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Heterobimetallic [Ru(II)/Fe(II)] complexes: On the formation of *trans*- and *cis*-[$RuCl_2$(dppf)(diimines)]

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Abstract

The synthesis and characterization of *trans*/*cis*-[$RuCl_2$(dppf)(diimines)], dppf = 1,1′-bis(diphenylphosphino)ferrocene; diimines = 2,2′-bipyridine (*trans*/*cis*-(**1**)), the new complexes with 4,4′-dimethyl-2,2′-bipyridine (*trans*/*cis*-(**2**)) and 1,10-phenanthroline (*cis*-(**3**)) are presented. The complexes were synthesized using two routes and the *trans*/*cis*-isomer formation is dependent upon conditions and the precursor applied. The *trans*-isomer (kinetic) readily isomerizes to the *cis*-isomer (thermodynamic) when exposed to light (fluorescent) and this process was followed by cyclic voltammetry and UV–vis. The electrochemical studies on these complexes reveal that $Fe^{(III)}/Fe^{(II)}$ couples are insensitive to the isomer (*trans*/*cis*) formed, but the $Ru^{(III)}/Ru^{(II)}$ couples are dependent on the isomer. Transfer-hydrogenation reactions for reduction of acetophenone were conducted using complexes *cis*-(**1**) and *cis*-(**2**) and the results are compared with that obtained for similar complexes. X-ray structure for *cis*-(**3**) are presented and discussed.

Keywords: Ruthenium; Heterobimetallic; Dppf; Electrochemistry; Isomerization; Transfer-hydrogenation

1. Introduction

The chemistry of "$Ru^{(II)}$(P–P)(N–N)" (P–P = 1,4-bis-(diphenylphosphino)butane-dppb, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl-binap and N–N = diamines or diimines) has been widely studied and several complexes containing this core have been synthesized [1–7]. The interest in such system has strongly increased, mainly after the works published by Noyori [8–10] and Morris [3–5] using mixed ruthenium phosphine and diamine complexes. These reactions lead themselves for selecting C=O or C=N bonds over C=C bonds by a ligand-assisted mechanism, where an ancillary ligand *cis* to the hydride must have an NH or OH group [8–10]. The observed selection is due to the interaction of C=O or C=N groups with the "RuH–NH" unit of the catalyst in an outer-sphere mechanism. In addition, higher productivity and enantioselection are achieved.

The chemistry of dppf (1,1′-bis[diphenylphosphino]ferrocene) is well documented [11] and the interest in such species is mainly focused on structural [12,13], electrochemical [14,15] and catalytical [16,17] studies. This diphosphine is a very versatile ligand since it can be coordinated to a transition metal as a *cis*-chelate, *trans*-spanning and bridging, leading to a great diversity of structures and properties for its complexes [11].

Very recently, a work published by James and coworkers [18] presented a series of complexes with dppf and diimines or di- and triamines. Complexes with diamines were isolated as *trans*-isomers (*trans*-dichlorides), but for the diimines were only isolated as *cis*-isomers. The reason claimed for the non-observation of *trans*-[$RuCl_2$(dppf)(diimines)] (diimines such as 2,2-bipyridine and phenanthroline) is the

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rigid character of such diimines in contrast with the flexible character of diamines.

This fact was quite surprising for us, since we had synthesized previously to the publication of James [18] the *trans*-isomer using the same one-pot synthesis, but the reaction was carried out in the dark and short period of time.

Our group have been working with complexes *trans*/*cis*-[$RuCl_2$(P–P)(N–X)], where P–P is mono- or diphosphines and N–X is diimines, acetyl and benzoyl-pyridines, with the interest in structural and isomerization, transfer-hydrogenation and epoxidation [1,2,19–23]. In these works we showed that the reaction conditions are a key role for the isolation of desired isomer [1,23].

In this work we present the syntheses, characterization, and electrochemical studies of four complexes *trans*/*cis*-[$RuCl_2$(dppf)(diimines)]. In addition, we show that the *trans*-isomer can be synthesized and isolated in disagreement with the recently published work [18], and the isomerization *trans* → *cis* was followed by cyclic voltammetry and UV–vis spectroscopy. The catalytic activity of *cis*-[$RuCl_2$(dppf)(diimines)] complexes (N–N = 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine) for reduction of acetophenone was tested and the results are compared with analogous complexes. X-ray structure *cis*-[$RuCl_2$(dppf)(phen)] is presented and discussed.

2. Experimental section

2.1. Material and instrumentation

All manipulations were carried out under purified argon using standard Schlenk techniques. Reagent grade solvents were appropriately distilled and dried before use. The $RuCl_3 \cdot 3H_2O$ was supplied by Johnson Matthey Ltd. or purchased from Aldrich. Triphenylphosphine (PPh_3) (Aldrich), 1,4-bis(diphenylphosphino)butane (dppb) (Aldrich), 1,1′-bis(diphenylphosphino)ferrocene (Strem), 2,2′-bipyridine (bipy) (Aldrich), 1,10-phenanthroline (phen) (Aldrich) and 4,4′-dimethyl-2,2′-bipyridine (Me-bipy) (Aldrich) were used as received. The [$RuCl_2(PPh_3)_3$] [24] and [$RuCl_2(PPh_3)_2$(diimines)] [21] complexes were synthesized following published procedures.

Cyclic voltammetry (CV) experiments were carried out at room temperature in CH_2Cl_2 using a BAS-100B/W Bioanalytical Systems Instruments; the working and auxiliary electrodes were stationary Pt foils, and the reference electrode was Ag/AgCl, 0.10 M $Bu_4N^+ClO_4^-$ (TBAP) (Fluka Purum), a medium in which ferrocene is oxidized at 0.43 V (Fc^+/Fc). Elemental analyses were performed in the Chemistry Department at Universidade Federal de São Carlos. All NMR experiments were recorded at 298 K on a Bruker AVANCE 400 equipment operating at 9.4 T, observing ^1H at 400.13 MHz and ^{31}P at 161.98 MHz.

2.2. Synthesis of complexes

2.2.1. *trans*-[$RuCl_2$(dppf)(bipy)] *trans*-(**1**) and *trans*-[$RuCl_2$(dppf)(Me-bipy)] *trans*-(**2**)

A Schlenk flask containing a degassed dichloromethane (10.0 mL) solution of [$RuCl_2(PPh_3)_3$] (100 mg; 0.104 mmol) and dppf (57.6 mg; 0.104 mmol) was stirred for 5 min, the reaction was protected from exposure to light and the 2,2′-bipyridine (16.2 mg; 0.104 mmol) was added. The reaction was stirred for additional 2 min and *n*-hexane was added to yield a dark red solid. After filtration the solid was washed with *n*-hexane and diethyl ether and dried under vacuum. The resulting red solution was concentrated and addition of diethyl ether afforded a red solid, which was collected, washed with diethyl ether and dried under vacuum. Yield: 87.4 mg (95%). ^1H NMR: 3.87 (s, 4H, C_5H_4), 4.12 (s, 4H, C_5H_4), 6.50 (t, 2H, *J* 6.3, bipy), 6.78 (t, 8H, *J* 7.5, Ph), 6.96 (t, 4H, *J* 7.2, Ph), 7.40 (t, 2H, *J* 7.4, bipy), 7.56 (br m, 8H, Ph), 7.76 (d, 2H, *J* 4.4, bipy), 8.38 (br d, 2H, *J* 4.4, bipy). IR (KBr pellet): 1602 m; 1481 m; 1471 m; 1433 s; 1384 w; 1309 w; 1188 w; 1155 m; 1086 m; 1035 m; 827 w; 745 s; 696 s; 640 m; 545 s; 516 s; 495 s; 476 m; 428 m; 330 w; 303 w; 281 w. Anal. Calc. for $C_{44}H_{36}N_2Cl_2P_2FeRu \cdot H_2O$: C, 58.68; H, 4.25; N, 3.11. Found: C, 58.82; H, 4.05; N, 3.40%. UV–vis (CH_2Cl_2, 10^{-3} M): λ/nm (ε/$M^{-1}\,cm^{-1}$) 302 (14900), 351 (3600), 498 (2600).

Complex *trans*-(**2**) was synthesized following the same procedure for the synthesis of *trans*-(**1**), but the reaction was carried out in a NMR tube for direct analysis by ^{31}P NMR.

2.2.2. *cis*-[$RuCl_2$(dppf)(bipy)]*cis*-(**1**)

The *cis*-isomer can be isolated by two methods: *Method A*: isomerization of *trans*-isomer in dichloromethane at room temperature and exposure to light (fluorescent). *Method B*: (A representative method for direct synthesis of the *cis*-isomer is as follow), *cis*-[$RuCl_2$(dppf)(bipy)] *cis*-(**1**): A Schlenk flask containing degassed dichloromethane (20.0 mL) solution of *cis*-[$RuCl_2(PPh_3)_2$(bipy)] (100 mg; 0.117 mmol) and dppf (71.5 mg; 0.129 mmol) was refluxed for 3 h. The resulting red solution was concentrated and addition of diethyl ether afforded a red solid, which was collected, washed with diethyl ether and dried under vacuum. Yield: 82.8 mg (80%). ^1H NMR: 3.41 (s, 1H, C_5H_4), 4.15 (s, 1H, C_5H_4), 4.24 (s, 1H, C_5H_4), 4.34 (s, 1H, C_5H_4), 4.47 (s, 2H, C_5H_4), 4.97 (s, 1H, C_5H_4), 5.98 (s, 1H, C_5H_4), 6.43 (t, 1H, *J* 6.5, bipy), 6.92 (t, 2H, *J* 7.1, Ph), 6.99 (m, 2H, Ph), 7.11 (m, 8H, Ph), 7.38 (m, 4H, Ph), 7.48 (s, 1H, bipy), 7.61 (d, 1H, *J* 7.9, bipy), 7.64 (d, 1H, *J* 6.1, bipy), 7.68 (d, 1H, *J* 7.5, bipy), 7.74 (d, 1H, *J* 7.9, bipy), 7.83 (d, 1H, *J* 7.9, bipy), 8.12 (m, 2H, Ph), 8.38 (t, 2H, *J* 8.1, Ph), 9.32 (d, 1H, *J* 5.0, bipy). IR (KBr pellet): 1603 m; 1482 m; 1468 m; 1432 s; 1383 w; 1308 w; 1190 w; 1158 m; 1089 m; 1035 m; 816 w; 747 s; 696 s; 636 m; 546 s; 518 s; 499 s; 474 m; 427 m; 348 w; 319 w; 294 w. Anal. Calc. for $C_{44}H_{36}N_2Cl_2P_2FeRu$: C, 59.88; H, 4.11; N, 3.17. Found: C, 60.13; H, 4.35; N,

3.23%. UV–vis (CH_2Cl_2, 10^{-3} M): λ/nm (ε/M^{-1} cm^{-1}) 300 (15 500), 351 (3600), 453 (2500), 530 (sh).

*2.2.3. cis-[RuCl$_2$(dppf)(Me-bipy)] cis-(**2**)*

Yield: 87.9 mg (85%). ^{1}H NMR: 2.27 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.44 (s, 1H, C_5H_4), 4.17 (s, 1H, C_5H_4), 4.25 (s, 1H, C_5H_4), 4.35 (s, 1H, C_5H_4), 4.47 (m, 2H, C_5H_4), 4.98 (s, 1H, C_5H_4), 5.97 (d, 1H, *J* 1.2, C_5H_4), 6.29 (d, 1H, *J* 6.0, bipy), 6.85 (d, 1H, *J* 5.6, bipy), 6.94 (m, 2H, Ph), 7.01 (m, 2H, Ph), 7.14 (m, 8H, Ph), 7.37 (m, 4H, Ph), 7.57 (s, 1H, bipy), 7.67 (s, 1H, bipy), 7.89 (d, 1H, *J* 5.2, bipy), 8.15 (m, 2H, Ph), 8.41 (t, 2H, *J* 8.0, Ph), 9.20 (dd, 1H, *J* 8.6, 2.7, bipy). IR (KBr pellet): 1618 m; 1482 m; 1432 s; 1384 w; 1304 w; 1189 w; 1161 m; 1157 m; 1115 m; 1091 m; 1071 m; 1036 m; 816 w; 747 s; 696 s; 636 m; 546 s; 518 s; 499 s; 474 m; 427 m; 348 w; 319 w; 294 w. Anal. Calc. for $C_{46}H_{40}N_2Cl_2P_2FeRu$: C, 60.67; H, 4.43; N, 3.08. Found: C, 60.35; H, 4.25; N, 3.15%. UV–vis (CH_2Cl_2, 10^{-3} M): λ/nm (ε/M^{-1} cm^{-1}) 296 (8800), 441 (1500), 520 (sh).

*2.2.4. cis-[RuCl$_2$(dppf)(phen)] cis-(**3**)*

Yield: 82.7 mg (80%). ^{1}H NMR: 3.38 (m, 1H, C_5H_4), 4.15 (m, 1H, C_5H_4), 4.27 (m, 1H, C_5H_4), 4.37 (m, 1H, C_5H_4), 4.42 (m, 1H, C_5H_4), 4.51 (m, 1H, C_5H_4), 5.07 (m, 1H, C_5H_4), 6.12 (m, 1H, C_5H_4), 6.78 (m, 4H, Ph), 6.83 (dd, 1H, *J* 8.1, 5.5, phen), 6.91 (m, 2H, Ph), 7.08 (m, 4H, Ph), 7.19 (m, 4H, Ph), 7.40 (m, 4H, Ph), 7.70 (d, 1H, *J* 8.7, phen), 7.82 (d, 1H, *J* 8.7, phen), 7.95 (dd, 1H, *J* 8.1, 1.2, phen), 8.18 (dd, *J* 8.1, 1.5, 1H, phen), 8.22 (dd, 1H, *J* 9.6, 1.5 phen), 8.28 (d, *J* 5.5, 1H, phen), 8.50 (t, *J* 8.6, 2H, Ph), 9.60 (m, 1H, phen). IR (KBr pellet): 1585 m; 1482 m; 1432 s; 1384 w; 1305 w; 1260 w; 1190 w; 1159 m; 1090 m; 1036 m; 840 w; 810 w; 745 s; 696 s; 640 m; 545 s; 518 s; 494 s; 472 m; 428 m; 336 w; 307 w; 281 w. Anal. Calc. for $C_{46}H_{36}N_2Cl_2P_2FeRu \cdot H_2O$: C, 59.76; H, 4.14; N, 3.03. Found: C, 59.42; H, 4.02; N, 3.09%. UV–vis (CH_2Cl_2, 10^{-3} M): λ/nm (ε/M^{-1} cm^{-1}) 271 (22 500), 438 (3400), 521 (sh).

3. Results and discussion

In this work we present the synthesis, electrochemistry, X-ray structure and preliminary transfer-hydrogenation reactions studies of the heterobimetallic *trans*/*cis*-[$RuCl_2$(dppf)(diimines)], diimines = 2,2′-bipyridine *trans*/*cis*-(**1**), 4,4′-dimethyl-2,2′-bipyridine *trans*/*cis*-(**2**) and 1,10-phenanthroline *cis*-(**3**). These complexes were synthesized by two methods: Starting from [$RuCl_2(PPh_3)_3$], dppf and diimines ligands for the synthesis of the *trans*-(**1**) and *trans*-(**2**); and by phosphine exchange from the precursor *cis*-[$RuCl_2(PPh_3)_2$(diimines)]. When the starting compound is *cis*-[$RuCl_2(PPh_3)_2$(diimines)] [21], independently of the conditions, only the *cis*-[$RuCl_2$(dppf)(diimines)] complex is obtained, which is in agreement with our previous work with the dcype ligand [2]. When the starting compound is the [$RuCl_2(PPh_3)_3$], the conditions of the reaction can be modified to isolate the *trans*- or the *cis*-isomer. The *cis*-configuration was confirmed by $^{31}P\{^1H\}$ NMR. The spectra were obtained in CH_2Cl_2 (with D_2O capillary tube) and presented a well defined AX spin system with chemical shifts for *cis*-(**1**), *cis*-(**2**) and *cis*-(**3**) at 42.15, 36.50 ($^2J_{P-P}$ = 30.7 Hz); 43.02, 36.90 ($^2J_{P-P}$ = 31.6 Hz) and 43.6, 37.4 ($^2J_{P-P}$ = 30.6 Hz), respectively. The *trans*-(**1**) (isolated) and *trans*-(**2**) (*in situ*, NMR tube) were obtained by one-pot reaction starting from [$RuCl_2(PPh_3)_3$] in absence of light and at short reaction time (2 min, after addition of diimines). The $^{31}P\{^1H\}$ spectra present a singlet signal for both complexes, which is in agreement with equivalent phosphorus (*trans*-(**1**) and *trans*-(**2**), 41.91 and 42.47 ppm, respectively). The isomerization *trans*(kinetic) → *cis*(thermodynamic) for the complex *trans*-(**1**) was followed by cyclic voltammetry and UV–vis spectroscopy and will be discussed below (see Fig. 1).

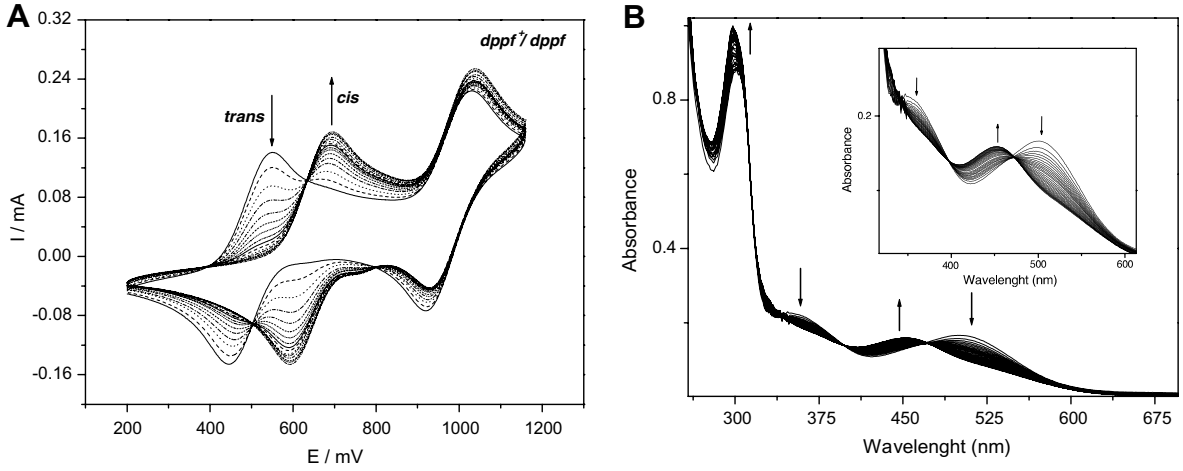

Fig. 1. Isomerization process of *trans*-[$RuCl_2$(dppf)(bipy)]. (A) Cyclic voltammetry (CH_2Cl_2 solution, 10^{-3} M, working and auxiliary electrodes were stationary Pt foils, and the reference electrode was Ag/AgCl, 0.10 M $Bu_4N^+ClO_4^-$). (B) UV–vis spectroscopy (CH_2Cl_2 solution, 10^{-3} M).

The ^{1}H NMR spectra of the *cis*-[$RuCl_2$(dppf)(diimines)] complexes showed signals for the phenyl groups of the phosphine as a series of multiplets in the 6.80–8.50 ppm region corresponding to 20 hydrogens. The ferrocenyl hydrogens show resonances in the region δ 3.40–6.10, appearing as seven lines, one of them with twice the intensity of the others for *cis*-(**1**) and *cis*-(**2**), however this is not the case of *cis*-(**3**) in which eight lines are observed for these hydrogens. This is a consequence of the non-equivalence of the phosphorus atoms attached to the Cp rings, as observed by the two doublets in the $^{31}P\{^1H\}$ NMR spectra. In complex *cis*-(**1**) the expected $^3J_{H-H}$ coupling for the Cp hydrogens is not resolved, and the resonances are seen as singlets. This is in contrast with the pattern found for *cis*-(**2**) and *cis*-(**3**), where for the first complex a multiplet is observed at 4.47 and a doublet at 5.97 ppm, besides five other singlet signals while for the other all the eight signals are multiplets for the Cp hydrogens. The diimines (N–N) hydrogens resonances are observed in the typical region. For the complexes *cis*-(**1**) and *cis*-(**3**) the expected eight aromatic hydrogens environments (relative intensity 1H each) appears as a series of doublets or double doublets in the 6.43–7.83 ppm region for *cis*-(**1**) and in the range 6.83–8.28 ppm for *cis*-(**3**). Additionally, both complexes showed the characteristic deshielded signal at 9.32 ppm for *cis*-(**1**) and at 9.60 ppm for *cis*-(**3**), corresponding to one of the *ortho* hydrogens of the (N–N) ligand. For the complex *cis*-(**2**) the six aromatic hydrogens of Me-bipy are observed as two singlets, three doublets and a double doublet at 9.20 ppm corresponding to one of the *ortho* hydrogens of the pyridine rings. For the CH_3 groups two singlets at 2.42 and 2.27 ppm are observed. In contrast with the *cis*-(**1**) isomer the *trans*-(**1**) (*trans*-[$RuCl_2$(dppf)(bipy)]) complex has a C_2 axis. This difference was reflected in the ^{1}H NMR spectrum which showed less signals than the *cis* analogous. The aromatic hydrogens resonances are in the range 6.78–7.56 ppm corresponding to 20 hydrogens. The ferrocenyl hydrogens show singlet resonances at 3.87 and 4.12 ppm (relative intensity 4H each) suggesting that the ferrocene rings are eclipsed and are essentially co-planar. This is clearly contrasting with the seven resonances for the similar hydrogens in the *cis* species. Finally, the bipy hydrogens show resonances at 8.38 and 7.76 (doublets) and at 7.40 and 6.50 (triplets) with relative intensity of 2H each, indicating that the two pyridyl rings are equivalent.

As mentioned before the *trans*-[$RuCl_2$(dppf)(diimines)] can be selectively synthesized starting from [$RuCl_2(PPh_3)_3$], dppf and diimines. The key role for this is carrying out the reaction in absence of light and at shortest reaction time (2 min, after addition of diimines). The *trans*-[$RuCl_2$(dppf)(bipy)] (kinetic isomer) when exposed to light readily isomerizes leading to the formation of *cis*-isomer (thermodynamic isomer). This process is similar to the observed for the *trans*-[$RuCl_2$(dppb)(bipy)] complex [1]. This isomerization process was followed by cyclic voltammetry and UV–vis spectroscopy (see Fig. 1). Thus, in conclusion, formation of *trans*- or *cis*-isomer is dependent upon the starting complex and conditions of the reaction.

The electrochemical data obtained for the studied complexes and for similar species from the literature are in Table 1.

The electrochemical behaviors of the *trans*/*cis*-[$RuCl_2$(dppf)(diimines)] complexes are similar to the observed for *trans*/*cis*-[$RuCl_2$(dppb)(bipy)] [1], but in this case besides the $Ru^{(III)}/Ru^{(II)}$ couples are also observed the processes for $Fe^{(III)}/Fe^{(II)}$ couples. The $Ru^{(III)}/Ru^{(II)}$ process for the *trans*-isomer is less anodic than for the *cis*-isomer. This is in agreement with the observed for the *trans*/*cis*-[$RuCl_2$(dppb)(diimines)] species [1]. For the $Fe^{(III)}/Fe^{(II)}$ processes are observed only a negligible difference on $E_{1/2}$ between *trans*- and *cis*-isomers (see Fig. 1). This variation on potentials and the similarity with other ruthenium complexes [1,2] allowed us to attribute the processes centered on ruthenium as the lower potentials (less anodic) and consequently the higher potentials to the iron of the coordinated dppf ligand.

The *trans*- to *cis*-isomerization was accompanied by spectral changes in the UV–vis spectra (Fig. 1(B)). The bands in the UV–vis spectra initially at 301 nm slightly change to 298 nm with an increase of intensity while the 360 nm band has its intensity greatly diminished. In the visible region the initial band at 500 nm was gradually substituted by a similar one at 452 nm with the formation of two isosbestic points at 397 and 472 nm. The visible bands are tentatively assigned to MLCT (Ru → bipy) transitions and the increase of the energy transition in the *cis*-isomer is in agreement with the lowest electron density of this isomer when compared with the *trans* species, as previously showed in the electrochemical data.

Recrystallization from dichloromethane/hexane solution led to formation of red single crystals of complex *cis*-(**3**) which were analysed by X-ray diffraction. The solved structure is presented in Fig. 2. Attempts to isolate single crystals of the *trans*-isomer were unsuccessful leading only to formation of single crystals of the *cis*-isomer.

The X-ray structure of the *cis*-(**3**) complex revealed that the Ru(II) ion is in a distorted octahedral geometry, as evidenced by P–Ru–P 99.37°, Cl–Ru–Cl 86.85° and N–Ru–N 78.60°. The Ru–Cl, Ru–N, Ru–P distances found for the *cis*-(**3**) are in the typical range reported in the literature

Table 1
Electrochemical data ($E_{1/2}$ in volts) for *trans*/*cis*-[$RuCl_2$(P–P)(N–N)]

	dppb [1] $Ru^{(III)}/Ru^{(II)}$	dcype [2] $Ru^{(III)}/Ru^{(II)}$	dppf[a] $Ru^{(III)}/Ru^{(II)}$ ($Fe^{(III)}/Fe^{(II)}$)[b]
trans/bipy	0.45	–	0.50 (0.97)
cis/bipy	0.60	0.41	0.64 (0.98)
trans/phen	0.47	–	–
cis/phen	0.63	0.41	0.65 (1.00)
cis/Me-bipy	–	0.35	0.62 (0.99)

[a] This work.
[b] $E_{1/2}$ for free dppf is 0.62 V.

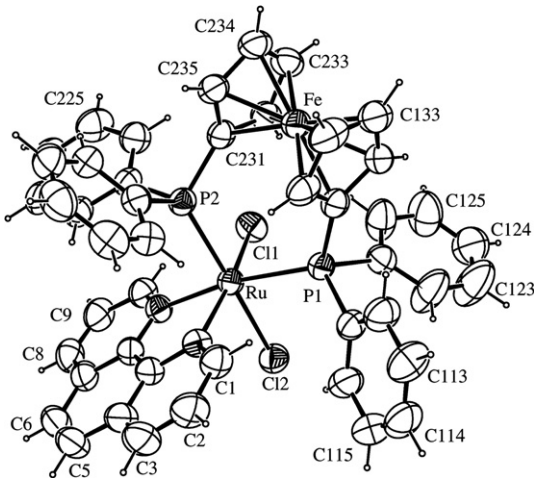

Fig. 2. ORTEP [26] view of the complex *cis*-[$RuCl_2$(dppf)(phen)]·$2CH_2Cl_2$, showing the atoms labelling and the 50% probability ellipsoids. *Bond lengths* (Å): Ru–N(1) 2.108(3), Ru–N(2) 2.122(3), Ru–P(2) 2.3210(8), Ru–P(1) 2.3664(8), Ru–Cl(1) 2.4206(8), Ru–Cl(2) 2.4621(8), Fe–C(231) 2.019(3), Fe–C(131) 2.024(3), Fe–C(135) 2.024(3), Fe–C(232) 2.029(3), Fe–C(235) 2.037(3), Fe–C(132) 2.048(4), Fe–C(134) 2.056(4), Fe–C(133) 2.058(4), Fe–C(234) 2.060(3), Fe–C(233) 2.064(4). *Bond angles* (°): N(1)–Ru–N(2) 78.60(10), N(1)–Ru–P(2) 98.96(7), N(2)–Ru–P(2) 90.85(7), N(1)–Ru–P(1) 98.68(8), N(2)–Ru–P(1) 169.73(7), P(2)–Ru–P(1) 99.37(3), N(1)–Ru–Cl(1) 165.86(8), N(2)–Ru–Cl(1) 87.86(8), P(2)–Ru–Cl(1) 85.17(3), P(1)–Ru–Cl(1) 93.94(3), N(1)–Ru–Cl(2) 87.44(7), N(2)–Ru–Cl(2) 82.95(7), P(2)–Ru–Cl(2) 170.07(3), P(1)–Ru–Cl(2) 87.05(3), Cl(1)–Ru–Cl(2) 86.85(3).

Table 2
Crystal data and structure refinement for *cis*-(**3**)

Empirical formula	$C_{46}H_{36}N_2P_2Cl_2FeRu \cdot 2CH_2Cl_2$
Formula weight	1076.38
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	38.9410(9)
b (Å)	14.1620(3)
c (Å)	17.9160(5)
Volume (Å^3)	9078.1(4)
Z	8
D_{calc} (Mg/m^3)	1.575
Absorption coefficient (mm^{-1})	1.113
F(000)	4352
Crystal size (mm^3)	0.24 × 0.16 × 0.06
Theta range for data collection (°)	3.42–26.40
Index ranges	$-46 \leqslant h \leqslant 48$, $-17 \leqslant k \leqslant 16$, $-22 \leqslant l \leqslant 22$
Reflections collected	27041
Independent reflections [*R*(int)]	9040 [0.0448]
Completeness to theta = 27.50°	97.0%
Maximum and minimum transmission	0.855 and 0.733
Data/restraints/parameters	9040/0/577
Goodness-of-fit on F^2	1.042
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0491$, $wR_2 = 0.1295$
R indices (all data)	$R_1 = 0.0621$, $wR_2 = 0.1399$
Largest difference in peak and hole (e Å^{-3})	0.675 and −1.024

[1,2,6,18,22]. As expected, the Ru–P bond length is longer for the phosphorus *trans* to nitrogen than for the phosphorus *trans*-chloride, but the Ru–P bond lengths are longer for *cis*-(**3**) (Ru–$P_{(av)}$, 2.344 Å) than for its analogue *cis*-[$RuCl_2$(dppf)(bipy)] (Ru–$P_{(av)}$, 2.317 Å) [18,25]. It is worth noting that the conformation for *cis*-(**3**) is synclinical staggered, as previously discussed by Bandoli and Dolmella [11], but the torsion angle P–C–C–P for *cis*-[$RuCl_2$(dppf)-(bipy)] is 19.70° and for *cis*-(**3**) is 35.54° and can be due to the more rigid ring of phenanthroline than the bipyridine (Table 2).

The catalytic activities of *cis*-(**1**) and *cis*-(**2**) were tested for reduction of acetophenone and the results are presented in Table 3 with another complexes [2]. The complexes presented in this work and the ones in Table 3 do not present an "NH" group, but they are active for converting acetophenone in 1-phenylethanol in good yield. The dppf complexes are less active than the [$RuCl_2$(P–P)(diimines)] (P–P = dppb or $(PPh_3)_2$) complexes for the reduction of acetophenone as can be seen in Table 3 and Fig. 3, giving low final conversions in 3 h (*cis*-(**1**), 47%; *cis*-(**2**), 33%) and lower rates. The lower activity of dppf complexes can be rationalized as a function of the bulkiness of the dppf ligand when compared with dppb or PPh_3. These complexes (*cis*-(**1**) and *cis*-(**2**)) promote the reduction of acetophenone via hydrogen transfer mechanism only in presence of isopropanol and base. Similar results were found by James [18] with the complexes *cis*-[$RuCl_2$(dppf)(bipy)] and *cis*-[$RuCl_2$(dppf)(phen)]. The presence of H_2 in the reaction system does not affect the activity of the catalysts and the final conversion of the acetophenone. Quite the opposite is observed for the complex *cis*-[$RuCl_2$(dppb)-(bipy)] [2] which has its activity improved under H_2 atmosphere (1 atm). In absence of H_2 the reaction is very slow achieving only 50% of conversion in 24 h, but under H_2 (1 atm) this complex reduces acetophenone in 78% of conversion in 3 h.

Table 3
Results for acetophenone reduction by mixed phosphines/diimines ruthenium complexes

Complexes	Conversion[a] (%)	$TOF_{30\,min}$ (h^{-1})
cis-[$RuCl_2$(dppb)(bipy)] [2]	78	760
cis-[$RuCl_2$(dppb)(bipy)] [2]	86	940[b]
cis-[$RuCl_2(PPh_3)_2$(bipy)] [2]	90	280
cis-[$RuCl_2(PPh_3)_2$(Me-bipy)] [2]	81	400
cis-[$RuCl_2$(dppf)(bipy)],[d] *cis*-(**1**)	47	360[c]
cis-[$RuCl_2$(dppf)(Me-bipy)],[d] *cis*-(**2**)	33	120[c]

[a] Conditions: Acetophenone (10 mmol, 0.2 M) in 2-propanol, 1 mL of KOH (0.2 M) in 2-propanol; precatalyst (10 μmol); $P(H_{2(g)}) = 1$ atm, temp. = 82 °C, time = 3 h; acetophenone/precatalyst/KOH 1000:1:20.
[b] $P(H_{2(g)}) = 3$ atm.
[c] With $H_{2(g)}$ (1 atm) or without the results are the essentially the same.
[d] This work.

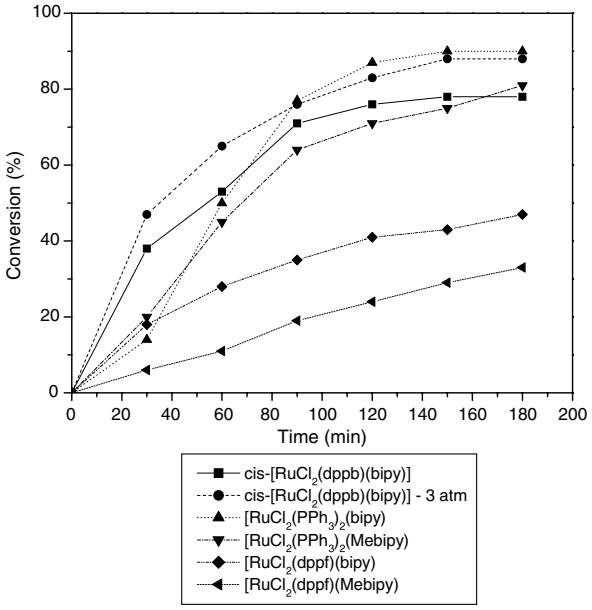

Fig. 3. Performance of *cis*-[$RuCl_2$(dppf)(diimines)] compared with similar complexes containing mono- and diphosphines in reduction of acetophenone.

4. Conclusion

In this work we present the successful synthesis of the *trans*/*cis*-[$RuCl_2$(dppf)(diimines)] (diimines = 2,2′-bipyridine) (*trans*/*cis*-(**1**)), 4,4′-dimethyl-2,2′-bipyridine (*trans*/*cis*-(**2**)) and 1,10-phenanthroline (*cis*-(**3**)) complexes and their characterization by $^{31}P\{^1H\}$ and ^1H NMR, cyclic voltammetry, elemental analysis, UV–vis spectroscopy and X-ray structures for two complexes, *cis*-(**1**) [25] and *cis*-(**3**). In disagreement with stated in the recently published paper [18] the *trans*-isomers (*trans*-[$RuCl_2$(dppf)(diimines)], diimines = bipy or Me-bipy) were synthesized. The isomerization of the *trans*-[$RuCl_2$(dppf)(bipy)] isomer was followed using cyclic voltammetry and UV–vis. The precursor and conditions applied are of fundamental importance for the synthesis of the desired *trans*- or *cis*-isomer. The catalytic activity of dppf complexes *cis*-(**1**) and *cis*-(**2**) was tested and these complexes presented a low performance when compared with other [$RuCl_2$(P–P)(diimines)] complexes. Improvement on these complexes should be made and new dppf systems will be tested.

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Appendix A. Supplementary material

CCDC 632660 and 638566 contain the supplementary crystallographic data for *cis*-[$RuCl_2$(dppf)(bipy)] and *cis*-[$RuCl_2$(dppf)(phen)]. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.038.

References

[1] S.L. Queiroz, A.A. Batista, G. Oliva, M. Gambardella, R.H.A. Santos, K.S. MacFarlane, S.J. Rettig, B.R. James, Inorg. Chim. Acta 267 (1998) 209.
[2] M.P. de Araujo, A.T. de Figueiredo, A.L. Bogado, G. Von Poelhsitz, J. Ellena, E.E. Castellano, C.L. Donnici, J.V. Comasseto, A.A. Batista, Organometallics 24 (2005) 6159.
[3] K. Abdur-Rashid, S.E. Clapham, A. Hadzovic, J.N. Harvey, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 124 (2002) 15104.
[4] K. Abdur-Rashid, A.J. Lough, R.H. Morris, Organometallics 20 (2001) 1047.
[5] S.E. Clapham, A. Hadzovic, R.H. Morris, Coord. Chem. Rev. 248 (2004) 2201.
[6] S.L. Queiroz, M.P. de Araujo, A.A. Batista, K.S. MacFarlane, B.R. James, J. Chem. Educ. 78 (2001) 87.
[7] S.L. Queiroz, M.P. de Araujo, A.A. Batista, K.S. MacFarlane, B.R. James, J. Chem. Educ. 78 (2001) 89.
[8] R. Noyori, T. Ohkuma, Angew. Chem., Int. Ed. 40 (2001) 40.
[9] R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345.
[10] K.J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem., Int. Ed. Engl. 36 (1997) 285.
[11] G. Bandoli, A. Dolmella, Coord. Chem. Rev. 209 (2000) 161.
[12] T.A. Peganova, N.V. Vologdin, P.V. Petrovskii, I.D. Nesterov, K.A. Lyssenko, O.V. Gusev, Russ. Chem. Bull. 55 (2006) 683.
[13] X.L. Lu, S.Y. Ng, J.J. Vittal, G.K. Tan, L.Y. Goh, T.S.A. Hor, J. Organomet. Chem. 688 (2003) 100.
[14] B. Therrien, L. Vieille-Petit, J. Jeanneret-Gris, P. Stepnicka, G. Suss-Fink, J. Organomet. Chem. 689 (2004) 2456.
[15] T. Sixt, J. Fiedler, W. Kaim, Inorg. Chem. Commun. 3 (2000) 80.
[16] V. Cadierno, P. Crochet, J. Diez, S.E. Garcia-Garrido, J. Gimeno, Organometallics 22 (2003) 5226.
[17] V. Cadierno, P. Crochet, J. Diez, S.E. Garcia-Garrido, J. Gimeno, Organometallics 23 (2004) 4836.
[18] G. Ma, R. McDonald, M. Ferguson, R.G. Cavell, B.O. Patrick, B.R. James, T.Q. Hu, Organometallics 26 (2007) 846.
[19] S.L. Queiroz, A.A. Batista, M.P. de Araujo, R.C. Bianchini, G. Oliva, J. Ellena, B.R. James, Can. J. Chem.-Rev. Can. Chim. 81 (2003) 1263.
[20] A.L. Bogado, R.F. de Souza, U. Schuchardt, A.A. Batista, J. Mol. Catal. A: Chem. 203 (2003) 129.
[21] A.A. Batista, M.O. Santiago, C.L. Donnici, I.S. Moreira, P.C. Healy, S.J. Berners-Price, S.L. Queiroz, Polyhedron 20 (2001) 2123.
[22] M.O. Santiago, A.A. Batista, M.P. de Araujo, C.L. Donnici, I.D. Moreira, E.E. Castellano, J. Ellena, S. dos Santos, S.L. Queiroz, Trans. Met. Chem. 30 (2005) 170.
[23] M.O. Santiago, C.L. Donnici, I.D. Moreira, R.M. Carlos, S.L. Queiroz, A.A. Batista, Polyhedron 22 (2003) 3205.
[24] T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 945.
[25] We also have solved the X-ray structure of *cis*-(**1**). This structure was already reported (see Ref. [18]), due to this the complete crystallographic data for this complex is presented in Supplementary material.
[26] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.