Ruthenium(II) Complexes with Triphosphane Ligands Combining Planar, Phosphorus, and Carbon Chirality: Application to Asymmetric Reduction of Trifluoroacetophenone

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Dichloro-, bis(acetonitrile)chloro-, and tris(acetonitrile)ruthenium(II) complexes with the triphosphane ligands $(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir and $(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir, combining planar, phosphorus, and carbon chirality, were prepared and structurally characterized in solution. The complexes were tested as catalyst precursors for the reduction of trifluoroacetophenone to (*R*)-α-(trifluoromethyl)benzyl alcohol by either hydrogenation or hydrogen transfer from *i*PrOH. The best conversion and enantioselectivity was obtained with the tris(acetonitrile) precursor [{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}Ru-$(CH_3CN)_3$]$(PF_6)_2$ in hydrogen-transfer conditions using a basic co-catalyst.

Introduction

The design of new, enantiomerically pure ligands leading to highly efficient and selective processes is a challenging issue attracting constant attention in the field of asymmetric catalysis. The large majority of stereoselective reactions catalysed by transition metal complexes involve chiral chelating diphosphane ligands, in particular those with C_2 symmetry.[1] Some attempts have been made to use chiral tridentate phosphanes, aimed at exploiting the superior stabilising effect and coordination versatility of tridentate ligands over bidentate ones.[2] However, due to the inherent difficulty of their synthesis, chiral stereohomogeneous triphosphanes have been scarcely investigated so far,[3] which has prevented an in-depth study of their great potential in asymmetric catalysis. In view of the large diversity of coordination modes accessible through tridentate ligands, the characterization and the knowledge of the structure of their metal complexes is of particular importance for the fine tuning of the catalytic activity and for the design of new active species.

The understanding of the chemical and physical factors that control the source of chiral information in metal complexes with tridentate phosphanes is a current research objective in our laboratories. As part of these studies, we have recently reported the synthesis of the *pseudo*-C_2-symmetric bis(ferrocenyl)triphosphanes Pigiphos (Figure 1), together with some applications of their Ru^{II}, Ni^{II} and Rh^{III} complexes in asymmetric catalysis.[4]

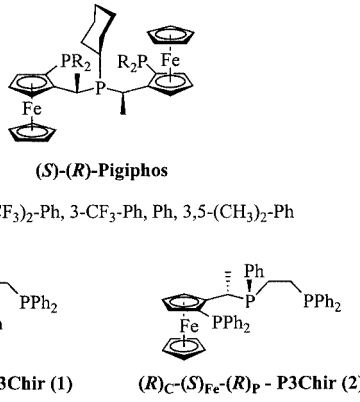

Figure 1. Sketch of the tridentate phosphane ligands (*S*)-(*R*)-Pigiphos = bis{(*S*)-1-[(*R*)-2-(diphenylphosphanyl)ferrocenyl]ethyl}-cyclohexylphosphane, $(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir (**1**) and $(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir (**2**) = (*R*)-1-[(*S*)-2-diphenylphosphanyl)ferrocenyl]-ethyl-(*R*)-[phenylphosphanyl-2-(diphenylphosphanyl)ethane]

The enantiomeric excesses (*ee*) obtained in the hydrogen-transfer reduction of acetophenone by (Pigiphos)Ru^{II} catalysis were relatively good, yet hardly comparable with those reported for the most efficient Ru^{II} systems modified with chiral chelating ligands.[5]

Since the tendency of Pigiphos to adopt a meridional (*mer*) coordination geometry and a *pseudo*-C_2 symmetry have been suggested to be unfavourable features for high asymmetric induction,[4b] we decided to design triphosphane ligands devoid of C_2 symmetry. Two ligands with these characteristics, namely $(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir (**1**) and

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$(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir (**2**), have been recently synthesized in diastereomerically pure form through an original procedure developed in our laboratories.[6] The peculiarity of the P3Chir ligands is to combine the planar chirality of the ferrocenyl moiety with phosphorus and carbon stereocenters in an unprecedented molecular assembly.

In this paper, we describe the synthesis and characterisation of the first ruthenium(II) complexes with the P3Chir ligands and also report a preliminary study of their use as catalyst precursors for the asymmetric reduction of trifluoroacetophenone by either hydrogenation or hydrogen transfer from *i*PrOH.

Results and Discussion

Synthesis and Characterization of the Dichlororuthenium Complexes

The diastereomeric, mononuclear Ru^{II} complexes [{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}$RuCl_2$] (**3**) and [{$(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir}$RuCl_2$] (**4**) were straightforwardly synthesized by treating $[RuCl_2(PPh_3)_3]$ in toluene with $(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir and $(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir, respectively (Figure 1). Both compounds were isolated in excellent yields as orange solids that are air-stable and soluble in solutions of non-coordinating, non-chlorinated solvents.

The $^{31}P\{^1H\}$ NMR spectroscopic data in [D_4]methanol for all the complexes described in this paper are listed in Table 1, whereas selected ^1H NMR spectroscopic data are reported in the Exp. Sect.

The $^{31}P\{^1H\}$ NMR spectra of **3** and **4** show the presence of several isomers in methanol solution at room temperature, in particular three isomers A/B/C in about a 5:2:1 molar ratio for **3** and four isomers A/B/C/D in about a 6:2:1.5:1 ratio for **4**. Stereochemical nonrigidity, leading to the formation of isomers in solution, is typical for five-coordinate Ru^{II} complexes with linear tridentate phosphane ligands.[7] Irrespective of the complex, the $^{31}P\{^1H\}$ NMR spectrum of each isomer consists of an AMQ pattern with $^2J_{P,P}$ values ranging from 19.2 to 41 Hz, which anticipates a facial (*fac*) arrangement of the tridentate ligands about the metal center (see Table 1 for the labelling scheme).[8,9]

Based on *trans* influence criteria,[3d,4b,7,10] all isomers have been assigned a square-pyramidal coordination geometry with an apical PhP(2) group (Scheme 1), though considerable distortions from an idealized geometry are possible due to the constraints imposed by the polydentate nature of the ligands. Indeed, from a comparison of the $^{31}P\{^1H\}$ NMR spectra of the Ru^{II} complexes **3** and **4** with those of the free ligands,[6] one may readily distinguish the apical phosphorus atoms (with no *trans* ligand) from the phosphorus atom *trans* to the chloride ion that experience a high-field shift of ca. 30−40 ppm, as previously reported for other dichloro(polyphosphane)ruthenium complexes.[3d,9,11] Once disregarded the formation of trigonal-bipyramidal Ru^{II} species, the isomers observed for **3** and **4** are apparently originated by the two chelate rings that may adopt either a boat or envelope conformation in each complex. A similar behaviour has already been observed in other Ru^{II} and Ir^{I} chiral ferrocenyltriphosphane complexes.[4b,12]

3, 4 **5, 6**

S = CH_3CN

Scheme 1

Conductivity measurements show the complexes to behave as non-electrolytes in methanol solution. In CD_3CN solution, the $^{31}P\{^1H\}$ NMR spectra of **3** and **4** are dramatically different from those recorded in [D_4]methanol due to the formation of acetonitrile adducts (see below).[13]

Synthesis and Characterization of the (Acetonitrile)ruthenium Complexes

Complexes **3** and **4** react at very different rates with acetonitrile to give the six-coordinate bis(acetonitrile)chloro

Table 1. $^{31}P\{^1H\}$ NMR spectroscopic data for the ruthenium complexes

Complex[a]	Isomer	δ(P1)	δ(P2)	δ(P3)	$^2J_{P1P2}$	$^2J_{P1P3}$	$^2J_{P2P3}$
3	A	41.48 (dd)	93.25 (dd)	65.38 (*t*)	40.7	27.5	24.0
	B	38.44 (dd)	95.15 (dd)	67.90 (*t*)	36.3	30.0	26.3
	C	35.51 (dd)	96.25 (dd)	60.90 (*t*)	40.0	29.1	22.9
4	A	35.63 (*t*)	100.14 (dd)	67.91 (dd)	37.2	32.0	19.8
	B	38.80 (dd)	106.12 (dd)	79.58 (dd)	41.0	31.9	18.8
	C	36.12 (dd)	104.02 (dd)	70.02 (*t*)	36.1	26.8	19.2
	D	36.91 (*t*)	100.82 (dd)	66.98 (dd)	34.5	29.1	21.3
5		35.92 (*t*)	95.64 (dd)	54.21 (dd)	38.9	32.7	21.2
6		41.21 (*t*)	92.77 (dd)	47.45 (dd)	34.1	31.6	19.2
7		39.03 (*t*)	92.53 (dd)	55.95 (dd)	34.2	33.4	19.6
8		38.65 (*t*)	91.34 (dd)	55.07 (dd)	34.8	29.8	18.8

[a] [D_4]Methanol, 161.98 MHz, 294 K. Chemical shifts in ppm, coupling constants in Hz. The labeling scheme adopted is: P(1) = Cp*P*Ph2, P(2) = *P*Ph, P(3) = *P*Ph_2 (see Figure 1). Isomers concentration A > B > C > D.

cationic derivatives [{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}RuCl-$(CH_3CN)_2$]Cl (**5**) and [{$(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir}RuCl-$(CH_3CN)_2$]Cl (**6**), respectively. Monitoring the reactions by $^{31}P\{^1H\}$ NMR spectroscopy in CD_3CN showed the conversion of **3** to occur within seconds at room temperature. In contrast, the quantitative conversion of **4** into **6** was achieved only by heating the solution at 75 °C for 2 h. In CD_3CN solution at room temperature, **5** and **6** exist as single isomers as shown by the $^{31}P\{^1H\}$ NMR spectra in which canonical AMQ spin systems are displayed,[13] with $^2J_{P,P}$ values indicative of a *fac* arrangement of the triphosphane ligands about the metal center.[8,9] The coordination geometry of **5** and **6** in solution can be established on the basis of the *trans* influence of the coligands discussed above, which decreases in the order $CH_3CN > Cl$.[9,11,14,15] In particular, from a comparison of the ^{31}P NMR chemical shifts in each complex with those observed for the corresponding nuclei in the free ligands and in the dichloro complexes **3** and **4**, the PhP(2) group is assigned a *trans* position to the chloride ion in both **5** and **6** (Scheme 1).

Compounds **5** and **6** behave as 1:1 electrolytes in acetonitrile solution, from which they can be isolated in the solid state by addition of diethyl ether (molar conductance in acetonitrile is 61 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ and 68 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for **5** and **6**, respectively). The IR spectra show weak absorptions in the region 2280−2360 cm^{-1}, where the ν(C≡N) absorption of coordinated CH_3CN is usually observed (see Exp. Sect.).[16] Both **5** and **6** dissolve in methanol generating a dissociation equilibrium concentration with the corresponding dichloro complexes. At room temperature, an approximate 30:70 molar ratio of the bis(acetonitrile) and dichloro complexes was determined on the basis of $^{31}P\{^1H\}$ NMR integration (Scheme 2). $^{31}P\{^1H\}$ NMR spectroscopic data for **5** and **6** in [D_4]methanol are listed in Table 1, whereas selected ^1H NMR spectroscopic data are reported in the Exp. Sect. When CH_3CN is used as solvent the bis(acetonitrile) adducts are stabilized and the equilibrium is completely shifted to the left.

$$\underset{\mathbf{5,\,6}}{[(P3Chir)RuCl(CH_3CN)_2]Cl} \rightleftharpoons \underset{\mathbf{3,\,4}}{(P3Chir)RuCl_2} + 2\,CH_3CN$$

P3Chir = $(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir **3, 5**
P3Chir = $(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir **4, 6**

Scheme 2

The occurrence of the equilibrium shown in Scheme 2 was further substantiated by a ^1H NOESY experiment carried out in [D_4]methanol, where the resonances due to the coordinated acetonitrile molecules can be detected. A section of the ^1H NOESY spectrum of **5** is shown in Figure 2. Strong exchange cross-peaks between coordinated [δ = 1.73 and 1.45 ppm (both s)] and free CH_3CN [δ = 2.06 ppm (s)] molecules are observed together with exchange peaks relating the CHCH_3 signals of **5** [δ = 1.59 ppm (dd)] with those of the A, B and C isomers of **3** [δ = 1.22, 1.16 and 0.94 ppm (all dd), respectively].

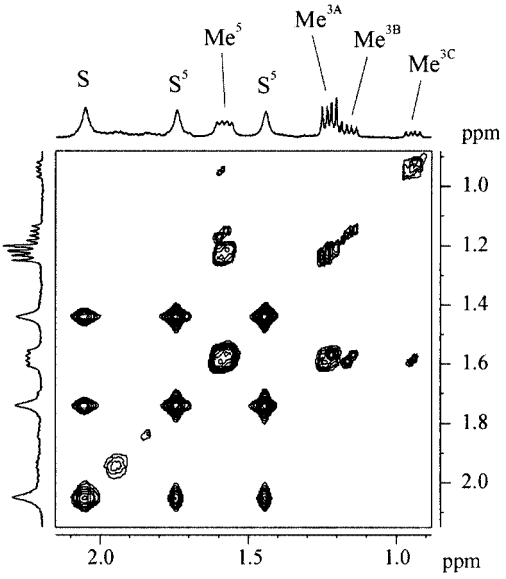


Figure 2. Section of the ^1H NOESY spectrum of **5** ([D_4]methanol, 294 K, 400.13 MHz, τ_m = 0.80 s); signals due to coordinated (S^5) and free (S) CH_3CN molecules and to the CHCH_3 protons of **5** (Me^5) and the A, B and C isomers of **3** (Me^{3A}, Me^{3B}, Me^{3C}) are displayed

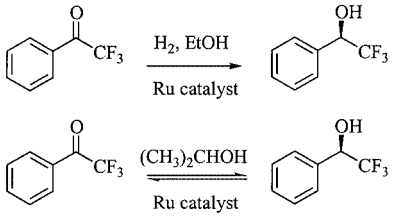
The ^1H and ^{13}C NMR resonances of the acetonitrile molecules in each complex could be unambiguously assigned by means of ^1H,^{13}C correlations. $^{13}C\{^1H\}$ NMR spectroscopic data for **5** and **6** in methanol solution are reported in the Exp. Sect.

The dicationic, tris(acetonitrile) adducts [{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}Ru$(CH_3CN)_3$]$(PF_6)_2$ (**7**) and [{$(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir}Ru$(CH_3CN)_3$]$(PF_6)_2$ (**8**) were obtained as orange microcrystals by treatment of the corresponding dichloro complexes **3** and **4** in CH_3CN with $TlPF_6$. The isolated compounds are quite stable in both the solid state and in deaerated methanol solution. The nujol IR spectra show absorptions in the range 2320−2390 cm^{-1}, characteristic of coordinated CH_3CN molecules (see Exp. Sect.).[16] Compounds **7** and **8** are stereochemically rigid on the NMR timescale at room temperature in [D_4]methanol, as shown by the $^{31}P\{^1H\}$ NMR spectra, which consist of canonical AMQ spin systems. A *fac* arrangement of the triphosphane ligands in the octahedral compounds can be assigned on the basis of the $^2J_{P,P}$ values, which range between 18.8 and 38.9 Hz.[8,9] The preservation of a *fac* arrangement of the tridentate ligand on going from chloro to acetonitrile complexes has been previously reported for other (triphosphane)Ru^{II} complexes.[4b,16a] The ^1H and ^{13}C NMR resonances of the acetonitrile molecules in **7** and **8** were readily assigned using ^1H,^{13}C correlations. The $^{13}C\{^1H\}$ NMR spectroscopic data in [D_4]methanol are reported in the Exp. Sect. Due to the small contribution of a neighbouring anisotropy effect,[9,17] ^{13}C chemical shifts generally provide more direct information concerning the electronic environment of a given ligand than proton shifts do. In the case at hand, the observed low-field shift of 0.43−2.01 ppm for the ^{13}C resonances of the CH_3CN carbon atoms, compared to the corresponding signals of free acetonitrile, is unequivo-

cally indicative of coordinated acetonitrile molecules.[4b,12,18]

Catalytic Reduction of Trifluoroacetophenone

Experiments with 2,2,2-trifluoroacetophenone showed that the Ru^{II} precursors with the P3Chir ligands can form effective asymmetric catalysts for the homogeneous reduction of prochiral ketones to optically pure secondary alcohols by either hydrogenation or hydrogen transfer (Scheme 3 and Table 2).



Scheme 3

The reduction of 2,2,2-trifluoroacetophenone to (*R*)-α-(trifluoromethyl)benzyl alcohol (Scheme 2) is a typical probe reaction to test the efficiency of chiral Ru^{II} catalysts. Indeed, asymmetric reductions of prochiral ketones can be carried out with Ru^{II} compounds through hydrogenation, hydrosilylation or hydrogen transfer. Most examples in the literature involve Ru^{II} complexes stabilised by bidentate ligands with P, N and O donor atoms.[1,19] The reduction of ketones catalyzed by complexes containing tri- and tetradentate ligands has been much less intensely studied.[4b,20]

The hydrogenation reactions were performed in ethanol at 60 °C under a H_2 pressure of 60 atm, while *i*PrOH was the solvent for the hydrogen-transfer reactions which, however, require the addition of *i*PrOK as basic co-catalyst to achieve the reduction of the ketone.[21] Irrespective of the hydrogen source, the yields of (*R*)-α-(trifluoromethyl)benzyl alcohol increased with the number of coordinated acetonitrile molecules in the {$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}ruthenium(II) precursors, which reflects the easier displacement of acetonitrile by the ketone as compared to the chloride ion (Table 2). Under the same experimental conditions, 2,2,2-trifluoroacetophenone was quantitatively hydrogenated after 19 h only with the tris(acetonitrile) complex **7** (Table 2, Entry 3), whereas a 78.7% and 23.4% yield was observed using the bis(acetonitrile) complex **5** and the dichloro complex **3**, respectively (Table 2, Entries 2 and 1). Although the hydrogen-transfer reactions occurred even at room temperature, relatively high temperatures (68 °C) were required to obtain appreciable reaction rates. Again, the best results were obtained with the tris(acetonitrile) complex **7**, which gave a nearly complete conversion of the ketone after 2.5 h (Table 2, Entry 6). Under these conditions, the yield of (*R*)-α-(trifluoromethyl)benzyl alcohol using **5** and **3** were 79.2% and 36.2%, respectively (Table 2, Entries 5 and 4). Besides higher activity, the hydrogen-transfer reactions also gave higher enantioselectivities (38−41%) than the hydrogenation reactions (19−23%). This finding prompted us to investigate the behaviour of the $(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir derivative **8** as a hydrogen-transfer catalyst precursor as well. This latter epimer gave a slightly better productivity than **7** in the same experimental conditions, yet the *ee* was almost negligible (Table 2, Entry 7). To summarise, the ruthenium(II) complexes described in this paper are efficient catalyst precursors either for the hydrogenation and the hydrogen-transfer reactions to prochiral ketones under mild conditions. In general, however, the *ee* values are lower than those achieved with other Ru^{II} chiral catalysts.[21a,22] The above results are consistent with those previously obtained in the transfer hydrogenation to acetophenone mediated by the dicationic Ru^{II} complex with the chiral triphosphane Pigiphos.[4b] This latter compound, however, was found to be the best preformed catalyst precursor containing a chiral tridentate ligand reported so far in terms of enantioselectivity for this reaction.[20d]

From a comparison of the results obtained with the P3Chir and Pigiphos ligands, one can see that the design of chiral tridentate ligands for diverse applications in asymmetric catalysis is still a challenging task. Indeed, other factors besides the presence/absence of C_2 symmetry or geometrical (*mer*/*fac*) isomerism of the tridentate ligand, seem to play an important role in controlling the chiral transfer ability.

Conclusion

Five- and six-coordinate Ru^{II} complexes with the first chiral tridentate phosphane ligands combining planar, phosphorus, and carbon chirality have been synthesized

Table 2. Asymmetric catalytic reduction of 2,2,2-trifluoroacetophenone with Ru^{II} complexes

Entry	Complex	*T* [°C]	Hydrogen source	*t* [h]	Yield [%][a]	*ee* [%][a]
1[b]	[{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}$RuCl_2$] (**3**)	60	H_2, 60 atm	19	22.0	21.9
2[b]	[{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}$RuCl(CH_3CN)_2$]Cl (**5**)	60	H_2, 60 atm	19	77.3	22.8
3[b]	[{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}$Ru(CH_3C)_3$]$(PF_6)_2$ (**7**)	60	H_2, 60 atm	19	99.0	19.0
4[c]	[{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}$RuCl_2$] (**3**)	68	*i*PrOH	2.5	35.3	38.2
5[c]	[{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}$RuCl(CH_3CN)_2$]Cl (**5**)	68	*i*PrOH	2.5	78.7	41.0
6[c]	[{$(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir}$Ru(CH_3CN)_3$]$(PF_6)_2$ (**7**)	68	*i*PrOH	2.5	93.7	40.9
7[c]	[{$(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir}$Ru(CH_3CN)_3$]$(PF_6)_2$ (**8**)	68	*i*PrOH	2.5	98.1	5.0

[a] Isolated yields. [b] Reaction conditions: Ru (0.0022 mmol), solvent ethanol (4 mL), 500 rpm, substrate/Ru mol. ratio 100:1. [c] Reaction conditions: Ru (0.0022 mmol), solvent *i*PrOH (4 mL), substrate/Ru/*i*PrO^-K^+ mol. ratio 100:1:1.

and fully characterized in solution. Irrespective of the co-ligands (chloro or acetonitrile), the absolute configuration of the stereocentres and the temperature, the triphosphane ligands wrap the metal centre in a facial arrangement.

The dichloro, bis(acetonitrile)chloro and tris(acetonitrile) complexes with $(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir and the tris(acetonitrile) complex with $(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir have been tested as catalyst precursors for the reduction of 2,2,2-trifluoroacetophenone to (*R*)-α-(trifluoromethyl)benzyl alcohol by either hydrogenation and hydrogen transfer from *i*PrOH. The catalytic activity was fairly good, particularly using the precursors bearing only acetonitrile co-ligands, yet the asymmetric induction was quite low.

To gain some insight into the chemical and physical factors (ligand conformation, steric and electronic properties of the donor groups) that may control the asymmetric induction by tridentate phosphane complexes, studies are presently ongoing in our laboratories and will be published in due course.

Experimental Section

General Remarks: All manipulations were performed under pure nitrogen unless otherwise stated. Diethyl ether was distilled from Na/benzophenone. Acetonitrile was distilled from CaH_2. Toluene was distilled from sodium. $[RuCl_2(PPh_3)_3]$,[23] $(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir (**1**) and $(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir (**2**)[6] were synthesized as previously reported. Unless otherwise stated, all the other chemicals were obtained from commercial suppliers and were used as received without further purification. The solid compounds were collected on sintered glass frits before being dried in a stream of nitrogen. $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker Avance DRX-400 spectrometer operating at 161.98 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 400.13 and 100.61 MHz, respectively, with a Bruker Avance DRX-400 spectrometer. Chemical shifts are calibrated against solvent resonances. The spectrometer was equipped with a variable-temperature control unit accurate to ±0.1 °C. The assignments of the signals were made from 1D spectra, $^1H\{^{31}P\}$ heteronuclear decoupling experiments, ^1H COSY and proton detected ^1H,^{13}C and ^1H,^{31}P correlations using degassed nonspinning samples. 2D NMR spectra were recorded using pulse sequences suitable for phase-sensitive representations using TPPI. The ^1H,^{13}C and ^1H,^{31}P correlations[24] were recorded using an HMQC sequence with decoupling during acquisition. A standard pulse sequence was used for the ^1H-NOESY[25] experiments. Infrared spectra were recorded with a Perkin−Elmer 1600 Series FT-IR spectrometer using samples mulled in Nujol between KBr plates. Reactions under a controlled pressure of hydrogen were performed with a stainless steel autoclave (10 mL internal volume) constructed at ICCOM-CNR (Firenze, Italy) and equipped with a magnetic stirrer, a Teflon inset and a pressure controller. The temperature control was achieved by an oil-bath thermostat accurate to ±0.2 °C. GC analyses were performed with a Shimadzu GC-17A gas chromatograph equipped with a flame-ionization detector and a 30-m (0.25 mm ID, 0.25 μm FT) SPB-1 Supelco fused-silica capillary column. The *ee* values were determined by GC analyses with a Shimadzu GC-17A gas chromatograph equipped with a flame-ionization detector and a 50 m × 0.25 mm ID Chiraldex G-TA capillary column and coupled with a Shimadzu C-R7A Chromatopac. Conductivities were measured with a Model 990101 Orion conductance cell connected to a Model 101 conductivity meter.

$[\{(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir$\}RuCl_2]$ (3): Solid $[RuCl_2(PPh_3)_3]$ (0.08 g, 0.08 mmol) was added to a solution of **1** (0.06 g, 0.08 mmol) in toluene (3 mL) and the suspension was refluxed with stirring for 3 h. During this time, a red solution was obtained from which red microcrystals separated slowly. After cooling to room temperature, the solid obtained was filtered off and washed with diethyl ether (25 mL). Yield: 62 mg (87%). ^1H NMR ([D$_4$]methanol, 400.13 MHz, 294 K): isomer A: δ = 4.51 (m, 1 H, C_5H_3), 4.18 (m, 1 H, C_5H_3), 3.85 (*s*, 5 H, C_5H_5), 3.63 (m, 1 H, C_5H_3), 3.61 (quint, $^3J_{H,H} = {}^2J_{H,P}$ = 7.0 Hz, 1 H, C*H*CH$_3$), 1.22 (dd, $^3J_{H,H}$ = 6.7, $^3J_{H,P}$ = 12.6 Hz, 3 H, CHC*H*$_3$); isomer B: δ = 4.62 (m, 1 H, C_5H_3), 4.46 (m, 1 H, C_5H_3), 4.07 (s, 5 H, C_5H_5), 3.98 (m, 1 H, C_5H_3), 3.75 (quint, $^3J_{H,H} = {}^2J_{H,P}$ = 7.4 Hz, 1 H, C*H*CH$_3$,), 1.16 (dd, $^3J_{H,H}$ = 6.7, $^3J_{H,P}$ = 12.8 Hz, 3 H, CHC*H*$_3$); isomer C: δ = 4.32 (m, 1 H, C_5H_3), 3.96 (s, 5 H, C_5H_5), 3.69 (m, 1 H, C_5H_3), 2.90 (quint, $^3J_{H,H} = {}^2J_{H,P}$ = 7.1 Hz, 1 H, C*H*CH$_3$), 0.94 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 12.4 Hz, 3 H, CHC*H*$_3$) ppm. $C_{44}H_{41}Cl_2FeP_3Ru$ (890.6): calcd. C 59.34, H 4.64; found C 59.40, H 4.65.

$[\{(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir$\}RuCl_2]$ (4): This compound was prepared as described above for **3** by using $(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir (**2**) instead of $(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir (**1**). Yield: 56 mg (78%). ^1H NMR ([D$_4$]methanol, 400.13 MHz, 294 K): isomer A: δ = 4.31 (s, 5 H, C_5H_5), 0.86 (dd, $^3J_{H,H}$ = 6.7, $^3J_{H,P}$ = 12.5 Hz, 3 H, CHC*H*$_3$); isomer B: δ = 4.52 (s, 5 H, C_5H_5), 1.42 (dd, $^3J_{H,H}$ = 6.8, $^3J_{H,P}$ = 13.2 Hz, 3 H, CHC*H*$_3$); isomer C: δ = 4.25 (s, 5 H, C_5H_5), 1.50 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,P}$ = 13.3 Hz, 3 H, CHC*H*$_3$); isomer D: δ = 4.20 (s, 5 H, C_5H_5), 1.62 (dd, $^3J_{H,H}$ = 7.8, $^3J_{H,P}$ = 13.5 Hz, 3 H, CHC*H*$_3$) ppm. $C_{44}H_{41}Cl_2FeP_3Ru$ (890.6): calcd. C 59.34, H 4.64; found C 59.28, H 4.63.

$[\{(R)_C$-$(S)_{Fe}$-$(S)_P$-P3Chir$\}RuCl(CH_3CN)_2]Cl$ (5): A solution of **3** (0.07 g, 0.08 mmol) in CH_3CN (2 mL) was stirred at room temperature for 1 h. Slow addition of diethyl ether (10 mL) caused the precipitation of an orange solid which was filtered off and washed with diethyl ether (15 mL). Yield: 72 mg (93%). ^1H NMR ([D$_4$]methanol, 400.13 MHz, 294 K): δ = 8.13 (m, 2 H, Ph), 7.91 (m, 2 H, Ph), 7.80 (m, 2 H, Ph), 7.6−7.1 (m, 17 H, Ph), 6.98 (m, 2 H, Ph), 4.86 (m, 1 H, C_5H_3), 4.62 (m, 1 H, C_5H_3), 4.41 (s, 5 H, C_5H_5), 3.80 (quint, $^3J_{H,H} = {}^2J_{H,P}$ = 7.1 Hz, 1 H, C*H*CH$_3$), 3.42 (m, 1 H, C_5H_3), 2.60 (ddddd, $^3J_{H,H}$ = 2.7, $^3J_{H,H}$ = 5.5, $^3J_{H,P}$ = 12.2, $^2J_{H,H}$ = 14.6, $^2J_{H,P}$ = 43.9 Hz, 1 H, PC*H*H), 2.38 (ddddd, $^3J_{H,H}$ = 2.3, $^3J_{H,H}$ = 5.8, $^3J_{H,P}$ = 10.8, $^2J_{H,H}$ = 14.1, $^2J_{H,P}$ = 42.9 Hz, 1 H, PC*H*H), 1.84 (m, 1 H, PCH*H*), 1.73 (s, 3 H, CH_3CN), 1.59 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 13.2 Hz, 3 H, CHC*H*$_3$), 1.45 (s, 3 H, CH_3CN), 0.74 (tdt, $^3J_{H,H}$ = 5.6, $^2J_{H,H}$ = 14.7, $J_{H,P}$ = 19.2 Hz, 1 H, PCH*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_4$]methanol, 100.61 MHz, 294 K): δ = 76.79 (d, $J_{C,P}$ = 7.2 Hz, 1 C, C_5H_3), 70.65 (s, 5 C, C_5H_5), 70.15 (d, $J_{C,P}$ = 7.7 Hz, 1 C, C_5H_3), 68.71 (d, C_5H_3, $J_{C,P}$ = 7.5 Hz, 1 C), 32.00 (d, $^1J_{C,P}$ = 19.9 Hz, 1 C, *C*HCH$_3$), 22.80 (dd, $^1J_{C,P}$ = 34.0, $^2J_{C,P}$ = 10.8 Hz, 1 C, PCH$_2$), 15.70 (dd, $^1J_{C,P}$ = 28.8, $^2J_{C,P}$ = 8.6 Hz, 1 C, PCH$_2$), 13.08 (s, 1 C, CH*C*H$_3$), 1.67 (s, 1 C, *C*H$_3$CN), 1.58 (s, 1 C, *C*H$_3$CN) ppm. $C_{48}H_{47}Cl_2FeN_2P_3Ru$ (972.7): calcd. C 59.27, H 4.87, N 2.88; found C 59.35, H 4.81, N 2.85. IR: $\tilde{\nu}$ = 2319 ν(C≡N) cm^{-1}.

$[\{(R)_C$-$(S)_{Fe}$-$(R)_P$-P3Chir$\}RuCl(CH_3CN)_2]Cl$ (6): A solution of **4** (0.07 g, 0.08 mmol) in CH_3CN (3 mL) was heated with stirring at 70 °C for 2 h. After cooling to room temperature, diethyl ether (15 mL) was added causing the precipitation of an orange solid. This was filtered off and washed with diethyl ether (15 mL). Yield: 66 mg (85%). ^1H NMR ([D$_4$]methanol, 400.13 MHz, 294 K): δ =

8.25 (m, 2 H, Ph), 8.06 (m, 2 H, Ph), 7.63 (m, 2 H, Ph), 7.6−7.2 (m, 17 H, Ph), 7.12 (m, 2 H, Ph), 5.03 (m, 1 H, C_5H_3), 4.44 (m, 1 H, C_5H_3), 4.32 (s, 5 H, C_5H_5), 3.94 (quint, $^3J_{H,H} = {}^2J_{H,P} = 6.8$ Hz, 1 H, C*H*CH_3), 3.29 (m, 1 H, C_5H_3), 2.73 (m, 1 H, PC*H*H), 2.45 (m, 1 H, PC*H*H), 1.87 (m, 1 H, PCH*H*), 1.72 (s, 3 H, CH_3CN), 1.61 (dd, $^3J_{H,H} = 6.8$, $^3J_{H,P} = 13.8$ Hz, 3 H, CHC*H*$_3$), 1.37 (s, 3 H, CH_3CN), 0.88 (m, 1 H, PCH*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_4$]methanol, 100.61 MHz, 294 K): δ = 76.82 (d, $J_{C,P} = 7.3$ Hz, 1 C, C_5H_3), 70.45 (s, 5 C, C_5H_5), 70.22 (d, $J_{C,P} = 7.8$ Hz, 1 C, C_5H_3), 68.69 (d, $J_{C,P} = 7.5$ Hz, 1 C, C_5H_3), 31.88 (d, $^1J_{C,P} = 19.7$ Hz, 1 C, *C*HCH$_3$), 23.30 (dd, $^1J_{C,P} = 33.8$, $^2J_{C,P} = 10.6$ Hz, 1 C, PCH_2), 15.52 (dd, $^1J_{C,P} = 28.6$, $^2J_{C,P} = 8.6$ Hz, 1 C, PCH_2), 12.87 (s, 1 C, CH*C*H$_3$), 1.88 (s, 1 C, *C*H$_3$CN), 1.68 (s, 1 C, *C*H$_3$CN) ppm. $C_{48}H_{47}Cl_2FeN_2P_3Ru$ (972.7): calcd. C 59.27, H 4.87, N 2.88; found C 59.28, H 4.85, N 2.84. IR: $\tilde{\nu}$ = 2323 ν(C≡N) cm^{-1}.

[{(R)$_C$-(S)$_{Fe}$-(S)$_P$-P3Chir}Ru(CH$_3$CN)$_3$](PF$_6$)$_2$ (7): Solid $TlPF_6$ (0.06 g, 0.16 mmol) was added to a solution of **3** (0.07 g, 0.08 mmol) in CH_3CN (5 mL). After stirring for 20 min, the mixture was decanted and TlCl was filtered off. Upon addition of diethyl ether (20 mL) to the resulting solution, orange microcrystals separated. The crystals were filtered and washed with diethyl ether (20 mL). Yield: 175 mg (89%). ^1H NMR ([D$_4$]methanol, 400.13 MHz, 294 K): δ = 7.9−7.8 (m, 4 H, Ph), 7.7−7.4 (m, 12 H, Ph), 7.3−7.1 (m, 9 H, Ph), 5.02 (m, 1 H, C_5H_3), 4.73 (m, 1 H, C_5H_3), 4.46 (s, 5 H, C_5H_5), 4.03 (quint, $^3J_{H,H} = {}^2J_{H,P} = 7.1$ Hz, 1 H, C*H*CH$_3$), 3.70 (m, 1 H, C_5H_3), 2.76 (m, 1 H, PC*H*H), 2.64 (s, 3 H, CH_3CN), 2.44 (m, 1 H, PCH*H*), 2.18 (m, 1 H, PC*H*H), 1.79 (s, 3 H, CH_3CN), 1.65 (dd, $^3J_{H,H} = 7.1$, $^3J_{H,P} = 13.9$ Hz, 3 H, CHC*H*$_3$), 1.54 (s, 3 H, CH_3CN), 1.22 (m, 1 H, PCH*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_4$]methanol, 100.61 MHz, 294 K): δ = 89.77 (m, 1 C, C_5), 84.52 (m, 1 C, C_5), 76.89 (s, 1 C, C_5H_3), 70.81 (s, 5 C, C_5H_5), 70.50 (s, 1 C, C_5H_3), 68.89 (s, 1 C, C_5H_3), 31.59 (d, $^1J_{C,P}$ = 17.7 Hz), 1 C, *C*HCH$_3$, 24.02 (d, $^1J_{C,P} = 42.3$ Hz, 1 C, PCH_2), 15.51 (dd, $^1J_{C,P} = 30.7$, $^2J_{C,P} = 8.6$ Hz, 1 C, PCH_2), 12.46 (s, 1 C, CH*C*H$_3$), 1.72 (s, 1 C, *C*H$_3$CN), 0.95 (s, 1 C, *C*H$_3$CN), 0.87 (s, 1 C, *C*H$_3$CN) ppm. $C_{50}H_{50}F_{12}FeN_3P_5Ru$ (1232.7): calcd. C 48.72, H 4.09, N 3.41; found C 48.69, H 4.02, N 3.52. IR: $\tilde{\nu}$ = 2319, 2388 ν(C≡N), 832 (P−F) cm^{-1}.

[{(R)$_C$-(S)$_{Fe}$-(R)$_P$-P3Chir}Ru(CH$_3$CN)$_3$](PF$_6$)$_2$ (8): Solid $TlPF_6$ (0.03 g, 0.08 mmol) was added to a solution of **4** (0.04 g, 0.04 mmol) in CH_3CN (5 mL). After stirring at 50 °C for 30 min, the mixture was cooled to room temperature, decanted and TlCl was filtered off. Upon addition of diethyl ether (20 mL) to the resulting solution, an orange solid separated which was filtered and washed with diethyl ether (20 mL). Yield: 84 mg (85%). ^1H NMR ([D$_4$]methanol, 400.13 MHz, 294 K): δ = 7.8−7.7 (m, 2 H, Ph), 7.6−7.2 (m, 14 H, Ph), 7.1−7.0 (m, 9 H, Ph), 5.13 (m, 1 H, C_5H_3), 4.44 (m, 1 H, C_5H_3), 4.15 (s, 5 H, C_5H_5), 3.40 (quint, $^3J_{H,H} = {}^2J_{H,P} = 6.5$ Hz, 1 H, C*H*CH$_3$), 2.96 (m, 1 H, C_5H_3), 2.75 (s, 3 H, CH_3CN), 2.50 (m, 1 H, PC*H*H), 2.46 (m, 1 H, PCH*H*), 2.18 (s, 3 H, CH_3CN), 1.78 (m, 1 H, PC*H*H), 1.55 (dd, $^3J_{H,H} = 6.7$, $^3J_{H,P} = 13.7$ Hz, 3 H, CHC*H*$_3$), 1.47 (m, 1 H, PCH*H*), 1.39 (s, 3 H, CH_3CN) ppm. $^{13}C\{^1H\}$ NMR ([D$_4$]methanol, 100.61 MHz, 294 K): δ = 92.10 (m, 1 C, C_5), 87.45(m, 1 C, C_5), 77.02 (s, 1 C, C_5H_3), 69.86 (s, 5 C, C_5H_5), 69.54 (s, 1 C, C_5H_3), 68.74 (s, 1 C, C_5H_3), 32.54 (d, $^1J_{C,P} = 17.8$ Hz, 1 C, *C*HCH$_3$), 25.08 (d, 1 C, PCH_2, $^1J_{C,P} = 41.9$ Hz), 15.47 (dd, $^1J_{C,P} = 30.5$, $^2J_{C,P} = 8.8$ Hz, 1 C, PCH_2), 12.44 (s, 1 C, CH*C*H$_3$), 2.31 (s, 1 C, *C*H$_3$CN), 1.12 (s, 1 C, *C*H$_3$CN), 0.73 (s, 1 C, *C*H$_3$CN) ppm. $C_{50}H_{50}F_{12}FeN_3P_5Ru$ (1232.7): calcd. C 48.72, H 4.09, N 3.41; found C 48.68, H 4.05, N 3.50. IR: $\tilde{\nu}$ = 2321, 2384 ν(C≡N); 840 (P−F) cm^{-1}.

General Procedure for the Reduction of 2,2,2-Trifluoroacetophenone by Hydrogen Transfer: In a typical reaction, a catalyst precursor (0.002 mmol) and freshly distilled 2,2,2-trifluoroacetophenone (28 μL, 0.2 mmol) were introduced under Ar into a flask equipped with a condenser and containing 5 mL of anhydrous *i*PrOH. The mixture was heated at 68 °C with stirring. After 10 min, freshly prepared *i*PrOK (0.1 M in *i*PrOH, 22 μL, 0.002 mmol) was introduced. The addition of *i*PrOK was considered as the starting time of the reaction. The solution was stirred at 68 °C for 3 h. During this time the reaction progress was monitored by GC (SPB-1 capillary column). After cooling the reaction mixture to room temperature, the solvent was removed in vacuo. The residue was dissolved in 1 mL of diethyl ether and chromatographed by short-column chromatography on silica gel using diethyl ether as eluent. The enantiomeric excess was determined on the resulting solution by GC analysis.

General Procedure for the Enantioselective Hydrogenation of 2,2,2-Trifluoroacetophenone: In a typical experiment, a suspension of the catalyst precursor (0.002 mmol) in ethanol (4 mL) was stirred at 60 °C under argon until the complete dissolution of the starting complex occurred (ca. 15 min). 2,2,2-Trifluoroacetophenone (28 μL, 0.2 mmol) was added at room temperature and the resulting solution was transferred via a Teflon capillary into a 10-mL autoclave under argon. Argon was then replaced by hydrogen with three cycles of 5 bar/normal pressure. The autoclave was finally charged with the desired pressure of H_2 and then heated using a thermostatted oil bath with magnetic stirring. After the desired time, the reactor was cooled to room temperature and a sample of the reaction mixture was analyzed by GC.

Acknowledgments

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[13] **3**: $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_3CN, 294 K): $\delta = -36.04$ (*t*, P1), 94.69 (dd, P2), 54.26 (dd, P3), $^2J_{P1P2} = 37.4$, $^2J_{P1P3} = 32.8$, $^2J_{P2P3} = 19.8$ Hz. **4**: $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_3CN, 294 K, after heating at 75 °C for 2 h): $\delta = -40.06$ (*t*, P1), 93.82 (dd, P2), 47.72 (dd, P3), $^2J_{P1P2} = 33.3$, $^2J_{P1P3} = 32.0$, $^2J_{P2P3} = 19.1$ Hz.
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