

Asymmetric Hydrogenation Catalyzed by Cationic Ferrocenylphosphine Rhodium(I) Complexes and the Crystal Structure of a Catalyst Precursor

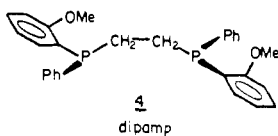
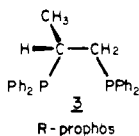
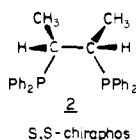
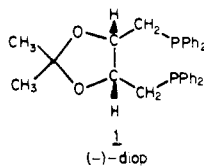
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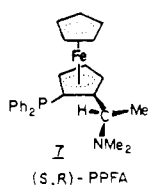
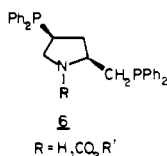
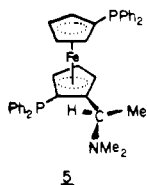
Abstract: The asymmetric hydrogenation of acylaminocinnamic acid and acylaminoacrylic acid is catalyzed by the cationic rhodium(I) complexes $[(+)-\text{or } (-)\text{-PPFA}]\text{Rh}(\text{diene})\text{X}$ [$(+)-\text{or } (-)\text{-PPFA} = (S,R)\text{-or } (R,S)\text{-}\alpha\text{-}(2\text{-diphenylphosphinoferrocenyl})\text{ethylidimethylamine}$, diene = norbornadiene or cyclooctadiene, X = ClO_4 , PF_6 , $\text{B}(\text{C}_6\text{H}_5)_4$, BF_4 , but not all combinations]. The reactions take place in alcohol solutions at 32 °C ($p\text{H}_2 = 1$ atm). The cinnamic acid derivative is hydrogenated in high chemical (~90%) and optical yield (~80%). The acrylic acid is hydrogenated faster but the optical yields are lower. $[(\text{PPFA})\text{Rh}(\text{NBD})]\text{PF}_6$ crystallizes in the space group $P2_1/c$ with $a = 9.406$ (6) Å, $b = 29.68$ (2) Å, $c = 11.600$ (8) Å, $\beta = 94.55$ (3)°, and $Z = 4$. The structure was solved by heavy-atom procedures and refined to a final R_1 of 0.083. The ligand chelates to the metal center through the N and P and the geometry around the rhodium atom is square planar. Models based on this structure indicate that the diastereotopic discrimination necessary for asymmetric reduction to occur probably arises because of steric interactions between the olefin substrate and the bound PPFA ligand. This model successfully predicts the absolute configuration of the products.

In recent years there has been considerable interest in the asymmetric hydrogenation of prochiral olefins catalyzed by rhodium(I) derivatives of chiral phosphines.² In particular the Monsanto Co. is producing L-Dopa by this method using an appropriate amino acid precursor as substrate.³ High optical yields can be obtained using chelating di(tertiary phosphine) ligands such as **1**–**4**^{4–7} among others.^{2c,d,8} Rhodium catalysts



containing chiral diphosphinites are also effective as asymmetric catalysts for olefin hydrogenation² and recently considerable success has been achieved when the backbone of the ligand is a sugar derivative.⁹

The two di(tertiary phosphines) **5**¹⁰ and **6**¹¹ have also been



used as ligands in rhodium(I) complexes which catalyze the hydrogenation of substrates such as (*Z*)- α -acylaminoacinnamic acid and in this paper we describe the use of **7** PPFA in the asymmetric hydrogenation of similar substrates.¹² The ligand **7** is easier to prepare and isolate than **2**–**5**, is readily available in either hand, and seems to be as effective a ligand as **1**.

Although the origin of the diastereotopic discrimination which leads to the high optical yields in these catalytic reactions is unknown, suggestions have been made on the basis of the structures^{7,14} of $[(\text{dipamp})\text{Rh}(\text{COD})]^+$ and $[(\text{chiraphos})-$

$\text{Rh}(\text{COD})]^+$ that the orientation of the four aryl groups on the two phosphorus atoms is important. In this paper we report the structure of $[(\text{PPFA})\text{Rh}(\text{NBD})]\text{PF}_6$ in which the rhodium atom is coordinated by nitrogen and phosphorus and which contains only two phenyl groups which could interact with the substrate.

Experimental Section

Air-sensitive reagents and products were manipulated in a N₂ or Ar atmosphere.

Conductivity measurements were made in nitromethane at 25 °C using a Wayne Kerr Universal Bridge B221A. Infrared spectra were run on a Perkin-Elmer 457 spectrometer and nuclear magnetic resonance spectra on Varian HA-100 and T-60 instruments. Chemical shifts are given in parts per million downfield from internal Me₄Si. Optical rotations were monitored on a Perkin-Elmer 141 polarimeter. Cell lengths of 1 and 10 cm were used and the light source was the sodium D line (589 nm).

N,N-Dimethyl- α -ferrocenylamine was prepared and resolved using (*R*)-(+)-tartaric acid as previously described.¹⁵

Microanalyses were done by Mr. Peter Borda, Chemistry Department, University of British Columbia.

Preparation of (S,R)- and (R,S)- α -(2-Diphenylphosphinoferrocenyl)ethylidimethylamine, (R,S)-(-)-PPFA and (S,R)-(+)-PPFA. The method is based on published reports.^{13,16,17} A solution of *n*-butyllithium in hexane (21 mL, 2.2 M) was added to 10 g of (*R*)-(+)-*N,N*-dimethyl- α -ferrocenylamine in diethyl ether (60 mL) at 23 °C. The mixture was stirred for 1.5 h and slowly treated with chlorodiphenylphosphine (17.5 g). The mixture was refluxed for 2 h. An aqueous slurry (80 mL) of NaHCO₃ was slowly added with stirring (20 min). The precipitate was filtered and washed with diethyl ether until all the yellow compound had been dissolved. The ether was dried (MgSO₄). A brown-yellow solid was obtained by evaporating the ether solution to dryness and cooling the resulting oil to 4 °C overnight. This solid was recrystallized from ethanol to give brown-yellow crystals of (*R,S*)-(-)-PPFA, mp 136 °C, $[\alpha]^{25}_D -364^\circ$ (*c* 0.42, ethanol).

(*S*)-(-)-*N,N*-Dimethyl- α -ferrocenylamine was treated in the same way to give (*S,R*)-(+)-PPFA: mp 135 °C; $[\alpha]^{25}_D +361.4^\circ$ (*c* 0.381, ethanol) [lit. mp 139 °C, $[\alpha]^{25}_D +361^\circ$ (*c* 0.6, ethanol)¹³]; NMR (CDCl₃) 1.17 (d, *J* = 7 Hz, CCH₃), 1.80 (s, N(CH₃)₂), 3.9 (s, FeC₅H₅), 3.5–4.5 (m, FeC₅H₄ and CH), 6.9–7.85 ppm (m, C₆H₅). Anal. Calcd for C₂₀H₂₈FeNP: C, 70.7; H, 6.35; N, 3.17. Found: C, 70.4; H, 6.33; N, 3.14.

Preparation of $[(\text{NBD})\text{Rh}(\text{PPFA})]\text{PF}_6$. A THF solution (2 mL) of PPFA (0.685 g, 1.55 mmol) was added to a solution of $[\text{NBDRhCl}]_2$ ¹⁸ (250 mg, 0.56 mmol) in benzene (8 mL). To the mixture was added

Table I. Crystal Data

$C_{33}H_{36}F_6FeNP_2Rh$	mol wt	781.3
space group $P2_1/c$	μ	11.1 cm^{-1}
a	ρ_0^a	1.59 g cm^{-3}
b	$\rho_c (Z = 4)$	1.608 g cm^{-3}
c	final R_1^b	0.083
β	final R_2^c	0.082
U		3228.2 \AA^3

^a Flotation in aqueous $ZnBr_2$ solution. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum F_o^2)^{1/2}$.

NH_4PF_6 (0.171 g) in acetone. A precipitate formed which was filtered and washed with a small quantity of dichloromethane. The filtrate and washings were concentrated in vacuo to give two liquid phases.

The turbid bottom phase was isolated and concentrated to approximately one-half its volume. A red solid precipitated from the solution after 12 h at $20^\circ C$.¹⁹ This was filtered off, washed with diethyl ether, and dried. The red solid was recrystallized from a minimum quantity of dichloromethane by the addition of ethanol and diethyl ether: mp $192^\circ C$ dec; NMR ($CDCl_3$) 1.78 (d, $J = 6.4$ Hz, CCH_3) 2.42 (s, NCH_3), 3.19 (s, NCH_3), 3.61 (s, FeC_5H_5), 1.46 and 4.14 (s, NBD), 4.44 (m, FeC_5H_5), 7–8.5 (m, C_6H_5); $\Delta = 72.3 \Omega^{-1} \text{ cm}^{-1} \text{ M}^{-1}$. Anal. Calcd for $C_{37}H_{36}FeF_6NP_2Rh$: C, 50.7; H, 4.61; N, 1.79. Found: C, 47.7; H, 4.78; N, 1.48.

Preparation of [(COD)Rh(PPFA)ClO₄]. This was prepared from $Rh(COD)acac$ ²⁰ as described by Schrock and Osborn.²¹ Orange-red crystals, mp $185^\circ C$ dec, were obtained from ethanol. $\Delta = 73.6 \Omega^{-1} \text{ cm}^{-1} \text{ M}^{-1}$. Anal. Calcd for $C_{34}H_{40}ClFeNO_4PRh$: C, 55.2; H, 5.41; N, 1.89. Found: C, 54.6; H, 5.09; N, 1.90.

Similarly were prepared²¹ the following compounds.

[(COD)Rh(PPFA)]BF₄: an orange-red solid, mp $190^\circ C$ dec, recrystallized from ethanol. $\Delta = 73.9 \Omega^{-1} \text{ cm}^{-1} \text{ M}^{-1}$. Anal. Calcd for $C_{34}H_{40}BF_4FeNPRh$: C, 55.2; H, 5.41; N, 1.89. Found: C, 55.2; H, 5.31; N, 1.89.

[(NBD)Rh(PPFA)ClO₄]: an orange-brown solid, mp $190^\circ C$ dec. Anal. Calcd for $C_{33}H_{36}ClFeNO_4PRh$: C, 53.8; H, 4.89; N, 1.90. Found: C, 53.5; H, 4.84; N, 1.83.

[(COD)Rh(PPFA)](C₆H₅)₄: an orange-yellow solid, mp 150 – $152^\circ C$ dec, $\Delta = 50.13 \Omega^{-1} \text{ cm}^{-1} \text{ M}^{-1}$. Anal. Calcd for $C_{58}H_{60}BF_6FeNPRh$: C, 71.7; H, 6.22; N, 1.44. Found: C, 71.4; H, 6.10; N, 1.44.

Preparation of (PPFA)Rh(CO)Cl. Using the procedure of Vallarino²² $Rh(CO)_2Cl_2$ (0.13 g) in benzene (2–5 mL) was treated with 0.3 g of ligand in benzene (25 mL). The resulting complex (immediate reaction) was recrystallized from benzene, mp 124 – $125^\circ C$ (80% yield), IR $\nu(CO)$ 1990 cm^{-1} . Anal. Calcd for $C_{33}H_{34}ClFeNOPRh$: C, 58.2; H, 4.99; N, 2.05; Cl, 5.21. Found: C, 58.1; H, 5.10; N, 1.80; Cl, 5.08.

Preparation of (PPFA)Ni(CO)₃. As described by King²³ PPFA (3.4 g) in diethyl ether was heated with $Ni(CO)_4$ (1.31 g). An orange-yellow solid precipitated. This was washed with diethyl ether to afford orange-yellow crystals: mp $135^\circ C$ (86% yield); IR (C_6H_{12} solution) $\nu(CO)$ 1980, 2000, 2060 cm^{-1} . Anal. Calcd for $C_{29}H_{28}FeNNiO_3P$: C, 59.6; H, 4.79; N, 2.40. Found: C, 59.4; H, 4.83; N, 2.44.

Hydrogenation Experiments. These were conducted in a simple gas uptake apparatus. The reaction flask was maintained at $32^\circ C$ and the H_2 pressure was 1 atm. Details are given in Tables IV and V. Optical yields were calculated on the basis of the reported values for the optically pure compounds (*N*-acetyl-(*R*)-phenylalanine, $[\alpha]_D^{26} -51.8^\circ$ (c 1, EtOH);²⁴ *N*-acetyl-(*S*)-phenylalanine, $[\alpha]_D^{26} +46.0^\circ$ (c 1, EtOH);²⁵ *N*-acetyl-(*R*)-alanine, $[\alpha]_D^{26} +66.5^\circ$ (c 2, H_2O)²⁶) and the pure *S* isomer was assumed to have the same degree of optical rotation but with opposite direction. The reaction products were isolated by removing the solvent under a vacuum. In the case of *N*-acetylphenylalanine the solid was washed with 4 mL of dichloromethane (three times) to remove the catalyst and to avoid a recrystallization from water. For *N*-acetylalanine the solid reaction product was dissolved in 10 mL of water filtered through Celite (two times). The product was obtained by freeze drying this solution.

Structure Determination of [(PPFA)Rh(NBD)]PF₆. Derivatives of chiral and racemic [(PPFA)Rh(NBD)]⁺ and [(PPFA)Rh(COD)]⁺ with various counterions were prepared in attempts to make crystals suitable for X-ray crystallographic studies. In all cases the crystals were small or badly formed. The best crystals which could be obtained were of racemic [(±)-(PPFA)Rh(NBD)]PF₆. An orange single

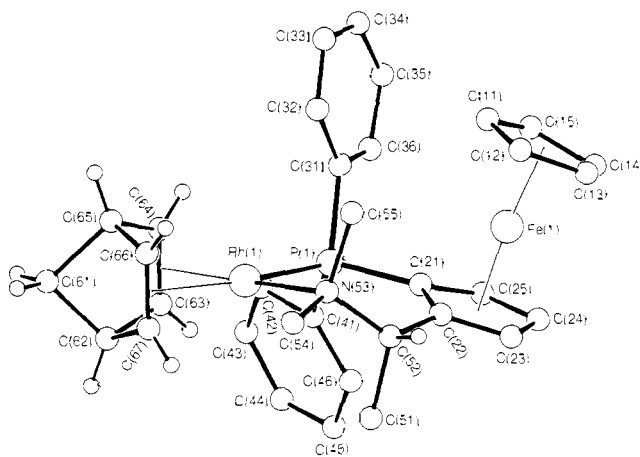


Figure 1. Projected view of the cation showing atomic labeling scheme. Cyclopentadienyl and phenyl hydrogen atoms have been deleted for clarity; each hydrogen atom is given the index of the carbon atom to which it is attached.

crystal $0.22 \times 0.18 \times 0.18 \text{ mm}$ was used in the X-ray study. Photographs taken with $Cu K\alpha$ radiation revealed Laue $2/m$ symmetry and systematic absences which uniquely determined the space group to be $P2_1/c$. Accurate cell dimensions were obtained by least squares from the setting angles of 12 reflections which were accurately centered on a Picker FACS-1 four-circle automated diffractometer employing graphite monochromatized $Mo K\alpha_1$ radiation ($\lambda = 0.70926 \text{ \AA}$). Crystal data are given in Table I.

The intensities of 1318 unique reflections with $3^\circ < 2\theta < 30^\circ$ were measured, and of these 847 with $I > 2.3\sigma_I$ (σ_I is the standard deviation derived from counter statistics and a precision factor of 0.03) were regarded as observed and used in structure solution and refinement. Reflections with $2\theta > 30^\circ$ were generally very weak and therefore were not measured. Data were collected by a θ - 2θ scan running at 2° min^{-1} with a scan width of 1.5° plus a correction for $K\alpha_1$ - $K\alpha_2$ separation. Stationary-crystal, stationary-counter 20-s background counts were measured after every 73 data points. Data were scaled according to the variation in the standards but there was no evidence of decomposition. A temperature of 295 K was maintained throughout. No correction was made for absorption.

Determination and Refinement of the Structure. The structure was solved by conventional heavy-atom procedures. Full-matrix least-squares refinement of all nonhydrogen atoms with isotropic temperature factors yielded a value of 0.097 for R_1 . $Rh(1)$, $Fe(1)$, and $P(2)$ were assigned anisotropic temperature factors in further refinement which resulted in $R_1 = 0.091$. The positions of the nonmethyl hydrogen atoms were determined geometrically (sp^2 or sp^3 geometry at the carbon atom, $r_{C-H} = 0.95 \text{ \AA}$). These atoms were incorporated in further least squares using the temperature factors of the carbon atoms to which they are attached; the parameters were not refined, but were recalculated several times during subsequent refinement. A difference Fourier map at this stage revealed a number of peaks and troughs in the vicinity of the PF_6 anion which suggested that the fluorine atoms should have anisotropic temperature factors. However, they turned nonpositive definite when refined, presumably owing to the weakness of the data set and the low observations/variable ratio (3.7), and so isotropic temperature factors were retained. Final R_1 was 0.083.

In the later stages of refinement a weighting scheme of the form $w = 1/\sigma_F^2$ was used. All shift-to-error ratios were less than 0.1 in the final cycle. Neutral scattering factors were employed²⁷ and anomalous dispersion corrections applied for rhodium, iron, and phosphorus.²⁸ The atom-labeling scheme is shown in Figure 1. Final atomic parameters are given in Table II, interatomic distances and angles in Table III, and least-squares planes in Table IV.

Results and Discussion

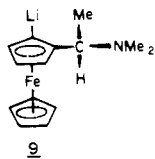
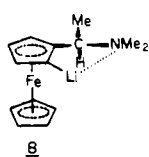
Ugi and co-workers^{15,29} showed that lithiation of (*R*)-*N,N*-dimethyl-1-ferrocenylethylamine affords the stabilized derivative **8** in high yield and in high stereospecificity (95%) with only a small proportion of the diastereomer of structure **9**. Reaction of the mixture with chlorodiphenylphosphine af-

Table II. Final Positional and Thermal Parameters for [(PPFA)Rh(NBD)]PF₆^{a,b}

atom	x	y	z	U
Rh(1)	0.4735(4)	0.4379(1)	0.2922(3)	
Fe(1)	0.7711(7)	0.3073(2)	0.2156(6)	
P(1)	0.5227(12)	0.3682(4)	0.3677(9)	
C(11)	0.624(4)	0.285(2)	0.094(4)	0.04(2)
C(12)	0.741(5)	0.303(2)	0.038(4)	0.06(2)
C(13)	0.850(5)	0.275(2)	0.079(4)	0.05(2)
C(14)	0.811(6)	0.246(2)	0.164(4)	0.09(2)
C(15)	0.664(5)	0.252(2)	0.163(4)	0.05(2)
C(21)	0.696(4)	0.348(1)	0.341(3)	0.04(1)
C(22)	0.800(5)	0.373(2)	0.275(3)	0.04(2)
C(23)	0.924(4)	0.350(1)	0.293(3)	0.03(1)
C(24)	0.903(5)	0.310(2)	0.361(4)	0.07(2)
C(25)	0.768(4)	0.309(2)	0.393(3)	0.04(1)
C(31)	0.401(4)	0.322(2)	0.313(4)	0.03(1)
C(32)	0.323(5)	0.325(2)	0.212(4)	0.06(2)
C(33)	0.240(4)	0.293(2)	0.167(4)	0.04(2)
C(34)	0.236(4)	0.254(2)	0.226(4)	0.05(2)
C(35)	0.308(4)	0.247(1)	0.325(4)	0.04(1)
C(36)	0.391(5)	0.284(2)	0.371(4)	0.06(2)
C(41)	0.518(5)	0.367(1)	0.524(3)	0.04(1)
C(42)	0.383(4)	0.361(1)	0.571(4)	0.04(1)
C(43)	0.381(6)	0.362(2)	0.695(4)	0.09(2)
C(44)	0.510(6)	0.368(2)	0.760(4)	0.08(2)
C(45)	0.643(4)	0.371(1)	0.720(3)	0.02(1)
C(46)	0.647(4)	0.370(1)	0.596(3)	0.01(1)
C(51)	0.845(4)	0.450(1)	0.336(4)	0.06(2)
C(52)	0.785(4)	0.422(1)	0.236(3)	0.03(1)
N(53)	0.653(3)	0.438(1)	0.174(3)	0.04(1)
C(54)	0.678(5)	0.484(2)	0.129(4)	0.07(2)
C(55)	0.601(4)	0.406(1)	0.079(3)	0.03(1)
C(61)	0.189(4)	0.517(1)	0.337(3)	0.05(2)
C(62)	0.338(4)	0.509(1)	0.394(3)	0.03(1)
C(63)	0.342(4)	0.457(1)	0.419(3)	0.03(1)
C(64)	0.254(4)	0.436(1)	0.334(3)	0.03(1)
C(65)	0.211(4)	0.475(1)	0.253(3)	0.05(2)
C(66)	0.336(5)	0.491(2)	0.200(4)	0.06(2)
C(67)	0.424(4)	0.512(1)	0.289(3)	0.03(1)
P(2)	0.080(2)	0.401(1)	0.928(2)	
F(1)	0.068(3)	0.386(1)	1.055(3)	0.12(1)
F(2)	0.097(3)	0.416(1)	0.803(3)	0.16(2)
F(3)	0.145(5)	0.357(2)	0.905(4)	0.20(2)
F(4)	0.024(5)	0.447(2)	0.954(4)	0.24(2)
F(5)	0.237(5)	0.412(1)	0.961(4)	0.22(2)
F(6)	-0.069(5)	0.393(2)	0.895(4)	0.20(2)

atom	Anisotropic Thermal Parameters ($\times 10^3$) ^c					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	36(3)	36(3)	46(3)	-5(3)	10(2)	4(3)
Fe(1)	40(6)	46(7)	56(6)	1(5)	14(4)	-15(5)
P(1)	29(10)	49(11)	30(9)	-3(8)	15(7)	-1(8)
P(2)	79(19)	195(27)	75(16)	47(17)	27(13)	62(15)

^a Estimated standard derivations of the least significant figures are given in parentheses here and in succeeding tables. ^b Positional and thermal parameters for the H atoms are deposited as supplementary material. ^c Anisotropic thermal parameters are in the form $\exp[-2\pi^2(U_{11}h^2a^*2 + \dots + 2U_{23}klb^*c^*)]$.



fords (*R,S*)-PPFA in good yield. Here the “*R*” refers to the configuration at the carbon atom of the -CH(CH₃)NMe₂ group and “*S*” to the chirality of the disubstituted ferrocene ring (planar chirality). The optical isomer (*S,R*)-PPFA (**7**) is obtained by the same procedure from the (*S*)-ferrocenylamine. A crystal structure determination established that (+)-PPFA has the *S,R* configuration.³⁰ Since the ligands **1-4**

are either chiral at phosphorus or in the hydrocarbon backbone it was of interest to study the properties of **7** and its enantiomer because of the existence of two sources of chirality. In addition the ligands contain a very bulky ferrocenyl group which could also show some electronic effects once complexed to a metal.

Nickel carbonyl and PPFA react easily to afford (PPFA)-Ni(CO)₃. Here, only the phosphorus atom is bonded to nickel and we were unable to persuade the ligand to chelate to give the Ni(CO)₂ derivative. Furthermore, even in the presence of excess PPFA only monosubstitution takes place. Chelation does take place when PPFA is reacted with [(CO)₂RhCl]₂. The product (PPFA)Rh(CO)Cl has the -NMe₂ group bonded because the NMR spectrum shows the presence of inequivalent

Table III. Selected Interatomic Distances (Å) and Angles (deg) for [(PPFA)Rh(NBD)]PF₆^{a,b}

Rh(1)-P(1)	2.28(1), 2.31(1)	Rh(1)-N(53)	2.26(3)
Rh(1)-C(63)	2.08(4)	Rh(1)-C(66)	2.27(4)
Rh(1)-C(64)	2.16(4)	Rh(1)-C(67)	2.24(4)
Fe(1)-C(11)	2.00(4)	Fe(1)-C(21)	2.06(4)
Fe(1)-C(12)	2.07(4)	Fe(1)-C(22)	2.08(5)
Fe(1)-C(13)	2.04(4)	Fe(1)-C(23)	2.06(4)
Fe(1)-C(14)	1.97(5)	Fe(1)-C(24)	2.02(5)
Fe(1)-C(15)	2.00(4)	Fe(1)-C(25)	2.06(4)
P(1)-C(31)	1.87(4)	P(1)-C(41)	1.82(4)
P(1)-C(21)	1.79(4)	N(53)-C(52)	1.46(4)
N(53)-C(54)	1.49(5)	N(53)-C(55)	1.49(4)
C(52)-C(22)	1.54(5)	C(52)-C(51)	1.49(5)
C(61)-C(62)	1.52(5)	C(61)-C(65)	1.61(5)
C(62)-C(63)	1.58(5)	C(62)-C(67)	1.52(4)
C(63)-C(64)	1.39(4)	C(67)-C(66)	1.41(5)
C(64)-C(65)	1.53(5)	C(66)-C(65)	1.45(5)
P(1)-Rh(1)-N(53)	95(1)	MP(1)-Rh(1)-MP(2)	71
P(1)-Rh(1)-MP(1)	94	N(53)-Rh(1)-MP(2)	99
P(1)-Rh(1)-MP(2)	165	N(53)-Rh(1)-MP(1)	170
Cp(1)-Fe(1)-Cp(2)	173	Rh(1)-N(53)-C(52)	110(2)
Rh(1)-P(1)-C(21)	113(1)	Rh(1)-N(53)-C(54)	111(3)
Rh(1)-P(1)-C(31)	116(2)	Rh(1)-N(53)-C(55)	104(2)
Rh(1)-P(1)-C(41)	112(1)	C(52)-N(53)-C(54)	108(3)
C(21)-P(1)-C(31)	104(2)	C(52)-N(53)-C(55)	113(3)
C(21)-P(1)-C(41)	105(2)	C(54)-N(53)-C(55)	111(3)
C(31)-P(1)-C(41)	105(2)	C(52)-C(22)-C(21)	125(4)
P(1)-C(21)-C(25)	127(3)	C(52)-C(22)-C(23)	126(4)
P(1)-C(21)-C(22)	125(3)	P(1)-C(41)-C(42)	118(3)
P(1)-C(31)-C(32)	121(4)	P(1)-C(41)-C(46)	120(3)
P(1)-C(31)-C(36)	121(4)	C(51)-C(52)-N(53)	118(4)
C(22)-C(52)-N(53)	120(3)	C(65)-C(61)-C(62)	89(3)
C(22)-C(52)-C(51)	105(3)	C(61)-C(62)-C(67)	100(3)
C(61)-C(62)-C(63)	104(3)	C(62)-C(67)-C(66)	105(3)
C(62)-C(63)-C(64)	108(3)	C(67)-C(66)-C(65)	106(4)
C(63)-C(64)-C(65)	102(4)	C(66)-C(65)-C(61)	98(4)
C(64)-C(65)-C(61)	105(3)	C(63)-C(62)-C(67)	101(3)
C(64)-C(65)-C(66)	110(4)		

^a MP(1) is the midpoint between C(63) and C(64); MP(2) is the midpoint between C(66) and C(67); Cp(1) is the centroid of C(11)-C(15); Cp(2) is the centroid of C(21)-C(25). ^b Average C-C distance in cyclopentadienyl rings is 1.39 (5) Å, in phenyl rings 1.38 (5) Å. ^c Interatomic distance averaged over thermal motion, assuming the atoms to be moving independently.

Table IV. Homogeneous Hydrogenation of α -Acetamidocinnamic Acid^a

catalyst precursor	solvent	time, h	conversion, %	optical yield, %	configuration
[(COD)Rh((-)-PPFA)]ClO ₄	methanol	25	91	80	<i>S</i>
[(COD)Rh(+)-PPFA)]ClO ₄	methanol	25	93	73	<i>R</i>
[(COD)Rh((-)-PPFA)]BF ₄	ethanol	40	83	75	<i>S</i>
[(NBD)Rh((-)-PPFA)]ClO ₄	methanol	25	93	78	<i>S</i>
[(COD)Rh(+)-PPFA)]BF ₄	ethanol	48	91	83	<i>R</i>
[(NBD)Rh(+)-PPFA)]PF ₆	2-propanol	48	>96	80	<i>R</i>
[(NBD)Rh(+)-PPFA)]PF ₆	ethanol	22	88	84	<i>R</i>
[(COD)Rh((-)-PPFA)]B(C ₆ H ₅) ₄	methanol	<i>b</i>	<i>b</i>	<i>b</i>	

^a Reactions were carried out at 1 atm H₂ and 32 °C. The concentration of the catalyst was 1.0 × 10⁻³ M and the substrate 1.0 × 10⁻¹ M. Optical yields are based on the rotation of the isolated product in ethanol. ^b The reaction rate was too low to be measured.

methyl groups. Other examples of similar chelate complexes are known,³¹ although they are not common and are not (P---N) bonded.

Because of this demonstration of chelation to rhodium and because of the effectiveness of cationic complexes such as [(Ph₃P)₂Rh(diene)]PF₆ as catalyst precursors for hydrogenation reactions,³² we prepared similar derivatives of PPFA using well-established procedures.²¹ The NMR spectra of the complexes [(PPFA)Rh(diene)]⁺A⁻ (diene = NBD, COD; A⁻ = PF₆⁻, ClO₄⁻, BF₄⁻, BPh₄⁻, but not all combinations; see Tables IV and V) show inequivalent NCH₃ groups as expected and the complexes are 1:1 electrolytes with conductivities of approximately 74 Ω⁻¹ cm⁻¹ M⁻¹ except for the PPh₄⁻ salt of

[(PPFA)Rh(COD)]⁺, which is considerably lower (50.1 Ω⁻¹ cm⁻¹ M⁻¹). The lower value may indicate some interaction between anion and cation of the sort described below. Attempts to prepare complexes with two PPFA ligands per rhodium(I) atom were unsuccessful.

Confirmation of the chelate structure comes from the X-ray investigation of [(PPFA)Rh(NBD)]PF₆. Within the unit cell there is a racemic mixture of [(+)-PPFA)Rh(NBD)]⁺ and [(-)-PPFA)Rh(NBD)]⁺ cations. The absolute configuration of the former is shown in Figure 1. PPFA coordinates to the Rh atom through the P and N atoms. The Rh atom can be viewed as having a square-planar environment (assuming that each NBD C=C bond is filling a single coordination site). The

Table V. Homogeneous Hydrogenation of α -Acetamidoacrylic Acid^a

catalyst precursor	solvent	time, h	conversion, %	optical yield, %	configuration
[(COD)Rh((-)-PPFA)]BF ₄	methanol	7	100	58	S
[(COD)Rh(+)-PPFA]ClO ₄	methanol	7	100	55	R
[(COD)Rh((-)-PPFA)]ClO ₄	methanol	6	100	43	S
[(COD)Rh((-)-PPFA)]B(C ₆ H ₅) ₄	methanol	92	90	26	S

^a Reactions were carried out at 1 atm H₂ and 32 °C. The concentration of the catalyst was 1.0×10^{-3} M and the substrate 1.0×10^{-1} M. Optical yields are based on the rotation of the isolated product in water.

Rh-P distance of 2.28 (1) Å is similar to those reported in [(S,S-chiraphos)Rh(COD)]⁺ (2.275 and 2.266 (1) Å).¹⁴ In both these complexes the Rh-P bonds are trans to olefin groups. When a Cl atom is in the trans position the Rh-P distance is generally shorter but Rh-P is longer when there is a trans phosphine.³³ The Rh-N bond length is 2.26 (3) Å.

The Rh-C distances are 2.08 and 2.16 (4) Å for one double bond and 2.27 and 2.24 (4) Å for the other. Although the average distance for the former C=C (opposite the N atom) is shorter than for the latter, the esd's are too large to draw any conclusions about the possible asymmetry of the Rh-C distances within each pair. Both equal^{34,35} and unequal³⁶ metal-olefin distances have been reported for NBD complexes. Rh-C distances for the related complexes [Rh₂(COD)₂(2,2'-biimidazole)] (av 2.11 (1) Å),³⁷ [Rh(COD)Cl]₂ (av 2.12 (3) Å),³⁸ and [(S,S-chiraphos)Rh(COD)]⁺ (av 2.243 (5) Å)¹⁴ show that the nature of the other ligands has an appreciable effect on the strength of the Rh-olefin bonds. The C-C distances and angles within the NBD group are within experimental range of their normal values.³⁴

Complexation causes PPFA to assume a different conformation from that found in the crystal structure of the uncoordinated ligand.³⁰ (There is a rotation of 40° about the P(1)-C(21) and of 116° about C(52)-C(22)). The rotation about P(1)-C(21) brings phenyl group 3 into proximity with the ferrocenyl moiety and forces this ring to be "edge-on" to the Rh atom and ring 4 to be "face-on". The ramifications of these steric factors upon the catalytic action of the complex are discussed below. Generally the bond lengths and angles of the PPFA group are similar to those of the free ligand, the exceptions being around C(52) where the angle C(22)-C(52)-N(53) increases from 107.4 (7)³⁰ to 120 (3)° to allow formation of the six-membered chelate ring (angle P(1)-Rh(1)-N(53) is 95 (1)°). A consequence of this is a decrease in angle C(22)-C(52)-C(51) from 114.1 (8) to 105 (3)°.

The model of the PF₆⁻ anion is poor (as is commonly found) owing to its high thermal motion coupled with the other crystallographic problems mentioned above.

The cationic complexes [(PPFA)Rh(diene)]⁺A⁻ are generally good catalyst precursors for the hydrogenation of the acrylic and cinnamic acid derivatives (Tables IV and V). The catalytic species is probably [(PPFA)Rh(solvent)₂]⁺³⁹⁻⁴¹ rather than the hydride [(PPFA)RhH₂]⁺ expected on the basis of the work of Schrock and Osborn.³² Certainly in the absence of substrate H₂ (1 atm, 32 °C) reacts with [(PPFA)Rh(diene)]⁺ with the loss of color. The catalyzed reduction of the cinnamic acid derivative is slower than that of the acrylic acid. The rates are not very dependent on the nature of the anion apart from the PPh₄⁻ derivative, which is inactive in one case and not very effective in the other. This loss of activity is probably due to complex formation between the arene rings and the rhodium(I) center.^{39,42,43} In contrast Knowles and co-workers report that [((±)-ACMP)₂Rh(COD)]PPh₄ (ACMP = *o*-CH₃C₆H₄(CH₃)(C₆H₁₁)P) is as good a catalyst precursor as the same cation complexed with BF₄⁻ or PF₆⁻.⁴⁴ Possibly the difference is due to a different reduction mechanism with the dihydride³² being the active species.

Substrates without acylamino groups such as α -phenylcinnamic acid, α -methylcinnamic acid, β -methylcinnamic acid, and atropic acid are not hydrogenated using the PPFA-based catalyst. These results together with arguments based on optical yields and product configuration suggested to us¹² that bonding of the substrate carbonyl group to the rhodium in addition to the olefinic bond is an important part of the catalytic pathway. Others⁴⁵ have also made this suggestion and recently it has been put on a factual basis by the determination of the crystal structure of [(diphos)RhPhCH=C(COOMe)NHCOME]⁺ (diphos = Ph₂PCH₂CH₂PPh₂) prepared from [(diphos)Rh(solvent)₂]⁺ plus substrate.⁴⁶ Here both C=C and C=O are coordinated to the rhodium. This binding of the substrate at two sites probably accounts for the difference in rates between the more bulky cinnamic acid and acrylic acid derivatives. However, it must be noted that the interaction between substrate and catalyst is very important when optical yields are considered because it is this same interaction which gives rise to the diastereotopic discrimination necessary for asymmetric reactions to occur. Recently Brown and Chaloner⁴¹ have shown that [((+)-diop)Rh(solvent)₂] interacts with only one face of (Z)-PhCH=C(COOH)NHCOPh. Thus the slower rate of reduction of the cinnamic acid correlates with the much higher optical yield of product.

We have built models of the type [((R,S)-PPFA)Rh(substrate)]⁺ and [((R,S)-PPFA)Rh(substrate)H₂]⁺ making the assumption that the substrate is bound at both C=C and C=O and that the H atoms are cis to allow for cis transfer to the olefin. In both cases it is clear that only one face of the substrate can bind easily to the rhodium because of steric interactions and that the bound face if hydrogenated would give rise to the reaction product with the experimentally observed absolute configuration. These repulsive interactions are less in the case of the acrylic acid derivative and hence the discrimination is lower (and the reaction rate faster).

Although these simplistic arguments account for the reactions of the PPFA complexes, they can at best be only part of the whole truth since electronic effects undoubtedly play some part especially when less symmetrical ligands (from an electronic point of view) are bound to the metal center.⁴⁷ The behavior of [((R)-prophos)Rh(COD)]ClO₄ is such that high optical yields are obtained, 90 ± 3%, for the hydrogenation of a range of substrates⁶ in spite of a considerable difference in turnover numbers (e.g., CH₂=C(COOH)NHCOME, 600 h⁻¹, to *p*-MeC₆H₄CH=C(COOH)NHCOME, 50 h⁻¹) corresponding to times of about 0.5–3 h for 100% reaction. Thus the cationic PPFA complexes are not as efficient as those derived from prophos (although they are easier to prepare).

Finally, it should be pointed out that the in situ catalysts derived from **5** and [Rh(1,5-hexadiene)Cl]₂ which are effective for the slow (20 h) hydrogenation (50 atm) of the usual substrates RCH=C(COOH)NHCOME probably have a similar structure to that determined in this investigation (Figure 1). Thus they could be chelated through the P and N atoms on the same ring and not through the two P atoms as assumed by Kumada and co-workers. Shifts between these two bonding possibilities or even to a monodentate phosphine mode could

account for some of the solvent effects on optical yield. For example, in Kumada's system when R = 4-acetoxyphenyl the optical yield of product is 8% in MeOH and 87% in H₂O/MeOH (1:3) and this cannot be discussed without knowing the identity of the catalytic species.¹⁰

In a similar vein in the reduction of ketones by derivatives of **5** and **7** Kumada and co-workers⁴⁸ have shown that MeC-OOH is reduced to MeCHOHCOOH in 16% optical yield. A much higher optical yield (55%, the highest reported for ketone reduction) is obtained if the ligand is modified by replacing the NMe₂ by OH. In the latter case the configuration of the product is also changed. It is likely that this sort of result is due to a change in bonding from P—N to P—P. It is also likely that the bonding in catalysts derived from **6** can vary in a similar manner.

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Supplementary Material Available: Calculated atomic coordinates for H atoms, interatomic distances and angles within the cyclopentadienyl and phenyl rings and PF₆⁻ group, least-squares planes, and a listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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