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Octahedral ruthenium(II) complexes containing the chiral ligand (4S)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN). X-Ray crystal structures of *fac*-[$RuCl_2(PMe_3)_2$(FcPN)] and *fac*-[$RuCl_2$(dppm)(FcPN)] (dppm = bis(diphenylphosphino)methane)

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Abstract

Octahedral ruthenium(II) complexes containing the chiral ligand (4S)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN) have been prepared from complex [$RuCl_2(PPh_3)$(FcPN)] (**1**) via phosphine exchange reactions. Complex **1** reacts with PMe_3, PMe_2Ph, bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) affording in good yield the complexes [$RuCl_2L_2$(FcPN)] (L = PMe_3 (**2a**), PMe_2Ph (**2b**)) and [$RuCl_2$(L–L)(FcPN)] (L–L = dppm (**3a**), dppe (**4**)). The processes are stereoselective giving rise to the thermodynamically stable *fac* isomers. The kinetically controlled formation of the *mer* isomer [$RuCl_2$(dppm)(FcPN)] (**3b**) is also described. Structural characterization of the complexes has been carried out by means of ^{1}H-, ^{31}P{^{1}H}- and ^{13}C{^{1}H}-NMR spectroscopy and the crystal structures of the complexes **2a** and **3a** have been determined by X-ray diffraction methods.

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

1. Introduction

The chemistry of complexes containing phosphorus–nitrogen ligands, particularly those with *hemilabile* properties, has raised great interest during the last few years due to their catalytic applications [1]. In this respect those ligands with planar chirality are specially attractive due to their potential in asymmetric induction.

Phosphinoferrocenyloxazoline derivatives (**I**) [2] belong to this class of ligands showing a remarkable versatility since the substituents in the oxazoline group allow the modulation of the chiral center which is located close to the N donor atom [3]. The catalytic activity of a series of rhodium, iridium, ruthenium and palladium complexes is now well established [4–8], most of them having been formed in situ; the stoichiometric chemistry, however, has been comparatively less studied. In the context of our recent interest in the chemistry of chiral ruthenium(II) complexes [9] herein we report the stereoselective synthesis of the first octahedral Ru(II) complexes containing the ligand (4S)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN) (**II** and **III**) (Scheme 1).

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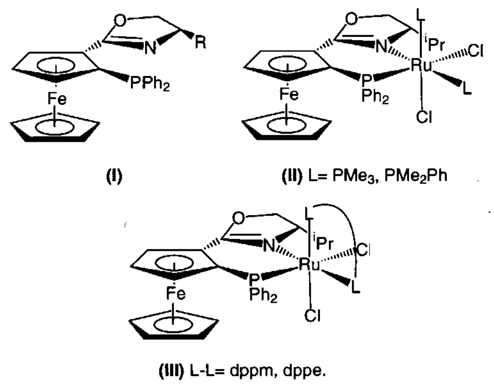


Scheme 1.

2. Results and discussion

Complexes **(II)** and **(III)** have been prepared in good yield from the known five-coordinate complex $[RuCl_2(PPh_3)(FcPN)]$ (**1**) [8c] via phosphine exchange reactions. Thus, the reactions with PMe_3 and PMe_2Ph at room temperature afford complexes **2a** and **2b** as air stable solids (73% (**2a**), 72% (**2b**) yields) (Eq. (1)).

$$[RuCl_2(PPh_3)(FcPN)] + 2\,L \xrightarrow[25^\circ C]{CH_2Cl_2 \text{ or } THF} [RuCl_2L_2(FcPN)] + PPh_3 \qquad (1)$$

L= PMe_3(**2a**), PMe_2Ph (**2b**).

Complexes **2a** and **2b** have been characterized by elemental analyses and ^1H-, $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectroscopy which have confirmed the proposed formulations. In particular $^{31}P\{^1H\}$-NMR spectra are informative for the structural elucidation since *fac* and *mer* stereoisomers are possible for each complex. Thus, $^{31}P\{^1H\}$-NMR spectra of **2a,b** show three resonances each of them as a doublet of doublets signal with coupling constants in the range of 29.9–38.8 Hz. These are consistent with an ABX system typical of three unequivalent phosphines coordinated in an octahedral ruthenium complex with a *fac* arrangement. In accordance with this, carbon resonances of the oxazoline group and the substituted carbon atoms of the cyclopentadienyl ring appear in the $^{13}C\{^1H\}$ spectra as multiplets with J_{CP} values in the range of 6.0–36.3 Hz (see Section 4 for details). In addition the structure of the complex **2a.1/2CH₂Cl₂** has been confirmed by an X-ray diffraction study. Fig. 1 shows the molecular structure together with the atomic numbering system; selected bond distances and angles are given in Table 1. In the crystals, complexes $[RuCl_2(PMe_3)_2(FcPN)]$ and dichloromethane molecules of solvation are present.

The Ru atom is octahedrally coordinated by the P and N atoms of the chelating ligand FcPN, by two Cl atoms and by two P atoms from the PMe_3 ligands with the three P atoms in a *fac* configuration. The chelating chiral FcPN ligand forms a nearly planar six-membered ring [maximum deviation for C8 atom 0.23(1) Å]. The three Ru–P bond distances [2.293(2) Å with FcPN and 2.298(2), 2.315(2) Å with the PMe_3 ligands] are comparable. These Ru–P bond distances, the Ru–Cl [2.471(2), 2.488(2) Å] and the Ru–N ones [2.206(5) Å] are much longer than those found in the five-coordinate complex **1** [Ru–P = 2.197(4), 2.26(2) Å, Ru–Cl = 2.406(5), 2.428(5) Å and Ru–N = 2.10(1) Å, respectively] [8c]. The oxazoline ring presents an envelope conformation with C2 atom deviation of 0.36(1) Å from the mean plane defined by C1,N1,O1,C3. The

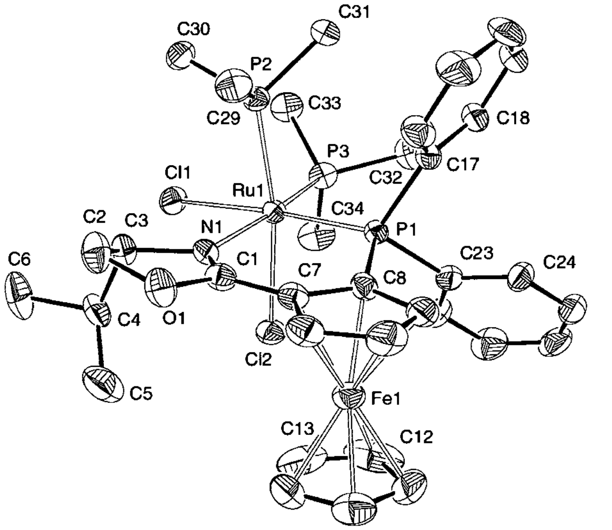


Fig. 1. View of the molecular structure of the molecule **2a.1/2CH₂Cl₂** together with the atomic numbering system. Thermal ellipsoids are drawn at the 30% probability level.

Table 1
Selected bond lengths (Å) and bond angles (°) for **2a.1/2CH₂Cl₂**

Bond length			
Ru(1)–N(1)	2.206(5)	N(1)–C(3)	1.51(1)
Ru(1)–P(1)	2.293(2)	O(1)–C(1)	1.36(1)
Ru(1)–P(2)	2.298(2)	O(1)–C(2)	1.47(1)
Ru(1)–P(3)	2.315(2)	P(1)–C(8)	1.818(6)
Ru(1)–Cl(1)	2.471(2)	C(1)–C(7)	1.432(9)
Ru(1)–Cl(2)	2.488(2)	C(2)–C(3)	1.507(9)
Fe(1)–M(1)	1.643(5)	C(3)–C(4)	1.542(9)
Fe(1)–M(2)	1.662(5)	C(7)–C(8)	1.436(9)
N(1)–C(1)	1.27(1)		
Bond angles			
N(1)–Ru(1)–P(1)	91.6(1)	P(3)–Ru(1)–Cl(2)	93.44(6)
N(1)–Ru(1)–P(2)	89.1(1)	Cl(1)–Ru(1)–Cl(2)	83.69(6)
P(1)–Ru(1)–P(2)	95.73(6)	M(1)–Fe(1)–M(2)	176.6(4)
P(1)–Ru(1)–P(3)	98.01(6)	C(1)–N(1)–Ru(1)	131.0(4)
P(2)–Ru(1)–P(3)	93.09(7)	C(1)–O(1)–C(2)	106.0(5)
N(1)–Ru(1)–Cl(1)	89.7(1)	C(8)–P(1)–Ru(1)	113.1(2)
P(2)–Ru(1)–Cl(1)	89.75(6)	N(1)–C(1)–C(7)	129.2(6)
P(3)–Ru(1)–Cl(1)	80.41(6)	C(8)–C(7)–C(1)	128.5(5)
N(1)–Ru(1)–Cl(2)	83.2(1)	C(7)–C(8)–P(1)	124.0(5)
P(1)–Ru(1)–Cl(2)	91.05(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).

absolute configurations of the chiral C3 atom is *S*, of the chiral plane is S_p and of the Ru atom is *OC*-63-2-*A*. Noteworthy, the *fac* arrangement of phosphines is such that one of the PMe_3 ligands is located in the opposite side as the ferrocenyl moiety and the isopropyl group. Probably the steric hindrance governs the selective formation of this isomer.

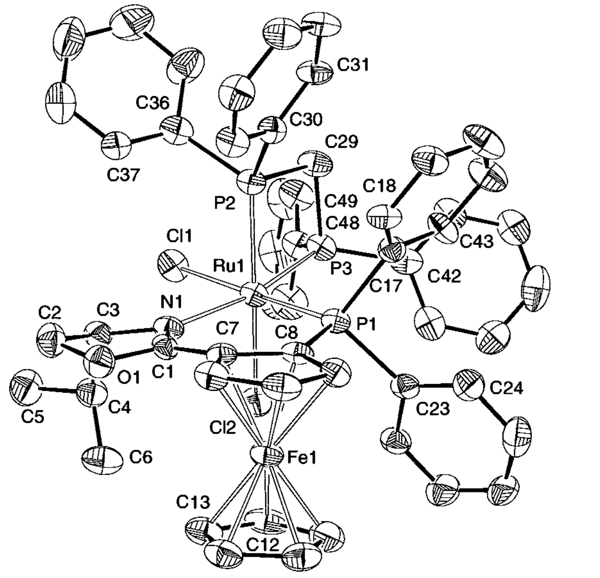


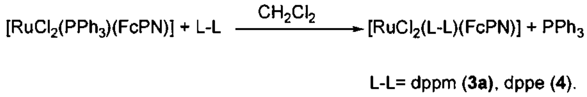
Fig. 2. View of the molecular structure of the molecule B of **3a.0.75C$_5$H$_{12}$** together with the atomic numbering system. Thermal ellipsoids are drawn at the 30% probability level.

Table 2
Selected bond lengths (Å) and bond angles (°) for one of the two independent molecules in **3a.0.75C$_5$H$_{12}$**

Bond length			
Ru(1)–N(1)	2.208(6)	O(1)–C(1)	1.343(8)
Ru(1)–P(3)	2.288(2)	O(1)–C(2)	1.442(9)
Ru(1)–P(2)	2.297(2)	P(1)–C(8)	1.833(7)
Ru(1)–P(1)	2.328(2)	P(2)–C(29)	1.867(8)
Ru(1)–Cl(1)	2.455(2)	P(3)–C(29)	1.835(8)
Ru(1)–Cl(2)	2.462(2)	C(1)–C(7)	1.43(1)
Fe(1)–M(1)	1.642(7)	C(2)–C(3)	1.52(1)
Fe(1)–M(2)	1.656(7)	C(3)–C(4)	1.55(1)
N(1)–C(1)	1.293(9)	C(7)–C(8)	1.44(1)
N(1)–C(3)	1.497(9)		
Bond angles			
N(1)–Ru(1)–P(2)	100.2(2)	P(1)–Ru(1)–Cl(2)	94.65(7)
P(3)–Ru(1)–P(2)	72.86(7)	Cl(1)–Ru(1)–Cl(2)	86.74(7)
N(1)–Ru(1)–P(1)	92.2(2)	M(1)–Fe(1)–M(2)	176.5(4)
P(3)–Ru(1)–P(1)	98.38(7)	C(1)–N(1)–Ru(1)	131.0(5)
P(2)–Ru(1)–P(1)	96.38(7)	C(1)–O(1)–C(2)	106.6(6)
N(1)–Ru(1)–Cl(1)	87.4(2)	C(8)–P(1)–Ru(1)	112.2(3)
P(3)–Ru(1)–Cl(1)	81.84(7)	N(1)–C(1)–C(7)	128.9(7)
P(2)–Ru(1)–Cl(1)	82.31(8)	C(1)–C(7)–C(8)	128.8(6)
N(1)–Ru(1)–Cl(2)	88.8(1)	C(7)–C(8)–P(1)	125.3(5)
P(3)–Ru(1)–Cl(2)	96.18(8)	P(3)–C(29)–P(2)	94.7(4)

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).

Similarly complexes [RuCl$_2$(L–L)(FcPN)] (L–L = dppm (**3a**); dppe (**4**)) (dppm = bis(diphenylphosphino)-methane, dppe = 1,2-bis(diphenylphosphino)ethane) have been obtained by reacting complex **1** with dppm or dppe in CH_2Cl_2 (**3a**: at room temperature, 50% yield; **4**: heating under reflux, 54% yield) after column chromatography (silica; MeOH/CH_2Cl_2) (Eq. (2)).



(2)

Complexes **3a** and **4** are yellow air stable solids. Elemental analyses and NMR spectroscopic data support this formulation. As was discussed above for complexes **2a** and **2b** $^{31}P\{^1H\}$-NMR spectra show resonances expected for a ABX system with coupling constants indicating a *fac* arrangement of the three phosphorus nuclei (**3a**: δ −0.46 (36.0, 53.0 Hz), 5.58 (28.6, 53.0 Hz), 24.74 (28.6, 36.0 Hz.); **4**: δ 25.15 (28.0, 32.6 Hz), 47.93 (18.6, 32.6 Hz), 52.84 (18.6, 28.0 Hz)). The structure of the complex **3a** has been confirmed by an X-ray study. In the crystals, two crystallographically independent, but very similar [RuCl$_2$(dppm)(FcPN)] complexes and disordered molecules of pentane are present. Fig. 2 shows the molecular structure of one of them, together with the atomic numbering system; selected bond distances and angles are given in Table 2.

Both complexes are very similar to **2a**, except for the presence of a chelating dppm ligand replacing two PMe_3 ligands. The structural features are comparable, except for those influenced by the narrow bite of chelating dppm ligand, [72.9(7)°]. In the dppm ligand the P2–C29–P3 bond angle is also rather narrow [94.7(4)°], due to the strained four-membered chelating ring [maximum deviation of 0.14(1) Å for the C29 atom from the mean plane defined by P1,C29,P2,Ru1]. The chelating chiral FcPN ligand forms a nearly planar six-membered ring [maximum deviation for C7 atom 0.13(1) Å]. It is noteworthy that the Ru–N bond distances both in **2a** and **3a** [2.206(5) Å in **2a** and 2.208(6) Å in **3a**] are much longer than those found in all Ru complexes in which the Ru atom is involved in a bond with a N atom of a ligand containing the C–N=C moiety (in the 2.02–2.16 Å range, from the structural data collected by the Cambridge Structural Database). As in **2a** the oxazoline ring shows an envelope conformation, with a C2 deviation of 0.31(1) Å from the mean plane defined by C1,N1,O1,C3. As in **2a** the absolute configurations of the chiral C3 atom is *S*, of the chiral plane is S_p and of the Ru atom is *OC*-63-2-*A*.

The reactions were monitored by $^{31}P\{^1H\}$-NMR at room temperature and *mer* isomers were detected. The spectrum of the reaction with dppm exhibits three sets of signals which are consistent with an ABX system showing typical coupling constants which reveal the presence of two phosphorus nuclei in *trans* (δ −28.47 and 22.57 (36.6, 345.5 Hz), 9.49 (36.6 Hz)). After 2 h of refluxing the spectrum remains unchanged. The partial evaporation of this reaction mixture and subsequent crystallization in hexane leads to the isolation of a yellow air-stable solid (91% yield) identified as the complex *mer* [$RuCl_2$(dppm)(FcPN)] (**3b**). Although elemental analyses and ^{1}H-, $^{31}P\{^{1}H\}$- and $^{13}C\{^{1}H\}$-NMR spectroscopy support this formulation these data do not allow to assign unequivocally the molecular structure since three different *mer* isomers are possible. Recrystallization of complex **3b** in methanol or the purification of this solid by column chromatography (SiO_2; eluting with a 9:1 mixture CH_2Cl_2/MeOH) gives the *fac* isomer **3a**. This seems to indicate that **3a** is the thermodynamically stable isomer and its formation proceeds through the *mer* isomer **3b** which is the kinetically controlled product.

In contrast, after 2 h, the spectrum of the reaction with dppe shows a complex pattern consisting of six doublet of doublets signals. Coupling constants indicate that along the complex *fac*-[$RuCl_2$(dppe)(FcPN)] (**4**) a *mer* isomer is also present (δ 66.94 (13.4, 30.7 Hz), 41.57 (13.4, 331.1 Hz), 10.73 (30.7, 331.1 Hz)). After 34 h of refluxing, the spectrum of the resulting solution only shows the pattern of the *fac* isomer (**4**) indicating the total transformation of the *mer* into the *fac* isomer.

3. Conclusions

In summary, we have synthesized in good yields novel chiral ruthenium(II) complexes containing the chelating (4*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline (FcPN) ligand, which are the first octahedral complexes described in the literature for this chiral planar ligand. The synthetic approach is stereoselective since either *fac* or *mer* isomer can be isolated by selecting the reaction conditions. Since it has been shown that the *fac* isomers are the thermodynamically stable species, novel derivatives of this type can be designed properly in order to use them for studies on the catalytic activity in asymmetric synthesis.

4. Experimental

4.1. General methods

All manipulations involving organoruthenium complexes were performed under an 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)] was prepared according to the literature procedure [8c]. All other chemicals were obtained from Aldrich 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.

4.2. Synthesis of *fac*-[$RuCl_2(PR_3)_2$(FcPN)] ($PR_3 = PMe_3$ (**2a**), PMe_2Ph (**2b**))

To a solution of [$RuCl_2(PPh_3)$(FcPN)] (**1**) (0.458 g, 0.5 mmol) in 50 ml of the corresponding solvent (CH_2Cl_2 for **2a**; THF for **2b**) the phosphine [PMe_3 (127 µl, 1.25 mmol) for **2a**, PMe_2Ph (178 µl, 1.25 mmol) for **2b**] was added at room temperature (r.t.). The mixture was stirred at r.t. for 2 and 3 h, respectively, and then evaporated to dryness. The resulting solid residue was purified using a silica column recovering the fraction eluting with the corresponding mixture of solvents: Et_2O/CH_2Cl_2 4:1 for complex **2a**, CH_2Cl_2/MeOH 22:3 for complex **2b**. The solution was evaporated to dryness, washed with hexane (40 ml) and vacuum-dried to yield the complexes as yellow solids. **2a**: (0.294 g, 73%), $^{31}P\{^{1}H\}$-NMR ($CDCl_3$, δ) 4.77 (m, $P(CH_3)_3$), 11.02 (dd, $P(CH_3)_3$, $^{2}J_{PP} = 32.6$, 38.8 Hz), 40.06 (dd, PPh_2, $^{2}J_{PP} = 32.6$, 35.7 Hz); ^{1}H-NMR ($CDCl_3$, δ) 0.74 (d, 9H, $P(CH_3)_3$), $^{2}J_{HP} = 8.5$ Hz), 0.90 (d, 3H, CH_3, $^{3}J_{HH} = 6.8$ Hz), 0.97 (d, 3H, CH_3, $^{3}J_{HH} = 6.8$ Hz), 1.55 (d, 9H, $P(CH_3)_3$, $^{2}J_{HP} = 9.1$ Hz), 3.47 (sept d, $C\underline{H}(CH_3)_2$, $^{3}J_{HH} = 1.4$, 6.8 Hz), 4.07 (m, 1H, CHN), 4.11 (s, 5H, C_5H_5), 4.30 (s, br, 1H, C_5H_3), 4.45 (dd, 1H, OCH_2, $^{2}J_{HH} = 2.0$, $^{3}J_{HH} = 8.5$ Hz), 4.56 (m, 2H, C_5H_3 and OCH_2), 5.04 (s, br, 1H, C_5H_3), 6.80–8.82 (m, 10H, Ph); $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, δ) 15.24 (s, CH_3), 19.04 (d, $P(CH_3)_3$, $J_{CP} = 30.2$ Hz), 19.11 (s, CH_3), 20.07 (d, $P(CH_3)_3$, $J_{CP} = 31.7$ Hz), 28.31 (s, $\underline{C}H(CH_3)_2$), 67.95 (s, OCH_2), 71.52 (d, C_5H_3, $^{2}J_{CP} = 6.0$ Hz), 71.90 (s, C_5H_5), 72.56 (d, CHN, $^{3}J_{CP} = 3.8$ Hz), 73.44 (m, 2C, C_5H_3), 74.64 (d, $\underline{C}CPPh_2$, $^{2}J_{CP} = 17.9$ Hz), 79.33 (d, $CPPh_2$, $J_{CP} = 36.3$ Hz), 127.02–137.02 (Ph), 166.74 (s, br, $\underline{C}OCH_2$); Anal. Calc. for [$RuCl_2(PMe_3)_2$(FcPN)]: C, 50.69; H, 5.76; N, 1.74. Found: C, 49.50; H, 5.74; N, 1.66; **2b**: (0.334 g, 72%), $^{31}P\{^{1}H\}$-NMR ($CDCl_3$, δ) 5.98 (m, $P(CH_3)_2Ph$), 11.95 (m, $P(CH_3)_2Ph$), 32.32 (dd, PPh_2, $^{2}J_{PP} = 29.9$, 36.6 Hz); ^{1}H-NMR ($CDCl_3$, δ) 0.15 (d, 3H, $P(CH_3)_2Ph$, $^{2}J_{HP} = 8.2$ Hz), 0.79 (d, 3H, CH_3, $^{3}J_{HH} = 6.9$ Hz), 0.92 (d, 3H, CH_3, $^{3}J_{HH} = 6.7$ Hz), 1.17 (d, 3H, $P(CH_3)_2Ph$, $^{2}J_{HP} = 9.0$ Hz), 1.78 (d, 3H, $P(CH_3)_2Ph$, $^{2}J_{HP} = 8.7$ Hz), 2.12 (d, 3H, $P(CH_3)_2Ph$, $^{2}J_{HP} = 9.2$ Hz), 2.77 (vt, CHN, $^{3}J_{HH} = 8.2$ Hz), 3.46 (m, $C\underline{H}(CH_3)_2$), 3.99 (dd, 1H, OCH_2, $^{2}J_{HH} = 2.8$, $^{3}J_{HH} = 8.2$ Hz), 4.09 (s, 5H, C_5H_5), 4.15 (s, br, 1H, C_5H_3), 4.39 (m, 1H, OCH_2), 4.55 (s, br, 1H, C_5H_3), 4.92 (s, br, 1H, C_5H_3), 6.84–8.60 (m, 20H, Ph); $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ) 15.43 (s, CH_3), 16.77 (d, $P(CH_3)_2Ph$, $J_{CP}=26.7$ Hz), 17.80 (d, $P(CH_3)_2Ph$, $J_{CP}=34.4$ Hz), 19.23 (s, CH_3), 19.32 (d, $P(CH_3)_2Ph$, $J_{CP}=32.5$ Hz), 20.36 (d, $P(CH_3)_2Ph$, $J_{CP}=29.9$ Hz), 27.82 (s, $\underline{C}H(CH_3)_2$), 66.95 (s, OCH_2), 71.89 (m, C_5H_5, CHN and C_5H_3), 74.30 (d, $\underline{C}CPPh_2$, $^2J_{CP}=14.6$ Hz), 75.28 (s, br, C_5H_3), 77.22 (s, br, C_5H_3), 79.23 (d, $CPPh_2$, $J_{CP}=36.2$ Hz), 126.72–143.50 (Ph), 166.64 (s, br, $\underline{C}OCH_2$); Anal. Calc. for $[RuCl_2(PMe_2Ph)_2(FcPN)]$: C, 56.84; H, 5.42; N, 1.51. Found: C, 57.39; H, 5.78; N, 1.44.

4.3. Synthesis of *fac*-$[RuCl_2(dppm)(FcPN)]$ (**3a**)

To a solution of $[RuCl_2(PPh_3)(FcPN)]$ (**1**) (0.092 g, 0.1 mmol) in 10 ml of CH_2Cl_2 dppm (0.042 g, 0.11 mmol) was added at r.t. The mixture was stirred at r.t. for 2 h, and then evaporated to dryness. The residue was dissolved in 5 ml of MeOH, and stirred at r.t. for 30 min. The solvent was removed at reduced pressure and the resulting solid residue was purified using a silica column recovering the fraction eluting with a mixture of CH_2Cl_2/MeOH 9:1. The solution was evaporated to dryness, washed with hexane (30 ml) and vacuum-dried to yield complex **3a** as a yellow solid. Yield: 0.052 g, 50%. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, δ) −0.46 (dd, dppm, $^2J_{PP}=36.0$, 53.0 Hz), 5.58 (dd, dppm, $^2J_{PP}=28.6$, 53.0 Hz), 24.74 (dd, PPh_2, $^2J_{PP}=28.6$, 36.0 Hz); ^1H-NMR (CD_2Cl_2, δ) 0.71 (d, 3H, CH_3, $^3J_{HH}=7.1$ Hz), 1.04 (d, 3H, CH_3, $^3J_{HH}=6.8$ Hz), 3.37 (m, $C\underline{H}(CH_3)_2$), 3.73 (m, 1H, CH_2 of dppm), 4.07 (m, 6H, C_5H_5 and C_5H_3), 4.25 (vt, CHN, $^3J_{HH}=8.8$ Hz), 4.53 (dd, 1H, OCH_2, $^2J_{HH}=2.1$, $^3J_{HH}=8.8$ Hz), 4.59 (s, br, 1H, C_5H_3), 4.94 (m, 1H, OCH_2), 5.12 (m, 1H, CH_2 of dppm), 5.19 (s, br, 1H, C_5H_3), 5.73–8.76 (m, 30H, Ph); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, δ) 15.59 (s, CH_3), 18.96 (s, CH_3), 27.76 (s, $\underline{C}H(CH_3)_2$), 42.91 (t, CH_2 of dppm, $J_{CP}=21.9$ Hz), 68.21 (s, OCH_2), 72.34 (m, C_5H_5 and C_5H_3), 73.24 (d, CHN, $^3J_{CP}=3.8$ Hz), 73.86 (d, $\underline{C}CPPh_2$, $^2J_{CP}=17.2$ Hz), 76.46 (s, br, C_5H_3), 79.47 (d, $CPPh_2$, $J_{CP}=35.6$ Hz), 126.17–141.03 (Ph), 167.73 (s, $\underline{C}OCH_2$); Anal. Calc. for $[RuCl_2(dppm)(FcPN)]$: C, 61.34; H, 4.86; N, 1.34. Found: C, 61.33; H, 4.82; N, 1.24.

4.4. Synthesis of *mer*-$[RuCl_2(dppm)(FcPN)]$ (**3b**)

To a solution of $[RuCl_2(PPh_3)(FcPN)]$ (**1**) (0.458 g, 0.5 mmol) in 50 ml of CH_2Cl_2 dppm (0.211 g, 0.55 mmol) was added at r.t. The mixture was refluxed for 2 h. The solution was concentrated at reduced pressure till 5 ml of CH_2Cl_2, and then 40 ml of hexane were added to precipitate the complex. The solvents were decanted, the solid obtained was washed with 40 ml of hexane and vacuum-dried to yield the complex **3b** as a yellow solid. Yield: 0.472 g, 91%. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, δ) −28.47 (dd, dppm, $^2J_{PP}=36.6$, 345.5 Hz), 9.49 (vt, dppm, $^2J_{PP}=36.6$ Hz), 22.57 (dd, PPh_2, $^2J_{PP}=36.6$, 345.5 Hz); ^1H-NMR (CD_2Cl_2, δ) 0.00 (d, 3H, CH_3, $^3J_{HH}=6.8$ Hz), 0.91 (d, 3H, CH_3, $^3J_{HH}=6.8$ Hz), 2.70 (m, $C\underline{H}(CH_3)_2$), 3.86 (s, 5H, C_5H_5), 4.06–4.26 (m, 3H, CHN and OCH_2), 4.31 (s, 1H, C_5H_3), 4.56 (m, 1H, C_5H_3), 4.73 (vt, 2H, CH_2 of dppm, $^2J_{HP}=10.2$ Hz), 4.99 (s, br, 1H, C_5H_3), 6.53–8.50 (m, 30H, Ph); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, δ) 15.37 (s, CH_3), 18.13 (s, CH_3), 27.98 (s, $\underline{C}H(CH_3)_2$), 48.48 (t, CH_2 of dppm, $J_{CP}=19.5$ Hz), 67.61 (s, OCH_2), 71.72 (s, C_5H_5), 72.02 (d, CHN, $^3J_{CP}=6.1$ Hz), 72.31 (s, br, C_5H_3), 75.16 (d, $\underline{C}CPPh_2$, $^2J_{CP}=19.5$ Hz), 75.63 (s, br, C_5H_3), 79.08 (d, C_5H_3, $^2J_{CP}=9.8$ Hz), 81.62 (dd, $CPPh_2$, $^3J_{CP}=2.4$ Hz, $J_{CP}=31.7$ Hz), 126.15–140.39 (Ph), 168.68 (s, $\underline{C}OCH_2$); Anal. Calc. for $[RuCl_2(dppm)(FcPN)]$: C, 61.34; H, 4.86; N, 1.34. Found: C, 61.28; H, 5.14; N, 1.33.

4.5. Synthesis of *fac*-$[RuCl_2(dppe)(FcPN)]$ (**4**)

To a solution of $[RuCl_2(PPh_3)(FcPN)]$ (**1**) (0.092 g, 0.1 mmol) in 10 ml of CH_2Cl_2 dppe (0.064 g, 0.16 mmol) was added at r.t. The mixture was refluxed for 34 h, and then evaporated to dryness. The resulting solid residue was purified using a silica column recovering the fraction eluting with a mixture of CH_2Cl_2/MeOH 5:1. The solution was evaporated to dryness, washed with hexane (30 ml) and vacuum-dried. Yield: 0.057 g, 54%. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ) 25.15 (dd, $^2J_{PP}=28.0$, 32.6 Hz), 47.93 (dd, $^2J_{PP}=18.6$, 32.6 Hz), 52.84 (dd, $^2J_{PP}=18.6$, 28.0 Hz); ^1H-NMR ($CDCl_3$, δ) 0.61 (d, 3H, CH_3, $^3J_{HH}=6.8$ Hz), 1.15 (d, 3H, CH_3, $^3J_{HH}=6.6$ Hz), 1.77 (m, 1H, CH_2 of dppe), 2.60–3.87 (m, 2H, CH_2 of dppe), 3.52 (m, 2H, CH_2 of dppe and $C\underline{H}(CH_3)_2$), 3.87 (s, 1H, C_5H_3), 4.25 (m, 6H, C_5H_5 and CHN), 4.40 (d, 1H, OCH_2, $^3J_{HH}=8.3$ Hz), 4.56 (m, 2H, C_5H_3 and OCH_2), 5.21 (s, 1H, C_5H_3), 5.74–8.53 (m, 30H, Ph); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, δ) 16.07 (s, CH_3), 19.10 (s, CH_3), 25.07 (dd, CH_2 of dppe, $^2J_{CP}=10.4$ Hz, $J_{CP}=32.1$ Hz), 27.78 (s, $\underline{C}H(CH_3)_2$), 68.82 (s, OCH_2), 72.21 (s, br, CHN), 72.65 (s, C_5H_5), 72.78 (m, 2C, C_5H_3), 73.95 (d, $\underline{C}CPPh_2$, $^2J_{CP}=17.3$ Hz), 77.17 (s, C_5H_3), 79.23 (d, $CPPh_2$, $J_{CP}=36.3$ Hz), 126.04–141.23 (Ph), 168.47 (s, $\underline{C}OCH_2$); Anal. Calc. for $[RuCl_2(dppe)(FcPN)]$: C, 61.67; H, 4.98; N, 1.33. Found: C, 61.36; H, 5.00; N, 1.08.

4.6. X-Ray structure determination of **2a.1/2CH_2Cl_2** and **3a.0.75C_5H_{12}**

The intensity data of the complexes 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 structures are summarized in Table 3.

Table 3
Crystal data and structure refinement for **2a.1/2CH$_2$Cl$_2$** and **3a.0.75C$_5$H$_{12}$**

	2a	**3a**
Empirical formula	RuFeP$_3$Cl$_2$NOC$_{34}$-H$_{46}$.0.5CH$_2$Cl$_2$	RuFeP$_3$Cl$_2$NOC$_{53}$H$_{50}$.0.75C$_5$H$_{12}$
Formula weight	847.91	1104.38
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Flack parameter	+0.04(3)	−0.01(2)
a (Å)	11.368(4)	19.308(4)
b (Å)	12.827(4)	22.121(5)
c (Å)	27.512(5)	25.437(5)
V (Å^3)	4012(2)	10 864(4)
Z	4	8
D_{calc} (g cm^{-3})	1.404	1.350
F(000)	1740	4608
Crystal size (mm)	0.26×0.27×0.37	0.23×0.18×0.21
μ (cm^{-1})	10.84	7.71
Reflections collected	24 351, 8696 [$R_{int}=0.0628$]	49 150, 15 674 [$R_{int}=0.0527$]
Reflections observed	5657 [$I>2\sigma(I)$]	11 386 [$I>2\sigma(I)$]
Final R indices [$I>2\sigma(I)$]	$R_1=0.0443$, $wR_2=0.0965$	$R_1=0.0446$, $wR_2=0.1067$
R indices (all data)	$R_1=0.0834$, $wR_2=0.1152$	$R_1=0.0780$, $wR_2=0.1264$

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

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms excepting for the carbon atoms of the disordered pentane molecules in **3a.0.75C$_5$H$_{12}$**. In the crystals of **2a.1/2CH$_2$Cl$_2$** molecules of CH$_2$Cl$_2$ were also found. In both structures the hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms, excepted for those of the solvent molecules. In the final cycles of refinement, a weighting scheme $w=1/[\sigma^2F_o^2+(0.0522P)^2]$ (**2a.1/2CH$_2$Cl$_2$**) and $w=1/[\sigma^2F_o^2+(0.0794P)^2]$ (**3a.0.75C$_5$H$_{12}$**) 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 [10].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 157012 for **2a.1/2CH$_2$Cl$_2$** and no. 157013 for **3a.0.75C$_5$H$_{12}$**. 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).

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