DALTON
FULL PAPER

Hydrogen-transfer catalyzed by half-sandwich Ru(II) aminophosphine complexes †

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The syntheses of and catalytic studies on some Ru(II) complexes bearing the aminophosphine ligands *N,N*-dimethyl-2-diphenylphosphinoethylamine (PN), optically pure (R_C,S_{pl})-2-{1-(*N,N*-dimethylamino)ethyl}-1-diphenylphosphinoferrocene (PPFA), and *N,N*-dimethyl-2-diphenylphosphinoaniline (DBD) are described, $[RuCp(CH_3CN)_3]^+$ reacts with these ligands to give the cationic complexes $[RuCp(PN\text{-}\kappa N,\kappa P)(CH_3CN)]^+$ (**1a**), [(S_{Ru},R_C,S_{pl})-RuCp(PPFA-κ*N*,κ*P*)$(CH_3CN)]^+$ (**1b**), and $[RuCp(DBD\text{-}\kappa N,\kappa P)(CH_3CN)]^+$ (**1c**), respectively, in high yields. From these, in turn, the residual CH_3CN ligand can be replaced by Br^- upon addition of NEt_4Br in CH_2Cl_2, resulting in the formation of the neutral complexes RuCp(PN)Br (**2a**), (S_{Ru},R_C,S_{pl})-RuCp(PPFA)Br (**2b**), and RuCp(DBD)Br (**2c**), again in good yields. Similarly, $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ reacts with 1 equiv. of PN or PPFA to give $Ru(\eta^6\text{-}p\text{-cymene})(PN\text{-}\kappa P)Cl_2$ (**3a**) and $Ru(\eta^6\text{-}p\text{-cymene})(PPFA\text{-}\kappa P)Cl_2$ (**3b**). Furthermore, treatment of **3** with $TlCF_3SO_3$ in THF at room temperature affords the cationic complexes $[Ru(\eta^6\text{-}p\text{-cymene})(PN\text{-}\kappa N,\kappa P)Cl]CF_3SO_3$ (**4a**) and [(R_{Ru},R_C,S_{pl})-Ru(η^6-*p*-cymene)-(PPFA-κ*N*,κ*P*)Cl]CF_3SO_3 (**4b**). The absolute configuration at the metal center of **2b** and **4b′** (BPh_4^- salt of **4b**) was determined by X-ray crystallography. Catalytic studies were performed with the racemic complexes **1a**, **2a**, **2c**, and **4a** and the diastereopure complexes **1b**, **2b**, and **4b**. All of these proved to be excellent precatalysts for the transfer hydrogenation of acetophenone and derivatives thereof, and cyclohexanone. With the enantiomerically pure systems **2b** and **4b**, only racemic products were obtained. This testifies to the hemilabile nature of the aforementioned aminophosphine ligands giving transient κ-*P*-bonding coordination. Since diastereoface selection of incoming substrates is based on the planar chirality of the ferrocene moiety, rather than the metal centered chirality, no enantioselective reaction takes place.

Introduction

Transition metal complexes containing chelating ligands with different donor atoms such as C, N, O, and P can induce increased selectivity due to the different electronic properties of these atoms which are relayed to the reactive metal site.[1] We[2] and others[3] have previously shown that aminophosphine ligands are readily introduced into RuCp, RuTp, and Ru(arene) systems. In the case of optically pure aminophosphine ligands, diastereopure complexes are often obtained in a single step with de's >98%. Consequently, such complexes could be useful precatalysts for various organic reactions. One has to keep in mind, however, that aminophosphines are hemilabile, particularly if the nitrogen site is sufficiently bulky (NMe_2 < NEt_2 < N-*i*-Pr_2). These soft/hard assemblies are able to coordinate reversibly to a metal center providing, or protecting temporarily, a vacant coordination site, a feature very desirable for catalysts. On the other hand, this very property may result in the loss of chiral information in the vicinity of a prochiral substrate and consequently rendering enantioselective reactions impossible or at least very difficult.

In the present contribution, we report on the synthesis of some Ru(II) Cp and *p*-cymene complexes featuring the phosphinoamine ligands *N,N*-dimethyl-2-diphenylphosphinoethylamine (PN), optically pure (R_C,S_{pl})-2-{1-(*N*,*N*-dimethylamino)-ethyl}-1-diphenylphosphinoferrocene (PPFA), and *N*,*N*-dimethyl-2-diphenylphosphinoaniline (DBD) and whether these compounds are suitable precatalysts for the transfer hydrogenation of prochiral ketones such as acetophenone and derivatives thereof, and cyclohexanone.[4–7] The counterions are PF_6^- and $CF_3SO_3^-$ for the RuCp and Ru(*p*-cymene) complexes, respectively.

Results and discussion

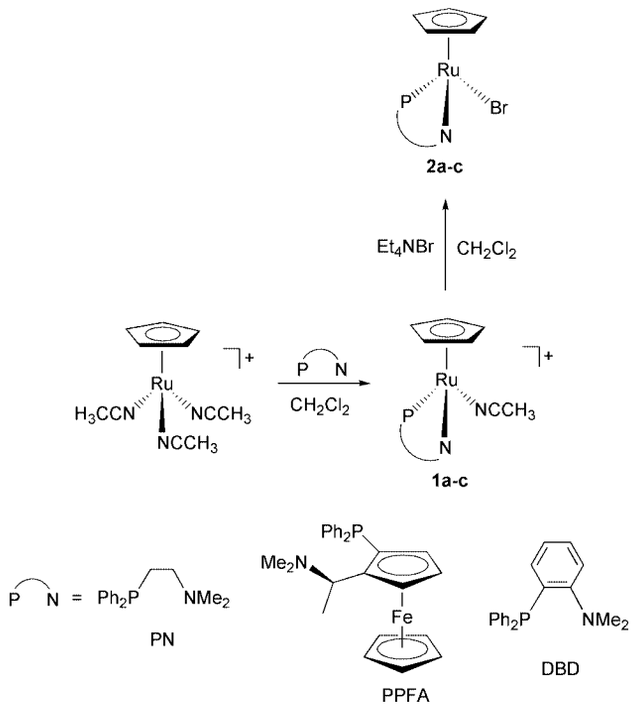
Synthesis and characterization of ruthenium(II) Cp and *p*-cymene complexes

We have recently shown[8,9] that the cationic complexes $[RuCp(PN\text{-}\kappa N,\kappa P)(CH_3CN)]^+$ (**1a**) and [(S_{Ru},R_C,S_{pl})-RuCp(PPFA-κ*N*,κ*P*)$(CH_3CN)]^+$ (**1b**) are formed in high yields by the reaction of $[RuCp(CH_3CN)_3]^+$ with the phosphinoamine ligands PN and PPFA, respectively. Most notably, the formation of **1b** is highly diastereoselective (de > 98%). Complex $[RuCp(DBD\text{-}\kappa P,\kappa N)(CH_3CN)]PF_6$ (**1c**), not previously reported, is obtained in a similar fashion.

Upon addition of NEt_4Br to a solution of **1** in CH_2Cl_2, the color is immediately changed from yellow to orange to afford,

† Electronic supplementary information (ESI) available: experimental details and NMR data for **1c** and **2c**. See http://www.rsc.org/suppdata/dt/b1/b104128m/

on workup, the neutral complexes RuCp(PN)Br (**2a**), (S_{Ru},R_C,S_{pl})-RuCp(PPFA)Br (**2b**), and RuCp(DBD)Br (**2c**) (Scheme 1) in good yields.

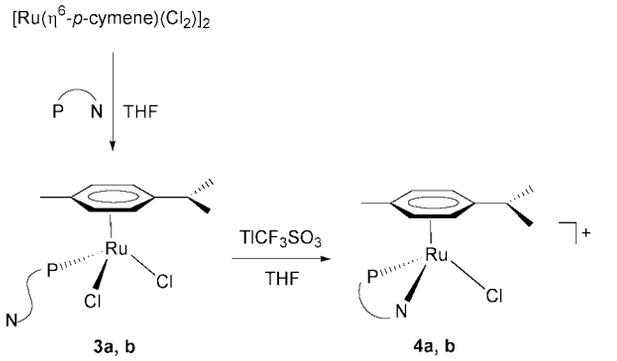


Scheme 1

All complexes have been characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies and elemental analysis. The formation of the bromide complex **2b** is again highly diastereoselective (de > 98%), with retention of configuration at ruthenium, as established by X-ray crystallography (Fig 1). Selected bond distances and angles are reported in the caption.

Accordingly, **2b** (in the form of its crystalline $CHCl_3$ solvate) adopts a three-legged piano stool conformation with Br and the N and P atoms of the bidentate PPFA ligand as the legs. There are two independent, but stereochemically similar, complexes in the asymmetric unit of the monoclinic cell. Their mean Ru–Br, Ru–N, and Ru–P bond lengths are 2.604(2), 2.266(6), and 2.287(2) Å, respectively, with Br–Ru–N, Br–Ru–P, and N–Ru–P angles of 87.5(1), 96.6(1), and 91.9(1)°. The Ru-bonded Cp rings are essentially planar with C–C bond distances in the range 1.32(1)–1.45(1) Å, giving a mean value of 1.39(1) Å. The Ru–C distances range from 2.147(7) to 2.222(7) Å [mean 2.183(7) Å].

Treatment of [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ with 1 equiv. of PN and PPFA in THF at room temperature afforded Ru(η^6-*p*-cymene)(PN-κ*P*)Cl$_2$ (**3a**) and Ru(η^6-*p*-cymene)(PPFA-κ*P*)Cl$_2$ (**3b**) in 80 and 87% isolated yields (Scheme 2) as orange air-stable complexes. Complexes **3a** and **3b** have been characterized



Scheme 2

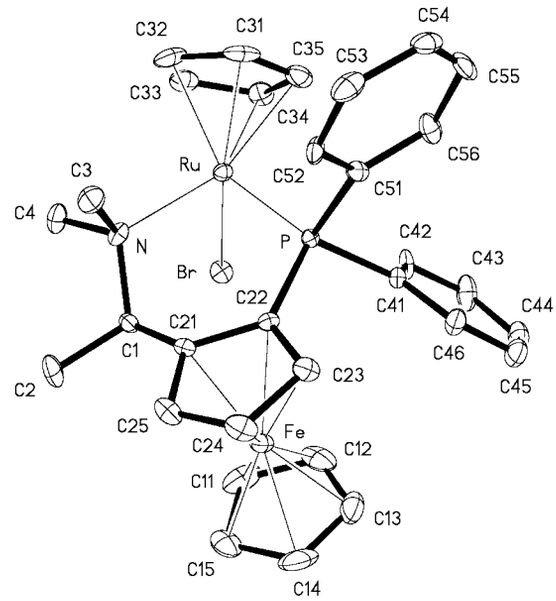


Fig. 1 Structural view of one of the two independent Ru complexes in (S_{Ru},R_C,S_{pl})-RuCp(PPFA-κ*N*,κ*P*)Br·$CHCl_3$ (**2b**·$CHCl_3$) showing 20% thermal ellipsoids. Priority for the assignment of the absolute configuration at Ru: Br > Cp > PPh_2 > NMe_2. Selected bond lengths (Å) and angles (°): Ru–C(31–35)$_{av}$ 2.176(7), Ru–P 2.288(2), Ru–N 2.269(6), Ru–Br 2.589(2); P–Ru–N 92.3(1), N–Ru–Br 87.3(1), Br–Ru–P 94.7(1).

by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies as well as elemental analysis. In the ^{1}H NMR spectra of **3a** and **3b**, the NMe_2 group of the coordinated ligand displays a singlet at a δ value nearly that of the 'free' ligand, indicating that the ligand is monodentate P-bonded. The ^{31}P{^{1}H} NMR spectra exhibit a singlet at 21.6 and 23.3 ppm, respectively.

Treatment of **3** with $TlCF_3SO_3$ (1 equiv.) in THF at room temperature affords, on workup, the cationic complexes [Ru(η^6-*p*-cymene)(PN-κ*N*,κ*P*)Cl]CF_3SO_3 (**4a**) and [(R_{Ru},R_C,S_{pl})-Ru(η^6-*p*-cymene)(PPFA-κ*N*,κ*P*)Cl]CF_3SO_3 (**4b**) in 52 and 86% isolated yield (Scheme 2). Characterization of these complexes was again accomplished by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies as well as elemental analysis. In the ^{31}P{^{1}H} NMR, the phosphorus atom of the κ*N*,κ*P*-coordinated phosphinoamine displays a singlet at 59.0 and 28.2 ppm (*cf.* 21.6 and 23.3 ppm in **3a** and **3b**, respectively, where the phosphinoamine ligand is κ*P*-coordinated). It is also evident from ^{31}P{^{1}H} NMR spectroscopy that, in the case of **4b**, only one diastereoisomer is formed. In order to assign the absolute configuration at the metal center, an X-ray diffraction study of **4b′** (BPh_4^- salt of **4b**) has been undertaken. The structure is depicted in Fig. 2, with selected bond distances and angles reported in the caption.

Complex **4b′** (in the form of its crystalline acetone–diethyl ether solvate) adopts a typical three-legged piano stool conformation with Cl and the N and P atoms of the bidentate PPFA ligand as the legs. The configuration at the Ru atom is *R*. As in **2b**·$CHCl_3$, there are two independent but stereochemically similar complexes in the asymmetric part of the unit cell. Their Ru–Cl, Ru–N, and Ru–P distances average to 2.388(2), 2.289(5), and 2.346(2) Å, respectively, with Cl–Ru–N, Cl–Ru–P, and N–Ru–P angles of 85.9(1), 87.5(1), and 90.0(1)°. The *p*-cymene rings show C–C arene bond distances in the range 1.381(9)–1.438(8) Å, giving a mean value of 1.411 Å. The Ru–C distances range from 2.186(6) to 2.324(6) Å (mean 2.250 Å).

Catalytic transfer hydrogenation of ketones

Catalytic studies with the racemic complexes **1a**, **2a**, **2c**, and **4a** and the diastereo- and enantiopure complexes **1b**, **2b**, and **4b**

Table 1 Reduction of acetophenone by **1**, **2**, and **4** with *i*-PrOH/*i*-PrONa as the reducing agent[a]

Precatalyst	*T*/°C	Time/h	Yield (%)
1a	25	24	>99
1a	82	2.5	>99
1b	25	24	no reaction
1b	82	2.5	<5
2a	25	24	>99
2a	82	2.5	>99
2b	25	24	no reaction
2b	82	48	>99
2c	25	24	no reaction
2c	82	2.5	27
4a	25	24	<5
4a	82	24	>99
4b	25	24	no reaction
4b	82	48	>99

[a] 0.1 M 2-propanol solution of acetophenone containing 5 mg of the precatalyst (acetophenone : precatalyst : *i*-PrONa = 200 : 1 : 2).

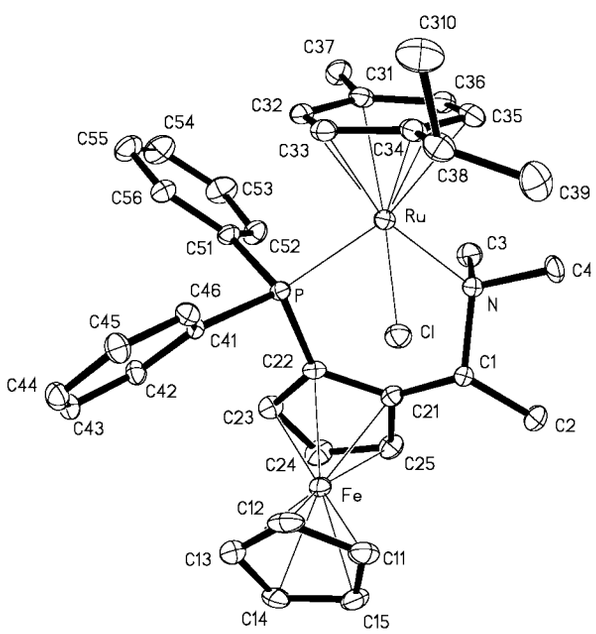
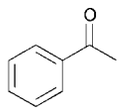
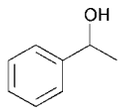
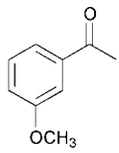
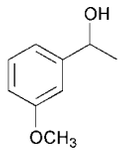
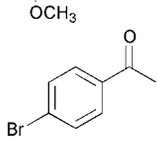
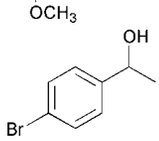
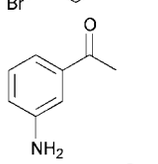
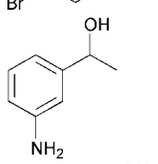
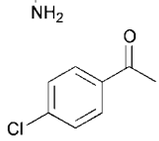
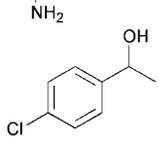
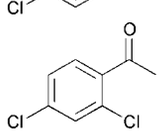
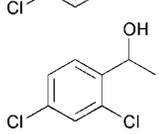
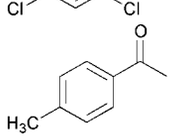
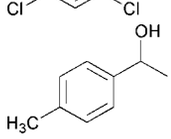
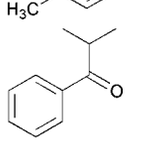
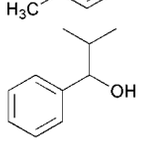
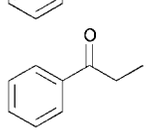
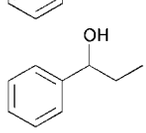
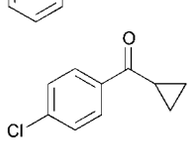
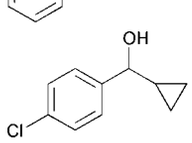
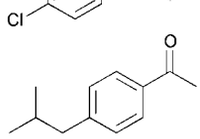
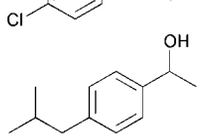
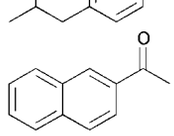
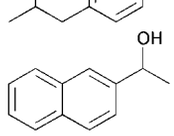
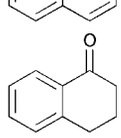
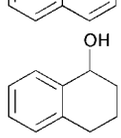
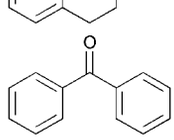
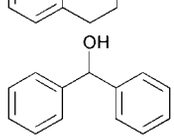
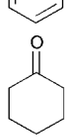
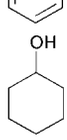


Fig. 2 Structural view of one of the two independent Ru complexes in $[(R_{Ru},R_C,S_{pl})$-Ru(η^6-*p*-cymene)(PPFA-κ*N*,κ*P*)Cl]BPh_4·½$(CH_3)_2$CO·½$(C_2H_5)_2$O (**4b′**·½$(CH_3)_2$CO·½$(C_2H_5)_2$O) showing 20% thermal ellipsoids. Priority for the assignment of the absolute configuration at Ru: *p*-cymene > Cl > PPh_2 > NMe_2. Selected bond lengths (Å) and angles (°): Ru–C(31–36)$_{av}$ 2.249(6), Ru–P 2.346(2), Ru–N 2.293(5), Ru–Cl 2.383(2); P–Ru–N 89.6(1), N–Ru–Cl 86.1(1), Cl–Ru–P 87.4(1).

for the transfer hydrogenation of acetophenone revealed that the RuCp and Ru(*p*-cymene) complexes with the simple PN ligand are much more effective than those with PPFA or DBD (Table 1). For instance, while **1a** and **2a** convert acetophenone to 1-phenylethanol quantitatively at room temperature after 24 h, compounds **1b**, **2b**, **2c**, **4a**, and **4b** require both prolonged reaction times (24 h or longer) and elevated temperatures (82 °C). At 82 °C the reduction of acetophenone with **1a** and **2a** as precatalysts is already complete after 2.5 h. By and large, complexes **2a** and **4a** are excellent precatalysts for the transfer hydrogenation of acetophenone derivatives and cyclohexanone in boiling 2-propanol for 48 h, as shown in Table 2. In most cases, the conversion to the respective alcohols is essentially quantitative.

Expanding the transfer hydrogenation of acetophenone and its derivatives to the optically pure systems **2b** and **4b** revealed that at elevated temperatures these complexes are also efficient precatalysts, comparable in reactivity to **2a** and **4a**. However, in all cases only racemic products were obtained. Racemization

Table 2 Reduction of various ketones by **2a** (**4a**) with *i*-PrOH/*i*-PrONa as the reducing agent[a]

Substrate	Product	Yield (%)
		>99
		78 (>99)
		75 (>99)
		62 (>99)
		>99
		>99
		61 (>99)
		>99
		78 (>99)
		33 (72)
		45 (>99)
		>99
		50 (80)
		>99 (80)[b]
		>99

[a] 0.1 M 2-propanol solution of the ketone containing 5 mg of **2a** (**4a**) (ketone : cat : *i*-PrONa = 200 : 1 : 2), T = 82 °C, t = 48 h. [b] t = 92 h.

of the final products seems not to take place since treatment of an optically pure sample of (*R*)-1-phenylethanol under the same reaction conditions did not result in racemization. Thus, we suggest that the aminophosphine ligands are hemilabile under the reaction conditions, forming reactive intermediates with κ*P*-bonded aminophosphine ligands, an observation perhaps not too surprising. However, since ^{1}H or $^{31}P\{^{1}H\}$ NMR spectra of **2a** (the most reactive complex) in CD_3NO_2 at 100 °C did not significantly change as compared to the room temperature spectra, there was no indication of any dynamic processes. In fact, the presence of two ^{1}H signals due to the diastereotopic NMe_2 groups is very indicative of a κ*N*,κ*P* coordination and a species with a monodentate P-bonded ligand must be present only in very small concentrations.

A reasonable mechanism for the transfer hydrogenation of ketones is summarized in Scheme 3 (exemplified for RuCp aminophosphine complexes). After Br^- dissociation, which is favored in polar solvents such as 2-propanol, the alkoxide anion attacks the metal center giving complex **A**. β-Elimination from **A** yields the hydride complex **B** and acetone. This process already requires an additional vacant coordination site. DFT calculations on related ruthenium arene systems revealed that β-elimination could involve ring slippage.[10,11] On the other hand, in our systems, Ru–N bond cleavage may occur as well, leading to reactive monodentate P-bonded intermediates. The decrease in reactivity on going from PN to DBD and PPFA may be partially explained by such a ring opening process. PPFA and DBD are certainly more rigid than PN due to their aromatic backbone. Furthermore, PPFA is sterically more demanding than both PN and DBD. In the following step, the substrate has to coordinate to **B**, requiring again a vacant coordination site. Accordingly, Ru–N bond cleavage or η^5 to η^3 ring slippage of the Cp ligand (in the case of arenes η^6 to η^4 ring slippage) has to take place, leading to intermediates **C** and/or **D**, respectively. However, since the two diastereopure PPFA systems were not enantioselective in the hydrogenation of 15 different substrates (Table 2), it is most likely that the catalytic reaction involves Ru–N bond cleavage. Thus, since diastereoface selection of incoming labile substrates is based on the planar chirality of the ferrocene moiety, rather than the metal centered chirality, as has been shown previously,[9] no enantioselective reaction takes place. On the other hand, in the case of ring slippage, even if the enantioselectivities are poor, there still should be some discrimination between the two diastereofaces of complexes **2b** and **4b**. The assumption that ring opening has to occur is further supported by the fact that the monophosphine complex $[RuCp(PPh_3)(CH_3CN)_2]^+$ is an even more efficient precatalyst for the above reductions than **1a** and **2a**.

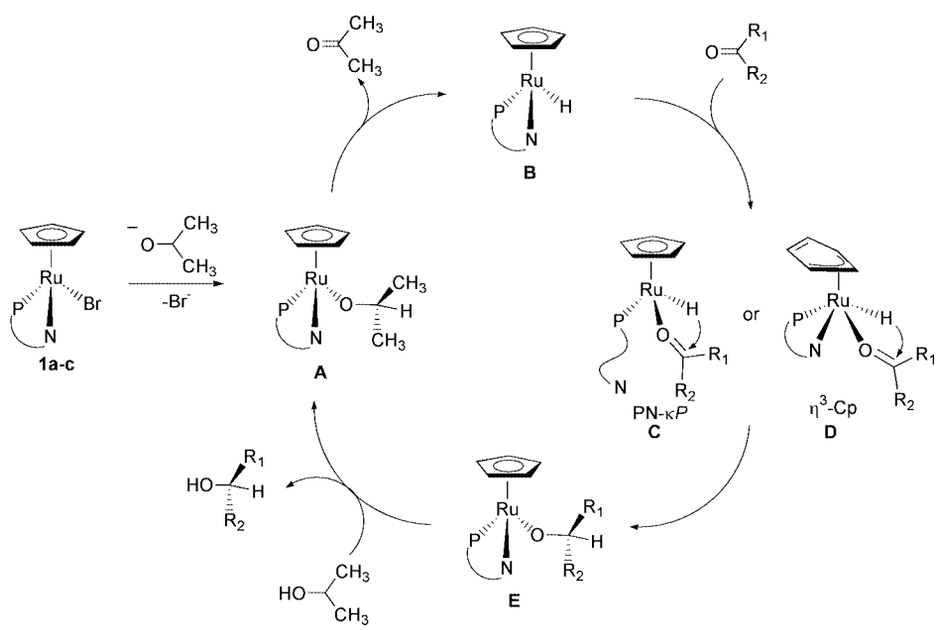
In conclusion, we have shown that ruthenium(II) half-sandwich complexes containing aminophosphine ligands are excellent precatalysts for the transfer hydrogenation of acetophenone derivatives and cyclohexanone. However, due to the hemilability of these ligands, there is no longer a discrimination between the two diastereofaces of the chiral complexes (the planar chirality of the PPFA ligand is important). Consequently, at least at elevated temperatures, such ligand systems are not suitable for enantioselective transfer hydrogenations. In fact, analogous complexes with monodentate phosphine ligands are much better suited for these types of reactions.

Experimental

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[12] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp(CH_3CN)_3]PF_6$ and $[RuCp(PPh_3)(CH_3CN)_2]PF_6$,[8,13] $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$,[14] [RuCp(PN-κ*N*, κ*P*)(CH_3CN)]PF_6 (**1a**), and [(S_{Ru},R_C,S_{pl})-RuCp(PPFA-κ*N*, κ*P*)(CH_3CN)]PF_6 (**1b**)[9] were prepared according to the literature. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to $SiMe_4$ and H_3PO_4 (85%). IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer. For analytical HPLC runs a Hewlett Packard HP1090 liquid chromatograph was used. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OB (250 × 4.6 mm) column. Separation conditions: flow 0.5 mL/min^{-1}, column temperature: 25 °C, eluent: hexane–isopropanol 9 : 1, c = 20 mg mL^{-1}, sample volume: 5 μl; t_R = 12.4 and 18.2 min.

Synthesis

RuCp(PN-κ*N*,κ*P*)Br (2a). To a solution of **1a** (100 mg, 0.164 mmol) in CH_2Cl_2 (3 mL), NEt_4Br (50.5 mg, 0.328 mmol) was added and the mixture was stirred for 20 h at room temperature. On addition of Et_2O, a precipitate of NEt_4PF_6



Scheme 3

was formed which was removed by filtration over Na_2SO_4. The solvent of the remaining dark red solution was then removed under reduced pressure and a red precipitate was obtained which was collected on a glass frit, washed with Et_2O and petroleum ether (1 : 5), and dried under vacuum. Yield: 68.1 mg (82.3%). $C_{21}H_{25}BrNPRu$ requires: C, 50.11; H, 5.01; N, 2.78. Found: C, 50.29; H, 5.06; N, 2.90%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.88 (m, 2H, Ph), 7.49–7.30 (m, 8H, Ph), 4.15 (s, 5H, Cp), 3.38 (s, 3H, NMe_2), 3.05 (s, 3H, NMe_2), 2.99–1.90 (m, 4H). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 142.1 (d, $^1J_{CP}$ = 42.9 Hz, 1C, Ph^1), 135.0 (d, $^2J_{CP}$ = 11.4 Hz, 2C, Ph^{2,6}), 132.5 (d, $^1J_{CP}$ = 40.1 Hz, 1C, Ph$^{1'}$), 131.1 (d, $^2J_{CP}$ = 10.5 Hz, 2C, Ph$^{2',6'}$), 130.1 (d, $^4J_{CP}$ = 1.9 Hz, 1C, Ph^4), 129.1 (d, $^4J_{CP}$ = 1.9 Hz, 1C, Ph$^{4'}$), 128.6 (d, $^3J_{CP}$ = 8.6 Hz, 2C, Ph^{3,5}), 128.2 (d, $^3J_{CP}$ = 10.5 Hz, 2C, Ph$^{3',5'}$), 73.0 (d, $^2J_{CP}$ = 2.9 Hz, 5C, Cp), 61.7 (d, $^2J_{CP}$ = 7.6 Hz, 1C, PCH_2CH_2N), 58.0 (s, 1C, NMe_2), 57.8 (s, 1C, NMe_2), 29.6 (d, $^1J_{CP}$ = 18.1 Hz, PCH_2CH_2N). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 64.9 (PPh$_2$)

(S_{Ru},R_C,S_{pl})-RuCp(PPFA-κ*N*,κ*P*)Br (2b). This complex has been prepared analogously to **2a** with **1b** (300 mg, 0.391 mmol) and NEt_4Br as the starting materials. Yield: 0.216 mg (84%). $C_{31}H_{33}BrFeNPRu$ requires: C, 54.17; H, 4.83; N, 2.04. Found: C, 54.29; H, 4.95; N, 2.10%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 8.39–8.27 (m, 2H, Ph), 7.53–7.44 (m, 3H, Ph), 7.20–7.11 (m, 3H, Ph), 6.98–6.87 (m, 2H, Ph), 5.38 (q, $^3J_{HH}$ = 6.78 Hz, 1H, C*H*(Me)NMe_2), 4.42–4.40 (m, 1H, FeCp^s), 4.39–4.34 (m, 2H, FeCp^s), 3.79 (s, 5H, RuCp), 3.70 (s, 5H, FeCp), 3.46 (s, 3H, NMe_2), 2.45 (s, 3H, NMe_2), 1.25 (d, $^3J_{HH}$ = 7.00 Hz, 3H, CH(*Me*)NMe_2). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 148.2 (d, $^1J_{CP}$ = 48.8 Hz, 1C, Ph^1), 137.5 (d, $^1J_{CP}$ = 42.7 Hz, 1C, Ph$^{1'}$), 137.4 (d, $^2J_{CP}$ = 12.2 Hz, 2C, Ph^{2,6}), 131.4 (d, $^2J_{CP}$ = 9.2 Hz, 2C, Ph$^{2',6'}$), 130.2 (d, $^4J_{CP}$ = 2.3 Hz, 1C, Ph^4), 127.9 (d, $^4J_{CP}$ = 1.5 Hz, 1C, Ph$^{4'}$), 127.5 (d, $^3J_{CP}$ = 9.2 Hz, 2C, Ph^{3,5}), 127.5 (d, $^3J_{CP}$ = 10.7 Hz, 2C, Ph$^{3',5'}$), 94.7 (d, $^2J_{CP}$ = 22.9 Hz, 1C, FeCp^2), 75.5 (d, J_{CP} = 2.3 Hz, 1C, FeCp^s), 74.3 (d, $^2J_{CP}$ = 3.0 Hz, 5C, CpRu), 74.3 (d, $^1J_{CP}$ = 27.5 Hz, 1C, FeCp^1), 71.0 (s, 5C, FeCp), 70.2 (d, J_{CP} = 3.8 Hz, 1C, FeCp^s), 70.0 (d, J_{CP} = 9.2 Hz, 1C, FeCp^s), 59.0 (d, $^3J_{CP}$ = 1.5 Hz, 1C, *C*H(Me)NMe_2), 56.1 (d, $^3J_{CP}$ = 2.3 Hz, 1C, NMe_2), 48.6 (d, $^3J_{CP}$ = 1.5 Hz, 1C, NMe_2), 10.3 (s, 1C, CH(*Me*)NMe_2). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 37.4 (PPh$_2$).

Ru(η^6-*p*-cymene)(PN-κ*P*)Cl$_2$ (3a). A solution of $[RuCl_2(\eta^6$-*p*-cymene)$]_2$ (250 mg, 0.410 mmol) in THF (10 mL) was treated with PN (0.211 g, 0.820 mmol) for 3 h at room temperature. After removal of the solvent under reduced pressure, the solid was collected on a glass frit, washed with Et_2O, and dried under vacuum. Yield: 0.201 g (80%). $C_{26}H_{34}Cl_2NPRu$ requires: C, 55.42; H, 6.08; N, 2.49. Found: C, 55.50; H, 6.02; N, 2.43%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.90–7.50 (m, 10H, Ph), 5.25 (d, J_{HH} = 5.3 Hz, 2H, Cy), 5.11 (d, J_{HH} = 6.0 Hz, 2H, Cy), 2.84–2.81 (m, 2H, PCH_2CH_2N), 2.11 (s, 6H, NMe_2), 2.30–2.09 (m, 2H, PCH_2CH_2N), 2.60 (m, J_{HH} = 7.1 Hz, 1H, Cy–C*H*Me_2), 1.91 (s, 3H, Cy–CH_3), 0.90 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Cy–CH*Me*$_2$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 133.3 (d, $^2J_{CP}$ = 9.9 Hz, 4C, Ph^{2,6}), 132.9 (d, $^1J_{CP}$ = 42.2 Hz, 2C, Ph^1), 130.9 (d, $^4J_{CP}$ = 1.8 Hz, 2C, Ph^4), 128.6 (d, $^3J_{CP}$ = 9.9 Hz, 4C, Ph^{3,5}), 108.8 (s, 1C, Cy), 94.4 (s, 1C, Cy), 90.4 (d, J_{CP} = 3.6 Hz, 2C, Cy), 85.9 (d, J_{CP} = 5.4 Hz, 2C, Cy), 53.6 (m, 1C, PCH_2CH_2N), 44.6 (s, 2C, NMe_2), 30.2 (s, 1C, Cy–C*H*Me_2), 21.6 (s, 2C, Cy–CH*Me*$_2$), 21.1 (d, $^1J_{CP}$ = 29.6 Hz, 1C, PCH_2CH_2N), 17.6 (s, 1C, Cy–CH_3). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 21.6 (PPh$_2$).

(R_C,S_{pl})-Ru(η^6-*p*-cymene)(PPFA-κ*P*)Cl$_2$ (3b). A solution of $[RuCl_2(\eta^6$-*p*-cymene)$]_2$ (250 mg, 0.410 mmol) in THF was treated with PPFA (361 mg, 0.820 mmol) for 1 h at room temperature. During that time, an orange precipitate began to form. After removal of the solvent under reduced pressure, the solid was collected on a glass frit, washed with Et_2O, and dried under vacuum. Yield: 0.529 g (87%). $C_{36}H_{42}Cl_2FeNPRu$ requires: C, 57.84; H, 5.66; N, 1.87. Found: C, 58.65; H, 5.80; N, 2.03%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.05–7.96 (m, 2H, Ph), 7.79–7.68 (m, 2H, Ph), 7.50–7.39 (m, 3H, Ph), 7.31–7.16 (m, 3H, Ph), 5.67–5.56 (m, 2H, Cy), 5.09–5.04 (m, 1H, FeCp^s), 5.04–4.96 (m, 2H, Cy), 4.63–4.59 (m, 1H, FeCp^s), 4.48–4.45 (m, 1H, FeCp^s), 4.03 (s, 5H, FeCp), 3.17 (q, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*(Me)NMe_2), 2.68 (m, J_{HH} = 6.9 Hz, 1H, Cy–C*H*Me_2), 1.96 (s, 3H, Cy–CH_3), 1.73 (s, 6H, CH(Me)N*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CH(*Me*)NMe_2), 1.11 (d, $^3J_{HH}$ = 7.13 Hz, 3H, Cy–CH*Me*$_2$), 1.05 (d, $^3J_{HH}$ = 6.56 Hz, 3H, Cy–CH*Me*$_2$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 136.2 (d, $^2J_{CP}$ = 10.5 Hz, 2C, Ph^{2,6}), 135.8 (d, $^2J_{CP}$ = 8.6 Hz, 2C, Ph$^{2',6'}$), 134.3 (d, $^1J_{CP}$ = 49.6 Hz, 1C, Ph^1), 133.7 (d, $^1J_{CP}$ = 48.6 Hz, 1C, Ph$^{1'}$), 130.8 (d, $^4J_{CP}$ = 1.9 Hz, 1C, Ph^4), 129.4 (d, $^4J_{CP}$ = 3.8 Hz, 1C, Ph$^{4'}$), 127.7 (d, $^3J_{CP}$ = 9.5 Hz, 2C, Ph^{3,5}), 126.0 (d, $^3J_{CP}$ = 9.5 Hz, 2C, Ph$^{3',5'}$), 107.1 (s, 1C, Cy), 95.5 (s, 1C, Cy), 92.8 (d, $^1J_{CP}$ = 32.4 Hz, 1C, FeCp^1), 91.3 (s, 1C, Cy), 88.9 (s, 1C, Cy), 86.4 (d, J_{CP} = 4.8 Hz, 1C, Cy), 85.6 (d, J_{CP} = 3.8 Hz, 1C, Cy), 78.0 (d, J_{CP} = 17.2 Hz, 1C, FeCp^2), 70.2 (d, J_{CP} = 18.1 Hz, 1C, FeCp^s), 69.9 (d, J_{CP} = 2.9 Hz, 1C, FeCp^s), 69.2 (d, J_{CP} = 7.6 Hz, 1C, FeCp^s), 54.7 (s, 2C, NMe_2), 39.9 (s, 1C, *C*H(Me)NMe_2), 30.4 (s, 1C, Cy–*C*HMe_2), 23.1 (s, 1C, Cy–CH*Me*$_2$), 22.4 (s, 1C, Cy–CH*Me*$_2$), 18.0 (s, 1C, Cy–*C*H_3), 9.8 (s, 1C, CH(*Me*)NMe_2). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 23.3 (PPh$_2$).

[Ru(η^6-*p*-cymene)(PN-κ*N*,κ*P*)Cl]CF_3SO_3 (4a). To a solution of **3a** (200 mg, 0.355 mmol) in THF (10 mL), $TlCF_3SO_3$ (150 mg, 0.426 mmol) was added and stirred for 30 min at room temperature. The reaction mixture was evaporated to dryness and the residue redissolved in CH_2Cl_2 (1 mL). Insoluble materials (TlCl) were then removed by filtation over Na_2SO_4. Upon addition of Et_2O (4 mL), a red precipitate was formed which was collected on a glass frit, washed with Et_2O (3 × 2 mL), and dried *in vacuo*. Yield: 116 mg (52%). $C_{27}H_{34}ClF_3NO_3PRuS$ requires: C, 47.89; H, 5.06; N, 2.07. Found: C, 47.81; H, 5.11; N, 2.13%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.75–7.40 (m, 10H, Ph), 6.25 (d, J_{HH} = 5.8 Hz, 1H, Cy), 5.99 (d, J_{HH} = 6.5 Hz, 1H, Cy), 5.36–5.16 (m, 2H, Cy), 3.22 (s, 3H, NMe_2), 3.16 (s, 3H, NMe_2), 3.04–2.47 (m, 4H, PCH_2CH_2N), 3.04–2.47 (m, 1H, Cy–C*H*Me_2), 1.27 (d, $^3J_{HH}$ = 6.5 Hz, 3H, Cy–CH*Me*$_2$), 1.20 (s, 3H, Cy–CH_3), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 3H, Cy–CH*Me*$_2$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 134.6 (d, $^2J_{CP}$ = 9.9 Hz, 2C, Ph^{2,6}), 134.0 (d, $^1J_{CP}$ = 47.6 Hz, 1C, Ph^1), 133.3 (d, $^2J_{CP}$ = 9.9 Hz, 2C, Ph$^{2',6'}$), 133.1 (d, $^1J_{CP}$ = 47.6 Hz, 1C, Ph$^{1'}$), 131.8 (d, $^4J_{CP}$ = 2.7 Hz, 1C, Ph^4), 131.6 (d, $^3J_{CP}$ = 9.0 Hz, 2C, Ph^{3,5}), 131.5 (d, $^4J_{CP}$ = 2.7 Hz, 1C, Ph$^{4'}$), 129.4 (d, $^3J_{CP}$ = 9.9 Hz, 2C, Ph$^{3',5'}$), 97.3 (s, 1C, Cy), 92.8 (s, 1C, Cy), 89.8 (d, J_{CP} = 8.9 Hz, 1C, Cy), 89.5 (d, J_{CP} = 3.6 Hz, 1C, Cy), 87.9 (s, 1C, Cy), 87.0 (d, J_{CP} = 5.4 Hz, 1C, Cy), 61.2 (d, $^2J_{CP}$ = 3.6 Hz, 1C, PCH_2CH_2N), 58.9 (s, 1C, NMe_2), 57.4 (s, 1C, NMe_2), 31.0 (s, 1C, Cy–*C*HMe_2), 22.3 (d, $^1J_{CP}$ = 28.7 Hz, 1C, PCH_2CH_2N), 20.7 (s, 1C, Cy–CH*Me*$_2$), 18.0 (s, 1C, Cy–CH*Me*$_2$), 15.9 (s, 1C, Cy–*C*H_3). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 59.0 (PPh$_2$).

[(R_{Ru},R_C,S_{pl})-Ru(η^6-*p*-cymene)(PPFA-κ*N*,κ*P*)Cl]CF_3SO_3 (4b). This complex has been prepared analogously to **4a** using **3b** (200 mg, 0.268 mmol) as starting material. Yield: 198 mg (86%). $C_{37}H_{42}ClF_3FeNO_3PRuS$ requires: C, 51.61; H, 4.92; N, 1.63. Found: C, 51.84; H, 5.13; N, 1.76%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.17–8.07 (m, 2H, Ph), 7.64–7.53 (m, 3H, Ph), 7.46–7.36 (m, 3H, Ph), 7.10–6.97 (m, 2H, Ph), 6.46–6.43 (m, 1H, Cy), 6.14–6.08 (m, 1H, Cy), 5.44 (q, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*(Me)-NMe_2), 5.27–5.20 (m, 1H, Cy), 4.91–4.85 (m, 1H, Cy), 4.56–4.50 (m, 1H, FeCp^s), 4.45–4.40 (m, 1H, FeCp^s), 4.38–4.33 (m, 1H, FeCp^s), 3.68 (s, 5H, FeCp), 3.45 (s, 3H, CH(Me)N*Me*$_2$), 2.79 (m, $^3J_{HH}$ = 6.8 Hz, 1H, Cy–C*H*Me_2), 2.57 (s, 3H, CH-(Me)N*Me*$_2$), 1.39 (d, $^3J_{HH}$ = 6.68 Hz, 3H, Cy–CH*Me*$_2$), 1.34 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH(*Me*)NMe_2), 1.31 (d, $^3J_{HH}$ = 7.0 Hz, 3H, Cy–CH*Me*$_2$), 0.93 (s, 3H, Cy–CH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 140.4 (d, $^1J_{CP}$ = 53.4 Hz, 1C, Ph^1), 136.2 (d, $^2J_{CP}$ = 10.5 Hz, 2C, Ph^{2,6}), 133.6 (d, $^1J_{CP}$ = 56.3 Hz, 1C, Ph$^{1'}$), 133.5 (d,

Table 3 Crystallographic data for **2b**·$CHCl_3$ and **4b′**·½$(CH_3)_2CO$·½$(C_2H_5)_2O$

	2b·$CHCl_3$	**4b′**·½$(CH_3)_2CO$·½$(C_2H_5)_2O$
Formula	$C_{32}H_{34}BrCl_3FeNPRu$	$C_{63.5}H_{70}BClFeNOPRu$
Fw	806.75	1097.36
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$ (no. 4)	$P2_1$ (no. 4)
a/Å	9.542(6)	13.439(6)
b/Å	34.54(2)	23.913(11)
c/Å	10.164(6)	17.169(8)
β/°	109.67(3)	90.84(3)
V/Å^3	3155(3)	5517(4)
Z	4	4
T/K	223(2)	223(2)
μ(Mo-Kα)/mm^{-1}	2.53	0.66
Measured rflns	31779	79805
Indep rflns	10891	23774
$2\theta_{max}$/°	49.8	54
No. of params	722	1271
R_1 [$I > 2\sigma(I)$] [a]	0.043	0.045
R_1 (all data) [a]	0.049	0.054
wR_2 (all data) [b]	0.102	0.118

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$

$^2J_{CP}$ = 8.6 Hz, 2C, Ph$^{2',6'}$), 132.1 (d, $^4J_{CP}$ = 2.9 Hz, 1C, Ph^4), 131.1 (d, $^4J_{CP}$ = 2.9 Hz, 1C, Ph$^{4'}$), 128.9 (d, $^3J_{CP}$ = 10.5 Hz, 2C, Ph^{3,5}), 128.5 (d, $^2J_{CP}$ = 10.5 Hz, 2C, Ph$^{3',5'}$), 96.8 (d, $^1J_{CP}$ = 21.0 Hz, 1C, FeCp^1), 96.6 (s, 1C, Cy), 93.4 (d, $^2J_{CP}$ = 20.0 Hz, 1C, FeCp^2), 93.4 (s, 1C, Cy), 91.8 (s, 1C, Cy), 91.6 (s, 1C, Cy), 88.7 (d, J_{CP} = 3.8 Hz, 1C, Cy), 85.3 (s, 1C, Cy), 72.1 (d, J_{CP} = 14.3 Hz, 1C, FeCp^s), 71.6 (s, 5C, FeCp), 71.4 (d, J_{CP} = 4.8 Hz, 1C, FeCp^s), 71.3 (d, J_{CP} = 1.9 Hz, 1C, FeCp^s), 57.8 (s, 1C, NMe_2), 57.3 (s, 1C, NMe_2), 49.5 (d, $^1J_{CP}$ = 1.9 Hz, 1C, *C*H(Me)NMe_2), 31.7 (s, 1C, Cy–*C*HMe_2), 22.4 (s, 1C, Cy–CH*Me*$_2$), 20.7 (s, 1C, Cy–CH*Me*$_2$), 15.0 (s, 1C, Cy–*C*H_3), 10.2 (s, 1C, CH(*Me*)NMe_2). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 28.2 (*P*Ph_2). The BPh_4^- salt of **4b**, [(R_{Ru},R_C,S_{pl})-Ru(η^6-*p*-cymene)(PPFA-κ*N*,κ*P*)Cl]BPh_4 (**4b′**), has been prepared by anion metathesis with $NaBPh_4$ in MeOH as the solvent.

Hydrogen transfer catalysis with the precatalysts 1a–c, 2a–c, 4a, and 4b

In a typical procedure, to a 0.1 M solution of the ketone in 2-propanol, the precatalyst (5 mg) and *i*-PrONa were added (ketone : precatalyst : *i*-PrONa = 200 : 1 : 2) to a Schlenk tube and heated in an oil bath at 82 °C for 48 h (see Tables 1 and 2). After that time, the solvent was removed under reduced pressure and the product distribution was determined by ^{1}H NMR spectroscopy. In the case of chiral precatalysts the enantiomeric excess was determined by HPLC.

X-Ray structure determination for 2b·$CHCl_3$ and 4b′·½$(CH_3)_2$-CO·½$(C_2H_5)_2$O

Crystals of **2b** and **4b′** in the form of their solvates **2b**·$CHCl_3$ and **4b′**·½$(CH_3)_2CO$·½$(C_2H_5)_2O$ were obtained by liquid phase diffusion of petroleum ether into $CHCl_3$ solutions and by gas phase diffusion of Et_2O into acetone solutions, respectively. Crystal data and experimental details are given in Table 3. X-Ray data were collected on a Bruker SMART CCD area detector diffractometer (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å, 0.3° ω-scan frames covering complete spheres of the reciprocal space). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. Both structures were solved by direct methods using the program SHELXS97.[15] Structure refinement on F^2 was carried out with program SHELXL97.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. **2b**·$CHCl_3$ contains two crystallographically independent Ru complexes of similar stereochemistry and conformation, but with differing environments, *e.g.* by the two independent $CHCl_3$ molecules. **4b′**·½$(CH_3)_2CO$·½$(C_2H_5)_2O$ also contains two crystallographically independent Ru complexes of similar comformation arranged in a pseudo-2_1-like fashion along the *c*-axis of the monoclinic unit cell. This compound stands out in containing two different but well-ordered solvent molecules.

CCDC reference numbers 164452 and 164453.

See http://www.rsc.org/suppdata/dt/b1/b104128m/ for crystallographic data in CIF or other electronic format.

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