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Highly Productive CNN Pincer Ruthenium Catalysts for the Asymmetric Reduction of Alkyl Aryl Ketones

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Abstract: Chiral pincer ruthenium complexes of formula [RuCl(CNN)(Josiphos)] (**2**–**7**; Josiphos = 1-[1-(dicyclohexylphosphano)ethyl]-2-(diarylphosphano)ferrocene) have been prepared by treating $[RuCl_2(PPh_3)_3]$ with (*S*,*R*)-Josiphos diphosphanes and 1-substituted-1-(6-arylpyridin-2-yl)methanamines (HCNN; substituent = H (**1a**), Me (**1b**), and *t*Bu (**1c**)) with NEt_3. By using **1b** and **1c** as a racemic mixture, complexes **4**–**7** were obtained through a diastereoselective synthesis promoted by acetic acid. These pincer complexes, which display correctly matched chiral PP and CNN ligands, are remarkably active catalysts for the asymmetric reduction of alkyl aryl ketones in basic alcohol media by both transfer hydrogenation (TH) and hydrogenation (HY), achieving enantioselectivities of up to 99%. In 2-propanol, the enantioselective TH of ketones was accomplished by using a catalyst loading as low as 0.002 mol% and afforded a turnover frequency (TOF) of 10^5–$10^6\ h^{-1}$ (60 and 82 °C). In methanol/ethanol mixtures, the CNN pincer complexes catalyzed the asymmetric HY of ketones with H_2 (5 atm) at 0.01 mol% relative to the complex with a TOF of $\approx 10^4\ h^{-1}$ at 40 °C.

Keywords: asymmetric catalysis · chiral resolution · hydrogen transfer · hydrogenation · ruthenium

Introduction

The design of selective and productive transition-metal catalysts is a crucial issue in the asymmetric synthesis of organic compounds. High catalyst efficiency is of paramount importance for industrial applications, allowing the use of precious chiral complexes in small amounts and leading to products with low metal content.[1] Enantioselective hydrogenation (HY)[2] and transfer hydrogenation (TH)[3] of carbonyl compounds are core processes in chemistry, which are usually performed with complexes derived from elements of Groups 8 and 9, with ruthenium being the metal of choice. A crucial contribution to catalytic HY and TH was made by Noyori and Ikariya and co-workers, which led to the synthesis of *trans*-[$RuCl_2$(diphosphane)(1,2-diamine)][4] and [(η^6-arene)RuCl(H_2NCHPhCHPhNTs)].[5] These catalytic systems inspired the development of a large number of catalysts.[2a,6] In the last decade, asymmetric HY systems have achieved an extremely high level of efficiency in terms of rate and productivity.[2] By contrast, TH usually requires a relatively large amount of a chiral complex (0.01–1 mol%)[5–7] on account of easy catalyst deactivation.

The robust CNN pincer complexes [RuCl(CNN)(PP)][8] (PP = $Ph_2P(CH_2)_4PPh_2$), prepared from 1-[6-(4′-methylphenyl)pyridin-2-yl]methanamine (HCNN, **1a**), have proven to be the most active and productive catalysts[9] for the achiral TH of carbonyl compounds (turnover frequencies (TOFs) up to $2.5\times10^6\ h^{-1}$) at a loading of 0.005–0.001 mol%. The development of the chiral version of this pincer system would result in catalysts that display both high productivity and enantioselectivity and thereby make TH a valid complement to HY. Recently, we found a practical route to the related chiral complexes *cis*-[$RuCl_2$(diphosphane)(aminopyridine)] by using racemic nitrogen ligands through a diastereoselective reaction.[10] Furthermore, CNN pincer osmium complexes [OsCl(CNN)(PP)] have recently been proven to efficiently catalyze the asymmetric TH and HY of carbonyl compounds.[11]

We report herein that the preparation of the novel chiral pincer catalysts [RuCl(CNN)(Josiphos)] (Josiphos = 1-[1-(dicyclohexylphosphano)ethyl]-2-(diarylphosphano)ferrocene)

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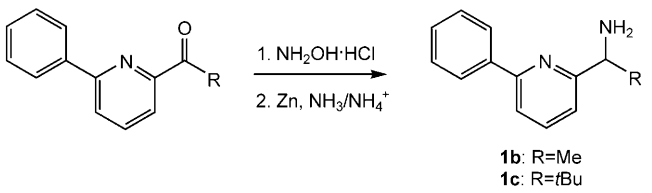
is greatly simplified through a one-pot synthesis that entails the use of $[RuCl_2(PPh_3)_3]$, a Josiphos diphosphane, and a racemic mixture of a 1-substituted HCNN ligand in the presence of acetic acid, which avoids the isolation of the pincer ligands in enantiopure form. These complexes, which contain correctly matched PP/CNN chiral ligands, are highly efficient catalysts for the asymmetric TH and HY of alkyl aryl ketones with TOFs of up to $10^6\ h^{-1}$ at a catalyst loading as low as 0.002 mol%.

Results and Discussion

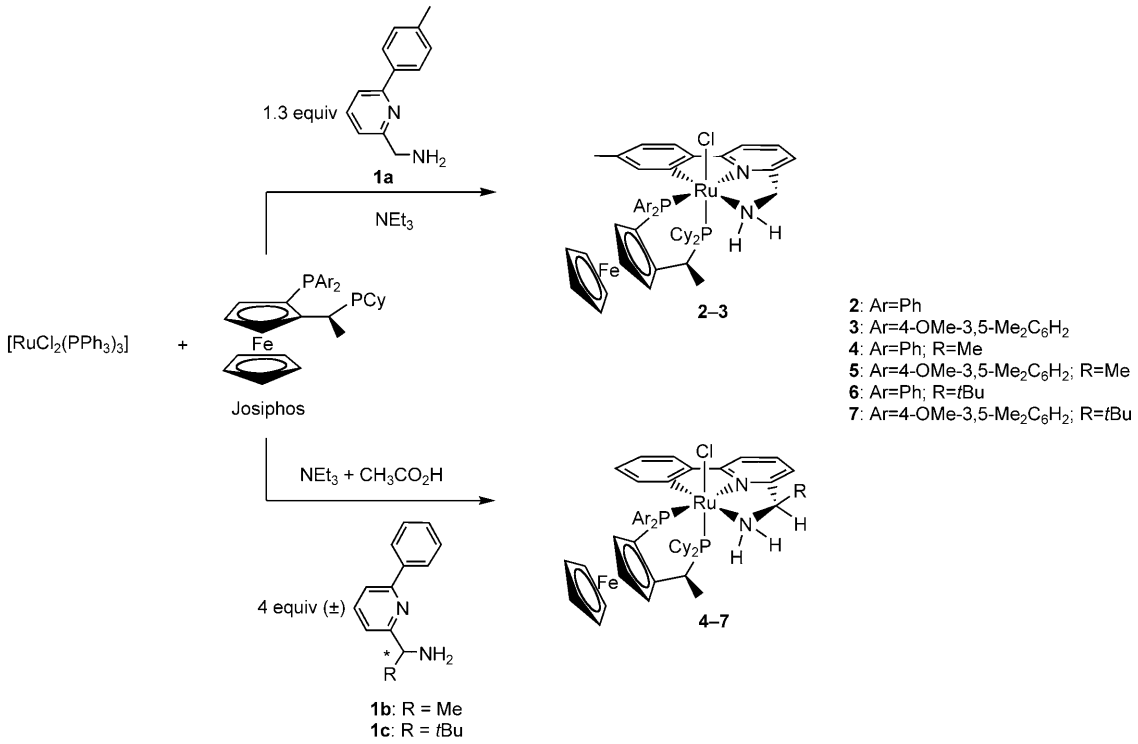
Preparation of the chiral pincer complexes [RuCl(CNN)-(Josiphos)]: The racemic ligands **1b** and **1c**, with a methyl and a *tert*-butyl group bonded to the carbon atom connected to the NH_2 moiety, were easily synthesized by treating the corresponding ketones with $NH_2OH{\cdot}HCl$ and reduction of the oxime intermediate with Zn/ammonium acetate/NH_4OH (91 and 67% yields, respectively), as shown in Scheme 1.



Scheme 1. Synthesis of the ligands **1b** and **1c**.

The ligands **1a**–**1c** were used to prepare the CNN pincer ruthenium complexes for the asymmetric reduction of ketones. The in situ generated derivative [RuCl(CNN)-(Josiphos)], obtained from $[RuCl_2(PPh_3)_3]$, (*S*,*R*)-Josiphos, and **1a**,[12] promotes the quantitative TH of acetophenone to (*S*)-1-phenylethanol (30 min, 65% enantiomeric excess (*ee*)) in 2-propanol with NaO*i*Pr (2 mol%) at a ruthenium loading of as low as 0.005 mol% (TOF = $1.1\times10^5\ h^{-1}$ at 60°C). Interestingly, an increase in enantioselectivity was achieved by using a racemic mixture of the 1-methyl-substituted pincer ligand **1b** in place of **1a** (75% *ee*, TOF = $1.0\times10^5\ h^{-1}$) (Scheme 2).

Employment of **1a** with the bulkier diphosphane (*S*,*R*)-Josiphos*, with 4-OMe-3,5-$Me_2C_6H_2$ instead of Ph, led to the *S* alcohol with 90% *ee* (TOF = $1.2\times10^5\ h^{-1}$). On account of the high productivity of these in situ generated catalysts, we decided to isolate the corresponding complexes. The thermally stable ortho-metalated chiral derivative **2** was easily prepared (67% yield) by treatment of $[RuCl_2(PPh_3)_3]$ with 1.2 equiv of (*S*,*R*)-Josiphos in toluene (105°C, 2 h), followed by reaction with **1a** (1.3 equiv) and NEt_3 in 2-propanol at reflux temperature (2 h; see Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two doublets at $\delta = 67.2$ and 40.8 ppm ($^2J(P,P) = 41.3$ Hz), which indicates the formation of a single stereoisomer. The $^{13}C\{^1H\}$ NMR signal for the NCH_2 group is at $\delta = 46.1$ ppm, whereas the ortho-metalated signal is at $\delta = 185.9$ ppm (dd, $J(C,P) = 13.1$, 8.5 Hz). Similarly to **2**, complex **3** was prepared by reaction of $[RuCl_2(PPh_3)_3]$ with the bulkier (*S*,*R*)-Josiphos* and **1a** (74% yield). Treatment of (*S*,*R*)-Josiphos with a racemic mixture of **1b** resulted in



Scheme 2. Synthesis of the chiral pincer CNN complexes **2**–**7**.

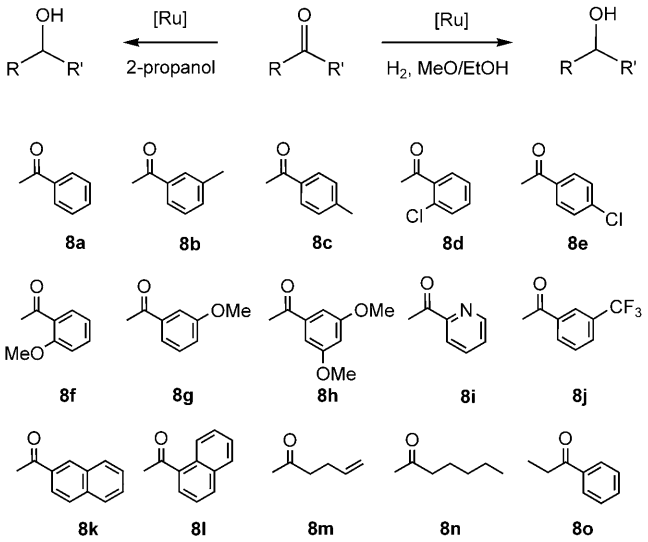
the formation of two ruthenium diastereoisomers in a ratio of about 1:1, as inferred from the $^{31}P\{^1H\}$ NMR spectrum.[13] Interestingly, by performing the reaction with an excess of (±)-**1b** (4 equiv) in the presence of NEt_3 and 0.5 equiv of acetic acid, complex **4** was formed predominantly as one stereoisomer (>92% major isomer) and was isolated in 70% yield (Scheme 2). Under these conditions, the combination of (*S*,*R*)-Josiphos* and (±)-**1b** led to the species **5** (>93% major isomer), isolated in 63% yield. The weak acid proved to facilitate the formation of the thermodynamically most stable diastereoisomer, possibly through protonation and decoordination of the ortho-metalated CNN ligand of the kinetic product. Control experiments showed that reaction of the $[RuCl_2(PPh_3)_3]$/(*S*,*R*)-Josiphos or (*S*,*R*)-Josiphos* system with the chiral ligand (*R*)-**1b** led to **4** and **5** as single stereoisomers, namely, the major isomers obtained in the synthesis of **4** and **5** from (±)-**1b**. In addition, the use of (±)-**1b** or (*R*)-**1b** leads to complexes that display the same catalytic activity. Finally, derivatives **6** and **7** were isolated as single isomers (65 and 67% yields) from $[RuCl_2(PPh_3)_3]$, (*S*,*R*)-Josiphos or (*S*,*R*)-Josiphos*, and (±)-**1c** in the presence of CH_3CO_2H. In these cases, the higher steric hindrance exerted by the *t*Bu group of **1c** relative to the Me group of **1b** resulted in an increase in the diastereoselectivity. Attempts to obtain suitable crystals for X-ray analysis failed. The stereochemistry of the pincer complexes [RuCl(CNN)(Josiphos)] was proposed on the basis of the NMR control experiments and the structures of the analogous [RuCl(CNN)(PP)][8a,b] and the related *cis*-$[RuCl_2$(Josiphos)(aminopyridine)][10] derivatives.

The synthesis of complexes **4–7** represents a straightforward approach to the preparation of catalysts containing both chiral phosphane and pincer ligands, which enable a high level of asymmetric induction in catalysis to be achieved without the need to synthesize the optically active 1-substituted-1-(6-arylpyridin-2-yl)methanamines.[8b]

Catalytic results: Complexes **2–7** were found to be highly efficient catalysts for the TH and HY of ketones in basic alcohol media (Scheme 3).

In 2-propanol and with NaO*i*Pr (2 mol%), TH occurred at a high rate (TOF $\approx 10^5$–10^6 h^{-1}) at a remarkably low catalyst loading (0.005–0.002 mol%). Derivative **2** catalyzed the quantitative reduction of acetophenone **8a** (0.1 M) to (*S*)-1-phenylethanol (70% *ee*) at 60°C in 30 min with TOF $= 1.3 \times 10^5$ h^{-1} (Table 1).

With **3**, with a bulkier diphosphane, the *S* alcohol was obtained with 92% *ee*. Employment of **4** and **5**, which contain the methyl–substituted CNN ligand, led to a slightly higher rate (TOFs up to 1.8×10^5 h^{-1}) and a significant increase in the *ee* of the *S* alcohol (81 and 95% *ee*, respectively) compared with **2** and **3**. By using a lower amount of **5** (0.002 mol%), neither erosion of the enantioselectivity or a decrease in the rate was observed (TOF $= 2.1 \times 10^5$ h^{-1}, 95% *ee*). To the best of our knowledge, no complexes capable of catalyzing asymmetric TH at such a low loading have been reported, which indicates that these pincer systems can find practical applications in the preparation of chiral alcohols. The derivatives **6** and **7**, with a *t*Bu group, catalyzed the TH of **8a** with TOFs of up to 1.1×10^5 h^{-1} and 85 and 95% *ee* of the *S* alcohol, respectively. These results show that the bulkiness of the diphosphane aryl groups plays a crucial role in the attainment of high asymmetric induction and further improvement is achieved by using the 1-substituted HCNN ligands. With complexes **3**, **5**, and **7**, a number of ketones were quickly converted into the *S* alcohols. Chemoselective TH of the aliphatic ketone 5-hexen-2-one (**8m**)



Scheme 3. Asymmetric TH and HY of ketones catalyzed by the chiral pincer complexes **2–7**.

Table 1. Catalytic TH of alkyl aryl ketones with **2–7** and NaO*i*Pr in 2-propanol at 60°C.[a]

Complex	Ketone	Conv.[b] [%]	*t* [min]	TOF[c] [h^{-1}]	*ee*[b] [%]
2	**8a**	97	30	1.3×10^5	70 *S*
3	**8a**	94	30	1.0×10^5	92 *S*
4	**8a**	98	30	1.6×10^5	81 *S*
5	**8a**	98	10	1.8×10^5	95 *S*
5[d]	**8a**	94	30	2.1×10^5	95 *S*
5	**8e**	97	10	1.5×10^5	96 *S*
5	**8g**	97	30	1.4×10^5	97 *S*
5	**8h**	97	10	1.8×10^5	98 *S*
5[e]	**8h**	98	2	1.3×10^6	95 *S*
5	**8i**	99	30	1.2×10^5	93 *S*
5	**8j**	98	30	1.6×10^5	95 *S*
5[d]	**8j**	96	30	2.1×10^5	95 *S*
5[f]	**8k**	97	5	2.0×10^5	97 *S*
5[f]	**8l**	98	60	5.5×10^4	98 *S*
5	**8o**	98	60	1.1×10^4	99 *S*
6	**8a**	95	30	1.1×10^5	85 *S*
7	**8a**	96	30	9.0×10^4	95 *S*
7	**8b**	96	30	1.3×10^5	92 *S*
7	**8d**	92	60	7.0×10^4	91 *S*
7	**8h**	95	10	1.6×10^5	97 *S*

[a] Unless stated otherwise the following reagents were used: 0.1 M alkyl aryl ketones, 0.005 mol% **2–7**, and 2 mol% NaO*i*Pr. [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] [Ru] = 0.002 mol%. [e] $T = 82$°C. [f] [Ru] = 0.01 mol%.

was observed with **3** (0.01 mol%), but with only low enantioselectivity (30% *ee*), whereas heptan-2-one (**8n**) was reduced to the linear *S* alcohol with 50% *ee*. The substrates 4′-chloroacetophenone (**8e**), 3′-methoxyacetophenone (**8g**), and 3′,5′-dimethoxyacetophenone (**8h**) in the presence of **5** (0.005 mol%) gave the corresponding alcohols with TOFs of up to $1.8\times10^5\ h^{-1}$ and 96, 97, and 98% *ee*, respectively. When the TH of **8h** was carried out in 2-propanol at reflux, the alcohol was formed within 2 min (98% conversion) with a remarkably high rate ($TOF=1.3\times10^6\ h^{-1}$) and a slightly lower enantioselectivity (95% *ee*) (Table 1). Notably, the heterocyclic ketone 2-acetylpyridine (**8i**) was rapidly converted into the intermediate (*S*)-1-(2-pyridyl)ethanol (93% *ee*), whereas (*S*)-1-(3-trifluoromethylphenyl)ethanol, which is a building block in the synthesis of the wide-spectrum agricultural fungicide (*S*)-MA20565, was obtained in 95% *ee* from **8j** in 30 min ($TOF=1.6\times10^5\ h^{-1}$).[14] The latter ketone **8j** was also reduced with **5** at a loading as low as 0.002 mol% (30 min; $TOF=2.1\times10^5\ h^{-1}$), without deactivation of the catalyst or erosion of the enantioselectivity. To show the practical potential of this system, (*S*)-1-(3-trifluoromethylphenyl)ethanol (4.10 g, 95% *ee*, 90% yield) were obtained from **8j** (4.53 g) in 1 h at 60°C, using complex **5** (0.50 mg, 0.002 mol%). In addition the TH of the bulky naphthyl ketones **8k** and **8l** led to the *S* alcohols with 97 and 98% *ee*, respectively. Interestingly, with **5** (0.005 mol%), propiophenone (**8o**) was efficiently converted (1 h) into (*S*)-1-phenyl-1-propanol with 99% *ee*. By using catalyst **7**, with a *t*Bu group, the substrates 3′-methylacetophenone (**8b**), 2′-chloroacetophenone (**8d**), and **8h** were reduced to *S* alcohols with TOFs of up to $1.6\times10^5\ h^{-1}$ and 92, 91, and 97% *ee*, respectively (Table 1). The high performance of these pincer complexes has led to a new standard in the asymmetric TH of ketones in terms of productivity and rate, such that TH is an alternative to HY. To investigate the matched/mismatched ligand effect, the in situ prepared catalytic system $[RuCl_2(PPh_3)_3]$/(*R*,*S*)-Josiphos*/(*R*)-**1b** afforded a slow reduction of **8a** to (*R*)-1-phenylethanol ($TOF=3.6\times10^4\ h^{-1}$, 74% *ee*), whereas the use of (*S*,*R*)-Josiphos* led to the *S* alcohol with a higher rate and enantioselectivity ($TOF=1.6\times10^5\ h^{-1}$, 94% *ee*), with values similar to those observed with the isolated complex **5**. These results and the NMR control experiments indicate that (*S*,*R*)-Josiphos*/(*R*)-**1b** is the correctly matched combination for the catalysis and complex **5**, obtained from (±)-**1b**, displays the same ligand combination.

A few ruthenium systems have been found to efficiently catalyze both asymmetric TH and HY of carbonyl compounds.[5,7b,d,15] Interestingly, the chiral pincer complexes **2**, **3**, and **5** also display high catalytic activity in the asymmetric HY of ketones in ethanol or methanol/ethanol under 5 atm of dihydrogen (Scheme 3). With **2** (0.02 mol%) and KO*t*Bu (6 mol%) in EtOH, the substrate **8a** was rapidly and quantitatively reduced to (*S*)-1-phenylethanol at 40°C (30 min, $TOF=4.3\times10^4\ h^{-1}$, 70% *ee*; Table 2).

The catalytic activity and selectivity of **3** in the HY of **8a** was strongly affected by the alcohol medium. Addition of methanol to ethanol resulted in a decrease in the rate ($TOF=3.6\times10^4$, 2.9×10^4, and $2.5\times10^4\ h^{-1}$) and an increase of enantioselectivity (71, 88, and 88% *ee*; MeOH/EtOH = 0, 3:7, and 1 by volume). Conversely, with **5** (0.01 mol%), addition of MeOH led to an increase in both activity ($TOF=1.7\times10^4$, 2.8×10^4, and $3.3\times10^4\ h^{-1}$) and enantioselectivity (77, 87, and 90% *ee*; MeOH/EtOH = 0, 3:7, and 1). In methanol the reduction of **8a** (0.5 M) with **5** under dihydrogen has to be regarded as pure HY, affording 89% *ee* (78% conversion in 3 h), whereas in 2-propanol the *S* alcohol was formed by TH with a negligible contribution from HY (91% *ee* and 75% conversion). These results suggest that the alcohol solvent plays an important role in the HY of ketones mediated by these pincer complexes. By using the mixture MeOH/EtOH = 1, complex **5** has been shown to catalyze rapidly the HY of different substrates. Thus, compounds **8b**, **8c**, **8f**, and **8k** have been reduced to the corresponding *S* alcohols within 30 min (TOFs of up to $3.8\times10^4\ h^{-1}$) and 90–93% *ee*. Finally, ketone **8o** was efficiently hydrogenated under these conditions to the corresponding *S* alcohol with 99% *ee*, an identical result to that observed in the TH using the same complex.

Table 2. Catalytic HY of alkyl aryl ketones with **2**, **3**, and **5**, and KO*t*Bu under H_2 at 40°C.[a]

Complex	Ketone	Solvent[b]	Conv.[c] [%]	*t* [min]	TOF[d] [$10^4\ h^{-1}$]	*ee*[c] [%]
2	**8a**	EtOH	>99	30	4.3	70 *S*
3	**8a**	EtOH	99	30	3.6	71 *S*
3	**8a**	MeOH/EtOH = 3:7	>99	30	2.9	88 *S*
3	**8a**	MeOH/EtOH = 1	94	90	2.5	88 *S*
5[e]	**8a**	EtOH	>99	60	1.7	77 *S*
5[e]	**8a**	MeOH/EtOH = 3:7	>99	30	2.8	87 *S*
5[e]	**8a**	MeOH/EtOH = 1	>99	30	3.3	90 *S*
5	**8b**	MeOH/EtOH = 1	99	20	3.8	93 *S*
5	**8c**	MeOH/EtOH = 1	99	30	3.0	90 *S*
5	**8f**	MeOH/EtOH = 1	>99	30	2.9	91 *S*
5	**8k**	MeOH/EtOH = 1	>99	30	3.6	93 *S*
5	**8o**	MeOH/EtOH = 1	>99	30	2.5	99 *S*

[a] Unless stated otherwise the following reagents were used: 0.5 M alkyl aryl ketones, 0.02 mol% **2**, **3**, and **5**, 6 mol% KO*t*Bu, and 5 atm of H_2. [b] Ratio by volume. [c] The conversion and *ee* were determined by GC analysis. [d] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [e] [Ru] = 0.01 mol%.

With regards to the mechanism for the reduction of ketones in basic alcohol media, the formation of alkoxide and hydride ruthenium complexes is expected.[16] The reaction of **5** with NaO*i*Pr (2 equiv) in 2-propanol/C_6D_6 (1:1 by volume) at RT leads to the quantitative formation of a new species, which was ascribed to the corresponding isopropoxide complex [Ru(O*i*Pr)(CNN){(*S*,*R*)-Josiphos*}] ($^{31}P\{^1H\}$ NMR: $\delta=$ 64.5 and 42.5 ppm with $^2J(P,P)=40.5$ Hz) on the basis of a study of analogous alkoxides [Ru(O*i*Pr)(CNN)(PP)] (PP = 1,4-bis(diphenylphosphino)butane (dppb), (2*S*,4*S*)-bis(diphenylphosphano)pentane).[17a] Evaporation of this solution leads to the formation of a mixture of complexes that contains the hydride [RuH(CNN){(*S*,*R*)-Josiphos*}] as the main product, which is formed by a β-hydrogen elimination reaction from the ruthenium alkoxide, as observed for [RuH-

(CNN)(dppb)].[8a,17a] In the ^{1}H NMR spectrum recorded in C_6D_6, the hydride appears as a doublet of doublets at $\delta = -7.87$ ppm with $^2J(H,P) = 88.6$ and 30.2 Hz due to the presence of *trans* and *cis* phosphorus atoms, whereas the $^{31}P\{^1H\}$ NMR signals are at $\delta = 55.8$ and 41.7 ppm, with a significantly small $^2J(P,P) = 24.7$ Hz, as reported for [RuH(CNN)(dppb)].[8a] Thus, it is likely that in the catalytic TH and HY reactions in alcohol media, the alkoxide and hydride intermediates [RuX(CNN)(PP)] (X = OR, H)[17] are the species involved in the catalysis.[18] Recently, evidence for the formation of the ruthenium alkoxide [RuH(OCHMePh)(binap)(dpen)] (dpen = 1,2-diphenylethylenediamine, binap = 2,2′-bis(diphenylphosphano)-1,1′-binaphthyl) from acetophenone and [Ru(H)$_2$(binap)(dpen)], a putative step in the catalytic hydrogenation of ketones, was provided by Hamilton and Bergens.[19]

Conclusion

The chiral pincer complexes [RuCl(CNN)(Josiphos)], obtained from (±)-HCNN ligands by diastereoselective synthesis, are efficient catalysts for the asymmetric transfer hydrogenation (TH) and hydrogenation (HY) of alkyl aryl ketones. High enantioselectivity (up to 99%) has been achieved in TH with a remarkably high rate (TOF = 10^5–10^6 h^{-1}) and low catalyst loading (0.005–0.002 mol%). By changing the reaction parameters, these pincer complexes also catalyze the HY of ketones (0.02–0.01 mol% of Ru) with H_2 (5 atm) to give up to 99% *ee*. On account of the remarkably high activity and productivity of these complexes, this class of ruthenium derivatives has potential for application in homogeneous asymmetric catalysis.

Experimental Section

General: All reactions were carried out under an argon atmosphere by using standard Schlenk techniques. The solvents and ketones were carefully dried by standard methods and distilled under argon before use. The diphosphane ligands and all other chemicals were purchased from Aldrich and Strem and used without further purification. Compounds **1a**,[8b] 1-(6-phenylpyridin-2-yl)ethanone,[20] 2,2-dimethyl-1-(6-phenylpyridin-2-yl)propan-1-one,[20] and [RuCl$_2$(PPh$_3$)$_3$][21] were prepared according to literature procedures. NMR spectra were recorded on a Bruker AC 200 spectrometer and the chemical shifts were measured in ppm relative to TMS for ^{1}H and $^{13}C\{^1H\}$ NMR and 85% H_3PO_4 for $^{31}P\{^1H\}$ NMR. Elemental analyses (C, H, and N) were carried out with a Carlo Erba 1106 elemental analyzer. GC analyses were performed with a Varian GP-3380 gas chromatograph equipped with a MEGADEX-ETTBDMS-β chiral column.

1-(6-Phenylpyridin-2-yl)ethanone oxime: A solution of 1-(6-phenylpyridin-2-yl)ethanone (4.70 g, 23.8 mmol) and hydroxylamine hydrochloride (3.06 g, 44.0 mmol) in 96% ethanol (150 mL) was stirred for 24 h at room temperature. The solvent was removed under reduced pressure and the residue was taken up with CH_2Cl_2 and a saturated solution of $NaHCO_3$. The resulting mixture was vigorously stirred for 30 min, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2×20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated to give 1-(6-phenylpyridin-2-yl)-ethanone oxime as a white solid, which was used in the next step without further purification (4.81 g, 95%). M.p. 85–87 °C; ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): $\delta = 9.76$ (s, 1H), 8.08 (dd, $^3J(H,H) = 7.8$, $J(H,H) = 1.8$ Hz, 2H), 7.81–7.65 (m, 3H), 7.54–7.35 (m, 3H), 2.52 ppm (s, 3H); elemental analysis calcd (%) for $C_{13}H_{12}N_2O$: C 73.56, H 5.70, N 13.20; found: C 73.67, H 5.73, N 13.15.

1-(6-Phenylpyridin-2-yl)ethanamine (1b): 1-(6-Phenylpyridin-2-yl)ethanone oxime (4.81 g, 22.7 mmol) and ammonium acetate (2.16 g, 28.0 mmol) in a solution of 30% NH_3/H_2O/96% EtOH (81.3, 54.2, and 54.2 mL) were stirred for 30 min at room temperature. Powdered zinc (8.13 g) was added portionwise over a period of 2 h at room temperature and then the reaction mixture was heated under reflux for 3 h. The grey precipitate was filtered under reduced pressure and the solvent was evaporated to give a residue, which was made alkaline with 10% NaOH and extracted with diethyl ether (3×30 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated to give **1b** as a pale-orange oil (4.34 g, 96%). ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): $\delta = 8.06$–7.98 (m, 2H), 7.64 (t, $^3J(H,H) = 7.5$ Hz, 1H), 7.54 (d, $^3J(H,H) = 7.5$ Hz, 1H), 7.50–7.33 (m, 3H), 7.16 (d, $^3J(H,H) = 7.5$ Hz, 1H), 4.16 (q, $^3J(H,H) = 6.6$ Hz, 1H), 2.05 (s, 2H), 1.45 ppm (d, $^3J(H,H) = 6.6$ Hz, 3H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): $\delta = 165.2$, 156.1, 139.2, 137.0, 128.6, 128.4, 126.6, 118.2, 118.1, 52.2, 24.3 ppm; elemental analysis calcd (%) for $C_{13}H_{14}N_2$: C 78.75, H 7.12, N 14.13, found: C 78.87, H 7.15, N 14.11.

2,2-Dimethyl-1-(6-phenylpyridin-2-yl)propan-1-one oxime: A mixture of 2,2-dimethyl-1-(6-phenylpyridin-2-yl)propanone (0.95 g, 3.97 mmol) and hydroxylamine hydrochloride (0.50 g, 7.19 mmol) in 96% ethanol (35.5 mL) was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was taken up with CH_2Cl_2 and with a saturated solution of $NaHCO_3$. The resulting mixture was vigorously stirred for 30 min, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2×20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated to give 2,2-dimethyl-1-(6-phenylpyridin-2-yl)propan-1-one oxime as a white solid, which was used in the next step without further purification (0.95 g, 94%). M.p. 190–191 °C; ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): $\delta = 8.30$ (s, 1H), 8.05 (dd, $J(H,H) = 8.4$, 1.8 Hz, 2H), 7.82–7.68 (m, 2H), 7.52–7.37 (m, 3H), 7.17 (dd, $J(H,H) = 7.8$, 0.9 Hz, 1H), 1.26 ppm (s, 9H); elemental analysis calcd (%) for $C_{16}H_{18}N_2O$: C 75.56, H 7.13, N 11.01; found: C 75.44, H 7.16, N 11.04.

2,2-Dimethyl-1-(6-phenylpyridin-2-yl)propan-1-amine (1c): 1-(6-Phenylpyridin-2-yl) *tert*-butyl ketoxime (0.92 g, 3.62 mmol) and ammonium acetate (0.344 g, 4.46 mmol) in a solution of 30% NH_3/H_2O/96% EtOH (12.9, 8.6, and 8.6 mL) were stirred for 30 min at room temperature. Powdered zinc (1.29 g) was added portionwise over a period of 2 h at room temperature and then the reaction mixture was heated under reflux for 3 h. The grey precipitate was filtered under reduced pressure and the solvent was evaporated to give a residue, which was made alkaline with 10% NaOH and extracted with diethyl ether (3×20 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated to give **1c** as a colorless oil (0.62 g, 71%). ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): $\delta = 8.03$ (d, $^3J(H,H) = 6.9$ Hz, 2H), 7.65–7.57 (m, 2H), 7.48–7.38 (m, 3H), 7.09 (dd, $J(H,H) = 7.5$, 1.5 Hz, 1H), 3.71 (s, 1H), 1.89 (s, 2H), 0.97 ppm (s, 9H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): $\delta = 162.1$, 155.7, 139.5, 136.1, 128.7, 128.6, 126.8, 121.9, 118.2, 65.7, 35.4, 26.7 ppm; elemental analysis calcd (%) for $C_{16}H_{20}N_2$: C 79.96, H 8.39, N 11.66; found: C 79.84, H 8.41, N 11.68.

Synthesis of 2: [RuCl$_2$(PPh$_3$)$_3$] (100 mg, 0.104 mmol) and (*S*,*R*)-Josiphos·C_2H_5OH (80 mg, 0.125 mmol) were treated with toluene (2 mL); the suspension was stirred at 105 °C for 2 h, and the solvent was evaporated. The ligand **1a** (27 mg, 0.136 mmol) and triethylamine (176 μL, 1.26 mmol) were added to the complex suspended in 2-propanol (2 mL) and the mixture was heated at reflux for 2 h. The solution was concentrated to 0.5 mL and addition of pentane afforded an orange precipitate, which was filtered and dried under reduced pressure. The solid was dissolved in dichloromethane (2 mL) and the filtrate was concentrated. Addition of pentane gave a yellow precipitate, which was filtered and dried under reduced pressure (65 mg, 67%). ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): $\delta = 8.13$ (t, $^3J(H,H) = 7.8$ Hz, 2H; aromatic protons), 7.87 (s, 1H;

aromatic proton), 7.80–7.17 (m, 11H; aromatic protons), 6.93 (d, ^3J(H,H) = 7.2 Hz, 1H; aromatic proton), 6.78 (d, ^3J(H,H) = 8.0 Hz, 1H; aromatic proton), 4.67 (s, 1H; PCH), 4.50–4.28 (m, 3H; C_5H_3), 4.12 (dd, ^3J(H,H) = 15.6, 4.6 Hz, 1H; CH_2N), 3.91 (m, 1H; CH_2N), 3.73 (s, 5H; C_5H_5), 3.16 (brs, 1H; NH_2), 2.26 (s, 3H; CH_3), 1.95–0.60 ppm (m, 26H; CH_3, Cy, NH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 185.9 (dd, J(C,P) = 13.1, 8.5 Hz; CRu), 165.5 (s; N*C*C), 158.9 (s; NCCH$_2$), 148.2–116.3 (m; aromatic carbons), 97.5 (dd, J(C,P) = 21.4, 3.2 Hz; *ipso*-FeC_5H_3), 74.3 (s; FeC_5H_3), 72.7 (dd, J(C,P) = 35.9, 4.9 Hz; *ipso*-FeC_5H_3), 70.5 (s; FeC_5H_5), 68.5–68.1 (m; FeC_5H_3), 46.1 (s; CH_2N), 40.5 (d, J(C,P) = 15.8 Hz; CH of Cy), 37.8 (d, J(C,P) = 18.0 Hz; CH of Cy), 31.6–30.0 (m; CH_2 of Cy), 29.3 (dd, J(C,P) = 21.0, 4.0 Hz; P*C*Me), 28.8–23.7 (m; CH_2 of Cy), 21.3 (s; CH_3), 15.6 ppm (d, J(C,P) = 6.8 Hz; PC*Me*); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 67.2 (d, ^2J(P,P) = 41.3 Hz), 40.8 ppm (d, ^2J(P,P) = 41.3 Hz); elemental analysis calcd (%) for $C_{49}H_{57}ClFeN_2P_2Ru$: C 63.40, H 6.19, N 3.02; found: C 63.70, H 6.28, N 3.14.

Synthesis of 3: $[RuCl_2(PPh_3)_3]$ (50 mg, 0.052 mmol) and (*S*,*R*)-Josiphos* (44 mg, 0.062 mmol) were treated with dichloromethane (2 mL); the solution was stirred at room temperature for 2 h, and the solvent was evaporated. The ligand **1a** (12 mg, 0.061 mmol) and triethylamine (85 μL, 0.61 mmol) were added to the complex suspended in 2-propanol (2 mL) and the mixture was heated at reflux for 3 h. The solution was concentrated to 0.5 mL and addition of pentane (2 mL) afforded an orange precipitate, which was filtered and dried under reduced pressure. The solid was dissolved in dichloromethane (2 mL) and the filtrate was concentrated. Addition of pentane gave a yellow-orange precipitate, which was filtered and dried under reduced pressure (40 mg, 74%). ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.81 (brs, 3H; aromatic protons), 7.76 (s, 1H; aromatic proton), 7.62 (m, 2H; aromatic protons), 7.28 (d, ^3J(H,H) = 8.6 Hz, 2H; aromatic protons), 6.93 (d, ^3J(H,H) = 7.6 Hz, 1H; aromatic proton), 6.76 (d, ^3J(H,H) = 8.6 Hz, 1H; aromatic proton), 4.71 (m, 1H; PCH), 4.48–4.42 (m, 2H; C_5H_3), 4.29–3.92 (m, 3H; C_5H_3, CH_2N), 3.71 (s, 6H; OMe), 3.70 (s, 5H; C_5H_5), 3.05 (m, 1H; NH_2), 2.25 (s, 3H; Me), 2.19 (s, 6H; Me), 2.17 (s, 6H; Me), 1.94–0.58 ppm (m, 26H; CH_3, Cy, NH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 186.4 (dd, J(C,P) = 13.2, 7.7 Hz; CRu), 165.5–116.1 (m; aromatic carbons), 97.3 (dd, J(C,P) = 21.5, 3.6 Hz; *ipso*-FeC_5H_3), 74.5 (s; FeC_5H_3), 73.9 (dd, J(C,P) = 34.6, 4.2 Hz; *ipso*-FeC_5H_3), 70.3 (s; FeC_5H_5), 68.2–68.1 (m; FeC_5H_3), 59.7 (s; OMe), 52.8 (s; CH_2N), 40.7 (d, J(C,P) = 14.9 Hz; PCH of Cy), 37.8 (d, J(C,P) = 18.8 Hz; PCH of Cy), 31.8 (s; CH_2 of Cy), 30.5 (s; CH_2 of Cy), 29.1 (dd, J(C,P) = 21.3, 3.8 Hz; P*C*Me), 29.0–26.7 (m; CH_2 of Cy), 21.7 (s; Me), 16.5 (s; Me), 16.2 (s; Me), 15.6 ppm (d, J(C,P) = 6.9 Hz; PC*Me*); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 67.2 (d, ^2J(P,P) = 41.3 Hz), 37.4 ppm (d, ^2J(P,P) = 41.3 Hz); elemental analysis calcd (%) for $C_{55}H_{69}ClFeN_2O_2P_2Ru$: C 63.25, H 6.66, N 2.68; found: C 63.68, H 6.89, N 2.76.

Synthesis of 4

Method a: $[RuCl_2(PPh_3)_3]$ (50 mg, 0.052 mmol) and (*S*,*R*)-Josiphos·C_2H_5OH (40 mg, 0.062 mmol) were treated with toluene (2 mL); the suspension was stirred at 105 °C for 2 h, and the solvent was evaporated. Addition of (±)-**1b** (41 mg, 0.207 mmol), acetic acid (1.5 μL, 0.026 mmol), and triethylamine (85 μL, 0.61 mmol) to the complex suspended in 2-propanol (2 mL) led to a solution that was heated at reflux for 4 h and concentrated to give an oily product. Pentane (2 mL) was added to afford an orange precipitate, which was filtered and dried under reduced pressure. The solid was treated with dichloromethane (1 mL) and after filtration pentane (2 mL) was added to the solution to give an orange precipitate, which was filtered and dried under reduced pressure (34 mg, 70%; >92% major isomer).

Method b: Complex **4** was synthesized as described in Method a by using (*R*)-**1b** (26 mg, 0.131 mmol, enantiomeric ratio 80:20) in place of (±)-**1b**. Yield: 30 mg (62%). ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 8.22–6.90 (m, 17H; aromatic protons), 4.68 (m, 1H; PCH), 4.53–4.36 (m, 3H; C_5H_3), 4.01 (m, 1H; CHMe), 3.74 (s, 5H; C_5H_5), 3.12 (t, J(H,H) = 11.6 Hz, 1H; NH_2), 2.00–0.52 ppm (m, 29H; Me, Cy, NH); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 187.2 (m; CRu), 165.7–116.9 (m; aromatic carbons), 74.1 (s; FeC_5H_3), 70.3 (s; FeC_5H_5), 68.6–68.4 (m; FeC_5H_3), 57.9 (d, J(C,P) = 2.5 Hz; *C*HNH$_2$) 40.3 (d, J(C,P) = 14.5 Hz; CH of Cy), 37.8 (d, J(C,P) = 18.5 Hz; CH of Cy), 31.6–26.5 (m; CH_2 of Cy, P*C*Me), 23.2 (s; NC*Me*), 15.5 ppm (d, J(C,P) = 6.7 Hz; PC*Me*); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 66.1 (d, ^2J(P,P) = 42.3 Hz), 41.3 ppm (d, ^2J(P,P) = 42.3 Hz); elemental analysis calcd (%) for $C_{49}H_{57}ClFeN_2P_2Ru$: C 63.40, H 6.19, N 3.02; found: C 63.64, H 6.33, N 3.09.

Synthesis of 5

Method a: $[RuCl_2(PPh_3)_3]$ (50 mg, 0.052 mmol) and (*S*,*R*)-Josiphos* (44 mg, 0.062 mmol) were treated with dichloromethane (2 mL), the solution was stirred at room temperature for 2 h, and the solvent was evaporated. Addition of (±)-**1b** (41 mg, 0.207 mmol), acetic acid (1.5 μL, 0.026 mmol), and triethylamine (85 μL, 0.61 mmol) to the complex suspended in 2-propanol (2 mL) led to a solution that was heated at reflux for 4 h and concentrated to give an oily product. Pentane (2 mL) was added to afford an orange precipitate, which was filtered and dried under reduced pressure. The solid was treated with dichloromethane (1 mL) and after filtration pentane (2 mL) was added to the solution to give an orange precipitate, which was filtered and dried under reduced pressure (34 mg, 63%; >93% major isomer).

Method b: Complex **5** was synthesized as described in Method a by using (*R*)-**1b** (26 mg, 0.131 mmol, enantiomeric ratio 80:20) in place of (±)-**1b**. Yield: 37 mg (68%). ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ = 8.15–6.89 (m, 11H; aromatic protons), 4.70 (m, 1H; PCH), 4.44–4.26 (m, 3H; C_5H_3), 3.97 (m, 1H; NC*H*Me), 3.71 (s, 6H; OMe), 3.68 (s, 5H; C_5H_5), 3.18 (m, 1H; NH_2), 2.19 (s, 12H; Me), 1.80–0.50 ppm (m, 29H; CH_3, Cy, NH); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ = 185.8 (m; CRu), 165.5–116.2 (m; aromatic carbons), 97.0 (dd, J(C,P) = 17.7, 3.3 Hz; *ipso*-FeC_5H_3), 74.0 (s; FeC_5H_3), 69.8 (s; FeC_5H_5), 67.8–67.3 (m; FeC_5H_3), 59.6 (s; OMe), 59.5 (s; OMe), 57.5 (s; CHNH$_2$), 40.1 (d, J(C,P) = 15.2 Hz; CH of Cy), 37.6 (d, J(C,P) = 17.8 Hz; CH of Cy), 31.9–25.3 (m; CH_2 of Cy, P*C*Me), 22.9 (s; NCH*Me*), 16.4 (s; Me), 16.1 (s; Me), 15.4 ppm (d, J(C,P) = 7.0 Hz; PC*Me*); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ = 66.4 (d, ^2J(P,P) = 41.0 Hz), 38.2 ppm (d, ^2J(P,P) = 41.0 Hz); elemental analysis calcd (%) for $C_{55}H_{69}ClFeN_2O_2P_2Ru$: C 63.25, H 6.66, N 2.68; found: C 63.69, H 6.87, N 2.82.

Synthesis of 6: Complex **6** was synthesized as described for **4** (Method a) by using (±)-**1c** (50 mg, 0.208 mmol) in place of (±)-**1b**. Yield: 33 mg (65%). ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 8.21–6.98 (m, 17H; aromatic protons), 4.69 (m, 1H; PCH), 4.52–4.36 (m, 3H; C_5H_3), 3.92 (brs, 1H; C*H*t*B*u), 3.76 (s, 5H; C_5H_5), 3.10 (t, J(H,H) = 11.6 Hz, 1H; NH_2), 2.00–0.99 (m, 24H; Me, Cy, NH), 0.97 (s, 9H; *t*Bu), 0.54 ppm (m, 2H; Cy); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 187.6 (m; CRu), 166.7–116.9 (m; aromatic carbons), 97.3 (dd, J(C,P) = 21.1, 3.4 Hz; *ipso*-FeC_5H_3), 73.7 (s; FeC_5H_3), 72.5 (m; *ipso*-FeC_5H_3), 71.9 (d, J(C,P) = 2.4 Hz; CHNH$_2$), 70.3 (s; FeC_5H_5), 68.6 (d, J(C,P) = 4.3 Hz; FeC_5H_3), 68.3 (d, J(C,P) = 8.0 Hz; FeC_5H_3), 40.2 (d, J(C,P) = 14.6 Hz; CH of Cy), 38.0 (d, J(C,P) = 18.5 Hz; CH of Cy), 35.2–30.9 (m; CH_2 of Cy and *C*Me$_3$), 28.8 (dd, J(C,P) = 21.9, 4.2 Hz; P*C*Me), 28.2–27.5 (m; CH_2 of Cy), 27.3 (s; C*Me*$_3$), 26.9 (s; CH_2 of Cy), 26.4 (s; CH_2 of Cy), 15.5 ppm (d, J(C,P) = 6.8 Hz; PC*Me*); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 65.7 (d, ^2J(P,P) = 42.6 Hz), 42.0 ppm (d, ^2J(P,P) = 42.6 Hz); elemental analysis calcd (%) for $C_{52}H_{63}ClFeN_2P_2Ru$: C 64.36, H 6.54, N 2.89; found: C 64.88, H 6.72, N 2.65.

Synthesis of 7: Complex **7** was synthesized as described for **5** (Method a) by using (±)-**1c** (50 mg, 0.208 mmol) in place of (±)-**1b**. Yield: 38 mg (67%). ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 8.18 (m, 2H; aromatic protons), 7.87 (d, ^3J(H,H) = 8.0 Hz, 1H; aromatic proton), 7.76–7.31 (m, 6H; aromatic protons), 6.97 (m, 2H; aromatic protons), 4.70 (m, 1H; PCH), 4.49–4.31 (m, 4H; C_5H_3, C*H*NH$_2$), 3.73 (s, 5H; C_5H_5), 3.70 (s, 3H; OMe), 3.66 (s, 3H; OMe), 3.13 (t, J(H,H) = 11.5 Hz, 1H; NH_2), 2.19 (s, 12H; Me), 2.00–1.10 (m, 20H; CH_3, Cy, NH_2), 1.02 (s, 9H; CMe_3), 0.98–0.52 ppm (m, 6H; Cy); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 188.0 (m; CRu), 166.7–117.1 (m; aromatic carbons), 97.5 (d, J(C,P) = 24.7 Hz; *ipso*-FeC_5H_3), 73.9 (s; FeC_5H_3), 72.0 (s; CHNH$_2$), 70.2 (s; FeC_5H_5), 68.4 (d, J(C,P) = 7.9 Hz; FeC_5H_3), 68.1 (d, J(C,P) = 4.1 Hz; FeC_5H_3), 59.8 (s; OMe), 40.3 (d, J(C,P) = 14.2 Hz; CH of Cy), 38.0 (d, J(C,P) = 18.5 Hz; CH of Cy), 35.3–27.5 (m; CH_2 of Cy, P*C*Me, and *C*Me$_3$), 27.3 (s; C*Me*$_3$), 16.5 (s; Me), 16.2 (s; Me), 15.5 ppm (d, J(C,P) = 6.9 Hz;

PC*Me*); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): $\delta = 65.8$ (d, $^2J(P,P) = 42.8$ Hz), 38.4 ppm (d, $^2J(P,P) = 42.8$ Hz); elemental analysis calcd (%) for $C_{58}H_{75}ClFeN_2O_2P_2Ru$: C 64.11, H 6.96, N 2.58: found: C 64.28, H 7.12, N 2.65.

Typical procedure for the catalytic TH of ketones: The ruthenium complex (2.50 μmol) was dissolved in 2-propanol (5 mL). The ketone (2.00 mmol) was dissolved in 2-propanol (final volume 19.6 mL) and the solution was heated at 60 °C under argon. The ketone was reduced by the addition of NaO*i*Pr (0.1 M, 400 μL, 40 μmol) in 2-propanol and the catalyst solution (200 μL, 0.1 μmol) to the ketone solution. The yield of the product was determined by GC (Ru 0.005 mol %, NaO*i*Pr 2 mol %, ketone 0.1 M).

Typical procedure for the catalytic HY of ketones: The ruthenium complex (1.72 μmol) was dissolved in alcohol (1 mL of EtOH or MeOH/EtOH mixture). The ketone (4.30 mmol), KO*t*Bu (0.26 mmol), and the catalyst solution (500 μL, 0.86 μmol) were added to alcohol (final volume 8.6 mL). The resulting solution was transferred into a thermostated reactor at 40 °C and the reduction was performed by introducing dihydrogen at a pressure of 5 atm (Ru 0.02 mol %, KO*t*Bu 6 mol %, ketone 0.5 M).

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[13] $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): $\delta = 66.1$, 41.3 (d, $^2J(P,P) = 42.3$ Hz), 64.7, 40.9 ppm (d, $^2J(P,P) = 41.0$ Hz).

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