Chiral Mono- and Bidentate Ligands Derived from D-Mannitol and Their Application in Rhodium(I)-Catalyzed Asymmetric Hydrogenation Reactions

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The new monodentate phosphoramidites **8a**–**g** and bidentate phospholanes **13a**–**e** are prepared in an ex-chiral-pool synthesis from D-mannitol. Chiral diols **7a**–**g**, obtained via nucleophilic ring opening of bis(epoxides) **6a**–**b**, are the key intermediates for the production of both classes of ligands. Treatment of **8a**–**g** or **13a**–**e** with $[PdCl_2(COD)]$ or $[Rh(COD)_2][SO_3CF_3]$ yield the corresponding Pd (**10a, 10f, 15a**) and Rh compounds (**9a**–**g** and **14a**–**e**), respectively. The C_2 symmetry of the complexes in the solid state is demonstrated by X-ray structure investigations performed on **10a**, **10f** and **15a**. Surprisingly high enantioselectivities in the asymmetric hydrogenation of itaconic acid (94% *ee*) and α-acetamidocinnamic acid (89% *ee*) are observed on using the Rh complex **9g** bearing two monodentate phosphoramidite ligands. Although the chelating bis(phospholanes) described herein are more effective, the adjustable synthesis of the monodentate phosphoramidites may permit the optimization of asymmetric catalytic reactions.

Introduction

The enantioselective hydrogenation of prochiral olefins plays an important role in the application of homogeneous catalysts. The development of suitable ligands for rhodium(I) species started in 1968 with Wilkinson-type complexes.[1,2] They used chiral monophosphane ligands, e.g. methyl(phenyl)(*n*-propyl)phosphane, which led to poor enantioselectivities in rhodium(I)-catalyzed hydrogenation reactions (3−15% *ee*). Also, other monodentate ligands failed to produce high enantioselectivities, while cyclohexyl(*o*-anisyl)methylphosphane (CAMP) was one of the rare exceptions (90% *ee* for hydrogenation of dehydroamino acids).[3] With the introduction of Kagan's DIOP, the first chiral diphosphane,[4] the research focussed on bidentate ligands. Knowles et al. showed that DIPAMP, another chelating diphosphane, is superior to PAMP, the corresponding monodentate species, with respect to rhodium-catalyzed hydrogenation reactions.[5] The use of bidentate ligands such as BINAP[6] and DuPHOS,[7] have also led to extremely high enantiomeric excess values. These chelating compounds are supposed to be superior because of the resulting rigid catalysts which favor effective chiral induction.[8] Monodentate ligands have been neglected in asymmetric hydrogenation reactions until Pringle et al. questioned the superiority of the bidentate species. They found higher enantioselectivities (92% *ee*) when using an asymmetric monophosphonite compared with the corresponding C_2-symmetric diphosphonite in the hydrogenation of methyl 2-(acetamido)acrylate.[9] Excellent enantioselectivities (> 99% *ee*) are also reported with monodentate phosphites[10] and phosphoramidites.[11] These new monodentate ligands have an enantiomerically pure binaphthol fragment in common. Based on the X-ray data of a platinum(II) complex, Pringle showed that the *cis* coordination of two sterically demanding monophosphonite ligands favors one stable conformation at the metal center, so that rotation about the M−P bond is prevented. Quadrant diagrams demonstrate the edge-on conformation of the bulky binaphthol moiety, presumably causing the asymmetric induction.[9]

Our approach to achieve high enantioselectivities in asymmetric hydrogenation reactions is not based on a single chiral auxiliary group. We present a highly variable ex-chiral-pool synthesis in order to generate monodentate phosphoramidites bearing four stereogenic centers, differing in the absolute configuration of carbon atoms and the steric demand of the substituents. This synthetic protocol also offers access to functionalized bidentate DuPHOS derivatives. Both types of ligands were tested in the rhodium(I)-catalyzed hydrogenation reaction of itaconic and α-(acetamido)-cinammic acid. The hydrogenation results can be explained with the help of quadrant diagrams based on X-ray data of corresponding palladium(II) complexes.

Ligand and Complex Synthesis

Our approach starts with the chiral building block D-mannitol[12] (**1**, Figure 1), which is converted into the

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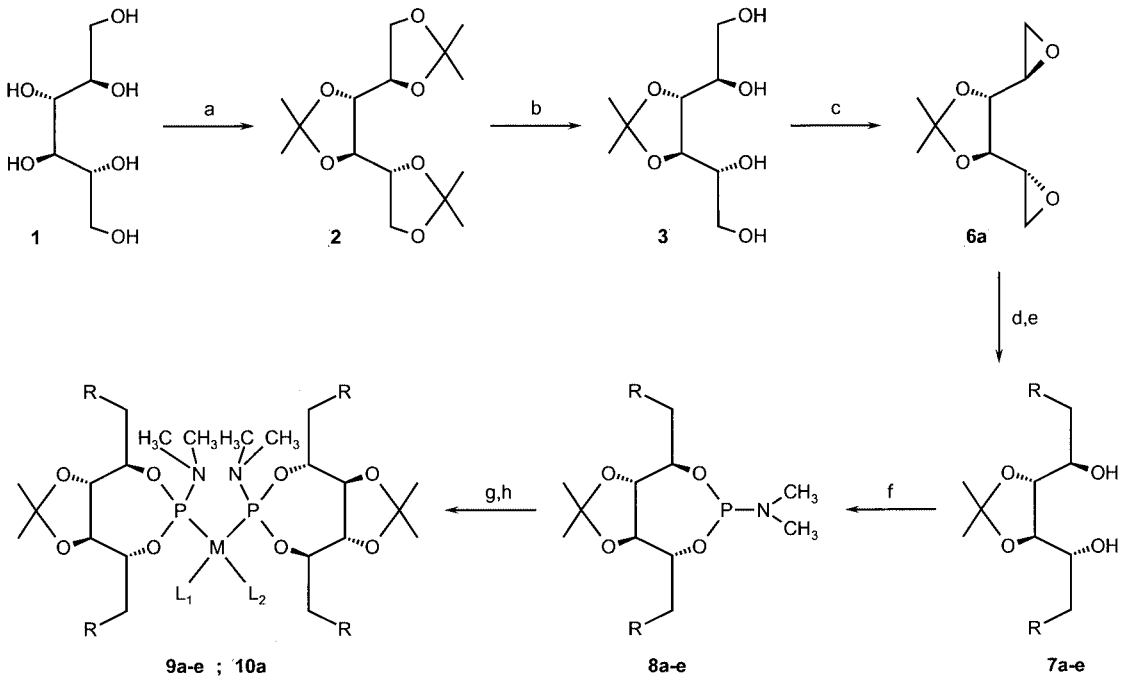


Figure 1. a) acetone, H_2SO_4; b) AcOH, H_2O, 40 °C; c) (i) trimethyl orthoacetate, PPTS, (ii) NEt_3, AcBr, (iii) K_2CO_3, MeOH; d) $LiAlH_4$, Et_2O, R = H (**7a**); e) CuBr·SMe_2, RMgBr, THF/Et_2O, −40 °C, R = CH_3 (**7b**), C_2H_5 (**7c**), iC_4H_9 (**7d**), C_6H_5 (**7e**); f) HMTAP, toluene, reflux; g) $[Rh(COD)_2][SO_3CF_3]$, CH_2Cl_2, **9a**−**e**: M = Rh, L_1-L_2 = COD; h) $[PdCl_2(COD)]$, CH_2Cl_2, **10a**: M = Pd, $L_1 = L_2$ = Cl

1,2;3,4;5,6-tri-*O*-isopropylidene (**2**) and the 3,4-*O*-isopropylidene derivative (**3**).[13,14] The syntheses of 1,2;5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol (**6a**),[15] the corresponding chiral diols **7a**−**e**,[16,17] the monodentate phosphoramidites **8a**−**e**, the Rh complexes **9a**−**e** and the Pd complex **10a** were recently reported by us.[18]

The highly variable synthetic strategy allows for the conversion of compound **3** (Figure 1) to the diastereomeric bis(epoxide) 1,2;5,6-dianhydro-3,4-*O*-isopropylidene-L-iditol (**6b**, Figure 2), with a changed configuration at carbon atoms C2 and C5 (dibenzoylation of **3**, ditosylation of **4**, subsequent transesterification with concomitant intramole-

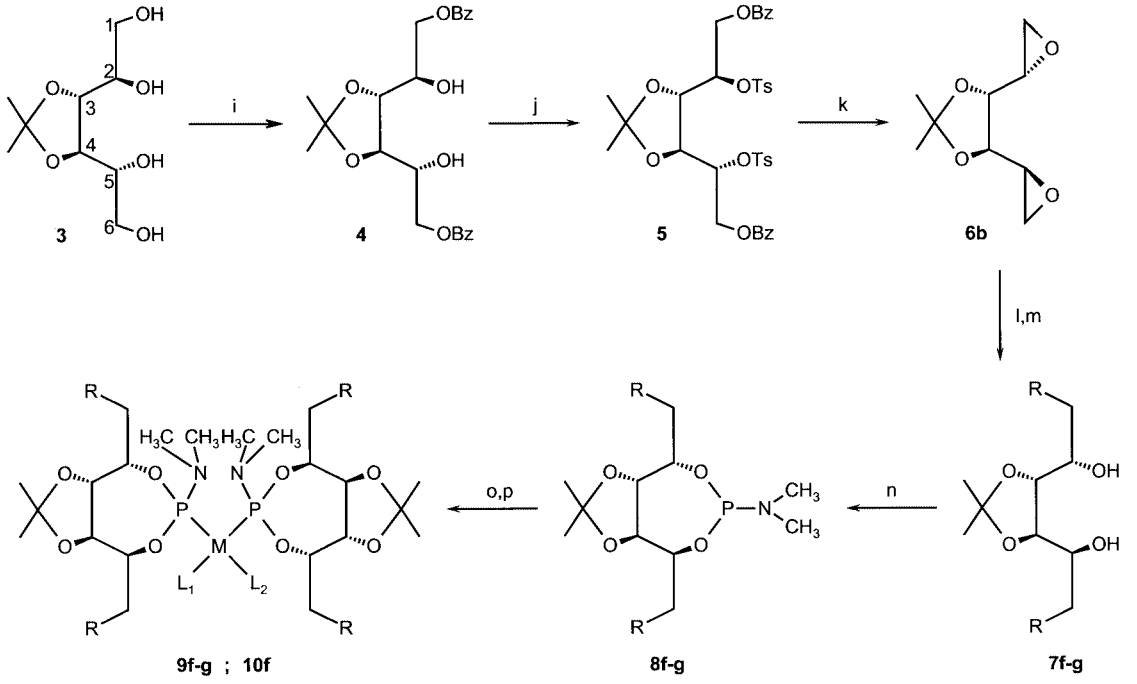


Figure 2. i) benzoyl chloride, pyridine, CH_2Cl_2, −80 °C; j) tosyl chloride, NEt_3, 4-(dimethylamino)pyridine, CH_2Cl_2; k) K_2CO_3, MeOH; l) $LiAlH_4$, Et_2O, R = H (**7f**); m) CuBr·SMe_2, PhMgBr, THF/Et_2O, −40 °C, R = C_6H_5 (**7g**); n) HMTAP, toluene, reflux; o) $[Rh(COD)_2][SO_3CF_3]$, CH_2Cl_2, **9f**−**g**: M = Rh, L_1-L_2 = COD; p) $[PdCl_2(COD)]$, CH_2Cl_2, **10f**: M = Pd, $L_1 = L_2$ = Cl

cular S_N2 reaction of **5**).[13] Nucleophilic attack of $LiAlH_4$ opens the epoxide rings of **6b** to form (2*S*,3*R*,4*R*,5*S*)-3,4-*O*-isopropylidene-2,3,4,5-hexanetetraol (**7f**) in a clean reaction.[16,19] Larger substituents [e.g. (2*S*,3*R*,4*R*,5*S*)-3,4-*O*-isopropylidene-1,6-diphenyl-2,3,4,5-hexanetetraol, **7g**, R = phenyl] can be introduced by nucleophilic ring-opening of **6b** with organocuprate reagents generated from the copper(I) bromide−dimethylsulfide complex and suitable Grignard reagents in diethyl ether.[17,20] Subsequently, the monodentate phosphoramidites **8f**−**g** were synthesized in high yields by refluxing **7f**−**g** and hexamethyltriaminophosphane (HMTAP) in toluene. The corresponding orange Rh complexes **9f**−**g** and the pale yellow Pd compound **10f** were prepared by stirring 2 equiv. of monodentate ligand **9f**−**g** with $[Rh(COD)_2][SO_3CF_3]$ or $[PdCl_2(COD)]$ in dichloromethane.

Access to functionalized DuPHOS ligands was offered by branching off from the key intermediates **7a**−**e** (Figure 3), which were readily converted into the corresponding cyclic sulfates **11a**−**e** by reaction with thionyl chloride, followed by in situ oxidation of the intermediate cyclic sulfite with catalytic amounts of RuO_4.[21,22] The 1,2-bis(phospholano)-benzenes **12a**−**e** were prepared by successive treatment of 1,2-bis(phosphanyl)benzene with 2 equiv. of *n*BuLi, followed by the addition of 2 equiv. of the corresponding cyclic sulfate **11a**−**e** and an additional 2.2 equiv. of *n*BuLi.[8] The chiral bis(phospholanes) **13a**−**e** bearing four free hydroxy groups were synthesized by cleavage of the protecting groups (refluxing **12a**−**e** with methanesulfonic acid in water/methanol).[23−25] The resulting chiral bis(phospholanes) **13a**−**e** were converted into the corresponding yellow-orange Rh complexes **14a**−**e** and the pale yellow Pd analog **15a** by stirring 1 equiv. of **13a**−**e** with $[Rh(COD)_2][SO_3CF_3]$ or $[PdCl_2(COD)]$ in tetrahydrofuran or dichloromethane, respectively.

Structure of $PdCl_2$ Complexes

We were not able to grow suitable crystals of the rhodium complexes for X-ray analysis, but we succeeded in crystallizing the isoelectronic $PdCl_2$ species **10a**, **10f** (from methanol) and **15a** (from acetone/ethyl acetate). The crystallographic data of **10a** (Figure 4) were already reported on in our latest report.[18] The X-ray structure of **10a** (C2, C11, C5, C14: *R*; C3, C12, C4, C13: *S*; "*RSSR*") indicates the *cis* coordination of the two monodentate ligands **8a**, and the expected square-planar coordination environment of Pd^{II} [see (a) in Figure 4, front-view] with a chiral, C_2-symmetric arrangement of both ligands [see (b) in Figure 4, side-view]. Furthermore, Figure 4 (b) clearly shows that the tunable substituents (Figure 1, CH_2−R) of the monodentate phosphoramidites (Figure 4; C1, C10: R = H) occupy the top-left and bottom-right quadrants [see (c) in Figure 4], thereby defining a chiral cage around the metal center. The size of the cage is influenced by the nucleophile (R) used for the epoxide ring opening.

The diastereomeric $PdCl_2$ complex **10f** (C2−C5, C11−C14: *S*; "*SSSS*") also bears two *cis*-coordinated monodentate phosphoramidites **8f**. The C_2 symmetry and the square-planar geometry around the Pd^{II} center was determined by an X-ray structure investigation (Figure 5). The corresponding crystallographic data are listed in Table 1

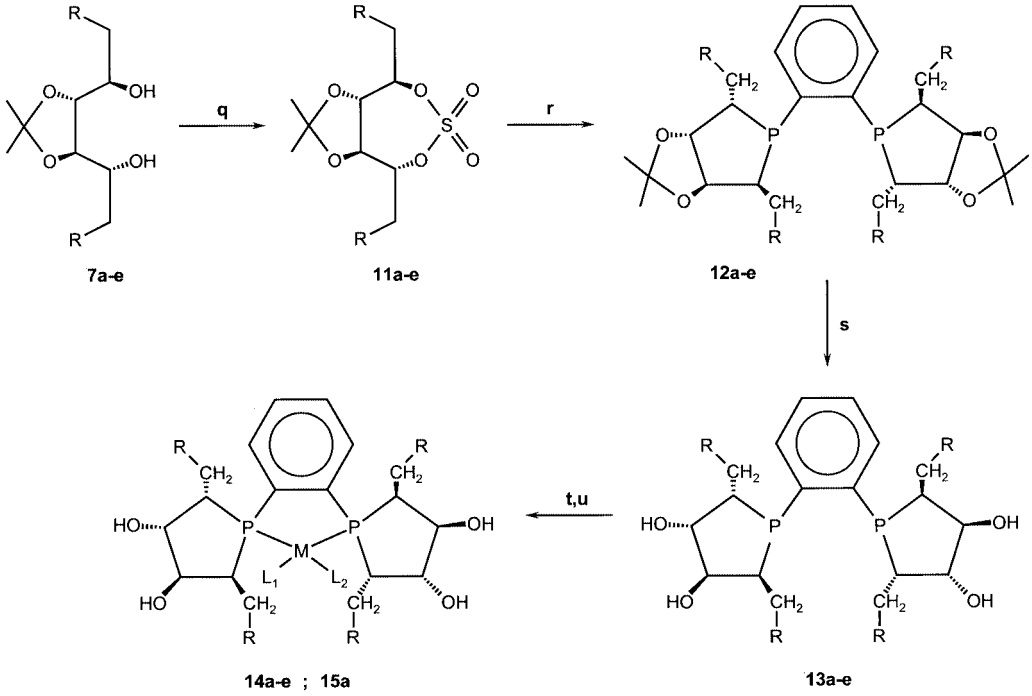
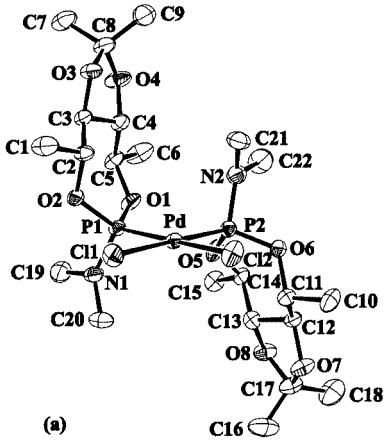
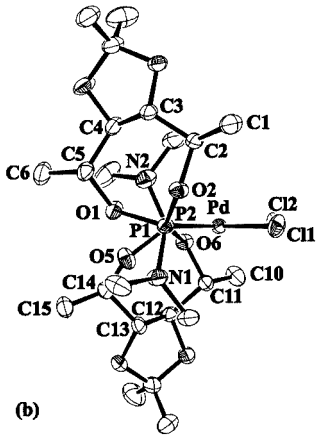


Figure 3. q) (i) $SOCl_2$, NEt_3, CH_2Cl_2; (ii) $NaIO_4/RuCl_3$, $CH_2Cl_2/MeCN/H_2O$; r) (i) 1,2-bis(phosphanyl)benzene, *n*BuLi, THF; (ii) *n*BuLi, THF; s) CH_3SO_3H, MeOH/H_2O, reflux; t) $[Rh(COD)_2][SO_3CF_3]$, THF, **14a**−**e**: M = Rh, L_1-L_2 = COD; u) $[PdCl_2(COD)]$, CH_2Cl_2, **15a**: M = Pd, $L_1 = L_2$ = Cl





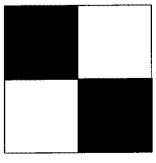
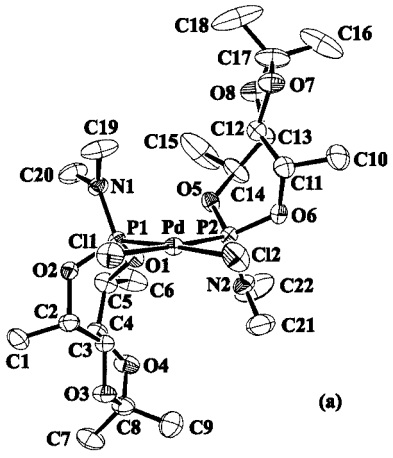
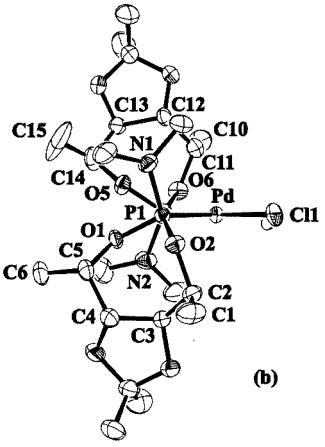


Figure 4. Molecular structure of **10a** (*RSSR*); (a) front-view: square-planar environment of Pd^{II}; (b) side-view: C_2-symmetric arrangement; hydrogen atoms have been omitted for clarity; (c) quadrant diagram





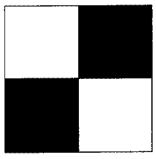


Figure 5. Molecular structure of **10f** (*SSSS*); (a) front-view: square-planar environment of Pd^{II}; (b) side-view: C_2-symmetric arrangement; hydrogen atoms have been omitted for clarity; (c) quadrant diagram

and 3. The side-view shows that the tunable substituents (Figure 2, CH_2-R) of the monodentate ligands (Figure 5; C1, C10: R = H) now occupy the top-right and bottom-left quadrants less effectively than in **10a** [see (c) in Figure 5].

In contrast to **10a** and **10f**, which bear two monodentate ligands each, the Pd^{II} complex **15a** (C2−C5, C8−C11: *S*; "*SSSS*") consists of a chelating bis(phospholane) (**13a**). Figure 6 (a) shows the five-membered phospholane rings and the planarity of the 1,2-phenylene moiety. The top view in Figure 6 (b) verifies the almost perpendicular orientation of the substituents (C1, C6, C7, C12 = CH_3) in the equatorial positions of the phospholane ring relative to the square-planar Pd^{II} environment. The effective occupation of the top-right and bottom-left quadrants is especially due to the free hydroxy groups (O2, O4) in the axial positions of the five-membered rings [Figure 6 (c); Table 2 and 3].

Results in the Asymmetric Hydrogenation Reactions

The synthesized Rh^{I} complexes bearing two monodentate phosphoramidite ligands (**9a**−**g**) or a chelating bis(phospholan)e (**14a**−**e**) were tested in the asymmetric hydrogenation reactions of α-(acetamido)cinnamic acid (**16**) and itaconic acid (**18**). Complexes **9a**−**e** ["*RSSR*", see (A) in Figure 7] produce a small excess of *N*-acetyl-(*R*)-phenylalanine in the hydrogenation of **16** (Table 4, Entries 1−5), ranging

Table 1. Selected bond lengths [Å] and angles [°] in **10f**

Bond lengths			
Pd−Cl1	2.3581(11)	C1−C2	1.501(6)
Pd−Cl2	2.3518(10)	C2−C3	1.499(5)
Pd−P1	2.2412(8)	C3−C4	1.506(5)
Pd−P2	2.2324(10)	C4−C5	1.534(5)
P1−O1	1.585(2)	C5−C6	1.510(6)
P1−O2	1.599(2)	C7−C8	1.512(6)
P1−N1	1.631(3)	C8−C9	1.498(7)
N1−C19	1.471(6)	O3−C3	1.420(4)
N1−C20	1.441(5)	O3−C8	1.441(5)
O1−C5	1.461(4)	O4−C4	1.426(5)
O2−C2	1.475(4)	O4−C8	1.430(5)
Bond angles			
Cl1−Pd−Cl2	90.20(5)	C1−C2−C3	116.5(3)
P1−Pd−Cl1	88.57(4)	C2−C3−C4	115.8(3)
P1−Pd−P2	90.77(4)	C2−C3−O3	113.4(3)
P2−Pd−Cl2	90.53(5)	C3−O3−C8	106.4(3)
P1−Pd−Cl2	177.57(3)	O3−C3−C4	102.2(3)
P2−Pd−Cl1	177.82(4)	O3−C8−C7	107.8(4)
Pd−P1−O1	113.13(10)	O3−C8−C9	110.4(4)
Pd−P1−O2	115.58(9)	O3−C8−O4	106.1(3)
Pd−P1−N1	113.88(12)	C7−C8−C9	113.8(4)
O1−P1−O2	103.14(13)	C7−C8−O4	111.1(4)
O1−P1−N1	106.15(15)	C9−C8−O4	107.4(4)
O2−P1−N1	103.80(15)	C8−O4−C4	106.4(3)
P1−N1−C19	121.3(3)	O4−C4−C5	114.3(3)
P1−N1−C20	123.4(3)	O4−C4−C3	100.1(3)
C19−N1−C20	114.6(3)	C3−C4−C5	116.8(3)
P1−O1−C5	124.4(2)	C4−C5−C6	113.8(4)
P1−O2−C2	123.2(2)	C4−C5−O1	110.9(3)
C1−C2−O2	105.8(3)	O1−C5−C6	106.1(4)
C3−C2−O2	106.8(3)		

from 3 to 36% *ee*. The highest value in this series (36% *ee*) is achieved with **9e** which bears the sterically most demanding benzyl substituent. The absolute configuration (*R*) of our hydrogenation products is in accordance with the prediction of Knowles[26] that the reaction to form (*R*)-amino acids is favored if the top-right quadrant of the catalyst's chiral cage is not occupied [Figure 4 (c)]. On the other hand, the diastereomeric Rh^{I} complexes **9f−g** ["*SSSS*", Figure 7 (B)], with the opposite quadrant geometry [cf. Pd^{II} complex **10f**, Figure 5 (c)], deliver an excess of the (*S*) form of *N*-acetylphenylalanine (**17**) (Entries 6−7). Complex **9g** remarkably yields an 89% *ee* (*S*) due to the benzyl groups, whereas the methyl-substituted analog **9f** only gives a 14% *ee* (*S*).

The methyl substituents in **9a** [Figure 7 (a), *RSSR*, C1, C10] occupy the "front-side" of the catalyst, whereas the same groups in **9f** [Figure 7 (B), *SSSS*, C1, C10] are oriented "sidewards". This leads to overall low enantioselectivities in the case of the methyl derivatives **9a**, **9f** (R = H), but with a trend to better results for **9a**. This situation changes completely for the benzyl-substituted species **9e** [Figure 7 (A)] and **9g** [Figure 7 (B)]. Computer models suggest that the sterically demanding benzyl groups (R = Ph) in **9e** are most probably oriented away from the P1−Pd−P2 plane, pointing into the "free-areas" above and below the coordination plane [Figure 7 (A)]. The changed stereochemistry of C2 and C11 (both *S*) in **9g** provides a "tight chiral cage" in the case of the demanding benzyl substituents in

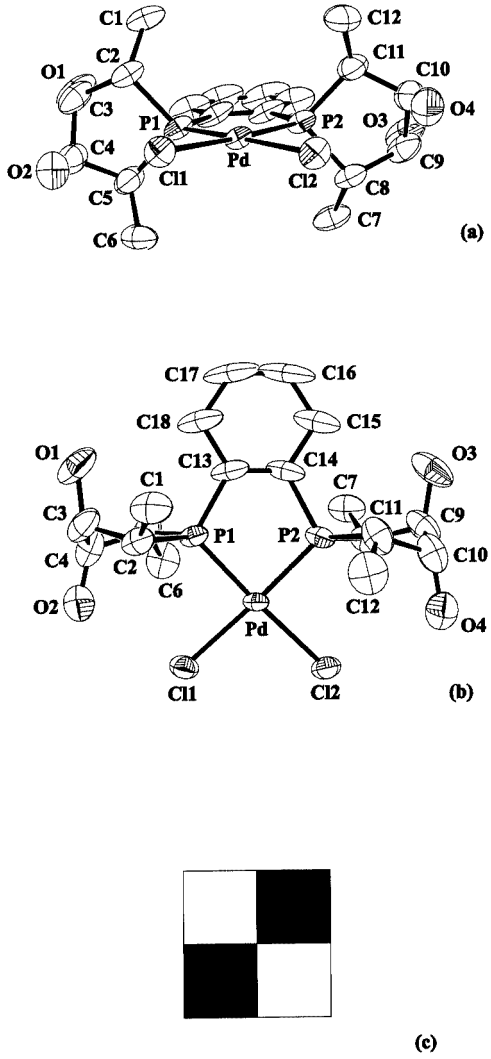


Figure 6. Molecular structure of **15a** (*SSSS*); (a) front-view: square-planar environment of Pd^{II}; (b) top-view: C_2-symmetric arrangement; hydrogen atoms have been omitted for clarity; (c) quadrant diagram

9g, and induces high enantioselectivities due to the "front orientation" of the phenyl fragments. In contrast, the small methyl substituents in **9f** lead to an "open chiral cage" of low enantioselectivity.

Itaconic acid (**18**), our second test olefin, gave the (*S*)-configured product after hydrogenation with **9a−e** ("*RSSR*"). The % *ee* values are higher with increasing steric demand of the substituents at the stereogenic centers C2 and C11 (Table 5, Entries 1−5). Therefore, **9e** gives the best result (61% *ee*) in this series; **9f** also produces a small excess (10% *ee*) of (*S*)-methylsuccinic acid (**19**); **9g** follows the opposite quadrant geometry relative to the former diastereomeric complexes, yielding **19** in an outstanding 94% *ee* (*R*) (Entries 6−7). This indicates that the steric arguments used above (Figure 7) also hold true for other substrates.

The Rh^{I} complexes **14a−e** bearing bidentate ligands once again demonstrate their outstanding ability to induce excellent enantioselectivities in asymmetric hydrogenation reactions. Compounds **14a−e**, with a quadrant diagram ident-

Table 2. Selected bond lengths [Å] and angles [°] in **15a**

Bond lengths			
Pd−Cl1	2.3786(7)	C3−C4	1.535(5)
Pd−P1	2.2301(7)	C4−O2	1.417(4)
P1−C2	1.852(3)	C4−C5	1.555(5)
P1−C5	1.856(4)	C5−C6	1.528(5)
P1−C13	1.815(3)	C13−C14	1.386(7)
C1−C2	1.525(5)	C13−C18	1.399(5)
C2−C3	1.542(4)	C17−C18	1.375(6)
C3−O1	1.421(4)	C16−C17	1.371(10)
Bond angles			
Cl1−Pd−Cl2	94.85(3)	C13−C18−C17	118.6(4)
P1−Pd−Cl1	88.66(2)	C18−C17−C16	121.2(3)
P1−Pd−P2	87.95(4)	C1−C2−C3	116.1(3)
P1−Pd−Cl2	175.73(3)	C2−C3−C4	108.5(2)
Pd−P1−C2	113.95(10)	C2−C3−O1	112.5(3)
Pd−P1−C5	121.13(11)	O1−C3−C4	107.8(3)
Pd−P1−C13	107.90(11)	C3−C4−C5	106.6(3)
P1−C2−C1	114.9(2)	C3−C4−O2	111.6(3)
P1−C2−C3	105.2(2)	O2−C4−C5	113.9(3)
P1−C5−C6	117.4(2)	C4−C5−C6	114.8(3)
P1−C5−C4	105.9(2)	C2−P1−C5	95.09(15)
P1−C13−C14	118.11(10)	C2−P1−C13	110.33(14)
P1−C13−C18	121.7(3)	C5−P1−C13	107.73(15)
C14−C13−C18	120.2(2)		

Table 3. Crystal data and refinement details for **15a** and **10f**

	15a	**10f**
Formula	$C_{18}H_{28}Cl_2O_4P_2Pd$	$C_{22}H_{44}Cl_2N_2O_8P_2Pd$
M_r	547.64	703.83
Crystal system	trigonal	orthorhombic
Space group	$P3_121$	$P2_12_12_1$
T [K]	203	293
a [Å]	10.554(1)	13.969(3)
b [Å]	10.554(1)	14.464(3)
c [Å]	17.876(2)	15.756(4)
V [Å^3]	1724.3(2)	3183.5(12)
Z	3	4
$D_{calcd.}$ [g cm^{-3}]	1.582	1.469
μ [mm^{-1}]	1.20	0.89
Crystal size [mm]	0.30 × 0.18 × 0.12	0.50 × 0.50 × 0.30
θ range [°]	2.23-25.85	2.82−25.98
Measured reflections	13451	33823
Unique reflections	2218	6165
R_{int}	0.048	0.060
Reflections with $I > 2\sigma(I)$	2049	5008
Goodness-of-fit	0.949	0.993
$R_1[F, I > 2\sigma(I)]$	0.020	0.029
$R_1(F$, all data)	0.023	0.041
$wR_2(F^2$, all data)	0.047	0.067
Min./Max. in ΔF [e Å^{-3}]	−0.33/0.33	−0.23/0.39
Absolute struct. parameter	−0.01(3)	−0.02(2)

ical to **10f**, also produce the (*S*) form of **17** in excellent enantioselectivities (up to 99% *ee* for *N*-acetylphenylalanine). This is clearly a consequence of the enhanced rigidity of the phenylene backbone (Table 4, Entries 8−12). The %

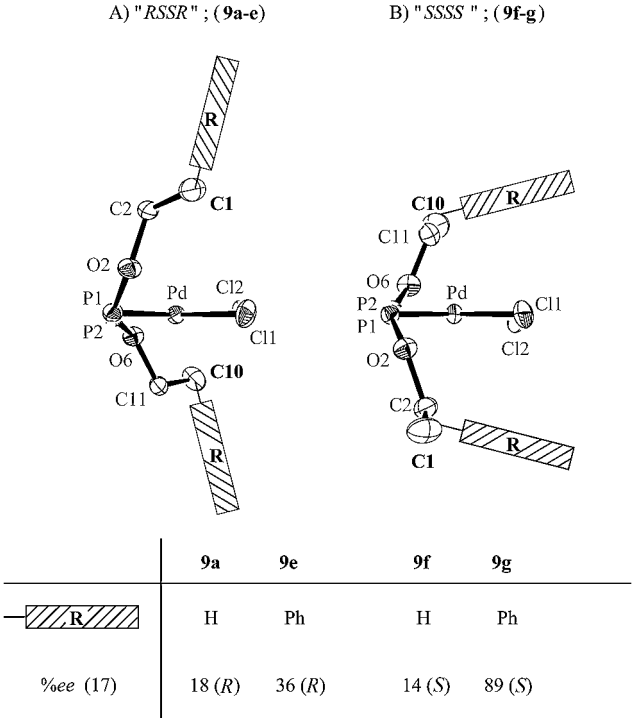
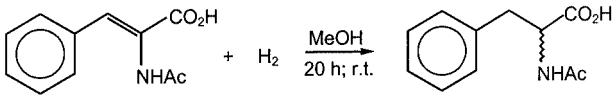


Figure 7. A) Section of Figure 4 (b); "*RSSR*" stereochemistry: aryl substituents occupy top-left and bottom-right quadrant "face-on"; B) section of Figure 5 (b); "*SSSS*" stereochemistry: "edge-on" orientation of aryl substituents in top-right and bottom-left quadrant, defining an effective chiral cage; the given % *ee* values of asymmetric hydrogenation reactions using **9a**,**e**,**f**,**g** are related to *N*-acetylphenylalanine (**17**)

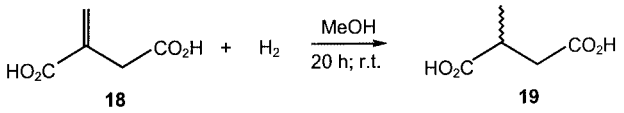
Table 4. Asymmetric hydrogenation of α-(acetamido)cinnamic acid (**16**); the reactions were carried out at room temp. under 1.3 bar of H_2 for 20 h in 5 mL of MeOH with a substrate/[Rh] (10 μmol) ratio of 244; all reactions achieved 100% conversion; the absolute configurations and % *ee* values were determined by chiral HPLC using Daicel chiral column Chiralpak WH 10 μm (250 mm × 4.6) with a Waters HPLC 2690 with UV/Vis detection (λ = 254 nm)



16 **17**

Entry	Catalyst	*ee* (%)
1	**9a**	18 (*R*)
2	**9b**	3 (*R*)
3	**9c**	5 (*R*)
4	**9d**	10 (*R*)
5	**9e**	36 (*R*)
6	**9f**	14 (*S*)
7	**9g**	89 (*S*)
8	**14a**	99 (*S*)
9	**14b**	98 (*S*)
10	**14c**	98 (*S*)
11	**14d**	97 (*S*)
12	**14e**	96 (*S*)

Table 5. Asymmetric hydrogenation of itaconic acid (**18**); the reactions were carried out at room temp. under 1.3 bar of H_2 for 20 h in 5 mL of MeOH with a substrate/[Rh] (10 μmol) ratio of 192; all reactions achieved 100% conversion; the absolute configurations and % *ee* values were determined by chiral HPLC using Daicel chiral column Chiralcel OD 10 μm (250 mm × 4.6) with a Waters HPLC 2690 with UV/Vis detection (λ = 220 nm)



18 **19**

Entry	Catalyst	*ee* (%)
1	**9a**	18 (*S*)
2	**9b**	27 (*S*)
3	**9c**	27 (*S*)
4	**9d**	44 (*S*)
5	**9e**	61 (*S*)
6	**9f**	10 (*S*)
7	**9g**	94 (*R*)
8	**14a**	> 99 (*R*)
9	**14b**	> 99 (*R*)
10	**14c**	98 (*R*)
11	**14d**	99 (*R*)
12	**14e**	98 (*R*)

ee values obtained with the hydroxy-substituted bis(phospholanes) **13a**−**e** are as high as that for the DuPHOS case, but we did not find a maximal enantioselectivity for the *n*-propyl derivative.[8] An increase in the steric demand of our tunable ligands **13a**−**e** lowers the resulting enantiomeric excess of the amino acids produced. Figure 6 (b) shows that mainly the free hydroxy groups in the axial positions claim the top-right and bottom-left quadrant. Raising the steric demand of the equatorial substituents cannot improve the occupation of the crucial areas.

The (*R*) form of methylsuccinic acid (**19**) is produced throughout with very high enantiomeric excess values (up to > 99% *ee*) (Table 5, Entries 8−12). The best enantioselectivities are again produced with the catalysts **14a**,**b** with the smallest substituents in the 2,5-positions of the phospholane moiety.

Conclusion

Recently developed chiral monodentate P-ligands based on binaphthol as the chiral building block show remarkable selectivities in asymmetric hydrogenation reactions. Here, we presented an efficient ex-chiral-pool synthesis starting from D-mannitol, which allows for the tailoring of monodentate phosphoramidites and bidentate phospholanes. The diastereoisomers of these new monodenate ligands allow the exact positioning of substituents with a defined steric demand at the stereogenic centers. The benzyl-substituted Rh^I complex **9g** (up to 94% *ee*) proved that monodentate ligands can be designed for high enantioselectivities in asymmetric catalytic reactions of different substrates. This opens the possibility to fine-tune our ligands and the corresponding metal complexes for given prochiral substrates. A suitable design strategy can be based on relatively simple steric considerations, e.g. the "quadrant model" of Knowles et al. Our results were in accordance with the carefully drawn structure-selectivity relations based on such quadrant diagrams derived from X-ray structures of the corresponding Pd^{II} species.

Experimental Section

General Remarks: All reactions and manipulations were performed using standard Schlenk techniques. The reagents were obtained from Aldrich, Fluka, Merck and Strem and used without purification. Diethyl ether, tetrahydrofuran, toluene and pentane were distilled from $LiAlH_4$, dichloromethane was distilled from CaH_2 under nitrogen. Dry methanol (secco solv) was purchased from Merck. Melting points were determined using a Büchi Melting Point B-540 apparatus and are uncorrected. Optical rotations were obtained using a POLAR monitor from IBZ Messtechnik. Elemental analyses were carried out using an Elementar Vario EL. Mass spectrometry was performed using a Finnigan MAT, TSQ 7000 (FAB; matrix: 2-nitrophenyl octyl ether) and a Finnigan MAT, SSQ 7000 (CI: CH_4; EI: 70 eV). ^1H, ^{13}C, ^{31}P NMR spectra were recorded with a Bruker DRX 400 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane, with the solvent as the internal standard or 85% H_3PO_4 as the external standard. Enantiomeric excess (% *ee*) values were measured using Daicel chiral HPLC columns Chiralcel OD and Chiralpak WH 10 μ m (250 mm × 4.6) with a Waters HPLC 2690 with a Knauer variable UV/Vis detector. Hydrogen (5.0) was purchased from mti. All compounds shown in Figure 1 were reported in our latest report.[18]

Synthesis of Chiral Diols 7f−g

(2*S*,3*R*,4*R*,5*S*)-3,4-*O*-Isopropylidene-2,3,4,5-hexanetetraol (7f): A solution of **6b** (8.85 g, 47.5 mmol) in 50 mL of diethyl ether was slowly added to a stirred suspension of $LiAlH_4$ (3.61 g, 95.1 mmol) in 130 mL of diethyl ether. After refluxing for 3 h, the reaction mixture was carefully hydrolyzed at 0 °C, subsequently with water and diluted sulfuric acid until the white precipitate dissolved. Extraction with diethyl ether, washing the organic layer with $NaHCO_3$, drying with Na_2SO_4 and evaporation of the solvent yielded **7f** as a colorless oil. Yield: 5.60 g, 62.0%. $[\alpha]_D^{25}$ = +26.1 (*c* = 0.44, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, 6 H, CH_3), 1.40 (s, 6 H, CH_3), 3.68−3.75 (m, 2 H, CH), 3.76−3.78 (m, 2 H, CH) ppm. ^{13}C NMR: δ = 20.1, 27.4, 67.1, 81.4, 109.4 ppm. MS (CI): *m*/*z* = 335 [MH^+] (+MSTFA). $C_9H_{18}O_4$ (190.24): calcd. C 56.82, H 9.54; found C 54.43, H 9.31.

(2*S*,3*R*,4*R*,5*S*)-3,4-*O*-Isopropylidene-1,6-diphenyl-2,3,4,5-hexanetetraol (7g): $CuBr{\cdot}SMe_2$ (0.62 g, 3 mmol) was added to a stirred suspension of phenylmagnesium bromide (120 mmol) in 100 mL of diethyl ether at −40 °C. After stirring at −40 °C for 2 h, a solution of **6b** (5.59 g, 30 mmol) in 30 mL of tetrahydrofuran was added. After 1 h of stirring at room temp., the mixture was poured into a saturated NH_4Cl solution. The organic layer was extracted, washed with water, dried with Na_2SO_4 and the solvents were evaporated to dryness to give **7g**, after flash chromatography (eluting with hexane/EtOAc, 7:3), as a colorless oil. Yield: 7.82 g, 76.1%. $[\alpha]_D^{21}$ = +10.2 (*c* = 0.53, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 6 H, CH_3), 2.70−2.83 (m, 4 H, CH_2), 3.66−3.71 (m, 2 H, CH), 3.95−3.99 (m, 2 H, CH), 7.13−7.26 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C

NMR: δ = 27.1, 41.1, 70.9, 78.6, 109.3, 126.4, 128.4, 129.2, 137.9 ppm. MS (CI): *m*/*z* = 343 [MH$^+$]. $C_{21}H_{26}O_4$ (342.4): calcd. C 73.66, H 7.65; found C 72.44, H 7.62.

General Procedure for the Synthesis of 8f−g: Chiral diols **7f−g** (6.2 mmol) and NH_4Cl (10 mg) were refluxed in 150 mL of toluene. HMTAP (1.24 mL, 6.8 mmol) was added to this refluxing solution and stirred for a further 8 h. The mixture was concentrated under reduced pressure affording colorless oils.

(4*S*,5*S*,6*S*,7*S*)-5,6-*O*-Isopropylidene-2-(dimethylamino)-4,7-dimethyl-1,3,2-dioxaphosphepane-5,6-diol (8f): Yield: 1.59 g, 97.3%. $[\alpha]_D^{23}$ = −67.1 (*c* = 0.41, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.42 (d, 3 H, CH_3), 2.57 (s, 3 H, N−CH_3), 2.60 (s, 3 H, N−CH_3), 4.24−4.27 (m, 1 H, CH), 4.41−4.56 (m, 3 H, CH) ppm. ^{13}C NMR: δ = 15.0, 16.4, 27.2, 34.8, 35.0, 68.4, 69.8, 75.7, 76.3, 110.3 ppm. ^{31}P NMR: δ = 140.48 (s) ppm. MS (CI): *m*/*z* = 264 [MH$^+$]. $C_{11}H_{22}NO_4P$ (263.3): calcd. C 50.18, H 8.42, N 5.32; found C 48.38, H 8.41, N 6.21.

(4*S*,5*S*,6*S*,7*S*)-5,6-*O*-Isopropylidene-2-(dimethylamino)-4,7-dibenzyl-1,3,2-dioxaphosphepane-5,6-diol (8g): Yield: 2.38 g, 92.4%. $[\alpha]_D^{21}$ = −50.0 (*c* = 0.01, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 6 H, CH_3), 2.45 (s, 3 H, N−CH_3), 2.48 (s, 3 H, N−CH_3), 2.70−2.78 (m, 1 H, CH_2), 3.09−3.25 (m, 3 H, CH_2), 4.43−4.61 (m, 3 H, CH), 4.73−4.79 (m, 1 H, CH), 7.17−7.29 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C NMR: δ = 27.0, 27.2, 34.3, 34.8, 35.0, 36.7, 73.3, 74.8, 76.4, 77.3, 110.6, 126.09, 126.13, 128.1, 128.2, 129.6, 129.8, 138.8, 139.1 ppm. ^{31}P NMR: δ = 140.24 (s) ppm. MS (CI): *m*/*z* = 417 [MH$^+$]. $C_{23}H_{30}NO_4P$ (415.5): calcd. C 66.49, H 7.28, N 3.37; found C 62.56, H 7.07, N 3.56.

General Procedure for the Synthesis of Rhodium(I) Complexes 9f−g: A solution of 2 equiv. of the corresponding monodentate phosphoramidite **8f−g** in 20 mL of dichloromethane was added to a stirred solution of $[Rh(COD)_2][SO_3CF_3]$ (300 mg, 0.64 mmol) in 30 mL of dichloromethane at 0 °C. After stirring for 2 h at room temp., the solvent was removed under reduced pressure. The resulting orange solid was washed twice with 50 mL of pentane and dried in vacuo.

{Bis[(4*S*,5*S*,6*S*,7*S*)-5,6-*O*-isopropylidene-2-(dimethylamino)-4,7-dimethyl-1,3,2-dioxaphosphepane]Rh^I(COD)} Trifluoromethanesulfonate (9f): Yield: 528 mg, 93.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, 6 H, CH_3), 1.33 (d, 6 H, CH_3), 1.38 (s, 12 H, CH_3), 2.31−2.57 (m, 8 H, $CH_{2,COD}$), 2.97−3.01 (m, 12 H, N−CH_3), 4.29−4.35 (m, 2 H, CH), 4.41−4.46 (m, 2 H, CH), 4.52−4.64 (m, 4 H, CH), 5.10−5.17 (m, 2 H, CH_{COD}), 5.52−5.59 (m, 2 H, CH_{COD}) ppm. ^{31}P NMR: δ = 117.06 (d) ppm. MS (FAB): *m*/*z* = 737 [(M − $SO_3CF_3^-$)$^+$]. $C_{31}H_{56}F_3N_2O_{11}P_2RhS$ (886.7): calcd. C 41.99, H 6.37, N 3.16; found C 41.87, H 6.48, N 2.55.

{Bis[(4*S*,5*S*,6*S*,7*S*)-5,6-*O*-isopropylidene-2-(dimethylamino)-4,7-dibenzyl-1,3,2-dioxaphosphepane]Rh^I(COD)} Trifluoromethanesulfonate (9g): Yield: 734 mg, 96.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 6 H, CH_3), 1.39 (s, 6 H, CH_3), 2.17−2.54 (m, 8 H, CH_{2COD}), 2.38−2.44 (m, 12 H, N−CH_3), 2.60−2.75 (m, 4 H, CH_2), 2.95−3.06 (m, 4 H, CH_2), 4.10−4.16 (m, 2 H, CH), 4.26−4.31 (m, 2 H, CH), 4.45−4.53 (m, 2 H, CH), 4.53−4.59 (m, 2 H, CH), 4.78−4.86 (m, 2 H, CH_{COD}), 5.45−5.53 (m, 2 H, CH_{COD}), 7.05−7.32 (m, 20 H, $CH_{arom.}$) ppm. ^{31}P NMR: δ = 116.60 (d) ppm. MS (FAB): *m*/*z* = 1041 [(M − $SO_3CF_3^-$)$^+$]. $C_{55}H_{72}F_3N_2O_{11}P_2RhS$ (1191.1): calcd. C 55.46, H 6.09, N 2.35; found C 54.28, H 6.22, N 2.31.

{Bis[(4*S*,5*S*,6*S*,7*S*)-5,6-*O*-isopropylidene-2-(dimethylamino)-4,7-dimethyl-1,3,2-dioxaphosphepane]}PdCl$_2$ (10f): A solution of 2 equiv. of the monodentate ligand **8f** in 50 mL of dichloromethane was added to a stirred solution of $[PdCl_2(COD)]$ (500 mg, 1.75 mmol) in 70 mL of dichloromethane at 0 °C. After stirring at room temp. for 2 h, the solvent was removed under reduced pressure. Washing of the residue twice with 50 mL of diethyl ether and drying in vacuo resulted in a pale yellow powder. Yield: 1.13 g, 91.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (d, 6 H, CH_3), 1.37 (s, 12 H, CH_3), 1.38 (d, 6 H, CH_3), 2.86−2.89 (m, 12 H, N−CH_3), 4.34−4.44 (m, 4 H, CH), 4.73−4.81 (m, 2 H, CH), 5.20−5.28 (m, 2 H, CH) ppm. ^{13}C NMR: δ = 15.4, 16.7, 26.7, 26.9, 38.1, 72.9, 74.4, 75.4, 75.9, 111.8 ppm. ^{31}P NMR: δ = 101.47 (s) ppm. MS (FAB): *m*/*z* = 669 [(M − Cl$^-$)$^+$]. $C_{22}H_{44}N_2O_8P_2PdCl_2$ (703.9): calcd. C 37.54, H 6.30, N 3.98; found C 35.66, H 6.45, N 4.18.

General Procedure for the Synthesis of the Cyclic Sulfates 11a−e: **11a**,**b** have already been reported.[24] A solution of thionyl chloride (1.91 mL, 26 mmol) in 20 mL of dichloromethane was added to a stirred solution of the corresponding chiral diol **7c−e** (24 mmol) and pyridine (4.26 mL, 53 mmol) in 100 mL of dichloromethane at 0 °C. After 3 h at room temp., the reaction mixture was washed with water and the organic layer extracted, dried with Na_2SO_4 and the solvents were evaporated to dryness. The resulting oil was redissolved in 40 mL of dichloromethane and 40 mL of acetonitrile, and $NaIO_4$ (10.25 g, 48 mmol) and $RuCl_3{\cdot}nH_2O$ (34 mg) in 60 mL of water were then added. After 1 h at room temp., the organic layer was extracted with dichloromethane, washed with brine, dried with Na_2SO_4 and the solvents were evaporated to dryness. The products were isolated by filtration through silica (eluent: dichloromethane). After concentration to dryness, the cyclic sulfates **11c−d** were obtained as colorless crystals, **11e** as a pale yellow oil.

(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-Isopropylidene-4,7-di-*n*-propyl-1,3,2-dioxathiepane 2,2-Dioxide (11c): Yield: 5.48 g, 74.2%; m.p. 36−38 °C. $[\alpha]_D^{24}$ = +45.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, 6 H, CH_3), 1.38 (s, 6 H, CH_3), 1.41−1.49 (m, 2 H, CH_2), 1.55−1.64 (m, 2 H, CH_2), 1.81−1.86 (m, 4 H, CH_2), 3.98−4.04 (m, 2 H, CH), 4.25−4.31 (m, 2 H, CH) ppm. ^{13}C NMR: δ = 13.5, 18.0, 26.7, 34.2, 79.6, 84.6, 110.5 ppm. MS (CI): *m*/*z* = 309 [MH$^+$]. $C_{13}H_{24}O_6S$ (308.4): calcd. C 50.63, H 7.84; found C 49.81, H 7.69.

(4*R*,5*S*,6*S*,7*R*)-4,7-Diisopentyl-5,6-*O*-isopropylidene-1,3,2-dioxathiepane 2,2-Dioxide (11d): Yield: 7.22 g, 82.6%; m.p. 36−38 °C. $[\alpha]_D^{24}$ = +45.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88−0.90 (m, 12 H, CH_3), 1.23−1.34 (m, 2 H, CH_2), 1.39 (s, 6 H, CH_3), 1.42−1.50 (m, 2 H, CH_2), 1.51−1.61 (m, 2 H, CH), 1.77−1.93 (m, 4 H, CH_2), 3.99−4.04 (m, 2 H, CH), 4.22−4.28 (m, 2 H, CH) ppm. ^{13}C NMR: δ = 22.2, 22.5, 26.8, 27.7, 30.2, 33.6, 79.7, 85.3, 110.6 ppm. MS (CI): *m*/*z* = 365 [MH$^+$]. $C_{17}H_{32}O_6S$ (364.5): calcd. C 56.02, H 8.85; found C 55.41, H 8.89.

(4*R*,5*S*,6*S*,7*R*)-4,7-Dibenzyl-5,6-*O*-isopropylidene-1,3,2-dioxathiepane 2,2-Dioxide (11e): Yield: 8.07 g, 83.2%. $[\alpha]_D^{23}$ = +54.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 6 H, CH_3), 3.07−3.18 (m, 4 H, CH_2), 4.02−4.07 (m, 2 H, CH), 4.39−4.45 (m, 2 H, CH), 7.18−7.28 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C NMR: δ = 26.8, 38.1, 78.7, 84.5, 110.9, 127.1, 128.5, 129.6, 135.1 ppm. MS (CI): *m*/*z* = 405 [MH$^+$]. $C_{21}H_{24}O_6S$ (404.49): calcd. C 62.39, H 5.98; found C 59.56, H 5.95.

General Procedure for the Synthesis of the Bis(phospholanes) 12a−e: **12a**,**b** have already been reported.[24] A solution of 1.6 M *n*-butyllithium (8.0 mL, 12.8 mmol) in *n*-hexane was added to a stirred solution of 1,2-bis(phosphanyl)benzene (0.91 g, 6.4 mmol) in 50 mL of

tetrahydrofuran. After 2 h at room temp., the corresponding cyclic sulfate **11c−e** (12.8 mmol) in 50 mL of tetrahydrofuran was added. After an additional 4 h at room temp., *n*-butyllithium (8.8 mL of 1.6 M solution, 14.1 mmol) in *n*-hexane was added. After 16 h at room temp., the excess *n*-butyllithium was hydrolyzed with 3 mL of methanol. The reaction solvents were evaporated to dryness. The resulting yellow oil was extracted twice with 50 mL *n*-pentane. After concentrating to dryness, the bidentate ligands were obtained as a white powder (**12d−e**) or a colorless oil (**12c**).

1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-*O*-isopropylidene-2,5-diisopropylphospholanyl]benzene (12c): Yield: 2.37 g, 65.8%. $[\alpha]_D^{24}$ = +189.3 (*c* = 0.783, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.57 (t, 6 H, CH_3), 0.69−0.78 (m, 2 H, CH_2), 0.85 (t, 6 H, CH_3), 0.95−1.05 (m, 2 H, CH_2), 1.23−1.35 (m, 6 H, CH_2), 1.37−1.42 (m, 2 H, CH_2), 1.44 (s, 6 H, CH_3), 1.45 (s, 6 H, CH_3), 1.47−1.56 (m, 2 H, CH_2), 1.81−1.97 (m, 2 H, CH_2), 2.24−2.29 (m, 2 H, CH), 2.61−2.73 (m, 2 H, CH), 4.33−4.46 (m, 4 H, CH), 7.30−7.38 (m, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR: δ = 13.90, 13.91, 21.6, 22.9, 27.2, 27.3, 29.8, 29.9, 30.6, 30.9, 81.3, 82.2, 117.0, 129.2, 131.1, 141.2 ppm. ^{31}P NMR: δ = 35.95 (s) ppm. MS (CI): *m*/*z* = 563 [MH^+]. $C_{32}H_{52}O_4P_2$ (562.7): calcd. C 68.30, H 9.31; found 64.18, H 8.56.

1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-2,5-diisopentyl-3,4-*O*-isopropylidenephospholanyl]benzene (12d): Yield: 3.00 g, 69.3%; m.p. 125−130 °C. $[\alpha]_D^{23}$ = +136.5 (*c* = 0.31, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.48 (d, 6 H, CH_3), 0.59 (d, 6 H, CH_3), 0.72−0.81 (m, 4 H, CH), 0.85 (d, 12 H, CH_3), 0.85−0.90 (m, 2 H, CH_2), 1.04−1.13 (m, 4 H, CH_2), 1.15−1.24 (m, 2 H, CH_2), 1.26−1.42 (m, 4 H, CH_2), 1.46 (s, 6 H, CH_3), 1.47 (s, 6 H, CH_3), 1.47−1.56 (m, 2 H, CH_2), 1.87−2.00 (m, 2 H, CH_2), 2.15−2.20 (m, 2 H, CH), 2.54−2.66 (m, 2 H, CH), 4.32−4.49 (m, 4 H, CH), 7.31−7.37 (m, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR: δ = 22.3, 22.4, 22.6, 22.7, 25.2, 26.1, 27.31, 27.33, 28.2, 28.4, 31.3, 31.4, 38.3, 38.9, 81.3, 82.4, 117.1, 129.2, 131.3, 141.2 ppm. ^{31}P NMR: δ = 36.71 (s) ppm. MS (CI): *m*/*z* = 676 [MH^+]. $C_{40}H_{68}O_4P_2$ (674.9): calcd. C 71.18, H 10.15; found C 67.24, H 9.69.

1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-2,5-dibenzyl-3,4-*O*-isopropylidenephospholanyl]benzene (12e): Yield: 2.64 g, 54.6%; m.p. 136−140 °C. $[\alpha]_D^{23}$ = +28.1 (*c* = 0.089, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (s, 12 H, CH_3), 2.05−2.10 (m, 2 H, CH_2), 2.49−2.55 (m, 2 H, CH_2), 2.67−2.73 (m, 2 H, CH_2), 2.79−2.88 (m, 2 H, CH_2), 3.12−3.26 (m, 4 H, CH), 4.43−4.63 (m, 4 H, CH), 6.89−7.44 (m, 24 H, $CH_{arom.}$) ppm. ^{13}C NMR: δ = 27.3, 27.4, 30.9, 32.2, 24.0, 35.1, 81.0, 81.9, 117.8, 125.6, 126.0, 127.8, 128.2, 128.6, 128.9, 129.0, 129.7, 130.8, 141.3, 141.4 ppm. ^{31}P NMR: δ = 42.39 (s) ppm. MS (CI): *m*/*z* = 755 [M^+]. $C_{48}H_{52}O_4P_2$ (754.9): calcd. C 76.37, H 6.94; found C 75.04, H 6.65.

General Procedure for the Synthesis of the Bis(phospholanes) 13a−e: 13a,**b** have already been reported.[24,25] Methanesulfonic acid (1 mL of a 70% solution) in water was added to a stirred solution of the corresponding bis(phospholane) **12c−e** (2.11 mmol) in 50 mL of methanol at room temp. After 2.5 h of stirring under reflux, the reaction solvents were evaporated to dryness. The residue was dissolved in 30 mL of ethyl acetate and 30 mL of water. K_2CO_3 was then added until neutral reaction of litmus. After stirring for several hours, the organic layer was separated and dried with Na_2SO_4. Concentration to dryness yielded bis(phospholanes) **13c−e** as white solids.

1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-dihydroxy-2,5-di-*n*-propylphospholanyl]benzene (13c): Yield: 0.73 g, 71.9%; m.p. 100−103 °C. $[\alpha]_D^{26}$ = +103.7 (*c* = 0.52, MeOH). ^{1}H NMR (400 MHz, MeOD): δ = 0.69−0.72 (t, 6 H, CH_3), 0.77−0.82 (t, 6 H, CH_3), 1.12−1.36 (m, 12 H, CH_2), 1.53−1.66 (m, 2 H, CH_2), 1.68−1.83 (m, 2 H, CH_2), 2.53−2.66 (m, 2 H, CH), 2.82−2.89 (m, 2 H, CH), 4.14−4.19 (m, 4 H, CH), 7.18−7.22 (m, 2 H, $CH_{arom.}$), 7.89−7.93 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR: δ = 14.9, 15.0, 23.8, 24.4, 30.6, 32.9, 41.7, 45.3, 80.0, 81.0, 129.1, 135.3, 144.8 ppm. ^{31}P NMR: δ = −10.36 (s) ppm. MS (CI): *m*/*z* = 483 [MH^+]. $C_{26}H_{44}O_4P_2$ (482.5): calcd. C 64.72, H 9.19; found C 62.77, H 9.00.

1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-dihydroxy-2,5-diisopentylphospholanyl]benzene (13d): Yield: 1.13 g, 90.2%; m.p. 150−155 °C. $[\alpha]_D^{24}$ = +89.2 (*c* = 0.25, MeOH). ^{1}H NMR (400 MHz, MeOD): δ = 0.68−0.81 (m, 24 H, CH_3), 0.83−0.90 (m, 4 H, CH), 1.04−1.27 (m, 6 H, CH_2), 1.31−1.40 (m, 4 H, CH_2), 1.42−1.52 (m, 2 H, CH_2), 1.53−1.65 (m, 2 H, CH_2), 1.77−1.91 (m, 2 H, CH_2), 2.50−2.63 (m, 2 H, CH), 2.77−2.87 (m, 2 H, CH), 4.16−4.20 (m, 4 H, CH), 7.18−7.22 (m, 2 H, $CH_{arom.}$), 7.88−7.92 (m, 2 H, $CH_{arom.}$) ppm. ^{31}P NMR: δ = −10.04 (s) ppm. MS (CI): *m*/*z* = 595 [M^+]. $C_{34}H_{60}O_4P_2$ (594.7): calcd. C 68.67, H 10.17; found C 66.22, H 9.89.

1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-2,5-dibenzyl-3,4-dihydroxyphospholanyl]benzene (13e): Yield: 0.81 g, 56.9%; m.p. 178−183 °C. $[\alpha]_D^{24}$ = +37.9 (*c* = 0.174, MeOH). ^{1}H NMR (400 MHz, MeOD): δ = 2.05−2.27 (m, 2 H, CH_2), 2.75−2.85 (m, 2 H, CH_2), 2.89−3.04 (m, 4 H, CH_2), 3.06−3.18 (m, 2 H, CH), 3.31−3.43 (m, 2 H, CH), 3.83−3.93 (m, 2 H, CH), 3.99−4.06 (m, 2 H, CH), 6.80−7.37 (m, 24 H, $CH_{arom.}$) ppm. ^{31}P NMR: δ = −11.13 (s) ppm. MS (CI): *m*/*z* = 675 [M^+]. $C_{42}H_{44}O_4P_2$ (674.7): calcd. C 74.77, H 6.57; found C 73.34, H 6.58.

General Procedure for the Synthesis of the Rhodium(I) Complexes 14a−e: A solution of 1 equiv. of the corresponding bis(phospholane) **13a−e** in 30 mL of tetrahydrofuran was added to a solution of $[Rh(COD)_2][SO_3CF_3]$ (400 mg, 0.85 mmol) in 50 mL of tetrahydrofuran at room temp. After 3 h of stirring at room temp., the reaction solvents were evaporated to dryness. The orange residue was washed twice with 50 mL of diethyl ether and dried in vacuo.

[{1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-dihydroxy-2,5-dimethylphospholanyl]benzene}Rh^I(COD)] Trifluoromethanesulfonate (14a): Yield: 582 mg, 93.3%. ^{1}H NMR (400 MHz, MeOD): δ = 0.91−0.96 (m, 6 H, CH_3), 1.34−1.40 (m, 6 H, CH_3), 2.17−2.64 (m, 8 H, CH_{2COD}), 2.79−2.89 (m, 4 H, CH), 4.06−4.14 (m, 2 H, CH), 4.16−4.24 (m, 2 H, CH), 5.54−5.61 (m, 2 H, CH_{COD}), 5.95−6.04 (m, 2 H, CH_{COD}), 7.55−7.58 (m, 2 H, $CH_{arom.}$), 8.62−8.66 (m, 2 H, $CH_{arom.}$) ppm. ^{31}P NMR: δ = 78.20 (d) ppm. MS (FAB): *m*/*z* = 581 [(M − $SO_3CF_3^-$)$^+$]. $C_{27}H_{40}F_3O_7P_2RhS$ (730.5): calcd. C 44.39, H 5.52; found C 43.36, H 5.78.

[{1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-dihydroxy-2,4-diethylphospholanyl]benzene}Rh^I(COD)] Trifluoromethanesulfonate (14b): Yield: 615 mg, 91.5%. ^{1}H NMR (400 MHz, MeOD): δ = 0.85−0.88 (t, 6 H, CH_3), 0.93−0.96 (t, 6 H, CH_3), 1.43−1.54 (m, 2 H, CH_2), 1.81−1.91 (m, 2 H, CH_2), 1.91−2.04 (m, 2 H, CH_2), 2.14−2.22 (m, 2 H, CH_2), 2.29−2.65 (m, 8 H, CH_{2COD}), 2.57−2.65 (m, 2 H, CH), 2.67−2.75 (m, 2 H, CH), 4.18−4.34 (m, 4 H, CH), 5.53−5.58 (m, 2 H, CH_{COD}), 5.89−5.95 (m, 2 H, CH_{COD}), 7.54−7.57 (m, 2 H, $CH_{arom.}$), 8.65−8.69 (m, 2 H, $CH_{arom.}$). ^{31}P NMR: δ = 71.50 (d) ppm. MS (FAB): *m*/*z* = 637 [(M − $SO_3CF_3^-$)$^+$]. $C_{31}H_{48}F_3O_7P_2RhS$ (786.6): calcd. C 47.33, H 6.15; found C 46.7, H 6.13.

[{1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-dihydroxy-2,5-di-*n*-propylphospholanyl]benzene}Rh^I(COD)] Trifluoromethanesulfonate (14c): Yield: 679 mg, 94.4%. ^{1}H NMR (400 MHz, MeOD): δ = 0.74−0.80 (m, 12 H, CH_3), 0.82−1.68 (m, 10 H, CH_2), 1.79−1.98 (m, 4 H, CH_2),

2.13−2.26 (m, 2 H, CH_2), 2.27−2.67 (m, 8 H, CH_{2COD}), 2.68−2.76 (m, 2 H, CH), 2.79−2.88 (m, 2 H, CH), 4.12−4.33 (m, 4 H, CH), 5.46−5.57 (m, 2 H, CH_{COD}), 5.88−5.99 (m, 2 H, CH_{COD}), 7.55−7.60 (m, 2 H, $CH_{arom.}$), 8.65−8.69 (m, 2 H, $CH_{arom.}$) ppm. ^{31}P NMR: δ = 71.87 (d) ppm. MS (FAB): *m*/*z* = 693 [(M − $SO_3CF_3^-$)$^+$]. $C_{35}H_{56}F_3O_7P_2RhS$ (842.7): calcd. C 49.89, H 6.70; found C 50.31, H 6.75.

[{1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-dihydroxy-2,5-diisopentylphospholanyl]benzene}Rh^I(COD)] Trifluoromethanesulfonate (14d): Yield: 763 mg, 93.5%. ^{1}H NMR (400 MHz, MeOD): δ = 0.66−0.69 (m, 12 H, CH_3), 0.78 (d, 6 H, CH_3), 0.83 (d, 6 H, CH_3), 0.86−0.95 (m, 4 H, CH), 0.99−1.66 (m, 12 H, CH_2), 1.71−1.83 (m, 2 H, CH_2), 2.00−2.14 (m, 2 H, CH_2), 2.14−2.65 (m, 8 H, CH_{2COD}), 2.65−2.80 (m, 4 H, CH), 4.15−4.34 (m, 4 H, CH), 5.50−5.57 (m, 2 H, CH_{COD}), 5.94−6.03 (m, 2 H, CH_{COD}), 7.53−7.61 (m, 2 H, $CH_{arom.}$), 8.62−8.69 (m, 2 H, $CH_{arom.}$) ppm. ^{31}P NMR: δ = 73.36 (d) ppm. MS (FAB): *m*/*z* = 805 [(M − $SO_3CF_3^-$)$^+$]. $C_{43}H_{72}F_3O_7P_2RhS$ (954.9): calcd. C 54.09, H 7.60; found C 52.00, H 7.47.

[{1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-2,5-dibenzyl-3,4-dihydroxyphospholanyl]benzene}Rh^I(COD)] Trifluoromethanesulfonate (14e): Yield: 803 mg, 90.9%. ^{1}H NMR (400 MHz, MeOD): δ = 2.19−2.63 (m, 8 H, CH_{2COD}), 2.68−2.89 (m, 4 H, CH_2), 2.91−2.99 (m, 2 H, CH_2), 3.00−3.08 (m, 2 H, CH_2), 3.09−3.24 (m, 2 H, CH), 3.41−3.53 (m, 2 H, CH), 3.91−4.16 (m, 4 H, CH), 5.41−5.49 (m, 2 H, CH_{COD}), 6.04−6.11 (m, 2 H, CH_{COD}), 6.77−8.85 (m, 24 H, $CH_{arom.}$) ppm. ^{31}P NMR: δ = 72.40 (d) ppm. MS (FAB): *m*/*z* = 885 [(M − $SO_3CF_3^-$)$^+$]. $C_{51}H_{56}F_3O_7P_2RhS$ (1034.8): calcd. C 59.19, H 5.45; found C 58.04, H 5.38.

{1,2-Bis[(2*S*,3*S*,4*S*,5*S*)-3,4-dihydroxy-2,5-dimethylphospholanyl]benzene}Pd^{II}Cl$_2$ (15a): A solution of **12a** (2.10 g, 4.66 mmol) in 50 mL of dichloromethane was added to a solution of [$PdCl_2$(COD)] (1.10 g, 3.85 mmol) in 50 mL of dichloromethane. The yellow solution was stirred for 1 h at room temp. and the solvents were evaporated to dryness. The residue was washed twice with 50 mL of *n*-pentane and dissolved in 50 mL of dichloromethane. On addition of 20 mL of water, and a small amount of hydrochloric acid, a pale yellow powder precipitated. After stirring for 1 h at room temp., the precipitate was filtered off, washed with dichloromethane and dried in vacuo. Yield: 1.87 g, 88.6%. ^{1}H NMR (400 MHz, MeOD): δ = 0.91−0.99 (m, 6 H, CH_3), 1.35−1.44 (m, 6 H, CH_3), 3.09−3.19 (m, 2 H, CH), 3.51−3.60 (m, 2 H, CH), 3.97−4.08 (m, 2 H, CH), 4.15−4.25 (m, 2 H, CH), 7.73−7.79 (m, 2 H, $CH_{arom.}$), 8.49−8.55 (m, 2 H, $CH_{arom.}$) ppm. ^{31}P NMR: δ = 104.99 (s) ppm. MS (FAB): *m*/*z* = 513 [(M − Cl^-)$^+$]. $C_{18}H_{28}Cl_2O_4P_2Pd$ (547.7): calcd. C 39.47, H 5.15; found C 39.47, H 5.09.

General Procedure for the Asymmetric Hydrogenation: Hydrogenation reactions were performed using standard Schlenk techniques. Methanol Secco Solv was purchased from Merck and stored over molecular sieves. In a Schlenk tube, the corresponding Rh^I complex, **9a**−**g**, **14a**−**e**, (10 μmol) and **16** (500 mg, 2.44 mmol) or **18** (250 mg, 1.92 mmol) were dissolved in 5 mL of methanol. After three vacuum/nitrogen cycles, followed by one vacuum/hydrogen cycle (1.3 bar), the reaction mixture was stirred at room temp. for 20 h. The reaction products were filtered through a short silica column and subjected to *ee* determination. Conversions were determined by means of ^{1}H NMR spectroscopy.

X-ray Crystallography of 15a and 10f: The crystals used in this study were mounted onto the ends of glass fibers. X-ray data were collected with a STOE IPDS unit (Imaging Plate Diffraction System). Graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) was used. Crystal data are listed in Table 3, together with refinement details. The lattice constants correspond to the temperatures indicated there. Absorption corrections were not applied. The structures were solved by the Patterson method with the SHELXS-86 program.[27] The atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined using the SHELXL-97 program;[28] full-matrix method on F^2 data. Hydrogen atoms were included in the final refinement cycles, except those of atoms C15, C16, C18, C19 and C22 of **10f**, since these were highly anisotropic. The riding model was used for the hydrogen atoms. By using the absolute structure parameter[29] as a criterion, it could be decided which of the enantiomers in both cases corresponds to the crystal investigated, and that in the case of **15a**, $P3_121$ is the correct space group and not $P3_221$. CCDC-177475 and -177476 for **15a** and **10f** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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