reactions using phosphanes and organometallic compounds were performed under Ar by using standard Schlenk techniques. Thin-layer chromatography was performed on pre-coated TLC plates (silica gel 60 F_{254}, Merck). Flash chromatography was carried out with silica gel 60 (particle size 0.040−0.063 mm, Merck). Melting points are corrected. NMR spectra were recorded at the following frequencies: 400.13 MHz (^{1}H), 100.63 MHz (^{13}C), 161.98 MHz (^{31}P). Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm downfield from TMS as internal standard. Chemical shifts of ^{31}P NMR spectra are referred to H_3PO_4 as external standard. Signals are quoted as s (singlet), d (doublet), br (broad) and m (multiplet). Elemental analyses of the phospholanes are not detailed. Owing to their high sensibility to oxidation values found were beyond the limit of 0.3%. Hydrogenation experiments of functionalized olefins have been carried out under normal pressure and isobaric conditions with an automatically recording gas measuring device (1.0 atm overall pressure over the solution). The experiments were performed with 0.01 mmol of precatalyst, 1.0 mmol of prochiral olefin in 15.0 mL of solvent at 25.0 °C. The conversion of the prochiral unsaturated amino acids and itaconic acid as well as the *ee* of the products were determined by GC. The acids were esterified with trimethylsilyldiazomethane before the GC-measurements [FID, carrier gas Ar (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]. The conversion into the saturated phosphonate and its *ee* were determined by HPLC (stationary phase Chiralcel OD-H; eluent *n*-hexane/ethanol). The conversion into methyl 3-(acetylamino)butanoate and its *ee* were determined by GC [Chiraldex β-PM 50 m × 0.25 mm (astec), 130 °C]. Hydrogenation experiments of ketones were carried out as detailed in Table 3. The *ee* values of the chiral alcohols obtained were determined either by HPLC (Chiralcel OD-H; eluent *n*-hexane/ethanol, 98:2) or by GC with a chiral column (50 m Lipodex A, 50 °C).

3,4-Dideoxy-2,5-*O*-isopropylidene-1,6-di-*O*-methyl-D-*threo*-hexitol (10): To a suspension of sodium hydride (1.06 g, 44 mmol) in THF (60 mL) was added at 0 °C a solution of the diol **9** (3.80 g, 20 mmol) in THF (30 mL). The suspension was stirred at room temperature for 2 h and then methyl iodide (6.21 g, 44 mmol) was added slowly. The stirring was continued for about 12 h at ambient temperature and then the excess sodium hydride was destroyed by carefully addition of water (30 mL). THF was removed using a rotary evaporator and the resulting aqueous residue was extracted with dichloromethane (3 × 50 mL). The combined organic washings were dried (Na_2SO_4), and after evaporation of the solvent the residue was purified by column chromatography (*n*-hexane/EtOAc, 2:1; R_f = 0.40) to yield a colorless syrup (3.68 g, 84% yield). $[\alpha]_D^{23}$= −32.8 (*c* = 1.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.31 (s, 6 H, CH_3), 1.34 (m, 2 H, H_a-CH_2), 1.67 (m, 2 H, H_b-CH_2), 3.23 (dd, $^2J_{a,b}$ = 9.9, $^3J_{H,H}$= 5.3 Hz, 2 H, H_a-CH_2O), 3.30 (s, 6 H, CH_3), 3.33 (dd, $^2J_{a,b}$ = 9.9, $^3J_{H,H}$= 6.3 Hz, 2 H, H_b-CH_2O), 3.92 (m, 2 H, CH). ^{13}C NMR ($CDCl_3$): δ = 25.6 (CH_3), 31.1 (C-3/4), 59.1 (OCH_3), 70.4 (C-2/5), 76.2 (C-1/6), 100.5 [$C(O)_2$]. IR (neat): ṽ = 2988, 2939, 2876, 2812, 1458, 1381, 1219, 1139, 1098, 1073, 987, 829 cm^{-1} − MS (EI): *m*/*z* (%) = 218 (1) [M], 203 (3) [M − Me], 173 (28) [M − CH_2OMe]. $C_{11}H_{22}O_4$ (218.3): calcd. C 60.52, H 10.16; found C 60.38, H 10.07.

(2*S*,5*S*)-1,6-Dimethoxyhexan-2,5-diol (7c): The dimethyl ether **10** (4.0 g, 18.3 mmol) was hydrolyzed in a mixture of THF (60 mL) and 1 N HCl (60 mL) within 30 min. After evaporation of the solvents, the residue was purified by column chromatography (EtOH/EtOAc, 1:3; R_f = 0.45) to yield a pale yellow syrup in nearly quantitative yield (3.14 g, 96% yield). $[\alpha]_D^{23}$= −7.2 (*c* = 1.09, CH_3OH). ^{1}H NMR (CD_3OD): δ = 1.56 (m, 4 H, CH_2), 3.23 (m, 4 H, CH_2O), 3.37 (s, 6 H, CH_3), 3.72 (m, 2 H, CH). ^{13}C NMR (CD_3OD): δ = 30.6 (C-3/4), 59.2 (OCH_3), 71.1 (C-2/5), 78.2 (C-1/6). IR (neat): ṽ = 3405, 2926, 2883, 2824, 1453, 1197, 1126, 965 cm^{-1}. $C_8H_{18}O_4$ (178.2): calcd. C 53.91, H 10.18; found C 53.38, H 10.01.

General Procedure for the Synthesis of (4*S*,7*S*)-4,7-Bis(alkoxymethyl)[1,3,2]dioxathiepane 2,2-Dioxide (11a) and (11b): To a solution of the diols **7a** or **7c** (10 mmol) in CCl_4 (70 mL) was slowly added thionyl chloride (1.43 g, 12 mmol) and the mixture heated under reflux for 90 min. After evaporation of the solvent, the residue was dissolved in a mixture of CCl_4 (45 mL), acetonitrile (45 mL) and water (65 mL) at 0 °C. Then, $RuCl_3$ trihydrate (15 mg, 0.06 mmol) and sodium periodate (4.28 g, 20 mmol) were added and the reaction mixture was stirred at ambient temperature for 1 h. After addition of water (60 mL), the solution was extracted with diethyl ether (3 × 75 mL) and the combined phases were washed with brine (1 × 50 mL). After drying with Na_2SO_4, the solution was filtered through SiO_2 and concentrated under vacuo. The nearly 5 mL of residue left was treated with *n*-hexane and the pure cyclic sulfates **11a** and **11b** precipitated in 80% yields. If the precipitation failed, the products could also be isolated by flash chromatography [**11a**: *n*-hexane/EtOAc (2:1), R_f = 0.20; **11b**: *n*-hexane/EtOAc (1:2), R_f = 0.40].

11a: M.p. 57−59 °C. $[\alpha]_D^{26}$ = −37.2 (*c* = 1.01; $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 2.01 (m, 4 H, CH_2), 3.56 (dd, $^2J_{a,b}$ = 10.8, $^3J_{H,H}$= 4.9 Hz, 2 H, H_a-CH_2O), 3.65 (dd, $^2J_{a,b}$ = 10.8, $^3J_{H,H}$= 5.4 Hz, 2 H, H_b-CH_2O), 4.57 (AB, $^2J_{a,b}$ = 12 Hz, 4 H, OCH_2Ph,), 4.78 (m, 2 H, CH), 7.27−7.37 (m, 10 H, arom. H). ^{13}C NMR ($CDCl_3$): δ = 28.9 (CH_2), 70.8 (CH_2Ph), 73.4 (CH_2O), 82.6 (CH), 127.7, 127.9, 128.4, 137.3 (arom. C). IR (KBr): ṽ = 3089, 3060, 3035, 2956, 2931, 2899, 2866, 1498, 1449, 1386, 1369, 1197, 1142, 1107, 1077, 1064, 987, 949, 913, 813, 751, 733, 697 cm^{-1}. MS (CI): *m*/*z* (%) = 301 (4) [M − C_7H_7], 271 (1) [M − CH_2OBn], 91 (100) [C_7H_7]. $C_{20}H_{24}O_6S$ (392.5): calcd. C 61.21, H 6.16, S 8.17; found C 61.03, H 6.23, S 8.07.

11b: M.p. 75−78 °C. $[\alpha]_D^{23}$ = −44.1 (*c* = 1.01; $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.92−2.04 (m, 4 H, CH_2), 3.37 (s, 6 H, OCH_3), 3.47 (dd, $^2J_{a,b}$ = 10.8, $^3J_{H,H}$= 4.7 Hz, 2 H, H_a-CH_2O,), 3.57 (dd, $^2J_{a,b}$ = 10.8, $^3J_{H,H}$= 5.4 Hz, 2 H, H_b-CH_2O), 4.72 (m, 2 H, CH). ^{13}C NMR ($CDCl_3$): δ = 28.8 (CH_2), 59.3 (OCH_3), 73.4 (CH_2O), 82.5 (CH). IR (KBr): ṽ = 2998, 2973, 2951, 2933, 2859, 2839, 2823, 1473, 1457, 1384, 1350, 1207, 1188, 1142, 1126, 1107, 1097, 958, 939, 913, 857, 815 cm^{-1}. MS (EI): *m*/*z* (%) = 240 (1) [M], 195 (1) [M − CH_2OMe], 45 (100) [CH_2OCH_3]. $C_8H_{16}O_6S$ (240.3) calcd. C 39.99, H 6.71, S 13.34; found C 40.06, H 6.75, S 13.27.

(4*S*,7*S*)-4,7-Bis(hydroxymethyl)[1,3,2]dioxathiepane 2,2-Dioxide (12): The *O*-benzyl-protected cyclic sulfate **11a** (4.80 g, 12.2 mmol)

was dissolved in methanol (40 mL) and stirred under 1 bar of hydrogen in the presence of palladium on charcoal (5%, 0.2 g) until the consumption of hydrogen ceased. After filtration of the suspension, the pure product **12** could be obtained by crystallization in methanol (2.40 g, 94%). In most runs the raw product was sufficiently pure and was used for the next step. M.p. 122−125 °C. $[\alpha]_D^{23} = -37.8$ (c = 1.01; CH_3OH). ^1H NMR (CD_3OD): δ = 1.97 (m, 4 H, CH_2), 3.63 (d, $^3J_{H,H}$= 5.2 Hz, 4 H, CH_2O), 4.62 (m, 2 H, CH). ^{13}C NMR (CD_3OD): δ = 29.5 (CH_2), 64.6 (CH_2O), 86.8 (CH). IR (KBr): $\tilde{\nu}$ = 3391, 2978, 2955, 2942, 1456, 1436, 1400, 1374, 1353, 1232, 1199, 1087, 1070, 1035, 1007, 983, 941, 905, 857, 813 cm^{-1}. MS (EI): m/z (%) = 181 (2) [M − CH_2OH], 121 (7), 87 (100), 57 (53) [C_3H_5O], 43 (20) [C_2H_3O], 31 (33) [CH_2OH]. $C_6H_{12}O_6S$ (212.2) calcd. C 33.96, H 5.70, S 15.11; found C 34.13, H 5.67, S 14.97.

(4*S*,7*S*)-4,7-Bis(*rac*-tetrahydropyran-2-yloxymethyl)[1,3,2]dioxathiepane 2,2-Dioxide (11c): To the diol **12** (3.00 g, 14.1 mmol), dissolved in dichloromethane (150 mL), were added pyridinium tosylate (0.59 g, 2.35 mmol) and 3,4-dihydro-2*H*-pyran (3.56 g, 42.3 mmol). After stirring for 2 h at ambient temperature, the solution was diluted with diethyl ether (250 mL) and washed with brine (2 × 75 mL). After drying and evaporation of the solvents, the residue was purified by column chromatography (*n*-hexane/EtOAc, 1:1; R_f = 0.20) to yield the diastereomeric mixture as a pale yellow oil (4.80 g, 89%). ^1H NMR ($CDCl_3$): δ = 1.45−2.10 (m, 16 H, CH_2), 3.55 (m, 4 H, CH_2O), 3.81 (m, 4 H, CH_2O), 4.62, 4.77 and 4.92 (m, 4 H, CH−O). ^{13}C NMR ($CDCl_3$): δ = 19.0 and 19.7 (CH_2), 25.3 (CH_2), 28.9 and 29.0 (CH_2), 30.2 (CH_2) 62.1, 62.2, (CH_2O), 68.0 and 68.2 (CH_2O), 82.5, 82.5, 82.9 and 83.0 (CH), 98.6 and 99.1 [$C(O)_2$]. $C_{16}H_{28}O_8S$ (380.5) calcd. C 50.51, H 7.42, S 8.83; found C 50.12, H 7.77, S 8.56.

General Procedure for the Synthesis of the Bis(phospholanes) 13a−c and 15a,b: To a solution of 1,2-bis(phosphanyl)benzene (0.57 g, 4.0 mmol) and 1,2-bis(phosphanyl)ethane (0.38 g, 4.0 mmol), respectively, in THF (60 mL) were added at a temperature of −78 °C 2 equiv. of *n*BuLi (1.6 M solution in *n*-hexane, 5.00 mL). The resulting yellow solution was stirred at 25 °C for 2 h. After cooling again at −78 °C, the sulfates **11a−c**, dissolved in THF (10 mL), were added dropwise. Stirring was continued at room temperature for 3 h. Then a second portion of *n*BuLi (5.5 mL, 8.8 mmol) was added at −78 °C and the mixture was stirred overnight at ambient temperature. For the syntheses of ethylene-bridged bis(phospholanes) **15a** and **15b** the reaction mixtures were cooled again to −10 °C and 3 equiv. of BH_3·THF complex (1 M solution in THF, 12 mL) were added and the mixtures were warmed to room temperature over a period of 2 h. The solvents were removed by concentration under vacuo and the residue was taken up with water (20 mL) and extracted under anaerobic conditions with dichloromethane (100 mL). After separation of the organic phase, the solvent was removed and the residue was purified by column chromatography to yield the bis(phospholane). The borane complexes **14a** and **14b** were dissolved in a solution of toluene (10 mL) and treated with 4 equiv. of DABCO by stirring at 40 °C under argon to yield the unprotected bis(phospholanes) **15a** and **15b**, respectively. The completion of reaction was monitored by TLC.

13a: 1.35 g (46% yield) of a pale yellow oil by column chromatography (*n*-hexane/EtOAc, 4:1; R_f = 0.35). ^1H NMR ($CDCl_3$): δ = 1.53−1.76 (m, 4 H, H_a-CH_2), 2.15 (m, 2 H, H_b-CH_2), 2.29 (m, 2 H, H_b-CH_2), 2.67 (m, 2 H, CH−P), 2.80−2.97 (m, 4 H, CH−P, CH_2O), 3.45−3.65 (m, 6 H, CH_2O), 4.01 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_a-CH_2Ph), 4.15 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_b-CH_2Ph), 4.44 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_a-CH_2Ph), 4.48 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_b-CH_2Ph), 7.10−7.45 (m, 24 H, arom. H). ^{13}C NMR ($CDCl_3$): δ = 30.4 (CH_2), 30.9 (CH_2), 38.9 (m, CH−P), 39.5 (CH−P), 72.5 (CH_2Ph), 73.0 (CH_2Ph), 74.1 (m, CH_2O), 127.1−128.4 and 131.8 (arom. C), 138.5 and 138.6 (*ipso*-C), 141.8 (dd, $^1J_{C,P}$ = 4.7, $^2J_{C,P}$ = 4.7 Hz, C_{ar}−P). ^{31}P NMR ($CDCl_3$): δ = −11.5.

13b: 1.05 g (62% yield) of a colorless syrup by column chromatography (*n*-hexane/EtOAc, 2:1; R_f = 0.20). ^1H NMR ($CDCl_3$): δ = 1.55 (m, 2 H, H_a-CH_2), 1.65 (m, 2 H, H_a-CH_2), 2.16 (m, 2 H, H_a-CH_2), 2.31 (m, 2 H, H_b-CH_2), 2.63 (m, 2 H, CH−P), 2.78 (m, 2 H, CH−P, CH_2), 2.91 (m, 2 H, CH_2O), 3.10 (s, 6 H, OCH_3), 3.35 (s, 3 H, OCH_3), 3.36 (m, 2 H, CH_2O), 3.55 (m, 4 H, CH_2O), 7.30 (m, 2 H, arom H), 7.45 (m, 2 H, arom. H). ^{13}C NMR ($CDCl_3$): δ = 30.3 (CH_2), 30.9 (CH_2), 39.0 (m, CH−P), 39.6 (CH−P), 58.2 (OCH_3), 58.8 (OCH_3), 74.5 (m, CH_2O), 76.6 (m, CH_2O), 128.4 and 131.8 (arom. C), 141.8 (dd, $^1J_{C,P}$ = 4.0, $^2J_{C,P}$ = 4.0 Hz, C_{ar}−P), − ^{31}P NMR ($CDCl_3$): δ = −11.7.

13c: 0.91 g (32% yield) of a pale yellow syrup by column chromatography (*n*-hexane/EtOAc, 2:1; R_f = 0.30). ^1H NMR ($CDCl_3$): δ = 1.32−1.85 (m, 28 H, CH_2), 2.19 (m, 2 H, CH_2), 2.35 (m, 2 H, CH_2), 2.66 (m, 2 H, CH−P), 2.91 (m, 2 H, CH−P), 3.10−4.00 (m, 16 H, CH_2O), 4.12−4.62 (m, 4 H, CH−O), 7.23 (m, 2 H, arom. H), 7.46 (m, 2 H, arom. H). ^{13}C NMR ($CDCl_3$) δ= 19.4−19.6 (CH_2), 25.4−25.5 (CH_2), 30.2−30.9 (CH_2), 38.7 (m, CH−P), 39.5 (m, CH−P), 61.6−62.3 (CH_2O), 69.3−71.1 (CH_2O), 98.0−99.5 (CHO), 128.3 and 131.8 (arom. C), 141.8 (m, C_{ar}−P). ^{31}P NMR ($CDCl_3$): δ = −11.5 to −12.3 (diastereomeric mixture).

14a: 0.42 g (15% yield) of a viscous syrup by column chromatography (*n*-hexane/EtOAc, 4:1; R_f = 0.25). ^1H NMR ($CDCl_3$): δ = 0.10−1.15 (br, 6 H, BH_3), 1.20−1.41 (m, 4 H, H_a-CH_2), 1.80−2.08 (m, 10 H, H_b-CH_2, CH_2, CH−P), 2.36 (m, 2 H, CH−P), 3.43 (m, 4 H, CH_2O), 3.38 (m, 4 H, CH_2O), 4.37 (AB, $^2J_{a,b}$ = 11 Hz, 2 H, H_a-CH_2Ph), 4.40 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_a-CH_2Ph), 4.43 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_b-CH_2Ph), 4.48 (AB, $^2J_{a,b}$ = 11 Hz, 2 H, H_b-CH_2Ph), 7.22−7.40 (m, 20 H, arom. H). ^{13}C NMR ($CDCl_3$): δ = 15.9 (m, CH_2P), 28.6 (CH_2), 29.1 (CH_2), 39.5 (m, CH−P), 68.4 (CH_2Ph), 69.4 (CH_2Ph), 72.7 (CH_2O), 73.2 (CH_2O), 127.4−128.3, 137.9 and 138.1 (arom. C). ^{31}P NMR ($CDCl_3$): δ = 40.2.

14b: 0.68 g (42% yield) of a white solid by column chromatography (*n*-hexane/EtOAc, 4:1; R_f = 0.20). m.p. 45−48 °C. $[\alpha]_D^{25} = 21.9$ (c = 1; $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 0.0−1.20 (br, 6 H, BH_3), 1.35−1.56 (m, 4 H, CH_2), 1.90−2.24 (m, 10 H, CH_2, CH−P), 2.36 (m, 2 H, CH−P), 3.32 (s, 6 H, OCH_3), 3.33 (s, 6 H, OCH_3), 3.51 (m, 8 H, CH_2O). ^{13}C NMR ($CDCl_3$): δ = 15.8 (m, CH_2P), 28.9 (CH_2), 29.1 (CH_2), 39.5 (m, CH−P), 58.7 (OCH_3), 58.7 (OCH_3), 70.7 (CH_2O), 71.6 (m, CH_2O). ^{31}P NMR ($CDCl_3$): δ = 40.4. IR (KBr): $\tilde{\nu}$ = 3240, 2947, 2927, 2902, 2872, 2827, 2811, 2739, 2388, 2332, 2252, 1453, 1410, 1384, 1192, 1111, 1062, 958, 924, 773, 748, 701 cm^{-1}.

15a: 0.21 g (73% yield) of a syrup by column chromatography (*n*-hexane/EtOAc, 4:1; R_f = 0.30). ^1H NMR ($CDCl_3$): δ = 1.25−1.51 (m, 8 H, CH_2), 2.02−2.38 (m, 8 H, CH_2, CH−P), 3.40−3.60 (m, 8 H, CH_2O), 4.40 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_a-CH_2Ph), 4.43 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_b-CH_2Ph), 4.48 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_a-CH_2Ph), 4.52 (AB, $^2J_{a,b}$ = 12 Hz, 2 H, H_b-CH_2Ph), 7.22−7.35 (m, 20 H, arom. H). ^{13}C NMR ($CDCl_3$): δ = 19.1 (m, CH_2P), 31.3 (CH_2), 31.4 (CH_2), 40.0 (m, CH−P), 43.7 (m, CH−P), 70.2 (CH_2Ph), 72.7 (CH_2Ph), 72.9 (CH_2O), 74.1 (CH_2O), 127.4−128.3, 138. and 138.6 (arom. C). ^{31}P NMR ($CDCl_3$): δ = −6.9.

15b: 0.39 g (71% yield) of a syrup by column chromatography (*n*-hexane/EtOAc, 3:2; R_f = 0.35). ^{1}H NMR ($CDCl_3$): δ = 1.13−2.46 (m, 16 H, CH_2, CH−P), 3.25(s, 6 H, OCH_3), 3.27 (s, 6 H, OCH_3), 3.41 (m, 8 H, CH_2O). ^{13}C NMR ($CDCl_3$): δ = 19.9 (m, CH_2P), 31.1 (CH_2), 31.2 (CH_2), 39.7 (m, CH−P), 43.3 (m, CH−P), 58.6 (OCH_3), 58.6 (OCH_3), 70.6 (CH_2O), 72.5 (CH_2O). ^{31}P NMR ($CDCl_3$): δ = −7.0.

General Procedure for the Preparation of the [{Bis(phospholane)}(COD)Rh]BF_4 Complexes: To solutions of bis(phospholanes) **13a**−**c** and **15a**,**b** (1 mmol) in THF (3 mL) was added at 0 °C 1 equiv. of [Rh(COD)$_2$]BF_4 (406 mg) and the mixture was stirred at ambient temperature for 1 h. Then the complex was precipitated by addition of ether (12 mL) and the solution was filtered. The residue was washed twice with ether (4 mL) and dried under vacuo to yield the rhodium complexes in yields of 40−70% as orange-yellow powder. For the deprotection of the hydroxy groups in complex of **13c** the THP groups were removed by stirring the rhodium complex (300 mg, 0.30 mmol) in MeOH (4 mL) with aq. HBF_4 (0.1 mL) over a period of 24 h. After evaporation of the solvent and addition of THF (2 mL), [Rh(COD)(**16**)]BF_4 was precipitated with ether (8 mL). Purification was carried out as described above. Selected ^{31}P NMR spectroscopic data are summarized in Table 1.

Crystal Structure Determinations for [Rh(COD)(13b)]BF_4: Crystals were obtained by slow diffusion of diethyl ether into a concentrated MeOH solution of the rhodium complex. Diffraction data were collected with an STOE-IPDS diffractometer using graphite-monochromated Mo-K_α radiation. The structure was solved by direct methods (SHELXS-97)[30] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[29] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed into theoretical positions and were refined by using a riding model. The weighting scheme used in the last cycles of refinement was $w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.0000P]$. Crystal and refinement data of [Rh(COD)(**13b**)]BF_4: empirical formula $C_{30}H_{48}BF_4O_4P_2Rh$, formula mass 724.34, crystal size 0.4 × 0.3 × 0.3 mm, space group $P2_12_12_1$, orthorhombic, a = 10.468(2), b = 17.379(3), c = 18.040(4) Å, V = 3281.9(11) Å^3, Z = 4, $\rho_{calcd.}$ = 1.466 g/cm^3, μ (Mo-K_α) = 0.674 mm^{-1}, T = 200 K, F(000) = 1504, Θ range for data collection 2.25−22.50 °, index range (h,k,l) −11/11, −18/18, −18/7, reflections collected 11290, observed reflections 3593, refined parameters 379, $R1$ [2σ(I)] = 0.0273, $R1$ (all data) = 0.0300. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-172512. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033]; E-mail: deposit@ccdc.cam.ac.uk].

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