Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 663 (2002) 204–212

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

New ruthenium(II) complexes containing the chiral ligand (4*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(methylethyl)oxazoline (FcPN). X-ray structures of *mer–trans*-[$RuCl_2$(dppm)(FcPN)] (dppm = bis(diphenylphosphino)methane) and *cis*-[$RuCl_2$(CO)(py)(FcPN)]

José Gimeno [a,*], Elena Lastra [a], César Madrigal [a], Claudia Graiff [b], Antonio Tiripicchio [b,*]

[a] *Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al C.S.I.C.), 33006 Oviedo, Spain*

[b] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17A, 43100 Parma, Italy*

Received 4 June 2002; accepted 23 September 2002

Dedicated to Professor Pascual Royo in recognition of his pioneering work and leadership in the field of Organometallic Chemistry in Spain

Abstract

fac–mer Isomerization processes of octahedral ruthenium(II) complexes [$RuCl_2$(dppm)(FcPN)] containing the chelate ligands (4*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(methylethyl)oxazoline (FcPN) and bis(diphenylphosphino)methane (dppm) are described. A five-coordinate intermediate [RuCl(dppm)(FcPN)][Cl] involved in this isomerization was isolated as its hexafluorophosphate salt. The alkynyl complex *mer*-[RuCl($C{\equiv}CC_6H_4CH_3$-4)(dppm)(FcPN)] (**4**) has been prepared by reaction of *fac*-[$RuCl_2$(dppm)(FcPN)] with $LiC{\equiv}CC_6H_4CH_3$-4. Azide complexes *fac*-[$Ru(N_3)_2(PR_3)_x$(FcPN)] (R = Ph, $x = 1$ (**5**), R = Me, $x = 2$ (**6**)) have also been prepared by treatment with NaN_3 of [$RuCl_2(PPh_3)$(FcPN)] and *fac*-[$RuCl_2(PMe_3)_2$(FcPN)], respectively. Bubbling CO through a dichloromethane solution of the five-coordinate complex [$RuCl_2(PPh_3)$(FcPN)] leads to [$RuCl_2(CO)(PPh_3)$(FcPN)] (**7**) which undergoes phosphine exchange with pyridine to yield *cis*-[$RuCl_2$(CO)(py)(FcPN)] (**8**). Reaction of **7** with dppm in the presence of $NaPF_6$ gives the cationic complex [RuCl(CO)(dppm)(FcPN)][PF_6] (**9**). X-ray structures of the complexes *mer–trans*-[$RuCl_2$(dppm)(FcPN)] (**1**) and *cis*-[$RuCl_2$(CO)(py)(FcPN)] (**8**) are also reported.

Keywords: Ruthenium(II); Chiral ligand; Ferrocenylphosphine; Ferrocenyloxazoline

1. Introduction

Metal mediated asymmetric catalysis has emerged as a synthetic tool to obtain enantiomerically pure substances [1]. In particular, ruthenium complexes containing chiral phosphinoferrocenyloxazolines as ligands [2] have proven to be good catalysts in reactions such as hydrosilylation [3] or transfer hydrogenation [4]. However, most of the active species have been formed "in situ" and therefore their coordination chemistry has been scarcely studied.

Recently we have reported the stereoselective synthesis of the complex *fac*-[$RuCl_2$(dppm)(FcPN)], the first octahedral ruthenium complex containing the chiral ligand (4*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(methylethyl)oxazoline (FcPN) [5]. Here we report the synthesis and characterization of further FcPN ruthenium chiral complexes potentially useful in catalytic

* Corresponding authors. Tel.: +34-98-510-3461; fax: +34-98-510-3446

E-mail addresses: jgh@sauron.quimica.uniovi.es (J. Gimeno), tiri@unipr.it (A. Tiripicchio).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)01963-0

reactions. These include: (a) five-coordinate species [RuCl(dppm)(FcPN)][PF_6] (**3**) and [Ru(N_3)$_2$(PPh_3)(FcPN)] (**5**) and (b) octahedral complexes *mer*-[RuClX(dppm)(FcPN)] (X = Cl (**1** and **2**), C≡$CC_6H_4CH_3$-4 (**4**)), *fac*-[Ru(N_3)$_2$(PMe_3)$_2$(FcPN)] (**6**), [RuCl_2(CO)(L)(FcPN)] (L = PPh_3 (**7**), py (**8**)), and [RuCl(CO)(dppm)(FcPN)][PF_6] (**9**).

2. Results and discussion

2.1. Synthesis and reactivity of mer–trans-[RuCl$_2$(dppm)(FcPN)] (1) and mer–cis-[RuCl$_2$(dppm)(FcPN)] (2)

We have previously reported [5] the synthesis of the *mer*- and *fac*-complexes [RuCl_2(dppm)(FcPN)] and the X-ray structure of the *fac* isomer. The former is formed at room temperature from the reaction of the five-coordinated complex [RuCl_2(PPh_3)(FcPN)] with dppm in CH_2Cl_2. The *fac* isomer is obtained from a methanol solution of **1**, followed by recrystallization in CH_2Cl_2 of the solid residue obtained by evaporation of the methanol (Eq. (1)).

$$[\mathrm{RuCl_2(PPh_3)(FcPN)}] \xrightarrow[\mathrm{dppm}]{\mathrm{CH_2Cl_2}} mer\text{-}[\mathrm{RuCl_2(dppm)(FcPN)}]_{(1)} \xrightarrow[\mathrm{ii.\ CH_2Cl_2}]{\mathrm{i.\ MeOH}} fac\text{-}[\mathrm{RuCl_2(dppm)(FcPN)}] \quad (1)$$

These isomers are obtained as the kinetic (*mer*) and thermodynamic (*fac*) controlled products. The *mer* isomer **1** (three stereoisomers are possible) has been now fully characterized by X-ray diffraction methods as the *mer*–*trans* complex.

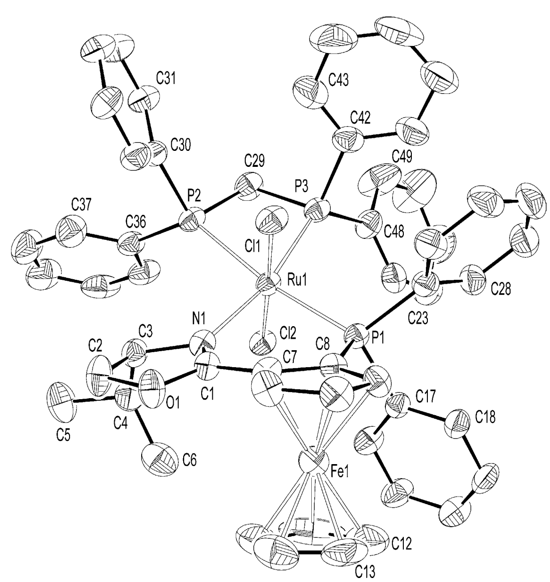


Fig. 1. Perspective view of the complex **1** with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Cl(1)–Ru(1)	2.407(2)	C(3)–N(1)	1.495(7)
Cl(2)–Ru(1)	2.427(2)	C(3)–C(4)	1.521(8)
N(1)–Ru(1)	2.154(4)	C(4)–C(6)	1.536(10)
P(1)–Ru(1)	2.367(2)	C(4)–C(5)	1.542(10)
P(2)–Ru(1)	2.395(2)	C(7)–C(8)	1.436(8)
P(3)–Ru(1)	2.287(2)	C(8)–P(1)	1.832(6)
Fe(1)–M(1)	1.648(5)	C(17)–P(1)	1.850(6)
Fe(1)–M(2)	1.659(5)	C(23)–P(1)	1.834(6)
C(1)–N(1)	1.289(7)	C(29)–P(3)	1.841(6)
C(1)–O(1)	1.352(7)	C(29)–P(2)	1.823(7)
C(1)–C(7)	1.465(8)	C(30)–P(2)	1.831(6)
C(2)–O(1)	1.453(7)	C(36)–P(2)	1.852(7)
C(2)–C(3)	1.528(9)	C(42)–P(3)	1.824(7)
		C(48)–P(3)	1.836(7)
Bond angles			
N(1)–C(1)–O(1)	118.3(5)	P(3)–Ru(1)–Cl(1)	92.52(6)
N(1)–C(1)–C(7)	129.0(5)	P(1)–Ru(1)–Cl(1)	83.03(6)
O(1)–C(1)–C(7)	112.7(5)	P(2)–Ru(1)–Cl(1)	92.84(6)
O(1)–C(2)–C(3)	104.8(5)	N(1)–Ru(1)–Cl(2)	93.36(14)
N(1)–C(3)–C(2)	103.7(5)	P(3)–Ru(1)–Cl(2)	88.36(6)
N(1)–C(3)–C(4)	112.6(5)	P(1)–Ru(1)–Cl(2)	97.88(5)
C(2)–C(3)–C(4)	115.5(6)	P(2)–Ru(1)–Cl(2)	86.38(6)
C(8)–C(7)–C(1)	127.6(5)	Cl(1)–Ru(1)–Cl(2)	178.60(6)
C(7)–C(8)–P(1)	124.8(4)	M(1)–Fe(1)–M(2)	174.96(4)
P(3)–C(29)–P(2)	97.4(3)	C(8)–P(1)–Ru(1)	107.68(19)
N(1)–Ru(1)–P(3)	167.62(12)	C(29)–P(2)–Ru(1)	91.7(2)
N(1)–Ru(1)–P(1)	91.23(13)	C(29)–P(3)–Ru(1)	94.7(2)
P(3)–Ru(1)–P(1)	100.69(6)	C(1)–N(1)–C(3)	106.3(5)
N(1)–Ru(1)–P(2)	95.85(13)	C(1)–N(1)–Ru(1)	126.0(4)
P(3)–Ru(1)–P(2)	72.00(6)	C(3)–N(1)–Ru(1)	125.3(4)
P(1)–Ru(1)–P(2)	171.52(6)	C(1)–O(1)–C(2)	105.9(5)
N(1)–Ru(1)–Cl(1)	85.55(14)		

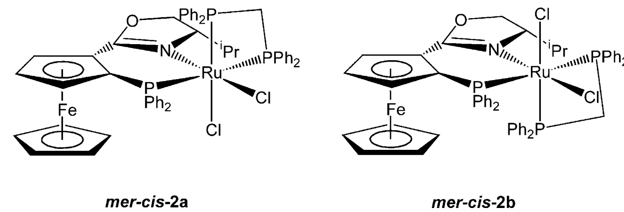
M(1) is the centroid of the Cp ring C(7) C(8) C(9) C(10) C(11). M(2) is the centroid of the Cp ring C(12) C(13) C(14) C(15) C(16).

Fig. 1 shows a view of the structure of complex **1** together with the atomic numbering system; selected bond distances and angles are given in Table 1.

The Ru atom is octahedrally coordinated by the P1 and N1 atoms of the chelating ligand FcPN, by two Cl atoms, in *trans* positions, and by two P atoms from the dppm ligand; the three P atoms are in a *mer* configuration. The six-membered ring formed by the chiral FcPN ligand with the Ru atom shows an envelope conformation [the Ru1 atom is out of 0.835(1) Å from the mean plane passing through the other five atoms]. The Ru–P(1) and Ru–P(2) bond distances involving two P atoms *trans* to one another are comparable [2.367(2) and 2.395(2) Å, respectively], and are longer than the Ru–P(3) one [2.287(2) Å], *trans* to the N1 atom of the oxazoline ring [Ru–N1 = 2.154(4) Å]. The Ru–Cl bond distances, involving the two Cl atoms in *trans*, 2.407(2) and 2.427(2) Å, are very similar. In the *fac*–*cis*-isomer [5] the two Ru–Cl distances, with the Cl atoms in *cis* positions, are again comparable, 2.455(2) and 2.462(2) Å, even if longer than those found in **1**. The Ru–P3 bond distance, 2.288(2) Å, with P(3) *trans* to N1 atom is very similar to that found in **1**, whereas the two Ru–P1 and Ru–P2 bond distances, both *trans* to Cl atoms, are very similar, 2.328(2) and 2.297(2) Å, respectively, but shorter than those found in **1** where the two atoms were *trans* to one another. Finally the Ru–N1 bond distance, 2.208(6) Å, was found to be longer than that in **1**. The bite angle of the chelating diphosphine ligand is narrow, 72.00(6)°, as in the *fac–cis*-isomer, 72.9(7)° due to the strained four member ring. The oxazoline ring in **1** presents an envelope conformation with C2 atom deviating of 0.151(1) Å from the mean plane defined by C1,N1,O1,C3. The absolute configuration of the chiral C3 atom is *S*, and that of the chiral plane is S_p.

As expected from its kinetic stability, the *mer–trans* isomer (**1**) is prone to undergo further isomerizations. Thus, the irradiation of a dichloromethane solution of **1** for 10 h at −20 °C gives complex *mer–cis*-[$RuCl_2$(dppm)(FcPN)] (**2**) (Scheme 1) as a yellow air stable solid (65%).

Complex **2** has been characterized by elemental analyses and ^{1}H- and ^{31}P{H}-NMR spectroscopy which confirms the *trans–cis* isomerization of the chloride ligands. Thus, ^{31}P{H}-NMR spectrum display the expected resonances for a *mer* disposition (ABX system) at δ −25.99 ($^2J_{PP}$ = 24.0, 375.2 Hz), 1.94 ($^2J_{PP}$ = 24.0, 34.1 Hz), 18.08 ($^2J_{PP}$ = 34.1, 375.2 Hz), which can be compared to those shown by the parent complex **1** ($^2J_{PP}$ = 36.6, 345.5 Hz). Although two stereoisomers *mer–cis*-**2a** and *mer–cis*-**2b** are consistent with these

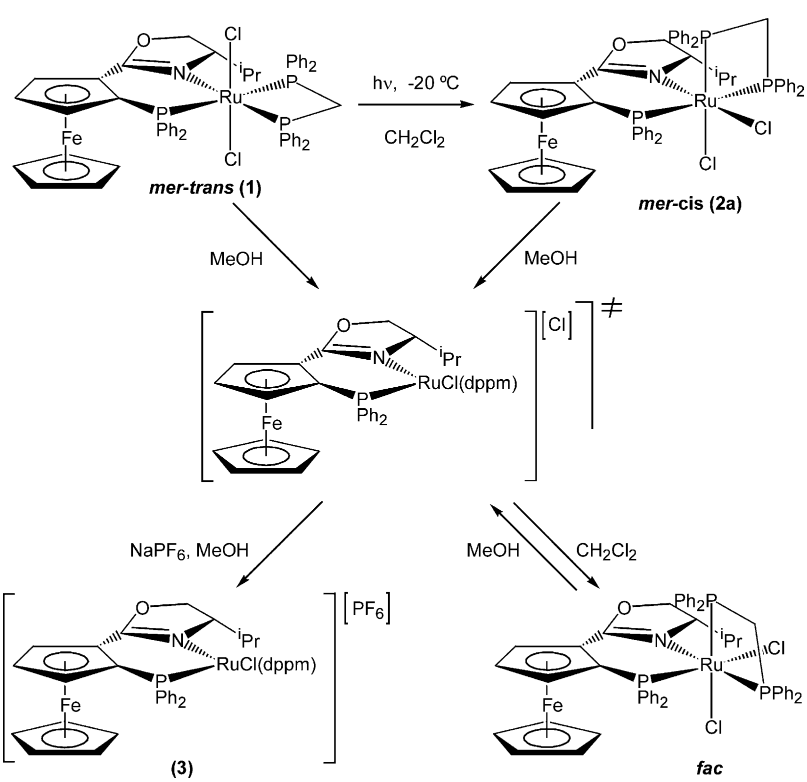


Scheme 2.

data (Scheme 2), the steric demanding of the isopropyl and ferrocenyl groups probably favours the structure of **2a**. This disposition minimizes the steric repulsion of the bulky phenyl groups of dppm with the isopropyl and ferrocenyl groups of FcPN since they are located relatively far away from each other.

As has been noted in Eq. (1), complex *fac*-[$RuCl_2$(dppm)(FcPN)] is isolated from a MeOH solution of **1**. The role of MeOH in this *mer* to *fac* thermodynamically favourable isomerization seems to indicate that it proceeds through the formation of a non-rigid five-coordinate complex generated in solution by dissociation of a chloride ligand (Scheme 1). This is supported by conductivity measurements of *fac* and *mer* isomers in methanol which show high values compared to neutral complexes [6].

The existence of the cationic complex is assessed by the addition of one equivalent of $NaPF_6$ to the MeOH solution of **1** which affords the complex [RuCl(dppm)(FcPN)][PF_6] (**3**) (Scheme 1), isolated as a



Scheme 1.

yellow air-stable solid. Elemental analyses, conductivity measurements in acetone (137.96 Ω^{-1} cm^2 mol^{-1}) and NMR spectroscopic data support this formulation. Thus, ^{31}P{^{1}H}-NMR spectrum of complex **3** shows resonances expected for a ABX system at δ −7.63 ($^2J_{PP}$ = 40.4, 62.1 Hz), 9.02 ($^2J_{PP}$ = 40.4, 62.1 Hz), 67.73 ($^2J_{PP}$ = 40.4 Hz) similar to those found for the methanol solutions of the octahedral isomers [7] indicating the formation of analogous five-coordinate species (Scheme 1).

2.2. Chloride substitution reactions

The ability of complex *fac*-[RuCl$_2$(dppm)(FcPN)] to dissociate the chloride ligand prompted us to explore nucleophilic substitution reactions. Thus, the reaction of *fac*-[RuCl$_2$(dppm)(FcPN)] with LiC≡CC$_6$H$_4$CH$_3$-4 (prepared in situ) at −20 °C in THF gives the acetylide complex *mer*-[RuCl(η^1-C≡CC$_6$H$_4$CH$_3$-4)(dppm)(Fc-PN)] (**4**) (Eq. (2)).

$$fac\text{-}[\mathrm{RuCl_2(dppm)(FcPN)}] \xrightarrow[-20\ ^\circ\mathrm{C,\ THF}]{\mathrm{LiC{\equiv}CC_6H_4CH_3\text{-}4}} mer\text{-}[\mathrm{RuCl}(\eta^1\text{-}\mathrm{C{\equiv}CC_6H_4CH_3\text{-}4})(\mathrm{dppm})(\mathrm{FcPN})]\ \underset{}{\mathbf{(4)}} \tag{2}$$

Complex **4** was characterized by conventional analytical and spectroscopic methods. IR spectrum (KBr) shows the expected weak ν(C≡C) absorption at 2067 cm^{-1}. The ^{31}P{^{1}H} spectrum shows three resonances at δ −20.63 ($^2J_{PP}$ = 40.7, 321.4), 11.72 ($^2J_{PP}$ = 40.7, 36.6), and 22.54 ($^2J_{PP}$ = 36.6, 321.4) indicating that a *fac*–*mer* isomerization has occurred.

Similarly, complexes [Ru(N$_3$)$_2$(PPh$_3$)(FcPN)] (**5**) and *fac*-[Ru(N$_3$)$_2$(PMe$_3$)$_2$(FcPN)] (**6**) are prepared by reactions of the five-coordinate complex [RuCl$_2$(PPh$_3$)(FcPN)] and *fac*-[RuCl$_2$(PMe$_3$)$_2$(FcPN)] with sodium azide (74 and 70% yield, respectively) (Eq. (3)).

$$[\mathrm{RuCl_2(PPh_3)(FcPN)}] \xrightarrow[\mathrm{CH_2Cl_2/MeOH}]{\mathrm{NaN_3}} [\mathrm{Ru(N_3)_2(PPh_3)(FcPN)}]\ \mathbf{(5)}$$
$$fac\text{-}[\mathrm{RuCl_2PMe_3)_2(FcPN)}] \xrightarrow[\mathrm{CH_2Cl_2/MeOH}]{\mathrm{NaN_3}} fac\text{-}[\mathrm{Ru(N_3)_2(PMe_3)(FcPN)}]\ \mathbf{(6)} \tag{3}$$

The analytical and spectroscopic data of **5** and **6** agree with the proposed structures (see Section 3) and seem to indicate that no isomerization process takes place in the course of the substitution reactions.

2.3. Synthesis of carbonyl complexes [RuCl$_2$(CO)(PPh$_3$)(FcPN)] (7) [RuCl$_2$(CO)(py)(FcPN)] (8), and [RuCl(CO)(dppm)(FcPN)][PF$_6$] (9)

When CO was bubbled through a THF solution of [RuCl$_2$(PPh$_3$)(FcPN)], the octahedral carbonyl complex [RuCl$_2$(CO)(PPh$_3$)(FcPN)] (**7**) is formed as expected from the coordinative unsaturation of the precursor complex (Eq. (4)). Complex **7** is isolated (82%) as an air stable solid, slightly soluble in THF and toluene and unsoluble in diethyl ether and hexane.

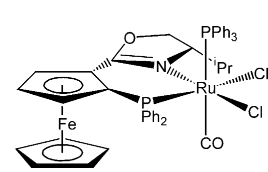
$$[\mathrm{RuCl_2(PPh_3)(FcPN)}] \xrightarrow[\mathrm{THF}]{\mathrm{CO}} [\mathrm{RuCl_2(CO)(PPh_3)(FcPN)}]_{\mathbf{(7)}} \xrightarrow{\mathrm{py}} [\mathrm{RuCl_2(CO)(py)(FcPN)}]\ \mathbf{(8)} \tag{4}$$

The IR spectrum in Nujol shows one strong ν(CO) band at 1987 cm^{-1} and two Ru–Cl weak bands at 311 and 273 cm^{-1} indicating that the two chloride ligands are located *cis* each other. The ^{31}P{^{1}H}-NMR shows two doublets at δ 31.95 and 1.44 ($^2J_{PP}$ = 27.2 Hz), indicating a *cis* disposition of the two phosphorus atoms. Although these data are consistent with various isomers, X-ray structure for analogous pyridine derivative (see below) allows tentative assignment of the structure of complex **7** as shown in Scheme 3.

The treatment of **7** with pyridine leads the substitution of the triphenylphosphine to give complex [RuCl$_2$(CO)(py)(FcPN)] (**8**) (Eq. (4)), which was characterized by conventional analytical and spectroscopic methods. IR spectrum (KBr) shows the ν(CO) band at 1954 cm^{-1}. ^{31}P{^{1}H}-NMR spectrum shows a singlet at δ 42.65 and ^{13}C{^{1}H}-NMR spectrum shows the carbonyl resonance as a doublet at δ 206.26 ($^2J_{CP}$ = 15.9 Hz), indicating a *cis* disposition of the phosphine and the CO. Due to the existence of more than one possible isomer for this complex, with the CO group *cis* to the PPh$_3$, an X-ray diffraction analysis was carried out.

Fig. 2 shows the structure of the complex together with the atomic numbering system; selected bond distances and angles are given in Table 2.

The Ru atom is octahedrally coordinated by the P1 and N1 atoms of the chelating ligand FcPN, by two Cl atoms, in *cis* positions, by the N2 atom of the pyridine and by the C22 atom of a terminal carbonyl. The Py and CO ligands are in *trans* positions occupying the axial coordination sites with the Cl1,Cl2,N1,P1 atoms the equatorial ones. The six-membered ring formed by the



Scheme 3.

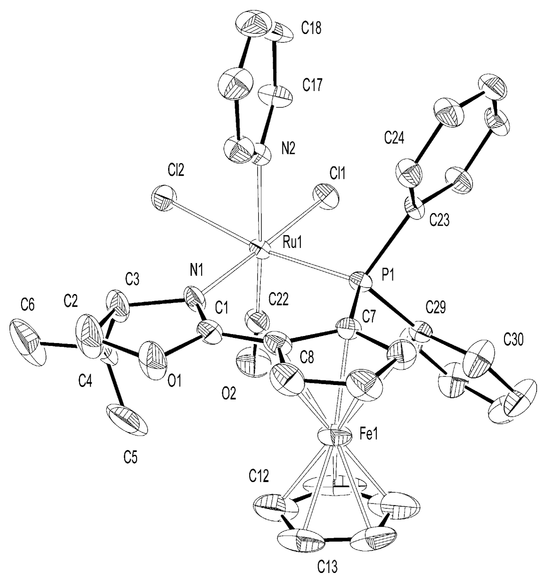


Fig. 2. Perspective view of the compound **8** with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

chiral FcPN ligand with the Ru atom is nearly planar being the Ru atom out only 0.170(1) Å from the mean plane passing through the other five atoms. The Ru1–P1 and Ru1–N1 bond distances involving the FcPN ligand [2.297(1) and 2.118(4) Å, respectively], both in *trans* with respect to Cl atoms, are shorter than those found in **1** (2.367(2) and 2.154(4) Å, respectively), both in *trans* with respect to P atoms. The Ru–Cl bond distances, involving the two Cl atoms in *cis*, are 2.414(1) and 2.468(1) Å, respectively. Finally the Ru–N2 bond distance, 2.206(6) Å, *trans* to the carbonyl, is longer than the Ru–N1 one.

The oxazoline ring in **8** presents an envelope conformation with C2 atom deviating 0.217(9) Å from the mean plane defined by C1,N1,O1,C3. The absolute configurations of the chiral C3 atom is *S*, of the chiral plane is S_p and of the Ru atom is *OC*-6-32-*A*.

The treatment of **7** with dppm in the presence of a halide abstractor, gives the cationic complex $[RuCl(CO)(dppm)(FcPN)][PF_6]$ (**9**) (Eq. (5)).

$$\underset{(\mathbf{7})}{[RuCl_2(CO)(PPh_3)(FcPN)]} \xrightarrow[\text{2) dppm}]{\text{1) MeOH, NaPF}_6} \underset{(\mathbf{9})}{[RuCl(CO)(dppm)(FcPN)][PF_6]} \quad (5)$$

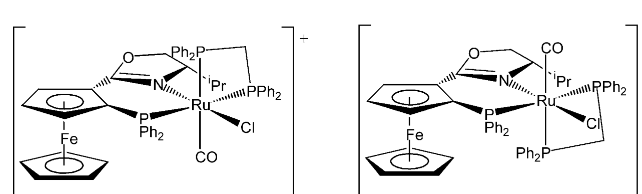
$^{31}P\{^1H\}$-NMR spectrum shows a *mer* disposition of the three phosphorous atoms (δ −37.74 ($^2J_{PP} = 16.3$, 28.5 Hz), −6.42 ($^2J_{PP} = 16.3$, 280.8 Hz), 23.30 ($^2J_{PP} = 28.5$, 280.8 Hz)). In the $^{13}C\{^1H\}$-NMR spectrum the expected carbonyl resonance appears as a doublet of multiplets at δ 202.80 ($^2J_{CP} = 104.8$ Hz) indicating the *trans* disposition of the CO group and one phosphorous atom of the dppm ligand.

Two stereoisomers **9a** and **9b** are consistent with these data (Scheme 4). However, the steric demanding of the isopropyl and ferrocenyl groups probably located as in complex **2**, favours the structure of **9a** in which the bulky phenyl groups of dppm are far away from the isopropyl and ferrocenyl groups of FcPN.

Table 2
Selected bond lengths (Å) and angles (°) for **9**

Bond lengths			
Ru(1)–C(22)	1.838(6)	P(1)–C(29)	1.83(1)
Ru(1)–N(1)	2.118(4)	C(1)–C(8)	1.43(1)
Ru(1)–N(2)	2.206(5)	C(2)–C(3)	1.53(1)
Ru(1)–P(1)	2.297(1)	C(3)–C(4)	1.50(1)
Ru(1)–Cl(1)	2.414(1)	C(4)–C(5)	1.50(1)
Ru(1)–Cl(2)	2.468(1)	C(4)–C(6)	1.53(1)
Fe(1)–M(1)	1.632(5)	C(7)–C(11)	1.44(1)
Fe(1)–M(2)	1.658(5)	C(7)–C(8)	1.47(1)
N(1)–C(1)	1.29(1)	C(8)–C(9)	1.43(1)
N(1)–C(3)	1.51(1)	C(9)–C(10)	1.40(1)
N(2)–C(17)	1.33(1)	C(10)–C(11)	1.42(1)
N(2)–C(21)	1.35(1)	C(12)–C(13)	1.38(1)
O(1)–C(1)	1.36(1)	C(12)–C(16)	1.42(1)
O(1)–C(2)	1.44(1)	C(13)–C(14)	1.34(1)
O(2)–C(22)	1.14(1)	C(14)–C(15)	1.32(1)
P(1)–C(7)	1.81(1)	C(15)–C(16)	1.41(1)
P(1)–C(23)	1.84(1)		
Bond angles			
C(22)–Ru(1)–N(1)	90.3(2)	C(1)–N(1)–Ru(1)	128.7(4)
C(22)–Ru(1)–N(2)	176.2(2)	C(3)–N(1)–Ru(1)	122.9(4)
N(1)–Ru(1)–N(2)	90.5(2)	C(17)–N(2)–C(21)	116.6(5)
C(22)–Ru(1)–P(1)	94.1(2)	C(17)–N(2)–Ru(1)	119.4(4)
N(1)–Ru(1)–P(1)	95.1(1)	C(21)–N(2)–Ru(1)	123.9(4)
N(2)–Ru(1)–P(1)	89.6(1)	C(1)–O(1)–C(2)	107.1(5)
C(22)–Ru(1)–Cl(1)	88.1(2)	C(7)–P(1)–Ru(1)	112.1(2)
N(1)–Ru(1)–Cl(1)	177.2(1)	N(1)–C(1)–O(1)	115.6(5)
N(2)–Ru(1)–Cl(1)	91.0(1)	N(1)–C(1)–C(8)	131.1(5)
P(1)–Ru(1)–Cl(1)	87.4(1)	O(1)–C(1)–C(8)	113.3(5)
C(22)–Ru(1)–Cl(2)	92.8(2)	O(1)–C(2)–C(3)	105.6(6)
N(1)–Ru(1)–Cl(2)	90.4(1)	C(4)–C(3)–N(1)	113.5(6)
N(2)–Ru(1)–Cl(2)	83.4(1)	C(4)–C(3)–C(2)	114.6(7)
P(1)–Ru(1)–Cl(2)	171.2(1)	N(1)–C(3)–C(2)	101.4(6)
Cl(1)–Ru(1)–Cl(2)	87.4(1)	C(8)–C(7)–P(1)	123.8(4)
M(1)–Fe(1)–M(2)	175.5(4)	C(1)–C(8)–C(7)	128.2(6)
C(1)–N(1)–C(3)	108.3(5)	O(2)–C(22)–Ru(1)	176.5(6)

M(1) is the centroid of the Cp ring C(7) C(8) C(9) C(10) C(11). M(2) is the centroid of the Cp ring C(12) C(13) C(14) C(15) C(16).



9a **9b**

Scheme 4.

3. Experimental

3.1. General methods

All manipulations involving organoruthenium complexes were performed under inert atmosphere of nitrogen, using standard Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. [$RuCl_2(PPh_3)$(FcPN)] [4c], *fac*-[$RuCl_2$(dppm)(FcPN)], *mer*–*trans*-[$RuCl_2$(dppm)(FcPN)] (**1**) and *fac*-[$RuCl_2(PMe_3)_2$(FcPN)] [5] were prepared according to the literature procedure. All other chemicals were obtained from Aldrich Chemical Co. and Acros Organics and used without further purification. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 instrument or a 300 DPX instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds.

3.2. Synthesis of *mer*–*cis*-[$RuCl_2$(dppm)(FcPN)] (2)

A solution of *mer*–*trans*-[$RuCl_2$(dppm)(FcPN)] (**1**) (0.519 g, 0.5 mmol) in 50 ml of CH_2Cl_2 was stirred for 10 h at −20 °C under ultraviolet light. The solution was concentrated at reduced pressure to ca. 5 ml and then 40 ml of hexane were added to precipitate the complex. The solvents were decanted, and the solid was washed with 40 ml of hexane and vacuum-dried to yield the complex **2** as a yellow solid. Yield: 0.337 g, 65%. ^{31}P{^{1}H}-NMR (CD_2Cl_2, δ) −25.99 (dd, dppm, $^2J_{PP}$ = 24.0, 375.2 Hz), 1.94 (dd, dppm, $^2J_{PP}$ = 24.0, 34.1 Hz), 18.08 (dd, PPh_2, $^2J_{PP}$ = 34.1, 375.2 Hz); ^{1}H-NMR (CD_2Cl_2, δ) 0.77 (m, 6H, CH_3), 2.46 (m, C$\underline{H}$($CH_3)_2$), 2.69 (vt, CHN, $^3J_{HH}$ = 7.6 Hz), 2.92 (m, 1H, OCH_2), 3.67 (m, 1H, OCH_2), 4.12 (s, 5H, C_5H_5), 4.37 (m, 1H, CH_2 of dppm), 4.53 (s, br, 1H, C_5H_3), 4.72 (s, br, 1H, C_5H_3), 4.90 (m, 1H, CH_2 of dppm), 5.07 (s, br, 1H, C_5H_3), 6.37–8.65 (m, 30H, Ph); ^{13}C{^{1}H}-NMR (CD_2Cl_2, δ) 16.98 (s, CH_3), 17.43 (s, CH_3), 27.76 (s, $\underline{C}$H($CH_3)_2$), 48.20 (dd, CH_2 of dppm, J_{CP} = 19.3, 23.8 Hz), 67.06 (s, OCH_2), 72.13 (s, C_5H_5), 72.66 (d, CHN, $^3J_{CP}$ = 6.3 Hz), 74.24 (s, br, C_5H_3), 74.41 (s, br, C_5H_3), 75.49 (d, $\underline{C}CPPh_2$, $^2J_{CP}$ = 18.0 Hz), 76.41 (d, $CPPh_2$, J_{CP} = 32.3 Hz), 78.94 (d, C_5H_3, $^2J_{CP}$ = 6.3 Hz), 126.57–141.45 (Ph), 169.23 (s, $\underline{C}OCH_2$); Anal. Calc. for [$RuCl_2$(dppm)(FcPN)]: C, 61.34; H, 4.86; N, 1.35. Found: C, 60.97; H, 5.01; N, 1.26%. Conductivity: 2.78 Ω^{-1} cm^2 mol^{-1} (acetone); 64.44 Ω^{-1} cm^2 mol^{-1} (MeOH).

3.3. Synthesis of [RuCl(dppm)(FcPN)][PF_6] (3)

A solution of *fac*-[$RuCl_2$(dppm)(FcPN)] (0.104 g, 0.1 mmol) in 10 ml of MeOH was stirred at room temperature (r.t.) for 20 min, and then $NaPF_6$ (0.042 g, 0.25 mmol) was added. The resulting solution was stirred for 30 min and the solvent was then removed at reduced pressure and the resulting solid residue was extracted with CH_2Cl_2. The solution was concentrated at reduced pressure to ca. 2 ml and then 20 ml of hexane were added to precipitate the complex. The solvents were decanted and the solid obtained was washed with 20 ml of hexane and vacuum-dried to yield the complex **3** as a dark-red solid. Yield: 0.060 g, 52%. ^{31}P{^{1}H}-NMR (CD_2Cl_2, δ) −7.63 (dd, $^2J_{PP}$ = 40.4, 62.1 Hz), 9.02 (dd, $^2J_{PP}$ = 40.4, 62.1 Hz), 67.73 (vt, $^2J_{PP}$ = 40.4 Hz); ^{1}H-NMR (CD_2Cl_2, δ) 0.53 (d, 3H, CH_3, $^3J_{HH}$ = 6.8 Hz), 1.08 (d, 3H, CH_3, $^3J_{HH}$ = 6.6 Hz), 2.58 (m, C$\underline{H}$($CH_3)_2$), 3.73 (m, 2H, OCH_2 and CH_2 of dppm), 4.07 (m, 6H, C_5H_5 and C_5H_3), 4.35 (vt, CHN, $^3J_{HH}$ = 9.4 Hz), 4.51 (dd, 1H, OCH_2, $^2J_{HH}$ = 5.8, $^3J_{HH}$ = 9.4 Hz), 4.68 (m, 1H, C_5H_3), 4.74 (m, 1H, CH_2 of dppm), 5.23 (s, br, 1H, C_5H_3), 6.01–8.28 (m, 30H, Ph); ^{13}C{^{1}H}-NMR (CD_2Cl_2, δ) 15.51 (s, CH_3), 20.39 (s, CH_3), 29.36 (s, $\underline{C}$H($CH_3)_2$), 45.03 (t, CH_2 of dppm, J_{CP} = 26.4 Hz), 69.03 (s, OCH_2), 71.30 (d, $\underline{C}CPPh_2$, $^2J_{CP}$ = 15.3 Hz), 72.81 (m, C_5H_5 and CHN), 73.07 (s, br, C_5H_3), 75.34 (d, C_5H_3, $^2J_{CP}$ = 6.2 Hz), 76.19 (s, br, C_5H_3), 77.02 (d, $CPPh_2$, J_{CP} = 52.0 Hz), 127.68–135.69 (Ph), 170.42 (s, br, $\underline{C}OCH_2$). IR(KBr, ν) 841 (PF_6) cm^{-1}; Anal. Calc. for [RuCl(dppm)(FcPN)][PF_6]: C, 55.49; H, 4.39; N, 1.22. Found: C, 55.71; H, 4.43; N, 1.25%. Conductivity: 137.96 Ω^{-1} cm^2 mol^{-1} (acetone).

3.4. Synthesis of *fac*-[RuCl{η^1-C≡C–$C_6H_4(CH_3)$}(dppm)(FcPN)] (4)

To a solution of the complex *fac*-[$RuCl_2$(dppm)(FcPN)] (0.200 g., 0.193 mmol) in 10 ml of THF at −20 °C, LiC≡$CC_6H_4CH_3$-4 (prepared in situ by addition of ^{n}BuLi (1.6 M in hexane, 361.4 μl, 0.578 mmol) to HC≡C–$C_6H_4(CH_3)$ (73.3 μl, 0.578 mmol) in 10 ml of THF at −20 °C) was added and the mixture was stirred for 40 min till the temperature of the cool-bath raised to −5 °C. The solvent was then removed at reduced pressure and the resulting solid residue was extracted with CH_2Cl_2, evaporated and the resulting solid washed with hexane (2 × 20 mL) and vacuum-dried to yield the complex **4** as a brown–yellow solid. Yield: 0.115 g, 53%. ^{31}P{^{1}H}-NMR (CD_2Cl_2, δ) −20.63 (dd, dppm, $^2J_{PP}$ = 40.7, 321.4 Hz), 11.72 (dd, dppm, $^2J_{PP}$ = 40.7, 36.6), 22.54 (dd, PPh_2, $^2J_{PP}$ = 36.6, 321.4 Hz); ^{1}H-NMR (CD_2Cl_2, δ) 0.07 (m, 3H, CH_3), 0.95 (d, 3H, CH_3, $^3J_{HH}$ = 5.6 Hz), 2.38 (s, 3H, $C_6H_4C\underline{H}_3$), 3.18 (m, 1H, C$\underline{H}$($CH_3)_2$), 3.67 (s, 5H, C_5H_5), 4.05, 4.25, 4.37, 4.52, 4.57, 4.74 and 4.92 (C_5H_3, OCH_2 CHN and CH_2 of dppm), 6.54–8.94 (m, 34H, Ph and C_6H_4); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, δ) 15.32 (s, CH_3), 17.89 (s, CH_3), 21.38 (s, $C_6H_4\underline{C}H_3$), 27.50 (s, $\underline{C}H(CH_3)_2$), 50.10 (vt, CH_2 of dppm, $J_{CP} = 21.3$ Hz), 67.08 (s, br, OCH_2), 71.51 (s, C_5H_5), 71.79 (m, C_5H_3 and CHN), 74.16 (d, $CPPh_2$, $J_{CP} = 48.1$ Hz), 75.20 (d, $\underline{C}CPPh_2$, $^2J_{CP} = 17.6$ Hz), 76.60 (s, br, C_5H_3), 79.92 (d, C_5H_3, $^2J_{CP} = 10.2$ Hz), 83.05 (d, Ru-Cα, $^2J_{CP} = 31.4$ Hz), 114.97 (s, br, Cβ), 126.16–141.64 (Ph and C_6H_4), 167.93 (s, br, $\underline{C}OCH_2$). IR(KBr, ν) 2067 (C≡C) cm^{-1}. Anal. Calc. for [RuCl{η^1-C≡C−$C_6H_4(CH_3)$}(dppm)(FcPN)]: C, 66.64; H, 5.14; N, 1.25. Found: C, 66.18; H, 5.06; N, 1.21%.

3.5. Synthesis of [Ru(N3)2(PPh3)(FcPN)] (5)

To a solution of [$RuCl_2(PPh_3)$(FcPN)] (0.366 g, 0.4 mmol) in 40 ml of CH_2Cl_2:MeOH (1:1), NaN_3 (0.065 g, 1 mmol) was added and the mixture was stirred for 1.5 h at r.t. The solvent was removed at reduced pressure and the solid residue extracted with CH_2Cl_2. The solvent was then concentrated to ca. 5 ml and 60 ml of hexane were added to precipitate the complex. The solvents were decanted and the solid washed with 60 ml of hexane and vacuum-dried to yield the complex **5** as a red–brown solid. Yield: 0.275 g, 74%. $^{31}P\{^1H\}$-NMR ($CDCl_3$) 39.51 (d, PPh_2, $^2J_{PP} = 32.6$ Hz), 44.94 (d, PPh_3, $^2J_{PP} = 32.6$ Hz); ^{1}H-NMR ($CDCl_3$, δ) 0.82 (d, 3H, CH_3, $^3J_{HH} = 6.5$ Hz), 0.87 (d, 3H, CH_3, $^3J_{HH} = 7.0$ Hz), 2.94 (m, $C\underline{H}(CH_3)_2$), 3.19 (t, CHN, $^3J_{HH} = 7.0$ Hz), 3.38 (d, 1H, OCH_2, $^3J_{HH} = 7.0$ Hz), 4.00 (s, 5H, C_5H_5), 4.25 (m, 1H, OCH_2), 4.59 (s, br, 1H, C_5H_3), 4.89 (s, br, 1H, C_5H_3), 5.11 (s, br, 1H, C_5H_3), 6.41–8.27 (m, 25H, Ph); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, δ) 14.40 (s, CH_3), 19.85 (s, CH_3), 28.98 (s, $\underline{C}H(CH_3)_2$), 68.65 (s, OCH_2), 72.28 (s, C_5H_5), 72.51 (d, C_5H_3, $^2J_{CP} = 7.1$ Hz), 73.66 (d, $CPPh_2$, $J_{CP} = 42.0$ Hz), 74.82 (d, $\underline{C}CPPh_2$, $^2J_{CP} = 7.1$ Hz), 74.93 (s, br), 75.09 (s, br), 75.46 (s, br) (C_5H_3 and CHN), 126.69–139.25 (Ph), 170.82 (s, $\underline{C}OCH_2$); IR (KBr, ν) 2062 (N_3) cm^{-1}; IR(CH_2Cl_2, ν) 2063 (N_3) cm^{-1}; Anal. Calc. for [$Ru(N_3)_2(PPh_3)$(FcPN)]·1/2CH_2Cl_2: C, 57.80; H, 4.59; N, 10.15. Found: C, 58.46; H, 4.71; N, 9.01%; MS-FAB (m/z) [$M^+ - N_3$-N_2] = 859, [$M^+ - N_3$-N_2-PPh_3] = 597.

3.6. Synthesis of [Ru(N3)2(PMe3)2(FcPN)] (6)

To a solution of [$RuCl_2(PMe_3)_2$(FcPN)] (0.155 g, 0.19 mmol) in 15 ml of CH_2Cl_2:MeOH (1:1), NaN_3 was added (0.031 g, 0.475 mmol) and the mixture was stirred for 30 min at r.t. The solvent was removed at reduced pressure and the solid residue extracted with CH_2Cl_2. The solvent was concentrated to ca. 5 ml and 60 ml of hexane were added to precipitate the complex. The solvents were decanted and the obtained solid washed with 60 ml of hexane and vacuum-dried to yield the complex **6** as a yellow solid. Yield: 0.109 g, 70%. $^{31}P\{^1H\}$-NMR (CH_2Cl_2/D_2O) 11.01 (vt, PMe_3, $^2J_{PP} = 36.6$ Hz), 13.52 (vt, PMe_3, $^2J_{PP} = 36.6$ Hz), 37.61 (vt, PPh_2, $^2J_{PP} = 36.6$ Hz); ^{1}H-NMR (CD_2Cl_2, δ) 0.67 (d, 9H, $P(CH_3)_3$, $^2J_{HP} = 7.7$ Hz), 1.04 (d, 3H, CH_3, $^3J_{HH} = 6.8$ Hz), 1.08 (d, 3H, CH_3, $^3J_{HH} = 6.8$ Hz), 1.49 (d, 9H, $P(CH_3)_3$, $^2J_{HP} = 8.0$ Hz), 3.05 (vsept, $C\underline{H}(CH_3)_2$, $^3J_{HH} = 6.8$ Hz), 4.01 (s, 5H, C_5H_5), 4.15 (m, 3H, CHN, OCH_2, and C_5H_3), 4.54 (m, 2H, OCH_2, and C_5H_3), 5.03 (s, br, C_5H_3), 6.84–8.49 (m, 10H, Ph); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, δ) 14.82 (s, CH_3), 18.12 (dd, $P(CH_3)_3$, $J_{CP} = 25.6$ Hz, $^3J_{CP} = 3.1$ Hz), 19.48 (dd, $P(CH_3)_3$, $J_{CP} = 26.4$ Hz, $^3J_{CP} = 2.8$ Hz), 20.42 (s, CH_3), 29.18 (s, $\underline{C}H(CH_3)_2$), 68.26 (s, OCH_2), 71.99 (s, C_5H_5), 72.21 (d, C_5H_3, $^2J_{CP} = 6.1$ Hz), 73.89 (d, CHN, $^3J_{CP} = 4.1$ Hz), 74.06 (m, $\underline{C}CPPh_2$ and C_5H_3), 74.38 (s, br, C_5H_3), 79.04 (d, $CPPh_2$, $J_{CP} = 36.4$ Hz), 127.99–143.13 (Ph), 168.33 (s, $\underline{C}OCH_2$); IR(KBr, ν) 2061 (N_3) cm^{-1}; IR(CH_2Cl_2, ν) 2080 (N_3) cm^{-1}; Anal. Calc. for [$Ru(N_3)_2(PMe_3)_2$(FcPN)]: C, 49.89; H, 5.66; N, 11.98. Found: C, 50.66; H, 5.74; N, 11.50%; MS-FAB (m/z) [$M^+ - N_3$] = 777, [$M^+ - N_3$-N_2-PMe_3] = 673, [$M^+ - 2N_3$-PMe_3] = 658, [$M^+ - N_2$-2PMe_3] = 639, [$M^+ - N_3$-N_2-2PMe_3] = 597.

3.7. Synthesis of [RuCl2(CO)(PPh3)(FcPN)] (7)

CO was bubbled for 35 min through a solution of [$RuCl_2(PPh_3)$(FcPN)] (1.832 g, 2 mmol) in 200 ml of THF at r.t. The solution was concentrated at reduced pressure to ca. 10 ml and then 80 ml of hexane were added to precipitate the complex. The solvents were decanted and the obtained solid washed with 80 ml of hexane and vacuum-dried to yield the complex **7** as a yellow solid. Yield: 1.547 g, 82%. $^{31}P\{^1H\}$-NMR (THF/D_2O, δ) 1.44 (d, PPh_3, $^2J_{PP} = 27.2$ Hz), 31.95 (d, PPh_2, $^2J_{PP} = 27.2$ Hz); ^{1}H-NMR (acetone-d_6, δ) 0.84 (d, 3H, CH_3, $^3J_{HH} = 7.1$ Hz), 0.92 (d, 3H, CH_3, $^3J_{HH} = 6.6$ Hz), 2.95 (vt, CHN, $^3J_{HH} = 8.8$ Hz), 3.26 (m, 2H, OCH_2 and $C\underline{H}(CH_3)_2$), 4.13 (s, 5H, C_5H_5), 4.21 (m, 1H, OCH_2), 5.09 (s, br, 2H, C_5H_3), 5.21 (s, br, 1H, C_5H_3), 6.63–7.70 (m, 23H, Ph), 8.78 (m, 2H, Ph); IR(Nujol, ν) 1987 (CO), 311, 273 (RuCl) cm^{-1}; IR(THF, ν) 1995 (CO) cm^{-1}; Anal. Calc. for [$RuCl_2(CO)(PPh_3)$(FcPN)]: C, 59.83; H, 4.59; N, 1.48. Found: C, 58.77; H, 4.75; N, 1.36%.

3.8. Synthesis of [RuCl2(CO)(py)(FcPN)] (8)

To a solution of [$RuCl_2(CO)(PPh_3)$(FcPN)] (**7**) (0.472 g, 0.5 mmol) in 50 mL of THF, pyridine (444 μl, 5.5 mmol) was added and the mixture stirred at r.t. for 4 h. The solution was then filtered, concentrated at reduced pressure to ca. 10 ml and 60 ml of hexane were added to precipitate the complex. The solvents were decanted and the obtained solid was washed with 60 ml of hexane and vacuum-dried to yield the complex **8** as a brown solid. Yield: 0.277 g, 73%. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, δ) 42.65

(s, PPh_2); ^{1}H-NMR (CD_2Cl_2, δ) 0.87 (d, 3H, CH_3, $^3J_{HH} = 6.6$ Hz), 0.98 (d, 3H, CH_3, $^3J_{HH} = 6.8$ Hz), 3.19 (m, $C\underline{H}(CH_3)_2$), 4.02 (m, CHN), 4.17 (m, 6H, C_5H_5 and OCH_2), 4.47 (d, 1H, OCH_2, $^3J_{HH} = 7.7$ Hz), 4.56 (s, br, 1H, C_5H_3), 4.89 (s, br, 1H, C_5H_3), 5.20 (s, br, 1H, C_5H_3), 6.81–8.32 (m, 15H, Ph and py); ^{13}C{^{1}H}-NMR (CD_2Cl_2, δ) 14.76 (s, CH_3), 18.95 (s, CH_3), 29.60 (s, $\underline{C}H(CH_3)_2$), 69.41 (s, OCH_2), 72.01 (s, C_5H_5), 73.15 (s, br, C_5H_3), 73.95 (m, $\underline{C}CPPh_2$), 74.11 (d, C_5H_3, $^2J_{CP} = 6.1$ Hz), 75.07 (s, br, C_5H_3), 75.18 (d, $CPPh_2$, $J_{CP} = 48.3$ Hz), 75.23 (d, CHN, $^3J_{CP} = 4.5$ Hz), 123.92 (s, *C-3 of py*), 127.65–136.50 (Ph), 137.18 (s, *C-4 of py*), 151.79 (s, *C-2 of py*), 170.51 (s, $\underline{C}OCH_2$), 206.26 (d, CO, $^2J_{CP} = 15.9$ Hz); IR(KBr, ν) 1954 (CO) cm^{-1}; IR(THF, ν) 1956 (CO) cm^{-1}; Anal. Calc. for [$RuCl_2$(CO)(py)(FcPN)]: C, 53.72; H, 4.38; N, 3.69. Found: C, 53.08; H, 4.51; N, 3.31%.

3.9. Synthesis of [RuCl(CO)(dppm)(FcPN)][PF_6] (9)

To a solution of [$RuCl_2$(CO)(PPh_3)(FcPN)] (**7**) (0.189 g, 0.2 mmol) in 20 mL of MeOH, $NaPF_6$ (0.039 g, 0.22 mmol) was added. After 10 min dppm (0.085 g, 0.22 mmol) was added and the mixture stirred for 1.5 h at r.t. The solvent was then removed at reduced pressure and the solid residue extracted with CH_2Cl_2, concentrated to ca. 5 ml, and 60 ml of Et_2O were added to precipitate the complex. The solvents were decanted and the obtained solid washed with 60 ml of Et_2O and vacuum-dried to yield the complex **9** as a red–orange solid. Yield: 0.148 g, 63%. ^{31}P{^{1}H}-NMR ($CDCl_3$) −37.74 (dd, dppm, $^2J_{PP} = 16.3$, 28.5 Hz), −6.42 (dd, dppm, $^2J_{PP} = 16.3$, 280.8 Hz), 23.30 (dd, PPh_2, $^2J_{PP} = 28.5$, 280.8 Hz); ^{1}H-NMR ($CDCl_3$, δ) −0.42 (d, 3H, CH_3, $^3J_{HH} = 6.5$ Hz), 0.78 (d, 3H, CH_3, $^3J_{HH} = 6.5$ Hz), 1.86 (m, $C\underline{H}(CH_3)_2$), 2.95 (m, 1H, OCH_2), 3.32 (vt, CHN, $^3J_{HH} = 9.4$ Hz), 3.95 (m, 6H, C_5H_5 and OCH_2), 4.51 (m, 1H, CH_2 of dppm), 4.71 (s, br, 1H, C_5H_3), 4.82 (m, 1H, CH_2 of dppm), 5.01 (vt, C_5H_3, $^3J_{HH} = 2.6$ Hz), 5.28 (s, br, 1H, C_5H_3), 6.58–8.13 (m, 30H, Ph); ^{13}C{^{1}H}-NMR ($CDCl_3$, δ) 14.96 (s, CH_3), 17.05 (s, CH_3), 28.06 (s, $\underline{C}H(CH_3)_2$), 43.01 (t, CH_2 of dppm, $J_{CP} = 24.6$ Hz), 66.95 (s, OCH_2), 71.77 (s, C_5H_5), 72.87 (d, $\underline{C}CPPh_2$, $^2J_{CP} = 19.5$ Hz), 74.45 (d, $CPPh_2$, $J_{CP} = 31.7$ Hz), 74.75 (d, C_5H_3, $^2J_{CP} = 5.6$ Hz), 74.88 (d, CHN, $^3J_{CP} = 4.6$ Hz), 76.09 (d, C_5H_3, $^3J_{CP} = 4.1$ Hz), 76.85 (m, C_5H_3), 125.70–136.61 (Ph), 171.66 (s, $\underline{C}OCH_2$), 202.80 (dm, $^2J_{CP} = 104.8$ Hz, CO); IR(KBr, ν) 1967 (CO), 842 (P–F) cm^{-1}; IR(CH_2Cl_2, ν) 1972 (CO) cm^{-1}; Anal. Calc. for [RuCl(CO)(dppm)(FcPN)][PF_6]·1/2CH_2Cl_2: C, 53.77; H, 4.22; N, 1.15. Found: C, 53.53; H, 4.41; N, 1.15%. Conductivity: 120.08 Ω^{-1} cm^2 mol^{-1} (acetone).

3.10. X-ray structure determination of complexes 1 and 8

The intensity data of complexes **1** and **8** were collected at r.t. on a Bruker AXS Smart 1000, equipped with an area detector diffractometer using a graphite monochromated Mo–K_α radiation. Crystallographic and experimental details for both structures are summarized in Table 3.

Both structures were solved by Patterson and Fourier methods [8] and refined by full-matrix least-squares procedures (based on F_o^2) [9] with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms.

In both structures the hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2F_o^2 + (0.0541P)^2]$ (**1**) and $w = 1/[\sigma^2F_o^2 + (0.0399P)^2]$ (**8**) where $P = (F_o^2 + 2F_c^2)/3$ was used.

All calculations were carried out on the DIGITAL AlphaStation 255 computers of the 'Centro di Studio per la Strutturistica Diffrattometrica' del CNR, Parma, using the SHELX-97 systems of crystallographic computer programs.

4. Supplementary material

The supplementary material for both structures includes the lists of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen

Table 3
Crystal data and structure refinement for **1** and **9**

	1	**9**
Formula	$RuFeP_3Cl_2NOC_{53}H_{50}$	$RuFePCl_2N_2O_2C_{34}H_{33}$
Formula weight	1037.67	760.41
Crystal system	Tetragonal	Orthorhombic
Space group	$P4_3$	$P2_12_12_1$
Flack parameter	−0.01(2)	−0.06(3)
a (Å)	18.771(5)	8.345(4)
b (Å)	18.771(5)	19.335(5)
c (Å)	15.734(5)	19.739(5)
V (Å^3)	5544(3)	3185(2)
Z	4	4
D_{calc} (g cm^{-3})	1.243	1.586
F(000)	2128	1544
Crystal size	0.18 × 0.22 × 0.15	0.21 × 0.17 × 0.27
μ (cm^{-1})	7.51	11.82
Reflections collected, unique	10 083, 7488 [$R_{int} = 0.0226$]	18 847, 6624 [$R_{int} = 0.0638$]
Reflections observed [$I > 2\sigma(I)$]	5591	4726
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0405$, $wR_2 = 0.0880$	$R_1 = 0.0444$, $wR_2 = 0.0847$
R indices (all data)	$R_1 = 0.0644$, $wR_2 = 0.0980$	$R_1 = 0.0770$, $wR_2 = 0.0945$

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

atoms, of anisotropic thermal parameters and complete lists of bond lengths and angles. The details of the crystal structure investigations have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 186642 (**1**) and 186643 (**8**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Dirección General de Investigación Científica y Técnica of Spain (FEDER 1FD97-0565 and MCT-00BQU 0227).

References

[1] (a) E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Vols. I–III, Springer-Verlag, 1999;
(b) I. Ojima (Ed.), Catalytic Asymmetric Synthesis, 2nd ed., Wiley VCH, 2000.

[2] (a) E.L. Stangeland, T. Sammakia, Tetrahedron 53 (1997) 16503;
(b) C.J. Richards, A.W. Mulvaney, Tetrahedron: Asymmetry 7 (1996) 1419;
(c) W. Deng, X. Hou, L. Dai, Y. Yu, W. Xia, Chem. Commun. (2000) 285;
(d) T. Sammakia, H.A. Latham, J. Org. Chem. 60 (1995) 6002.

[3] (a) Y. Nishibayashi, I. Takei, S. Uemura, M. Hidai, Organometallics 17 (1998) 3420;
(b) I. Takei, Y. Nishibayashi, Y. Arikawa, S. Uemura, M. Hidai, Organometallics 18 (1999) 2271;
(c) I. Takei, Y. Nishibayashi, Y. Ishii, Y. Mizobe, S. Uemura, M. Hidai, Chem. Commun. (2001) 2360.

[4] (a) T. Sammakia, E.L. Stangeland, J. Org. Chem. 62 (1997) 6104;
(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.

[5] J. Gimeno, E. Lastra, C. Madrigal, C. Graiff, A. Tiripicchio, J. Organomet. Chem. 637–639 (2001) 463.

[6] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.

[7] $^{31}P\{^{1}H\}$-NMR spectrum of *mer*-isomers (**1** and/or **2**) in MeOH solutions show two doublets at δ −7.66 ($^{2}J_{PP}=41.3$, 61.4 Hz), 9.09 ($^{2}J_{PP}=41.3$, 61.4 Hz) and a multiplet at δ 69.23, different from the $^{31}P\{^{1}H\}$-NMR spectra of *mer*-complexes in $CDCl_3$ (see Section 3) or the *fac* isomer (δ −0.46 ($^{2}J_{PP}=36.0$, 53.0 Hz), 5.58 ($^{2}J_{PP}=28.6$, 53.0 Hz), 24.74 ($^{2}J_{PP}=28.6$, 36.0 Hz)).

[8] G.M. Sheldrick, SHELXL-93, a Program for Crystal Structure Determination, University of Göttingen, Göttingen, Germany, 1993.

[9] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.