Synthesis of a New Class of Functionalized Chiral Bisphospholane Ligands and the Application in Enantioselective Hydrogenations

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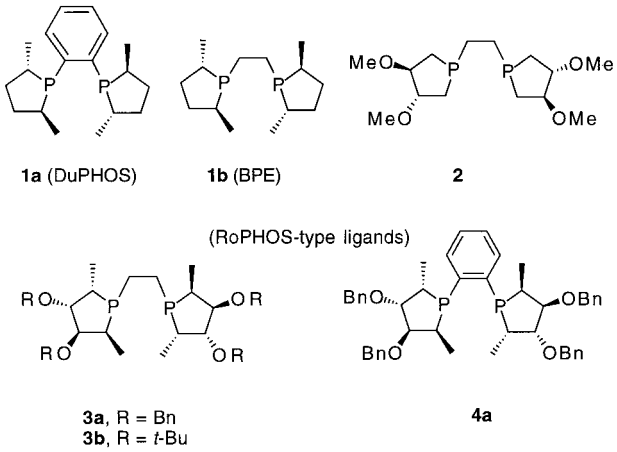
Introduction

The enantioselective hydrogenation of prochiral olefins or ketones with phosphine−metal complexes represents an extremely useful and versatile reaction.[1] Over the last years it has seen broad application in lab-scale organic synthesis as well as in the industrial scale for the production of fine chemicals.[2] Due to the increasing importance there is an ongoing interest focused on the design of new ligands and metal complexes.[3]

One of the most powerful classes of ligands associated to rhodium(I) hydrogenation catalysts constitutes chiral C_2-symmetric bis-phospholanes, e.g., 1,2-bis(2,5-dimethylphospholanyl)benzene (**1a**, DuPHOS), 1,2-bis(2,5-dimethylphospholanyl)ethane (**1b**, BPE),[4] and related ligands,[5] originally developed by Burk and co-workers at Du Pont de Nemours & Company, which has seen also application in other asymmetric reactions.[6]



1a (DuPHOS) **1b** (BPE) **2**

3a, R = Bn
3b, R = *t*-Bu

4a

The synthesis of these chiral phospholanes entails as key steps the asymmetric hydrogenation of β-keto esters affording the corresponding chiral hydroxy esters, followed by an electrochemical coupling procedure of the chiral units (Kolbe reaction). Due to this preparative protocol the self-made synthesis requires additional experience and equipment not always available in each laboratory. Inspection of the literature reveals that some alternatives for the construction of the chiral phospholane framework exist including stoichiometric asymmetric reactions as well as the employment of enzymatic methods.[7−10] However, none of the procedures delivers functionalized phospholanes, although the effect of additional functional groups in phosphine metal complexes is well documented. In particular ether functions known from the high efficiency of DIPAMP−Rh(I)-complexes[11] can advantageously contribute to the enantioface-discriminating ability of the catalyst.[12]

Considering these features, we decided to disclose a new and simple pathway to enantiopure and functionalized bis-phospholane ligands **3a**,**b** and **4a** starting from

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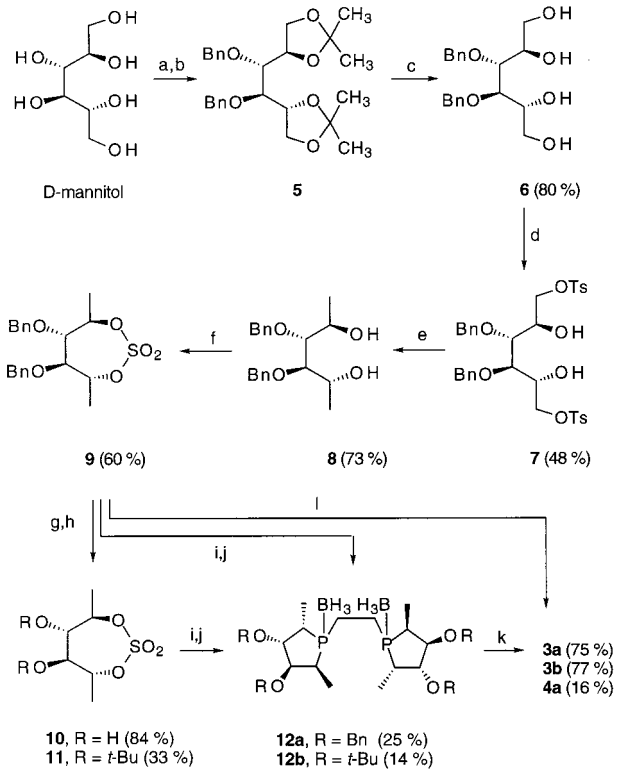
the "chiral pool".[13] The new phosphines bear ether groups in position 3 and 4 of the heterocycle. Already in 1987, Brunner reported the synthesis of bis-phospholane **2** employing (*R*,*R*)-tartaric acid as starting material.[14] However, due to the remote position of the chiral centers from the metal, asymmetric induction in the rhodium(I)-catalyzed hydrogenation of a prochiral test olefin was disappointingly low. In contrast to these results, our new family of ligands named "RoPHOS"[15] combines structural motifs of both ligand types and matches the high efficiency of DuPHOS-type complexes in asymmetric hydrogenations.

Results and Discussion

The starting material of our approach is the commercially available and inexpensive D-mannitol, which has been selectively converted into the 1,2;5,6-di-*O*-isopropylidene derivative by a known protocol.[16] *O*-Benzylation of the remaining alcoholic groups afforded 3,4-di-*O*-benzyl ether **5**.[17] Acidic cleavage of the acetal protective groups yielded the tetrol **6**.[17a,18] Both primary hydroxymethyl groups in turn were converted via tosylation (**7**)[19] and subsequent reduction with $LiAlH_4$ into methyl groups (**8**).[20] Esterification of the hydroxy groups with thionyl chloride and in situ oxidation of the intermediate sulfite with catalytic amounts of RuO_4 gave the cyclic sulfate **9**. The latter could be also used for a change of the *O*-protective groups. Thus, hydrogenolysis of the benzyl groups employing catalytic amounts of palladium on charcoal afforded alcohol **10**. Treatment of the hydroxy groups with isobutylene furnished *O*-*tert*-butyl-substituted sulfate **11**. Sulfates **9** and **11** were individually reacted with 1,2-diphosphinoethane in the presence of *n*-BuLi to give bis-phospholanes **3a**,**b**. For the purpose of purification the highly air-sensitive trialkylphosphines were converted in situ into the corresponding phosphine−borane adducts **12a**,**b** by treatment with an 1 M THF solution of BH_3.[21] After flash chromatography the phosphines were liberated with 1,4-diazabicyclo[2.2.2]octane (DABCO)[22] in toluene to afford the aspired phosphines **3a**,**b**. Alternatively, sulfate **9** was reacted with 1,2-diphosphinobenzene to give bis-phospholane **4a**. The latter was much less sensitive to air than **3a**,**b** and could be therefore simply purified by flash chromatography without prior conversion into its borane adduct.[23]

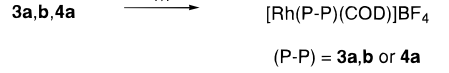
Complexation reactions of the new ligands with $[Rh(COD)_2]BF_4$ formed the expected five-membered *cis*-chelates $[Rh(\mathbf{3a})(COD)]BF_4$ ($^1J_{Rh-P} = 148.8$ Hz), $[Rh(\mathbf{3b})(COD)]BF_4$ ($^1J_{Rh-P} = 148.4$ Hz) and $[Rh(\mathbf{4a})(COD)]BF_4$ ($^1J_{Rh-P} = 152.6$ Hz) (Scheme 2). It is noteworthy that the undesired formation of catalytically inactive Rh(I) complexes bearing two chelating diphosphine ligands could be averted when the reaction was run below 0 °C.

Scheme 1[a]



[a] Key: (a) acetone, $ZnCl_2$, rt; (b) BnBr, NaOH, THF; (c) 70% aq HOAc, rt; (d) TsCl, pyridine, 0 °C; (e) $LiAlH_4$, THF; (f) (1) $SOCl_2$, (2) $RuCl_3$, $NaIO_4$, CH_3CN, H_2O, CCl_4; (g) H_2, Pd/C, MeOH, rt; (h) isobutylene, H_2SO_4, CH_2Cl_2, 5 d, rt; (i) BuLi, 1,2-$H_2P(CH_2)_2PH_2$, THF; (j) BH_3−THF; (k) DABCO, toluene, 40 °C, 48 h; (l) BuLi, 1,2-$H_2PC_6H_4PH_2$, THF, rt.

Scheme 2[a]



[a] Key: (m) $[Rh(COD)_2]BF_4$, THF, −10 °C.

The new complexes were tested in the hydrogenation of different prochiral olefins. As listed in Table 1 the catalysts tolerate a range of several functional groups attached to the double bond. In all cases, even in the hydrogenation of the unsaturated phosphonate,[24] enantioselectivities between 92.6 and 99.1% were achieved. Although the catalytic differences between ethylene- and phenylene-bridged phospholanes as well as the influence of the different *O*-protective groups upon the intrinsic enantioselectivity of the 2,4-dimethylphospholane complex are small, the effect is significant. Thus, by the proper choice of these structural features fine-tuning of the catalyst toward the special requirements of each substrate is possible.

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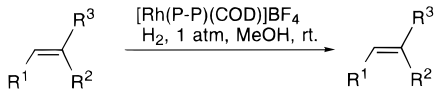
Table 1. Asymmetric Hydrogenations with Rh Complexes of RoPHOS Type[a]



ligand	R^1	R^2	R^3	time for 50% conversion (min)	ee[b] (%)/ config
3a	Ph	NHAc	COOH	62	93.5 (*S*)
3a	Ph	NHAc	COOMe	52	97.5 (*S*)
3a	H	CH_2COOH	COOH	24	98.0 (*R*)
3a	H	CH_2COOMe	COOMe	9	98.9 (*R*)
3a	Ph	NHBz	$P(O)(OMe)_2$	780	95.4 (*R*)
3b	Ph	NHAc	COOH	115	96.8 (*S*)
3b	Ph	NHAc	COOMe	125	98.4 (*S*)
3b	H	CH_2COOH	COOH	11	96.7 (*R*)
3b	H	CH_2COOMe	COOMe	8	99.1 (*R*)
3b	Ph	NHBz	$P(O)(OMe)_2$	500	98.8 (*R*)
4a	Ph	NHAc	COOH	75	93.0 (*S*)
4a	Ph	NHAc	COOMe	48	96.0 (*S*)
4a	H	CH_2COOH	COOH	10	97.5 (*R*)
4a	H	CH_2COOMe	COOMe	28	98.0 (*R*)
4a	Ph	NHBz	$P(O)(OMe)_2$	600	92.6 (*R*)

[a] Condition of the hydrogenation: 1.0 atm overall pressure over the solution. The experiments were carried out under standard conditions with 0.01 mmol of precatalyst and 1.0 mmol of prochiral olefin in 15 mL of solvent. [b] For the determination of the %ee, see Experimental Section.

In summary, we have prepared a new class of chiral functionalized chelating diphosphines by a convenient and simple synthetic sequence starting from D-mannitol.[25] The corresponding rhodium complexes are highly effective in the hydrogenation of a range of functionalized olefins.

Experimental Section

General. All reagents were obtained from Aldrich and Merck. Solvents were dried and freshly distilled under argon before use. Reactions using phosphines and organometallic compounds were performed under an Ar atmosphere by using standard Schlenk techniques. Thin-layer chromatography was performed on precoated 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 (multiplett).

Hydrogenation experiments have been 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 performed with 0.01 mmol precatalyst and 1.0 mmol of prochiral olefin in 15 mL of solvent at 25 °C. The conversion of the prochiral dehydroamino acids and the %ee were determined by GC. The acids were esterified with (trimethylsilyl)diazomethane before the GC-measurements: FID, Carrier gas: Ar: 1 mL/min; methyl *N*-acetylphenylalaninate: fused silica, 10 m, XE-60-L-valin-*tert*-butylamide, i.d. 0.2 mm; oven temperature: 150 °C; dimethyl methylsuccinate: fused silica, Lipodex E (Machery and Nagel), 25 m, i.d. 0.25 mm, oven temperature: 85 °C. The conversion to the saturated phosphonate and its %ee were determined by HPLC: stationary phase: Chiralcel OD-H, eluent: *n*-hexane/ethanol.

(2*R*,3*R*,4*R*,5*R*)-3,4-Di-*O*-benzylhexane-2,3,4,5-tetrol (8). A solution of ditosylate **7** (10 g, 14.9 mmol) in THF (30 mL) was added dropwise to a suspension of $LiAlH_4$ (2.25 g, 59.6 mmol) in THF (100 mL) under stirring at ambient temperature. After 1 h stirring, the suspension was heated for 2 h under reflux. After cooling the mixture to room temperature, the excess of $LiAlH_4$ was decomposed by careful addition of water (2.25 mL), 15% aqueous NaOH (2.25 mL), and water (6.75 mL). Then, the inorganic compounds were filtered off, and the residue was extracted with CH_2Cl_2 by means of a Soxhlet. The combined extracts were evaporated, and the residue was purified by flash chromatography (*n*-hexane:AcOEt = 1:2; R_f = 0.45) to provide **8** as a white solid (3.6 g, 73%): mp 46−50 °C; $[\alpha]^{26}_D = -4.7$ (*c* 0.990, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.40−7.25 (m, 10H), 4.65 (AB, J = 11.3 Hz, 2H), 4.64 (AB, J = 11.3 Hz, 2H), 4.09 (m, 2H), 3.53 (m, 2H), 2.96 (br, exchangeable with D_2O, 2H), 1.25 (d, J = 6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 137.4, 128.5, 128.2, 128.0, 81.5, 73.3, 67.3, 19.7; IR (KBr) 3417, 3287 cm^{-1}; MS (70 eV, *m*/*z*) 331 [M^+ + H] (1). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.79; H, 7.94.

(4*R*,5*S*,6*S*,7*R*)-5,6-Bis(benzyloxy)-4,7-dimethyl[1,3,2]-dioxathiepane 2,2-Dioxide (9). A suspension of diol **8** (4.75 g, 14.4 mmol) and $SOCl_2$ (1.3 mL) in CCl_4 (20 mL) was heated under reflux for 1.5 h. After cooling the mixture to room temperature, the solvent was removed under vacuum. The residue was dissolved in a mixture of CCl_4 (10 mL), acetonitrile (10 mL), and water (15 mL). The solution was cooled to 0 °C, and $RuCl_3 \cdot 3H_2O$ (0.021 g, 0.08 mmol) and sodium periodate (6.2 g, 29.0 mmol) were successively added. After 1 h of stirring, water (75 mL) was added and the solution extracted with diethyl ether (4 × 100 mL). The combined extracts were washed with brine, dried (Na_2SO_4), and filtered through silica gel. The ethereal solution was evaporated and the residue purified by flash chromatography (*n*-hexane:AcOEt = 9:1, R_f = 0.25) to give the sulfate **9** as colorless crystals (3.4 g, 60%): mp 90−94 °C; $[\alpha]^{23}_D = -2.8$ (*c* 1.012, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.32−7.18 (m, 10H), 4.79 (AB, J = 10.7 Hz, 2H), 4.64 (AB, J = 10.8 Hz, 2H), 4.60 (m, 2H), 3.48 (m, 2H), 1.46 (d, J = 6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 137.1, 128.6, 128.1, 127.7, 84.2, 79.4, 76.2, 17.9; MS (70 eV, *m*/*z*): 392 [M^+] (1). Anal. Calcd for $C_{20}H_{24}O_6S$: C, 61.21; H, 6.16; S, 8.17. Found: C, 61.20; H, 6.24; S, 8.08.

(4*R*,5*S*,6*S*,7*R*)-5,6-Dihydroxy-4,7-dimethyl[1,3,2]-dioxathiepane 2,2-Dioxide (10). A solution of dibenzyl ether **9** (8.60 g, 21.9 mmol) in MeOH (150 mL) was stirred in the presence of 10% Pd/C (300 mg) under a H_2 atmosphere (1 atm H_2 pressure) at room temperature. After completion of the hydrogen consumption, the mixture was filtered off and the solvent removed under vacuum. The residue was subjected to flash chromatography (*n*-hexane:AcOEt = 1:2, R_f = 0.4) to give **10** as colorless crystals (3.90 g, 84%): mp 118−123 °C (dec); $[\alpha]^{23}_D = -24.5°$ (*c* 1.028, CH_3OH); ^{1}H NMR (CD_3OD) δ 4.36 (m, 2H), 3.15 (m, 2H), 1.31 (d, J = 6.0 Hz, 6H); ^{13}C NMR (CD_3OD) δ 81.4, 77.8, 18.3; IR (KBr) 3452, 3375 cm^{-1}; MS (CI, *m*/*z*) 269 [$M^+ + C_4H_9$]. Anal. Calcd for $C_6H_{12}O_6S$: C, 33.96; H, 5.70; S, 15.11. Found: C, 34.13; H, 5.56; S, 14.87.

(4*R*,5*S*,6*S*,7*R*)-5,6-Bis(*tert*-butyloxy)-4,7-dimethyl[1,3,2]-dioxathiepane 2,2-Dioxide (11). A pressure vessel was fitted with a solution of alcohol **10** (3.61 g, 17.0 mmol) in CH_2Cl_2 (70 mL). After cooling the mixture to −78 °C, isobutylene (70 mL) and concentrated sulfuric acid (0.2 mL) were successively added. The vessel was closed and the solution stirred for 5 days at room temperature. Then, the solution was cooled to −78 °C and the excess of isobutylene carefully liberated. The remaining solution was washed with water (2 × 25 mL) and dried (Na_2SO_4). After filtration and removal of the solvent, the residue was subjected to flash chromatography (*n*-hexane:AcOEt = 4:1, R_f = 0.35) to afford **11** as colorless crystals (1.83 g, 33%): mp 112−117 °C; $[\alpha]^{24}_D = 21.5°$ (*c* 0.998, $CHCl_3$). Anal. Calcd for $C_{14}H_{28}O_6S$: C, 51.83; H, 8.70; S, 9.88%; Found: C, 51.91; H, 8.78; S, 9.72.

BH_3 Adduct of 1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-2,5-dimethylphospholanyl]ethane (12a). To a stirred solution of 1,2-diphosphinoethane (0.396 g, 4.21 mmol) in THF (70 mL) was added *n*-BuLi (1.6 M *n*-hexane solution, 5.26 mL, 8.42 mmol) dropwise via a syringe at room temperature. The resulting yellow solution was stirred for further 2 h. When a solution of sulfate **9** (3.30 g, 7.92 mmol) dissolved in THF (15 mL) was added, a change of the color from yellow to brown occurred. After 4 h of stirring, *n*-BuLi (1.6 M hexane solution, 5.79 mL, 9.26 mmol) was added and the solution kept for 16 h at room temperature. Then 2.2 equiv of BH_3−THF complex (1

(25) Dr. J. M. Brown (Oxford, UK) kindly informed us that his group recently succeeded in the synthesis of a DIPAMP−BPE hybrid ligand also starting from D-mannitol.

M solution in THF, 9.26 mL, 9.26 mmol) was added at 0 °C. After 2 h the solvents were removed under reduced pressure. To the residue was added water (20 mL) and the aqueous solution extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to afford the crude phospholane−borane as a colorless syrup. Purification was accomplished by flash chromatography (*n*-hexane:AcOEt = 4:1, R_f = 0.25) to give **12a** as a colorless syrup (750 mg, 25%): ^{1}H NMR ($CDCl_3$) δ 7.38−7.20 (m, 20H), 4.55−4.42 (m, 8H), 3.90 (m, 4H), 2.58 (m, 2H), 2.24 (m, 2H), 2.00−1.64 (m, 4H), 1.20−1.11 (m, 12H), 0.90−0.05 (b, 6H); ^{13}C NMR ($CDCl_3$) δ 137.8, 137.5, 128.5−127.4, 84.0, 82.3, 72.5, 72.3, 34.5 (d, J = 33.4 Hz), 34.0 (d, J = 31.5 Hz), 17.8, 10.0, 8.1; ^{31}P NMR ($CDCl_3$) δ 39.2. Anal. Calcd for $C_{42}H_{58}O_4B_2P_2$: C, 71.00; H, 8.23. Found: C, 71.42; H, 8.33.

BH_3 Adduct of 1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-bis(*tert*-butyloxy)-2,5-dimethylphospholanyl]ethane (12b). Analogously as described for the preparation of **12a** starting from 1,2-diphosphinoethane (0.352 g, 3.74 mmol) and sulfate **11** (2.43 g, 7.48 mmol). Purification of the phosphine−borane was finally carried out by flash chromatography (*n*-hexane:AcOEt = 9:1, R_f = 0.30) to give **12b** as a colorless syrup (310 mg, 14%): mp 200−210 °C; $[\alpha]^{24}_D$ = 27.3° (0.565, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 39.1; MS (EI, *m*/*z*) 573 [M^+ − H]. Anal. Calcd for $C_{30}H_{66}O_4P_2B_2$: C, 62.73; H, 11.58. Found: C, 63.13; H, 11.86.

1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-2,5-dimethylphospholanyl]ethane (3a). A solution consisting of phosphine−borane adduct **12a** (290 mg, 0.41 mmol) and 4 equiv of DABCO (183 mg, 1.64 mmol) in toluene (6 mL) was stirred for 48 h at 40 °C. The conversion was followed by TLC (*n*-hexane:AcOEt = 4:1, R_f of the phosphine = 0.3). After full conversion, the solution was passed through a short column. The toluene was removed under reduced pressure to give the phosphine (210 mg, 75%). ^{1}H NMR ($CDCl_3$) δ 7.37−7.15 (m, 20H), 4.54−4.34 (m, 8H), 3.96−3.78 (m, 4H), 2.53 (m, 2H), 2.10 (m, 2H), 1.73−1.50 (m, 4H), 1.30−1.05 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 138.7, 138.5, 128.3−127.3, 86.8, 85.1, 72.2, 71.9, 33.5, 22.6, 14.1, 9.4; ^{31}P NMR ($CDCl_3$) δ −1.5. Due to the high sensitivity of the phosphine to oxidation, it was immediately chelated to Rh(I).

1,2-Bis[(2*S*,3*S*,4*S*,5*S*]-3,4-bis(*tert*-butyloxy)-2,5-dimethylphospholanyl]ethane (3b). Analogously as described for the preparation of **3a** starting from the borane adduct **12b** (130 mg, 0.23 mmol) and 4 equiv of DABCO (101 mg, 0.92 mmol). After stirring for 48 h at 40 °C and workup by flash chromatography (*n*-hexane:AcOEt = 2:1, R_f of the phosphine 0.60) the extremely air-sensitive phosphine was obtained as a colorless syrup (95 mg, 77%). ^{31}P NMR ($CDCl_3$) δ −0.5. Due to the high sensitivity of the phosphine to oxidation, it was immediately chelated to Rh(I).

1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-2,5-dimethylphospholanyl]benzene (4a). To a stirred solution of 1,2-diphosphinobenzene (0.564 g, 3.96 mmol) in THF (70 mL) was added *n*-BuLi (1.6 M hexane solution, 4.95 mL, 7.93 mmol) at room temperature. The resulting yellow solution was stirred for further 2 h. Then a solution of sulfate **9** (3.11 g, 7.92 mmol) dissolved in THF (15 mL) was added. A change of the color from yellow to brown occurred. After 4 h of stirring *n*-BuLi (1.6 M hexane solution, 5.45 mL, 8.71 mmol) was added and the solution kept for another 16 h at room temperature. After addition of methanol (3 mL), the solvents were evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL), washed with water (20 mL), and dried (Na_2SO_4). After filtration and removal of the solvent, the crude phosphine was purified by flash chromatography (*n*-hexane:AcOEt = 9:1, R_f = 0.2) to give **4a** as a colorless syrup (0.46 g, 16%). ^{1}H NMR ($CDCl_3$) δ 7.55−7.19 (m, 24H), 4.63 (AB, J = 12.0 Hz, 2H), 4.59 (AB, J = 12.0 Hz, 2H), 4.58 (s, 4H), 4.05 (m, 4H), 2.98−2.82 (m, 4H), 1.29 (m, 6H), 0.84 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 142.3, 138.7, 131.7, 128.1−127.4, 84.4, 84.2, 72.0, 71.9, 31.9, 31.4, 14.3, 12.8; ^{31}P NMR ($CDCl_3$) δ −4.3; MS (FDpos) 731 [M^+ + H] (100). Anal. Calcd for $C_{46}H_{52}O_4P_2$: C, 75.60; H, 7.17. Found: C, 75.98; H, 7.42.

[Rh(3a)(COD)]BF_4. A solution of diphospholane **3a** (180 mg, 0.26 mmol) in THF (1.5 mL) was slowly added to [Rh(COD)$_2$]-BF_4 (107 mg, 0.26 mmol) dissolved in THF (1.5 mL) at −10 °C. The solution was stirred for 15 min at room temperature. After addition of diethyl ether (12 mL), a brownish oil was formed. Decantation and repeated washing with diethyl ether (3 × 5 mL) converted the oil into a solid. It was dried under vacuum to give the complex as orange-brown powder (134 mg, 52%). ^{1}H NMR ($CDCl_3$) δ 7.38−7.27 (m, 20H), 5.30 (m, 2H), 5.17 (m, 2H), 4.61−4.43 (m, 8H), 4.09−3.93 (m, 4H), 2.60−1.70 (m, 16H) 1.37−1.20 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 137.6, 137.2, 128.7−127.5, 101.8, 95.5, 83.8, 83.5, 73.0, 72.6, 41.9, 33.5, 31.3, 28.6, 25.6, 14.5, 8.8; ^{31}P NMR ($CDCl_3$) δ 72.7 (d, J_{Rh-P} = 148.8 Hz); MS (FDpos) 892 [M^+ − BF_4] (100). Anal. Calcd for $C_{50}H_{64}O_4P_2$-$RhBF_4$: C, 61.24; H, 6.58. Found: C, 61.55; H, 6.26.

[Rh(3b)(COD)]BF_4. Analogously as described for the preparation of **[Rh(3a)(COD)]BF_4** starting from diphospholane **3b** (95 mg, 0.173 mmol) and [Rh(COD)$_2$]BF_4 (72 mg, 0.173 mmol) to give the complex as orange powder (110 mg, 75%). ^{31}P NMR ($CDCl_3$) δ 74.3 (d, J_{Rh-P} = 148.4 Hz). Anal. Calcd for $C_{38}H_{72}O_4P_2$-$RhBF_4$: C, 54.04; H, 8.59. Found: C, 54.57; H, 8.61.

[Rh(4a)(COD)]BF_4. Analogously as described for the preparation of **[Rh(3a)(COD)]BF_4** starting from diphospholane **4a** (300 mg, 0.41 mmol) and [Rh(COD)$_2$]BF_4 (167 mg, 0.41 mmol) to give the complex as brown powder (200 mg, 47%). ^{31}P NMR ($CDCl_3$) δ 76.1 (d, J_{Rh-P} = 152.6 Hz); MS (FDpos) 941 [M^+ − BF_4] (10). Anal. Calcd for $C_{54}H_{64}O_4P_2RhBF_4$: C, 63.05; H, 6.27. Found: C, 62.58; H, 6.18.

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Supporting Information Available: A complete list of all IR and MS spectra, ^{1}H and ^{13}C NMR spectra of **11**, **12b**, **3b**, **[Rh(3b)(COD)]BF_4**, and **[Rh(4a)(COD)]BF_4** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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