absorption correction based upon a series of Ψ scans were applied to the data. The structure was solved by standard heavy-atom techniques with the SDP-VAX package.[42] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom H21 was located and refined with fixed isotropic thermal parameters. The remaining hydrogen atom positions were calculated and added to the structure factor calculations but not refined. Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[43]

Acknowledgment. We thank the NSF for support of this research and J. Bakke for preliminary observations and some data for **3g**.

Supplementary Material Available: ^{1}H NMR spectra of **4** in the presence of (+)-Eu(hfc)$_3$ (Figure 2) and tables of additional crystallographic data, bond lengths and angles, hydrogen atom parameters, and anisotropic thermal parameters for **3f** (6 pages); a table of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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Catalytic Asymmetric Hydrogenation of Imines. Use of Rhodium(I)/Phosphine Complexes and Characterization of Rhodium(I)/Imine Complexes

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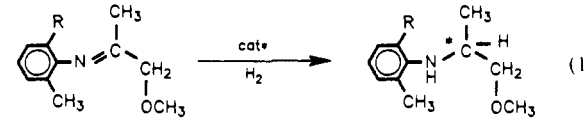
An in situ Rh^I(P-P) catalyst formed from [Rh(NBD)Cl]$_2$ and cycphos (P-P = 1,2-bis(diphenylphosphino)-1-cyclohexylethane) effects asymmetric hydrogenation of some commercially important and model imines in 1:1 benzene/methanol under 1000-1500 psig H_2 from -25 to +25 °C; a maximum of 91% ee is obtained for ArC(Me)=NCH$_2$Ph (Ar = 4-MeOC$_6$H$_4$) in the presence of iodide cocatalyst at -25 °C. Two [Rh(diphos)(imine)$_2$]BF$_4$ complexes have been isolated (diphos = 1,2-bis(diphenylphosphino)ethane): imine **8** = 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (complex **11**) or imine **4** with Ar = 2-MeOC$_6$H$_4$ (complex **16**). Complex **11** crystallizes in the triclinic system, space group $P\bar{1}$, with a = 12.564 (1) Å, b = 21.446 (2) Å, c = 10.521 (1) Å, α = 100.655 (9)°, β = 110.539 (8)°, γ = 79.102 (7)°, and Z = 2, the structure refining to R = 6.8% and R_w = 8.2% for 5881 reflections; the η^1-imines bind via nitrogen in a syn arrangement at the essentially square-planar Rh, while in solution an anti isomer is also evident. Other species [Rh(diphos)(η^1-imine)(MeOH)]$^+$ and Rh(P-P)Cl(η^1-imine), where P-P = diphos or chiral bis(tertiary phosphines), have been characterized in solution, and Rh(diop)(Cl) (**8**) has been isolated (diop = 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane). Complexes [Rh(diphos)(imine)]$^+$ containing a chelated imine (via the nitrogen lone pair and oxygen of a methoxy functionality) exist, but chelation is not essential for effective asymmetric induction. The catalytic hydrogenations appear to occur via an unsaturate route; a plausible intermediate is Rh(P-P)(X)(MeOH)(imine), where X = halide and the alcohol facilitates η^2-(C=N) binding.

Introduction

Although much is known about the asymmetric reduction of alkenes and ketones by dihydrogen, a reaction catalyzed by chiral metal complexes,[1] the analogous hydrogenation of imines has received much less attention.[2,3] Rhodium(I) and iridium(I) derivatives of chiral bis(tertiary phosphines) are the catalysts of choice for the few asymmetric imine reductions studied to date,[2,3] and the present work is concerned with extending our knowledge of the rhodium systems.

Our work in this area began with a search for a catalyst for the asymmetric reduction of the commercially important imines **1** (eq 1).[3a-c] Only the Z form of the E/Z mixture is shown.



(1)

1a R=CH$_3$
b R=C$_2$H$_5$

Optical yields of up to 69% were achieved by using low-temperature, H_2 pressure of >1000 psig, a solvent mixture of MeOH/benzene (or toluene), and a particular chiral bidentate phosphine, cycphos ($Ph_2PCH(C_6H_{11})CH_2PPh_2$), in conjunction with the [Rh(NBD)Cl]$_2$ precursor.[3a-c,4,5] The optimum conditions

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(2) Longley, C. J.; Goodwin, T. J.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1625.

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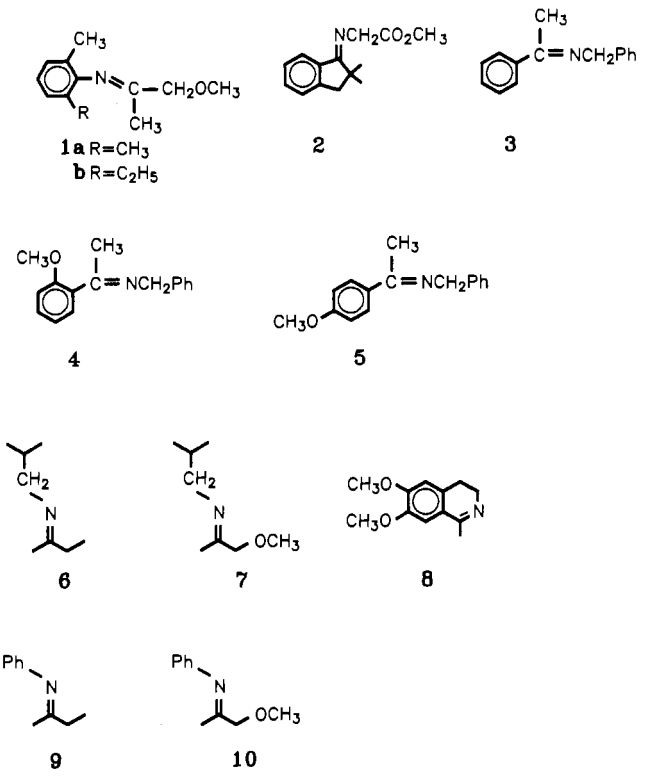
(4) Cycphos = $Ph_2PCH(C_6H_{11})CH_2PPh_2$, norphos = $Ph_2PCHCHCH{=}CHCH(CH_2)CHPPh_2$, chiraphos = $Ph_2PCH(CH_3)CH(CH_3)PPh_2$, skewphos = $Ph_2PCH(CH_3)CH_2CH(CH_3)PPh_2$, diphos = $Ph_2PCH_2CH_2PPh_2$, DPPP = $Ph_2P(CH_2)_3PPh_2$, diop = $Ph_2PCH_2CHOCMe_2OCHCH_2PPh_2$.

(5) Norphos is also effective as a ligand.[3b]

0020-1669/91/1330-5002$02.50/0

Chart I



are quite different from those for the asymmetric reductions of acylaminoacrylic acid derivatives that are catalyzed by rhodium(I) derivatives of ligands such as chiraphos,[1] and thus the mechanism of the reduction of imines is probably not the same as that established for the reduction of olefinic acids.

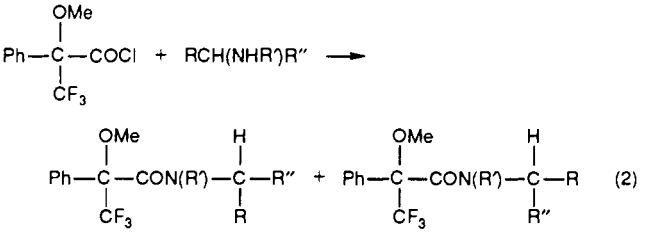
The present work extends our imine hydrogenation studies to the imine **2** (Chart I), which is of commercial interest, and to a range of "model" imines **3–10**. We demonstrate that the addition of iodide ion to the Rh system can be beneficial, with optical yields of up to 91% being obtainable.[6] The imines initially bind to the rhodium via the nitrogen lone pair, and unlike in the reduction of olefins,[1] chelation of the unsaturated substrate does not lead to higher optical yields.[7] Earlier publications from this group describe detailed work on the imines **1** and preliminary data for some of the model imines.[3a-c]

Experimental Section

Reagents and products were generally manipulated in Schlenk apparatus under an atmosphere of nitrogen or argon. NMR spectra were recorded by using Bruker or Varian spectrometers operating at 400 or 300 MHz, respectively. Mass spectral data were acquired by using a Kratos MS-50 spectrometer. Microanalyses were performed by Mr. Peter Borda of this Department. $^{31}P\{^1H\}$ NMR data, reported relative to 85% aqueous H_3PO_4, downfield being positive, are listed in Table V.

(*R*)-Cycphos was prepared from (*S*)-mandelic acid as described by Riley and Shumate: $[\alpha]^{22}_d$ = +102.6° (*c* 1.1, THF), lit.[8] $[\alpha]^{25}_D$ = +103.3° (*c* 1.0, THF). Imines **1** and **2** were gifts from Ciba Geigy. Imines **3–5**, **9**, and **10** were prepared from the appropriate amine and ketone by the usual water removal procedure (Dean Stark).[9] Imines **6** and **7** were prepared by using a molecular sieve to trap water as follows.[10] Ketone (0.2 mol) and isobutylamine (0.2 mol) were mixed together with 20 g of freshly activated 4-Å molecular sieve. An exothermic reaction occurred, and the mixture was left for 24 h. The imines were isolated by distillation after recovery of the molecular seives. Imine **8** was prepared from 3,4-$(CH_3O)_2C_6H_3CH_2CH_2NH_2$ and acetic anhydride.[11] The microanalytical results and NMR spectra of the imines were as expected.

Determination of Optical Yields by Forming Diastereomeric Amides.[12] This procedure was used for the products of the reductions of **4** and **5** (eq 2). For example, the product from the reduction of **4** (24 mg) was



(2)

added to a suspension of NaH (24 mg; 80% in oil) in THF (20 mL). The reaction mixture was stirred at 20 °C for 30 min, (*S*)-PhC(CF_3)(OMe)COCl (50 mg in 2 mL of THF) added, and stirring was continued for 18 h. Examination of the mixture by using TLC showed ~100% reaction. Water (20 mL) was added, and following acidification with 5% HCl the mixture was extracted with ether (50 mL). The ether layer was washed with 5% HCl (20 mL × 3), saturated Na_2CO_3 solution (20 mL), and finally water (20 mL × 2). The dried ether solution ($MgSO_4$) was evaporated and the residue purified by TLC (20:1 petroleum ether/ethyl acetate) to afford 42 mg of product, 91% yield. The ^1H NMR spectrum showed the presence of four isomers: *trans-R,R*, *trans-S,R*, *cis-R,R*, and *cis-S,R* with both *R,R*:*S,R* ratios being 1:4; thus the ee is 60% in favor of the *S* isomer.

[Rh(NBD)(*R*-cycphos)]PF_6, [Rh(NBD)(diphos)]BF_4, and [Rh(NBD)(*S,S*-chiraphos)]BF_4 were prepared by the method of Riley and Shumate;[8] $[Rh(NBD)Cl]_2$ was also prepared by a literature procedure.[13]

Preparation of [Rh(diphos)(8)$_2$]BF_4 (11). [Rh(NBD)(diphos)]BF_4 (68 mg, 0.1 mmol) was dissolved in MeOH (5 mL), and the solution was degassed and stirred under H_2 (1 atm) for 15 min, and then imine **8** (82 mg, 0.4 mmol) was added under Ar. The initially yellow solution was left at 20 °C for 24 h, during which period yellow crystals were formed. The solid product (56 mg, 50% yield) was isolated by filtration and dried at 40 °C (0.05 mmHg). ^1H NMR ($CDCl_3$): δ 7.20–8.10 (m, 20 H, aromatic, diphos), {6.62 (s, 1 H), 6.59 (s, 1 H), aromatic, imines of minor isomer}, {6.61 (s 1 H), 6.58 (s, 1 H), aromatic, imines of major isomer}, {3.81 (s, 3 H), 3.76 (s, 3 H), OMe, minor isomer}, {3.81 (s, 3 H), 3.79 (s, 3 H), OMe, major isomer}, 3.55–4.05 (m, 4 H, N–CH_2–), 1.95–2.55 (m, 8 H, P–CH_2–CH_2–P and N–CH_2–CH_2), 2.32 (s, 3 H, C–CH_3, major isomer), 2.22 (s, 3 H, C–CH_3, minor isomer). MS (FAB): *m/z* 912 ($[Rh(diphos)(8)_2]^+$), 706 ($[Rh(diphos)(8)]^+$), 501 ($[Rh(diphos)]^+$). Anal. Calcd for $C_{50}H_{54}BF_4N_2O_4P_2Rh$: C, 60.13; H, 5.45; N, 2.81. Found: C, 59.86; H, 5.48; N, 2.63.

Crystals suitable for X-ray studies were grown from CH_2Cl_2/hexanes by the layering technique.

Preparation of [Rh(diphos)(4)$_2$]BF_4 (16). [Rh(NBD)(diphos)]BF_4 (68 mg, 0.1 mmol) was dissolved in 10 mL of MeOH, and the solution was degassed and then stirred under H_2 (1 atm) for 20 min (20 °C). Imine **4** (96 mg, 0.4 mmol) was added under Ar and the volume of solution reduced to 1.5 mL in vacuo. Yellow-orange crystals formed when this solution was left at −25 °C (24 h). The solid (25 mg, 23% yield) was isolated by filtration and dried at 40 °C (0.05 mmHg). Anal. Calcd for $C_{58}H_{58}BF_4N_2O_2P_2Rh$: C, 63.30; H, 5.48; N, 2.63. Found: C, 63.33; H, 5.20; N, 2.57. The ^1H NMR spectrum of this compound is complicated in CD_3OD as well as in CD_2Cl_2, due to the dissociation of imine.

Preparation of Rh(diop)(Cl)(8) (22). $[Rh(NBD)Cl]_2$ (115 mg, 0.5 mmol) and diop (249 mg, 0.5 mmol) were dissolved in dry CH_2Cl_2 (10 mL), and the solution was stirred under H_2 (1 atm) for 1 h (20 °C), during which time the color of the solution changed from yellow to red. Removal of solvent afforded a red powder, identified as $[Rh(diop)Cl]_2$. ^1H NMR (CD_2Cl_2): δ 7.0–7.5 (m, 40 H, aromatic), 3.82 (m, 4 H, >CH), 2.65–2.25 (two sets of multiplet, 8 H, –CH_2), 1.19 (s, 12 H, –CH_3). Anal. Calcd for $C_{31}H_{32}ClO_2P_2Rh$: C, 58.46; H, 5.06. Found: C, 58.75; H, 5.31.

(6) The use of halide ion to promote higher optical yields in catalyzed imine reduction was first described in ref 3f, but these particular systems have low reproducibility.
(7) A solid of formula [Rh(diphos)(**1a**)]BF_4 can be isolated from the reaction of [Rh(diphos)$(MeOH)_2$]BF_4 with **1a**, with the imine bound through the nitrogen lone pair and the OMe group.[3b] If this chelate complex is present during the hydrogenation reaction, it certainly does not result in an increase in optical yield. Considerably higher results are obtained in the hydrogenation of imines such as **3** that cannot act as a bidentate ligand.[3a-c]
(8) Riley, D. P.; Shumate, R. E. *J. Org. Chem.* **1980**, *45*, 5189.
(9) *The Chemistry of Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970.
(10) Norton, D. G.; Haury, V. E.; Davis, F. C.; Mitchell, L. J.; Ballard, S. A. *J. Org. Chem.* **1954**, *19*, 1054.
(11) *Org. Synth.* **1977**, *56*, 3.
(12) Dale, J. A.; Diell, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.
(13) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1954**, 3178.

Table I. Crystallographic Data[a]

compd	**11**
formula	$C_{51}H_{58}BCl_2F_4O_5P_2Rh$
fw	1073.58
color, habit	yellow prism
cryst size, mm	0.10 × 0.15 × 0.35
cryst system	triclinic
space group	$P\bar{1}$
a, Å	12.564 (1)
b, Å	21.446 (2)
c, Å	10.521 (1)
α, deg	100.655 (9)
β, deg	110.539 (8)
γ, deg	79.102 (7)
V, Å^3	2585.2 (5)
Z	2
ρ_c, g/cm^3	1.38
$F(000)$	1108
radiation	Cu
wavelength, Å	1.541 78
μ, cm^{-1}	47.82
transm factors	0.663–1.00
scan type	ω–2θ
scan range, deg in ω	1.05 + 0.30 tan θ
scan speed, deg/min	32
data collcd	$+h,\pm k,\pm l$
$2\theta_{max}$, deg	155.7
cryst decay, %	9.9
tot. no. of reflcns	11 055
no. of unique reflcns	10 540
R_{merge}	0.038
no. of reflcns with $I > 3\sigma(I)$	5881
no. of variables	641
R	0.068
R_w	0.082
gof	2.12
max Δ/σ (final cycle)	0.13
resid density, e/Å^3	0.83

[a] Temperature 294 K, Rigaku AFC6S diffractometer, graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan:background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B) + (pF^2)^2]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count, $p = 0.040$ for **11**), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

$[Rh(diop)Cl]_2$ (63.7 mg, 0.05 mmol) and imine **8** (20.5 mg, 0.1 mmol) were dissolved in CH_2Cl_2 (5 mL), the volume of the solution was reduced to ~1 mL, and hexanes were added to precipitate the yellow solid product **22**, which was collected and dried in vacuo. ^1H NMR ($CDCl_3$): δ 7.1–8.3 (m, 20 H, aromatic, diop), {6.8 (s, 1 H), 6.43 (s, 1 H), aromatic, imine, major isomer}, {6.7 (s, 1 H), 6.48 (s, 1 H), aromatic, imine, minor isomer}, {3.86 (s, 3 H), 3.77 (s, 3 H), OMe major isomer}, {3.8 (s, 3 H), 3.75 (s, 3 H), OMe minor isomer}, 3.12 (s, 3 H, N=C—CH_3 major isomer), 2.80 (s, 3 H, N=C—CH_3 minor isomer), 1.20, 1.17 (2 s, 2 × 3 H, $(CH_3)_2C(O-)_2$, major isomer), 1.28, 1.07 (2 s, 2 × 3 H, $(CH_3)_2C(O-)_2$, minor isomer), 1.4–4.1 (m, 10 H, 4-CH_2 and 2-CH). Anal. Calcd for $C_{43}H_{47}ClNO_4P_2Rh$: C, 61.33; H, 5.63; N, 1.66. Found: C, 61.76; H, 5.77; N, 1.52.

Preparation of [Rh(chiraphos)I]$_2$. $[Rh(NBD)Cl]_2$ (124 mg, 0.54 mmol) was suspended in MeOH (20 mL), and chiraphos (250 mg, 0.59 mmol) was added slowly (5 min) with vigorous stirring. KI (450 mg, 2.7 mmol) was then added and the mixture stirred until a clear solution was obtained. A precipitate of the product formed overnight. The air-, light-, and water-sensitive solid was isolated, washed with MeOH, and recrystallized twice from CH_2Cl_2/hexanes by using the layering technique. ^{31}P NMR ($CDCl_3$): δ 80.9, J(Rh–P) = 187 Hz. Anal. Calcd for $C_{28}H_{28}IP_2Rh$: C, 49.87; H, 4.18; I, 18.8. Found: C, 50.26; H, 4.21; I, 18.9.

Hydrogenation Reactions. These were carried out as follows: The rhodium(I) precursor, usually $[Rh(NBD)Cl]_2$ (0.025 mmol), was dissolved in 10 mL of dry degassed solvent (usually benzene/methanol, 1:1) in a Schlenk tube under argon. The ligand (usually R-(+)-cycphos) (0.05 mmol) was then added followed by the imine substrate (5 mmol). The solution was transferred under argon to a steel autoclave. The reaction vessel was then flushed with hydrogen and pressurized with the same gas to, usually, 1000 psig, and the contents were stirred for noted times, normally 18 h, at 20 °C. The solvent was removed and the product isolated by distillation.

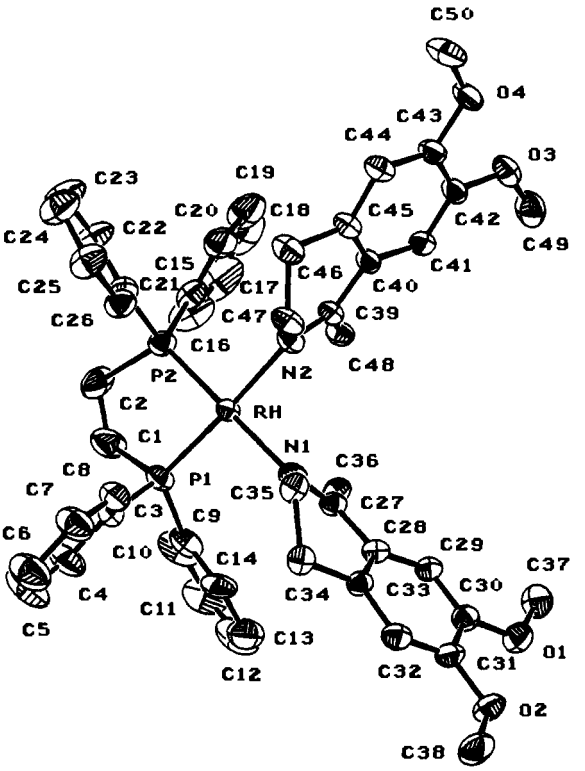


Figure 1. ORTEP plot of $[Rh(diphos)(\mathbf{8})_2]^+$ (**11**). Selected bond distances (Å) and angles (°): Rh–N(2) = 2.118 (7), Rh–N(1) = 2.122 (7), Rh–P(2) = 2.202 (2), Rh–P(1) = 2.214 (2), C(27)–N(1) = 1.29 (1), C(39)–N(2) = 1.28 (1); P(2)–Rh–P(1) = 84.9 (1), P(2)–Rh–N(2) = 92.6 (2), N(2)–Rh–N(1) = 86.3 (3), N(1)–Rh–P(1) = 95.6 (2).

X-ray Crystallographic Analysis of Compound 11. Crystallographic data are listed in Table I. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with $2\theta = 41$–51°. The intensities of three standard reflections, measured every 150 reflections throughout the data collections, decayed uniformly by 9.9%. The data were processed[14] and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans for four reflections).

The structure analysis was initiated in the centrosymmetric space group $P\bar{1}$, the choice being confirmed by the subsequent successful solution and refinement of the structure. The structure was solved by conventional heavy-atom methods, the coordinates of the metal atom being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The asymmetric unit contains one water and one dichloromethane solvate molecule in addition to the complex cation and tetrafluoroborate anion. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions ($d_{C-H} = 0.98$ Å, $B_H = 1.2B$ of the bonded atom) except for those associated with the water molecule, which could not be located. The BF_4 anion was found to be 2-fold disordered: the boron and one fluorine position are fully occupied with the disorder occurring as a rotation of the remaining F atoms about the B–F(1) bond. Both orientations were found to be 50% occupied. The thermal parameters of the dichloromethane carbon atom suggest possible disorder, but no attempt was made to model this disorder, the carbon atom being refined with full occupancy. Neutral-atom scattering factors and anomalous dispersions corrections for the non-hydrogen atoms were taken from ref 15. Final atomic coordinates are listed in Table II. An ORTEP plot of the cation is shown in Figure 1; some selected bond lengths

(14) TEXSAN/TEXRAY structure analysis package that includes versions of the following: DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

Table II. Positional Parameters and B(eq) Values

atom	x	y	z	B(eq), Å^2
Rh	0.24183 (6)	0.24179 (3)	0.49092 (7)	3.14 (2)
Cl(1)	0.5930 (5)	0.3109 (3)	1.0116 (6)	16.0 (4)
Cl(2)	0.3944 (6)	0.2965 (3)	1.0587 (7)	16.7 (4)
P(1)	0.4205 (2)	0.2041 (1)	0.4992 (3)	4.4 (1)
P(2)	0.2876 (2)	0.3349 (1)	0.4834 (3)	4.3 (1)
F(1)	0.934 (1)	0.1401 (5)	0.879 (1)	14.4 (7)
F(2)	0.970 (3)	0.235 (1)	0.858 (2)	12 (2)
F(3)	1.072 (2)	0.194 (2)	1.046 (4)	14 (2)
F(4)	0.902 (3)	0.222 (2)	1.010 (4)	15 (2)
F(5)	0.910 (3)	0.235 (1)	0.905 (4)	17 (2)
F(6)	1.004 (7)	0.184 (3)	1.051 (3)	27 (6)
F(7)	1.072 (2)	0.175 (1)	0.892 (3)	14 (2)
O(1)	0.1293 (6)	−0.0493 (3)	0.7844 (6)	5.3 (3)
O(2)	0.1257 (6)	−0.1258 (3)	0.5674 (6)	5.3 (3)
O(3)	−0.3159 (5)	0.3992 (3)	0.6989 (7)	5.6 (3)
O(4)	−0.4195 (5)	0.4377 (3)	0.4610 (7)	5.5 (3)
O(5)	0.238 (2)	−0.192 (1)	0.848 (2)	34 (2)
N(1)	0.1946 (6)	0.1520 (3)	0.4917 (7)	4.0 (3)
N(2)	0.0706 (6)	0.2812 (3)	0.4755 (7)	3.9 (3)
C(1)	0.506 (1)	0.2699 (5)	0.548 (1)	8.0 (6)
C(2)	0.439 (1)	0.3261 (5)	0.494 (1)	7.4 (6)
C(3)	0.4383 (8)	0.1628 (4)	0.341 (1)	4.5 (4)
C(4)	0.546 (1)	0.1333 (6)	0.332 (1)	7.2 (6)
C(5)	0.558 (1)	0.1021 (7)	0.210 (1)	9.6 (8)
C(6)	0.464 (1)	0.0983 (7)	0.096 (1)	8.7 (8)
C(7)	0.356 (1)	0.1264 (6)	0.100 (1)	6.8 (6)
C(8)	0.3467 (8)	0.1576 (5)	0.225 (1)	5.1 (4)
C(9)	0.5043 (8)	0.1478 (5)	0.620 (1)	5.5 (5)
C(10)	0.591 (1)	0.1627 (7)	0.739 (1)	8.6 (7)
C(11)	0.643 (1)	0.1156 (9)	0.831 (1)	9.8 (8)
C(12)	0.605 (1)	0.0571 (9)	0.800 (2)	10 (1)
C(13)	0.521 (1)	0.0417 (6)	0.684 (2)	8.0 (7)
C(14)	0.4713 (9)	0.0877 (5)	0.594 (1)	6.3 (5)
C(15)	0.266 (1)	0.3986 (5)	0.616 (1)	5.6 (5)
C(16)	0.350 (1)	0.4055 (6)	0.741 (1)	9.5 (8)
C(17)	0.327 (2)	0.451 (1)	0.847 (2)	13 (2)
C(18)	0.227 (3)	0.4858 (8)	0.830 (2)	13 (2)
C(19)	0.141 (2)	0.4793 (6)	0.705 (2)	10 (1)
C(20)	0.160 (1)	0.4352 (5)	0.598 (1)	6.9 (6)
C(21)	0.2164 (8)	0.3724 (4)	0.328 (1)	4.6 (4)
C(22)	0.214 (1)	0.4376 (4)	0.323 (1)	6.4 (5)
C(23)	0.160 (1)	0.4615 (5)	0.200 (1)	8.2 (7)
C(24)	0.110 (1)	0.4244 (6)	0.083 (1)	7.6 (7)
C(25)	0.111 (1)	0.3615 (5)	0.086 (1)	6.3 (6)
C(26)	0.1655 (9)	0.3350 (4)	0.208 (1)	5.1 (4)
C(27)	0.2110 (7)	0.1249 (4)	0.5978 (9)	3.7 (3)
C(28)	0.1772 (7)	0.0613 (4)	0.5850 (8)	3.7 (3)
C(29)	0.1653 (7)	0.0389 (4)	0.6961 (8)	3.9 (3)
C(30)	0.1452 (7)	−0.0229 (4)	0.6845 (9)	4.1 (4)
C(31)	0.1398 (7)	−0.0647 (4)	0.564 (1)	4.1 (4)
C(32)	0.1487 (7)	−0.0423 (4)	0.453 (1)	4.2 (4)
C(33)	0.1660 (7)	0.0205 (4)	0.4626 (8)	3.6 (3)
C(34)	0.1732 (7)	0.0474 (4)	0.3439 (8)	4.0 (4)
C(35)	0.1310 (7)	0.1189 (4)	0.3577 (8)	4.0 (4)
C(36)	0.2659 (8)	0.1571 (4)	0.7368 (9)	4.3 (4)
C(37)	0.123 (1)	−0.0079 (5)	0.904 (1)	6.2 (5)
C(38)	0.117 (1)	−0.1695 (5)	0.446 (1)	6.8 (6)
C(39)	0.0295 (7)	0.3091 (4)	0.5704 (8)	3.6 (3)
C(40)	−0.0904 (7)	0.3386 (4)	0.5403 (9)	3.6 (3)
C(41)	−0.1452 (7)	0.3526 (4)	0.6396 (9)	4.0 (4)
C(42)	−0.2557 (7)	0.3841 (4)	0.609 (1)	4.2 (4)
C(43)	−0.3109 (7)	0.4042 (4)	0.480 (1)	4.5 (4)
C(44)	−0.2602 (7)	0.3894 (4)	0.381 (1)	4.7 (4)
C(45)	−0.1502 (7)	0.3552 (4)	0.4094 (9)	4.1 (4)
C(46)	−0.0907 (8)	0.3355 (5)	0.304 (1)	5.1 (4)
C(47)	−0.0123 (7)	0.2737 (4)	0.3351 (8)	4.4 (4)
C(48)	0.1056 (8)	0.3121 (4)	0.7169 (9)	4.4 (4)
C(49)	−0.267 (1)	0.3759 (6)	0.825 (1)	7.0 (6)
C(50)	−0.479 (1)	0.4582 (5)	0.330 (1)	7.0 (6)
C(51)	0.534 (2)	0.260 (1)	1.069 (4)	23 (2)
B	0.981 (2)	0.1914 (9)	0.942 (2)	7.3 (9)

and angles are listed in the caption.

Results and Discussion

As mentioned in the Introduction, we were able to maximize the optical yield of the reduction described by eq 1 to about 69%.[3b]

Table III. Asymmetric Hydrogenation of Imine **2**

conditions[a]	ligand	time, days	yield, %[b]	ee, %[c]
normal	cycphos	2	3	51
normal	cycphos	8	45	53
1500 psig	cycphos	9	48	57
KI (1 equiv)	cycphos	11	9	60
52 °C	cycphos	4	27	51
1500 psig	(*S,S*)-chiraphos	8	34	7
normal	(+)-diop	4	20	11
normal	DPPP	3	15	

[a] Normal conditions are as described in the Experimental Section; departures from this are listed as appropriate. Apart from those identified as normal all other reactions were carried out with [Rh]:[imine] = 1:50, using 0.05 mM $[Rh(NBD)Cl]_2$. [b] By chromatography using an OV 101 capillary column. Conditions: T_1 = 80 °C, t_1 = 2 min, rate = 20 °C min^{-1}, T_2 = 200 °C. [c] Based on the value $[\alpha]^{25}_D$ = 47.9 (*c* 1.6, $CHCl_3$) provided by the Ciba Geigy Co.

We also established that there was no change in the ratio of the geometric isomers of the imine, initially a 5:1 mixture of anti and syn isomers for **1a** and **1b**, as a function of conversion; thus the catalytic system does not seem to produce one enantiomer by preferentially hydrogenating one stereoisomer of the imine.

It was of interest to establish if the stoichiometric reduction of **1** by a chiral borohydride would do any better. In our hands the literature procedure that affords high optical yield for the reduction of **8**[16] is only partly successful, 20% ee being obtained for the reduction of **1a**.[17]

When the catalytic system was used for the reduction of imine **2**, disappointing chemical and optical yields were obtained (Table III). The addition of KI slowed the reaction down considerably, although it did increase the optical yield somewhat. In the catalyzed reduction of **1a**, addition of KI effectively stops the reaction.[3b] The ligand DPPP, which is an achiral analogue of skewphos used successfully by a Hungarian group in imine hydrogenations,[3f] was not active enough to warrant further studies.

Imines **3–10** were prepared in order to study these reduction reactions further. We hoped to be able to find reactions that would proceed at faster rates and lower hydrogen pressures so that kinetic measurements could be made. Thus, the imines were chosen so that steric constraints would be less than those of **1** and **2**.

Experimental results are listed in Table IV. There are no dramatic increases in reaction rates or in optical yields when the conditions used for the reduction of **1** and **2**, the "normal" conditions, are used for the imines **3–10**. There may be some moderate increases in the rate of reduction of some imines, e.g. **3–6** and **10**, but optical yields for reactions carried out at 20 °C are considered moderate (up to 71% ee). Some corresponding values for the reduction of **1a** at 20 °C are 91% yield and 41% ee after 40 h and yield 58% and 40% ee after 12 h.[3b]

In the group of imines **6–10**, **9** and **10** are close in structure to **1**. Under normal conditions the ease of reduction and the optical yield for all these seem similar, although we were unable to determine the optical purity of the product of the reduction of **9** because it was unreactive toward the chiral acid chloride *S*-$PhC(CF_3)(OMe)COCl$.

(16) Yamada, K.; Takeda, M.; Iwakuma, T. *J. Chem. Soc., Perkin Trans. I* **1983**, 265.

(17) A solution of (*S*)-*N*-((benzyloxy)carbonyl)proline (45 mmol) in 10 mL of dry THF was added to a stirred suspension of $NaBH_4$ (1.5 mmol) in 3 mL of dry THF maintained at −10 °C.[16] The mixture was allowed to warm slowly to room temperature, left for a further 2 h, and then cooled to −30 °C. A solution of **1a** (1.15 mmol) in THF (10 mL) was added, and the reaction mixture was maintained at −30 °C for 10 h, quenched with 5% HCl, and then heated to 60 °C for 0.5 h. The bulk of the THF was removed by using a rotary evaporator. The residue was made basic with saturated K_2CO_3 solution and extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated, and the chemical yield was determined by gas chromatography (OV 101 capillary column). The secondary amine was isolated by TLC (silica gel, petroleum ether/ethyl acetate, 15:1); the chemical yield was 22%, and the optical yield 20%.

Table IV. Asymmetric Hydrogenation of Imines **3–10** with Catalyst Rh(I)/Cycphos

imine	conditions[a]	time, h	yield, %[b]	ee, %[c]
3	normal	18	100	67
4	normal	90	100	60
5	normal	18	100	71
5	1 atm of H_2	192	95	69
3	KBr	144	100	72
3	KI	90	100	79
4	KI	120	90	71
5	KI	72	100	84
5	KI, 4 °C, 1500 psig	90	100	87
5	KI, CH_3OH/toluene (10 mL/5 mL), −25 °C, 1500 psig	144	100	91
3	cation[d]	46	100	0
4	cation[d]	46	35	15[e]
5	cation[d]	46	100	0
6	normal	90	100	0
7, 8	normal	90	~0	
8	cation[f]	72	71	0
9	normal	96	74	*g*
10	normal	66	100	44

[a] Normal conditions are as described in the Experimental Section; departures from this are listed as appropriate. KBr or KI means that 1 equiv of the salt was added based on rhodium. [b] Chemical yields were determined by using gas chromatography OV 101 capillary column. Usual conditions T_1 = 100 °C, t_1 = 2 min, rate = 20 °C min^{-1}, and T_2 = 220 °C. [c] The configuration of the product was (−)-*S*. Optical yields, ee, were determined as follows: from **3** by rotation, $[\alpha]^{20}_D$ = 56.2° (*c* 1.07, EtOH) for (+)-*R* product (Parek, K. J. *Prakt. Chem.* **1912**, *86*, 287); from **4** and **5** by ^{1}H NMR spectra of diastereomeric amides (see Experimental Section); from **10** by use of an HPLC Pirkle Type 1A column. Base-line resolution was obtained (2-propanol/hexane eluant) but only for the product from **10**. [d] The salt [Rh(NBD)(*R*-cycphos)]PF_6 (0.05 mmol) was used in place of the in situ generated catalyst. [e] The configuration of the product was (+)-*R*. [f] [Rh(NBD)(*S*,*S*-chiraphos)]BF_4 was used. [g] The optical yield was not determined because the amine failed to react with $PhC(CF_3)(OMe)COCl$ (see Experimental Section); product $[\alpha]^{25}_{365}$ = −6.1° (*c* 2.28, hexanes).

The fastest rate of reaction is seen for **5**; this reduction does proceed slowly even at 1 atm of H_2. The optical yield is effectively unchanged on lowering the pressure. In contrast the optical yields from Rh-catalyzed olefin reductions can be sensitive to pressure.[1] The higher optical yields seem to be obtained from imines that cannot act as a bidentate ligand at the metal center of the catalyst; i.e., they bind only through the imine functionality.

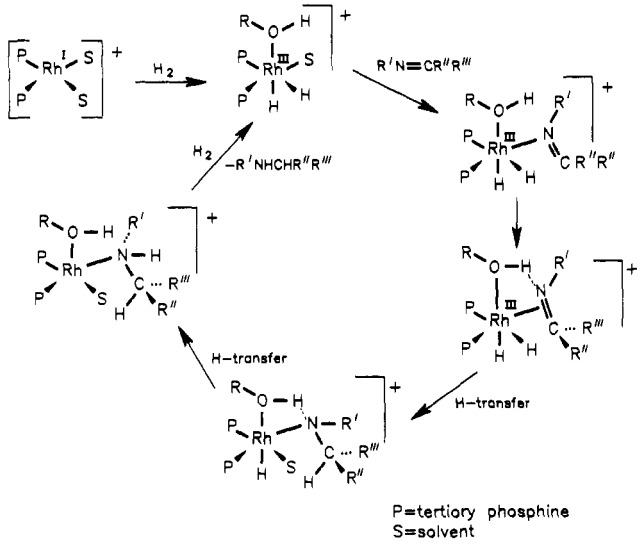
The pair of aliphatic imines **6** and **7** show markedly different behavior; the latter contains the same N=C—C—OMe grouping that is found in **1** and whose presence seems to result in slower rates. This contrasts with findings for olefinic and ketonic substrates where some secondary functionality induces, via chelate formation, higher optical yields. The reduction of **6** is more facile than **7**, but the product is racemic. The cyclic imine **8** is not reduced under the "normal" conditions. This imine was chosen for study because of the fixed geometry at nitrogen and also because of a report that related cyclic imines can be reduced by hydrogen in the presence of an in situ $RhCl_3$/diop catalyst.[18] This diop catalyst system does not reduce **8**.

The effect of the addition of halide ion to the catalytic system was examined for imines **3–5**. Reaction rates are slower, but optical yields are generally increased, as in the case of **2** (see above).

Increased optical yields (up to 69%) are observed when **1** is reduced at temperatures below 0 °C.[3a-c] These conditions were used for **5**, and as seen in Table IV, the combination of a lower temperature (−25 °C) together with the addition of 1 equiv of KI results in the highest optical yield of 91% ee.

A number of questions regarding metal–imine interactions need to be answered before the catalytic cycle can be considered in any detail. For example, the following questions may be posed: (a) How does the imine bind to the metal center initially? (b) How does the imine bind to the metal center during hydrogen transfer? (c) How many imines are bound to the metal center during the catalytic cycle? (d) How do these factors relate to optical yields?

Scheme I



As a model for discussion, we will use Scheme I, an adaption of the scheme proposed by Longley et al.[2,19]

In this scheme the hydride route is preferred, and with regard to question (a) above, the imine binding is assumed to take place via the nitrogen lone pair. It is also implied that vacant coordination sites have been created at the metal center prior to the initial imine–metal binding, that a $Rh^{III}(H)_2$ species is first formed, and that the function of the alcohol is to facilitate η^2-(C=N) bonding. In the present work we have endeavored to provide some information about these processes.

Figure 1 shows the crystal structure of the cation of compound **11**, which is prepared from imine **8** as outlined in eq 3. The cation

$$[Rh(NBD)(diphos)]BF_4 \xrightarrow[MeOH]{H_2} [Rh(diphos)(MeOH)_2]BF_4 \xrightarrow{8} [Rh(diphos)(\mathbf{8})_2]BF_4 \quad (3)$$
$$\mathbf{12} \qquad\qquad \mathbf{11}$$

has the expected, essentially square-planar geometry at the Rh. Of immediate interest is the binding of two imine molecules via the nitrogen lone pairs. The structure also shows that the geometrical arrangement of the imines is syn (i.e., the two CH_3–C groups are on the same side of the "square plane"). When the same complex is prepared from imine that is labeled with ^{13}C at >*C*=N, the $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2 of the coordinated imine shows a singlet for this carbon atom at δ 163.3. The spectrum of the labeled complex **11** in MeOH shows two unequal intensity resonances at 170.97 and 170.49 ppm that are not coupled to rhodium. Thus, the binding present in the solid state is preserved in solution, although the two resonances in MeOH probably indicate the presence of both syn and anti isomers. The $^{31}P\{^1H\}$ NMR spectrum of **11** generated in situ in MeOH-d_4 shows two doublets δ 72.2, J = 168 Hz, and δ 72.4, J = 168 Hz, with the former being major (see Table V, which lists the ^{31}P data for all the species discussed in this paper). This again indicates the presence of syn and anti isomers, as does the ^{1}H NMR spectrum.

When the reaction of eq 3 is carried out by using 1 equiv of imine **8**, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture in MeOH-d_4 shows a trace of the isomers of **11** and an ABX pattern that can be assigned to the molecule [Rh(diphos)(**8**)MeOH]BF_4 (**13**) (Table V); P^2 is defined as trans to the imine on the basis

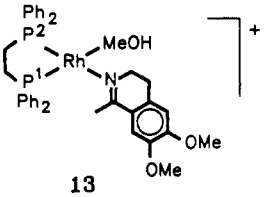
(18) Rice, K. C. U.S. Patent 748,854, June 26, 1985.

(19) The coordination number of 6 on the amine-bound Rh(I) center in the original of Scheme I[2] is unrealistic.

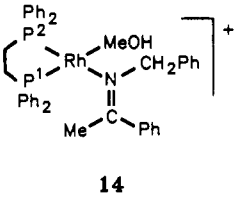
Table V. $^{31}P\{^1H\}$ NMR Data for Imine Complexes

compd	δ, ppm	J(Rh-P), Hz	J(P-P), Hz
11 (major)	72.2	168	
11 (minor)	72.4	168	
13	79.3 (P^1)	207	46
	71.5 (P^2)	170	
14 (major)	78.7 (P^1)	209	46
	70.3 (P^2)	171	
14 (minor)	76.2 (P^1)	214	47
	72.1 (P^2)	170	
15 (major)	78.7 (P^1)	209	46
	70.3 (P^2)	171	
15 (minor)	76.2 (P^1)	216	47
	72.0 (P^2)	170	
16	67	175	
17	77.1 (P^1)	210	46
	71.7 (P^2)	170	
18	65.2 (P^1)	175	43
	70.5 (P^2)	171	
19	77.3 (P^1)	217	52
	73.3 (P^2)	173	
21	72.5 (P^1)	198	42
	69.7 (P^2)	164	
22a (major)	31.1 (P^1)	197	53
	32.1 (P^2)	158	
22b (minor)	30.7 (P^1)	191	53
	31.1 (P^2)	163	
23a (major)	75.6 (P^1)	192	52
	73.8 (P^2)	161	
23b (minor)	74.1 (P^1)	191	52
	73.5 (P^2)	162	

of the spectrum of **11**, and P^1 as trans to MeOH on the basis of ^{31}P NMR data for **12**.[20]



13



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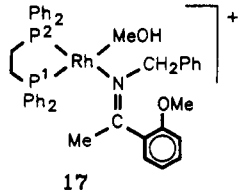
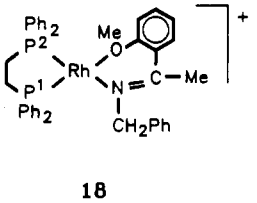
When the sequence of reactions of eq 3 is carried out with imine **3** (4 equiv), the $^{31}P\{^1H\}$ NMR spectrum of the in situ product shows the presence of two species that are probably isomers of the compound **14** (Table IV) that differ in the geometry of the imine; i.e., the single imine is bound as either the *Z* or *E* isomer. When labeled imine is used, $>^{13}C{=}N-$, the $^{13}C\{^1H\}$ NMR spectrum of **14** in CD_3OD shows only one resonance at 181 ppm in spite of the isomers evident in the $^{31}P\{^1H\}$ NMR spectrum; presumably the ^{13}C resonances for the two isomers are accidentally degenerate. The reaction of imine **5** with **12** similarly affords only the monoimine cation [Rh(diphos)(**5**)(MeOH)]$^+$ (**15**) analogous to **14**. However, when the *o*-methoxy-substituted imine **4** is used, the in situ product mixture contains three principal components as judged by the $^{31}P\{^1H\}$ NMR spectrum. The major product is the bis(imine) complex [Rh(diphos)(**4**)$_2$]BF_4 (**16**) assigned to the doublet at 67 ppm, *J*(Rh-P) = 175 Hz. Isomers are possible, but no pertinent information has been obtained. One of the minor components appears to be [Rh(diphos)(**4**)(MeOH)]BF_4 (**17**), as



17



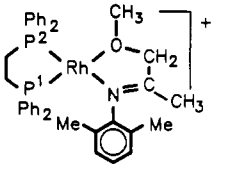
18

judged by the ^{31}P NMR parameters (Table V). Both *J* values of the other minor component, **18**, are ~170 Mz. Complexes of structure type **13** have one *J*(Rh-P) (P^2 trans to imine) of this magnitude and the other (P^1 trans to MeOH) greater than 200 Hz. Thus, **18** does not contain a coordinated MeOH. We suggest that **18** has the structure shown in which the imine is chelated to the metal center. Different geometric isomers of the imine are present in **17** and **18**.

The major product, **16**, can be isolated (see Experimental Section), and the microanalytical data fit the formulation. When **16** is dissolved in MeOH-d_4 the $^{31}P\{^1H\}$ NMR spectrum reveals that **17** is the major component of the solution showing that the imine is easily displaced (eq 4).

$$[\text{Rh(diphos)}(\mathbf{4})_2]^+ + \text{MeOH} \rightarrow \underset{\mathbf{16}}{} \qquad \underset{\mathbf{17}}{[\text{Rh(diphos)}(\mathbf{4})(\text{MeOH})]^+} + \mathbf{4} \quad (4)$$

The other potentially chelating imine studied is **1a**. The solid isolated from reaction of **1a** with **12** contains one imine per metal atom and is best formulated as **19**.[3b] The solution $^{31}P\{^1H\}$ NMR

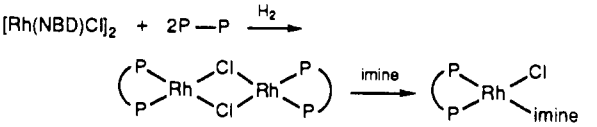


19

spectral data, however, perhaps indicate that the monoimine cation [Rh(diphos)(**1a**)(MeOH)]$^+$ is present in MeOH solution, the important coupling constants being 173 and 217 Hz. However, it is possible that there is not much difference in the donor strengths of CH_3OH vs CH_3OCH_2–.

These results show that imines generally react with a cationic catalyst precursor as monodentate ligands and generally prefer to occupy only one coordination site, with binding taking place through the nitrogen lone pair. Some imines such as **1a**, which possess a second basic site, are capable of chelating to the metal center although this structure may not be maintained to a great extent in MeOH solution.

Because the catalysts are often prepared in situ from [Rh(NBD)Cl]$_2$ and bis(tertiary phosphine), it is important to study the interaction of these systems with imines. The procedure used is described in general terms in eq 5, the synthetic work being carried



20 (5)

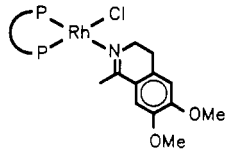
out in CH_2Cl_2. Although diphos was used in the work on cationic derivatives outlined above, because of the wish to simplify the results, this ligand affords more products than indicated by eq 5 when 1 equiv of **8** is used as the imine. Thus, the $^{31}P\{^1H\}$ NMR spectrum of the final reaction solution shows not only the eight-line pattern expected for the imine substitution product [Rh(diphos)Cl(**8**)] (**21**) (other analogues of this are discussed in more detail below) but also the presence of [Rh(diphos)$_2$]Cl (δ 57.5, *J*(Rh-P) = 132 Hz)[21] and another small doublet (δ 66, *J*(Rh-P) = 153 Hz), which could indicate the presence of [Rh(diphos)(NBD)Cl] (or [Rh(diphos)(NBD)]Cl).

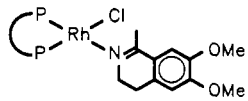
It turned out that the use of diop as ligand resulted in easier characterization of products. This allowed the isolation first of [Rh(diop)Cl]$_2$ (**20**) with P-P = diop, characterized by microanalysis and by its $^{31}P\{^1H\}$ NMR spectrum (δ 33, *J* = 190 Hz), and when this species is treated with 2 equiv of imine **8**, the monoimine product [Rh(diop)(Cl)(**8**)] (**22**) can be isolated. The microanalytical data agree with this formulation. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of two isomers, which are

(20) Slack, D. A.; Greveling, I.; Baird, M. C. *Inorg. Chem.* **1979**, *18*, 3125.

(21) James, B. R.; Majahan, D. *Can. J. Chem.* **1979**, *57*, 180.

probably **22a** and **22b**, implying restricted rotation about the Rh–N bond.





22a P—P=diop **22b**

23a P—P=chiraphos **23b**

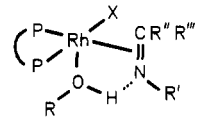
When **20**, P-P = chiraphos, prepared in situ, is treated with 1 equiv of **8**, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture is very similar to that of **22a** and **22b**. This means that the isomers of [Rh(chiraphos)(Cl)(**8**)] (**23a,b**) are undoubtedly formed.

The addition of excess iodide to an in situ catalyst solution prepared from $[Rh(NBD)Cl]_2$ and chiraphos results in a red precipitate that is the dimer $[Rh(chiraphos)I]_2$ (**24**). This is an analogue of **20** but is produced without a hydrogenation step. $^{31}P\{^1H\}$ NMR studies show that **24** is the major component in solution when Me_4NI is added to the in situ catalyst $[Rh(NBD)Cl]_2$/chiraphos in MeOH. (The in situ catalyst consists entirely of [Rh(NBD)(chiraphos)]Cl[8] if the reagents are mixed slowly. Otherwise some $[Rh(chiraphos)_2]Cl$[22] is formed as well.)

An optical yield of 78% ee is obtained when **24** is used as a catalyst for the hydrogenation of **3**. This value is greater than that obtained under "normal conditions" (70%), for the in situ $[Rh(NBD)Cl]_2$/chiraphos system, or normal conditions plus KI (1 equiv) (73%).

The literature mechanism outlined in Scheme I implies that the first step is the formation of a hydride (a so-called hydride route). Our studies indicate that imine binding to rhodium is a more facile process than hydride formation when chelating phosphines are used as ligands. Rhodium hydrides are not readily produced from 1:1 rhodium(I) complexes of ligands such as diop and diphos.[1a,c] Thus imine binding is probably the first step in the catalytic cycle with the production (in the in situ system) of intermediates akin to **22** and **23**. The addition of iodide to the catalytic system seems to result in the formation of dimers such as **24** that would also be cleaved by imines to afford analogues of **22** and **23**. The use of methanol in the solvent seems to be essential for catalytic hydrogenation to take place at a reasonable rate. Thus, the alcohol is probably bound to the metal and perhaps plays a role similar to that shown in Scheme I; namely, it facilitates change from the η^1 to η^2 binding of the imine group.[23] The effect of iodide is more difficult to rationalize. It slows down reaction but increases optical yields, which seems to imply that it occupies specific coordination sites in the metal that might be otherwise used for imine binding. In other words, it perhaps prevents the binding of two imines to the metal during the catalytic cycle. Two imines could bind with syn or anti geometries and could be hydrogenated on enantiotopic faces, thus leading to lower optical yields.

The data seem to imply a 5-coordinate intermediate such as **25**; this could form a monohydride by solvent- (or imine-) assisted



25 (X=halide)

heterolytic cleavage of H_2. The liberated proton could then be used to cleave the Rh–N bond following the usual insertion reaction (assuming this takes place in the direction shown in Scheme I). However, such speculation is hazardous given that high pressures are needed for reduction to take place. We are currently studying these systems by using high-pressure NMR techniques and have preliminary evidence indicating that dinuclear rhodium species are involved. Binuclear steps involving two rhodium species (e.g. a hydride and an alkylamido or aminoalkyl complex) cannot be excluded. Dinuclear iridium complexes are reported to be effective catalysts for imine hydrogenation; here, a dimer is equilibrating with small quantities of active monomer and monomer/imine species.[3j]

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Supplementary Material Available: A stereo ORTEP view of $[Rh(diphos)(\mathbf{8})_2]^+$ and Tables S1–S7, listing hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, intermolecular contacts, and least-squares planes, respectively (25 pages); Table S8, listing structure amplitudes (71 pages). Ordering information is given on any current masthead page.

(22) Young, C. G.; Rettig, S. J.; James, B. R. *Can. J. Chem.* **1986**, *64*, 51.

(23) Aqueous media have been found to increase reaction rates and optical yields in imine hydrogenation.[3i]