Novel P,N Ligands Derived from (*R*)- and (*S*)-1-Phenylethylamine with (2*R*,5*R*)-2,5-Dimethylphospholanyl Groups (DuPHAMIN) for Asymmetric Catalysis

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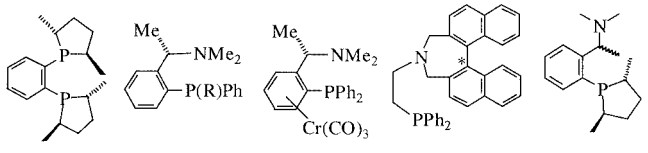
Novel P,N chelating ligands with three stereogenic centres in positions α to the donor atoms have been prepared in good yields and high enantiomeric purity by a series of reactions beginning with either (*R*)- or (*S*)-1-phenylethylamine. These isomers were first lithiated with *t*BuLi and converted into aminophosphanes **3a** by treatment with $(Et_2N)_2PCl$. They were transformed into the enantiomeric primary phosphanes **4** by quantitative solvolysis with ethanol to give the phosphonous acid esters **3b** and subsequent reduction with $LiAlH_4$. Stepwise treatment of **4** with *n*BuLi and the cyclic sulfate of (*S*,*S*)-2,5-hexanediol gave the isomeric tertiary phosphanes (*R*,*RR*)-**5** and (*S*,*RR*)-**5**. Treatment of the aminophosphane (*R*)-**3a** with (*R*)-2,2′-binaphthol yielded the aminophosphonite (*R*,*R*)-**6** in high yields. Cationic (COD)Rh complexes of **5** were prepared by treatment with $[Rh(COD)Cl]_2$, the PF_6^- salts **7a** being isolated. Analogous (2,5-norbornadiene)Rh complexes **7b** were prepared similarly. The chelate nature of the P,N ligands in these salts is indicated by their NMR spectra in solution and is confirmed by the crystal structures of (*R*,*RR*)-**7a** and (*S*,*RR*)-**7a**. With the exception of (*S*,*RR*)-**7a**, the complexes **7a** and **7b** are shown to catalyse the asymmetric hydrogenation of methyl acetamidocinnamate at room temperature. Differences in the catalytic activity of the complexes are related to the different dynamic behaviour detected by the ^1H EXSY spectra for the COD ligands of **7a**.

Introduction

Chiral chelates containing phosphorus and an electronically different donor atom can be highly effective coligands in a variety of transition-metal-catalysed asymmetric reactions. The enantioselectivities achieved in these systems[1] may well be comparable with those obtained by use of the established C_2-symmetrical diphosphanes of the DuPHOS type[2] (**1a**), attributed to the electronic asymmetry in the vicinity of the metallic coordination centre. For instance, the different *trans* effects of the coordinating atoms may enhance the steric influence exerted by the chiral substituents on the optical induction. The application of the concept of electronic disparity[3] has in the last decade resulted in the development of novel bidentate P,N hybrid ligands such as **1b**−**1d**[4] for enantioselective catalysis.[5]



1a **1b** **1c** **1d** **1e**

Ligands of type **1b** are derived from the cheap, commercially available (*R*)- and (*S*)-1-phenylethylamine. We wondered whether it is possible to introduce chiral 2,5-dialkylated phospholane units in place of the P(R)Ph groups of **1b**. Such a synthesis would yield hitherto unknown P,N hybrid ligands **1f** (“DuPHAMIN”) with three stereogenic centres in positions α to the donor atoms P and N. Their catalytic activity would be of particular interest because the interaction of the different types of chiral groups should give “matching” and “mismatching” effects[6] and potentially offer control over stereoselectivity in catalytic reactions.

Results

Lithiation of (*R*)-(+)-**2** with *t*BuLi[7] and subsequent treatment of the organolithium product with $(Et_2N)_2PCl$ gave the aminophosphane (*R*)-(+)-**3a** in 74% yield. (*S*)-(−)-**3a** was analogously derived from (*S*)-(−)-**2**. Solvolysis with ethanol quantitatively formed the corresponding phosphonous acid esters (*R*)-(+)- and (*S*)-(−)-**3b** (Scheme 1). These were reduced with $LiAlH_4$ to yield the two enantiomeric primary phosphanes **4**. The polyphosphane **4b** and the diphosphane **4a** were formed as side products, and these gave further primary phosphane **4** on treatment with potassium and subsequent hydrolysis {(*R*)-**4**: $[\alpha]_D^{20} = 73.3$ (*c* =

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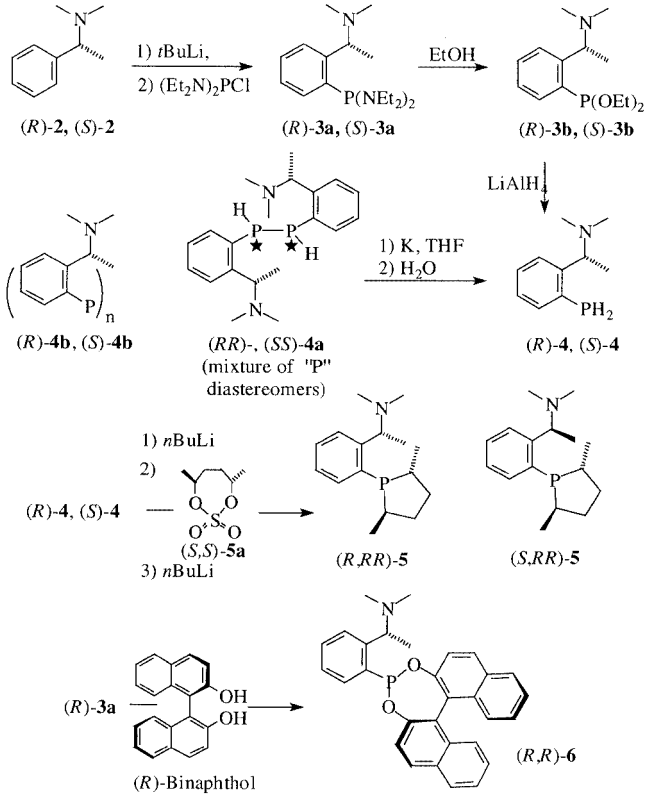
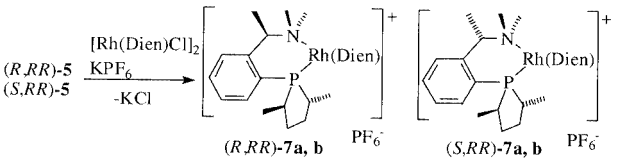
1.1, CH_2C1_2); (*S*)-**4**: $[\alpha]_D^{20} = -74.4$ (c = 1.1, CH_2C1_2)}. Enantiomers **4** each show a triplet in the $^{31}P\{^1H\}$ NMR spectrum at $\delta_P = -121.95$ ($^1J_{PH}$ = 200.5 Hz). No enantiomerically pure phenylphosphane derivatives of type **4** have previously been reported in the literature. They are synthons of broad applicability for the preparation of chiral P,N ligands by structural variation at the reactive PH_2 group. Thus, stepwise treatment of (*R*)-(+)-**4** with *n*BuLi and cyclic sulfate (*S,S*)-**5a**[8] resulted in the formation of the isomeric tertiary phosphanes (*R,RR*)-**5** in 82% yield, while (*S,RR*)-**5** was obtained analogously in 68% yield. They show singlets at $\delta = -7.10$ or -4.53 ppm, respectively, in the $^{31}P\{^1H\}$ NMR spectrum, no signals that might indicate the presence of additional diastereomers being detected. From the optical purity of the starting materials and the unlikelihood of simultaneous inversion of all three stereogenic centres, the enantiomeric purity of the phosphane ligands of type **5** should exceed 98%. The ^1H NMR spectra of (*R,RR*)-**5** and (*S,RR*)-**5** were analysed completely, and the ^1H NMR spectrum of the phospholane group was simulated as an $ABCDMNQ_3R_3X$ spin system {A, B, C, D = ^1H (C_2H_4); M, N = ^1H [C*H*(Me-P); Q, R = ^1H [CH(*Me*-P)]; X = ^{31}P}. As expected, fifteen resonances were observed in the $^{13}C\{^1H\}$ NMR spectra of both (*R,RR*)-**5** and (*S,RR*)-**5**, in part showing $^nJ_{PC}$ doublet fine structure (n = 1−3) (see Exp. Sect.).



Scheme 1. Syntheses of the chiral P,N ligands

Like (*R*)-**4** and (*S*)-**4**, the aminophosphanes (*R*)-**3a** and (*S*)-**3a** may also be employed as starting materials for the modular synthesis of P,N hybrid ligands based on commercially available (*R*)-and (*S*)-1-phenylethylamine. Treatment of (*R*)-**3a** with (*R*)-2,2′-dihydroxy-1,1′-binaphthyl afforded the novel, axially chiral aminophosphonite ligand (*R,R*)-**6** in high yield.

Treatment of each isomer of **5** with [Rh(1,5-cyclooctadiene)Cl]$_2$ or [Rh(2,5-norbornadiene)Cl]$_2$ and subsequent metathesis with KPF_6 gave the stable Rh^I complexes (*R,RR*)-**7a/b** and (*S,RR*)-**7a/b** (Scheme 2). The observation of two resonances for the diastereotopic Me groups of the NMe_2 unit in the ^1H NMR indicates the P,N coordination of both isomers of **5** in the Rh complexes in solution. This is corroborated by the ^{31}P-^{13}C-coupling fine structure [$^3J_{PC}$ = 2.5 Hz, (*R,RR*)-**7a**; 3.4 Hz, (*S,RR*)-**7a**] of one of the $^{13}C\{^1H\}$ NMR signals of the NMe_2 groups.[9] These observations rule out a rapid dissociation of the N donor of **5** on the NMR time scale.



Scheme 2. Syntheses of the complexes (*R,RR*)-**7a**, (*R,RR*)-**7b**, (*S,RR*)-**7a**, and (*S,RR*)-**7b**

Crystal Structures

The crystal structures of (*R,RR*)-**7a** and (*S,RR*)-**7a** have been determined by X-ray diffraction, and drawings of the cations are displayed in Figures 1 and 2. As shown by the distances and angles listed in Tables 1 and 2, good agreement is found for the Rh coordination in the two compounds. The studies confirm the P,N coordination of the novel ligands, the (*R*) configurations of the two carbon atoms α to the phospholane unit and the respective (*R*) and (*S*) configurations of the carbon atom α to the two $CH(Me)NMe_2$ groups.

Inspection of the bottom drawings in Figures 1 and 2 reveals that the inversion of configuration of the benzylic carbon atom is associated with a marked change in the conformation of the $Rh^a-P-C-C-C-N^b$(Rh^a-N^b) chelate ring. Cremer−Pople analysis[10] of their geometries shows that the puckering amplitude of (*S,RR*)-**7a** (0.673 Å) is greater than that of (*R,RR*)-**7a** (0.566 Å). The conformation of the former lies near the half-boat form with the N atom displaced by 0.873(3) Å (rms deviation 0.055 Å) from the plane defined by the other five ring atoms. In contrast, the screw-boat form appears to be the best description of the conformation of the chelate ring in the other isomer, the P1 and α-carbon C1 atoms deviating from the best plane (rms deviation 0.068 Å) of the other four ring atoms by 0.140 and 0.667 Å, respectively.

The methyl group at the α-carbon atom in each structure is found to occupy a pseudoaxial position on the chelate ring, thus avoiding close contact with the neighbouring

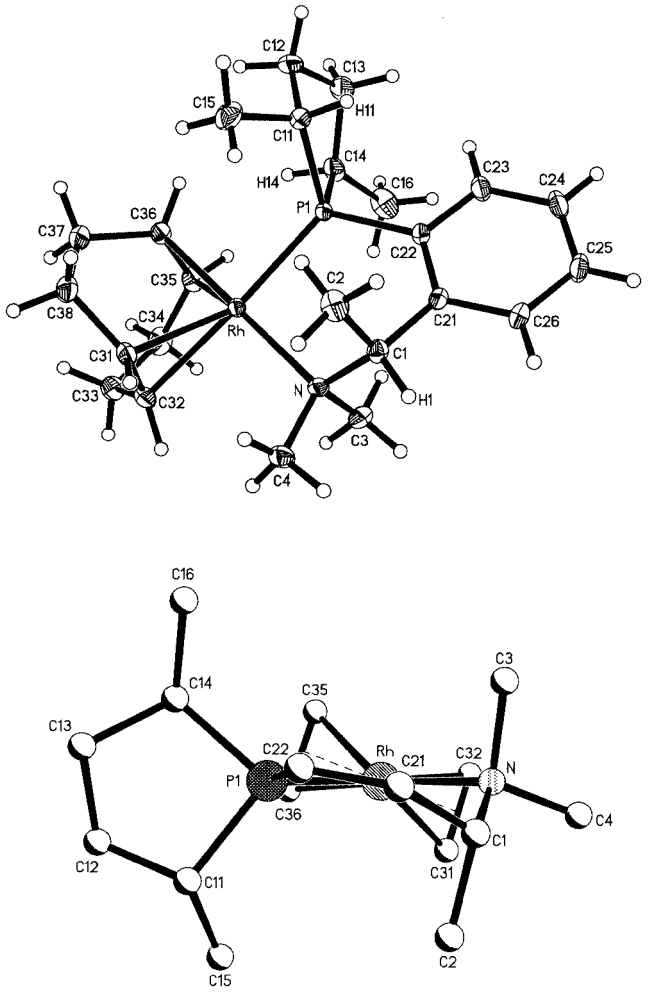


Figure 1. Structure of the cation of (*R*,*RR*)-**7a** (top); front view, showing the orientation of the phospholane group and the chelate ring of (*R*,*RR*)-**7a** (bottom); hydrogen atoms have been omitted for clarity

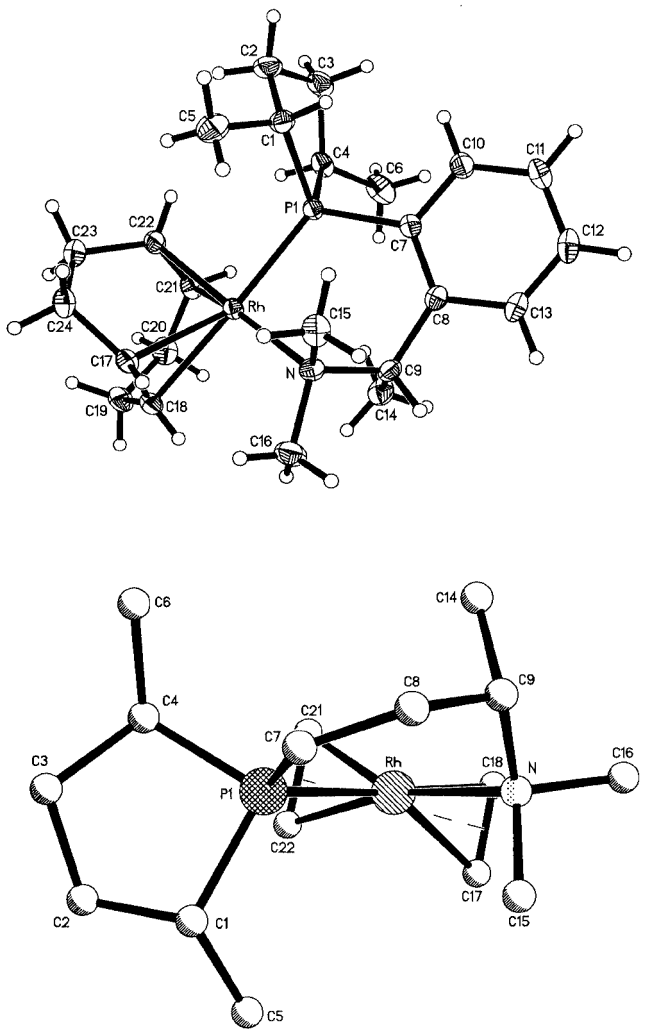


Figure 2. Structure of the cation of (*S*,*RR*)-**7a** (top); front view, showing the orientation of the phospholane group and the chelate ring of (*S*,*RR*)-**7a** (bottom); hydrogen atoms have been omitted for clarity

phenylene hydrogen atom. In (*R*,*RR*)-**7a** this methyl substituent C2 lies on the same side of the chelate ring as the phospholane methyl group C15, which is directed towards the COD ligand. Although these methyl groups are separated by six bonds, they are brought into contact distance [3.823(5) Å] by the screw-boat conformation adopted by the chelate ring. The corresponding methyl groups in (*S*,*RR*)-**7a** lie on opposite sides of the chelate ring. Here, the inwardly directed phospholane methyl group C5 makes a van der Waals contact with the pseudoaxial *N*-methyl group C15 [3.901(8) Å].

The centroids M1 (*trans* to P1) and M2 (*trans* to N) of the C=C double bonds do not lie in the P1−Rh−N plane. The dihedral angle formed by the normals to the M1−Rh−M2 and P1−Rh−N planes is significantly smaller in (*S*,*RR*)-**7a** (14.4°) than in (*R*,*RR*)-**7a** (21.4°). As an inspection of Figures 1 and 2 reveals, the sense of the out-of-plane twist of the COD ligands is the same in the two compounds. Apparently, the orientation of the COD ligands in the solid state reflects the arrangement of the phospholane ring more than it does the disposition of the NMe_2 group. While a similar value was found for this angle in [(COD)Rh{(*R*,*R*)-2,4-bis[(*R*,*R*)-2,5-dimethylphospholano]pentane}]OTf (mean value: 19.3°), a significantly smaller angle (mean 2.6°) was reported for the corresponding (*S*,*S*;*R*,*R*) isomer.[11]

Table 1. Selected distances [Å] and angles [°] in (*R*,*RR*)-**7a**

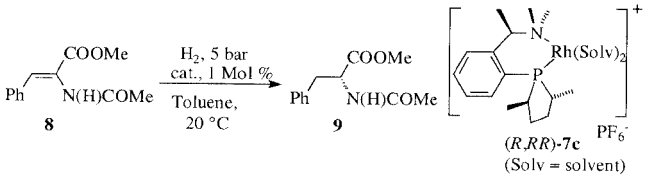
Rh−P1	2.3065(7)	P1−C22	1.830(3)
Rh−N	2.228(2)	N−C1	1.498(3)
Rh−C31	2.207(3)	C1−C2	1.528(4)
Rh−C32	2.292(3)	C1−C21	1.516(4)
Rh−M1	2.145(3)	C21−C22	1.399(4)
Rh−C35	2.114(3)	C31−C32	1.357(5)
Rh−C36	2.145(3)	C35−C36	1.394(4)
Rh−M2	2.012(3)		
N−Rh−P1	92.33(6)	N−C1−C21	116.1(2)
C22−P1−Rh	115.62(9)	C22−C21−C1	125.8(2)
C1−N−Rh	115.9(2)	C21−C22−P1	121.7(2)

Table 2. Selected distances [Å] and angles [°] in (*S*,*RR*)-**7a**

Rh−P1	2.3010(10)	P1−C7	1.837(4)
Rh−N	2.209(3)	N−C9	1.508(5)
Rh−C17	2.194(4)	C7−C8	1.392(5)
Rh−C18	2.275(4)	C8−C9	1.516(6)
Rh−M1	2.132(4)	C9−C14	1.526(6)
Rh−C21	2.114(4)	C17−C18	1.344(7)
Rh−C22	2.155(4)	C21−C22	1.376(7)
Rh−M2	2.021(4)		
N−Rh−P1	89.67(9)	N−C9−C8	115.0(3)
C7−P1−Rh	115.51(13)	C7−C8−C9	126.6(3)
C9−N−Rh	109.0(2)	C8−C7−P1	121.6(3)

Catalytic Properties

The hydrogenation of methyl (*Z*)-α-acetamidocinnamate (**8**) at 20 °C is catalysed by (*R*,*RR*)-**7a**. Under a hydrogen pressure of 5 bar, the (*R*) isomer of **9** was formed with 95% *ee*. (Scheme 3). No reaction was observed when (*S*,*RR*)-**7a** was employed as the catalyst under these conditions. At higher temperature (60 °C) the (*R*) isomer of **9** is formed with 60% *ee*.



Scheme 3. Hydrogenation of methyl (*Z*)-α-acetamidocinnamate

The difference in the activities of the isomers of **7a** indicates that the catalytically active species **7c** is formed more rapidly in the case of (*R*,*RR*)-**7a**. This is supported by the observation that (*R*,*RR*)-**7a**, on treatment at room temperature with hydrogen, yields cyclooctane, identified by ^{1}H NMR spectroscopy, while (*S*,*RR*)-**7a** did not react. The COD ligand in the latter isomer is obviously bound to the transition metal atom much more tightly than in (*R*,*RR*)-**7a**. This is also indicated by the different dynamic behaviour of the COD ligands in the two isomers as derived from the 400 MHz ^{1}H NOESY spectrum of the olefinic hydrogen atoms. While (*R*,*RR*)-**7a** shows EXSY peaks,[12] these are not observed in the case of (*S*,*RR*)-**7a** (Figure 3). This may be interpreted as a result of diolefin rotation[13] causing a rapid exchange of the CH=CH groups *trans* to the N and P atoms.

A simple mechanism for diolefin rotation at our square-planar d^8 transition metal centre is by cleavage of one Rh−olefin bond, rotation around the remaining Rh−olefin bond and recoordination of the free olefin to Rh either *cis* to the nitrogen atom or *cis* to the phosphorus atom. We assume that the addition of dihydrogen in (*R*,*RR*)-**7a** is favoured only during the short interval in which an olefin either is not coordinated or is in a distorted complex geometry. In this case, addition of dihydrogen to (*S*,*RR*)-**7a** at 20 °C may be much slower than that to the (*R*,*RR*) diastereomer because of the absence of diolefin rotation in the former under these conditions.

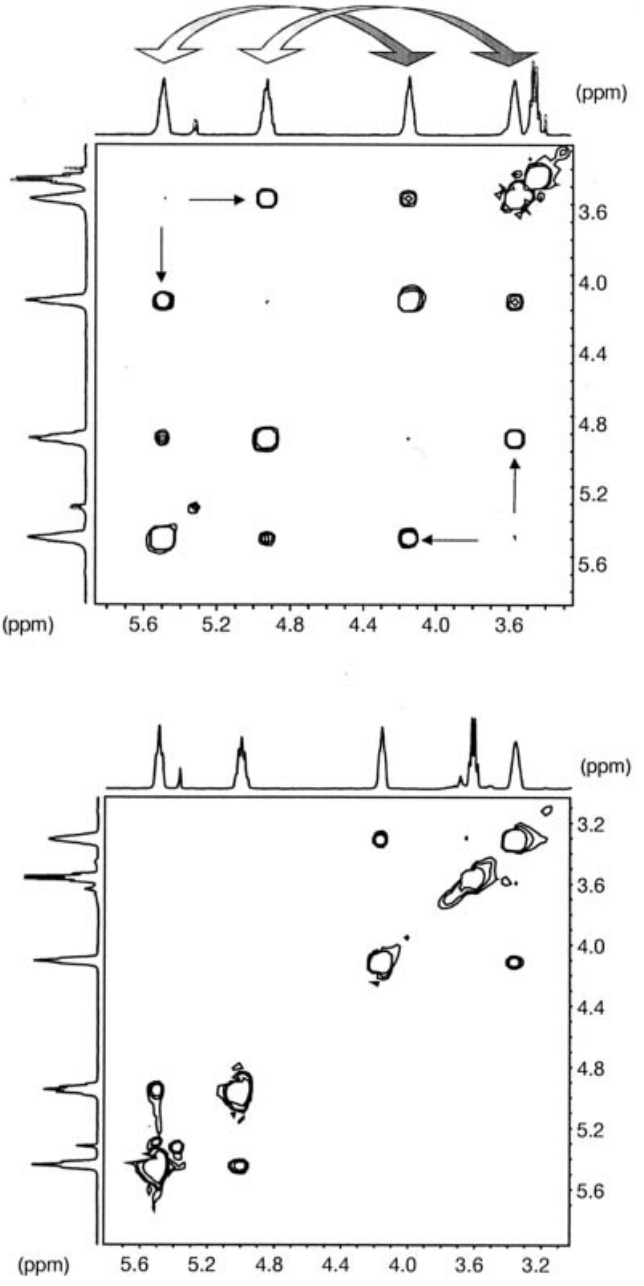


Figure 3. 400 MHz ^{1}H-NOESY spectra at 300 K in CD_2Cl_2 of (*R*,*RR*)-**7a** (top) and (*S*,*RR*)-**7a** (bottom); signals caused by chemical exchange are indicated with arrows; a mixing time of 1.0 s was used

Both norbornadiene complexes (*R*,*RR*)-**7b** and (*S*,*RR*)-**7b** were more active than the corresponding COD complexes. Differences between norbornadiene and COD complexes have also been reported in the literature for related catalytic complexes.[14] With (*R*,*RR*)-**7b** as the pre-catalyst, (*R*)-**9** was formed in 96% *ee*, which is similar to the yield obtained with (*R*,*RR*)-**7a**, while with (*S*,*RR*)-**7b** the hydrogenation product was obtained in only 60% *ee*.

Experimental Section

General: All reactions were performed under nitrogen by use of standard Schlenk techniques. Diethyl ether and pentane were distilled from $LiAlH_4$, THF and toluene from potassium under nitrogen. Dry CH_2Cl_2, methanol and ethanol were purchased from Aldrich in 99.9% purity and used without further purification. (*S*)- and (*R*)-1-Phenylethylamine (> 98% *ee*) were purchased from Aldrich and converted into the *N*,*N*-dimethyl derivatives by literature methods.[15] Enantiomerically pure (*S*,*S*)-2,5-hexanediol (> 99% *ee*) was purchased from Jülich Fine-Chemicals. The cyclic sulfate was prepared by the method described by Sharpless.[16]

NMR: Spectra were recorded with a Bruker ARX 400 MHz NMR spectrometer with use of standard pulse programs for HH-gs-NOESY measurements, spectra with various mixing times (0.1−1.0 s) being recorded. Positive ^1H, ^{13}C, or ^{31}P NMR chemical shifts are upfield from external Me_4Si or H_3PO_4 (85%).

Synthesis of (*R*)- and (*S*)-4

(*R*)-4: A solution of *t*BuLi (1.6 M, 29.0 mL) was added to a solution of (*R*)-**2** (6.91 g, 46.3 mmol) in *n*-pentane (50 mL) and the mixture was stirred at 20 °C for 14 h. The reaction mixture obtained was added at 0 °C to a solution of chlorobis(diethylamino)phosphane (8.86 g, 42.1 mmol) in dry diethyl ether (30 mL). The LiCl produced was removed by filtration, the solvent was evaporated, and the residue was distilled in vacuo (92 °C, 0.1 mbar). The aminophosphane (*R*)-**3a** (yield: 11.1 g, 74%) was dissolved in EtOH (40 mL) and the solution was heated at 60 °C for 48 h. All volatiles were then evaporated, leaving an oily residue, which was distilled in vacuo (76 °C, 0.1 mbar). Yield: 8.96 g (98%) of (*R*)-**3b**. Compound **3b**, as obtained above, was reduced with $LiAlH_4$ (1.18 g, 31.0 mmol) in THF at −30 to 20 °C. After hydrolytic workup of the reaction mixture with water (10.0 mL), the organic phase was separated and the solvent was evaporated. The remaining residue was dissolved in THF (20 mL), potassium (2.42 g, 62.0 mmol) was added, and the reaction mixture was heated at reflux for 4 h. Methanol (10 mL) was then added and the mixture was stirred for 1 h. All volatiles were removed in vacuo and the residue was distilled in vacuo (69 °C, 0.1 mbar). Yield: 4.59 g (76%), $[\alpha]_D^{20} = 73.3$, $c = 1.14$, CH_2Cl_2. (*S*)-**4** was obtained in an analogous manner from (*S*)-**2** as starting material. Yield: 4.21 g (76.0%). $[\alpha]_D^{20} = -74.4$, $c = 1.1$, CH_2Cl_2. ^1H NMR (C_6D_6): 1.13 (d, $J = 6.7$ Hz, 1 H, Me), 2.01 (s, 6 H, NMe), 3.48 (q, $J = 6.7$ Hz, 3 H, CH), 3.91 (dd, $J = 10.8$, 201.4 Hz, 1 H, PH_2), 4.02 (dd, $J = 10.8$, 198.9 Hz, 1 H, PH_2), 6.94 (m, 1 H, arom. H), 7.09 (m, 1 H, arom. H), 7.23 (m, 1 H, arom. H), 7.41 (m, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 15.14 (Me), 41.20 (NMe), 63.65 (d, $J = 6.1$ Hz, CH), 126.66 (d, $J = 2.0$ Hz, arom. C), 126.92 (d, $J = 3.05$ Hz, arom. C), 128.20 (s, arom. C), 130.66 (d, $J = 11.2$ Hz, arom. C), 136.45 (d, $J = 4.1$ Hz, arom. C), 148.55 (d, $J = 11.2$ Hz, arom. C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −121.95 (d, $J = 200.5$ Hz) ppm. MS (EI): $m/z = 181$ [M^+]. $C_{10}H_{16}NP$ (181.2): calcd. C 66.28, H 8.90, N 7.73; found C 65.62, H 8.70, N 7.60.

Synthesis of (*R*,*RR*)- and (*S*,*RR*)-5

(*R*,*RR*)-5: *n*BuLi (1.6 M solution in *n*-hexane, 10 mL) was added at 0 °C to a solution of (*R*)-**4** (2.87 g, 15.8 mmol) in THF (70 mL) and the reaction mixture was stirred at ambient temperature for 30 min. After addition of (*SS*)-**4a** (2.88 g, 15.8 mmol, dissolved in 10 mL of THF), the mixture was stirred for 30 min. Further *n*BuLi (1.6 M solution in *n*-hexane, 15 mL) was added and the reaction mixture was stirred for another 30 min. To remove excess *n*BuLi, methanol (10 mL) was added to the reaction mixture. All volatiles were then removed in vacuo and the remaining residue was distilled in vacuo (98−101 °C, 0.1 mbar) to afford (*R*,*RR*)-**5** as a colourless liquid. Yield 3.40 g (82%). $[\alpha]_D^{20} = +57.5$, $c = 1.1$, CH_2Cl_2. The isomer (*S*,*RR*)-**5** was synthesised in an analogous manner from (*S*)-**4**. Yield: 1.10 g (68%). $[\alpha]_D^{20} = -158.7$, $c = 1.5$, CH_2Cl_2.

(*R*,*RR*)-5: ^1H NMR (C_6D_6): δ = 0.80 (dd, $J = 6.9$, 9.32 Hz, 3 H, Me), 1.26 (m, $J = 2.8$, 6.3, 9.9, 11.6, −13.1 Hz, 3 H, CH_2), 1.28 (dd, $J = 7.2$, 18.7 Hz, 3 H, Me), 1.29 (d, $J = 6.6$ Hz, 6 H, Me), 1.53 (m, $J = 4.7$, 6.0, 10.5, 11.6, −12.8 Hz, 1 H, CH_2), 1.88 (m, $J = 2.6$, 6.3. 6.5, 8.9, −12.8 Hz, 1 H, CH_2), 2.08 (m, $J = 2.6$, 6.0, 7.3, −13.1, 15.0 Hz, 1 H, CH), 2.21 (s, 6 H, NMe), 2.23 (m, $J = 6.5$, 6.9, 10.5, 23.3 Hz, 1 H, CH), 2.52 (m, $J = 5.9$, 7.2, 7.3, 9.9 Hz, 1 H, CH), 4.68 (dq, $J = 6.6$, 9.1 Hz, 1 H, CH), 7.08 (m, $J = 1.5$, 7.4, 7.8 Hz, 1 H, arom. H), 7.22 (m, $J = 1.4$, 7.3, 7.8 Hz, 1 H, arom. H), 7.36 (m, $J = 1.5$, 1.7, 7.5 Hz, 1 H, arom. H), 7.71 (m, $J = 1.4$, 3.6, 7.9 Hz, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 16.44 (d, $J = 1.5$ Hz, Me), 20.99 (d, $J = 36.1$ Hz, Me), 21.11 (s, Me), 34.84 (d, $J = 13.2$ Hz, CH), 36.63 (d, $J = 3.1$ Hz, CH_2), 37.08 (d, $J = 12.2$ Hz, CH), 37.12 (CH_2), 43.48 (Me), 61.11 (d, $J = 26.4$ Hz, CH), 126.07 (arom. C), 127.53 (d, $J = 5.1$ Hz, arom. C), 129.03 (arom. C), 133.27 (d, $J = 3.1$ Hz, arom. C), 135.92 (d, $J = 31.0$ Hz, arom. C), 152.93 (d, $J = 23.4$ Hz, arom. C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −7.10 ppm. MS (EI): $m/z = 263$ [M^+]. $C_{16}H_{26}NP$ (263.4): calcd. C 72.97, H 9.95, N 5.32, P 11.76; found C 72.74, H 10.00, N 5.31, P 11.51.

(*S*,*RR*)-5: ^1H NMR (C_6D_6): δ = 0.84 (dd, $J = 7.0$, 9.1 Hz, 3 H, Me), 1.27 (dd, $J = 7.2$, 18.6 Hz, 3 H, Me), 1.27 (d, $J = 6.6$ Hz, 3 H, Me), 1.30 (m, $J = 3.4$, 6.1, 9.5, 11.2, −13.0 Hz, 1 H, CH_2), 1.53 (m, $J = 5.6$, 5.8, 9.7, 11.2, −12.6 Hz, 1 H, CH_2), 1.92 (m, $J = 3.4$, 6.1, 6.7, 8.8, −12.6 Hz, 1 H, CH_2), 2.07 (m, $J = 3.4$, 5.8, 7.3, −13.0, 14.7 Hz, 1 H, CH_2), 2.15 (s, 6 H, NMe), 2.34 (m, $J = 6.7$, 7.0, 9.7, 23.6 Hz, 1 H, CH), 2.49 (m, $J = 5.4$, 7.2, 7.3, 9.5 Hz, 1 H, CH), 4.53 (dq, $J = 6.8$, 6.9 Hz, 1 H, CH), 7.09 (m, $J = 1.6$, 7.4, 7.6 Hz, 1 H, arom. H), 7.20 (m, $J = 1.6$, 2.1, 7.7 Hz, 1 H, arom. H), 7.40 (m, $J = 1.5$, 3.8, 7.6 Hz, 1 H, arom. H), 7.64 (m, $J = 1.5$, 3.8, 7.7 Hz, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 17.03 (Me), 17.04 (d, $J = 1.5$ Hz, Me), 20.99 (d, $J = 37.1$, Me), 34.88 (d, $J = 13.7$ Hz, CH), 35.62(d, $J = 10.2$ Hz, CH_2), 36.42 (d, $J = 4.6$ Hz, CH), 37.03 (d, $J = 1.5$ Hz, CH), 42.38 (Me), 61.86 (d, $J = 24.4$ Hz, CH), 126.13 (arom. C), 126.60 (d, $J = 5.1$ Hz, arom. C), 128.74 (d, $J = 1.0$ Hz, arom. C), 133.63 (d, $J = 3.6$ Hz, arom. C), 136.31 (d, $J = 31.0$ Hz, arom. C), 152.47 (d, $J = 21.9$ Hz, arom. C) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −4.53 ppm. MS (EI): $m/z = 263$ [M^+]. $C_{16}H_{26}NP$ (263.4): calcd. C 72.97, H 9.95, N 5.32, P 11.76; found C 72.92, H 9.88, N 5.33, P 11.63.

Synthesis of (*R*,*R*)-6: Compound (*R*)-**3a** (1.72 g, 5.34 mmol) was added by syringe to a stirred suspension of (*R*)-2,2′-binaphthol (1.53 g, 5.34 mmol) in dry toluene (30 mL). The mixture cleared immediately and was heated at 80 °C for 2 h. After completion of the reaction, all volatiles were removed in vacuo (0.01 mbar, 40 °C, 12 h) to leave pure (*R*,*R*)-**6** as a colourless, microcrystalline solid. Yield 2.45 g (99%). $[\alpha]_D^{20} = -19.8$ ($c = 0.95$, CH_2Cl_2). ^1H NMR (C_6D_6): δ = 7.75 (m, 2 H), 7.69 (m, 3 H), 7.64 (m, 1 H), 7.59 (m, 1 H), 7.55 (m, 1 H), 7.15 (m, 3 H), 7.02 (m, 4 H), 6.90 (m, 2 H), 6.67 (m, 1 H), 3.89 (q, $J = 6.6$ Hz, 1 H), 2.04 (s, 6 H), 0.95 (qd, $J = 6.6$, 0.9 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 152.74 (d, $J = 1.7$ Hz, arom. C), 150.52 (d, $J = 13.6$ Hz), 147.70 (d, $J = 19.5$ Hz, arom. C), 139.20 (d, $J = 48.0$ Hz, arom. C), 133.73 (d, $J = 1.4$ Hz, arom. C), 133.44 (d, $J = 1.5$ Hz, arom. C), 131.66 (d, $J = 0.7$ Hz, arom. C), 131.29 (s, arom. C), 131.25 (d, $J = 2.3$ Hz, arom. C), 130.56 (d, $J = 0.8$ Hz, arom. C), 130.16 (s, arom. C),

128.94 (d, J = 1.7 Hz, arom. C), 128.78 (s, arom. C), 128.59 (d, J = 0.4 Hz, arom. C), 127.55 (s, arom. C), 127.22 (s, arom. C), 126.80 (s, arom. C), 126.31 (s arom. C), 126.26 (s, arom. C), 125.56 (d, J = 5.7 Hz, arom. C), 25.22 (d, J = 3.2, arom. C), 124.72 (s, arom. C), 124.47 (s, arom. C), 124.36 (d, J = 2.2 Hz, arom. C), 124.00 (s, arom. C), 123.03 (d, J = 1.0 Hz, arom. C), 58.16 (d, J = 7.9 Hz, NMe), 38.38 (d, J = 5.0 Hz, CH), 7.83 (d, J = 3.1 Hz, Me) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 150.2 ppm. MS (EI): m/z = 463 [M^+]. $C_{30}H_{26}NO_2P$ (463.5): calcd. C 77.74, H 5.65, N 3.02, P 6.68; found.: C 77.48, H 5.76, N 3.12, P 6.82.

Rh^I Complexes 7a and 7b: Either (*S*,*RR*)-**5** or (*R*,*RR*)-**5** (0.10 g, 0.38 mmol) was added to a solution of [Rh(1,5-cyclooctadiene)Cl]$_2$ (93.7 mg, 0.19 mmol) or [Rh(2,5-norbornadiene)Cl]$_2$ (87.6 mg, 0.19 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at ambient temperature for 20 min. A solution of KPF_6 (105 mg, 0.57 mmol) in water (5 mL) was added with stirring after 1 h. The aqueous phase was separated and the organic phase was washed with three aliquots of water (10 mL). After addition of a tenfold amount of diethyl ether, the Rh complexes were precipitated as red, crystalline solids in 90−95% yield. Crystals of (*S*,*RR*)- and (*R*,*RR*)-**7a** suitable for X-ray structural analysis could be obtained by slow concentration of the dichloromethane solutions.

Isomer (*S*,*RR*)-7a: $[\alpha]_D^{20}$ = 13.7 (c = 1.1, CH_2Cl_2). ^1H NMR (CD_2Cl_2): δ = 0.91 (dd, J = 6.4, 15.0 Hz, 3 H, Me), 1.81 (m, 1 H, CH_2), 1.82 (dd, J = 6.9, 18.1 Hz, 3 H, Me), 1.97 (m, 1 H, CH_2), 2.20 (m, 2 H, CH/CH_2), 2.26 (d, J = 6.5 Hz, 3 H, Me), 2.34 (s, 3 H, NMe), 2.40 (m, 1 H, CH), 2.53 (m, 1 H, CH_2), 2.70 (s, 3 H, NMe), 2.75 (m, 1 H), 2.87 (m, 1 H,), 3.31 (m, 1 H, olef. H), 3.56 (d, J = 6.5 Hz, 1 H, CH), 4.10 (m, 1 H, olef. H), 5.95 (m, 1 H, olef. H), 5.44 (m, 1 H, olef. H), 7.18 (m, 1 H, arom. H), 7.49 (m, 2 H, arom. H), 7.61 (m, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ =14.05 (d, J = 0.8 Hz, Me), 19.62 (d, J = 9.7 Hz, Me), 23.92 (d, J = 5.6 Hz, Me), 26.03 (d, J = 2.5 Hz, CH_2), 28.90 (d, J = 1.3 Hz, CH_2), 32.47 (s, CH_2), 33.46 (dd, J = 25.9, 1.0 Hz, CH), 35.63 (d, J = 3.8 Hz, CH_2), 36.05 (dd, J = 1.4, 1.4 Hz, CH_2), 38.11 (d, J = 2.3 Hz, CH_2), 44.14 (dd, J = 26.5, 1.3 Hz, CH), 51.57 (d, J =3.4 Hz, NMe), 52.19 (s, NMe), 68.54 (dd, J = 12.1, 1.0 Hz, olef. C), 73.64 (d, J = 6.1 Hz, CH), 81.72 (d, J = 12.5 Hz, olef. C), 100.41 (dd, J = 13.0, 7.1 Hz, olef. C), 106.06 (d, J = 8.4, 6.10 Hz, olef. C), 124.91 (d, J = 23.9 Hz, arom. C), 129.71 (d, J = 4.8 Hz, arom. C), 131.73 (d, J = 8.9 Hz, arom. C), 132.33 (d, J = 2.3 Hz, arom. C), 134.84 (dd, J = 1.1, 1.1 Hz, arom. C), 146.43 (d, J = 14.8 Hz, arom. C) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 28.30 (d, J = 150.4 Hz), −143.2 (sept, J = 710.6 Hz) ppm. $C_{24}H_{38}F_6NP_2Rh$ (619.4): calcd. C 46.54, H 6.18, N 2.26, P 10.00; found C 46.70, H 6.32, N 2.39, P 10.38.

Isomer (*R*,*RR*)-7a: $[\alpha]_D^{20}$ = 21.5 (c = 1.0, CH_2Cl_2). ^1H NMR (CD_2Cl_2): δ = 1.29 (dd, 3 H, J = 7.1, 14.2 Hz, Me), 1.49 (m, 1 H, CH_2), 1.70 (dd, 3 H, J = 7.1, 17.3 Hz, Me), 1.83 (d, J = 6.5 Hz, 3 H, Me), 2.09 (m, 2 H, CH_2), 2.23 (m, 1 H, CH_2), 2.41 (m, 1 H, CH), 2.58 (s, 3 H, NMe), 2.60 (m, 1 H, CH), 2.69 (s, 3 H, NMe), 3.47 (q, J = 6.5 Hz, 1 H CH), 3.58 (m, 1 H, olef. H), 4.15 (m, 1 H, olef. H), 4.93 (m, 1 H, olef. H), 5.50 (m, 1 H, olef. H), 7.0 (m, 1 H, arom. H), 7.48 (m, 2 H, arom. H), 7.60 (m, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ =13.54 (d, J = 1.3 Hz, Me), 18.02 (d, J = 6.6 Hz, Me), 25.89 (d, J = 4.1 Hz, Me), 27.96 (d, J = 2.0 Hz, CH_2), 30.31 (s, CH_2), 31.07 (d, J = 2.5 Hz, CH_2), 33.51 (d, J = 3.1 Hz, CH_2), 35.68 (dd, J = 25.2, 1.0 Hz, CH_2), 35.95 (dd, J = 1.7, 1.7 Hz, CH_2), 38.35 (d, J = 2.0 Hz, CH), 45.93 (dd, J = 25.6, 1.7 Hz, CH), 49.75 (d, J = 2.5 Hz, NMe), 51.11 (s, NMe), 69.52 (dd, J = 11.8, 0.9 Hz, olef. C), 73.15 (d, J = 5.9 Hz, CH), 81.70 (dd, J = 13.1, 0.9 Hz, olef. C), 101.33 (dd, J = 11.6, 7.3 Hz, olef. C), 105.38 (dd, J = 7.9, 7.9 Hz, olef. C), 124.88 (d, J = 23.1 Hz, arom. C), 129.79 (d, J = 5.1 Hz, arom. C), 132.01 (d, J = 2.3 Hz, arom. C), 132.31 (d, J = 8.9 Hz, arom. C), 134.11 (dd, J = 1.0, 1.0 Hz, arom. C), 145.91 (d, J = 14.8 Hz, arom. C) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 25.19 (d, J = 150.4 Hz), −141.0 (sept, J = 710.6 Hz) ppm. $C_{24}H_{38}F_6NP_2Rh$ (619.4): calcd. C 46.54, H 6.18, N 2.26, P 10.00; found C 46.55, H 6.11, N 2.37, P 10.36.

Isomer (*S*,*RR*)-7b: $[\alpha]_D^{20}$ = −100.3 (c = 1.1, CH_2Cl_2). ^1H NMR (CD_3COCD_3): δ = 0.89 (dd, J = 6.9, 14.2 Hz, 3 H, Me), 1.41 (m, 1 H, CH_2), 1.55 (m, 1 H, CH_2), 1.65 (m, 1 H, CH_2), 1.84 (dd, 3 H, J = 7.0, 18.2 Hz, Me), 1.91 (m, 1 H, CH_2), 2.07 (m, 1 H, CH), 2.13 (m, 1 H, CH_2), 2.22 (d, J = 6.6 Hz, 3 H, Me), 2.37 (m, 1 H, CH_2), 2.58 (s, 3 H, NMe), 2.86 (m, 1 H, CH), 2.87 (s, 3 H, NMe), 3.74 (dq, J = 1.6, 6.6 Hz, 1 H, CH), 4.02 (m, 1 H, CH), 4.05 (m, 1 H, olef. H), 4.10 (m, 1 H, CH), 4.16 (m, 1 H, olef. H), 5.43 (m, 1 H, olef. H), 5.67 (m, 1 H, olef. H), 7.29 (m, 1 H, arom. H), 7.49 (m, 1 H, arom. H), 7.52 (m, 1 H, arom H), 7.73 (m, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ = 14.31 (d, J = 2.0 Hz, Me), 18.91 (dd, J = 1.0, 10.7 Hz, Me), 24.35 (d, J = 3.8 Hz, Me), 33.17 (dd, J = 1.8, 28.0 Hz, CH), 36.67 (dd, J = 1.4, 1.4 Hz, CH_2), 38.34 (d, J = 4.3, CH_2), 44.91 (dd, J = 1.4, 26.6 Hz, CH), 50.65 (d, J = 2.8 Hz, NMe), 51.70 (s, NMe), 52.30 (dd, J = 2.0, 2.0 Hz, CH), 53.58 (dd, J = 1.3, 2.8 Hz, CH), 56.28 (d, J = 9.9 Hz, olef. C), 63.74 (d, J = 10.7 Hz, olef. C), 66.61 (dd, J = 1.7, 5.2 Hz, CH_2), 73.34 (d, J = 5.1 Hz, CH), 87.55 (dd, J = 5.3, 10.4 Hz, olef. C), 92.20 (dd, J = 6.2, 8.0 Hz, olef. C), 124.66 (d, J = 24.2 Hz, arom. C), 129.95 (d, J = 5.3 Hz, arom. C), 132.25 (d, J = 9.4 Hz, arom. C), 132.73 (d, J = 2.3 Hz arom. C), 136.08 (dd, J = 1.3, 1.3 Hz, arom. C), 148.52 (d, J = 15.3 Hz, arom. C) ppm. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ = 32.43(d,167.9 Hz), −143.0 (sept, J = 707.4 Hz) ppm. $C_{23}H_{34}F_6NP_2Rh$ (603.4): calcd. C 45.78, H 5.68, N 2.32, P 10.27; found C 45.60, H 5.59, N 2.30, P 10.05.

Isomer (*R*,*RR*)-7b: $[\alpha]_D^{20}$ = −78.1 (c = 1.1, CH_2Cl_2). ^1H NMR (CD_3COCD_3): δ = 1.18 (dd, J = 7.2, 14.2 Hz, 3 H, Me), 1.29 (m, 1 H, CH_2), 1.54 (m, 1 H, CH_2), 1.64 (m, 1 H, CH_2), 1.64 (dd, J = 7.1, 17.6 Hz, 3 H, Me), 1.87 (d, J = 0.5 Hz, 3 H, 6.6 Hz, Me), 1.95 (m, 1 H, CH_2), 2.23 (m, 1 H, CH), 2.27 (m, 1 H, CH), 2.54 (s, 3 H, NMe), 2.57 (m, 1 H, CH), 2.59 (s, 3 H, NMe), 2.61 (m, 1 H, CH), 3.64 (dq, J = 1.9, 6.6 Hz, 1 H, CH), 4.03 (m, 1 H, olef. H), 4.05 (m, 1 H, olef. H), 4.21 (m, 1 H, CH.), 4.32 (m, 1 H, CH), 5.38 (m, 1 H, olef. H), 5.58 (m, 1 H, olef. H), 7.30 (m, 1 H, arom. H), 7.48 (m, 1 H, arom. H), 7.52 (m, 1 H, arom H), 7.65 (m, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ = 14.80 (d, J = 2.53 Hz, Me), 18.15 (dd, J = 1.8, 8.1 Hz, Me), 26.65 (d, J = 3.8 Hz, Me), 35.46 (dd, J = 1.5, 27.0 Hz, CH), 37.11 (dd, J = 1.5, 1.5 Hz, CH_2), 38.51 (d, J = 4.1, CH_2), 46.51 (dd, J = 1.8, 26.2 Hz, CH), 49.64 (d, J = 1.8 Hz, NMe),51.57 (s, NMe), 53.55 (dd, J = 2.0, 2.0 Hz, CH),53.82 (dd, J = 1.3, 2.8 Hz, CH), 56.40 (d, J = 9.9 Hz, olef. C), 65.66 (d, J = 11.2 Hz, olef. C), 67.58 (dd, J = 1.8, 5.3 Hz, CH_2), 72.95 (dd, J = 5.6, CH), 87.22 (dd, J = 5.6, 9.7 Hz, olef. C), 92.01 (dd, J = 6.1, 8.9 Hz, olef. C), 125.17 (d, J = 23.9 Hz, arom. C), 130.73 (d, J = 5.1 Hz, arom. C), 133.13 (d, J = 9.2 Hz, arom. C), 133.20 (d, J = 2.3 Hz, arom. C), 136.38 (dd, J = 1.3, 1.3 Hz, arom. C), 148.80 (d, J = 15.3 Hz, arom. C) ppm. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ = 28.74 (d,167.9 Hz), −143.0 (sept, J = 707.4 Hz). $C_{23}H_{34}F_6NP_2Rh$ (603.4): calcd. C 45.78, H 5.68, N 2.32, P 10.27; found C 45.56, H 5.85, N 2.35, P 10.17.

Asymmetric Hydrogenation Reactions: A 100-mL glass autoclave was charged with a solution of methyl (*Z*)-α-acetamidocinnamate (**8**, 0.40 g, 1.8 mmol) in methanol (15 mL). After repeated vacuum/H_2 cycles, the catalyst (ca. 1 mol %) was added and the autoclave was pressurised to 5 bar with hydrogen. The reactions were allowed

to continue either at 20 °C or at 60 °C and the progress of the hydrogenation was monitored by ^{1}H NMR spectroscopy. After 10−12 h, all volatiles were removed in vacuo, and the residue was dissolved in chloroform (2−3 mL). To remove rhodium catalyst the solutions were filtered through silica gel and the filtrate was concentrated to dryness. Methyl *N*-acetylphenylalaninate (**9**) was obtained as a colourless powder. The *ee* values were determined by HPLC (CHIRACEL, *n*-heptane/2-propanol, flow rate 0.8 mL/h, UV detector) and ^{1}H NMR spectroscopy [chiral shift reagent Eu(hfc)$_3$]. Results are summarised in Table 3.

Table 3. Hydrogenation of methyl (*Z*)-α-acetamidocinnamate (**8**)

Catalyst	*T* [°C]	Time [h]	Yield (%)	*ee* (%)[a]
(*R*,*RR*)-**7a**	20	12	95	96
(*S*,*RR*)-**7a**	60	12	90	60
(*R*,*RR*)-**7b**	20	10	96	95
(*S*,*RR*)-**7b**	20	12	95	60

[a] The (*R*) configuration of **9** was found to be in excess in each case.

X-ray Crystallographic Studies: Crystals were glued to glass fibres and transferred to a Siemens P3 diffractometer, which employed Mo-K_α radiation (0.71073 Å) and was equipped with a graphite monochromator. Intensities were determined at 22 °C by a profile analysis of ω-scans and were corrected for absorption, the correction being made empirically for (*R*,*RR*)-**7a** and by integration for (*S*,*RR*)-**7a**. The structures were solved by direct methods and refined conventionally. Hydrogen atoms were positioned geometrically with the riding model, except for the olefinic hydrogen atoms of (*S*,*RR*)-**7a**, which were refined isotropically. An extinction correction was necessary only for the latter structure. Both structures were solved, refined and depicted with the aid of the SHELXTL program package. Crystal data are summarized in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166313 and -174251 for (*R*,*RR*)-**7a** and (*S*,*RR*)-**7a**, respectively. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Crystallographic data for (*R*,*RR*)-**7a** and (*S*,*RR*)-**7a**

	(*R*,*RR*)-**7a**	(*S*,*RR*)-**7a**
Empirical formula	$C_{24}H_{38}F_6NP_2Rh$	$C_{24}H_{38}F_6NP_2Rh$
Formula mass	619.40	619.40
Crystal system	orthorhombic	trigonal
Space group	$C222_1$	$P3_112$
a [Å]	9.853(2)	10.1362(13)
b [Å]	17.735(3)	10.1362(13)
c [Å]	29.904(5)	44.621(6)
V [Å^3]	5225.6(15)	3970.3(9)
Z	8	6
D(calcd.) [g cm^{-3}]	1.575	1.554
θ range[°]	2.30−30.00	2.32−25.00
Limiting indices	$-13 \le h \le 13$	$-12 \le h \le 9$
	$-24 \le k \le 24$	$-9 \le k \le 12$
	$-42 \le l \le 42$	$-53 \le l \le 53$
Reflections collected	8374	15557
Unique	7623	4648
R(int)	0.0179	0.0279
Observed [$I > 2\sigma(I)$]	6821	4444
Crystal size [mm]	0.80 × 0.70 × 0.30	0.54 × 0.48 × 0.48
μ [mm^{-1}]	0.833	0.822
Transmission	1.00000−0.80946	0.7539−0.7262
R1 (all data)	0.0361	0.0303
*wR*2 (all data)	0.0727	0.0695
Goodness-of-fit on F^2	0.965	1.043
Parameters	314	350
Δ*F* map [e·Å^{-3}]	0.429 to −0.590	0.379 to −0.391
Extinction parameter	−	0.0049(2)
Flack parameter	−0.02(2)	−0.01(3)

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