Novel Monodentate Phosphoramidites By Chiral Pool Synthesis Starting from D-Mannitol, and Their Pd^{II} and Rh^{I} Complexes

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The new monodentate phosphoramidites **6a**–**e** were prepared in an ex-chiral-pool synthesis from readily available D-mannitol in high yields. A ring opening of 1,2;5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol (**4**) with nucleophiles provides the chiral diols **5a**–**e** with different steric demand as key intermediates. The ligands **6a**–**e** are synthesized by refluxing **5a**–**e** with hexamethyltriaminophosphane (HMTAP) and lead, after treatment with $[PdCl_2(COD)]$ or $[Rh(COD)_2][SO_3CF_3]$, to the corresponding Pd complex **8a** and rhodium(I) complexes **7a**–**e**, respectively. The *cis*-arrangement of the ligands and the C_2-symmetry of the complexes in the solid state is demonstrated by an X-ray structure investigation performed on **8a**. In addition, variable temperature NMR experiments show that **8a** keeps its C_2-symmetric coordination geometry even at temperatures up to 90 °C (decomposition).

Introduction

Worldwide activity in the development of C_2-symmetric, bridged bisphosphane complexes for asymmetric catalyzed reactions began in the late 1970's and continued strongly until the end of the 1980's. Then, major emphasis was spent on the development of biocatalysts for catalytic organic transformations. It is well known that both enzymes and organometallic complexes occupy their own specific catalytic field. In organometallic chemistry bidentate ligands were supposed to be superior to the monodentate ones as the resulting rigidity of the catalysts favors effective chiral induction.[1] Consequently, monodentate ligands were neglected in asymmetric hydrogenations until Pringle et al. questioned the superiority of bidentate structures. These authors found higher enantioselectivities (92% *ee*) using an asymmetric monophosphonite rather then the corresponding C_2-symmetric diphosphonite in the hydrogenation of methyl-2-acetamido acrylate.[2] Excellent enantioselectivities (>99% *ee*) have also been reported with monodentate phosphites[3] and phosphoramidites,[4,5] inducing a renaissance in the investigation of monodentate ligands of the above type. However, a disadvantage of these species is their limitation to the binaphthol backbone, which does not allow a rational catalyst design.

We report here on a straightforward and highly variable synthetic protocol based on an ex-chiral-pool synthesis starting from D-mannitol[6] to generate monodentate phosphoramidites bearing four stereogenic centers. This approach allows us to introduce a variety of substituents with different steric demand at key positions at the stereogenic centers by using selected nucleophiles in epoxide ring-opening reactions. The structure and dynamic behavior of the corresponding Pd^{II} and Rh^{I} complexes was investigated by a combination of X-ray diffraction in the solid state and variable temperature NMR spectroscopy in solution.

Results and Discussion

The starting material for our synthetic strategy is the commercially available and cheap D-mannitol (**1**), which was converted into the 1,2;3,4;5,6-tri-*O*-isopropylidene derivative (**2**). Subsequent acidic cleavage of two protecting groups yielded the 3,4-*O*-isopropylidene-D-mannitol (**3**) selectively.[7,8] 1,2;5,6-Dianhydro-3,4-*O*-isopropylidene-D-mannitol (**4**) was prepared from **3** in a simple one pot synthesis according to a literature procedure.[9] The stereoisomer 1,2;5,6-dianhydro-3,4-*O*-isopropylidene-L-iditol,[7] with a different configuration at carbon atoms C2 and C5, is also available and provides access to additional chiral diols. Ring-opening reactions using organolithium or Grignard compounds afford the chiral key-diols **5a**−**e**. Nucleophilic attack of $LiAlH_4$ opens the epoxide ring to form (2*R*,3*R*,4*R*,5*R*)-3,4-*O*-isopropylidene-2,3,4,5-hexanetetraol (**5a**).[10] Compounds **5b**−**e** were prepared by treatment with organocuprates − generated from the copper(I) bromide−dimethyl sulfide complex − and the correspond-

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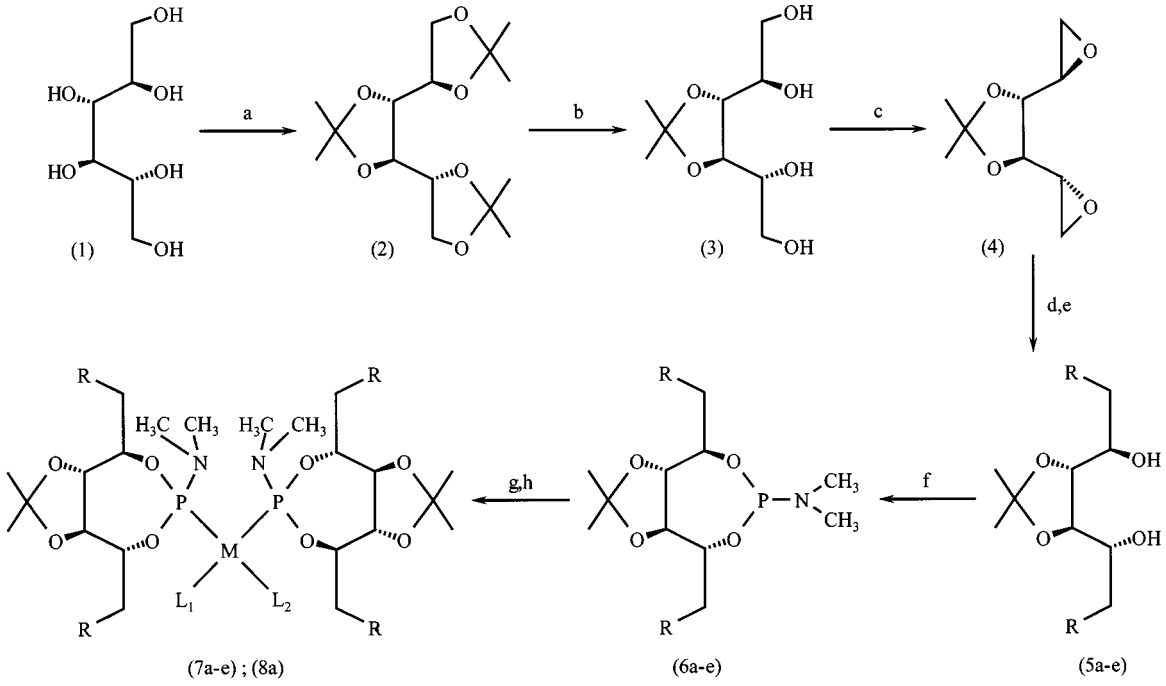

Figure 1. a) acetone, H_2SO_4; b) AcOH, H_2O, 40 °C; c) (i) trimethyl orthoacetate, PPTS, (ii) NEt_3, AcBr, (iii) K_2CO_3, MeOH; d) $LiAlH_4$, Et_2O, R = H; e) CuBr·SMe_2, RMgBr, THF/Et_2O, −40 °C, R = CH_3, C_2H_5, i-C_4H_9, C_6H_5; f) HMTAP, toluene, reflux; g) $Rh^I(COD)_2(SO_3CF_3)$, CH_2Cl_2, **7a**−**e**: M = Rh, L_1-L_2 = COD; h) $Pd^{II}(COD)Cl_2$, CH_2Cl_2, **8a**: M = Pd; L_1,L_2 = Cl

ing alkyl- or phenylmagnesium bromides in diethyl ether.[11] The monodentate phosphoramidites (**6a**−**e**) were formed in high yields by refluxing **5a**−**e** and HMTAP in toluene (Figure 1).

The corresponding yellow-orange Rh^I complexes **7a**−**e** and the pale yellow Pd^{II} complex **8a** were prepared by stirring two equivalents of monodentate ligand **6a**−**e** with $[Rh(COD)_2][SO_3CF_3]$ or $[PdCl_2(COD)]$ in dichloromethane.

We were not able to obtain suitable crystals of one of the rhodium(I) complexes for X-ray diffraction, but we succeeded in crystallizing the isoelectronic Pd^{II} species **8a** from methanol. Its X-ray structure clearly shows the *cis*-coordination of the two monodentate phosphoramidite ligands **6a** and the expected square-planar coordination environment of Pd^{II} (Figure 2a, Table 1) with a chiral, C_2-symmetric arrangement of both P ligands (Figure 2b).

No sign of other diastereomers (rotamers) could be found, indicating a stable chiral conformation, at least in the solid state. The side-view (Figure 2b) furthermore shows that the tunable substituents (Figure 1, CH_2−R) of the monodentate phosphoramidites (Figure 2, R = H; C1, C10) occupy the top-left and bottom-right quadrants, thus defining a chiral cage around the metal center, the size of which is determined by the nucleophile used for the epoxide ring-opening. Quadrant diagrams have often been used to explain the achieved enantioselectivity with several known asymmetric diphosphane-rhodium catalysts in hydrogenations. Knowles suggested to use X-ray structures to predict the absolute configuration of hydrogenation products from the chiral cage of the catalyst.[12] We are looking forward to check these predictions in applying **7a**−**e** in the asymmetric hydrogenation of prochiral olefins. The rigidity of the C_2-symmetric ligand arrangement in solution is further supported by variable temperature ^{31}P NMR spectroscopy. The spectra of **8a** show a sharp singlet at δ = 102.49, which remains unaltered between −30 °C and +90 °C (decomposition). The Rh^I complexes **7a**−**e** have ^{31}P NMR spectra with a single sharp doublet. Variable temperature NMR experiments performed on **7a** show an unaltered signal at δ = 118.92 between −30 °C and +60 °C, which again indicates the presence of a single isomer. At higher temperatures a second doublet grows at δ = 86.67, which could be due to a further complex species. This second species undergoes decomposition, as we noticed from a NMR measurement the next day, while the initial Rh^I complex is still present.

Conclusion

We have introduced an efficient, ex-chiral-pool synthetic route to a new family of chiral, monodentate phosphorus ligands with different steric demand. Their corresponding C_2-symmetric Rh^I and Pd^{II} complexes bear two *cis*-arranged ligands both in the solid state and in solution. In addition, the complexes are thermally stable up to 60 and 90 °C, respectively. Due to the variability of the ligand synthesis, changes of the configuration of the stereogenic cen-

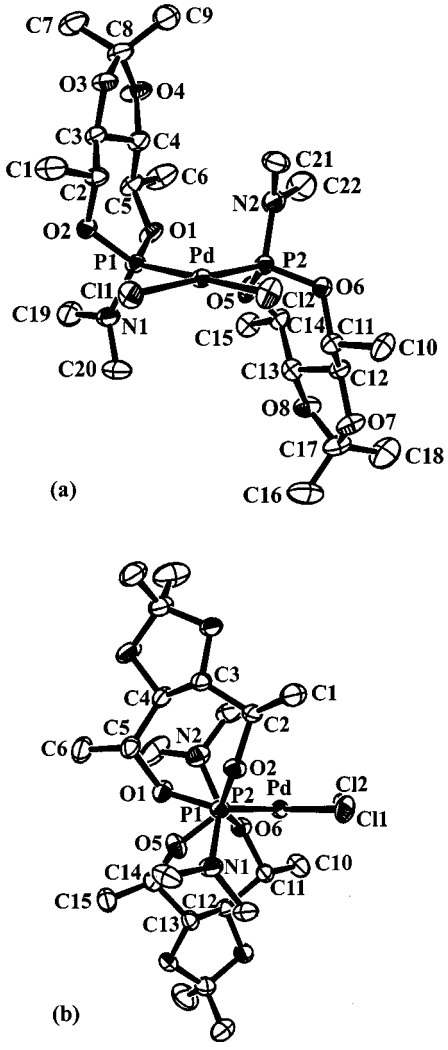

Figure 2. Molecular structure of **8a**; (a) front view: square-planar environment of Pd^{II}; (b) side view: C_2-symmetric arrangement; hydrogen atoms have been omitted for clarity

ters (Figure 2, C2, C5 and C11, C14) and modifications of their substitution can easily be introduced. This is a prerequisite for adopting the catalysts to new substrates in asymmetric transformations. Investigations on this topic are underway.

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.

Melting points were determined on a Büchi Melting Point B-540 and are uncorrected. Optical rotation was obtained on a POLARmonitor from IBZ Messtechnik. Elemental analyses were carried out on a Elementar Vario EL. Mass spectrometry was performed on a Finnigan MAT, TSQ 7000 (FAB, matrix: 2-nitrophenyloctyl ether) and a Finnigan MAT, SSQ 7000 (CI: CH_4. EI: 70 eV). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on 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.

Table 1. Selected bond lengths [Å] and angles [°] in **8a**

Bond lengths			
Pd−Cl1	2.3461(9)	C1−C2	1.500(4)
Pd−Cl2	2.3416(10)	C2−C3	1.510(4)
Pd−P1	2.2462(9)	C3−C4	1.507(4)
Pd−P2	2.2360(9)	C4−C5	1.519(4)
P1−O1	1.592(2)	C5−C6	1.503(5)
P1−O2	1.6082(18)	C7−C8	1.495(5)
P1−N1	1.620(3)	C8−C9	1.513(5)
N1−C19	1.474(4)	O3−C3	1.419(3)
N1−C20	1.461(4)	O3−C8	1.438(4)
O1−C5	1.459(3)	O4−C4	1.422(4)
O2−C2	1.462(3)	O4−C8	1.447(4)
Bond angles			
Cl1−Pd−Cl2	88.90(3)	C1−C2−C3	113.4(2)
P1−Pd−Cl1	86.92(3)	C2−C3−C4	115.7(2)
P1−Pd−P2	93.05(3)	C2−C3−O3	111.3(2)
P2−Pd−Cl2	91.16(3)	C3−O3−C8	105.7(2)
P1−Pd−Cl2	175.49(3)	O3−C3−C4	101.7(2)
P2−Pd−Cl1	179.10(3)	O3−C8−C7	107.7(3)
Pd−P1−O1	117.44(8)	O3−C8−C9	110.1(3)
Pd−P1−O2	112.22(7)	O3−C8−O4	105.8(2)
Pd−P1−N1	113.58(9)	C7−C8−C9	114.3(3)
O1−P1−O2	103.26(11)	C7−C8−O4	110.4(3)
O1−P1−N1	103.78(13)	C9−C8−O4	108.2(3)
O2−P1−N1	105.27(13)	C8−O4−C4	107.1(2)
P1−N1−C19	120.8(2)	O4−C4−C5	111.3(2)
P1−N1−C20	122.9(2)	O4−C4−C3	101.1(2)
C19−N1−C20	116.2(3)	C3−C4−C5	116.4(3)
P1−O1−C5	129.59(18)	C4−C5−C6	113.8(3)
P1−O2−C2	121.45(18)	C4−C5−O1	108.4(2)
C1−C2−O2	108.6(3)	O1−C5−C6	105.8(2)
C3−C2−O2	104.1(2)		

Synthesis of Chiral Diols 5a−e: The diols **5a** and **5b** were prepared according to known procedures.[10,11]

General Procedure for the Synthesis of 5c−e: $CuBr{\cdot}SMe_2$ (3 mmol) was added to a stirred suspension of the appropriate alkyl- or phenylmagnesium bromide (120 mmol) in diethyl ether (100 mL) at −40 °C. After stirring at −40 °C for 2 h, **4** (30 mmol) in 30 mL tetrahydrofuran was added. After 1 h stirring at room temperature the mixture was poured into a saturated aqueous NH_4Cl solution. The organic layer was extracted, washed with water, dried over Na_2SO_4 and the solvents evaporated to dryness to give the pure products **(5c−e)** after flash chromatography (eluting with hexane/EtOAc; 7:3).

(4*R*,5*R*,6*R*,7*R*)-5,6-*O*-isopropylidene-4,5,6,7-decanetetraol (5c): Oil. Yield: 6.78 g, 91.8%. $[\alpha]_D^{23} = +25.8$ ($c = 1.0$, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.61−3.59 (m, 2 H, CH), 3.55−3.49 (m, 2 H, CH), 1.74−1.66 (m, 2 H, CH_2), 1.58−1.45 (m, 2 H, CH_2), 1.45−1.33 (m, 4 H, CH_2), 1.32 (s, 6 H, CH_3), 0.91 (t, 6 H, CH_3). ^{13}C NMR: δ = 108.67, 83.24, 72.88, 36.34, 26.85, 18.26, 14.00. MS (CI): $MH^+ = 391$ (+MSTFA). $C_{13}H_{26}O_4$ (246.3): calcd. C 63.39, H 10.64; found C 62.68, H 10.60.

(5*R*,6*R*,7*R*,8*R*)-6,7-*O*-isopropylidene-2,11-dimethyl-5,6,7,8-dodecanetetraol (5d): Oil. Yield: 8.63 g, 95.1%. $[\alpha]_D^{24}$ = +29.2 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.65−3.63 (m, 2 H, CH), 3.55−3.48 (m, 2 H, CH), 1.80−1.71 (m, 2 H, CH_2), 1.60−1.50 (m, 2 H, CH_2), 1.44−1.35 (m, 4 H, CH_2), 1.34 (s, 6 H, CH_3), 1.28−1.18 (m, 2 H, CH), 0.89−0.86 (m, 12 H, CH_3). ^{13}C NMR: δ = 108.72, 83.16, 73.48, 34.20, 32.06, 28.11, 26.90, 22.81, 22.38. MS (CI): MH^+ = 447 (+MSTFA). $C_{17}H_{34}O_4$ (302.5): calcd. C 67.51, H 11.33; found C 66.37, H 10.97.

(2*R*,3*R*,4*R*,5*R*)-3,4-*O*-Isopropylidene-1,6-diphenyl-2,3,4,5-hexanetetraol (5e): Oil. Yield: 9.20 g, 89.6%. $[\alpha]_D^{23}$ = +43.2 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33−7.20 (m, 10 H, $CH_{arom.}$), 3.82−3.72 (m, 4 H, CH), 3.18−3.13 (m, 2 H, CH_2), 2.74−2.68 (m, 2 H, CH_2), 1.48 (s, 6 H, CH_3). ^{13}C NMR: δ = 137.66, 129.68, 128.39, 126.42, 109.02, 82.34, 73.54, 40.26, 26.93. MS (CI): MH^+ = 343 (+MSTFA). $C_{21}H_{26}O_4$ (342.4): calcd. C 73.66, H 7.65; found C 72.56, H 7.63.

General Procedure for the Synthesis of 6a−e: Chiral diols **5a−e** (6.5 mmol), HMTAP (8.23 mmol) and 10 mg NH_4Cl were refluxed in toluene for 7 h. The mixture was concentrated under reduced pressure affording an oil. The oil was stirred in a small amount of diethyl ether, after which crystals formed.

(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-Isopropylidene-2-dimethylamino-4,7-dimethyl-1,3,2-dioxaphosphepane-5,6-diol (6a): Yield: 1.66 g, 97.2%; m.p. 70 °C. $[\alpha]_D^{23}$= +10.2 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.95−3.85 (m, 3 H, CH), 3.53−3.48 (m, 1 H, CH), 2.58 (s, 3 H, N−CH_3), 2.56 (s, 3 H, N−CH_3), 1.38 (d, 3 H, CH_3), 1.34 (s, 6 H, CH_3), 1.33 (d, 3 H, CH_3). ^{13}C NMR: δ = 109.30, 83.72, 83.59, 72.39, 71.16, 35.00, 34.81, 26.95, 21.25, 19.98. ^{31}P NMR: δ = 142.71 (s). MS (CI): MH^+ = 264. $C_{11}H_{22}NO_4P$ (263.3): calcd. C 50.18, H 8.42, N 5.32; found C 49.16, H 8.35, N 5.40.

(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-isopropylidene-2-dimethylamino-4,7-diethyl-1,3,2-dioxaphosphepane-5,6-diol (6b): Yield: 1.77 g, 93.7%; m.p. 44 °C. $[\alpha]_D^{23}$= +31.3 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.86−3.70 (m, 3 H, CH), 3.60−3.55 (m, 1 H, CH), 2.60 (s, 3 H, N−CH_3), 2.57 (s, 3 H, N−CH_3), 1.88−1.73 (m, 2 H, CH_2), 1.66−1.51 (m, 2 H, CH_2), 1.34 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 0.97 (t, 3 H, CH_3), 0.95 (t, 3 H, CH_3). ^{13}C NMR: δ = 109.29, 82.34, 82.10, 76.68, 75.17, 35.09, 34.89, 27.48, 26.91, 26.31, 9.26, 8.83. ^{31}P NMR: δ = 141.72 (s). MS (CI): MH^+ = 292. $C_{13}H_{26}NO_4P$ (291.3): calcd. C 53.60, H 9.00, N 4.81; found C 51.59, H 9.02, N 5.04.

(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-Isopropylidene-2-dimethylamino-4,7-dipropyl-1,3,2-dioxaphosphe-pane-5,6-diol (6c): yield: 1.94 g, 93.6%; m.p. 87 °C. $[\alpha]_D^{23}$= +36.8 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.88−3.76 (m, 3 H, CH), 3.58−3.54 (m, 1 H, CH), 2.59 (s, 3 H, N−CH_3), 2.57 (s, 3 H, N−CH_3), 1.79−1.65 (m, 2 H, CH_2), 1.64−1.46 (m, 4 H, CH_2), 1.44−1.35 (m, 2 H, CH_2), 1.35 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 0.91 (t, 3 H, CH_3), 0.90 (t, 3 H, CH_3). ^{13}C NMR: δ = 109.32, 82.80, 82.62, 75.35, 74.04, 36.70, 35.46, 35.15, 34.95, 26.94, 26.87, 18.29, 17.89, 13.97. ^{31}P NMR: δ = 141.10 (s). MS (CI): MH^+ = 320. $C_{15}H_{30}NO_4P$ (319.4): calcd. C 56.41, H 9.47, N 4.39; found C 54.43, H 9.30, N 4.73.

(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-Isopropylidene-2-dimethylamino-4,7-di-*iso*-pentyl-1,3,2-dioxaphosphe-pane-5,6-diol (6d): Yield: 2.33 g, 95.3%; mp: 67 °C. $[\alpha]_D^{23}$= +37.5 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.83−3.72 (m, 3 H, CH), 3.58−3.53 (m, 1 H, CH), 2.59 (s, 3 H, N−CH_3), 2.56 (s, 3 H, N−CH_3), 1.83−1.70 (m, 2 H, CH), 1.61−1.46 (m, 4 H, CH_2), 1.45−1.35 (m, 2 H, CH_2), 1.35 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.27−1.18 (m, 2 H, CH_2), 0.88−0.85 (m, 12 H, CH_3). ^{13}C NMR: δ = 109.30, 82.88, 82.61, 75.79, 74.60, 34.16, 33.97, 33.17, 32.97, 31.44, 31.41, 30.26, 30.19, 27.00, 25.97, 25.89, 21.82, 21.45. ^{31}P NMR: δ = 140.83 (s). MS (CI): MH^+ = 376. $C_{19}H_{38}NO_4P$ (375.5): calcd. C 60.78, H 10.20, N 3.73; found C 58.54, H 10.10, N 4.28.

(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-isopropylidene-2-dimethylamino-4,7-dibenzyl-1,3,2-dioxaphosphepane-5,6-diol (6e): Yield: 2.61 g, 96.7%; mp: 64 °C. $[\alpha]_D^{23}$= +29.5 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24−7.12 (m, 10 H, $CH_{arom.}$), 4.02−3.96 (m, 1 H, CH), 3.93−3.88 (m, 2 H, CH), 3.51−3.47 (m, 1 H, CH), 3.09−3.00 (m, 2 H, CH_2), 2.90−2.82 (m, 2 H, CH_2), 2.40 (s, 3 H, N−CH_3), 2.38 (s, 3 H, N−CH_3), 1.41 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3). ^{13}C NMR: δ = 137.78, 137.31, 130.24, 129.99, 127.88, 127.70, 126.16, 126.11, 109.58, 81.46, 81.16, 75.83, 74.05, 40.27, 39.18, 35.01, 34.88, 27.01, 26.89. ^{31}P NMR: δ = 141.30 (s). MS (CI): MH^+ = 416. $C_{23}H_{30}NO_4P$ (415.5): calcd. C 66.49, H 7.28, N 3.37; found C 64.02, H 7.33, N 4.22.

Synthesis of Rhodium(I) Complexes. General Procedure for the Synthesis of 7a−e: A solution of 2 equivalents of the corresponding monodentate phosphoramidite **6a−e** in 20 mL 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 temperature, the solvent was removed under reduced pressure. The resulting orange solid was washed twice with 50 mL pentane and dried in vacuo.

{Bis[(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-isopropylidene-2-dimethylamino-4,7-dimethyl-1,3,2-dioxaphosphepane]Rh(COD)} Trifluoromethanesulfonate (7a): Yield: 557 mg, 98.2%. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.53−5.45 (m, 2 H, CH_{COD}), 5.19−5.11 (m, 2 H, CH_{COD}), 4.33−4.23 (m, 2 H, CH), 4.09−3.99 (m, 2 H, CH), 3.42−3.36 (m, 2 H, CH), 3.30−3.24 (m, 2 H, CH), 3.03−2.98 (m, 12 H, N−CH_3), 2.77−2.31 (m, 8 H, CH_2 $_{COD}$), 1.39 (s, 6 H, CH_3), 1.36 (s, 6 H, CH_3), 1.33 (d, 6 H, CH_3), 1.29 (d, 6 H, CH_3). ^{31}P NMR: δ = 118.92 (d). MS (FAB): $[M - SO_3CF_3^-]^+$ = 737. $C_{31}H_{56}F_3N_2O_{11}P_2RhS$ (886.7): calcd. C 41.99, H 6.37, N 3.16; found C 41.42, H 5.97, N 3.18.

{Bis[(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-isopropylidene-2-dimethylamino-4,7-diethyl-1,3,2-dioxaphosphepane]Rh(COD)} Trifluoromethanesulfonate (7b): Yield: 477 mg, 79.1%. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.60−5.53 (m, 2 H, CH_{COD}), 5.32−5.25 (m, 2 H, CH_{COD}), 4.09−3.98 (m, 4 H, CH), 3.59−3.52 (m, 2 H, CH), 3.39−3.32 (m, 2 H, CH), 3.06−3.01 (m, 12 H, N−CH_3), 2.76−2.33 (m, 8 H, CH_2 $_{COD}$), 1.86−1.77 (m, 4 H, CH_2), 1.77−1.66 (m, 2 H, CH_2), 1.55−1.43 (m, 2 H, CH_2), 1.40 (s, 6 H, CH_3), 1.37 (s, 6 H, CH_3), 0.99−0.91 (m, 12 H, CH_3). ^{31}P NMR: δ = 118.06 (d). MS (FAB): $[M - SO_3CF_3^-]^+$ = 793. $C_{35}H_{64}F_3N_2O_{11}P_2RhS$ (942.8): calcd. C 44.59, H 6.84, N 2.97; found C 45.12, H 6.97, N 2.97.

{Bis[(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-isopropylidene-2-dimethylamino-4,7-dipropyl-1,3,2-dioxaphosphepane]Rh(COD)} Trifluoromethanesulfonate (7c): Yield: 558 mg, 87.2%. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.55−5.46 (m, 2 H, CH_{COD}), 5.29−5.21 (m, 2 H, CH_{COD}), 4.10−3.98 (m, 4 H, CH), 3.55−3.47 (m, 2 H, CH), 3.32−3.27 (m, 2 H, CH), 3.03−2.97 (m, 12 H, N−CH_3), 2.74−2.32 (m, 8 H, CH_2 $_{COD}$), 1.79−1.63 (m, 4 H, CH_2), 1.61−1.50 (m, 2 H, CH_2), 1.49−1.39 (m, 6 H, CH_2), 1.38 (s, 6 H, CH_3), 1.35 (s, 6 H, CH_3), 1.33−1.20 (m, 4 H, CH_2),0.94−0.87 (m, 12 H, CH_3). ^{31}P NMR: δ = 117.93 (d). MS (FAB): $[M - SO_3CF_3^-]^+$ = 849. $C_{39}H_{72}F_3N_2O_{11}P_2RhS$ (998.9): calcd. C 46.89, H 7.26, N 2.80; found C 46.38, H 7.11, N 2.87.

{Bis[(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-isopropylidene-2-dimethylamino-4,7-di-*iso*-pentyl-1,3,2-dioxaphosphepane]Rh(COD)} Trifluoromethanesul-

fonate (7d): Yield: 692 mg, 97.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.55−5.48 (m, 2 H, CH_{COD}), 5.32−5.25 (m, 2 H, CH_{COD}), 4.11−3.96 (m, 4 H, CH), 3.54−3.48 (m, 2 H, CH), 3.36−3.30 (m, 2 H, CH), 3.03−2.97 (m, 12 H, N−CH_3), 2.75−2.32 (m, 8 H, CH_2 $_{COD}$), 1.81−1.69 (m, 4 H, CH_2), 1.68−1.58 (m, 2 H, CH), 1.57−1.46 (m, 4 H, CH_2), 1.45−1.40 (m, 2 H, CH), 1.39 (s, 6 H, CH_3), 1.36 (s, 6 H, CH_3), 1.32−1.11 (m, 8 H, CH_2), 0.91−0.82 (m, 24 H, CH_3). ^{31}P NMR: δ = 118.01 (d). MS (FAB): [M − $SO_3CF_3^-$]$^+$ = 961. $C_{47}H_{88}F_3N_2O_{11}P_2RhS$ (1111.1): calcd. C 50.81, H 7.98, N 2.52; found C 50.35, H 7.91, N 2.68.

{Bis[(4*R*,5*S*,6*S*,7*R*)-5,6-*O*-ispropylidene-2-dimethylamino-4,7-dibenzyl-1,3,2-dioxaphosphe-pane]Rh(COD)} Trifluoromethanesulfonate (7e): Yield: 743 mg, 97.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37−7.08 (m, 20 H, $CH_{arom.}$), 5.47−5.39 (m, 2 H, CH_{COD}), 5.22−5.16 (m, 2 H, CH_{COD}), 4.44−4.38 (m, 2 H, CH), 4.13−4.05 (m, 2 H, CH), 3.53−3.48 (m, 2 H, CH), 3.17−3.10 (m, 2 H, CH), 2.75−2.33 (m, 8 H, CH_2 $_{COD}$), 2.52−2.47 (m, 12 H, N−CH_3), 1.50−1.45 (m, 2 H, CH_2), 1.44 (s, 6 H, CH_3), 1.43−1.36 (m, 2 H, CH_2), 1.32−1.24 (m, 2 H, CH_2), 1.24 (s, 6 H, CH_3), 1.23−1.15 (m, 2 H, CH_2). ^{31}P NMR: δ = 118.35 (d). MS (FAB): [M − $SO_3CF_{33}^-$]$^+$ = 1041. $C_{55}H_{72}F_3N_2O_{11}P_2RhS$ (1191.1): calcd. C 55.46, H 6.09, N 2.35; found C 54.25, H 6.19, N 2.67.

{Bis((4*R*,5*S*,6*S*,7*R*)-5,6-*O*-isopropylidene-2-dimethylamino-4,7-dimethyl-1,3,2-dioxaphosphepane]}$PdCl_2$ (8a): A solution of 2 equivalents of monodentate ligand **6a** in 50 mL 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 temperature for 2 h, the solvent was removed under reduced pressure. Washing the residue twice with 50 mL of diethyl ether and drying in vacuo resulted in a pale yellow powder. Yield: 749 mg, 60.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.82−4.73 (m, 2 H, CH), 4.38−4.31 (m, 2 H, CH), 3.64−3.60 (m, 2 H, CH), 3.49−3.45 (m, 2 H, CH), 2.92−2.89 (m, 12 H, N−CH_3), 1.47 (d, 6 H, CH_3), 1.37 (s, 12 H, CH_3), 1.36 (d, 6 H, CH_3). ^{13}C NMR: δ = 110.05, 83.61, 82.38, 74.13, 37.08, 26.75, 26.55, 18.89, 18.82. ^{31}P NMR: δ = 102.49 (s). MS (FAB): [M − $SO_3CF_3^-$]$^+$ = 669. $C_{22}H_{44}Cl_2N_2O_8P_2Pd$ (703.9): calcd. C 37.54, H 6.30, N 3.98; found C 36.80, H 6.34, N 4.09.

Table 2. Crystal data and refinement details for **8a**

	8a
Formula	$C_{22}H_{44}Cl_2N_2O_8P_2Pd$
M_r	703.83
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	8.098(2)
b (Å)	14.460(2)
c (Å)	13.910(3)
β (°)	96.06(3)
V (Å^3)	1619.6(6)
Z	2
$D_{calcd.}$ (g·cm^{-3})	1.443
μ (mm^{-1})	0.88
Crystal size (mm^3)	0.40 × 0.30 × 0.10
θ range (°)	2.04−25.98
Measured reflections	14673
Unique reflections	5968
R_{int}	0.039
Reflections with $I > 2\sigma(I)$	5543
Goodness-of-fit	1.01
R_1 [F, $I > 2\sigma(I)$]	0.025
R_1 (F, all data)	0.029
wR_2 (F^2, all data)	0.053
Min./max. in ΔF (e·Å^{-3})	−0.46/0.37
Absolute struct. parameter	−0.03

X-ray Crystallography of 8a: The crystal used in this study was mounted onto the end of an glass fiber. X-ray data were collected at −100 °C on a STOE IPDS unit (Imaging Plate Diffraction System). Graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) was used. Crystal data are listed in Table 2 together with refinement details. Absorption corrections were not applied. The structure was solved by the Patterson method with the SHELXS-86 program.[13] The atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined using the SHELXL-97 program;[14] full-matrix method, F^2 data. Hydrogen atoms were included in the final refinement cycles in a riding mode.
Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-165693. 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; Email: deposit@ccdc.cam.ac.uk].

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