Terdentate RuX(CNN)(PP) (X = Cl, H, OR) Complexes: Synthesis, Properties, and Catalytic Activity in Fast Transfer Hydrogenation

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Terdentate ruthenium(II) complexes of general formula RuX(CNN)(dppb) (X = chloride, hydride, alkoxide; dppb = $Ph_2P(CH_2)_4PPh_2$), where CNN is a deprotonated 2-aminomethyl-6-arylpyridine ligand, have been prepared. The orthometalated derivative RuCl(**b**)(dppb) (**1**) has been obtained by reaction of $RuCl_2(PPh_3)$(dppb) with *N*,*N*-dimethyl-2-aminomethyl-6-(4-methylphenyl)pyridine (H**b**) in 2-propanol and in the presence of triethylamine by elimination of PPh_3 and HCl. Similarly, RuCl(**a**)(dppb) (**2**) and the chiral analogue RuCl(**c**)(dppb) (**3**), containing primary amine ligands, have been isolated starting from 2-aminomethyl-6-(4-methylphenyl)pyridine (H**a**) and (*R*)-2,2-dimethyl-1-(6-phenylpyridin-2-yl)-propylamine (H**c**), respectively. The synthesis of the functionalized pyridines H**a**−H**c** is here described, whereas the crystal structure of **3** has been determined through an X-ray diffraction experiment. Treatment of **1**−**3** with sodium or potassium isopropoxide gives the corresponding hydrides RuH(**b**)(dppb) (**4**), RuH(**a**)(dppb) (**5**), and RuH(**c**)(dppb) (**6**) from the ruthenium isopropoxide complexes, via a β-H elimination process. Studies in solution show that the isopropoxides bearing a NH donor group are in equilibrium with the corresponding hydrides (**5** and **6**). Reaction of **5** with benzophenone leads to the alkoxide Ru($OCHPh_2$)(**a**)(dppb) (**7**), which has been proven to interact with benzhydrol in C_6D_6, leading to the adduct **7**·($HOCHPh_2$), the alkoxide ligand, and the alcohol being in rapid exchange. Complexes **2** and **3** display a remarkable high catalytic activity for the transfer hydrogenation of ketones to alcohol in 2-propanol using a very small amount of catalyst. With the chiral complex **3** (0.005 mol %) methyl-aryl ketones can be quickly reduced (TOF ranging from 5.4×10^5 to 1.4×10^6 h^{-1}) with an enatiomeric excess up to 88%.

Introduction

The reduction of ketones using catalytic hydrogen-transfer conditions, with 2-propanol as hydrogen source, has been largely investigated in the last years, and several ruthenium complexes have proven to be efficient catalyst precursors in transfer hydrogenation.[1] Many efforts have been made for designing highly efficient catalysts for selective transformations, but for large-scale application increasing activity and productivity of catalytic reactions is still a target of primary importance.[2]

In the search for new catalytic systems we have recently reported on novel terdentate complexes of ruthenium(II), containing a diphosphine, prepared from 2-aminomethyl-6-(4-methylphenyl)pyridine of formula RuX(CNN)(dppb) (X = Cl, H; dppb = $Ph_2P(CH_2)_4PPh_2$), in which the CNN moiety is connected to the metal via a sp^2 aryl−carbon σ bond and one sp^2 and one sp^3 N donor site, giving two stable five-membered cyclometalated rings.[3] To the best of our knowledge the ruthenium complex **2** (Figure 1) is the most active transfer hydrogenation catalytic precursor (TOF and TON up to 2.5×10^6 h^{-1} and 1.7×10^5) for the reduction of ketones in basic 2-propanol reported to date.[4]

The pincer terdentate ligand is designed to combine the 2-aminomethylpyridine (ampy) moiety, which shows a particularly high ligand acceleration effect in the ruthenium(II) transfer hydrogenation of ketones,[5] and 2-phenylpyridine derivatives,

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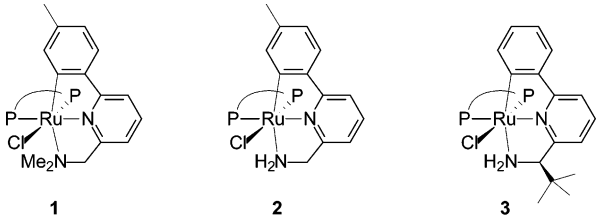


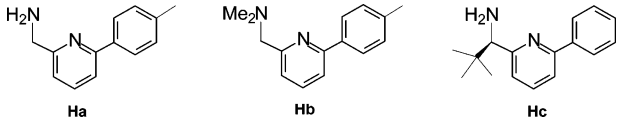
1 2 3

Figure 1.

which are known to easily give access to CN orthometalated ruthenium species. Complexes of monoanionic C-aryl ligands, such as **2**, belong to the class of pincer metal complexes containing P- and N-donor atoms (ZCZ′; Z, Z′ = N, P),[6] which have recently attracted much attention because of their relevance in a number of metal-mediated organic transformations.[7] In particular, ruthenium complexes containing monoanionic terdentate NCN and PCP ligands of the type $[C_6H_3(CH_2ZR_2)_2\text{-}2,6]^-$ (Z = N or P) are active catalysts in base-cocatalyzed hydrogen-transfer reactions of ketones with 2-propanol.[8] In the ligand the central aryl−carbon σ bond is complemented by two sp^3 N- or P-donor atoms. The presence of a metal−carbon bond generally gives compounds with a high degree of thermal stability and prevents to a large extent the metal dissociation from the ligand. Fine-tuning of the catalytic properties of these complexes can also be achieved by controlling the electronic and steric properties of the substituents of the ZCZ′ ligand.

So far the majority of investigations with nitrogen-containing pincer ligands have been focused on the NCN-type, while the CNN motif has received much less attention. As a matter of fact, only a few CNN complexes have been described, namely, those prepared from $BrC_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2$[6a] and more recently the palladium(II) and platinum (II) derivatives obtained from 6-phenyl-2-(2-aminoisopropyl)pyridine.[9] It should be noted that despite the importance that Ru compounds have as mediators and catalysts of organic transformations,[10] no examples of "pincer" CNN Ru catalysts have been reported before our communication.[3]

As found for several other ruthenium(II) complexes, the catalytic activity of **2** in transfer hydrogenation is promoted by addition of a base (^{i}PrOH/NaOH), which leads to the formation of the corresponding hydride, which is an active catalytic species. It is worth pointing out that for the CNN ligands the presence of the $-NH_2$ group is crucial in enhancing the activity of the catalysts, in agreement with the "NH effect" extensively described by Noyori and co-workers.[11] Evidence has been provided in systems containing the RuH/NH_2 motif (bifunctional catalysts) of a mechanism involving a concerted transfer of a proton and of a hydride to the substrate, without coordination of either alcohol or ketone to the metal and without formation of a ruthenium alkoxide.[11,12] It should be noted that in the case of complex **2** containing the CNN ligand, the corresponding hydride reacts with ketones to give the corresponding alkoxides,[3] thus suggesting a possible different mechanism from that proposed by Noyori.



Ha Hb Hc

Figure 2.

As part of our current work dealing with the chemistry of ruthenium complexes containing CNN ligands, we report herein the synthesis and characterization of complexes of formula RuX(CNN)(dppb) (X = Cl, H, or alkoxide) prepared from the 2-aminomethyl-6-arylpyridine-type ligands H**a**−H**c** (Figure 2).

In addition to the ligand H**a** containing the NH_2 group, the *N*,*N*-dimethyl analogue H**b** has been synthesized to prepare the corresponding ruthenium complex RuCl(**b**)(dppb) (**1**) (Figure 1), with the aim to gain more insights in the mechanism of transfer hydrogenation. Because asymmetric reduction of prochiral ketones via hydrogen transfer represents an attractive route for preparation of optically active alcohols, we have also isolated the chiral analogue (*R*)-2,2-dimethyl-1-(6-phenylpyridin-2-yl)-propylamine (H**c**), by introducing chirality at the C-NH_2 carbon atom. The resulting new chiral ruthenium derivative RuCl(**c**)(dppb) (**3**) (Figure 1), which has also been characterized by a structural X-ray analysis, displays a very high catalytic activity for asymmetric transfer hydrogenation (TOF up to 1.4×10^6 h^{-1}, ee up to 88%) with very low loading (0.005 mol %). The reactivity of the ruthenium alkoxide complexes Ru(OR)(CNN)(dppb) and their role as key species in the catalytic transfer hydrogenation is discussed.

Results and Discussion

Synthesis of the Ligands Ha−Hc. The asymmetric 2,6-functionalized pyridine ligands H**a** and H**b** were prepared according to Scheme 1.

Thus, oxidation of 2-(4-methylphenyl)pyridine with hydrogen peroxide in glacial acetic acid leads to the corresponding *N*-oxide, which by treatment with dimethylcarbamyl chloride and trimethylsilyl cyanide in dichloromethane gives 2-cyano-6-(4-methylphenyl)pyridine in almost quantitative yield. Subsequent reduction of the cyano group with $LiAlH_4$ in THF−Et_2O leads in 46% yield to the amino pyridine ligand H**a**, which was finally converted into the *N*,*N*-dimethylamine ligand H**b** by reaction with formaldehyde in an aqueous solution of formic acid (58% yield). The procedure described herein for the synthesis of H**a** is more straightforward with respect to the routes reported for related 2-pyridylamines containing an aryl sub-

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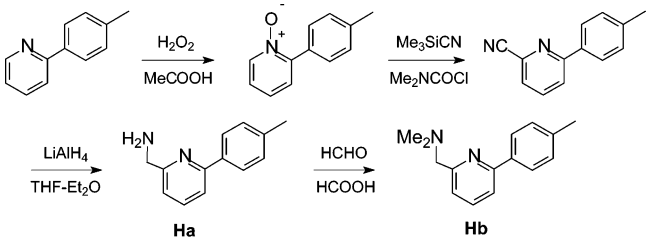
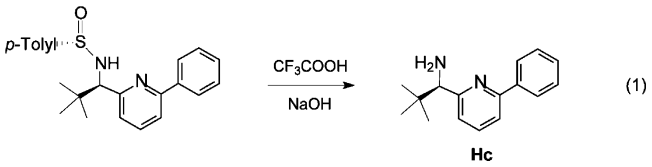
Scheme 1



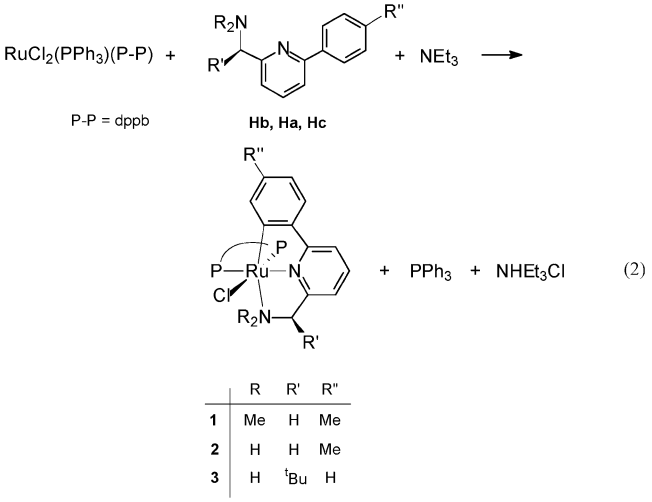
stituent in the 6-position of the pyridine ring, using 6-bromopicolylaldehyde[13] or 2,6-dibromopyridine[9] as starting compounds.

The optically active ligand H**c** has been obtained in high yield by trifloroacetic acid-mediated hydrolysis of the recently described (S_S,*R*)-*N*-(*p*-toluenesulfinyl)-2,2-dimethyl-1-(6-phenylpyridin-2-yl)propylamine, in turn accessible in 98% de via diastereoselective reduction of the related enantiopure *N*-*p*-toluenesulfinylpyridyl ketimine[14] (eq 1).



(1)

CNN Ruthenium(II) Chloride Complexes. It is well known that cyclometalated CN and CNN ruthenium complexes involving the 2-phenylpyridine and the 6-phenyl-2,2′-bipyridine motifs have been prepared through direct metalation in the ortho position of the aryl group, resulting in stable five-membered chelate rings.[15] Alternatively, some CN complexes have also been obtained in high yield via transmetalation using Ar_2Hg.[16] We have found that when the functionalized pyridine H**b**, displaying a NMe_2 group, is allowed to react with $RuCl_2(PPh_3)$-(dppb) in 2-propanol at reflux and in the presence of triethylamine, the orthometalated ruthenium(II) complex **1** is easily obtained by displacement of PPh_3 and elimination of HCl (eq 2).



(2)

	R	R'	R"
1	Me	H	Me
2	H	H	Me
3	H	^{t}Bu	H

In the solid state the yellow, thermally stable derivative **1** can be kept in air, but in solution it is fairly oxygen sensitive and decomposes if air is admitted. The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 shows two doublets at δ 50.8 and 35.5 with $^2J(PP) = 37.3$ Hz, and these data do not change significantly in the range of temperatures between +30 and −90 °C. In the ^1H NMR spectrum at room temperature the protons of the NCH_2 moiety are at δ 3.50 and 3.09 with $^2J(HH) = 13.6$ Hz, whereas the two *N*-methyl groups give a relatively sharp singlet at δ 1.77. Upon cooling, the latter signal broadens, revealing a coalescence temperature of about −50 °C and leading at −90 °C to two resonances at δ 1.79 and 1.29 for two nonequivalent methyl groups, indicating that the dynamic process involving the methyl groups can be frozen out. The approximation to the Eyring equation $\Delta G^{\ddagger} = RT_c[22.96 + \ln(T_c/\Delta\nu)]$[17] ($\Delta\nu = 100$ Hz) affords a relatively low value for $\Delta G^{\ddagger}_{223}$ (10.5 ± 0.2 kcal/mol) of the fluxional process. The $^{13}C\{^1H\}$ NMR spectrum at room temperature shows one signal for the CH_2 at δ 70.7 and one single resonance for the two Me groups at δ 50.7, shifted downfield of δ 4.1 and 5.0, respectively, compared to the free ligand, and indicating that the NMe_2 group is coordinated to the metal center. Conversely, the $^{13}C\{^1H\}$ NMR spectrum at −90 °C reveals two signals at δ 50.6 and 50.0 for two *N*-methyl groups, whereas the orthometalated carbon resonance appears at low field[15a,18] at δ 174.6 as a doublet of doublets ($^2J(CP) = 17.8$ and 7.5 Hz).[19] Addition of $[PPh_4]Cl$ to **1** in CD_2Cl_2, aiming to prevent a possible chloride dissociation from the complex, does not affect the ^1H and ^{31}P NMR spectra. Therefore, these data suggest that **1** exhibits a hemilabile terdentate CNN ligand with the NMe_2 group that undergoes an easy pyramidal inversion at the nitrogen atom through decoordination from the Ru metal center, favored by the presence of the aryl group, exerting a strong trans influence.[20] Despite the fact the *N*-alkyl substituents are expected to increase the σ-donating properties of the N atom, it is generally accepted that the metal−nitrogen bond is intrinsically weaker for tertiary amine ligands, compared to the primary or secondary ones. This has been ascribed to different factors, such as elongation due to the steric hindrance and elimination of intra- or intermolecular M−N−H···X hydrogen bonds with a decrease of the outer sphere solvation energy of the complex.[21]

Reaction of $RuCl_2(PPh_3)$(dppb) with the ligand H**a**, showing a NH_2 group instead of NMe_2, leads to complex **2**, which was isolated in high yield (eq 2). By comparison with **1**, the reaction for **2** requires a shorter time (2 h) to be completed, suggesting that orthometalation occurs more easily. The VT ^1H NMR measurements of **2** ($CDCl_2CDCl_2$) show that the broad resonance at δ 3.41 (at 20 °C), attributable to one NH_2 proton, which undergoes H/D exchange in basic (NaOH) D_2O, is still distinct at 60 °C, indicating that decoordination of the NH_2 moiety in **2** is more hindered compared to that of the NMe_2 group in **1**.

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Table 1. Crystal Data and Details of Structure Refinements of 3

formula	$C_{44}H_{47}ClN_2P_2Ru$
fw	802.30
cryst syst	orthorhombic
space group	$P\,2_12_12_1$
a (Å)	12.047(3)
b (Å)	15.900(3)
c (Å)	21.476(5)
V (Å^3)	4113.7(16)
Z	4
D_{calc} (g cm^{-3})	1.295
μ(Mo Kα) (mm^{-1})	0.555
F(000)	1664
θ range	1.59−29.66
no. of reflns collected	47 070
no. of unique reflns	10 978 [R_{int} = 0.0360]
no. of observed reflns $I > 2\sigma(I)$	9416
no. of params refined	451
Flack parameter	−0.020(19)
goodness-of-fit (F^2)	0.975
R1 ($I > 2\sigma$(I))[a]	0.0340
wR2[a]	0.0832
$\Delta\rho$ (e Å^{-3})	0.685, −0.311

[a] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3

Ru−C(1)	2.047(3)	Ru−P(1)	2.251(1)
Ru−N(1)	2.055(2)	Ru−P(2)	2.295(1)
Ru−N(2)	2.221(2)	Ru−Cl(1)	2.498(1)
C(1)−Ru−N(1)	80.97(10)	N(1)−Ru−Cl(1)	82.86(6)
C(1)−Ru−N(2)	154.71(9)	N(2)−Ru−P(1)	103.37(6)
C(1)−Ru−P(1)	86.70(7)	N(2)−Ru−P(2)	96.86(6)
C(1)−Ru−P(2)	105.54(7)	N(2)−Ru−Cl(1)	79.15(6)
C(1)−Ru−Cl(1)	88.95(7)	P(1)−Ru−P(2)	94.36(3)
N(1)−Ru−N(2)	75.50(9)	P(1)−Ru−Cl(1)	174.23(3)
N(1)−Ru−P(1)	92.70(6)	P(2)−Ru−Cl(1)	90.46(2)
N(1)−Ru−P(2)	170.64(6)	C(12)−N(2)−Ru	109.63(16)

The $^{13}C\{^1H\}$ NMR resonance of the terdentate ligand of **2** presents a signal at δ 52.5 for the NH_2CH_2 moiety, shifted downfield by about δ 4.3 compared to the free ligand, similarly to **1**. The resonance of the orthometalated carbon is at δ 181.8, strongly shifted downfield with respect to the free ligand **a** ($\Delta\delta$ 54.8) and coupled with two phosphorus atoms with ^2J(CP) = 16.3 and 7.8 Hz, as for **1**.

According to eq 2, the chiral complex **3** can be prepared by reaction of $RuCl_2(PPh_3)$(dppb) with the ligand H**c**. The $^{31}P\{^1H\}$ NMR spectrum displays two doublets similar to those of **2**, indicating that **3** is present in solution as a single stereoisomer with chirality at the metal center.[22] The ^1H and ^{13}C NMR data are related to those of **2** and are in agreement with the formation of a terdentate CNN complex. The molecular structure of **3** was confirmed by X-ray analysis carried out on a single crystal. Crystallographic data are summarized in Table 1, and selected bond distances and angles are reported in Table 2. The ruthenium center of **3** is in a pseudo-octahedral environment with the orthometalated **c** ligand bound to the metal in a terdentate fashion, forming two five-membered chelate rings (Figure 3).With respect to the terdentate ligand plane, the ^{t}Bu group bound to the chiral carbon atom (*R* configuration) is pointing to the side of the chloride, away from the phosphine phenyl groups. The solid-state structural features of **3** are closely related to those described for **2**.[3] The Ru−N1 bond length of the pyridine trans to the phosphorus atom is significantly shorter

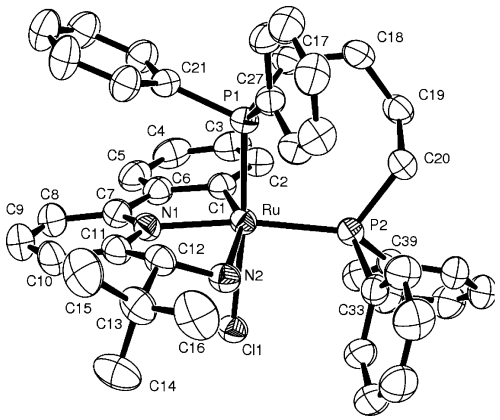

Figure 3. Molecular structure of **3** (ORTEP drawing, thermal ellipsoids at 40% probability level).

(2.055(2) Å) compared to the corresponding values measured in *cis*-$RuCl_2$(diphosphine)(ampy) complexes (2.138(2)−2.148(2) Å).[5c] This fact may be ascribed to the geometrical constraints of the terdentate ligand, showing narrow C(1)−Ru−N(1) and N(1)−Ru−N(2) bond angles (80.97(10)°, 75.50(9)°). In addition, the Ru−N amino bond distance (2.221(2) Å) is similar to that of **2** (2.246(3) Å) and significantly longer than that found in the aforementioned ampy complexes (2.104(3)−2.116(2) Å) that display the NH_2 group trans to a chloride, in agreement with the higher trans influence of the aryl compared to the chloride ligand. The carbon bearing the ^{t}Bu group and the amino nitrogen N(2) are displaced by +0.059(4) and −0.647(4) Å, respectively, from the best-fit plane through the terdentate ligand. This arrangement leads one N−H bond to be almost parallel to the Ru−Cl bond (H−N(2)−Ru−Cl dihedral angle of about 8.2°, with a H···Cl distance of 2.62 Å), suggesting a possible intramolecular hydrogen bond interaction.[23] As for **2**, there is also a relatively short contact between the pyridine nitrogen atom and the ipso carbon atom C(21) of the phosphine phenyl (3.12 Å), indicating a stacking between the pyridine and phenyl rings. Similar features have also been observed in **2** and in *cis*-$RuCl_2$(diphosphine)(ampy) complexes. Consequently, solid-state studies and NMR data in solution for **1**−**3** are consistent with the relatively weak σ-donation of the amino group to the ruthenium center in the CNN ligands, because of the trans influence of the aryl group, with the Ru−NH_2 bond being stronger than the Ru−NMe_2 one.

CNN Ruthenium(II) Hydride Complexes. The chemistry of transition metal hydrides continues to attract a great deal of attention because of the unique M−H bonding properties (e.g., insertion reactions, acidic vs hydridic character, hydrogen-bonding interactions) that allow the use of these species in stoichiometric reactions and catalysis.[24] Among the different procedures for obtaining late transition metal hydride complexes, a method generally employed entails the reaction of halide precursor complexes with sodium or potassium alkoxides displaying a hydrogen in the β-position. The resulting covalent metal alkoxides are generally reactive intermediates that undergo a facile β-hydrogen elimination reaction, affording hydride complexes (alkoxide route).[25] When the ruthenium complex **1**

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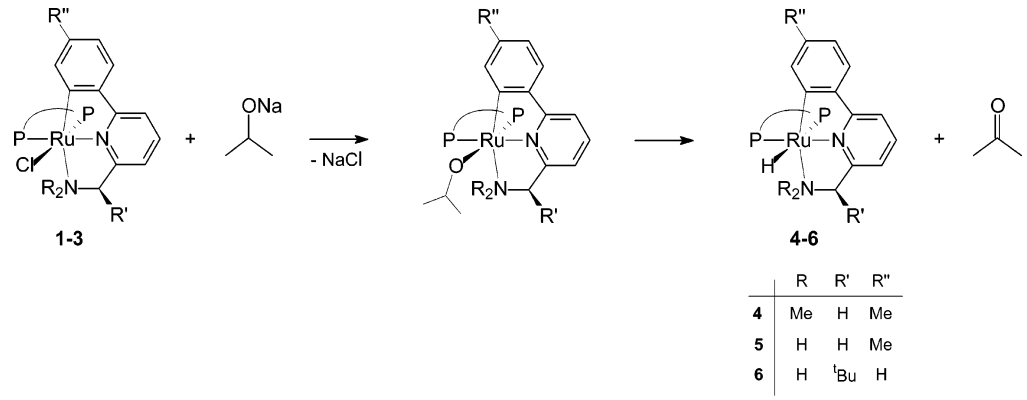
Scheme 2



is treated with 1.5 equiv of NaO^{i}Pr in 2-propanol−toluene at room temperature, the solution quickly turns red, affording an intermediate alkoxide, as inferred by $^{31}P\{^1H\}$ NMR spectroscopy (δ 46.4 and 35.8, $^2J(PP) = 32.5$ Hz, C_6D_6 (10% in volume) as inside lock) (Scheme 2).

As will be described in a further part of this work, all ruthenium alkoxides of this type assume a red-orange color and are characterized by a $^2J(PP)$ of about 32−34 Hz, which differ significantly from those of the chloride and hydride complexes. Heating of this solution above 50 °C results in the slow and irreversible formation of the hydride complex **4** through elimination of acetone. The $^{31}P\{^1H\}$ NMR spectrum of **4** in C_6D_6 at room temperature exhibits two doublets at δ 62.5 and 30.4, the latter being trans to the hydride as proven by a ^1H-coupled ^{31}P NMR measurement, with a significantly small phosphorus−phosphorus coupling constant ($^2J(PP) = 15.5$ Hz), compared to that of the chloride analogue ($^2J(PP) = 37.3$ Hz). The ^1H NMR signal for the hydride appears as a doublet of doublets at δ −5.79 with $^2J(HP) = 87.7$ and 28.6 Hz, in agreement with the data reported for other ruthenium hydride complexes bearing the phosphorus atoms trans and cis to the hydride, respectively.[26] At room temperature the CH_2NMe_2 moiety presents two doublets at δ 3.25 and 2.61 ($^2J(HH) =$ 13.3 Hz) for the nonequivalent methylene protons, whereas the methyl groups show two resonances at δ 2.13 and 2.10, at variance with **1**. This clearly indicates that replacement of the chloride with a hydride leads to a stronger coordinated NMe_2 amino group, and this is likely to be ascribed to the lesser steric hindrance of H vs Cl. In addition, for the chloride derivative a π-donation of the adjacent lone pairs of the halide can also promote the opening of the arm trans to the aryl group, destabilizing the six-coordinate complex vs the corresponding 16-electron species.[27]

Reaction of **2** with NaO^{i}Pr in 2-propanol−toluene gives at 50 °C a red solution containing a ruthenium alkoxide species as the main product, as inferred by $^{31}P\{^1H\}$ NMR spectroscopy (δ 54.3 and 44.6, $^2J(PP) = 34.2$ Hz, C_6D_6 lock) (Scheme 2). The use of a mixture of 2-propanol−toluene (1:1 in volume) is necessary for the solubilization of both the ruthenium chloride **2** and sodium isopropoxide, leading quickly to the ruthenium alkoxide and formation of NaCl. As a matter of fact, when the reaction is carried out in a single solvent, slow or poor conversion is observed. It is likely that the favorable effect of 2-propanol, which displays good polarity favoring the dissociation of the chloride, for the ruthenium alkoxide formation may be due to an acid/conjugate base metathesis approach, according to the route suggested by Bergman for the preparation of late transition metal amido complexes using $NaNH_2$ in the presence of its conjugate acid NH_3 in THF.[28] Employment of potassium isopropoxide with **2** leads the reaction to be completed at room temperature in a few minutes, suggesting that the reactivity is affected by the different ion pairing of potassium vs sodium isopropoxide in 2-propanol.[29] We want to point out that, by contrast to **4**, heating the ruthenium isopropoxide solution results in the reversible formation of the hydride **5**, as inferred by $^{31}P\{^1H\}$ NMR spectroscopy. As a matter of fact, a solution prepared from **2** and NaOH (molar ratio = 1/2) in 2-propanol−C_6D_6 shows the presence of the Ru-isopropoxide as essentially the only product at 20 °C, whereas at higher temperatures the Ru-H/Ru-alkoxide ratio increases (i.e., about 1:2 at 60 °C), indicating that the formation of the hydride is an endothermic process. Due to the lability of this system, the hydride complex **5** can be isolated from the reaction mixture by shifting the equilibrium reaction to the right, removing acetone through evaporation of the 2-propanol−toluene media (Scheme 2). The ^1H NMR spectrum of **5** shows the hydride signal at δ −5.58 (dd, $^2J(HP) = 89.1$, 26.4 Hz), close to that of the NMe_2 derivative **4**, with two broad resonances at δ 2.75 and 1.02 for the nonequivalent NH_2 protons. A $^1H-^1H$ NOESY experiment shows contacts of the Ru-H with two different ortho phenyl protons and with both N-H protons, but no exchange has been apparently observed. The Ru-H stretching bands of **5** and **4** are 1743 and 1811 cm^{-1}, respectively, and these low wavelengths are in agreement with the presence of a phosphine trans to hydride. Furthermore, the significantly lower value for **5** compared to **4** can be ascribed to a possible RuH···HN hydrogen bonding interaction. Complex **5** can be easily protonated by weak acids, such as CH_3COOH, leading to the corresponding acetate derivative via elimination of dihydrogen, as will be described elsewhere. Dissolution of **5** in $CHCl_3$ or CH_2Cl_2 results in the fast conversion into the chloride **2**, indicating that the hydride **5** is highly active and halogenated solvents cannot be employed. Examination of the reactivity of the hydrides **4** and **5** with acetone in C_6D_6 in the presence of 2-propanol shows

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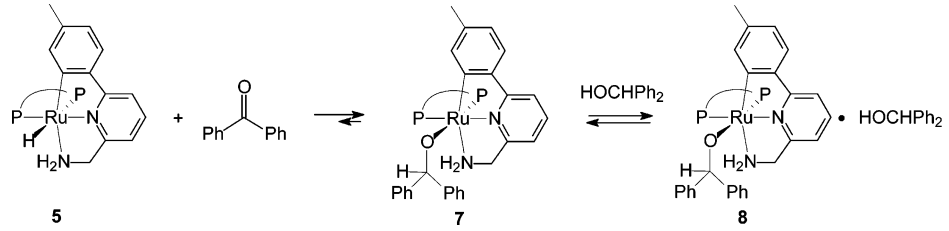
Scheme 3



5 7 8

that the two complexes have a substantially different behavior. As a matter of fact, the presence of the NH_2 group in **5** leads to the thermodynamically stable and kinetically labile isopropoxide species, with respect to the hydride−acetone system. For the NMe_2 derivative **4** the β-hydrogen elimination is a relatively slow and irreversible process, the reaction being completely shifted to the right. The stability of the isopropoxide bearing a NH_2 group can be tentatively ascribed to the lesser steric bulkiness of the H vs Me, in combination with the possible formation of a O···H hydrogen bond.

Similarly to **2**, treatment of the chiral precursor **3** with potassium isopropoxide in 2-propanol−toluene at room temperature affords a mixture of the ruthenium isopropoxide species ($^{31}P\{^1H\}$ NMR: δ 53.6 and 46.2 with $^2J(PP) = 34.6$ Hz, C_6D_6 lock) and the ruthenium hydride **6** ($^{31}P\{^1H\}$ NMR: δ 64.8 and 35.3 with $^2J(PP) = 16.5$ Hz) in 4:1 molar ratio, respectively. Likewise to the alkoxide prepared from **2**, heating the solution results in shifting the equilibrium toward the hydride complex, with a Ru-isopropoxide/Ru-H molar ratio of about 1.5:1 and 1:3 at 50 and 70 °C, respectively. The hydride **6** shows a doublet of doublets at δ −5.59 (dd, $^2J(HP) = 89.8$, 26.1 Hz), which are values very close to those of the hydrides **4** and **5**. Attempts to isolate **6** by removing acetone failed, leading to a mixture of **6** (about 70%) and the isopropoxide as main products.

Reaction of the Ruthenium Hydride 5 with Ketones. Insertion of unsaturated compounds into a metal−hydrogen bond is a fundamental step of stoichiometric and catalytic transformations.[30] However, insertion of ketones into a Ru−H bond is sparingly documented,[31] whereas the reverse β-hydrogen elimination is a well-exploited procedure for the synthesis of ruthenium hydrides.[25] Reaction of the hydride **4** with an equimolar amount of different ketones, such as acetone or benzophenone, results in no formation of the corresponding alkoxides, as observed by NMR measurements. By contrast when complex **5** in d_8-toluene is treated with benzophenone, insertion of the carbonyl group into the Ru−H bond occurs promptly, as depicted in Scheme 3.

The ^{31}P NMR spectrum of **7** shows two doublets at $\delta = 57.0$ and 37.3, showing a $^2J(PP) = 34.2$ Hz, which is similar to those of the ruthenium isopropoxide intermediates obtained from **1** and **2**. In the ^1H NMR spectrum the resonance at 4.80 is for the alkoxide CH group, and by cooling at 0 °C it turns into a doublet with a $^4J(HP) = 3.7$ Hz, as inferred through a $^1H\{^{31}P\}$ NMR experiment, which indicates that the alkoxide is directly bound to ruthenium. The broad signal at $\delta = 5.30$ is for one proton of the amine group at low field, compared to the other amine proton ($\delta = 1.45$), and this large difference may be consistent with a NH···O hydrogen bond interaction, which could stabilize the alkoxide **7**. Furthermore, the doublet at $\delta = 5.50$ ($^3J(HH) = 7.6$ Hz) is for one proton of the pyridine in the position 5, as established via a $^1H-^1H$ COSY experiment, shifted upfield compared to those in **2** and **5** and which may be due to a possible interaction between the pyridine ring and a phenyl of the alkoxide. The ^{13}C NMR spectrum of the complex in benzene-d_6 displays a signal at 80.1, shifted downfield compared to benzhydrol ($\Delta\delta = 4.0$). This value can be compared with those of other transition metal alkoxide complexes, which show a similar trend.[32] Addition of benzhydrol in about 1:1 molar ratio results in the formation of a new species, **8**, which can be ascribed to an alkoxide−alcohol adduct, in equilibrium with the original alkoxide **7**.[33,34] Interestingly, this new complex **8** displays two doublets in the ^{31}P NMR spectrum at $\delta = 55.0$ and 42.8 with a $^2J(PP) = 34.2$ Hz, a value identical to that of the alkoxide **7**. Addition of alcohol leads to the increase of the signals for **8**, with a high-field resonance that shifts progressively to lower field (δ up to 45.0). In the ^1H NMR spectrum the signal at $\delta = 5.45$ is for the benzhydrol OCH moiety, which is in rapid exchange with the coordinated OCH group at 4.80, as revealed through a ^1H 1D sel-NOESY experiment. As a matter of fact, the latter signal is converted into that of benzhydrol in 70 ms (plateau, 40% conv.), following an exponential behavior. This clearly indicates that the alkoxide in Ru(amine)(alkoxide) exchanges rapidly with alcohol, and this process can be possibly mediated via a RuOR···HOR hydrogen bond, according to the studies of Bergman and other authors.[33] By increasing the temperature to about 50 °C the two OCH signals (and also the low-field NH resonance) disappear in the baseline, leading at 70 °C to only one broad signal at $\delta = 5.10$. The NCH_2 group shows a singlet at $\delta = 3.22$ for the two protons, apparently not coupled with the NH protons, probably because of their fast exchange, whereas the carbon signal is, at $\delta = 52.0$, almost identical to that of **7**, indicating that the nitrogen is coordinated as amine to ruthenium. At room temperature the CH_3 groups of the tolyl moiety of **7** and **8** are at $\delta = 2.28$ and 2.35, while at higher temperature they broaden, leading to a singlet at $\delta = 2.29$ at 70 °C. Also in the ^{31}P NMR spectra the signals of **7** and **8** broaden when the temperature is increased, and at about 70 °C the two species lead only to two resonances at $\delta = 57.2$ and 39.5, indicating that these complexes are involved in a fast exchange process. Furthermore, at temperatures higher than 70 °C, the spectra show the signals of the hydride **5**, which equilibrates with the species **7** and **8**. The reversible insertion of a ketone into the metal−hydride bond has been described previously by Hoffmann on a rhenium isopropoxide system.[35] On the other hand, there are only a few reports on stable ruthenium alkoxides obtained through Ru-H insertion of ketones, namely, those containing electron-withdrawing group, such as

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CF_3,[31a] or ketoesters, which can lead to bidentate alkoxides.[31b] Although it has been well established that NH hydrogens increase the activity of ruthenium catalysts in hydrogenation, far less is known about the role of these hydrogen in stabilizing Ru-O species, such as alkoxides or carboxylates. Interestingly, Koike and Ikariya have reported that the presence of NH hydrogens allows insertion of carbon dioxide into the Ru−H bond.[36] Furthermore, these authors and Morris have given evidence of the formation of ruthenium alkoxide−amine species.[37]

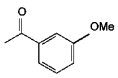
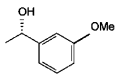
Addition of acetophenone to the hydride **5** in C_6D_6 leads to the corresponding alkoxide Ru(OCHMePh)(**a**)(dppb) with ^{31}P NMR data ($\delta = 56.1$ and 37.9; $^2J(PP) = 34.3$ Hz) that resemble those of **7**, whereas addition of 1-phenylethanol (2 equiv) leads to a new alcohol adduct at $\delta = 54.5$ and 41.6 with a $^2J(PP) = 33.8$ Hz in equilibrium with the alkoxide. By addition of subsequent amounts of alcohol the latter resonance shifts to lower field (to 46.2) as for **8**, the four doublets being relatively broad ($\Delta\nu_{1/2} \approx 70$ Hz), indicating that a rapid exchange process occurs between the alkoxide and the alkoxide−alcohol adduct.

Therefore, our NMR data show that the Ru alkoxides of the type Ru(OR)(CNN)(PP) are in rapid exchange with alcohols (<0.1 s) and also with the corresponding hydrides, allowing very fast equilibration of the alcohol and ketone species. This represents a central point for the transfer hydrogenation catalysis in which Ru-alkoxides are effective key species. Since the exchange between the alkoxide **7** and the corresponding alcohol adduct **8** is very fast compared to the β-hydrogen elimination reaction, we cannot rule out that the presence of alcohol could be fundamental in facilitating the formation of the hydride **5**. This point has been raised by Milstein for the *trans*-$HIr(OCH_3)(C_6H_5)(PMe_3)_3$ system, which leads to the corresponding dihydride without requiring a vacant cis coordination site and possibly through a hydrogen-bonding network with methanol.[38]

Catalytic Transfer Hydrogenation with 1−3. The catalytic precursor **2** has been shown to be extremely active for the selective reduction of a large number of ketones to alcohols in 2-propanol and in the presence of NaOH.[3] Thus, acetophenone has been quantitatively converted in 5 min using 0.005% mol of **2** in refluxing 2-propanol, with a remarkable speed (TOF of 1.1×10^6 h^{-1}). The robust frame of **2** allows the reaction to be carried out even at lower catalyst loading. Different ketones, such as acetophenone and benzophenone, have been easily reduced using 0.001 mol % of **2**, indicating that this protocol can be applied for the medium-scale preparation of alcohols and, therefore, may be of interest for industrial applications. It is noteworthy that most of the described hydrogen-transfer catalysts work with relatively higher loading (>0.01% mol) and lead to incomplete conversion of substrate when the amount of catalyst is reduced.

It is significant that complex **1**, which shows a NMe_2 group instead of NH_2, displays a much lower catalytic activity for the reduction of ketones. Under identical catalytic conditions used for **2**, complex **1** (0.005 mol %, NaOH 2 mol %) leads only to 30% conversion of acetophenone after 3 h. As reported in the previous part, when **1** reacts with sodium isopropoxide, the hydride **4** is easily formed, but this species does not give insertion of ketones and no formation of ruthenium alkoxides has been observed by NMR measurements. This provide additional evidence for the key role of alkoxides in the fast transfer hydrogenation and suggests that the effectiveness of complexes containing an amino NH group could be related to their ability to favor the formation of ruthenium alkoxides. When the chiral complex **3** is used, again fast reduction of different methyl-aryl ketones is observed under the same experimental conditions employed for **2**, and the results are reported in Table 3.

Table 3. Catalytic Transfer Hydrogenation of Methyl-Aryl Ketones with Complex 3[a]

Complex	Ketone	Alcohol	Conversion % (min)[b]	TOF (h^{-1})[c]	*ee* (%)[b]
3			98 (5)	9.3×10^5	71 *S*
3			99 (5)	6.8×10^5	70 *S*
3			96 (5)	5.4×10^5	88 *S*
3			97 (2)	1.4×10^6	71 *S*
in situ[d]			98 (10)	6.6×10^5	72 *S*
in situ[d]			98 (5)	6.8×10^5	70 *S*
in situ[d]			95 (5)	6.0×10^5	88 *S*

[a] Conditions: reactions were carried out at 82 °C, ketone 0.1 M in 2-propanol, ketone/Ru/NaOiPr = 20000/1/400. [b] The conversion and ee were determined by GC analysis. [c] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [d] Complex **3** was prepared in situ by treatment of $RuCl_2(PPh_3)$(dppb) with the ligand H**c** (1:2 molar ratio) in 2-propanol at reflux for 10 min.

The values of the rate of reduction are comparable to those of **2**, leading to the corresponding alcohols in a few minutes (TOF in the range 5.4×10^5 to 1.4×10^6 h^{-1}) and with fairly good to good enantiomeric excess (70−88%), the best result being obtained with 2-methoxyacetophenone. These data indicate that **3** can be employed for the fast enatioselective reduction of prochiral ketones using very low catalyst loading (substrate/catalyst up to 20 000). Furthermore, the same catalytic performance can be obtained generating the catalyst in situ, by reaction of $RuCl_2(PPh_3)$(dppb) with the ligand H**c** (2 equiv) in 2-propanol at reflux, showing that the formation of **3** is quite straightforward (Table 3).

As regards the mechanism of the transfer hydrogenation of ketones mediated by RuX(CNN)(PP) complexes, the first step is the reaction of the chloride catalytic precursor with alkaline isopropoxides, affording the ruthenium isopropoxide derivative. This species gives the ruthenium hydride, which then reacts with the ketone substrate, affording the corresponding ruthenium

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alkoxide.[39] Subsequent reaction with 2-propanol, which is present in large excess, leads to the formation of the ruthenium isopropoxide, which closes the cycle. This route is supported by stoichiometric reactions that show that the ruthenium isopropoxide CNN complexes, formed by chloride displacement, are in equilibrium with the hydrides (such as **5**, **6**), when a NH_2 group is present. This shows that for the above complexes the alkoxide β-elimination and the insertion of ketones into the Ru−H bond is a relatively easy and rapid process. Furthermore, the fast exchange of the alkoxide with alcohol, as observed for **5**, which is likely to occur via hydrogen bond interactions, indicates that the last step of the catalytic cycle also takes place rapidly. Therefore, these studies show that the Ru(OR)(CNN)-(PP) complexes bearing a NH donor group display rapid hydride/alkoxide and alkoxide/alcohol equilibrium processes as well as fast catalytic transfer hydrogenation.

Concluding Remarks

In summary, we have described a novel class of terdentate complexes of formula RuCl(CNN)(dppb) also with a chiral CNN moiety that are extremely active catalysts for transfer hydrogenation in basic conditions. Reaction of these complexes with MO^iPr (M = Na, K) leads to the corresponding isopropoxides, which, when a NH_2 group is present, are in equilibrium with the hydrides. These complexes react with ketones with formation of alkoxides, which are in rapid exchange with the alcohol. Because the new highly active catalysts RuCl(CNN)(PP) can be easily prepared combining 6-aryl-2-aminomethylpyridines with a large number of commercially available diphosphines, this new group of complexes appears to be very promising for application in homogeneous catalysis. Work is in progress to extend this chemistry to chiral diphosphines for obtaining very fast enantioselective catalysts.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use. The ruthenium complex $RuCl_2(PPh_3)$(dppb)[40] and (S_S,*R*)-*N*-(*p*-toluenesulfinyl)-2,2-dimethyl-1-(6-phenylpyridin-2-yl)propylamine[14] were prepared according to literature procedures, whereas all other chemicals were purchased from Aldrich and used without further purification. NMR measurements were recorded on a Bruker AC 200 spectrometer and a Bruker AVANCE 400 spectrometer equipped with a 5 mm multinuclear z-gradient probe. 2D COSY, 2D HSQC, and 1D sel-NOESY experiments were performed using the standard pulse sequences from the Bruker library. Chemical shifts, in ppm, are relative to TMS for ^1H and $^{13}C\{^1H\}$, whereas 85% H_3PO_4 was used for $^{31}P\{^1H\}$. Infrared measurements were obtained using a Brucker Vector 22 FT-IR spectrometer. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 elemental analyzer.

Synthesis of 2-Cyano-6-(4-methylphenyl)pyridine. 2-(4-Methylphenyl)pyridine was converted into the *N*-oxide by oxidation with 30% hydrogen peroxide in glacial acetic acid at 70 °C for 13 h according to Ochiai[41] (84% yield, mp 119−120 °C). To a solution of the *N*-oxide (9.21 g, 49.7 mmol) in anhydrous CH_2Cl_2 (130 mL) were added dropwise in sequence dimethylcarbamyl chloride (5.35 g, 4.58 mL, 49.7 mol) and trimethylsilyl cyanide (5.19 g, 6.97 mL, 52.3 mol). The solution was stirred at room temperature for 3 days and then heated under reflux for 9 h. After cooling, a 10% solution of K_2CO_3 was added and stirring continued for 15 min. The organic phase was separated and dried (Na_2SO_4), the solvent was evaporated, and the residue was purified by flash chromatography (petroleum ether−EtOAc, 95:5). Yield: 9.23 g (96%). Mp: 131−132 °C. Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.52; H, 5.17; N, 14.44. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 7.94−7.91 (m, 3H), 7.88 (t, *J*(HH) = 9.6 Hz, 1H), 7.59 (dd, *J*(HH) = 1.2, 1.2 Hz, 1H), 7.31 (dd, *J*(HH) = 0.6, 0.6 Hz, 2H), 2.42 (s, 3H; CH_3).

Synthesis of 2-Aminomethyl-6-(4-methylphenyl)pyridine (Ha). 2-Cyano-6-(4-methylphenyl)pyridine (0.970 g, 5.00 mmol) was added portionwise to a solution prepared by mixing anhydrous Et_2O (10 mL) with a 1 M solution of $LiAlH_4$ in THF (6.92 mL, 6.92 mmol). The mixture was stirred at room temperature for 1 h and then heated at 40 °C for 3 h. After cooling, a 40% aqueous solution of NaOH (5 mL) was cautiously added, and stirring continued for 1 h. The organic phase was separated and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by flash chromatography (methanol). Yield: 0.46 g (46%). Mp: 59−60 °C. Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.66; H, 7.14; N, 14.14. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 7.92 (d, *J*(HH) = 8.1 Hz, 2H), 7.68 (t, *J*(HH) = 7.5 Hz, 1H), 7.57 (d, *J*(HH) = 7.5 Hz, 1H), 7.27 (d, *J*(HH) = 8.1 Hz, 2H), 7.15 (d, *J*(HH) = 7.5, 1H), 4.01 (s, 2H; CH_2), 2.40 (s, 3H; CH_3), 1.86 (s, 2H; NH_2).

Synthesis of *N*,*N*-Dimethyl-2-aminomethyl-6-(4-methylphenyl)pyridine (Hb). 2-Aminomethyl-6-(4-methylphenyl)pyridine (H**a**) (0.30 g, 1.5 mmol) was slowly added to a cooled (0 °C) 90% aqueous solution of formic acid (0.460 g, 9.0 mmol). Then a 35% aqueous solution of formaldehyde (0.283 g, 3.3 mmol) was added, and the resulting mixture was heated at 70 °C for 4 h. After cooling, the mixture was basified with a 10% aqueous solution of NaOH (10 mL) and then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried (Na_2SO_4), the solvent was evaporated, and the residue was purified by flash chromatography (CH_2Cl_2−MeOH, 9:1), affording a pale yellow oil. Yield: 0.197 g (58%). Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.93; H, 8.05; N, 12.39. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 7.90 (d, *J*(HH) = 8.1 Hz, 2H), 7.68 (t, *J*(HH) = 7.5 Hz, 1H), 7.55 (d, *J*(HH) = 7.5 Hz, 1H), 7.32 (d, *J*(HH) = 7.5 Hz, 1H), 7.25 (d, *J*(HH) = 8.1 Hz, 2H), 3.67 (s, 2H; CH_2), 2.39 (s, 3H; CH_3), 2.34 (s, 6H; NMe_2).

Synthesis of (*R*)-2,2-Dimethyl-1-(6-phenylpyridin-2-yl)propylamine (Hc). Trifluoroacetic acid (1.4 g, 12.2 mmol) was added dropwise to a cooled (0 °C) solution of (S_S,*R*)-*N*-(*p*-toluenesulfinyl)-2,2-dimethyl-1-(6-phenylpyridin-2-yl)propylamine (1.12 g, 2.96 mmol, 98% de) in CH_3OH (12 mL). After 24 h stirring at room temperature, H_2O (10 mL) was added and the MeOH was evaporated under vacuum. The aqueous residue was taken up in CH_2Cl_2 (100 mL), and the resulting solution was washed with 10% NaOH (3 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The residue was purified by flash chromatography (methanol), obtaining a yellow oil. Yield: 0.67 g (94%). $[\alpha]^{25}_D = -39.4$ (*c* 0.13, $CHCl_3$). Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.66. Found: C, 79.65; H, 8.41; N, 11.64. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.03 (d, *J*(HH) = 7.2 Hz, 2H), 7.66−7.58 (m, 2H), 7.49−7.37 (m, 3H), 7.10 (d, *J*(HH) = 7.2 Hz, 1H), 3.72 (s, 1H; CHN), 1.99 (s, 2H; NH_2), 0.97 (s, 9H; CMe_3).

Synthesis of 1. To a suspension of $RuCl_2(PPh_3)$(dppb) (0.400 g, 0.465 mmol) in 2-propanol (4 mL) were added the ligand H**b** (0.148 g, 0.654 mmol) and triethylamine (0.9 mL, 6.46 mmol). The mixture was refluxed overnight, and the orange precipitate was filtered, washed with methanol, and dried under reduced pressure. Yield: 0.260 g (71%). Anal. Calcd for $C_{43}H_{45}ClN_2P_2Ru$: C 65.52;

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H, 5.75; N 3.55. Found: C, 65.21; H, 5.68; N, 3.32. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 8.19−6.60 (m, 24H; aromatic protons), 6.19 (t, J(HH) = 8.0 Hz, 2H; m-Ph), 3.50 (d, J(HH) = 13.6, 1H; CH_2N), 3.09 (d, J(HH) = 13.6 Hz, 1H; CH_2N), 3.24−0.90 (m, 8H; CH_2), 2.20 (s, 3H; CH_3), 1.77 (s, 6H; $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): 164.2 (s; N*C*C), 157.6 (s; N*C*CH_2), 150.2−116.5 (m; aromatic carbons), 70.7 (s, *C*H_2N), 50.7 (s, $N(CH_3)_2$), 34.5 (d, J(CP) = 23.3 Hz; *C*H_2P), 32.5 (d, J(CP) = 32.0 Hz; *C*H_2P), 27.1 (s; CH_2), 21.8 (s; CH_2), 21.6 (s, CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ 50.8 (d, J(PP) = 37.3 Hz), 35.5 (d, J(PP) = 37.3 Hz).

Synthesis of 2. The synthesis of **2** was carried out in a way similar to that described for **1**, using H**a** instead of H**b**. To a suspension of $RuCl_2(PPh_3)$(dppb) (1.17 g, 1.36 mmol) in 2-propanol (15 mL) were added the ligand H**a** (0.300 g, 1.51 mmol) and triethylamine (1.9 mL, 13.6 mmol). The mixture was refluxed for 2 h, and the yellow precipitate was filtered, washed with methanol, and dried under reduced pressure. Yield: 810 mg (78%). Anal. Calcd for $C_{41}H_{41}ClN_2P_2Ru$: C, 64.77; H, 5.44; N, 3.68. Found: C, 64.36; H, 5.52; N, 3.70. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 8.10−6.57 (m, 24H; aromatic protons), 6.00 (t, J(HH) = 8.1 Hz, 2H; m-Ph), 4.12 (dd, J(HH) = 15.5, 4.4 Hz, 1H; CH_2N), 3.72 (td, J(HH) = 15.5, 4.1 Hz, 1H; CH_2N), 3.41 (m, 1H; NH_2), 3.05 (m, 2H; CH_2P), 2.46−0.90 (m, 7H; NH and CH_2), 2.23 (s, 3H; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ 181.8 (dd, J(CP) = 16.3, 7.8 Hz; CRu), 163.2 (s; N*C*C), 155.9 (s; N*C*CH_2), 149.2−116.0 (m; aromatic carbons), 52.5 (d, J(CP) = 2.7 Hz; *C*H_2N), 33.4 (d, J(CP) = 26.3 Hz; *C*H_2P), 30.7 (d, J(CP) = 31.6 Hz; *C*H_2P), 26.8 (s; CH_2), 22.1 (s; CH_2), 21.8 (s, CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ 57.3 (d, J(PP) = 38.3 Hz), 42.6 (d, J(PP) = 38.3 Hz).

Synthesis of 3. The synthesis of **3** was carried out in a way similar to that described for **1**, using H**c** instead of H**b**. To a suspension of $RuCl_2(PPh_3)$(dppb) (1.35 g, 1.57 mmol) in 2-propanol (20 mL) were added the ligand H**c** (0.470 g, 1.96 mmol) and triethylamine (2.20 mL, 15.8 mmol). The mixture was refluxed overnight, and the light brown precipitate was filtered, washed with methanol, and dried under reduced pressure. Yield: 1.07 g (85%). Anal. Calcd for $C_{44}H_{47}ClN_2P_2Ru$: C 65.87; H, 5.90; N 3.49. Found: C, 65.61; H, 5.78; N, 3.32. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 8.16−6.57 (m, 25H; aromatic protons), 5.93 (t, J(HH) = 8.6 Hz, 2H; m-Ph), 3.40 (d, J(HH) = 13.1, 1H; CHN), 3.22 (dd, J(HH) = 13.2, 9.5 Hz, 1H; NH_2), 3.04 (m, 2H; PCH_2), 2.30−1.05 (m, 7H; PCH_2, CH_2 and NH_2), 0.95 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): 183.6 (dd, J(CP) = 16.3, 7.7 Hz; CRu), 165.1 (s; N*C*C), 156.5 (s; N*C*CH_2), 150.2−116.5 (m; aromatic carbons), 72.2 (d, J(CP) = 2.53 Hz; *C*HN), 35.1 (s, *C*CH_3), 33.3 (d, J(CP) = 24.8 Hz; *C*H_2P), 30.6 (d, J(CP) = 32.0 Hz; *C*H_2P), 27.2 (s; $C(CH_3)_3$), 26.9 (s; CH_2), 21.8 (s; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): 56.8 (d, J(PP) = 38.8 Hz), 43.7 (d, J(PP) = 38.8 Hz).

Synthesis of 4. Complex **1** (0.200 g, 0.254 mmol) was suspended in toluene (4.0 mL), and 4.0 mL of a solution 0.1 M of NaO^iPr in 2-propanol (0.4 mmol) was added. After 2 h at 60 °C the solution was concentrated, stirred at room temperature for 30 min, and filtered on Celite (fine frit). The solvent was eliminated under reduced pressure, and the solid was extracted with pentane, affording an orange product, which was dried under reduced pressure. Yield: 0.099 g (52%). Anal. Calcd for $C_{43}H_{46}N_2P_2Ru$: C, 68.51; H, 6.15; N, 3.72. Found: C, 68.33; H, 6.02; N, 3.51. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.50−6.10 (m, 26H; aromatic protons), 3.25 (d, J(HH) = 13.3 Hz, 1H; CH_2N), 2.83 (m, 2H; PCH_2), 2.61 (d, J(HH) = 13.3 Hz, 1H; CH_2N), 2.23−0.90 (m, 6H; CH_2), 2.18 (s, 3H; CH_3), 2.13 (s, 3H; $N(CH_3)_2$), 2.10 (s, 3H; $N(CH_3)_2$), −5.79 (dd, J(HP) = 87.7, 28.6 Hz, 1H; RuH). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20 °C): δ 184.5 (s br; CRu), 163.6 (s; N*C*C), 154.3 (s; N*C*CH_2), 148.7−114.8 (m; aromatic carbons), 72.9 (s, *C*H_2N), 33.4 (d, J(CP) = 18.1, 5.0 Hz; CH_2P), 31.6 (d, J(CP) = 22.5 Hz; *C*H_2P), 27.0 (s; CH_2), 23.1 (s; CH_2), 22.1 (s; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ 62.5 (d, J(PP) = 15.5 Hz), 30.4 (d, J(PP) = 15.5 Hz). IR (Nujol): 1811 cm^{-1} (br, Ru−H).

Synthesis of 5. Complex **2** (516 mg, 0.679 mmol) was suspended in toluene (10 mL), and 10 mL of a solution of NaO^iPr (0.1 M, 1.00 mmol) in 2-propanol was added. After 1 h at 60 °C the solution was concentrated, stirred at room temperature, and after addition of toluene filtered on Celite (fine frit). The filtrate was evaporated, and the solid was precipitated from toluene and filtered, affording a bright orange product, which was dried under reduced pressure. Yield: 395 mg (80%). Anal. Calcd for $C_{41}H_{42}N_2P_2Ru$: C, 67.85; H, 5.83; N, 3.86. Found: C, 66.80; H, 5.63; N, 3.57. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.55−5.90 (m, 26H; aromatic protons), 3.10−0.9 (m, 12H; CH_2 and NH_2), 2.30 (s, 3H; CH_3), −5.58 (dd, J(HP) = 89.1, 26.4 Hz, 1H; RuH). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 45 °C): δ 189.1 (s; CRu), 163.0 (s; N*C*C), 154.8 (s; N*C*CH_2), 149.2−113.2 (m; aromatic carbons), 52.1 (d, J(CP) = 2.8 Hz; *C*H_2N), 32.5 (d, J(CP) = 13.8 Hz; *C*H_2P), 30.0 (d, J(CP) = 21.3 Hz; *C*H_2P), 27.0 (s; CH_2), 22.8 (s; CH_2), 22.0 (s; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 45 °C): δ 65.7 (d, J(PP) = 17.2 Hz), 34.6 (d, J(PP) = 17.2 Hz). IR (Nujol): 1743 cm^{-1} (br, Ru−H).

Synthesis of 7. To a suspension of **5** (160 mg, 0.220 mmol) in toluene (2 mL) was added benzophenone (45 mg, 0.247 mmol), and the solution was stirred for 15 min. The solution was concentrated and addition of pentane afforded a dark orange precipitate, which was filtered and dried under reduced pressure. Yield: 140 mg (70%). Anal. Calcd for $C_{54}H_{52}N_2OP_2Ru$: C, 71.43; H, 5.77; N, 3.09. Found: C, 70.51; H, 5.39; N, 2.81. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.40−5.80 (m, 35H; aromatic protons), 5.58 (d, J(HH) = 7.2 Hz, 1H; aromatic proton), 5.35 (br s, 1H; NH_2), 4.86 (s, 1H; OCH), 3.20−2.60 (m, 5H), 2.25 (s, 3H; CH_3), 2.10−0.9 (m, 6H). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20 °C): δ 187.6 (s; CRu), 163.8 (s; N*C*C), 157.4 (s; N*C*CH_2), 155.7−112.4 (m; aromatic carbons), 80.1 (s; OCH), 52.0 (s; *C*H_2N), 31.6 (d, J(CP) = 29.2 Hz; *C*H_2P), 30.9 (d, J(CP) = 26.7 Hz; *C*H_2P), 27.0 (s; CH_2), 22.6 (s; CH_2), 22.1 (s; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ 57.0 (d, J(PP) = 34.2 Hz), 37.3 (d, J(PP) = 34.2 Hz).

Typical Procedure for the Catalytic Transfer Hydrogenation. The ruthenium complex **3** (3.2 mg, 4.0 μmol) was dissolved in 8 mL of 2-propanol. The ketone (2 mmol) was dissolved in 19 mL of 2-propanol, and the solution was heated to reflux under argon. By addition of NaO^iPr (0.1 M, 0.4 mL) and the solution containing the ruthenium complex (0.2 mL) the reduction of the ketone starts immediately (**3** 0.005 mol %, NaO^iPr 2 mol %), and the yield was determined by GC analysis using a MEGADEX-ETTBDMS-β chiral column.

X-ray Structure Determination of 3. Data collection for **3** was carried out at 293(2) K on a Nonius DIP-1030H system, with graphite-monochromatized Mo Kα radiation. A total of 30 frames were collected, each with an exposure time of 20 min, over a half of reciprocal space with a rotation of 6° about φ, the detector being at 80 mm from the crystal. Cell refinement, indexing, and scaling of the data set were carried out using the programs Denzo and Scalepack.[42] The structure was solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[43] Anisotropic temperature factors were obtained for all non-H atoms of the complex. The contribution of hydrogen atoms at calculated positions was included in the final cycles of refinements. All the calculations were performed using

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the WinGX System, Ver 1.70.00.[44] Details of the X-ray experiment, data reduction, and final structure refinement calculation are summarized in Table 1.

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Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for **3** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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