Journal of Organometallic Chemistry 693 (2008) 2535–2540

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Asymmetric transfer hydrogenation of ketones catalyzed by ruthenium(II) complexes bearing a chiral phosphinoferrocenyloxazoline ligand

Cesar A. Madrigal, Almudena García-Fernández, José Gimeno, Elena Lastra *

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica "Enrique Moles"(Unidad Asociada al C.S.I.C.), Universidad de Oviedo, 33006 Oviedo, Principado de Asturias, Spain

ARTICLE INFO

Article history:
Received 6 February 2008
Received in revised form 21 April 2008
Accepted 21 April 2008
Available online 29 April 2008

Keywords:
Ruthenium(II) catalysts
Asymmetric hydrogen transfer
Ferrocenyl oxazoline
Ferrocenylphosphine
Indenyl complexes
Arene complexes

ABSTRACT

The catalytic activity in asymmetric transfer hydrogenation of ketones using octahedral and half-sandwich (η^5-indenyl and η^6-arene) ruthenium(II) complexes containing the chiral ligand (4*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN) has been explored. Catalytic studies with complex *fac*-[$RuCl_2\{\eta^2(P,N)$-FcPN$\}(PMe_3)_2$] (**1**) show excellent TOF values (9600 h^{-1}). Experiments in the presence of free FcPN, which lead to an increase in conversion rates and ee values when the catalyst is complex [$Ru(\eta^5$-$C_9H_7)\{\kappa^2(P,N)$-FcPN$\}(PPh_3)][PF_6]$ (**4**) have been carried out. The characterization of the new complexes *mer–trans*-[$RuCl_2\{P(OMe)_3\}_2\{\kappa^2(P,N)$-FcPN$\}$] and of the water-soluble complexes *fac*- and *mer–trans*-[$RuCl_2(PTA)_2\{\kappa^2(P,N)$-FcPN$\}$] is also reported.

1. Introduction

Metal catalyzed asymmetric reduction of prochiral ketones has emerged as a very valuable synthetic tool to obtain optically pure substances [1,2]. Ruthenium complexes are among the most efficient catalysts in transfer hydrogenation of ketones [2] displaying excellent performances and asymmetric inductions [3–5]. In particular, ruthenium complexes containing phosphinoferrocenyloxazoline ligands (Fig. 1) featuring substituents in the oxazoline group close to the N donor atom, are especially attractive since they easily allow subtle modifications in the asymmetric induction of the ligand [6].

Besides the outstanding performance of Noyori's catalysts [5] containing chiral ligands with N–H functionalities, the five-coordinate complex [$RuCl_2(PPh_3)\{\kappa^2$-(P,N)-FcPN$\}$] bearing the chiral ligand (4*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN) (Fig. 1) has proven to be one of the best catalysts displaying high ee values and excellent conversions [7].

We have recently reported the diastereoselective synthesis of a number of ruthenium complexes containing the chiral ligand (S_p,*S*)-FcPN of two different types (Fig. 2): (a) six-coordinate complexes [8] of general formula [$RuCl_2L_2$ $\{\kappa^2$-(P,N)-FcPN$\}$] (L = PMe_3 (**1**), PMe_2Ph (**2**), dppm (**3**)) and (b) chiral at metal η^5-indenyl and η^6-arene ruthenium(II) complexes [$Ru(\eta^5$-$C_9H_7)(PPh_3)\{\kappa^2(P,N)$-FcPN$\}][PF_6]$ (**4**), [$RuCl(\eta^5$-$C_9H_7)\{\kappa^2(P,N)$-FcPN$\}$] (**5**) and [$RuX(\eta^6$-arene$)\{\kappa^2(P,N)$-FcPN$\}][PF_6]$ (X = Cl (**6**), H (**7**); arene = *p*-cymene, 1,2,3,4-tetramethylbencene (**8**)) which have been isolated as single diastereoisomers (S_{Ru} for η^5-indenyl complexes and R_{Ru} for η^6-arene complexes) [9].

Herein, we describe the synthesis of new six-coordinate ruthenium(II) complexes *mer–trans*-[$RuCl_2\{P(OMe)_3\}_2\{\kappa^2(P,N)$-FcPN$\}$] (**9**), *mer–trans*-[$RuCl_2(PTA)_2\{\kappa^2(P,N)$-FcPN$\}$] (**10a**) and *fac*-[$RuCl_2(PTA)_2\{\kappa^2(P,N)$-FcPN$\}$] (**10b**) (PTA = 1,3,5-triaza-7-phosphadamantane). The catalytic activity of these complexes in asymmetric transfer hydrogenation of ketones along with that of six-coordinate **1**–**3** and half-sandwich **4**–**8** ruthenium(II) complexes previously reported by us [8,9], is also described.

2. Results and discussion

2.1. Synthesis of *mer–trans*-[$RuCl_2\{P(OMe)_3\}_2\{\kappa^2(P,N)$-FcPN$\}$] (**9**), *mer–trans*-[$RuCl_2(PTA)_2(\kappa^2(P,N)$-FcPN$)$] (**10a**) and *fac*-[$RuCl_2(PTA)_2$-$(\kappa^2(P,N)$-FcPN$)$] (**10b**)

Complex **9** has been prepared (85% yield) stereoselectively from the reaction of the five-coordinate complex [$RuCl_2(PPh_3)\{\kappa^2(P,N)$-FcPN$\}$] [11] with a light excess of $P(OMe)_3$ in CH_2Cl_2 at room temperature (Eq. 1):

* Corresponding author. Tel.: +34 985102995; fax: +34 985103446.
E-mail address: elb@uniovi.es (E. Lastra).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.04.027

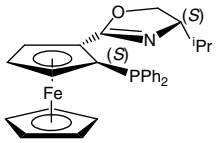


Fig. 1. (4S)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN) ligand.

$$[RuCl_2(PPh_3)\{\kappa^2(P,N)\text{-FcPN}\}] \xrightarrow[CH_2Cl_2,rt]{P(OMe)_3} \textit{mer–trans}\text{-}[RuCl_2\{P(OMe)_3\}_2\{\kappa^2(P,N)\text{-FcPN}\}] \quad (1)$$

Complex **9** is isolated as a yellow solid and has been characterized by elemental analyses and ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy which confirm the proposed formulation and stereochemistry. Thus, the $^{31}P\{^1H\}$ NMR spectrum displays three set of signals expected for a ABX system at 5.6 ($^2J_{PP}$ = 47 and 547 Hz), 117.8 ($^2J_{PP}$ = 65 and 547 Hz) and 136.0 ($^2J_{PP}$ = 47 and 65 Hz) ppm. The high $^2J_{PP}$ value (547 Hz) arises from the *trans* disposition of one of phosphite ligands with respect to the PPh_2 group of the FcPN ligand and is in accordance with a *mer* disposition of the phosphorus atoms. Although these data are consistent with three *mer* stereoisomers (Fig. 3A–C), we tentatively assign the structure *mer–trans* **C** in analogy with that found in the related complex *mer–trans*-[$RuCl_2$(dppm){κ^2(*P,N*)-FcPN}] which has been determined by X-ray crystallography [10].

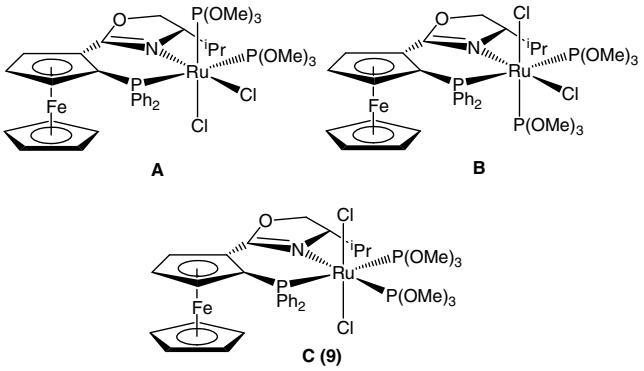
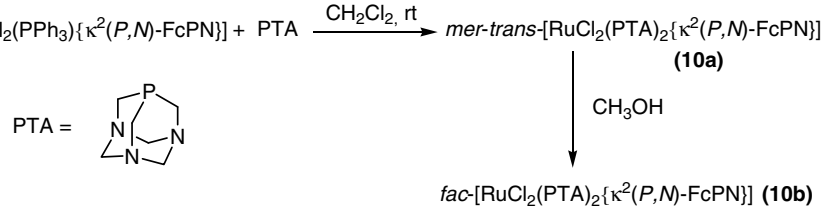


Fig. 3. *mer* stereoisomers for complex **9**.

Following the same synthetic route of **9**, the complex *mer–trans*-[$RuCl_2(PTA)_2\{\kappa^2$ (*P,N*)-FcPN}] (**10a**) has been obtained stereoselectively. Thus, the reaction of complex [$RuCl_2(PPh_3)\{\kappa^2$(*P,N*)-FcPN}] [11] with the water-soluble phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) in CH_2Cl_2 at room temperature affords complex **10a** isolated as an orange solid in 60% yield (Eq. 2):



(2)

Complex **10a** has been characterized by elemental analyses and ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **10a**, which is similar to that of **9**, also exhibits a three set of signals (ABX system), namely, a triplet at 43.6 ($^2J_{PP}$ = 28 Hz) and two doublet of doublets at −54.8 and −72.7 ($^2J_{PP}$ = 319 and 28 Hz, respectively) ppm. As for complex **9**, the formation of the *mer–trans* isomer can be proposed (Fig. 4).

A solution of complex **10a** in methanol affords the isomer *fac*-[$RuCl_2(PTA)_2\{\kappa^2$(*P,N*)-FcPN}] (**10b**) (Fig. 4) [12]. Elemental analysis and spectroscopic data are consistent with the proposed formulation and stereochemistry (see Section 4 for details). In particular,$^{31}P\{^1H\}$ NMR spectrum is very informative showing resonances expected for a ABX system i.e. a doublet of doublets for the PPh_2 group at 37.1 ppm ($^2J_{PP}$ = 34 and 33 Hz), and two triplets for the PTA phosphorous atoms at −30.8 ($^2J_{PP}$ = 33 Hz) and −35.0 ($^2J_{PP}$ = 34 Hz) ppm. These coupling constant values are consistent with a *fac*- disposition of the phosphorus atoms of the ligands. All other signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra are also in accordance with the proposed structure.

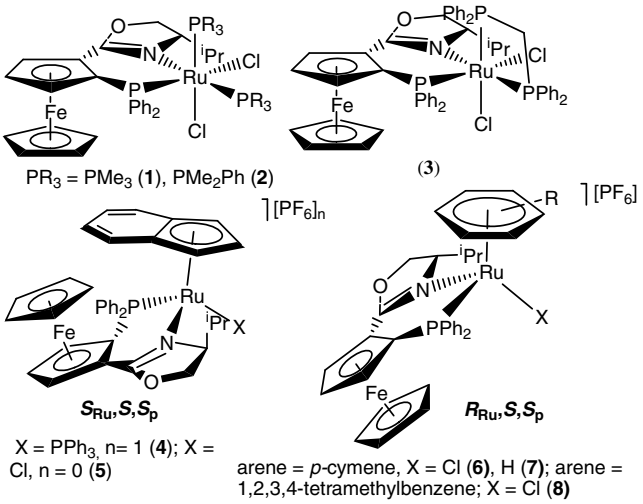


Fig. 2. Six-coordinated and half-sandwich ruthenium(II) complexes.

2.2. Catalytic transfer hydrogenation of acetophenone

The reduction of acetophenone by propan-2-ol was used as a model. In a typical experiment, NaOH was added to a *i*PrOH solution of the ruthenium catalyst precursor (0.2 mol%) and the ketone at 82 °C and the reaction was monitored by gas chromatography.

Table 1 shows the catalytic activity of the studied complexes under optimized reaction conditions.

Octahedral complexes are, in general, better catalysts than half-sandwich complexes. The most remarkable features are (i) very rapid conversions are achieved with catalysts *fac*-[$RuCl_2$(P-$Me_3)_2\{\kappa^2$(*P,N*)-FcPN}] (**1**) and *fac*-[$RuCl_2(PMe_2Ph)_2\{\kappa^2$(*P,N*)-FcPN}] (**2**) (TOF 9600 and 7275 h^{-1}, respectively). The reaction becomes

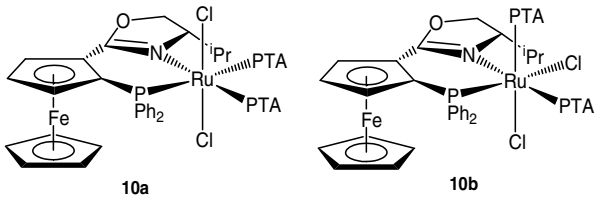


Fig. 4. Ruthenium(II) complexes containing FcPN and PTA ligands.

notably slower as the temperature decreases with no enhancement of the enantioselectivity [13]; (ii) the catalytic activity is dependent on the basicity of the phosphines i.e. *fac*-[$RuCl_2(PMe_3)_2$-{κ^2(*P*,*N*)-FcPN}] (**1**) (entry 1) > *fac*-[$RuCl_2(PMe_2Ph)_2\{\kappa^2(P,N)$-FcPN}] (**2**) (entry 2) > *mer–trans*-[$RuCl_2\{P(OMe)_3\}_2\{\kappa^2(P,N)$-FcPN}] (**9**) (entry 4). It is worth to note the relatively lower activity of the complex *fac*-[$RuCl_2$(dppm){κ^2(*P*,*N*)-FcPN}] (**3**) (entry 3), a fact probably arising from the chelate effect of dppm which is reluctant to generate the required coordination site; (iii) complex **9** featuring a *mer–trans* stereochemistry gives rise to the highest asymmetric induction (ee 94%) (entry 4). This is probably related to the position of the vacant site resulting from the dissociation of the chloride ligand.

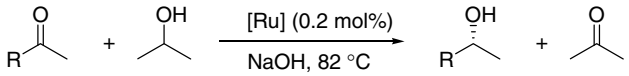
Although complex **10b** containing the hydrosoluble ligand PTA is an active catalyst (entry 5) all attempts to perform the catalysis using water as solvent and sodium formate as hydrogen source [14], failed (3% conversion and no ee was observed after 40 min).

All half-sandwich complexes are active catalysts performing almost quantitative conversion in 40–120 min albeit with moderate ee values (31–76%). (entries 6–10).

Although no mechanistic study was carried out, we believed of interest to find out whether the required coordination vacancy [15] to bind the entering ketones is generated through ligand dissociation. To this regard, a set of experiments in the presence of free phosphines were carried out. Table 2 shows the results in the presence of either the chiral FcPN ligand or PPh_3.

For octahedral **1**, **2** and half-sandwich **5**, **6** catalysts (entries 1–4 and 10–13) no significative change in the ee was observed in the presence of free FcPN. This seems to indicate that no dissociation of the coordinated FcPN ligand takes place. However, the reaction rate decreases due probably to a competition of the added ligand FcPN with the incoming ketone for the vacant coordination site of the catalyst. In contrast, for the cationic complex

Table 1
Catalytic transfer hydrogenation of acetophenone[a]



	Complex	*t* (min)	Conv.[c] (%)	Ee (%)	TOF (h^{-1})[d]
1	*fac*-[$RuCl_2(PMe_3)_2\{\kappa^2(P,N)$-FcPN}] (**1**)[b]	3	96	72 (*R*)	9600
2	*fac*-[$RuCl_2(PMe_2Ph)_2\{\kappa^2(P,N)$-FcPN}] (**2**)[b]	4	97	81 (*R*)	7275
3	*fac*-[$RuCl_2$(dppm)]{κ^2(*P*,*N*)-FcPN} (**3**)	150	92	47 (*R*)	184
4	*mer–trans*-[$RuCl_2\{P(OMe)_3\}_2\{\kappa^2(P,N)$-FcPN}] (**9**)	120	96	94 (*R*)	240
5	*fac*-[$RuCl_2(PTA)_2(\kappa^2(P,N)$-FcPN)] (**10b**)	10	54	23 (*R*)	1633
6	[$Ru(\eta^5$-$C_9H_7)(PPh_3)\{\kappa^2(P,N)$-FcPN}][$PF_6$] (**4**)	120	92	76 (*R*)	230
7	[$RuCl(\eta^5$-$C_9H_7)\{\kappa^2(P,N)$-FcPN}] (**5**)	90	92	31 (*R*)	307
8	[$RuCl(\eta^6$-*p*-cymene){$\kappa^2(P,N)$-FcPN}][PF_6] (**6**)	50	93	47 (*R*)	560
9	[$RuH(\eta^6$-*p*-cymene){$\kappa^2(P,N)$-FcPN}][PF_6] (**7**)	60	91	41 (*R*)	455
10	[$RuCl(\eta^6$-1,2,3,4-tetramethylbenzene){$\kappa^2(P,N)$-FcPN}][PF_6] (**8**)	40	97	43 (*R*)	724

[a] 0.2 mol% catalyst, 0.1 M acetophenone in 50 ml *i*PrOH, 4.8 mol% NaOH.
[b] 2.0 mol% NaOH.
[c] Conversion calculated by GC analyses.
[d] Turnover frequency (mol product/mol Ru/time), calculated at the time indicated in each case.

Table 2
Catalytic transfer hydrogenation of acetophenone in the presence of free phosphine[a]

Entry	Cat.	FcPN (mol%)	PPh_3 (mol%)	*t* (min)	Conv.[c] (%)	Ee (%)	TOF (h^{-1})[d]
1	**1**[b]			3	92	72 (*R*)	9600
2	**1**[b]	0.2		10	94	73 (*R*)	2820
3	**2**[b]			4	97	81 (*R*)	7275
4	**2**[b]	0.2		15	93	82 (*R*)	1860
5	**4**			120	92	76 (*R*)	230
6	**4**	0.2		20	93	86 (*R*)	1395
7	**4**	0.4		20	96	86 (*R*)	1440
8	**4**		0.2	80	94	81 (*R*)	352
9	**4**		0.4	80	94	82 (*R*)	352
10	**5**			90	92	31 (*R*)	307
11	**5**	0.2		120	90	29 (*R*)	225
12	**6**			50	93	47 (*R*)	560
13	**6**	0.2		70	91	46 (*R*)	390

[a] 0.2 mol% catalyst, 0.1 M acetophenone in 50 mL *i*PrOH, 4.8 mol% NaOH.
[b] 2.0 mol% NaOH.
[c] Conversion calculated by GC analyses.
[d] Turnover frequency (mol product/mol Ru/time), calculated at the time indicated in each case.

[Ru(η^5-C_9H_7)(PPh_3){κ^2(*P*,*N*)-FcPN}][PF_6] (**4**), both the reaction rate and the ee values increase upon addition of FcPN (0.2–0.4 mol%) (entries 6 and 7 vs. entry 5). For instance, a conversion of 96% and 86% ee is achieved after 20 min (entry 7) when 0.4 mol% of FcPN is added to the reaction mixture, vs. a conversion of 92% and 76% ee after 120 min in the absence of the free FcPN. Thus, the indenyl complex **4** in the presence of free FcPN is among the most efficient half-sandwich ruthenium(II) catalytic systems reported to date [2,4].

This behaviour is also observed adding PPh_3. This fact is consistent with the liberation of free coordination sites by the indenyl ligand favoured by the well-known ability to undergo a haptotropic η^5-η^3-η^1 slippage [16]. It seems that the added phosphines can favour the stabilization of the coordinatively unsaturated hydride intermediate which is able to induce more rapid conversions (120 vs. 80–20 min) and better asymmetric induction (76% vs. 81–86% ee) (entries 5–9).

2.3. Catalytic transfer hydrogenation of methyl-aryl ketones

The catalytic transformations of a series of methyl-arylketones have also been studied. The results are collected in Table 3.

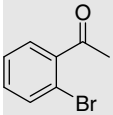
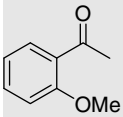
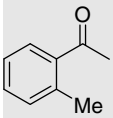
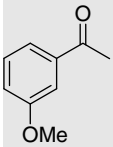
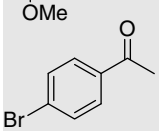
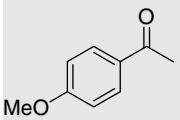
The following features are noteworthy: (i) In general, reactions are slower than those shown in Table 1 for acetophenone; (ii) for all the ketones, the best ee values are obtained using complex *mer*–*trans*-[$RuCl_2${$P(OMe)_3$}$_2${κ^2(*P*,*N*)-FcPN}] **(9)** as catalyst, obtaining ee values up to 92% for 2-acetylanisole and 94% ee for 3-acetylanisole (entries 8 and 18, respectively); (iii) except for the *ortho*-substituted 2′-methylacetophenone (entries 11–15), which undergoes relatively faster conversions (15–60 min), the *para*-substitution (entries 21–30) leads to relatively faster conversions compared with the *ortho* substitution (entries 1–10) due probably to the steric effects involved in the coordination to the active catalytic species.

3. Conclusions

Herein we describe the catalytic activity of six-coordinate and half-sandwich ruthenium(II) complexes containing the chiral ligand (4*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN) in the asymmetric transfer hydrogenation of methyl-aryl ketones with propan-2-ol affording the corresponding *sec*-alcohol. Six-coordinate complexes [$RuCl_2L_2${κ^2(*P*,*N*)-FcPN}] are the most active catalysts with fairly high TOF values (9600 and 7675 h^{-1} for *fac* isomers L = PMe_3(**1**), and PMe_2Ph (**2**), respectively) and moderate ee values (up to 94% using complex *mer*–*trans*-[$RuCl_2${$P(OMe)_3$}$_2${κ^2(*P*,*N*)-FcPN}] (**9**)). Half-sandwich complexes are relatively less active catalysts, best performances being achieved by the cationic complexes [Ru(η^5-C_9H_7)(PPh_3){κ^2(*P*,*N*)-FcPN}][PF_6] (**4**) and [RuCl(η^6-*p*-cymene){κ^2(*P*,*N*)-FcPN}][PF_6] (**6**).

The influence of free phosphines PPh_3 and FcPN on the catalytic activity has been investigated. In particular, a significant increase of conversion rate is observed in the presence of both phosphines leading to excellent TOF values (up to 1440 h^{-1} by using the indenyl complex **4** as catalyst) and ee values up to 86%. These results seem to indicate that (i) the formation of the required coordination vacant is favoured by the indenyl ring and (ii) the coordinatively unsaturated hydride intermediate is stabilized in the presence of the free phosphines allowing a favourable transition state where the substrates are coordinated. In

Table 3
Catalytic transfer hydrogenation of methyl-arylketones[a]

Ketone	Entry	Cat.	*t* (min)	Conv.[c] (%)	Ee (%)	TOF (h^{-1})[d]
	1	**1**[b]	15	42	44 (*R*)	840
	2	**2**[b]	10	28	52 (*R*)	840
	3	**9**	600	93	73 (*R*)	47
	4	**4**	360	7	7 (*R*)	6
	5	**6**	300	31	0	31
	6	**1**[b]	60	95	63 (*R*)	475
	7	**2**[b]	75	94	73 (*R*)	376
	8	**9**	240	97	92 (*R*)	121
	9	**4**	240	97	75 (*R*)	121
	10	**6**	90	96	28 (*R*)	320
	11	**1**[b]	30	98	50 (*R*)	975
	12	**2**[b]	40	99	63 (*R*)	744
	13	**9**	60	98	83 (*R*)	491
	14	**4**	15	97	86 (*R*)	1032
	15	**6**	30	98	37 (*R*)	978
	16	**1**[b]	10	87	71 (*R*)	2610
	17	**2**[b]	5	93	78 (*R*)	5580
	18	**9**	240	92	94 (*R*)	115
	19	**4**	90	94	80 (*R*)	313
	20	**6**	40	92	32 (*R*)	690
	21	**1**[b]	15	93	69 (*R*)	1860
	22	**2**[b]	7	93	73 (*R*)	3986
	23	**9**	5	97	84 (*R*)	5820
	24	**4**	300	94	63 (*R*)	94
	25	**6**	70	96	22 (*R*)	411
	26	**1**[b]	5	64	32 (*R*)	3857
	27	**2**[b]	10	78	65 (*R*)	2341
	28	**9**	60	86	66 (*R*)	430
	29	**4**	390	90	52 (*R*)	69
	30	**6**	180	86	11 (*R*)	144

[a] 0.2 mol% catalyst, 0.1 M acetophenone in 50 mL *i*PrOH. 4.8 mol% NaOH.
[b] 2.0 mol% NaOH.
[c] Conversion calculated by GC analyses.
[d] Turnover frequency (mol product/mol Ru/time), calculated at the time indicated in each case.

such conditions, the indenyl complex **4** is among the most efficient half-sandwich ruthenium(II) catalysts reported to date.

4. Experimental

4.1. General procedures

All manipulations involving organoruthenium complexes were performed under inert atmosphere on nitrogen, using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds *fac*-[$RuCl_2(PR_3)_2\{\kappa^2(P,N)$-FcPN}] ($PR_3 = PMe_3$ (**1**), PMe_2Ph (**2**)) [8], *fac*-[$RuCl_2$(dppm)$\{\kappa^2(P,N)$-FcPN}] (**3**) [8], [Ru(η^5-C_9H_7)$\{\kappa^2(P,N)$-FcPN}(PPh_3)][PF_6] (**4**) [9], [RuCl(η^5-C_9H_7)$\{\kappa^2(P,N)$-FcPN}] (**5**) [9] and [RuX(η^6-arene)$\{\kappa^2(P,N)$-FcPN}][PF_6] (η^6-arene = *p*-cymene, X = Cl (**6**), H (**7**); η^6-arene = 1,2,3,4-tetramethylbenzene, X = Cl (**8**)) [9] were prepared by previously reported methods. [$RuCl_2(PPh_3)$-$\{\kappa^2(P,N)$-FcPN}] [11] and PTA [17] phosphane were prepared according to the literature procedure. All other chemicals were obtained from Aldrich Chemical Co. and Acros Organics and used without further purification. The C, H, and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC-400 instruments at 400.1 MHz (^{1}H), 161.9 (^{31}P) or 100.6 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments were carried out for all the compounds. Abbreviations used: br, broad signal; d, doublet; dd, double doublet; m, multiplet; sept, septuplet; s, singlet; t, triplet. Gas chromatographic measurements were made on Hewlett–Packard HP6890 equipment using a Supelco Beta-Dex 120 (30 m, 250 μm) column.

4.2. Synthesis of mer–trans-[$RuCl_2\{P(OMe)_3\}_2\{\kappa^2(P,N)$-FcPN}] (**9**)

$P(OMe)_3$ (28 μL, 0.24 mmol) was added to a solution of [$RuCl_2(PPh_3)\{\kappa^2(P,N)$-FcPN}] (0.100 g, 0.11 mmol) in dichloromethane (10 mL). The mixture was stirred for 1.5 h at room temperature and then concentrated under vacuum to a volume of approx. 0.5 mL. Addition of hexane afforded a yellow precipitate. The solvents were decanted and the solid was washed with hexane (3 × 20 mL) and dried under reduced pressure to afford complex **9**. Yield: 90 mg (85%). ^{31}P{^{1}H} NMR (CD_2Cl_2, 273 K, δ) 5.6 (dd, PPh_2, $^2J_{PP}$ = 47, 547 Hz), 117.8 (dd, $P(OMe)_3$, $^2J_{PP}$ = 65, 547 Hz), 136.0 (dd, $P(OMe)_3$, $^2J_{PP}$ = 47, 65 Hz) ppm. ^{1}H NMR (CD_2Cl_2, 293 K, δ) 8.71 (m, 2H, Ph), 7.13–7.47 (m, 8H, Ph), 4.94 (m, 1H, C_5H_3), 4.68 (m, 2H, C_5H_3), 4.40 (m, 1H, OCH_2), 4.28 (m, 1H, OCH_2), 4.03 (br, 11 H C_5H_5 $P(OCH_3)_3$), 3.97 (br, 3H, $P(OCH_3)_3$), 3.83 (t, 1H, *CH*N, $^3J_{HH}$ = 9.8 Hz), 3.25 (br, 3H, $P(OCH_3)_3$), 3.20 (br, 3H, $P(OCH_3)_3$), 2.93 (m, 1H, $CH(CH_3)_2$), 1.16 (d, 3H, CH_3, $^3J_{HH}$ = 6.2 Hz), 0.91 (m, 6H, CH_3 y $P(OCH_3)_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ) 168.5 (d, $COCH_2$, $^3J_{CP}$ = 3 Hz), 143.9–126.2 (Ph), 77.1 (br, C_5H_3), 76.2 (d, $CPPh_2$, $^2J_{CP}$ = 22 Hz), 75.7 (m, C_5H_3), 74.1 (d, $CPPh_2$, J_{CP} = 32 Hz), 73.4 (*CH*N), 72.9 (d, C_5H_3, $^2J_{CP}$ = 7 Hz), 72.1 (C_5H_5), 67.3 (OCH_2), 54.9 (br, $P(OCH_3)_3$), 54.8 (br, $P(OCH_3)_3$), 53.3 (m, 2C, $P(OCH_3)_3$), 53.2 (m, 2C, $P(OCH_3)_3$), 28.2 ($CH(CH_3)_2$), 19.4 (CH_3), 16.0 (CH_3) ppm. Anal. Calc. for [$RuCl_2\{P(OMe)_3\}_2$(FcPN)]: C, 45.30; H, 5.14; N, 1.55. Found: C, 45.73; H, 5.20; N, 1.65%.

4.3. Synthesis of mer–trans-[$RuCl_2(PTA)_2\{\kappa^2(P,N)$-FcPN}] (**10a**)

PTA (0.033 g, 0.21 mmol) was added to a solution of [$RuCl_2$ $(PPh_3)\{\kappa^2(P,N)$-FcPN}] (0.100 g, 0.10 mmol) in dichloromethane (10 mL). The mixture was stirred for 2 h at room temperature and then concentrated under vacuum to a volume of approx. 0.5 mL. Addition of hexane afforded an orange precipitate. The solvents were decanted and the solid was washed with hexane (4 × 10 mL) and dried under reduced pressure to afford complex **10a**. Yield: 60 mg (62%). ^{31}P{^{1}H} NMR (CD_2Cl_2, 273 K, δ) 43.6 (t, PPh_2 $^2J_{PP}$ = 28 Hz), −54.8 (dd, PTA, $^2J_{PP}$ = 319, 28 Hz), −72.7 (dd, PTA, $^2J_{PP}$ = 319, 28 Hz) ppm. ^{1}H NMR (CD_2Cl_2, 293 K, δ) 8.00–6.33 (m, 10H, Ph), 5.12 (AB spin system, 3H, PTA, J_{HAHB} = 12 Hz), 4.92 (AB spin system, 3H, PTA, J_{HAHB} = 12 Hz), 4.83–4.36 (m, 18H, C_5H_3, OCH_2, *CH*N and PTA), 4.18 (s, 5H, C_5H_5), 3.83 (AB spin system, 3H, PTA, J_{HAHB} = 16 Hz), 3.69 (AB spin system, 3H, PTA, J_{HAHB} = 16 Hz), 2.36 (m, 1H, $CH(CH_3)_2$), 1.08 (d, 3H, CH_3, $^3J_{HH}$ = 7 Hz), 0.92 (d, 3H, CH_3, $^3J_{HH}$ = 7 Hz) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ) 169.5 ($COCH_2$), 146.1–127.4 (Ph), 86.8 (d, $CPPh_2$, J_{CP} = 37 Hz), 75.9 (C_5H_3), 73.5 (C_5H_3), 72.9 (m, $CCPPh_2$), 72.7 (br, 6C, NCH_2N), 71.9 (C_5H_5), 71.0 (C_5H_3), 69.8 (*CH*N), 67.3 (OCH_2), 50.6 (br, 3C, NCH_2P), 49.8 (br, 3C, NCH_2P), 27.3 ($CH(CH_3)_2$), 19.7 (CH_3), 14.9 (CH_3) ppm. Anal. Calc. for [$RuCl_2(PTA)_2$(FcPN)] · $1.5CH_2Cl_2$: C, 45.52; H, 5.06; N, 8.95. Found: C, 45.01; H, 5.52; N, 9.27%.

4.4. Synthesis of fac-[$RuCl_2(PTA)_2\{\kappa^2(P,N)$-FcPN}] (**10b**)

A solution of *mer–trans*-[$RuCl_2(PTA)_2\{\kappa^2(P,N)$-FcPN}] (100 mg, 0.1 mmol) in CH_3OH (5 mL) was stirred at room temperature for 10 min. The solvent was then removed at reduced pressure and the resulting solid extracted with dichloromethane. The resulting solution was concentrated under vacuum to a volume of approx. 0.5 mL. Addition of hexane afforded an orange precipitate. The solvents were decanted and the solid was washed with hexane (2 × 10 mL) and dried under reduced pressure to afford complex **10b**. Yield: 87 mg (85%). ^{31}P{^{1}H}-NMR (CD_3OD, 293 K, δ) 37.1 (dd, PPh_2 $^2J_{PP}$ = 34, 33 Hz), −30.8 (t, PTA, $^2J_{PP}$ = $^2J_{PP}$ = 33 Hz), −35.0 (t, PTA, $^2J_{PP}$ = $^2J_{PP}$ = 34 Hz) ppm. ^{1}H NMR (CD_2Cl_2, 293 K, δ) 8.82–7.02 (m, 10H, Ph), 5.50 (s, 1H, C_5H_3), 4.91 (s, 1H, C_5H_3), 4.79–3.96 (m, 24H, C_5H_3, OCH_2, *CH*N, PTA), 4.11 (s, 5H, C_5H_5), 3.76 (AB spin system, 3H, J_{HAHB} = 16 Hz, PTA), 3.31 (m, 1H, $CH(CH_3)_2$), 3.11 (AB spin system, 3H, J_{HAHB} = 16 Hz, PTA), 1.10 (d, CH_3, $^3J_{HH}$ = 4 Hz), 0.98 (d, CH_3, $^3J_{HH}$ = 4 Hz) ppm.^{13}C{^{1}H}-NMR (CD_3OD, 293 K, δ) 168.8 ($COCH_2$), 146.4 - 127.7 (Ph), 78.1 (d, $CPPh_2$, J_{CP} = 40 Hz), 74.4 (C_5H_3), 74.3 (d, $OCCCPPh_2$, $^2J_{CP}$ = 17 Hz), 74.0 (d, *CH*N, $^3J_{CP}$ = 4 Hz), 73.6 (C_5H_3), 72.8 (d, $CCPPh_2$, $^2J_{CP}$ = 16 Hz), 72.3 (d, 3C, NCH_2N, $^3J_{CP}$ = 5 Hz), 72.1 (C_5H_5), 71.5 (d, 3C, NCH_2N, $^3J_{CP}$ = 6 Hz), 68.4 (OCH_2), 54.5 (d, 3C, NCH_2P, J_{CP} = 17 Hz), 52.7 (d, 3C, NCH_2P, J_{CP} = 16 Hz), 28.6 ($CH(CH_3)_2$), 18.3 (CH_3), 15.1 (CH_3) ppm. Anal. Calc. for [$RuCl_2(PTA)_2$(FcPN)]: C, 49.65; H, 5.42; N, 10.13. Found: C, 49.21; H, 5.03; N, 9.78%.

4.5. Transfer hydrogenation of ketones ? General procedure

The samples were typically prepared as follows: the ketone (5 mmol), ruthenium catalyst precursor (0.01 mmol, 0.2 mol% of Ru) and propan-2-ol (47 mL) were introduced into a Schlenk tube fitted with a condenser and heated at 82 °C for 15 min in an inert atmosphere. NaOH was then added (3 mL of a 0.08 M solution in propan-2-ol, 4.8 mol%) and the reaction monitored by gas chromatography. The corresponding alcohol and acetone were the only products detected in all cases. The identity of the alcohol was assessed by comparison with commercially available (Aldrich Chemical Co. or Acros Organics) pure samples.

Acknowledgements

This work was supported by the Spanish M.C.T. (BQU2003-00255) Consolider Ingenio 2010 (CSD2007-00006). Cesar A. Madrigal and A. García-Fernández thanks the Spanish Ministerio de Educación, Cultura y Deporte for a scholarship.

References

[1] (a) S.A. Clapham, A. Hadzovic, R.H. Morris, Coord. Chem. Rev. 248 (2004) 2201; (b) R. Noyori, Angew. Chem., Int. Ed. 41 (2002) 2008;

(c) I. Ojima (Ed.), Catalytic Asymmetric Synthesis, 2nd ed., Wiley VCH, 2000;
(d) E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vols. I–III, Springer-Verlag, 1999.
[2] (a) J.S.M. Samec, J.E. Bäckvall, P.G. Andersson, P. Brandt, Chem. Soc. Rev. 35 (2006) 237;
(b) S. Gladiali, E. Alberico, Chem. Soc. Rev. 35 (2006) 226 and references therein.
[3] (a) For recent examples see: W. Baratta, G. Chelucci, E. Herdtweck, S. Magnolia, K. Siega, P. Rigo, Angew. Chem., Int. Ed. 46 (2007) 7651;
(b) W. Baratta, K. Siega, P. Rigo, Chem. Eur. J. 13 (2007) 7479;
(c) W. Baratta, M. Bosco, G. Chelucci, A. Del Zotto, K. Siega, M. Toniutti, P. Rigo, E. Zangrando, P. Rigo, Angew. Chem., Int. Ed. 46 (2007) 7651;
(d) W. Baratta, E. Herdtweck, K. Siega, M. Toniutti, P. Rigo, Organometallics 24 (2005) 1660;
(e) W. Baratta, G. Chelucci, S. Gladiali, K. Siega, M. Toniutti, M. Zanette, E. Zangrando, P. Rigo, Angew. Chem., Int. Ed. 44 (2005) 6214;
(f) D. Cuervo, M.P. Gamasa, J. Gimeno, Chem. Eur. J. 10 (2004) 425;
(g) J. Hannedouche, G.J. Clarkson, M. Wills, J. Am. Chem. Soc. 126 (2004) 986;
(h) C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, J. Chem. Soc., Dalton Trans. (2001) 2989;
(i) T. Langer, G. Helmchen, Tetrahedron Lett. 37 (1996) 1381.
[4] (a) For recent examples in half-sandwich catalysts see: P. Västila, A.B. Zaitsev, J. Wettergren, T. Privalov, H. Adolfsson, Chem. Eur. J. 12 (2006) 3218;
(b) A.M. Hayes, D.J. Morris, G.J. Clarkson, M. Wills, J. Am. Chem. Soc. 127 (2005) 7318;
(c) C. Hedberg, K. Källstrom, P.I. Arvidsson, P. Brandt, P.G. Andersson, J. Am. Chem. Soc. 127 (2005) 15083;
(d) P. Pelagatti, M. Carcelli, F. Calbiani, C. Cassi, L. Elviri, C. Pelizzi, U. Rizzotti, D. Rogolino, Organometallics 24 (2005) 5836.
[5] (a) R. Noyori, M. Yamakawa, S. Hashiguchi, J. Org. Chem. 66 (2001) 7931;
(b) R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97;
(c) K.J. Hashiguchi, S. Haack, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem., Int. Ed. 36 (1997) 285;
(d) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 2521;
(e) S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 117 (1995) 7562.
[6] (a) S. Cabrera, O.G. Mancheno, R.G. Arrayas, I. Alonso, P. Mauleon, J.C. Carretero, Pure Appl. Chem. 78 (2006) 257;
(b) G.C. Fu, Acc. Chem. Res. 37 (2004) 542;
(c) P. Barbaro, C. Bianchini, G. Giambastiani, S.L. Parisel, Coord. Chem. Rev. 248 (2004) 2131;
(d) L.X. Dai, T. Tu, S.L. You, W.P. Deng, X.L. Hou, Acc. Chem. Res. 36 (2003) 659;
(e) T.J. Colacot, Chem. Rev. 103 (2003) 3101.
[7] (a) G. Onodera, Y. Nishibayashi, S. Uemura, Angew. Chem., Int. Ed. 45 (2006) 3819;
(b) Y. Nishibayashi, I. Takei, S. Uemura, M. Hidai, Organometallics 18 (1999) 2291;
(c) Y. Arikawa, M. Ueoka, K. Matoba, Y. Nishibayashi, M. Hidai, S. Uemura, J. Organomet. Chem. 572 (1999) 163;
(d) Y. Nishibayashi, I. Takei, S. Uemura, M. Hidai, Organometallics 17 (1998) 3420;
(e) T. Sammakia, E.L. Stangeland, J. Org. Chem. 62 (1997) 6104.
[8] J. Gimeno, E. Lastra, C. Madrigal, C. Graiff, A. Tiripicchio, J. Organomet. Chem. 637–639 (2001) 463.
[9] A. Garcia-Fernandez, J. Gimeno, E. Lastra, C. Madrigal, C. Graiff, A. Tiripicchio, Eur. J. Inorg. Chem. (2007) 732.
[10] J. Gimeno, E. Lastra, C. Madrigal, C. Graiff, A. Tiripicchio, J. Organomet. Chem. 663 (2002) 204.
[11] Y. Arikawa, M. Ueoka, K. Matoba, Y. Nishibayashi, M. Hidai, S. Uemura, J. Organomet. Chem. 572 (1999) 163.
[12] Complex **10b** is also obtained from CH_2Cl_2 solutions of complex **10a** after a week.
[13] For instance, using *fac*-[$RuCl_2(PMe_3)_2\{\kappa^2(P,N)$-FcPN}] (**1**) as catalyst 94% conversion and 66% ee was achieved at 65 °C after 25 min (6% conversion and 11% ee at 20 °C after 8 h).
[14] (a) C.A. Mebi, R.P. Nair, B.J. Frost, Organometallics 26 (2007) 429;
(b) X. Wu, J. Xiao, Chem. Commun. (2007) 2449;
(c) H.Y. Rhyoo, H.-J. Park, W.H. Suh, Y.K. Chung, Tetrahedron Lett. 43 (2002) 269;
(d) A. Schlatter, M.K. Kundu, W.-D. Woggon, Angew. Chem., Int. Ed. 43 (2004) 6731.
[15] (a) J.S.M. Samec, J.E. Bäckvall, P.G. Andersson, P. Brandt, Chem. Soc. Rev. 35 (2006) 237;
(b) J.E. Bäckvall, J. Organomet. Chem. 652 (2002) 105;
(c) O. Pàmies, J.E. Bäckvall, Chem. Eur. J. 7 (2001) 5052;
(d) Y.R.S. Laxmi, J.E. Bäckvall, Chem. Commun. (2000) 611;
(e) A. Aranyos, G. Csjernyik, K.J. Szabó, J.E. Bäckvall, Chem. Commun. (1999) 351.
[16] Complete dissociation of the indenyl ring cannot be discarded.
[17] D.J. Daigle, Inorg. Synth. 32 (1998) 40.