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# Phosphine-Free Cp*Ru(Diamine) Catalysts in the Hydrogenation of Imines

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*Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday*

**Abstract:** We previously reported the phosphine-free Cp*Ru(diamine)-catalyzed hydrogenation of aryl methyl ketones. Herein we present the first report of ruthenium–diamine-catalyzed imine hydrogenation to form amines. The most effective catalyst, **I**/KO*t*Bu, completely converted several imines to amines at room temperature. The effect of electron-donating and -withdrawing groups on the reaction was investigated using a suitable series of substrates. The asymmetric version of the reaction was studied for two substrates, and the chiral amine products could be obtained in moderate enantiomeric excess.

**Keywords:** diamine ligands · hydrogenations · imines · ruthenium

## Introduction

Ruthenium-based hydrogenation catalysts have undergone a meteoric rise in popularity since the early 1990s,[1] and the chiral ruthenium catalysts that earned Professor Noyori the Nobel Prize in 2001[2] have played a major role in driving this trend. Noyori, Takaya, Akutagawa, and co-workers reported the highly enantioselective hydrogenation of functionalized ketones by ruthenium complexes in the late 1980s,[3,4] and Noyori and colleagues reported the same reaction for "simple" ketones (those in which the only other functional groups are aromatic rings) in 1995.[5] Highly active and selective ruthenium catalysts for transfer hydrogenation were developed concurrently by Noyori and others.[6] These breakthroughs have driven ruthenium compounds to the forefront of the ketone hydrogenation field,[4] and therefore these compounds have also been applied to the less-studied imine hydrogenation reactions.[7,8] Although recent work on ketone and imine hydrogenations has focused on enantioselective reduction, the industrial advantages of even achiral or racemic catalysts for ketone[9a] and C=Y (Y=N or O)[9b] hydrogenation have been discussed.

The four types of ruthenium precatalysts most commonly used for ketone (and, in some cases, imine) hydrogenation and transfer hydrogenation are shown in Figure 1. Each of these catalyst precursors reacts with base (usually an alkoxide or a hydroxide) to form the active catalyst via deprotonation of an NH or OH moiety on the ligand. Most of the precatalysts described by **A**–**D** in Figure 1 are active for either the direct or the transfer hydrogenation of ketones; Rautenstrauch, Morris, and co-workers demonstrated that a few can be catalysts for both transformations, albeit by forming different active catalysts in each mode.[9] The catalyst precursors **A** are useful in transfer hydrogenations[10] and are advantageous because some 1,2-aminoalcohol ligands (such as norephedrine) that give highly active catalysts are available relatively cheaply in both enantiomers.[6]

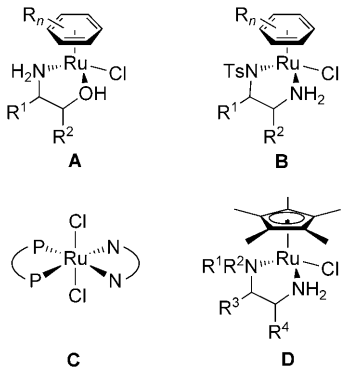


Figure 1. Ruthenium-based precatalysts for the direct and transfer hydrogenation of ketones and, in some cases, imines.

In 1995, Noyori and co-workers described the phosphine-free Ru–arene/diamine complexes **B**.[11] After activation by a strong base, these (in particular, the complex **B** with

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$R^1,R^2$ = (*R*,*R*)- or (*S*,*S*)-diphenyl and $\eta^6$-arene = *p*-cymene) catalyzed the asymmetric transfer hydrogenation of ketones using *i*PrOH or, better still, a mixture of formic acid and triethylamine, as the $H_2$ source.[12] The latter system also catalyzed the transfer hydrogenation of imines effectively and stereoselectively,[13] offering a major improvement over the previous state of the art. The structures **B** have served as templates for many related catalysts.[14]

The development of the ruthenium-catalyzed, direct asymmetric hydrogenation of imines has also drawn considerably on the analogous ketone reductions, but the imine reduction has lagged behind.[15] Although early reports of the ruthenium-catalyzed homogeneous hydrogenation of oximes[16] demonstrated this metal's activity towards C=N double bonds, the (diphosphine)ruthenium catalysts that work so well for ketone hydrogenation can be deactivated in the presence of bases, which complicates their application to imine hydrogenation.[5] James and co-workers applied Noyori's BINAP-ligated ruthenium catalysts[2] to imine hydrogenation, and found that they performed poorly for asymmetric imine hydrogenation.[17] However, they did find other $RuP_2$ systems that gave moderate conversions and modest *ee* values in the hydrogenation of imines to amines.

In 1995 Noyori and co-workers demonstrated that ruthenium complexes bearing a chelating diphosphine (or two monodentate phosphines) and a chelating diamine ligand (structure **C**), upon activation with an alkoxide or hydroxide base, catalyzed the asymmetric hydrogenation of ketones.[5] These catalysts are highly active and chemoselective for ketone hydrogenation, even in the presence of olefin functionalities.[18] Recently, $[RuP_2N_2]$ complexes have been applied toward catalytic imine hydrogenation by Abdur-Rashid et al. (who used [Ru(diphosphine)-(diamine)HCl][19,20] and $[Ru(phosphine)_2(diamine)HCl]$[21] precatalysts) and Cobley and Henschke (who used $[Ru(diphosphine)(diamine)Cl_2]$ precatalysts).[22]

Later, Ikariya and co-workers published the phosphine-free RuCp*(diamine) complexes **D**,[23] which are isoelectronic to **B**. The complexes **D** can be activated with KOH to form catalysts for the direct hydrogenation of ketones. The authors examined the effect of various diamine ligands on the reaction and concluded that diamines bearing one primary and one tertiary amino function showed the highest activity. Additionally, Ikariya and colleagues found that alcohols such as isopropanol and ethanol are the best solvents for these reactions. Deuterium labeling studies revealed that the alcohol solvent participates in the reaction by forming a hydrogen bond network that facilitates the scission of $H_2$ to produce an active ruthenium hydride species.

Our research group has employed *Cinchona* alkaloid-derived diamines as chiral ligands in **D** to produce precatalysts for exceptionally rapid, highly selective ketone hydrogenations.[24] We also studied the reaction computationally, and found a mechanism that accurately predicts the sense of enantiomeric discrimination for the hydrogenation of substrates by several catalysts. Our mechanism was in accord with that proposed by Ikariya; in particular, we calculated that the activation energy for $H_2$ cleavage was decreased by 7–10 kcal mol$^{-1}$ in the case of alcohol-mediated cleavage.

Despite the remarkable ability of **D**/alkoxide and **D**/hydroxide systems to catalyze the hydrogenation of ketones, they have not yet been applied to the hydrogenation of other C=Y bonds. This encouraged us to investigate the possible hydrogenation of imines using a similar catalytic system.

## Results and Discussion

Earlier reports indicated that the diamine ligand in a catalyst of type **D** must contain one tertiary and one primary nitrogen atom to produce a fast catalyst for ketone hydrogenation. Recently, Noyori[25] and Baratta[26] used 2-(aminomethyl)pyridine as a ligand in the $[RuP_2N_2]$-catalyzed hydrogenation and transfer hydrogenation, respectively, of ketones; this demonstrates the potential of unsaturated diamines in ketone reduction. Therefore, our preliminary studies included two types of ligands (Figure 2): ligands of the first type (**I**–**III**) have one $sp^2$ and one $sp^3$ nitrogen each, whereas those of the second type (**IV**–**VI**) have two $sp^3$ nitrogen atoms each. Additionally, the different basicities of the donor $sp^2$ nitrogen atoms of **I** and **II** allowed us to study how this parameter affects the hydrogenation reaction.

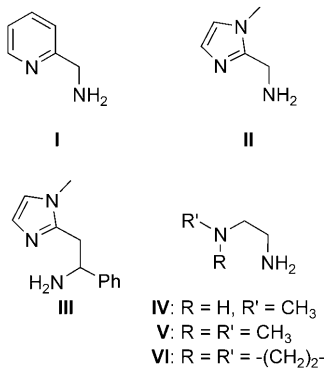
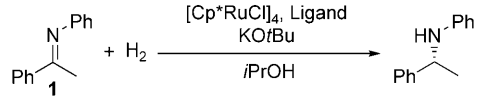



Figure 2. Diamine ligands used in the initial hydrogenation studies.

*N*-(1-Phenylethylidene)aniline (**1**) was chosen as the test substrate for hydrogenation. Test reactions were carried out in *i*PrOH containing the substrate, $[Cp^*RuCl]_4$, diamine, and potassium *tert*-butoxide at room temperature and at 50 °C under $H_2$ (100 bar) for 18 h. The results of these initial catalyst screening reactions are summarized in Table 1. Among the ligands tested, 2-(aminomethyl)pyridine (**I**, Table 1, Entries 2 and 3) produced the most active catalyst, which completely converted **1** to the corresponding amine even after 12 h at room temperature (Entry 3). The imidazole-based ligands **II** and **III** (Entries 4 and 5) also performed well, but at room temperature produced lower conversions than ligand **I**. Reactions performed with *N*-methylethylenediamine (**IV**, Entry 6), *N*,*N*-dimethylethylenedia-

Table 1. Hydrogenation of *N*-(1-phenylethylidene)aniline catalyzed by $[Cp^*RuCl]_4$, KO*t*Bu, and various diamine ligands.[a]

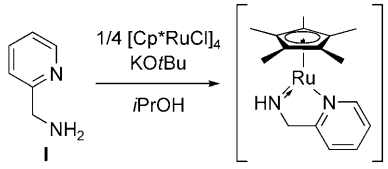



| Entry | Ligand | Conv. [%][b] | TOF [$h^{-1}$][c] | Conv.(50) [%][d] |
|---|---|---|---|---|
| 1 | none | <5 | <0.28 | 10 |
| 2 | **I** | >99 | >5.5 | >99 |
| 3[e] | **I** | >99 | >8.3 | –[f] |
| 4 | **II** | 80 | 4.4 | >99 |
| 5 | **III** | 90 | 5.0 | >99 |
| 6 | **IV** | 12 | 0.67 | 20 |
| | | 18 | 1.0 | 30 |
| 8 | **VI** | 25 | 1.4 | 25 |

[a] Experimental conditions: **1**/ligand/$[Cp^*RuCl]_4$=100:1:0.25, $P(H_2)$= 100 bar, $t$=18 h. [b] Conversion of the reaction performed at room temperature as determined by $^1H$ NMR spectroscopy. [c] Turnover frequency for the reaction performed at room temperature as determined from the conversion. [d] Conversion of the reaction performed at 50 °C as determined by $^1H$ NMR spectroscopy. [e] Reaction was run for 12 h. [f] Not determined.

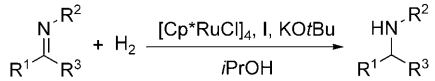
mine (**V**, Entry 7), and 1-(2-aminoethyl)pyrrolidine (**VI**, Entry 8) as ligands gave only modest conversions. Thus in general, ligands containing one aromatic donor $sp^2$ and one aliphatic $sp^3$ nitrogen each produced active catalysts at both temperatures tested. The ligands that possess two aliphatic $sp^3$ nitrogen functionalities (one tertiary and one primary) showed inferior conversions. This is in contrast to the case of ketone hydrogenation by this type of catalyst, for which the latter ligand class was ideal.[23] In a control experiment, the attempted hydrogenation of **1** using $[Cp^*RuCl]_4$ without any ligand (Entry 1) showed very low conversion even at elevated temperature; therefore the ruthenium source alone is not a competent catalyst for the reaction.

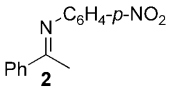
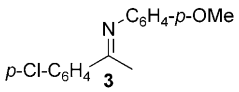
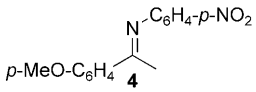
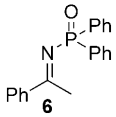
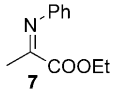
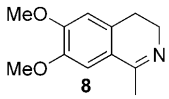
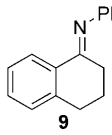
Because this is the first hydrogenation of C=N bonds using [Cp*Ru(diamine)] complexes, we sought to probe the scope of the reaction. Based on its success in the hydrogenation of **1**, the complex formed from ligand **I** and $[Cp^*RuCl]_4$ in the presence of KO*t*Bu (Scheme 1) was tested in the hydrogenations of various imines (Table 2) under the conditions described above, but with overnight reactions. Consistent with the data in Table 1, the hydrogenation of **1** using $H_2$ (100 bar) at room temperature proceeded to full conversion overnight (Table 2, Entry 1). Introducing electron-withdrawing or -donating groups at the para positions of either phenyl moiety led to lower conversions. For example, substrate **2** (Entry 2), which bears an electron-withdrawing




Scheme 1. In situ formation of the catalyst from **I**, $[Cp^*RuCl]_4$, and KO*t*Bu.

Table 2. Hydrogenation of imine substrates by $[Cp^*RuCl]_4$/**I**.[a]




| Entry | Substrate | Conv. [%][b] | TOF [$h^{-1}$][c] |
|---|---|---|---|
| 1 |  **1** | >99 | >5.5 |
| 2 |  **2** | 70 | 3.9 |
| 3 |  **3** | 50 | 2.8 |
| 4 |  **4** | 50 | 2.8 |
| 5 |  **5** | 94 | 5.2 |
| 6 |  **6** | 90 | 5.0 |
| 7 |  **7** | 60 | 3.3 |
| 8 |  **8** | 87 | 4.8 |
| 9 |  **9** | 38 | 2.1 |

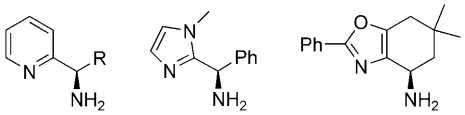
[a] Experimental conditions: imine/**I**/$[Cp^*RuCl]_4$=100:1:0.25, $T$=room temperature, $P(H_2)$=100 bar, $t$=overnight. [b] Substrate conversion as determined by $^1H$ NMR spectroscopy. [c] Turnover frequency as calculated from conversion.

group at the para position of the *N*-phenyl group, was 70% hydrogenated over the same time period. Substrate **3** (Entry 3), with an electron-donating group on the *N*-phenyl and an electron-withdrawing group on the *C*-phenyl moiety, was hydrogenated even more slowly. Switching the electronic character of the phenyl rings to give **4** (Entry 4) did not alter this effect, as **3** and **4** were both 50% hydrogenated at room temperature under 100 bar $H_2$. Substrates **5** and **6**, bearing electron-withdrawing *p*-toluenesulfonyl (Ts) and diphenylphosphine oxide (dpp) protecting groups, respectively, gave 91 and 90% conversion (Entries 5 and 6). The imino ester **7** (Entry 7) was also reduced, in 60% conversion. Finally, we attempted the hydrogenation of cyclic imines. The endocyclic imine **8** (Entry 8) was quite reactive (87% conversion), whereas the exocyclic imine **9** (Entry 9) was much less so (38% conversion).

Encouraged by the ability of [Cp*Ru(diamine)] complexes to catalyze the hydrogenation of imines, we pursued

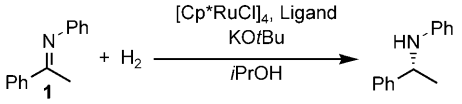
a chiral version of the catalyst (Figure 3). To begin, we modified the ligand **I** by introducing alkyl groups on the side chain, yielding **VII** and **VIII**. Though this did not diminish the conversion, it unfortunately did not induce enantioselectivity (Table 3, Entries 1 and 2). Ligand **IX**, a chiral variant of **II**, was also unable to direct the stereochemistry of the reaction (Entry 3).




**VII**: R = Me
**VIII**: R = *i*Pr
**IX**
**X**

Figure 3. Chiral diamine ligands used in this study.

Table 3. Asymmetric hydrogenation of **1** using $[Cp^*RuCl]_4$ and chiral diamine ligands.[a]

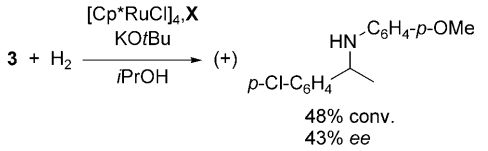



| Ligand | Conv. [%][b] | TOF [$h^{-1}$][c] | *ee* [%][d] |
|---|---|---|---|
| **VII** | >99 | >5.5 | *rac* |
| **VIII** | >99 | >5.5 | *rac* |
| **IX** | 52 | 2.9 | *rac* |
| **X** | 80 | 4.4 | 51 (*R*) |

[a] Experimental conditions: **1**/ligand/$[Cp^*RuCl]_4$ = 100:1:0.25, $T$ = room temperature, $P(H_2)$ = 100 bar, $t$ = overnight. [b] Conversion as determined by $^1H$ NMR spectroscopy. [c] Turnover frequency as calculated from conversion. [d] Determined by chiral HPLC.

Our research group reported previously on the synthesis of N,P ligands similar to **X** for use in iridium-catalyzed asymmetric hydrogenation of unfunctionalized olefins[27] and Ru-catalyzed asymmetric ketone hydrogenations.[28] Like the 1,4-diamines used in catalysts **I**–**IX**, this ligand features one aromatic $sp^2$ nitrogen atom and one primary amine, and we therefore considered that it might form an active catalyst in the present system. Indeed, the catalyst that formed when **X** was combined with $[Cp^*RuCl]_4$ and KO*t*Bu in *i*PrOH showed good conversion and promising enantioselectivity (80% conversion, 52% *ee*) in the hydrogenation of **1**. Application of this same catalyst system to the substituted substrate **3**, which was hydrogenated by $[Cp^*RuCl]_4$/**I**/KO*t*Bu much more slowly than **1**, resulted in a lower conversion (48%) and a slightly lower enantiomeric excess (43% *ee*), although the stereoselectivity was in the same range (Scheme 2). The asymmetric reduction of additional prochiral olefins and, more importantly, the development of more effective chiral ligands for this new reaction are now underway in our laboratory.

We have not yet investigated the mechanism by which this class of catalysts hydrogenates imines. However it is probable that, analogous to the hydrogenation of ketones by




Scheme 2. Asymmetric hydrogenation of substrate **3** with $[Cp^*RuCl]_4$/**X**/KO*t*Bu. The optical rotation was assigned based on comparison of the HPLC retention time of the product to the reported compound.[29]

catalysts based on the complexes **D**, this reaction is a case of solvent-assisted $H_2$ cleavage.[23] Thus, we propose that the ruthenium center activates $H_2$ to form a ruthenium-bound dihydrogen species, the subsequent heterolytic splitting of which is assisted by the *i*PrOH solvent.

## Conclusions

We have described the direct hydrogenation of a range of imines to amines using base-activated Cp*Ru(diamine) complexes as catalysts. Catalyst **I** completely hydrogenates **1** to amine in an overnight reaction at room temperature. The chiral ligand **X** produced a catalyst that hydrogenated **1** to the corresponding *R*-configured amine in moderate enantiomeric excess, and similar enantioselectivity was observed for the reduction of **3**, an imine with different electronic properties. We therefore consider this an auspicious system for the asymmetric hydrogenation of imines. To our knowledge, this is the first study to use phosphine-free Cp*Ru/diamine complexes as catalysts for the reduction of C=N double bonds. The development of more effective chiral diamine ligands and the expansion of the substrate scope for this transformation are underway in our research group.

## Experimental Section

2-(Aminomethyl)pyridine (Lancaster), and $[Cp^*RuCl]_4$ (Strem) were used as received. *i*PrOH was dried over $CaH_2$ prior to use. Samples for NMR spectroscopy were prepared in $CDCl_3$ and run at room temperature. $^1H$ (400 MHz) and $^{13}C$ (100 MHz) NMR spectra were recorded on a 400 MHz Varian Unity spectrometer. $^{31}P$ (121 MHz) NMR spectra were recorded on a 300 MHz Varian Mercury spectrometer. Imines and diamine ligands were synthesized according to published procedures.[30]

**Hydrogenation**: A solution of 2-(aminomethyl)pyridine (0.015 mmol) in dry *i*PrOH (2 mL) was added to $[Cp^*RuCl]_4$ (0.0037 mmol) in a dry Schlenk tube. The resulting solution was stirred under argon for 30 min. Imine (1.5 mmol) was weighed into a glass vial and dissolved in dry $CH_2Cl_2$ (0.5 mL). The vial was flushed with argon and sealed with a rubber septum to maintain an inert atmosphere. The catalyst solution was transferred to the reaction vial under argon, and a solution of KO*t*Bu (0.11 M) in *i*PrOH (0.136 mL, 0.015 mmol) was added. The hydrogenation vial was transferred to a high-pressure hydrogenation apparatus fitted with a steel bomb. Nitrogen gas was introduced to the steel bomb and vented carefully. After it was purged in this way three times, the bomb was pressurized with $H_2$ to 100 bar. The reaction mixture was stirred at this pressure and 50 °C overnight. After careful venting, the reaction mixture was transferred to a 50-mL round-bottom flask. The solvents were evaporated under reduced pressure, and the residue was dissolved in $CH_2Cl_2$ and filtered through a short plug of silica. The solvent was evaporated, and the sample was analyzed by $^1H$ NMR spectroscopy.

## Acknowledgements

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