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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

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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).

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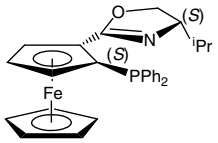


Fig. 1. (4S)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN) ligand.

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

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].

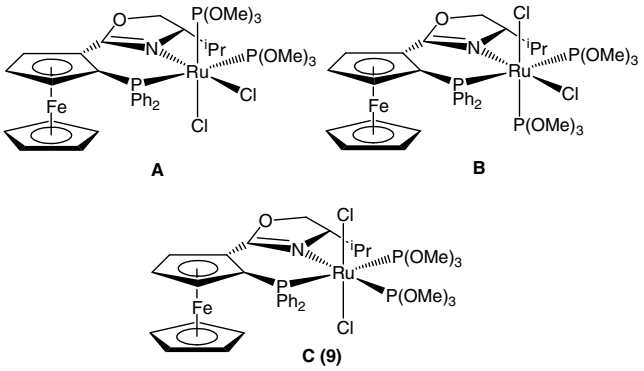
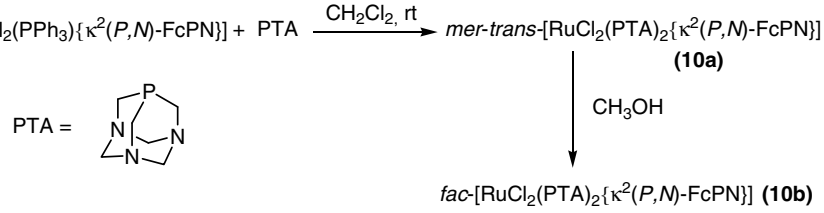


Fig. 3. *mer* stereoisomers for complex **9**.

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.

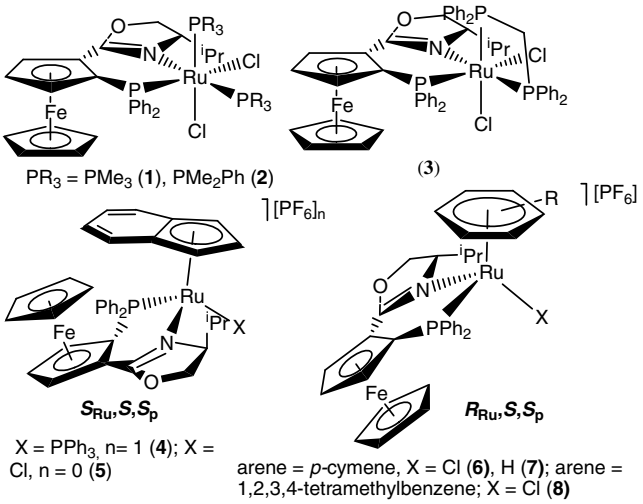


Fig. 2. Six-coordinated and half-sandwich ruthenium(II) complexes.

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