$[RuCl_2(PPh_3)(PNN')]$ Complexes as Efficient Catalysts in Transfer Hydrogenation of Ketones

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Ruthenium complexes of the general formula $[RuCl_2(PPh_3)(PNN')]$ have been obtained from tridentate PNN′ ligands containing phosphine (P), amine or imine (N), and pyridyl donor groups (N′). The imino ligand $Ph_2P(o,o'\text{-}C_6H_4CH{=}NCH_2C_5H_4N)$ (**a**) has been synthesized from $Ph_2P(2\text{-}C_6H_4CHO)$ and 2-(aminomethyl)pyridine, whereas amino $Ph_2P(o,o'\text{-}C_6H_4CH_2NHCH_2C_5H_4N)$ (**b**) is prepared by the reduction of **a** with $NaBH_4$. The complexes *trans*-$[RuCl_2(PPh_3)(PNN')]$ [PNN′ = **b**, (**1**); **a**, (**2**)] containing a five-membered NN′ cycle have been isolated in high yield by the reaction of $RuCl_2(PPh_3)_3$ with **b** and **a**, respectively. By the same route and using the ligand $Ph_2P(o,o'\text{-}C_6H_4CH{=}NCH_2CH_2C_5H_4N)]$ (**c**), the complex *cis*-$[RuCl_2(PPh_3)$(**c**)] (**3**) was isolated, and it displays a different stereochemistry as a result of the different size of the tridentate ligand. For the amino derivative **1**, an X-ray diffraction experiment was carried out. Treatment of $[RuHCl(PPh_3)_3]$ with the ligands **a** or **b** leads to the monohydride complexes *trans*-$[RuHCl(PPh_3)(PNN')]$ [PNN′ = **b**, (**4**); **a**, (**5**)]. Complexes **1**−**5** have been proven to catalyze the transfer hydrogenation of linear, cyclic, and aromatic ketones to secondary alcohols in 2-propanol at reflux and in the presence of $(CH_3)_2CHONa$ with a very high rate (TOF values up to 250 000 h^{-1}). The trans derivatives **1** and **2** containing the amino and imino functions catalyze the reduction of acetophenone with the same activity (TOF = 190 000 and 185 000 h^{-1}, respectively), suggesting that the C=N group is reduced during catalysis. A lower activity has been observed for complexes **3**−**5**.

Introduction

The catalytic transfer hydrogenation of polarized unsaturated compounds using 2-propanol or formic acid as the hydrogen source is a widely investigated reaction that is promoted by different transition metal complexes.[1] Employment of highly active catalytic systems makes this approach quite attracting for the preparation of alcohols, rivaling the well-established hydrogenation process, which necessitates hydrogen under pressure. The most active systems are based on Ru, Rh, and Ir bearing nitrogen- and/or phosphorus-containing ligands, which allow the easy formation of catalytically active hydride species.

Ruthenium complexes containing suitable combinations of P and N or mixed PN ligands have proven to be highly efficient catalysts for the hydrogenation and transfer hydrogenation of carbonyl compounds. Thus, bi-, tri-, and tetradentate achiral and chiral ligands have successfully been used to prepared five- and six-coordinate complexes for the transfer hydrogenation, namely, $[RuCl_2(P)_2(NN)]$ and $[RuCl_2(PP)(NN)]$ (P = phosphine; PP = diphosphine; NN = diamine, dipyridine),[2] $[RuCl_2(P)(PN)]$ (PN = amino- or imino-phosphine and oxazolinylferrocenylphosphine),[3] $[RuCl_2(PN)_2]$,[3a,4] $[RuCl(p\text{-cymene})(PN)][BF_4]$ (PN = phosphole-pyridine),[5] $[RuCl(p\text{-cymene})(NN)][BF_4]$,[6] $[RuCl_2(P)(NPN)]$,[7] $[RuCl_2(NPN)]$,[8] $[RuCl_2(P)(NNN)]$[9] (NPN and NNN = oxazoline based ligands), and $[RuCl_2(PNNP)]$ (PNNP = diphosphine/diamine ligand).[10] A particularly active complex

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is [RuCl$_2$(P)(PNO)],[11] which contains a mixed tridentate ligand with a labile oxygen donor atom. In addition, enantioselective catalytic systems have been obtained by the in situ reaction of ruthenium precursors (i.e., [RuCl$_2$(PPh$_3$)$_3$], [RuCl$_2$(η^6-arene)]$_2$, or [RuCl$_2$(DMSO)$_4$]) with the NNN,[12] NPN,[13] PNP,[14] PNN,[15] and PNO[16] ligands.

The complexes Ru(η^6-arene) containing diamines or aminoalcohols, discovered by Noyori and co-workers, are highly enantioselective and show a high rate of reaction due to the presence of primary amine ligands.[17] Recently, we have found that highly active ruthenium catalysts are obtained using 2-(aminomethyl)pyridine (ampy) as the bidentate NN′ ligand (ligand acceleration effect).[18] Particularly attractive are the complexes of the general formula [RuCl$_2$(PP)(ampy)], which are active for both transfer hydrogenation and hydrogenation.[19] As an extension of this chemistry with ampy, we have prepared terdentate complexes [RuCl(CNN)(PP)] (HCNN = 6-(aryl)-2-pyridinemethanamines), which display the highest rate in the transfer hydrogenation of ketones (turnover frequency (TOF) up to 10^6 h^{-1}).[20] In all these systems containing amine ligands, the presence of the NH$_2$ function has been proven to be crucial for achieving a highly efficient transfer hydrogenation of ketones (bifunctional catalysis). According to the studies of Noyori and co-workers on the [RuCl$_2$(PNNP)] systems, the imino derivatives display a very low activity as compared to the amino analogues.[10a,c,21] By contrast, catalytic studies performed by Gimeno and co-workers on [RuCl$_2$(P)(PN)][3b] show that amino and imino derivatives have the same activity.

We describe here the synthesis and characterization of the complexes **1**−**5** of the general formula [RuClX(PPh$_3$)(PNN′)] (X = Cl, H), bearing tridentate ligands showing phosphine, imino versus amino and pyridine donors, obtained from Ph$_2$P(2-C$_6$H$_4$CHO) and ampy or 2-(aminoethyl)pyridine (Figure 1). These complexes in a basic 2-propanol solution at reflux efficiently catalyze the transfer hydrogenation of numerous ketones with a very high rate (TOF up to 250 000 h^{-1}).

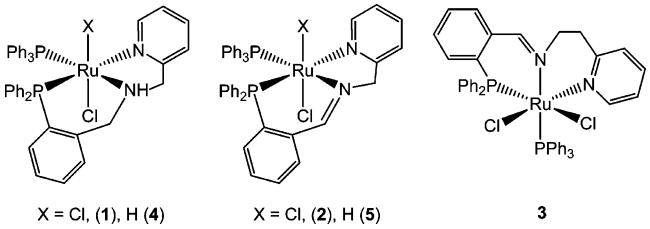


Figure 1.

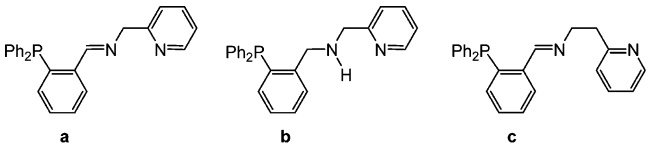


Figure 2.

Furthermore, under analogous experimental conditions, the imine and amine derivatives display the same catalytic activity.

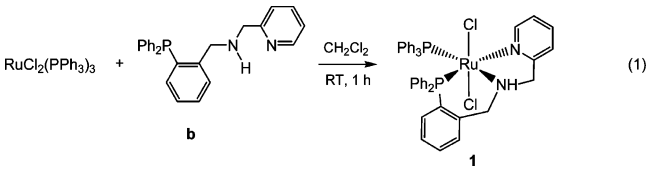
Results and Discussion

Synthesis and Characterization of Ligands and Complexes. The tridentate PNN′ ligands (N = imine or amine donor and N′ = pyridine) employed in this work show a combination of triphenylphosphine and ortho substituted pyridines with a C_1 or C_2 chain and linked through an imine or amine moiety (Figure 2).

Similar to the synthesis of **c**,[22] the ligand **a** was prepared by treatment of 2-(diphenylphosphino)benzaldehyde with ampy in toluene at reflux (Scheme 1).

It should be noted that few rhodium complexes have been described with **a**, but this compound was not characterized.[23] The amino PNN′ ligand **b** was isolated in good yield by reduction of the in situ formed **a**, prepared in methanol in the presence of Na$_2$SO$_4$ with NaBH$_4$ at room temperature (Scheme 1).

The thermally stable complex *trans*-[RuCl$_2$(PPh$_3$)(**a**)] (**1**) was easily synthesized by treatment of [RuCl$_2$(PPh$_3$)$_3$] with 1.1 equiv of **a** in dichloromethane at room temperature for 1 h (eq 1).



(1)

The ^{31}P{^{1}H} NMR spectrum of **1** in the CD$_2$Cl$_2$ solution shows two doublets at δ 46.6 and 41.8 with ^2J(PP) = 29.6 Hz, indicating a cis arrangement of the two phosphorus atoms.[24] The ^{1}H NMR signals for the methylene groups appear at δ 4.61, 4.46, 4.09, and 3.77, whereas in the ^{13}C{^{1}H} spectrum, the two CH$_2$ groups are at δ 60.2 and 53.8 (d, J(CP) = 5.1 Hz), the latter attributable to the carbon bound to the phenyl ring. The IR spectrum of complex **1** shows a single ν_{Ru-Cl} band at 321 cm^{-1}, which supports a trans arrangement of the Cl atoms. The molecular structure of **1** was definitively confirmed by an X-ray

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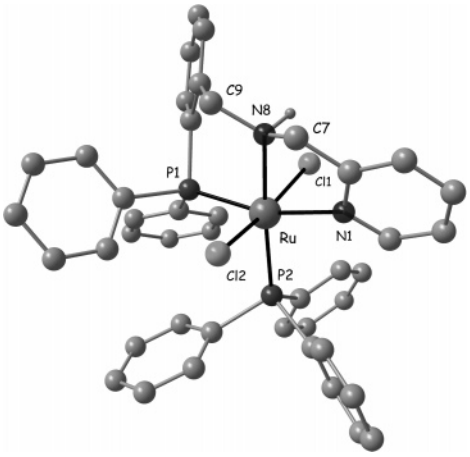

Figure 3. Ball-and-stick model[25,26] of **1** in the solid state. Selected bond lengths (Å): Ru−Cl1 2.413(2), Ru−Cl2 2.391(2), Ru−P1 2.297(2), Ru−P2 2.321(2), Ru−N1 2.170(5), Ru−N8 2.148(5), N8−C7 1.478(9), and N8−C9 1.480(9) and bond angles (deg): Cl1−Ru−Cl2 169.18(6), Cl1−Ru−P1 88.24(6), Cl1−Ru−P2 101.19(6), Cl−Ru−N1 85.3(2), Cl1−Ru−N8 81.9(1), Cl2−Ru−P1 93.90(6), Cl2−Ru−P2 89.04(6), C2−Ru−N1 89.8(2), Cl2−Ru−N8 87.5(1), P1−Ru−P2 97.79(6), P1−Ru−N1 163.7(1), P1−Ru−N8 88.7(1), P2−Ru−N1 98.1(1), P2−Ru−N8 172.9(1), N1−Ru−N8 75.7(2), and C7−N8−C9 111.7(5).

analysis carried out on a single crystal. The ruthenium center of **1** is in a pseudo-octahedral environment with the tridentate PNN ligand adopting a mer arrangement with two cis phosphorus atoms and two trans chlorides (Figure 3). The Ru−N1 and the Ru−N8 distances are similar (2.170(5) and 2.148(5) Å) and relatively long, due to the phosphine trans influence. The Cl1−Ru−Cl2 angle is 169.18(6)°, while the P1−Ru−N1 angle is 163.7(1)° with a short N1−Ru−N8 angle (75.7(2)°). The two phosphorus and two nitrogen atoms are displaced by +0.074(3) and −0.079(3) Å from the best-fit plane. The arrangement of the PNN ligand leads one N−H bond to be almost parallel to the Ru−Cl1 bond (H8−N8−Ru−Cl1 dihedral angle of about −10° with a H8···Cl1 distance of 2.46 Å), suggesting a possible intramolecular hydrogen bond interaction.[27] This structure resembles that of related *trans*-[$RuCl_2$-(PPh_3)(PNN)] and *trans*-[$RuCl_2$(PPh_3)(PNNP*)] complexes (P* denotes an uncoordinated phosphorus atom) bearing ligands with amino or imino groups.[28]

The reaction between [$RuCl_2(PPh_3)_3$] and appropriate imino PNN′ ligand in toluene at 90 °C afforded the six-coordinate complexes *trans*-[$RuCl_2(PPh_3)$(PNN′)] [PNN′ = **a**, (**2**); **c**, (**3**)], isolated in high yield (Scheme 2).

The $^{31}P\{^1H\}$ NMR spectra of **2** in CD_2Cl_2 solution shows two doublets at δ 33.2 and 53.2 [^2J(PP) = 28.3 Hz], whereas the resonances for **3** are at δ 31.5 and 49.4 [^2J(PP) = 29.1 Hz], indicating a cis P−Ru−P arrangement. In the ^1H NMR spectra of complexes **2** and **3**, the signal of the HC═N proton at δ ca. 8.8 shows ^4J(P,H) of 8.2 and 7.1 Hz, respectively, as established by heteronuclear $^{31}P-^1H$ correlation. These values are in accord with a mutual trans arrangement of the imine nitrogen and PPh_3.[29] As a matter of fact, in the related square-planar complexes [MCl(**c**)]PF_6 (M = Pd or Pt), in which the imine moiety is cis to the phosphorus atom, almost negligible ^4J(P,H) values for the HC═N proton (1.7 and 0.5 Hz, respectively) have been observed.[30] The IR spectrum of **2** exhibits a single Ru−Cl stretching mode at 320 cm^{-1}, indicating that this species is isostructural with **1**. On the contrary, two bands of comparable intensity at 312 and 320 cm^{-1} are observed for **3**, in agreement with a cis Cl−Ru−Cl arrangement. Therefore, while in complexes **1** and **2** the shorter tridentate ligand is mer coordinated, complex **3** shows a different stereochemistry with the longer ligand **c** displaying a fac arrangement. The vinylidene derivatives *trans*-[$RuCl_2$(CCHR)(**c**)] (R = Ph, ^{t}Bu) recently reported by Spivak and co-workers show a trans Cl−Ru−Cl arrangement.[31]

Complexes **2** and **3** are stable in the solid state but decompose slowly in solution. ^1H and ^{31}P NMR spectra indicate a fluxional behavior in the whole range of 293−183 K. ^1H spectra of **2** and **3**, as well as the $^{13}C\{^1H\}$ spectrum of the former complex, were recorded at 193 K, while even at low temperatures, **3** led to poor quality $^{13}C\{^1H\}$ NMR spectra. The ^{31}P NMR monitoring of $CDCl_3$ solutions of both **2** and **3** evidenced complicated patterns after a few hours, consistent with the formation of two derivatives bearing PPh_3 and PNN′ ligands as well as three species arising from the dissociation of PPh_3. Because of the formation of equilibrium mixtures, isolation of a single species was not possible. By contrast, the amino complex **1** is stable in solution, and the ^1H and ^{31}P spectra show sharp signals, suggesting that in **2** and **3**, the imino donor ligand exerts a trans-labilizing effect on triphenylphosphine, leading to the labile species.

The monohydride complex *trans*,*mer*-[RuHCl(PPh_3)(**b**)] (**4**) was isolated following the procedure adopted for the preparation of *trans*,*cis*-[RuHCl(PPh_3)$_2$(ampy)].[19a] The reaction between equimolar amounts of [RuHCl(PPh_3)$_3$] and **b** in refluxing heptane afforded a 3:1 mixture of **4** and a closely related monohydride isomer (^1H NMR for RuH at δ −16.91 with J(HP) = 21.6, 28.2 Hz; ^{31}P NMR: δ 66.5 and 62.7 with J(PP) = 32.8 Hz), which in dichloromethane converts into **4**. Similar to **4**, the complex *trans*,*mer*-[RuHCl(PPh_3)(**a**)] (**5**) was prepared from [RuHCl(PPh_3)$_3$] and **a** in heptane (Scheme 3).

The $^{31}P\{^1H\}$ NMR spectra of **4** and **5** show two doublets at δ 64.3 and 66.5 [J(PP) = 33.0 Hz] and δ 57.8 and 67.4 [J(PP) = 29.8 Hz], respectively, indicating a cis arrangement of the two phosphorus atoms. In the high field region of the ^1H NMR spectra, a doublet of doublets is present at ca. δ −17, and the

(25) Data collection was aborted due to low crystal quality. The quick solution revealed non-resolvable disordered solvent molecules. Compound **1**: [($C_{43}H_{38}Cl_2N_2P_2Ru$), n(CH_2Cl_2), light brown fragment (0.38 mm × 0.45 mm × 0.48 mm), monoclinic, *C*2/*c* (No. 15), a = 37.2956(10) Å, b = 9.9079(3) Å, c = 24.8352(5) Å, β = 90.938(2)°, V = 9175.9(4) Å^3, Z = 8. Preliminary examination and data collection were carried out on a κ-CCD device (Oxford Diffraction, Xcalibur) with an Oxford Cryosystems cooling system at the window of a sealed tube (Enhance X-ray Source, Spellman, DF3) with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection was performed at 153 K. Full-matrix least-squares refinements were aborted at R1 = 0.0686 (6984 intensities, $I_o > 2\sigma(I_o)$) and wR2 = 0.1693 (8431 intensities, all data).

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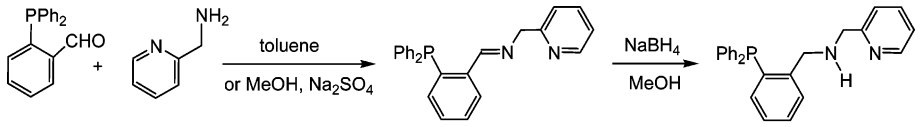
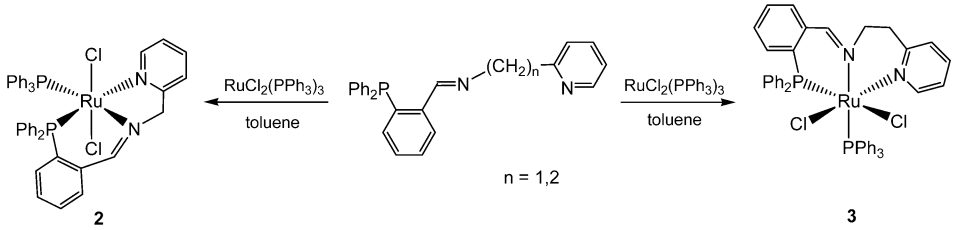
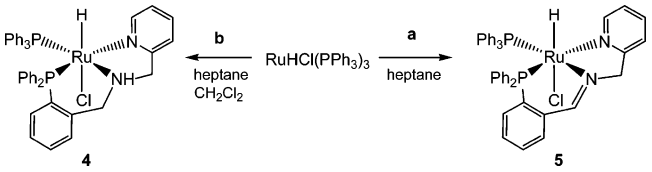
Scheme 1



Scheme 2

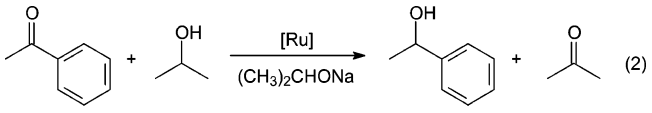


Scheme 3



two coupling constant values (in the range of 24−32 Hz) are in agreement with the presence of two P atoms both cis to hydride, as for *trans,cis*-[RuHCl(PPh$_3$)$_2$(ampy)].[19a] It should be noted that a trans H−Ru−Cl arrangement characterizes other Ru(II) complexes with a HClP$_2$N$_2$ donor set, namely, [RuHCl(P)$_2$(NN)],[32] [RuHCl(PP)(NN)],[33] [RuHCl(PN)$_2$],[34] and [RuHCl(PNNP)],[35] reported by Morris and co-workers.

Catalytic Transfer Hydrogenation. The reduction of acetophenone to 1-phenylethanol by 2-propanol has been chosen as a model reaction to explore the catalytic behavior of complexes **1**−**3** in transfer hydrogenation. The catalytic trials were carried out using a 0.1 M solution of the substrate, 0.1 mol % of catalyst, and 4 mol % of (CH$_3$)$_2$CHONa freshly prepared from elemental sodium (eq 2). A 2-propanol solution containing the catalyst and base was added to a 2-propanol solution of the substrate kept at reflux. During the dissolution of the Ru(II) complex into the alcohol, which was accomplished within few minutes, the color of the solution changed from red−brown to greenish yellow.



The amino complex **1** has been found to catalyze the quantitative reduction of acetophenone to 1-phenylethanol in 2 min, affording a turnover frequency number of 190 000 h^{-1} at 50% conversion, which is a value of the same order to that reported for the related complexes *cis,cis*-[RuCl$_2$(diphosphine)(ampy)].[19a] The imino derivatives **2** and **3**, displaying a trans and cis Cl−Ru−Cl arrangement, respectively, and a different size of the N,N′ bound rings, show a remarkable different activity. As a matter of fact, complex **2** resulted in being much more active than **3**, as inferred from the TOF values (**2**: 185 000 h^{-1}, **3**: 21 000 h^{-1}; Table 1). This is also consistent with our previous finding, which shows that the substitution of ampy with 2-(aminoethyl)pyridine, in the complexes [RuCl$_2$(PPh$_3$)$_2$(NN′)], resulted in lower catalytic performances.[36] Most probably, the presence of a five-membered chelate ring in **a** gives a higher stability to the six-coordinate complex with a neat increase of its catalytic efficiency. On the basis of the high activity shown by complex **2** in the transfer hydrogenation of acetophenone, we decided to further explore its catalytic potential in the reduction of other ketones. The results are listed in Table 2. Generally, a good efficiency of complex **2** as a precatalyst has been observed for all substrates employed. The higher TOFs (≈250 000 h^{-1}) were obtained for the acetophenone derivatives showing a chloro atom in the meta or para position (Table 2, entries 3 and 4). Conversely, the chloro atom in the ortho position leads to a much lower TOF (70 000 h^{-1}) (Table 2, entry 2). The whole trend can be rationalized in terms of steric hindrance, which is kinetically relevant when the chloro atom is in the ortho position. Lower TOFs with respect to that observed for acetophenone (Table 2, entry 1) were found for cyclic and linear aliphatic ketones (Table 2, entries 5−7). Using complex **2** as the catalyst, 1-phenylethanol was prepared on a gram-scale in nearly quantitative yield and 96% purity.

It is noteworthy that the amino and imino complexes **1** and **2** display the same activity for the reduction of acetophenone under these conditions. Similar catalytic activity for phosphine/imine versus phosphine/amine complexes [RuCl$_2$(PPh$_3$)(PN)] has been reported by Gimeno and co-workers.[3b] On the basis of these results, we were stimulated to investigate the catalytic behavior of the tetradentate diimino versus diamino complexes [RuCl$_2$(PNNP)$_2$] **6** and **7**, respectively (Figure 4). Complex **7** has been described by Gao et al. and Noyori et al.[10a,c] to be an excellent precatalyst for the transfer hydrogenation of ketones, while **6** showed a poor activity in the presence of a low base amount (base/Ru = 0.5).

In the catalytic conditions adopted by us (i.e., in the presence of an excess of base and under reflux), interestingly, complexes **6** and **7** showed substantially the same catalytic activity (TOF: **6**, 27 000 h^{-1}; **7**, 26 000 h^{-1}, Table 1), thus confirming that there is no difference between the catalytic performances of complexes with phosphine/imine or phosphine/amine ligands. These results may suggest that during catalysis, the imino

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Table 1. Catalytic Transfer Hydrogenation of Acetophenone with Complexes 1−7[a]

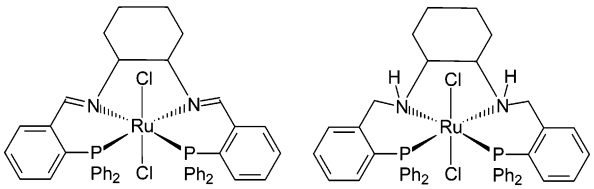
complex	yield % (min)[b]	TOF (h^{-1})[c]
1	98 (2)	190 000
2	98 (2)	185 000
2[d]	97 (12)	125 000
3	98 (15)	21 000
4	96 (15)	16 000
5	96 (15)	15 000
6	97 (20)	27 000
7	96 (20)	26 000

[a] Experimental conditions: reactions carried out at 82 °C, acetophenone 0.1 M in 2-propanol, acetophenone/complex/$(CH_3)_2CHONa$ = 1000:1:40. [b] Determined by GC analysis. [c] Turnover frequency (mol of substrate per mol of complex per hour) at 50% conversion. [d] Acetophenone/**2**/$(CH_3)_2CHONa$ = 5000:1:40.

Table 2. Catalytic Transfer Hydrogenation of Ketones with Complex 2[a]

Entry	Substrate	Product	Yield % (min)[b]	TOF (h^{-1})[c]
1			98(2)	185000
2			97(5)	70000
3			99(1)	250000
4			99(1)	240000
5			98(10)	33000
6			99(4)	54000
7			93(10)	18000

[a] Experimental conditions: reactions carried out at 82 °C, acetophenone 0.1 M in 2-propanol, acetophenone/complex/$(CH_3)_2CHONa$ = 1000:1:40. [b] Determined by GC or GC-MS analysis. [c] Turnover frequency (mol of substrate per mol of complex per hour) at 50% conversion.



6 **7**

Figure 4.

complex precursors are converted to amino species for which the presence of the N−H moiety is responsible for the high rate. The reduction of the C═N function of the coordinated ligand into a CH−NH bond is therefore favored by the excess of a strong base and at high temperature. Ruthenium complexes have been found to catalyze the transfer hydrogenation of aldimines in basic alcohol media at high temperatures.[37] The higher activity found for the tridentate PNN′ compounds **1** and **2**, as compared to the tetra- or bidentate $[RuCl_2(PNNP)]$ and $[RuCl_2(PPh_3)(PN)]$ complexes, is certainly due to the presence of the ampy moiety that, as we previously reported, enables fast hydrogen transfer reactions (i.e., a ligand acceleration effect).[18]

The monohydride complexes **4** and **5** do not catalyze the reduction of acetophenone in the absence of base, suggesting that a dihydride species should be involved in the catalysis. Under the catalytic conditions adopted with complexes **1**−**3**, also **4** and **5** induce the reduction of acetophenone but at lower rates (TOF = 16 000 h^{-1} **4**; 15 000 h^{-1} **5**), which can be ascribed to the formation of different isomer dihydride species. A lower performance of hydride versus chloride Ru(II) precatalysts has also been reported by other authors.[38] As regards the catalytic cycle, the precursors **1**−**5** undergo different rapid transformations to give the catalytically active species. With the imino ligands, the formation of Ru−hydride complexes leads to concomitant reduction of the C═N bond, affording amino ligands. According to our study on *cis*-$[RuCl_2(PP)(ampy)]$,[19a] it is likely that with **1**−**5**, the transfer hydrogenation occurs via the amino $[RuHX(PPh_3)(PNN')]$ (X = H, OR′) species, involving β-hydrogen elimination versus ketone insertion reactions.[1f,39]

Conclusion

In summary, we have described the ruthenium complexes $[RuCl_2(PPh_3)(PNN')]$ with tridentate PNN′ ligands containing phosphine (P), amine or imine (N), and pyridyl donor groups (N′), which are efficient catalytic precursors for the transfer hydrogenation of ketones. In the trans complexes **1** and **2**, the PNN′ ligands containing a five-membered NN′ cycle adopt a mer arrangement, while a fac geometry has been observed for the cis **3**, characterized by a six-membered NN′ cycle. Interestingly, in the catalytic transfer hydrogenation, the trans complexes **1** and **2** are the most active and show similar rates, suggesting that during the catalysis, the C═N group is reduced, affording the amine N−H moiety, which is a prerequisite to achieve high activity. Work is in progress to extend the chemistry of imino ruthenium complexes in asymmetric transfer hydrogenation.

Experimental Procedures

General Remarks and Instrumentation. All reagents were purchased from Aldrich and used without further purification. Commercial reagent grade solvents were dried according to standard methods and freshly distilled under argon before use. All syntheses and manipulations were carried out in an atmosphere of argon using standard Schlenk techniques. The ligand *N*-(2-(diphenylphosphino)-benzylidene)(2-(2-pyridyl)ethyl)amine (**c**)[22] and complexes $[RuCl_2(PPh_3)_3]$[40] and $[RuHCl(PPh_3)_3]$[41] were synthesized according to literature procedures.

The ^1H, ^{13}C, and ^{31}P NMR spectra (at 200.13, 50.32, and 81.02 MHz, respectively) were recorded on a Bruker AC 200 F QNP spectrometer. The ^1H and ^{13}C chemical shifts were referenced to $SiMe_4$, while positive ^{31}P chemical shifts were downfield from 85% H_3PO_4 as the external standard. The GC-MS analyses, run to control the identity of the compounds obtained in the catalytic trials, were carried out with a Fisons TRIO 2000 gas chromatograph-mass spectrometer working in the positive ion 70 eV electron impact

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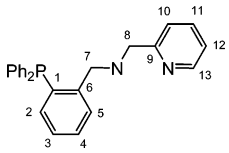

Figure 5.

mode. The injector temperature was kept at 250 °C, and the column (Supelco SE-54, 30 m long, 0.25 mm i.d., coated with a 0.5 μm phenyl methyl silicone film) temperature was programmed from 50 to 280 °C with a gradient of 10 °C/min. The GC analyses of the catalytic mixtures were run on a Fisons GC 8000 Series gas chromatograph equipped with a Supelco PTA-5 column (30 m long, 0.53 mm i.d., coated with a 3.0 μm poly(5% diphenyl-95% dimethylsiloxane) film). The injector and column temperatures were as indicated previously. The elemental analyses (C, H, and N) were carried out in the Microanalytical Laboratory of the Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, with a Carlo Erba 1106 elemental analyzer.

Synthesis of Ligand a. 2-(Diphenylphosphino)benzaldehyde (580 mg, 2.0 mmol) and 2-(aminomethyl)pyridine (238 mg, 2.2 mmol) were stirred in toluene (20 mL), and the mixture was refluxed for 1 h. A yellow oil was obtained upon elimination of the solvent under reduced pressure. Twice, the treatment with dichloromethane (10 mL)/cold *n*-hexane (50 mL) resulted in a purification of the product, which, however, did not crystallize. Yield: 657 mg, 86%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 295 K): δ −13.0. ^1H NMR ($CDCl_3$, 295 K): δ 9.05 (dt, J(HH) = 1.3 Hz, J_{HP} = 4.8 Hz, 1H, HC═N), 8.48 (ddd, J(HH) = 2.0, 0.7, 0.5 Hz, 1H, pyridine), 8.04 (ddd, J(HH) = 1.6, 0.6 Hz, J_{HP} = 3.9 Hz, 1H, aromatic), 7.47 (dt, J(HH) = 3.0, 0.7 Hz, 1H, pyridine), 7.4−7.0 (m, 12H, aromatic), 7.06 (ddd, J(HH) = 3.0, 2.0, 0.5 Hz, 1H, pyridine), 7.0−6.8 (m, 2H, pyridine and aromatic), 4.83 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K, see Figure 5 for the numbering of C atoms, $^{13}C-^{31}P$ coupling constants (in Hz) are reported in brackets): δ 162.0 [20.2] (C^7), 159.1 (C^9), 148.8 (C^{13}), 139.3 [17.7] (C^1), 136.5 [9.8] (C^i), 136.5 (C^{11}), 137.6 [19.5] (C^6), 133.9 [20.1] (C^o), 133.4 [9.5] (C^5), 130.4 [1.2] (C^4), 128.9 (C^3), 128.8 (C^p), 128.5 [8.5] (C^m), 128.1 (C^2), 122.1 (C^{10}), 121.7 (C^{12}), 66.5 (C^8).

Synthesis of Ligand b. 2-(Diphenylphosphino)benzaldehyde (580 mg, 2.0 mmol) and 2-(aminomethyl)pyridine (238 mg, 2.2 mmol) were stirred at room temperature in methanol (20 mL) in the presence of an excess of Na_2SO_4 (710 mg, 5.0 mmol) for 3 h. Then, after elimination of the solid by filtration, $NaBH_4$ (76 mg, 2.0 mmol) was added, and the mixture was gently warmed for 30 min at 45 °C. The solvent was eliminated under reduced pressure, and after the addition of water (10 mL), the organic material was extracted with ethyl ether (3 × 10 mL). The desired product was obtained as a yellow oil by pumping off the solvent under reduced pressure. Yield: 536 mg, 70%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = −15.3. ^1H NMR ($CDCl_3$, 295 K): 8.40 (d, J(HH) = 4.1 Hz, 1H, pyridine), 7.6−6.9 (m, 16H, aromatic and pyridine), 6.82 (dd, J(HH) = 4.1, 2.1 Hz, 1H, pyridine), 3.95 (s, 2H, CH_2), 3.73 (s, 2H, CH_2), 2.06 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K, see Figure 5 for the numbering of C atoms, $^{13}C-^{31}P$ coupling constants (in Hz) are reported in brackets): δ 159.9 (C^9), 149.1 (C^{13}), 144.3 [23.8] (C^1), 136.8 [10.2] (C^i), 136.3 (C^{11}), 135.7 [14.1] (C^6), 133.8 [19.6] (C^o), 131.9 [9.6] (C^5), 129.1 [5.4] (C^4), 129.0 (C^3), 128.8 (C^p), 128.6 [7.0] (C^m), 127.21 (C^2), 122.0 (C^{10}), 121.7 (C^{12}), 54.5 (C^8), 51.9 [21.0] (C^7).

Synthesis of *trans*-[RuCl₂(PPh₃)(b)] (1). $[RuCl_2(PPh_3)_3]$ (383 mg, 0.40 mmol) was dissolved in dichloromethane (5 mL), and to the solution was added **b** (168 mg, 0.44 mmol) dissolved in dichloromethane (1 mL). The solution was stirred at room temperature for 1 h and then concentrated to ca. 3 mL. The addition of ethyl ether (15 mL) afforded a light brown precipitate. The product was isolated by filtration, washed with ethyl ether, and dried under reduced pressure. Yield: 269 mg, 82%. Anal. calcd for $C_{43}H_{38}Cl_2N_2P_2Ru$ (816.72): C, 63.24%; H, 4.69%; N, 3.43%. Found: C, 62.93%; H, 4.68%; N, 3.38%. IR (polyethene): 321 cm^{-1} (ν_{Ru-Cl}). ^{31}P NMR (CD_2Cl_2, 295 K): δ 46.6 (d, J(PP) = 29.6 Hz), 41.8 (d, J(PP) = 29.6 Hz). ^1H NMR (CD_2Cl_2, 295 K): δ 8.27 (d, J(HH) = 4.0 Hz, 1H, pyridine), 7.8−6.9 (m, 27H, aromatic and pyridine), 6.61 (t, J(HH) = 7.1 Hz, 1H, pyridine), 6.55 (t, J(HH) = 7.1 Hz, 1H, pyridine), 5.94 (t, J(HH) = 8.2 Hz, 2H, aromatic), 5.55 (t, J(HH) = 12.4 Hz, 1H, aromatic), 4.61 (t, J(HH) = 8.4 Hz, 1H, CH_2), 4.46 (t, J(HH) = 8.4 Hz, 1H, CH_2), 4.09 (dt, J(HH) = 13.4, 3.2 Hz, 1H, CH_2), 3.77 (m, 1H, CH_2), 0.50 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 295 K, see Figure 5 for the numbering of C atoms, $^{13}C-^{31}P$ coupling constants (in Hz) are reported in brackets): δ 161.0 (C^9), 157.7 (C^{13}), 139.7 [13.8] (C^i), 136.7 (C^6), 135.9 (C^{11}), 135.1 [5.7] (C^4), 134.2 [8.9] (C^2), 132.6 (C^3), 131.2 [7.9] (C^5), 130.2 [54.7] (C^1), 129.2 [25.0] (C^o), 128.0 [4.2] (C^m), 127.1 (C^p), 121.3 (C^{10}), 121.1 (C^{12}), 60.2 (C^8), 56.7 [5.1] (C^7).

Synthesis of *trans*-[RuCl₂(PPh₃)(a)] (2). A mixture of $[RuCl_2(PPh_3)_3]$ (815 mg, 0.85 mmol), **a** (358 mg, 0.94 mmol), and toluene (20 mL) was stirred at 90 °C for 20 min. The resulting purple−red mixture was cooled, and *n*-hexane (20 mL) was added to complete the precipitation of the product. The pink−purple solid was filtered off, washed with *n*-hexane and ethyl ether, and dried under reduced pressure. Yield: 610 mg, 88%. Anal. calcd for $C_{43}H_{36}Cl_2N_2P_2Ru$ (814.70): C, 63.39%; H, 4.45%; N, 3.44%. Found: C, 63.15%; H, 4.48%; N, 3.33%. IR (polyethene): 320 cm^{-1} (ν_{Ru-Cl}). ^{31}P NMR (CD_2Cl_2, 295 K): δ 53.2 (d, J(PP) = 28.3 Hz), 33.2 (d, J(PP) = 28.3 Hz). ^1H NMR (CD_2Cl_2, 193 K): δ 8.84 (m, 1H, HC═N), 8.17 (m, 3H, aromatic and pyridine), 7.7−6.2 (m, 28H, aromatic and pyridine), 5.52 (m, 2H, aromatic), 5.16 (m, 1H, CH_2), 4.46 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 193 K, see Figure 5 for the numbering of C atoms, $^{13}C-^{31}P$ coupling constants (in Hz) are reported in brackets): δ 166.3 (C^9), 156.4 (C^{13}), 136.9 [14.5] (C^i), 136.5 (C^6), 135.5 (C^{11}), 135.4 [4.7] (C^4), 134.7 [7.3] (C^2), 133.7 (C^3), 132.0 [2.6] (C^5), 130.1 [49.3] (C^1), 129.6 [22.1] (C^o), 129.2 (C^p), 127.4 [5.0] (C^m), 125.5 (C^{10}), 122.4 (C^{12}), 74.5 (C^8), 55.1 [3.9] (C^7).

Synthesis of *cis*-[RuCl₂(PPh₃)(c)] (3). To $[RuCl_2(PPh_3)_3]$ (575 mg, 0.60 mmol) and **c** (260 mg, 0.66 mmol) was added 20 mL of toluene, and the slurry was stirred at 90 °C for 20 min. The resulting deep red mixture was cooled, and *n*-hexane (30 mL) was added to complete the precipitation of the product. The brick-red solid was filtered off, washed with *n*-hexane and ethyl ether, and dried under reduced pressure. Yield: 453 mg, 91%. Anal. calcd for $C_{44}H_{38}Cl_2N_2P_2Ru$ (828.72): C, 63.77%; H, 4.62%; N, 3.38%. Found: C, 63.04%; H, 4.60%; N, 3.29%. IR (polyethene): 320, 312 cm^{-1} (ν_{Ru-Cl}). ^{31}P NMR (CD_2Cl_2, 295 K): δ 49.4 (d, J(PP) = 29.1 Hz), 31.5 (d, J(PP) = 29.1 Hz). ^1H NMR (CD_2Cl_2, 193 K): δ 8.82 (m, 1H, HC═N), 8.58 (m, 1H, pyridine), 8.33 (m, 3H, aromatic and pyridine), 7.7−6.1 (m, 26H, aromatic and pyridine), 5.57 (m, 3H, aromatic), 4.03 (m, 2H, CH_2), 2.74 (m, 2H, CH_2).

Synthesis of *trans*-[RuHCl(PPh₃)(b)] (4). $[RuHCl(PPh_3)_3]$ (185 mg, 0.20 mmol) and **b** (84 mg, 0.22 mmol) were suspended in *n*-heptane (10 mL), and the slurry was refluxed for 2 h. The solid was filtered off, washed with ethyl ether, and dried under reduced pressure. The product was then dissolved in dichloromethane (5 mL), and the solution was stirred for 30 min. Concentration and addition of *n*-pentane afforded a red−brown precipitate, which was filtered, washed with *n*-pentane, and dried under reduced pressure. Yield: 92 mg, 59%. Anal. calcd for $C_{43}H_{39}ClN_2P_2Ru$ (782.28): C, 66.02%; H, 5.03%; N, 3.58%. Found: C, 65.93%; H, 4.98%; N, 3.51%. ^{31}P NMR (CD_2Cl_2, 295 K): δ 66.5 (d, J(PP) = 33.0 Hz), 64.3 (d, J(PP) = 33.0 Hz). ^1H NMR (CD_2Cl_2, 295 K): δ 7.96 (d, 1H, pyridine), 7.8−6.7 (m, 30H, aromatic and pyridine protons), 6.70 (t, 1H, aromatic), 6.46 (t, 1H, aromatic), 4.59 (t, 1H, CH_2), 4.30 (dt, 1H, CH_2), 3.89 (m, 2H, CH_2), 3.73 (m, 1H, NH), −17.72 (dd, J(HP) = 24.5, 31.6 Hz, 1H, Ru−H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2,

295 K, see Figure 5 for the numbering of C atoms, $^{13}C-^{31}P$ coupling constants (in Hz) are reported in brackets): δ 162.7 (C^9), 156.6 (C^{13}), 138.9 [14.2] (C^i), 137.1 [42.6] (C^1), 135.0 (C^6), 134.2 [8.2] (C^2), 134.8 (C^{11}), 134.3 [9.8] (C^4), 132.3 (C^3), 131.4 [7.2] (C^5), 129.2 [17.8] (C^o), 128.6 [2.3] (C^p), 127.4 [8.5] (C^m), 122.8 (C^{10}), 119.8 (C^{12}), 63.2 (C^8), 59.6 [7.1] (C^7).

Synthesis of *trans*-[RuHCl(PPh$_3$)(a)] (5). [RuHCl(PPh$_3$)$_3$] (232 mg, 0.25 mmol) and **a** (107 mg, 0.28 mmol) were suspended in *n*-heptane (15 mL), and the slurry was refluxed for 2 h. The brown solid was filtered off, washed with ethyl ether, and dried under reduced pressure. Yield: 134 mg, 68%. Anal. calcd for $C_{43}H_{37}ClN_2P_2Ru$ (780.26): C, 66.19%; H, 4.78%; N, 3.59%. Found: C, 66.01%; H, 4.71%; N, 3.50%. ^{31}P NMR (CD_2Cl_2, 295 K): δ 67.4 (d, J(PP) = 29.8 Hz), 57.8 (d, J(PP) = 29.8 Hz). ^1H NMR (CD_2Cl_2, 193 K): δ 8.59 (m, 1H, HC=N), 7.87 (m, 1H, pyridine), 7.7−6.4 (m, 31H, aromatic and pyridine), 5.51 (m, 1H, aromatic), 4.96 (m, 1H, CH_2), 4.29 (m, 1H, CH_2), −16.38 (dd, J(HP) = 24.6, 30.5 Hz, 1H, Ru−H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 193 K, see Figure 5 for the numbering of C atoms, $^{13}C-^{31}P$ coupling constants (in Hz) are reported in brackets): δ 158.1 (C^9), 149.7 (C^{13}), 139.1 [13.5] (C^i), 136.0 (C^6), 135.1 [44.3] (C^1), 134.9 (C^{11}), 134.6 [8.0] (C^2), 134.0 [6.7] (C^4), 132.9 (C^3), 131.4 [6.1] (C^5), 130.2 [12.9] (C^o), 128.4 [2.1] (C^p), 128.1 [8.8] (C^m), 124.2 (C^{10}), 121.8 (C^{12}), 65.3 (C^8), 58.9 [6.3] (C^7).

General Procedure for the Catalytic Transfer Hydrogenation. Solutions containing the substrate (a) and the catalyst (b) were prepared as follows: (a) the organic substrate (1 mmol) was dissolved into 9 mL of 2-propanol, and (b) the ruthenium complex (2.5 μmol) was suspended into 1.5 mL of 2-propanol, and to the mixture was added 1 mL of a 0.1 M solution of $(CH_3)_2CHONa$ in 2-propanol. Then, the slurry was gently warmed until complete dissolution of the complex was achieved. Finally, solution b (1 mL) was added to solution a kept at reflux, with immediate starting of the reaction. For the gas chromatographic analysis of the reaction mixture, 0.2 mL of solution was extracted by means of a syringe, cooled, and mixed with 1 mL of ethyl ether. The resulting solution was passed through a microcolumn filled with silica gel to eliminate any inorganic material.

Synthesis of (±)-1-Phenylethanol. A 500 mL three-necked round-bottomed flask, equipped with a magnetic stirrer and a condenser, was charged with complex **2** (40.9 mg, 50 μmol) and 200 mL of a sodium isopropoxide solution in 2-propanol prepared from Na (46 mg, 2 mmol). The mixture was gently warmed until a clear solution was obtained. Then, acetophenone (6.00 g, 0.05 mol) in 2-propanol (200 mL) was added, and the solution was refluxed for 30 min. After cooling, the solvent was pumped off, and the orange−brown residue was purified by column chromatography using silica gel and ethyl ether as the eluent. Elimination of the solvent afforded 5.92 g (97%) of the desired product, whose purity (96%) was checked by GC and ^1H NMR.

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Supporting Information Available: Tables of crystal and data collection parameters, bond lengths, and bond angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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