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Electrochemical and spectroscopic studies on $RuCl_2(PPh_3)_2(N)_2$ and $RuCl_2(PPh_3)_2(N{-}N)$ complexes (N = pyridine derivatives and N–N = phenanthroline or bipyridine derivatives). X-ray structure of $RuCl_2(PPh_3)_2(phen)$

Alzir A. Batista [a,*], Marcelo O. Santiago [a], Claudio L. Donnici [b], Icaro S. Moreira [c], Peter C. Healy [d], Susan J. Berners-Price [d], Salete L. Queiroz [d]

[a] *Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905 São Carlos, SP, Brazil*
[b] *Departamento de Química, Icex, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil*
[c] *Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, Fortaleza, CE, Brazil*
[d] *School of Science, Griffith University, Brisbane, Qld 4111, Australia*

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Abstract

A series of $RuCl_2(PPh_3)_2(N)_2$ and $RuCl_2(PPh_3)_2(N{-}N)$ complexes were synthesized from $RuCl_2(PPh_3)_3$, $(N)_2$ = pyridine (py), 4-(*N*,*N*-dimethylamino)pyridine (4-dmNpy), 4-*tert*-butylpyridine (4-^{t}Bu-py), 4-methylpyridine (4-Mepy), 4-vinylpyridine (4-Vpy), 4-phenylpyridine (4-Phpy), isonicotinamide (4-$CONH_2$py), 4-cyanopyridine (4-CNpy) N–N = 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), 2,2′-bipyridine-4,4′-dimethoxy (MeO-bipy), 2,2′-bipyridine-4,4′-dimethyl (Me-bipy), 2,2′-bipyridine-4,4′-dithiomethyl (MeS-bipy), 2,2′-bipyridine-4,4′-dichloro (Cl-bipy) and 2,2′-bipyridine-4,4′-dinitro (NO_2-bipy). The complexes were characterized by elemental analysis, cyclic voltammetry and UV–Vis, NMR and IR spectroscopies. The structure of the $RuCl_2(PPh_3)_2(phen)$ was established by single crystal X-ray crystallography. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ruthenium(II) complexes; Triphenylphosphine; N-donor ligands; Electrochemical and spectroscopic studies

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1. Introduction

Ruthenium(II) pyridyl complexes have been known for many years. They are characterized by strong metal-to-ligand charge transfer (MLCT) bands in the visible region which make these compounds highly colored. The presence of phosphines in this class of compounds can make them good catalysts for homogeneous hydrogenation of unsaturated organics [1–4]. This process depends on the dissociation of a coordinated ligand in order to generate an electronically unsaturated species which undergoes reactions with the substrate. The dissociation of pyridyl ligands can also supply the reaction medium of a base which is necessary to promote the easy heterolytic activation of H_2 [5]. It is clear that both electronic and steric effects play a decisive role in this process. We report here some electrochemical and spectroscopic characteristics of pyridyl/phosphine/ruthenium(II) complexes relating their half-wave potentials with the properties of the N-heterocyclic ligands and with the molecular structure of these complexes. Since the mechanism of hydrogenation reactions involves the oxidative addition of H_2 to the complex, this information is important in order to help select the best catalysts among possible isomers of the same complex.

2. Experimental

The chemicals employed in this work were of reagent grade quality (Aldrich). Ligands with general formula X-bipy (X = Cl, Me, MeO, MeS, NO_2) and the $RuCl_2(PPh_3)_3$ complex were synthesized as mentioned

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* Corresponding author. Tel.: + 55-16-2608285; fax: + 55-16-2608350.

E-mail address: daab@power.ufscar.br (A.A. Batista).

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in the literature [6]. Tetrabutylammonium perchlorate (Fluka purum) was recrystallized from ethanol–water and dried overnight, under vacuum, at 100°C. Reagent grade solvents (Merck) were appropriately distilled, dried and stored over Linde 4 Å molecular sieves. Purified argon was used for the removal of dissolved oxygen. Infrared spectra were recorded as CsI pellets on a Bomem–Michelson 102 instrument, and UV–Vis spectra in CH_2Cl_2 on a HP 8452A spectrophotometer and are given as λ_{max} (nm); log ε (M^{-1} cm^{-1}). $^{31}P\{^1H\}$ NMR spectra (^{31}P 161 MHz) were obtained in CH_2Cl_2 or $CDCl_3$ solution at room temperature (r.t.) with Bruker or Varian 400 MHz spectrometers and chemical shifts are reported relative to H_3PO_4 85%. Cyclic and differential pulse voltammetries were carried out at r.t. in freshly distilled dichloromethane containing 0.1 mol l^{-1} of $Bu_4N^+ClO_4^-$ (TBAP), using an EG&G/PARC electrochemical system consisting of a 273A potentiostat. A three-electrode system with resistance compensation was used throughout. The working and auxiliary electrodes were a stationary platinum foil and a wire, respectively. The reference electrode was Ag | AgCl in a Luggin capillary, 0.1 mol l^{-1} TBAP in CH_2Cl_2, a medium in which ferrocene is oxidized at 0.43 V (Fc^+/Fc); all potentials are referred to this electrode. Elemental analyses were performed at the Department of Chemistry, Federal University of São Carlos, São Carlos.

2.1. $RuCl_2(PPh_3)_2(N)_2$

Complexes with general formula $RuCl_2(PPh_3)_2(N)_2$ were prepared as ascribed in the literature with little modification [5]. A typical procedure for preparation of these complexes is: $[RuCl_2(PPh_3)_3]$ (0.1 g, 0.1 mmol) was dissolved in CH_2Cl_2 (5 ml) and excess of the ligand (0.5 mmol) was added. The solution was stirred under Ar for 1 h after what the volume was reduced to approximately 1.5 ml and ether was added to precipitate the complex which was filtered and well washed with hexane and ether and dried under vacuum. The yields of these syntheses ranged from 80 to 85%.

The microanalytical data for all $RuCl_2(PPh_3)_2(N)_2$ complexes synthesized in this work are consistent with the formulation shown below [experimental (calculated)]:

Complex	%C	%H	%N
$RuCl_2(PPh_3)_2(4\text{-dmNpy})_2$	63.83	5.36	5.95
	(63.52)	(5.79)	(6.01)
$RuCl_2(PPh_3)_2(4\text{-}^t\text{Bu-py})_2$	67.50	5.90	3.00
	(67.07)	(5.84)	(2.90)
$RuCl_2(PPh_3)_2(4\text{-Mepy})_2$	65.88	5.35	3.33
	(65.31)	(5.02)	(3.17)
$RuCl_2(PPh_3)_2(4\text{-Vpy})_2$	66.15	4.75	2.98
	(66.22)	(4.89)	(3.09)
$RuCl_2(PPh_3)_2(py)_2$	64.40	5.09	3.10
	(64.64)	(4.72)	(3.29)
$RuCl_2(PPh_3)_2(4\text{-Phpy})_2$	69.41	4.93	2.98
	(69.18)	(4.80)	(2.78)
$RuCl_2(PPh_3)_2$-(4-$CONH_2$py)	60.83	4.74	5.97
	(61.28)	(4.50)	(5.96)
$RuCl_2(PPh_3)_2(4\text{-CNpy})_2$	63.23	3.99	6.06
	(63.72)	(4.23)	(6.19)

2.2. $RuCl_2(PPh_3)_2$(X-bipy)

Complexes with general formula $RuCl_2(PPh_3)_2$(X-bipy) were synthesized as follows: $RuCl_2(PPh_3)_3$ (0.1 g, 0.1 mmol) was dissolved in CH_2Cl_2 (2 ml) and the X-bipy ligand (0.11 mmol) was added. The solution was stirred under Ar for 30 min and ether (6 ml) was added to precipitate the product of the reaction. The obtained solid was well washed with hexane and ether and dried under vacuum. The yields of these syntheses were approximately 80–90%.

The microanalytical data for all $RuCl_2(PPh_3)_2$(X-bipy) complexes synthesized in this work were consistent with the formulation shown below [experimental (calculated)]:

Complex	%C	%H	%N
$RuCl_2(PPh_3)_2$(MeO-bipy)	63.01	4.98	3.24
	(63.16)	(4.64)	(3.07)
$RuCl_2(PPh_3)_2$(Me-bipy)	64.98	4.90	3.46
	(65.46)	(4.81)	(3.18)
$RuCl_2(PPh_3)_2$(MeS-bipy)	60.88	5.01	3.05
	(61.01)	(4.48)	(2.96)
$RuCl_2(PPh_3)_2$(bipy)	64.36	4.79	3.20
	(64.79)	(4.49)	(3.29)
$RuCl_2(PPh_3)_2$(phen)	65.02	4.61	3.37
	(65.76)	(4.37)	(3.20)
$RuCl_2(PPh_3)_2$(Cl-bipy)	59.61	4.15	3.18
	(59.95)	(3.94)	(3.04)
$RuCl_2(PPh_3)_2(NO_2\text{-bipy})$	58.15	4.13	6.11
	(58.61)	(3.85)	(5.94)

2.3. Crystal structure determination for *cis*-$RuCl_2(PPh_3)_2$(phen)

2.3.1. Data collection, structure solution and refinement

A red prismatic crystal of the complex, suitable for X-ray diffraction studies, was grown by slow evaporation of a dichloromethane–diethyl ether solution. A unique data set was collected at 293 K on a crystal with dimensions 0.30 × 0.25 × 0.20 mm with a Rigaku AFC7R rotating anode diffractometer (ω–2θ scan mode, monochromated Mo K_α radiation $\lambda = 0.7107$ Å) to $2\theta_{\max} = 50°$, yielding 4029 independent reflections, 1971 with $I > 2\sigma(I)$ being considered 'observed'. An empirical absorption correction was applied based on ψ-scans with transmission factors ranging from 0.67 to 0.88. The structure was solved by heavy atom Patterson techniques, expanded by using Fourier techniques and refined by full-matrix least-squares on $|F|$ (program TEXSAN, 1997) [7]. Meaningful anisotropic refinement was found to be possible for the Ru, Cl and P atoms only; $(x, y, z, U_{\text{iso}})_H$ were included and constrained at estimated values. Statistical weights were employed. Conventional residues, R, R_w at convergence were 0.054 and 0.052.

2.3.2. Crystal data

[RuCl$_2$(PPh$_3$)$_2$(phen)], $C_{48}H_{38}Cl_2N_2P_2Ru$, M 876.8, orthorhombic space group $Pna2_1$ (no. 33), $a = 32.830(8)$, $b = 11.785(5)$, $c = 10.425(7)$ Å, $V = 4034$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.44$ g cm^{-3}, $F(000) = 1792$, $\mu = 6.4$ cm^{-1}.

Table 1
Electronic spectroscopic data for the RuCl$_2$(PPh$_3$)$_2$(X-bipy) complexes

Complex	CT1 [a]	CT2 [a]	CT3 [a]
RuCl$_2$(PPh$_3$)$_2$(MeO-bipy)	294(4.18)	338(3.77)	488(3.42)
RuCl$_2$(PPh$_3$)$_2$(Me-bipy)	300(4.30)	344(3.80)	492(3.52)
RuCl$_2$(PPh$_3$)$_2$(MeS-bipy)	300(4.34)	344(3.83)	488(3.56)
RuCl$_2$(PPh$_3$)$_2$(bipy)	304(4.23)	352(3.81)	488(3.60)
RuCl$_2$(PPh$_3$)$_2$(phen)	308(4.08)	353(3.71)	550(3.49)
RuCl$_2$(PPh$_3$)$_2$(Cl-bipy)	304(4.10)	366(3.74)	548(3.60)
RuCl$_2$(PPh$_3$)$_2$(NO$_2$-bipy)		336(3.67)	524(3.94)

[a] Electronic spectral data, in CH$_2$Cl$_2$ solution. $\lambda_{\max}$ (nm) (log $\varepsilon_{\max}$, M^{-1} cm^{-1}).

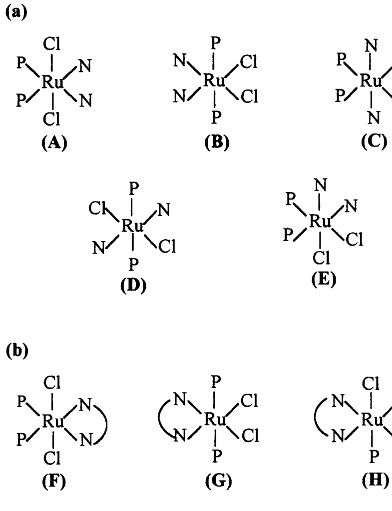

Fig. 1. The possible geometries of: (a) RuCl$_2$(PPh$_3$)$_2$(N)$_2$ and (b) RuCl$_2$(PPh$_3$)(N–N)$_2$, where N = nitrogen donor, P = PPh$_3$ and N–N = bidentated ligand (N and N–N see text).

3. Results and discussion

The electronic spectra of these ruthenium(II) complexes were studied in CH$_2$Cl$_2$ solutions The complexes formed very intense coloured solutions and thus very low concentrations have been used. In the UV–Vis region, intense bands below 300 nm present in the free ligand and assigned to $\pi \rightarrow \pi^*$ transitions from the aromatic rings are also present in the spectra of the complexes. In general three moderately intense bands are observed in the complexes which could be assigned to charge transfer (Ru(II) $d_\pi \rightarrow$ py p_{π^*}) [5,8–11]. Transitions of the metal ion (d–d transitions) can be obscured by charge transfer transitions at lower energies in these complexes [12]. The UV–Vis spectrum for our complexes with monodentate ligands are very similar with those mentioned in the literature [5] and the data for the compounds with bidentate ligands are shown in Table 1. As general tendency, bands for complexes with bidentate ligands are shifted to the UV region when compared with those for monodentate ones.

Complexes with general formula RuCl$_2$(PPh$_3$)(N)$_2$ where N is a N-donor monodentate ligand can show five possible geometries (Fig. 1(a)).

When the N-donor ligand is bidentate this number of geometries is reduced to three (Fig. 1(b)). From our previous study with complexes with general formula RuCl$_2$(dppb)(N)$_2$ (dppb = 1,4-bis(diphenylphosphino)-butane) it was well defined that isomers of type A or F (Fig. 1(a) and (b), respectively), where nitrogens are *trans* to phosphorus atoms, have $^{31}P\{^1H\}$ chemical shifts in the range 30–40 ppm [13] (coordination chemical shift, $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}) \cong 56$ ppm downfield). The *trans*-RuCl$_2$(dppb)(py)$_2$ complex was characterized by X-ray crystallography suggesting that indeed ruthenium(II) phosphine complexes with nitrogen atoms *trans* to phosphorus atoms present $^{31}P\{^1H\}$ NMR chemicall shift close to 30–40 ppm [13]. From this same study it was also inferred that isomers of type C undergo an upfield shift of $^{31}P\{^1H\}$ NMR to approximately 30 ppm ($\Delta\delta \cong 46$ ppm). For the present PPh$_3$ complexes, those with monodentate N-donor ligands show $^{31}P\{^1H\}$ chemical shifts of the order of range 30–40 ppm (Table 2) while complexes with bidentate N-donor ligands show their $^{31}P\{^1H\}$ resonances shifted upfield to approximately 20 ppm (Table 2). This result, by analogy with the corresponding shifts observed for the dppb complexes described above is consistent with the monodentate N-donor complexes in which the chlorides are in the *trans* position, consistent with geometry A (Fig. 1(a)) and the bidentate N-donor complexes with the chlorides in the *cis* position, consistent with geometry G (Fig. 1(b)). Our previous study with a series of RuCl$_2$(PPh$_3$)$_2$(CO)(N) complexes (where N = monodentate N-donor ligands and phosphorus *trans* phosphorus) [14] and other data from the literature [15] give

Table 2
pK_a, NMR, IR and cyclic voltametric data for the complexes $RuCl_2(PPh_3)_2(N)_2$ and $RuCl_2(PPh_3)_2(N–N)$ where N is a N-donor ligand

Complex	pK_a [a]	$^{31}P\{^1H\}$ NMR	IR ν(Ru–Cl) [b]	$E_{1/2}$ (Ru^{III}/Ru^{II}) (V)
$RuCl_2(PPh_3)_2$(4-dmNpy)$_2$	9.71 [d]	40.23	336	0.25
$RuCl_2(PPh_3)_2$(4-Mepy)$_2$	6.02 [c]	38.91	324	0.41
$RuCl_2(PPh_3)_2$(4-^{t}Bu-py)$_2$	5.99 [d]	30.00	332	0.31
$RuCl_2(PPh_3)_2$(4-Vpy)$_2$	5.72 [e]	37.00	337	0.45
$RuCl_2(PPh_3)_2$(4-Phpy)$_2$	5.55 [d]	37.05	331	0.46
$RuCl_2(PPh_3)_2(py)_2$	5.25 [c]	42.56	326	0.45
$RuCl_2(PPh_3)_2$(4-$CONH_2$py)	3.61 [d]	36.35	330	0.52
$RuCl_2(PPh_3)_2$(4-CNpy)$_2$	1.86 [c]	36.52	329	0.66
$RuCl_2(PPh_3)_2$(MeO-bipy)	4.96 [d]	21.83	278, 309	0.27
$RuCl_2(PPh_3)_2$(Me-bipy)	4.58 [d]	21.78	263, 294	0.31
$RuCl_2(PPh_3)_2$(MeS-bipy)	4.52 [d]	21.97	259, 291	0.36
$RuCl_2(PPh_3)_2$(bipy)	4.40 [f]	21.53	278, 295	0.42
$RuCl_2(PPh_3)_2$(Cl-bipy)	3.55 [d]	20.12	272, 289	0.43
$RuCl_2(PPh_3)_2$(NO_2-bipy)	2.09 [d]	19.66	266, 290	0.59
$RuCl_2(PPh_3)_2$(phen)	4.84 [c]	23.26	262, 295	0.43

[a] With respect to nitrogen of the pyridine ring.
[b] In cm^{-1}, very weak intensities.
[c] Ref. [20].
[d] Ref. [23].
[e] Values calculated using the equation p$K_a = 5.25–5.9\ \Sigma\ \sigma$, Ref. [21].
[f] Ref. [22].

support to this suggestion. In order to confirm the geometry of the series of complexes containing bidentate ligands we determined the single crystal X-ray structure of the $RuCl_2(PPh_3)_2$(phen) compound. The structure is consistent with the formulation of the complex as a monomeric six-coordinate molecular species with *trans* PPh_3 ligands and *cis* chloride anions. A representative view of the molecular structure is shown in Fig. 2 and relevant interatomic bond lengths and bond angles are in Table 3. The symmetry of the complex approximates C_m with a pseudo-plane of mirror symmetry passing through the phenantholine ligand, ruthenium(II) cation and chloride anions. The differences in degree of distortion of the complex away from exact C_m symmetry is reflected in the torsion angles of the phenyl rings Ru–P(n)–C(nm1)–C(nm2) -8, 50 and 78° for the $n = 1$ ligand and 6, -69 and -75° for the $n = 2$ ligand. The Ru–P distances of 2.401(4), 2.378(4) Å; Ru–Cl of 2.441(5), 2.425(5); Ru–N of 2.05(2), 2.07(2) are essentially the same as those recorded for the $(PPh_3)_2$Pt(μ-1,10-phenanthroline-5,6-diolato)Ru$(PPh_3)_2Cl_2$ and other *trans* $(PPh_3)_2$Ru complexes [16–18].

The single $^{31}P\{^1H\}$ chemical shift of this complex (sample prepared from crystals identical to that used for the structure analysis) in $CDCl_3$ is at 23.26 ppm, consistent with results reported in Table 2. In the IR spectra of the complexes sharp peaks are observed at about 520, 700 and 750 cm^{-1} due the presence of aromatic rings (triphenylphosphine or pyridines) [12,19]. The presence of two ν_{Ru-Cl} in the IR spectrum of these kind of complexes and only one in the $RuCl_2(PPh_3)_2(N)_2$ species (Table 2) also substantiate our attribution by $^{31}P\{^1H\}$ NMR of the geometries of these complexes [19]. The complex $RuCl_2(PPh_3)_2$(4-vinylpyridine)$_2$ was previously synthesised and its $^{31}P\{^1H\}$ chemical shift is very close to that found in this work (34.07 ppm in $CDCl_3$ solution) [5]. The authors of this work proposed a structure for this complex in which the chlorides are in *cis* position and the 4-

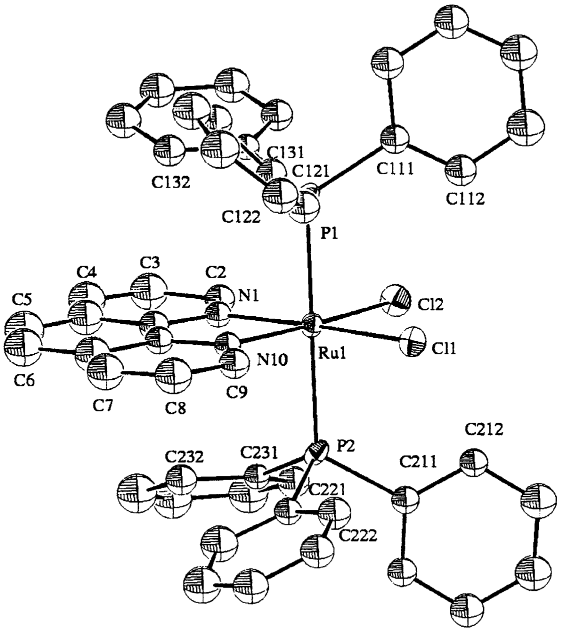

Fig. 2. The molecular structure of $RuCl_2(PPh_3)_2$(phen). 30% of thermal ellipsoids are shown for non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and bond angles (°) for $RuCl_2(PPh_3)_2(phen)$

Bond lengths			
Ru–Cl(1)	2.441(5)	C(8)–C(9)	1.39(2)
Ru–Cl(2)	2.425(5)	C(5)–C(6)	1.25(2)
Ru–P(1)	2.401(4)	P(1)–C(111)	1.90(2)
Ru–P(2)	2.378(4)	P(1)–C(121)	1.81(2)
Ru–N(1)	2.05(2)	P(1)–C(131)	1.83(2)
Ru–N(10)	2.07(2)	P(2)–C(211)	1.87(2)
N(1)–C(2)	1.34(2)	P(2)–C(221)	1.85(2)
N(1)–C(12)	1.35(2)	P(2)–C(231)	1.84(2)
C(2)–C(3)	1.45(2)	N(10)–C(9)	1.31(2)
C(3)–C(4)	1.31(3)	N(10)–C(11)	1.35(2)
Bond angles			
Cl(1)–Ru–Cl(2)	93.2(2)	P(1)–Ru–P(2)	179.9(2)
Cl(1)–Ru–P(1)	90.9(2)	P(1)–Ru–N(1)	89.7(4)
Cl(1)–Ru–P(2)	89.2(2)	P(1)–Ru–N(10)	90.5(4)
Cl(1)–Ru–N(1)	173.2(4)	P(2)–Ru–N(1)	90.2(4)
Cl(1)–Ru–N(10)	95.0(4)	P(2)–Ru–N(10)	89.5(4)
Cl(2)–Ru–P(1)	89.9(2)	N(1)–Ru–N(10)	78.2(6)
Cl(2)–Ru–P(2)	90.1(2)	Cl(2)–Ru–N(10)	171.7(5)
Cl(2)–Ru–N(1)	93.5(4)		

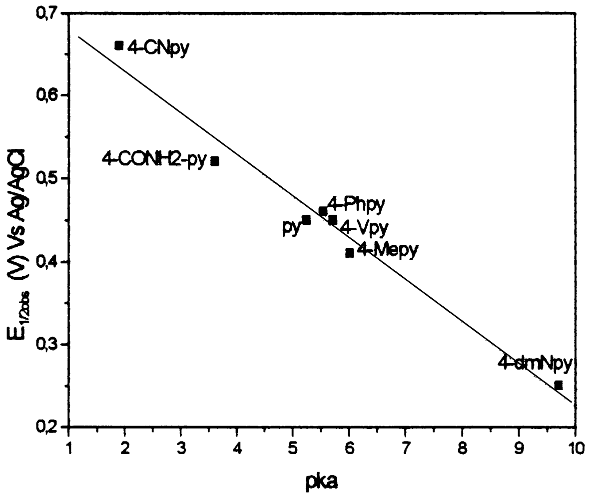

Fig. 3. Correlation of measured values of $E_{1/2}$ for the $RuCl_2(PPh_3)_2(N)_2$ complexes with pK_a of free ligands (N) (N = N-heterocycles) (see text for correlation coefficient).

vinylpyridine are also *cis* to each other which contrasts with our observations reported here. The $RuCl_2(PPh_3)_2(4\text{-CNpy})_2$ and $RuCl_2(PPh_3)_2(4\text{-Mepy})_2$ complexes were also synthesized previously and their $^{31}P\{^1H\}$ chemical shift were reported as 26.70 (s br) and 25.43 (s), respectively [5]. In this case the authors suggested the presence of isomers type B, differently of the found in this work (4-CNpy, $^{31}P\{^1H\} = 36.52$ ppm and 4-Mepy, $^{31}P\{^1H\} = 38.91$ ppm) were we suggest the geometry type of A. It is likely that the isolation of different isomers in this case is due to the use of different methodologies of syntheses in the respective studies.

In Table 2 the half-wave potentials are shown for the complexes studied in this work.

The cyclic voltammograms of all the complexes prepared consist of a pair of reversible peaks ($I_a/I_c \cong 1$), attributed to the one electron Ru(III)/Ru(II) couple. A general tendency is that where complexes containing monodentated ligands show higher half-wave potentials when compared with those with bidentate ligands with similar basicity. This can be explained by the strong competition between the two mutually *trans* phosphorus atoms for the same d electrons from the metal center (*trans* competitive effect [24]). This competition leaves the metal center rich in electrons making its reduction easier. This behavior has been detected by us for other ruthenium(II) phosphines complexes [25]. Indeed, for the series of substituted pyridine ligands a reasonable linear plot of $E_{1/2}$ versus pK_a (Fig. 3), correlation coefficient $R = -0.94$ was obtained. Similar results were obtained for the series of $RuCl_2(CO)(PPh_3)_2(N)$ [14]. If we had excluded the 4-^{t}Bu-py complex the R value would increase to -0.99. It is reasonable to assume that the low $E_{1/2}$ value obtained for the $RuCl_2(4\text{-}^t\text{Bu-py})_2(PPh_3)_2$ complex is due to the slow diffusion of this compound in solution caused by the bulky 4-^{t}Bu-py ligand. Similar correlation for complexes containing bipyridine ligands are in Fig. 4, where $R = -0.98$.

It is interesting to mention that our suggestions above for the geometries of the complexes studied in this work based on spectroscopic data find support in cyclic voltametric experiments. Thus the complexes $RuCl_2(dppb)(N)_2$, where N = 4-Mepy, 4-Vpy, py and 4-CNpy show their half-wave potentials equal 0.42, 0.42, 0.48 and 0.62 V which are practically the same found for the $RuCl_{2(}PPh_3)_2(N)_2$ series under similar conditions [13]. The same was found for the complexes

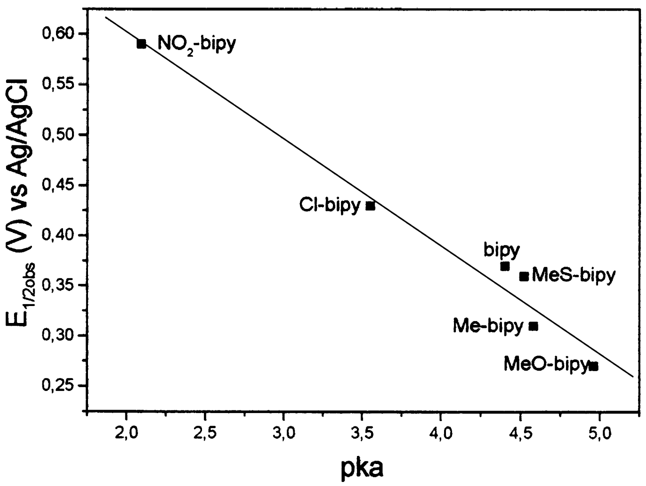

Fig. 4. Correlation of measured values of $E_{1/2}$ for the $RuCl_2(PPh_3)_2(N–N)$ complexes with pK_a of free ligands (N–N) (N–N = N-heterocycles) (see text for correlation coefficient).

with bipy and phen where the complexes $RuCl_2(dppb)(N-N)$ with these ligands shown their $E_{1/2}$ equal 0.45 and 0.47 V what is concordant with the data mentioned in Table 2 [13].

4. Conclusions

This study has demonstrated that for the $RuCl_2(PPh_3)_2(N\text{-heterocyclic})_2$ and $RuCl_2(PPh_3)_2(X\text{-bipy})$ series their $^{31}P\{^1H\}$ chemical shifts are well defined indicating the geometry of the complexes. The IR and cyclic voltametric data give support for the geometries of the complexes suggested by NMR experiments. The half-wave potentials of these complexes are correlate with the pK_a of the ligands. The structure of the $RuCl_2(PPh_3)_2(phen)$ complex was characterized by X-ray crystallography supporting the suggested geometry of this complex in solution.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 142909 for $RuCl_2(PPh_3)_2(phen)$. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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