Synthesis of Ruthenium Hydride Complexes Containing beta-Aminophosphine Ligands Derived from Amino Acids and their use in the H_2-Hydrogenation of Ketones and Imines

Kamaluddin Abdur-Rashid,[a,b] Rongwei Guo,[a] Alan J. Lough,[a] Robert H. Morris,[a,*] Datong Song[a]

[a] Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada
Fax: (+1)-416-9786962, e-mail: rmorris@chem.utoronto.ca
[b] Current address: Kanata Chemical Technologies Inc., 2240 Speakman Dr., Sheridan Science and Technology Park, Mississauga, Ontario LSK 1A9, Canada
E-mail: kamal@kctchem.com

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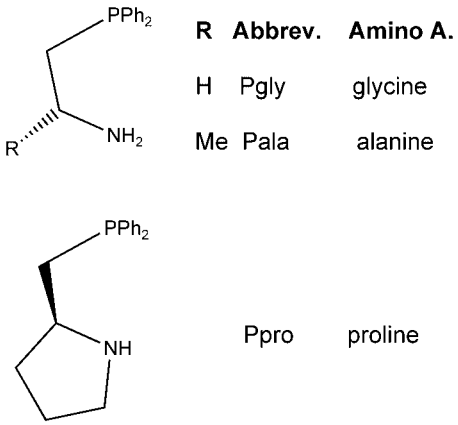
Abstract: The new complexes RuHCl(PPh_2CH_2-$CHRNH_2$)$_2$ and RuHCl($PPh_2CH_2CHRNH_2$)(R-binap), R = H (Pgly), R = Me [(*R*)-Pala] were prepared by the substitution of the PPh_3 ligands in RuHCl(PPh_3)$_3$ or RuHCl(PPh_3)[(*R*)-binap] with beta-aminophosphines derived from amino acids. The complex *trans*-RuHCl(Pgly)[(*R*)-binap] has been characterized by X-ray crystallography. The complex *trans*-RuHCl[(*S*)-Ppro]$_2$ where (*S*)-Ppro is derived from proline was also prepared and characterized by X-ray crystallography. These were used as catalyst precursors in the presence of a base (KOPr-*i* or KOBu-*t*) for the hydrogenation of various ketones and imines to the respective alcohols and amines with H_2 gas (1–11 atm) at room temperature. Acetophenone was hydrogenated to (*S*)-1-phenylethanol in low ee (up to 40%) when catalyzed by the enantiomerically pure complexes. These complexes are especially active in the hydrogenation of sterically congested and electronically deactivated ketones and imines and are selective for the hydrogenation of C=O bonds over C=C bonds.

Keywords: homogeneous catalysis; hydrogenation; imines; ketones; P,N ligands; ruthenium

Introduction

Diamine-diphosphine complexes of ruthenium such as *trans*-RuCl$_2$(diamine)(diphosphine)[1,2] and *trans*-RuHCl(diamine)(diphosphine)[3,4] are active catalyst precursors for the hydrogenation of ketones and imines.[5] The high activity and enantioselectivity of the complexes containing matched, enantiomerically pure ligands are attributed to the facile, outer-sphere transfer of H^-/H^+ equivalents from an RuH···HN hydridic-protonic unit to the ketone. The presence of an amino hydrogen is crucial for this mechanism and so this has been called metal-ligand bifunctional catalysis or the NH effect[1] or a ligand-assisted outer-sphere hydrogenation.[6]

Here we report the synthesis of the first complexes of the type *trans*-RuHCl(L)$_2$ where L is a beta-aminophosphine derived from amino acids (Figure 1)[7–9] and their use in the asymmetric hydrogenation of ketones and imines.[10] Since their overall geometry (**A**, Figure 2) is very similar to that of the successful diamine diphosphine complexes (**B**), it is of interest to see how the activity and selectivity compare. The use of the Ppro ligand was of particular interest as it could potentially give a rigid, asymmetric structure to the metal complex and increase enantioselectivity in asymmetric reactions.



R	Abbrev.	Amino A.
H	Pgly	glycine
Me	Pala	alanine
	Ppro	proline

Figure 1. Abbreviations for the beta-aminophosphines.

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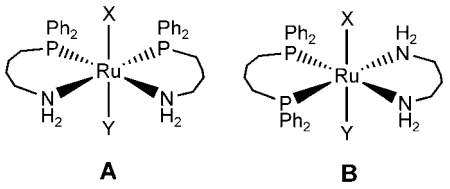


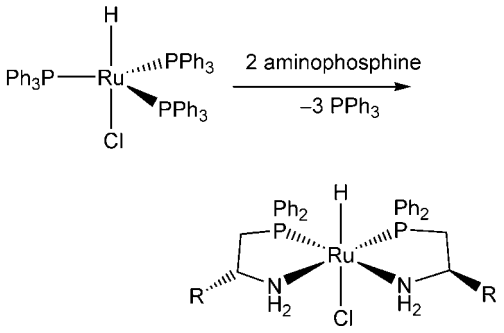
Figure 2. A comparison of the simplified geometry of the aminophosphine complexes (**A**), X = Cl or H, with that of the RuXY(diamine)(diphosphine) catalyst precursors (**B**) for the asymmetric hydrogenation of ketones.

A further point of interest is the geometry of such complexes. Quirmbach et al. [11] described the synthesis of the complex *cis*-$RuCl_2(Pval)_2$, Pval = (*S*)-PPh_2CH_2CH-(*i*-Pr)NH_2 (also known as valPHOS) by reacting the aminophosphine derived from (*S*)-valine with $RuCl_2(DMSO)_4$. A geometry with *trans*-PPh_2 groups was suggested on the basis of the ^{31}P NMR spectrum. This complex was a precatalyst for the hydrogenation of alkyl aryl ketones by transfer of hydrogen from 2-propanol. No enantioselectivity was observed. Kuznetsov and Alper[12] described the synthesis of the complex *trans, trans, trans*-$Ru(OAc)_2(Ppro)_2$ where Ppro is the beta-aminophosphine, 2-(*S*)-diphenylphosphinopyrrolidine derived from (*S*)-proline. A tridentate NPN ligand, also derived from (*S*)-proline, has been described and used for the asymmetric transfer hydrogenation of ketones catalyzed by ruthenium(II).[13] In work unrelated to catalysis, the preparation and crystal structure determination of the complex $RuCl_2(Pgly)_2$, Pgly = $PPh_2CH_2CH_2NH_2$, revealed that it has the geometry of **A** in Figure 2 with X, Y = Cl.[14]

We also describe a route to a potentially very diverse series of complexes containing one aminophosphine and one diphosphine, (*R*)-binap. The use of the enantiomerically pure (*R*)-binap ligand can facilitate or enhance the enantioselectivity of these catalyst types. Hydrogenation catalyst precursors with bidentate ligands such as $RuCl_2(binap)(diamine)$,[1,2,15] RuH(Cl)(binap)(diamine)[3] and $RuH(BH_4)(binap)(diamine)$[16] and hydrogenation catalysts $Ru(H)_2(binap)(diamine)$[4,17] are known but they do not contain an aminophosphine ligand. Ruthenium precatalysts with tetradentate $Ph_2P(C_6H_4)CH_2$ NH-Q-$NHCH_2(C_6H_4)PPh_2$ ligands, where Q is linking group, have also been reported for H_2-hydrogenation[18] and transfer hydrogenation[18,19] of ketones.

Results and Discussion

The hydride complexes *trans*-$RuHCl(PPh_2CH_2$-$CHRNH_2)_2$, R = H and Me, are prepared by refluxing the precursor complex $RuHCl(PPh_3)_3$ in toluene with two equivalents of the ligand [Pgly or (*R*)-Pala] as shown in Scheme 1.



Scheme 1. Preparation of the complexes *trans*-$RuHCl(PPh_2CH_2CHRNH_2)_2$.

The complexes are yellow, air sensitive solids. The complex $RuHCl(Pgly)_2$ has a low solubility in benzene or THF while $RuHCl(Pala)_2$ is more soluble. Although no crystals could be obtained, the complexes have the geometry shown in Scheme 1 on the basis of the NMR data and the similarity to $RuHCl(Ppro)_2$ (see below). In addition, dissolving $RuHCl(Pgly)_2$ in CH_2Cl_2 results in the formation of *trans*-$RuCl_2(Pgly)_2$ as shown by single crystal X-ray diffraction to have the same geometry as reported previously[14] with geometry **A** shown in Figure 2.

The complex *trans*-$RuHCl(Ppro)_2$ was prepared as a mixture of two diastereomers according to Scheme 2. There is a major diastereomer A and a minor diastereomer B in a ratio of 7:1.

The assignment of these diastereomers to the structures shown in Scheme 2 is based on the single crystal X-ray diffraction structure of diastereomer A (Figure 3). Crystals of *trans*-$RuHCl(Ppro)_2$ have two independent molecules in the asymmetric unit cell that are almost superimposable (Table 1). The azacyclopentane ring can take up two configurations that allow the nitrogen to be *R* or *S*. The major diastereomer has the nitrogens of opposite configuration so that both N–H are *syn* to the chloride and have favorable $N-H^{\delta+}\cdots Cl^{\delta-}$-Ru interactions as shown in Scheme 2. The nitrogen in the *R* configuration in Figure 3 is in an azacyclopentane ring that is nearly in the same plane as the Ru and P_2N_2 donor set (dihedral angle of 14°). The best plane through the other azacyclopentane ring containing the (*S*)-N is angled from the plane of the RuP_2N_2 atoms with a dihedral angle of approx. 39°. The Ru–Cl bond is tilted away from perpendicular to the RuP_2N_2 plane toward the NH groups, a motif that is common for RuHCl(diamine)(P-donor)$_2$ complexes.[3,4]

The structure is retained in solution according to the NMR spectra. The ^{31}P NMR spectrum shows two sets of doublets for each diastereomer as expected. The magnitude of the $^2J_{P,P}$ coupling constants indicates that the phosphorus atoms are *cis* and not *trans* in each diastereomer. The ^1H NMR spectra show doublet of doublet

Table 1. Selected bond lengths [Å] and angles [°].

trans-RuHCl[(S)-Ppro]$_2$ (two molecules)				*trans*-RuHCl[(R)-binap](Pgly)	
Ru(1)-H(1RU)	1.88(7)	not observed		Ru(1)-H(1RU)	1.58(2)
Ru(1)-N(1)	2.189(6)	Ru(2)-N(4)	2.185(6)	Ru(1)-N(1)	2.195(5)
Ru(1)-N(2)	2.203(6)	Ru(2)-N(3)	2.202(7)	Ru(1)-P(2)	2.255(2)
Ru(1)-P(2)	2.225(2)	Ru(2)-P(4)	2.227(2)	Ru(1)-P(3)	2.307(2)
Ru(1)-P(1)	2.227(2)	Ru(2)-P(3)	2.232(3)	Ru(1)-P(1)	2.340(2)
Ru(1)-Cl(1)	2.564(2)	Ru(2)-Cl(2)	2.549(2)	Ru(1)-Cl(1)	2.580(2)
H(1RU)-Ru(1)-N(1)	91(2)			H(1RU)-Ru(1)-N(1)	90(2)
H(1RU)-Ru(1)-N(2)	85(2)			H(1RU)-Ru(1)-P(2)	92(2)
N(1)-Ru(1)-N(2)	91.8(2)	N(4)-Ru(2)-N(3)	91.8(3)	N(1)-Ru(1)-P(2)	177.6(1)
H(1RU)-Ru(1)-P(2)	87(2)			H(1RU)-Ru(1)-P(3)	82(2)
N(1)-Ru(1)-P(2)	174.8(2)	N(3)-Ru(2)-P(4)	174.5(2)	N(1)-Ru(1)-P(3)	89.0 (2)
N(2)-Ru(1)-P(2)	83.6(2)	N(4)-Ru(2)-P(4)	82.8(2)	P(2)-Ru(1)-P(3)	90.67(6)
H(1RU)-Ru(1)-P(1)	95(2)			H(1RU)-Ru(1)-P(1)	82(2)
N(1)-Ru(1)-P(1)	83.2(2)	N(3)-Ru(2)-P(3)	83.5(2)	N(1)-Ru(1)-P(1)	81.2(2)
N(2)-Ru(1)-P(1)	174.96(2)	N(4)-Ru(2)-P(3)	174.6(2)	P(2)-Ru(1)-P(1)	99.81(6)
P(2)-Ru(1)-P(1)	101.44(8)	P(4)-Ru(2)-P(3)	101.88(9)	P(3)-Ru(1)-P(1)	161.14(6)
H(1RU)-Ru(1)-Cl(1)	164(2)			H(1RU)-Ru(1)-Cl(1)	167(2)
N(1)-Ru(1)-Cl(1)	79.5(2)	N(4)-Ru(2)-Cl(2)	80.5(2)	N(1)-Ru(1)-Cl(1)	78.7(12)
N(2)-Ru(1)-Cl(1)	82.4(2)	N(3)-Ru(2)-Cl(2)	82.6(2)	P(2)-Ru(1)-Cl(1)	99.08(6)
P(2)-Ru(1)-Cl(1)	102.19(8)	P(3)-Ru(2)-Cl(2)	101.47(8)	P(3)-Ru(1)-Cl(1)	104.43(6)
P(1)-Ru(1)-Cl(1)	96.29(8)	P(4)-Ru(2)-Cl(2)	95.49(8)	P(1)-Ru(1)-Cl(1)	89.46(6)

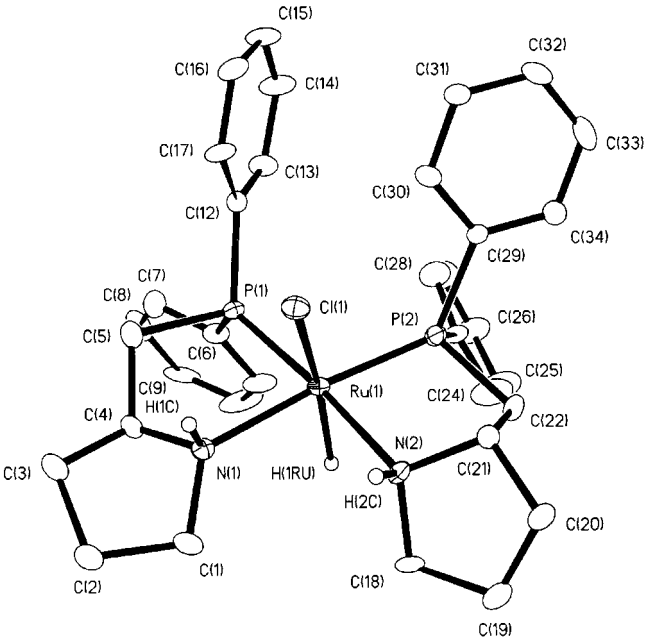
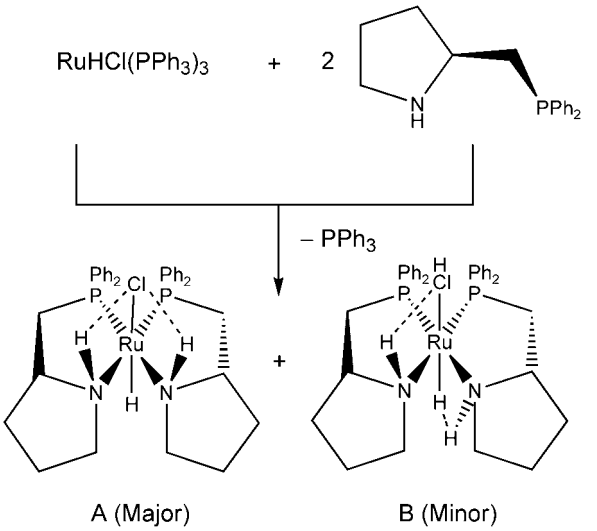


Figure 3. Molecular structure of one of the two molecules of *trans*-RuHCl[(S)-Ppro]$_2$ in the unit cell.

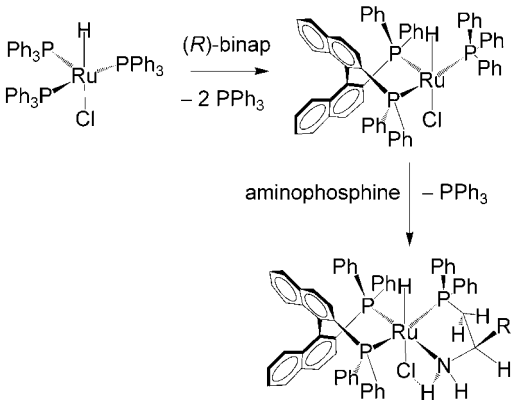


Scheme 2. Synthesis of *trans*-RuH(Cl)[(S)-Ppro]$_2$ as two diastereomers.

patterns for the hydride of each diastereomer and the magnitude of the coupling constants shows that the hydrides are *cis* to two non-equivalent phosphorus nuclei as expected on the basis of the structures in Scheme 2.

The structure of *trans*-RuHCl[(*S*)-Ppro]$_2$ contrasts with that of the complex *trans, trans, trans*-Ru(O$_2$CMe)$_2$[(*S*)-Ppro]$_2$ that has mutually *trans* phosphorus atoms.[12] This geometry is maintained in solution as evidenced by the large $^2J_{P,P}$ coupling of 335 Hz in the ^{31}P NMR spectrum. The phosphorus nuclei in this complex are non-equivalent because the 5-membered proline rings also take up two different configurations in the same molecule with the N atoms having opposite configurations. This supports our structural assignment of the two diastereomers in our *trans*-RuHCl[(*S*)-Ppro]$_2$ complex. Therefore this ligand is not as rigid as initially anticipated.

A series of hydridochlororuthenium(II) complexes containing enantiomerically pure bidentate diphosphine ligand and bidentate aminophosphine ligand



Scheme 3. The synthesis of complexes *trans*-RuHCl[(*R*)-binap]-(aminophosphine) (R=H, Me).

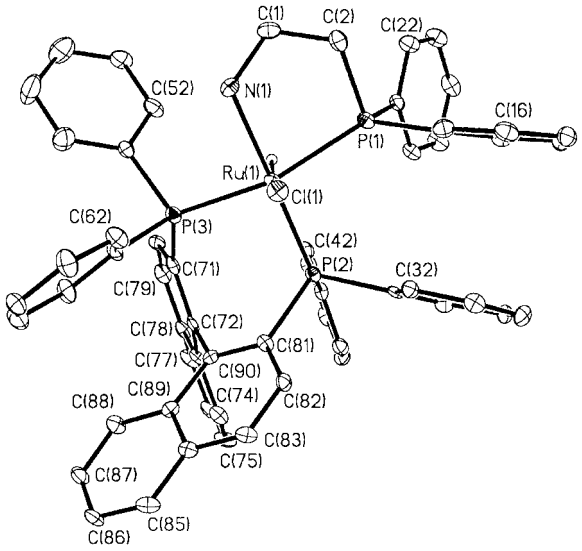


Figure 4. Molecular structure of *trans*-RuHCl[(R)-binap](Pgly).

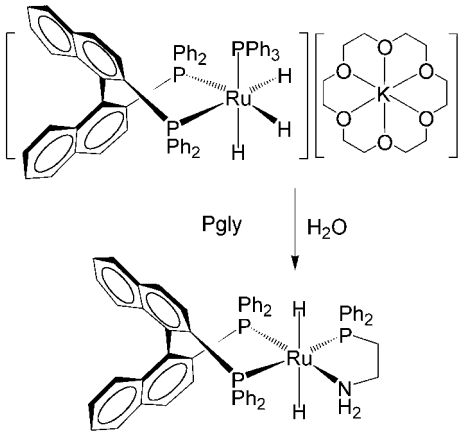


Figure 5. Generation of a *trans*-dihydride complex in solution.

were prepared in two steps (Scheme 3). In the first step RuHCl[(*R*)-binap](PPh$_3$) is prepared from RuHCl(PPh$_3$)$_3$ and (*R*)-binap as described previously.[3] The complexes RuHCl[(*R*)-binap][Ph$_2$PCH$_2$CH(R)(NH$_2$)] (R = H, CH$_3$) were then prepared as shown in Scheme 3.

For the preparation of *trans*-RuHCl[(*R*)-binap)(Pala), it is necessary to heat the mixture in toluene until the two isomers that initially form are converted into one isomer. The multiplet and ABX patterns in the ^{1}H and ^{31}P{^{1}H} NMR spectra, respectively, of *trans*-RuHCl[(*R*)-binap](aminophosphine) are consistent with a *trans* octahedral coordination geometry. The structure of RuHCl[(*R*)-binap](Pgly) was determined to have the geometry shown in Scheme 3 (R = H) by single crystal X-ray diffraction (Figure 4). There is an axial NH that is parallel to the Ru–Cl bond with an H···Cl distance of 2.6 Å.

Observation of a *trans*-Dihydride Complex

trans-Dihydrides are thought to be the active catalysts for the hydrogenation of ketones and the structure of *trans*-RuH$_2$[(*R*)-binap](tmen) has been determined.[4,17] The dihydride derived by the reaction of *trans*-RuHCl(Pgly)$_2$ with hydride reagents is extremely reactive and has not been observed by us to date. The *trans*-dihydride complex RuH$_2$[(*R*)-binap](Pgly) was generated *in situ* by mixing one equivalent of Pgly and the anionic hydride salt [(K-18-crown-6)]{RuH$_3$[(*R*)-binap](PPh$_3$)} in C$_6$D$_6$ and allowing the solution to stand for 12 hours at 20 °C (Figure 5).

The reaction is probably facilitated by adventitious moisture. An alternative interpretation is the formation of an anionic complex [(K-18-crown-6)]{RuH$_2$[(*R*)-binap](PPh$_2$CH$_2$CH$_2$NH)} where the hydrides are *trans* and there is an amido nitrogen created by deprotonation by the hydride with evolution of dihydrogen. However, such an anionic complex would be expected to be protonated by 2-propanol and this was not observed when a drop of this alcohol was added to the solution. Therefore it is probably a neutral dihydride. The complex was too reactive to be isolated. However the hydride chemical shifts and the *trans*-$J_{H,H}$ of 8 Hz of the complex are comparable to those typically observed in neutral *trans*-dihydride ruthenium(II) complexes.[17,20] The ACMNX pattern of the two hydride resonances was simulated exactly where A and C represent the two non-equivalent hydrides and M, N and X represent the three non-equivalent ^{31}P nuclei. The MNX pattern in the ^{31}P{^{1}H} NMR spectrum is also consistent with the structure shown in Figure 5.

Catalytic Hydrogenation of Ketones and Imines

All of these complexes provide very active catalysts for the hydrogenation of ketones or imines to alcohols or amines, respectively. The active catalyst solutions are

Table 2. Representative list of new ruthenium precatalysts, the conditions for the hydrogenation of acetophenone (**a**) and the yield and ee.[a]

Complex	Conditions	Yield of alcohol	ee of alcohol
$RuCl_2(Pgly)_2$	KOPr-*i*/neat PhCOMe/3 atm H_2/12 h/S : cat = 2200	100%	
$RuHCl(Pgly)_2$	KOPr-*i*/neat PhCOMe/3 atm H_2/12 h/S : cat = 2200	100%	
$RuHCl(Pala)_2$	KOPr-*i*/neat PhCOMe/3 atm H_2/12 h/S : cat = 2200	100%	
RuHCl((*R*)-binap)(Pgly)	KOBu-*t*/neat PhCOMe/3 atm H_2/12 h/S : cat = 4100	100%	10% (*S*)
RuHCl[(*R*)-binap][(*R*)-Pala]	KOBu-*t*/neat PhCOMe/3 atm H_2/12 h/S : cat = 4100	100%	40% (*S*)
trans-RuHCl[(*S*)-Ppro]$_2$	KOBu-*t*/C_6D_6/11 atm H_2/12 h/S : cat = 2000[b]	>99%	6% (*R*)

[a] Representative conditions: acetophenone (2.0 g) was added under a flow of hydrogen gas to a Schlenk flask containing $RuHCl(Pgly)_2$ (5 mg) and KOPr-*i* (5 mg). The flask was cooled to liquid nitrogen temperature, filled with H_2 gas, closed and allowed to gradually warm to room temperature in order to generate an initial pressure of about 3 atm H_2. The mixture was vigorously stirred for 12 hours.

[b] Acetophenone (500 mg, 4.2 mmol), KOBu-*t* (1.2 mg, 1.1×10^{-2} mmol), RuHCl[(*S*)-Ppro]$_2$ (1.4 mg, 2.1×10^{-3} mmol) and benzene added to 2.5 mL.

Table 3. Representative list of other ketones hydrogenated (see Figure 6).

Complex	Ketone	Conditions	% conversion to alcohol
$RuCl_2(Pgly)_2$	**c**	KOBu-*t*/C_6D_6/3 atm H_2/12 h/S : cat = 390	100
$RuHCl(Pgly)_2$	**c**	KOBu-*t*/C_6D_6/3 atm H_2/12 h/S : cat = 390	100
RuHCl[(*S*)-Ppro]$_2$	**c**	KOBu-*t*/C_6H_6/11 atm H_2/16 h/S : cat = 2000	50
$RuHCl(Pgly)_2$	**d**	KOBu-*t*/neat ketone/3 atm H_2/12 h/ S : cat = 4000	100
RuHCl[(*R*)-Pala]$_2$	**d**	KOBu-*t*/neat ketone/3 atm H_2/12 h/ S : cat = 4100	100
RuHCl[(*R*)-binap](Pgly)	**d**	KOBu-*t*/neat ketone/3 atm H_2/12 h/ S : cat = 3400	100
$RuCl_2(Pgly)_2$	**e**	KOBu-*t*/neat ketone/3 atm H_2/12 h/ S : cat = 2550	100
$RuHCl(Pgly)_2$	**e**	KOBu-*t*/neat ketone/3 atm H_2/12 h/ S : cat = 2400	100
RuHCl[(*R*)-Pala]$_2$	**e**	KOBu-*t*/neat ketone/3 atm H_2/12 h/S : cat = 620	100
RuHCl[(*S*)-Ppro]$_2$	**e**	KOBu-*t*/C_6H_6/11 atm H_2/16 h/S : cat = 2000	25
$RuHCl(Pgly)_2$	**f**[a]	KOBu-*t*/neat ketone/3 atm H_2/12 h/ S : cat = 2450	100
RuHCl[(*S*)-Ppro]$_2$	**g**	KOBu-*t*/C_6H_6/11 atm H_2/16 h/S : cat = 2000	100

[a] 5-Hexen-2-one (**f**, 3.0 g) was added under a flow of hydrogen gas to a Schlenk flask containing $RuHCl(Pgly)_2$ (5 mg) and KOBu-*t* (5 mg). Pure 5-hexen-2-ol was present when the sample was analyzed after 12 h.

obtained by mixing the complex with 3–5 equivalents of an alkoxide base and the neat substrate or a benzene solution of this substrate in a ratio of catalyst : base : substrate = 1 : (3 to 5) : (400 to 5000) and placing it under 1 to 11 atm of H_2 at 20 °C.

Under these mild conditions, the complexes catalyze the hydrogenation of several grams of acetophenone to 1-phenylethanol in less than 12 h (Table 2). Our qualitative observations indicate that the $(P,N)_2$ and (P,N)[(*R*)-binap] catalysts have similar activities. While the use of the $(P,N)_2$ complexes that have optically active P,N ligands produced the alcohol in very low ee, the use of the (P,N)((*R*)-binap) complexes lead to ee of up to 40% (S) for the (*R*)-Pala complex (Table 2).

These complexes are exceptionally active for the hydrogenation of a variety of other ketones (Table 3). The complexes $RuCl_2(Pgly)_2$ and $RuHCl(Pgly)_2$ produce more active catalysts than RuHCl[(*S*)-Ppro]$_2$ for the hydrogenation of the sterically hindered and electronically deactivated carbonyl group of pivalophenone (ketone **c**, Figure 6) and pinacolone (ketone **e**). All of the complexes can be used to efficiently hydrogenate acetone (ketone **d**) to 2-propanol. There is complete selectivity in the hydrogenation of the C=O over C=C bonds of α,β-unsaturated ketones (**f** and **g**) to produce exclusively the allyl alcohols. This is a hallmark of catalysts that employ the NH-assisted outer-sphere hydrogenation of polar bonds.[1,6]

The catalysts are also effective for the hydrogenation of imines (**h** to **m** of Figure 7) under very mild conditions when left overnight (Table 4). The aldimine **h** is readily reduced to *N*-benzylaniline. In fact the conversion was complete after 4 h in at least two of the cases. The more substituted ketimines with either *N*-phenyl or *N*-benzyl substituents are also readily reduced. The $RuCl_2(Pgly)_2$ catalyst system is tolerant of the quinuclidine functional group of imine **k** and easily reduces it to the corresponding *N*-phenylamine. Even the more challenging *N*-butyl-substituted imine (**m**) can be hydrogenated by use of $RuCl_2(Pgly)_2$ when the reaction is left for 36 h under the standard conditions.

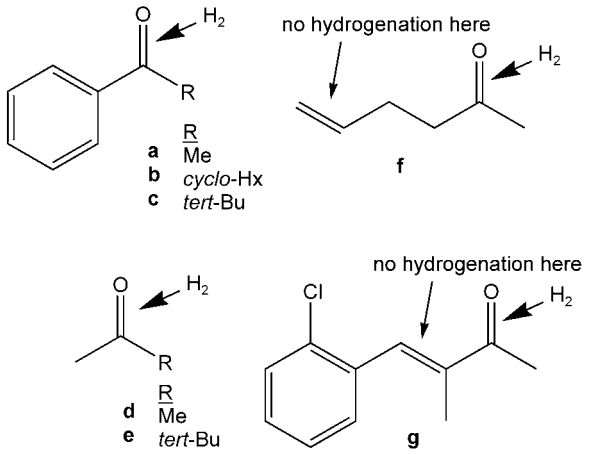


Figure 6. Ketone substrates and the location of reduction to produce alcohols.

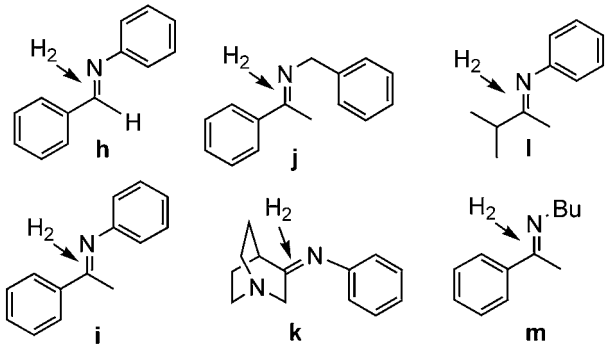


Figure 7. Imine substrates and the location of hydrogenation to produce amines.

Conclusions

A series of complexes $RuHCl(PPh_2CH_2CHRNH_2)_2$ and $RuHCl(PPh_2CH_2CHRNH_2)[(R)\text{-binap})]$, can be prepared by the substitution of the PPh_3 ligands in $RuHCl(PPh_3)_3$ or $RuHCl(PPh_3)[(R)\text{-binap}]$ with beta-aminophosphines derived from amino acids. These are catalyst precursors for the hydrogenation of a variety of ketones and imines under mild conditions and show excellent selectivity for C=O over C=C bonds. Unfortunately the ee values were low in the asymmetric hydrogenation of ketones. A *trans*-dihydride complex RuH_2 $[(R)\text{-binap}](Pgly)$ was generated *via* a novel anionic hydride intermediate. This might be the active hydrogenation catalyst that is formed by the reaction of the $RuHCl[(R)\text{-binap}](Pgly)$ precursor with base and dihydrogen.

The hydride complex $RuHCl[(S)\text{-Ppro}]_2$ prepared using the ligand derived from proline was an active ketone hydrogenation precatalyst but gave low enantioselectivity in the hydrogenation of acetophenone. This is probably explained by the existence of diastereomers generated by the unexpected flexibility of the proline rings with resulting mixed stereochemical configurations at the nitrogen atoms. Future work will concentrate on more rigid ligand systems.

Experimental Section

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. The ketones were washed with saturated

Table 4. Hydrogenation of imines (see Figure 7) to amines using ruthenium(II) aminophosphine complexes, potassium *tert*-butoxide base (3–5 equivs.) and 3 atm H_2.[a]

Complex	Imine	Conditions	% conversion to amine
$RuCl_2(Pgly)_2$	**h**	KOBu-*t*/C_6D_6/3 atm H_2/12 h/S : cat = 4200	100
$RuHCl(Pgly)_2$	**h**	KOBu-*t*/C_6D_6/3 atm H_2/4 h/S : cat = 370	100
$RuHCl[(R)\text{-Pala}]_2$	**h**	KOBu-*t*/C_6D_6/3 atm H_2/4 h/S : cat = 360	100
$RuHCl[(R)\text{-binap}](Pgly)$	**h**	KOBu-*t*/C_6D_6/3 atm H_2/12 h/S : cat = 550	100
$RuHCl[(R)\text{-binap}][(R)\text{-Pala}]$	**h**	KOBu-*t*/C_6D_6/3 atm H_2/12 h/S : cat = 550	100
$RuCl_2(Pgly)_2$	**i**	KOBu-*t*/C_6D_6/3 atm H_2/8 h/S : cat = 1000	100
$RuHCl(Pgly)_2$	**i**[b]	KOBu-*t*/C_6D_6/3 atm H_2/8 h/S : cat = 2600	100
$RuHCl[(R)\text{-Pala}]_2$	**i**	KOBu-*t*/C_6D_6/3 atm H_2/12 h/S : cat = 2000	100
$RuHCl[(R)\text{-binap}](Pgly)$	**i**	KOBu-*t*/C_6D_6/3 atm H_2/12 h/S : cat = 1000	100
$RuCl_2(Pgly)_2$	**j**	KOBu-*t*/neat imine/3 atm H_2/12 h/S : cat = 1800	100
$RuHCl(Pgly)_2$	**j**	KOBu-*t*/neat imine/3 atm H_2/12 h/S : cat = 1700	100
$RuHCl[(R)\text{-Pala}]_2$	**j**	KOBu-*t*/neat imine/3 atm H_2/12 h/S : cat = 1800	100
$RuHCl[(R)\text{-binap}](Pgly)$	**j**	KOBu-*t*/neat imine/3 atm H_2/24 h/S : cat = 950	100
$RuCl_2(Pgly)_2$	**k**	KOBu-*t*/C_6D_6/3 atm H_2/12 h/S : cat = 200	100
$RuCl_2(Pgly)_2$	**l**	KOBu-*t*/neat imine/3 atm H_2/12 h/S : cat = 2000	100
$RuCl_2(Pgly)_2$	**m**	KOBu-*t*/C_6D_6/3 atm H_2/36 h/S : cat = 500	100

[a] 1 g C_6D_6 added to solid imines **h**, **i**, **l**, **m**.

[b] *N*-(1-Phenylethylidene)-benzeneamine (4.0 g) and C_6D_6 (1 g) were added under a flow of hydrogen gas to a Schlenk flask containing $RuHCl(Pgly)_2$ (10 mg) and KOBu-*t* (10 mg). Pure *N*-phenyl-1-phenylethylamine was present when the sample was analyzed after 8 h.

K_2CO_3 solution and dried with anhydrous Na_2SO_4, then distilled prior to use. The enantiomeric excess value of the products was determined with a Perkin Elmer AutoSystem XL Gas Chromatograph system (column, Chirasil-DEX CB; 25 m × 0.25 mm, CHROMPACK, carrier gas, H_2). Varian Gemini 300, Unity 400 and Unity 500 spectrometers were used for NMR spectra. The program MestRe-C was used for simulation of the NMR spectra. Pgly was purchased from Fluka. The aminophosphine ligands can be prepared in excellent chemical and enantiomeric purity and fair yield when the intermediates are carefully isolated by chromatography under Ar. The ligand Pala was made from the unnatural (*R*)-alanine.[9,21] Ppro ($\delta^{31}P = -18.5$ in $CDCl_3$),[7] $RuHCl(PPh_3)_3$,[22] and RuHCl(binap)(PPh_3)[3] were prepared as described. The imines were prepared from the corresponding ketones and amines at reflux in toluene in the presence of molecular sieves. Other chemicals that were required were purchased from the Aldrich Chemical Company.

trans-RuHCl(Pgly)$_2$

Toluene (5 mL) was added to a mixture of $RuHCl(PPh_3)_3$ (300 mg, 1.07 mmol) and $Ph_2P(CH_2)_2(NH_2)$ (510 mg, 2.2 mmol) and the mixture refluxed for 12 hours under argon, during which a bright yellow solution formed. The solution was concentrated to 1.0 mL and hexanes (5 mL) added, resulting in the precipitation of a yellow solid which was then filtered using a sintered glass frit, washed with hexanes (3 × 5 mL) and vacuum dried. Recrystallization from toluene/hexanes afforded a pure sample of the complex; yield: 468 mg. ^{1}H NMR (C_6D_6): $\delta = -19.83$ (t, $^2J_{H,P} = 25.9$ Hz, 1H, RuH), 2.18–4.54 (m, 12H), 6.90–7.38 (m, 20H, Ph); $^{31}P\{^1H\}$ NMR: $d = 77.8$ (s); IR (Nujol): $\nu = 1924$ (νRuH), 3282, 3141 cm^{-1} (νNH); anal. calcd. for $C_{28}H_{33}ClN_2P_2Ru$: C 56.42, H 5.58, N 4.70; found: C 57.0, H 6.1, N 4.3. A small amount of hexanes in the crystals (detected by ^{1}H NMR) accounts for the differences.

trans-RuCl$_2$(Pgly)$_2$

A 50 mg sample of $RuHCl(Pgly)_2$ was dissolved in dichloromethane (1.0 mL) and the resulting solution was allowed to stand at room temperature for 24 hours. A bright yellow precipitate was obtained upon addition of diethyl ether (2 mL); yield: 43 mg (81%); ^{1}H NMR (CD_2Cl_2): $\delta = 1.68–3.72$ (m, 12H), 6.99–7.17 (m, 20H, Ph); $^{31}P\{^1H\}$ NMR: $\delta = 62.51$ ppm (s). The complex is modified when dissolved in DMSO-d_6 to produce the ^{31}P NMR spectrum reported previously.[14]

trans-RuHCl(Pala)$_2$

This complex was prepared using procedures similar to those described for $RuHCl(Pgly)_2$. ^{1}H NMR (C_6D_6): $\delta = -19.15$ (t, $^2J_{H,P} = 25.4$ Hz, 1H, RuH), 1.01–4.54 (m, 16H), 6.93–7.76 (m, 20H, Ph); $^{31}P\{^1H\}$ NMR: $\delta = 72.9$ (d), 72.4 (d, $^2J_{P,P} = 34.8$ Hz).

Preparation of the Mixture of Diastereomers A and B of RuHCl[(*S*)-Ppro]$_2$

The Ppro ligand (*S*)-2-(diphenylphosphinomethyl)pyrrolidine (285 mg, 1.06 mmol) and $RuHCl(PPh_3)_3$ (440 mg, 0.48 mmol) and dry THF (5 mL) were added to a 25-mL Schlenk flask. The resulting mixture was refluxed for 6 h under argon and cooled to room temperature. It was filtered under a nitrogen atmosphere and the solvent was removed under vacuum. The residue was washed with ether (3 × 10 mL) to remove PPh_3 and dried under vacuum. A yellow-green powder was obtained; yield: 308 mg (95%). It contained two isomers (the ratio of major isomer/minor isomer is about 6.5/1). Orange crystals of the major isomer were obtained by slow diffusion of hexanes into a C_6D_6 solution. ^{1}H NMR(300 MHz, C_6D_6): $\delta = -19.18$ (dd, $J_{H,P} = 24.9$ Hz, $J_{H,P} = 29.7$ Hz, major isomer); -18.85 (dd, $J_{H,P} = 24.6$ Hz, $J_{H,P} = 29.7$ Hz, minor isomer); ^{31}P NMR (121 MHz, C_6D_6): $\delta = 70.81$ (d, $J_{P,P} = 39.1$ Hz, major isomer), 76.64 (d, $J_{P,P} = 39.1$ Hz, major isomer), 69.62 (d, $J_{P,P} = 18.8$ Hz, minor isomer), 71.63 (d, $J = 18.8$ Hz, minor isomer); anal. calcd. for $C_{34}H_{41}ClN_2P_2Ru$: C 60.39, H 6.11, N 4.14; found: C 60.50, H 6.19, N 4.09.

RuHCl[(*R*)-binap](Pgly)

A mixture of RuHCl[(*R*)-binap](PPh_3) (300 mg, 0.29 mmol) and Pgly (70 mg, 0.30 mmol) in toluene (5 mL) was refluxed for 6 h. The resulting solution was concentrated to 1 mL and hexanes (10 mL) added, resulting in a bright yellow product; yield: 261 mg (90%). Crystals were obtained by the slow diffusion of hexanes into a THF solution of the complex to produce RuHCl[(*R*)-binap](Pgly)·3 THF. Anal. calcd. for $C_{70}H_{73}ClNO_3P_3Ru$: C 69.7, H 6.1, N 1.16; found: C 69.3, H 6.1, N 1.0; ^{1}H NMR (C_6D_6): $\delta = -17.75$ (dt, $^2J_{H,P} = 20.6$, 25.6 Hz, 1H, RuH), 0.95–3.68 (m, 6H), 6.22–8.83 (m, 42H); $^{31}P\{^1H\}$ NMR: $\delta = 38.1$ (dd, $^2J_{P,P} = 292$, 32.5 Hz), 40.6 (dd, $^2J_{P,P} = 292$, 31.4 Hz), 67.5 (dd, $^2J_{P,P} = 32.5$, 31.4 Hz); IR (Nujol): $\nu = 1986$ (νRuH), 3329, 3259 cm^{-1} (νNH).

RuHCl[(*R*)-binap](Pala)

This was prepared using a similar procedure; yield: 272 mg (93%); ^{1}H NMR (C_6D_6): $\delta = -17.36$ (ddd, $^2J_{H,P} = 21.7$, 21.0, 20.1 Hz, 1H, RuH), 0.85–3.00 (m, 8H), 6.22–8.88 (m, 42H); $^{31}P\{^1H\}$ NMR: $\delta = 29.4$ (ABX pattern, P^A, $^2J_{A,B} = 294$, $^2J_{A,X} = 32$ Hz), 32.9 (P^B, $^2J_{A,B} = 294$, $^2J_{B,X} = 32$ Hz), 63.4 (dd, $^2J_{B,X} = {}^2J_{A,X} = 32$ Hz); IR (Nujol): $\nu = 2006$ (νRuH), 3320, 3250 cm^{-1} (νNH). If benzene is used as the solvent, then two isomers form, a major one as above, and a minor one with the following $^{31}P\{^1H\}$ NMR properties: $\delta = 43.5$ (ABX pattern, P^A, $^2J_{A,B} = 290$, $^2J_{A,X} = 31$ Hz), 48.1 (P^B, $^2J_{A,B} = 290$, $^2J_{B,X} = 31$ Hz), 57.3 (P^X, $^2J_{B,X} = 32$, $^2J_{A,X} = 31$ Hz).

RuH$_2$[(*R*)-binap](Pgly):

(a) *Synthesis of precursor [K(18-crown-6)][RuH$_3$[*(R)*-binap](PPh$_3$)]:* THF (2 mL) was added to a mixture of RuHCl[(*R*)-binap]$(PPh_3)_3$ (100 mg, 0.10 mmol), KH (20 mg, 0.5 mmol) and 18-crown-6 (26 mg, 0.10 mmol) under an atmosphere of H_2 gas. The mixture was stirred for 5 hours, filtered un-

der a nitrogen atmosphere and hexanes (10 mL) added to the filtrate, precipitating a pale red-brown solid; yield: 95 mg (74%); ^{1}H NMR (C_6D_6, labelling as in Figure 8i): $\delta = -8.92$ (ACEMQX pattern, H^A, $J_{A,C}=7$, $J_{A,E}=6$, $J_{A,M}=76$, $J_{A,Q}=20$, $J_{A,X}=21$ Hz, RuH), -9.32 (H^C, $J_{A,C}=7$, $J_{C,E}=6$, $J_{C,M}=31$, $J_{C,Q}=76$, $J_{C,X}=12$ Hz, RuH), -9.94 (H^E, $J_{A,E}=6$, $J_{C,E}=6$, $J_{E,M}=14$, $J_{E,Q}=28$, $J_{E,X}=73$ Hz, RuH), 3.16 (s, 24H, CH_2), 6.24–8.76 (m, 47H); ^{31}P{^{1}H} NMR: $\delta=59.1$ (dd, P^X, $J_{M,X}=10$, $J_{Q,X}=8$ Hz), 61.2 (dd, P^Q, $J_{M,Q}=9$, $J_{Q,X}=8$ Hz), 64.7 (dd, P^M, $J_{M,Q}=9$, $J_{M,X}=10$ Hz); IR (Nujol): $\nu=1799$, 1836 cm^{-1} (νRuH).

(b) *RuH_2[(R)-binap](Pgly):* A mixture of {[K(18-crown-6)][RuH_3[(*R*)-binap](PPh$_3$)]} (100 mg, 77 mmol) and Pgly (20 mg, 86 mmol) in C_6D_6 (0.6 mL) was allowed to stand for 12 hours. The NMR spectra shows a clean formation of the *trans*-dihydride complex. Hydride region of ^{1}H NMR (C_6D_6, labelling as in Figure 8ii): $\delta = -5.11$ (ACMNX pattern, H^A, $J_{A,C}=8.2$, $J_{A,M}=-14.8$, $J_{A,N}=-20.2$, $J_{A,X}=-14.2$ Hz, RuH), -6.45 (H^C, $J_{A,C}=8.2$, $J_{C,M}=-26.3$, $J_{C,N}=-12.4$, $J_{C,X}=-22.3$ Hz, RuH); ^{31}P{^{1}H} NMR: $\delta=67.5$ (dd, P^M, $J_{M,N}=279$, $J_{M,X}=-33.5$ Hz), 72.8 (dd, P^N, $J_{M,N}=279$, $J_{N,X}=-38.6$ Hz), 81.6 (P^X, $J_{M,X}=-33.5$, $J_{N,X}=-38.6$ Hz).

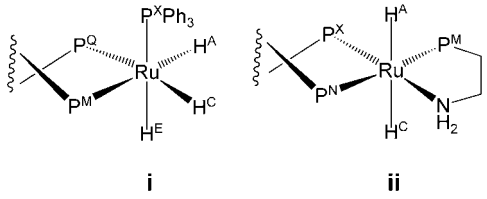


Figure 8. Labelling of the nuclei for [K(18-crown-6)][RuH_3[(*R*)-binap](PPh$_3$)] (**i**) and *trans*-RuH_2[(*R*)-binap](Pgly) (**ii**).

Catalytic Hydrogenation of Ketones and Imines

(a) *Reactions done at 3 atm H_2:* In a typical catalytic run, 1 to 5 g of the neat ketone or imine or their solution in benzene or THF were added under a flow of hydrogen gas to a Schlenk flask containing 5 to 10 mg of the precursor complex and 5 to 10 mg of base (KOPr-*i* or KOBu-*t*). The flask was then cooled to liquid nitrogen temperature, filled with H_2 gas, closed and allowed to gradually warm to room temperature. The mixture was vigorously stirred for 8 to 12 hours. Conversion of the substrate to the respective product was assayed by NMR spectroscopy and gas chromatography. The catalyst was oxidized and precipitated from the alcohols of low volatility by the addition of hexanes in the air and then removed by filtration through a 5 mm thick pad of silica gel. The hexanes were evaporated to yield the pure alcohol. The catalytic hydrogenation results are summarized in Tables 1–3.

(b) *Reactions done at higher pressures:* A solution of the substrate and base (5–10 mg of KOBu-*t*) was added to a Parr reaction vessel against a flow of H_2. A solution of the catalyst was then added and the vessel was pressurized and stirred. The products were analyzed by gas chromatography and NMR. Reaction conditions: ketone (4.2 mmol); KOBu-*t* (1.2 mg, 1.1×10^{-2} mmol); RuHCl[(*S*)-Ppro]$_2$ (1.4 mg, 2.1×10^{-3} mmol) ben-

Table 5. Crystallographic data.[a]

Compound	*trans*-RuHCl[(*S*)-Ppro]$_2$	*trans*-RuHCl[(*R*)-binap](Pgly)·3 THF
Formula	$C_{34}H_{41}ClN_2P_2Ru$	$C_{70}H_{73}ClNO_3P_3Ru$
Formula weight	676.15	1205.72
Temperature, K	150(2)	150(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	12.081(2)	10.9011(4)
b, Å	19.452(4)	20.2807(7)
c, Å	26.700(5)	26.733(1)
α, °	90	90
β, °	90	90
γ, °	90	90
Volume, Å^3	6274(2)	5910.1(4)
Z	8	4
D_{calcd}, g·cm^{-3}	1.432	1.355
μ, cm^{-1}	7.13	4.41
2θ max, °	54.94	50.00
No. of reflns measd	33461	20779
No of reflns used	13770	10195
No of parameters	725	736
Final R indices [I > 2sigma(I)]	$R_1=0.0756$	$R_1=0.0649$
	$wR_2=0.1105$	$wR_2=0.1042$
R indices (all data)	$R_1=0.1812$	$R_1=0.1019$
	$wR_2=0.1428$	$wR_2=0.1187$
Goodness-of-fit on F^2	1.026	1.052

[a] $R_1=\Sigma F_o - F_c/\Sigma F_o$; $wR_2=[\Sigma w[(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w=1/[^2(F_o^2)+(0.075P)^2]$, where $P=[\max(F_o^2,0)+2F_c^2]/3$.

zene added to 2.5 mL. Reaction carried out at 20 °C for 16 h. Pressure of H_2 is 11 bar.

X-Ray Crystallographic Studies

Data were collected on a Nonius Kappa-CCD diffractometer using MoKα radiation (Table 5). The CCD data were integrated and scaled using the DENZO-SMN software package and the structures were solved and refined using SHELXTL V6.0. Hydrides were located and refined with isotropic thermal parameters. The unit cell of RuHCl[(*R*)-binap](Pgly) contains three THF molecules (one disordered and 2 partially disordered).

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-249142 {RuHCl[(*S*)-Ppro]$_2$} and CCDC-249143 {RuHCl[(*R*)-binap](Pgly)}. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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