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# Photochemical isomerization of *trans*- to *cis*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] (X = –H, –NO$_2$, –Me, –COOH, –SMe, –O=SMe, –Cl, –OMe) complexes

Marcelo O. Santiago [a], Claudio L. Donicci Filho [b], Icaro de S. Moreira [c], Rose Maria Carlos [a], Salete L. Queiroz [d], Alzir A. Batista [a,*]

[a] *Departamento de Química, Universidade Federal de São Carlos, CP 676, 13565-905 São Carlos, SP, Brazil*
[b] *Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil*
[c] *Departamento de Química Orgânica e Inorgánica, Universidade Federal do Ceará, Fortaleza, CE, Brazil*
[d] *Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil*

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## Abstract

A series of [RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes was synthesized from [RuCl$_2$(dppb)(PPh$_3$)] and 4,4′-X$_2$-2,2′-bipy [dppb = 1,4-bis(diphenylphosphino)butane and 4,4′-X$_2$-2,2′-bipy = 2,2′-bipyridine (bipy), 4,4′-dimethoxy-2,2′-bipyridine (MeO-bipy), 4,4′-dimethyl-2,2′-bipyridine (Me-bipy), 4,4′-dicarboxy-2,2′-bipyridine (COOH-bipy), 4,4′-dithiomethyl-2,2′-bipyridine (MeS-bipy), 4,4′-dichloro-2,2′-bipyridine (Cl-bipy), 4,4′-dinitro-2,2′-bipyridine (NO$_2$-bipy), and 4,4′-dithiomethylsulphoxide-2,2′-bipyridine (MeS=O-bipy)]. The complexes were characterized by elemental analysis, cyclic voltammetry and differential pulse voltammetry, and by UV–Vis and $^{31}$P{$^1$H}NMR spectroscopies. The p$K_a$ of the ligands were determined. The *trans*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes were photoisomerized under white light and the isomerization rate constants from *trans* to *cis* isomers were consistent with first order reactions and were correlated with the p$K_a$ of the ligands and with the $E_{1/2}$ of the complexes. The suggested mechanism of isomerization reactions is consistent with an intramolecular twist process.

*Keywords:* Ruthenium(II)-bipy derivative complexes; Photoisomerization; 1,4-bis(diphenylphosphino)butane

## 1. Introduction

The 2,2′-bipyridine species has been used in a variety of studies dealing with structural coordination chemistry. Since its discovery at the end of the 19th century, bipyridine has been extensively used in the complexation of metal ions as a metal chelating ligand, due to its robust redox stability and ease of functionalization [1]. Ruthenium(II) is one of the most currently used ions for complexation with bipyridine ligands and complexes of this type have been known for many years. They are characterized by strong metal-to-ligand charge transfer (MLCT) bands in the visible region, which make them highly colored and, with the presence of phosphines, they often become good catalysts for homogeneous hydrogenation of unsaturated organics [2–6]. This property depends on the dissociation of a coordinated ligand in order to generate an electronically unsaturated species that undergoes reactions with the substrate.

The mechanism of stereochemical rearrangements of metal chelate compounds has been an important problem in coordination chemistry since the days of Alfred Werner [7]. For intramolecular rearrangements of octahedral chelates, two classes of mechanisms have been considered: (1) metal–ligand bond rupture to give a five-coordinate species and (2) twisting mechanisms that produce rearrangement without rupture of any metal–ligands bonds [8].

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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 present work we have studied the photochemical isomerization of *trans*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] to *cis*-isomers. Quantitative data show that the isomerization rate constants increase with the increasing p$K_a$ of the 4,4′-X$_2$-2,2′-bipy ligand. This study also leads us to propose that the isomerization process in the series progresses through a twisting mechanism.

## 2. Experimental

### 2.1. Materials

The chemicals employed were of reagent grade quality (Aldrich). Ligands with general formula 4,4′-X$_2$-2,2′-bipy (X = –H, –NO$_2$, –Me, –COOH, –SMe, –O=SMe, –Cl, –OMe) and the [RuCl$_2$(dppb)(PPh$_3$)] and the [RuCl$_2$(PPh$_3$)$_3$] complexes, were synthesized as described in the literature [9–11]. Tetrabutylammonium perchlorate (TBAP) (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.

### 2.2. Synthesis

A typical procedure for preparation of the *trans*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes was: (0.100 g; 0.110 mmols) of [RuCl$_2$(dppb)(PPh$_3$)] was dissolved in benzene (2 ml) and 0.120 mmols of the ligand was added. The solution was stirred under Ar for 30 min and hexane was subsequently added to precipitate the resulting powder, which was filtered, well washed with ether and dried under vacuum. The yield of these complexes was about 90%.

In a previous study was detected that heating the *trans*-isomers to reflux in CH$_2$Cl$_2$ or C$_6$H$_6$ results in isomerization to the *cis*-forms [12]. Thus, in this work the synthesis of the *trans*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes were performed at room temperature and in the dark to avoid the isomerization processes.

The microanalytical data for all *trans*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes synthesized are consistent with the formulation shown below [experimental(calculated)] (Table 1).

All complexes, including the products of the photochemical isomerizations, were characterized by cyclic voltammetric (CV) or differential pulse voltammetric (DPV) measurements and $^{31}$P{$^1$H}NMR spectroscopy.

Reinecke's salt (NH$_4$)[Cr(NH$_3$)$_2$(SCN)$_4$] (Eastman) used in the photochemical experiments was converted to the potassium salt by recrystallization from KNO$_3$ solution, prior to being used for actinometry at 519 nm [13]. Potassium(tris-oxalate)ferrate(III), used in actinometry at 304 and 370 nm, was prepared according to Calvert and Pitts [14].

### 2.3. Apparatus and methods

Monochromatic irradiation at 300, 370 and 500 nm is generated using a 200-W Xenon lamp in an Oriel mod. 68805 Universal Arc Lamp source selected with an appropriate interference filter (Oriel). The progress of the photoreaction was monitored by UV–Vis spectra on a HP 8452A spectrophotometer, or electrochemically by differential pulse voltammetry (DPV) on a EG&PARC electrochemical system consisting of a 273A potentiostat. This instrument was also used for characterization of the complexes. The working and auxiliary electrodes were a stationary platinum foil and wire, respectively. The reference electrode was Ag|AgCl in a Luggin capillary. The measurements were carried out at room temperature in freshly distilled CH$_2$Cl$_2$ containing 0.1 mol l$^{-1}$ of Bu$_4$N$^+$ClO$_4$$^-$ in the three-electrode system with resistance compensation, a medium in which ferrocene is oxidized at 0.43 V versus *Fc*$^+$/*Fc*; all potentials are referred to this electrode.

$^{31}$P{$^1$H} NMR spectra ($^{31}$P 161 MHz) were obtained in a CH$_2$Cl$_2$ or CDCl$_3$ solution at room temperature

Table 1
Micro analytical data for the *trans*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes

| RuCl$_2$(dppb)$_2$,(X-bipy), X = | %H(calc) | %C(calc) | %N(calc) |
|---|---|---|---|
| MeO– | 4.92(4.95) | 58.35(58.97) | 3.46(3.44) |
| Me– | 5.15(5.15) | 61.11(61.38) | 3.66(3.58) |
| MeS–[a] | 4.90(4.76) | 56.67(56.73) | 3.47(3.31) |
| H– | 4.90(4.85) | 60.48(60.50) | 3.81(3.75) |
| –COOH | 4.22(4.31) | 56.68(57.01) | 3.03(3.32) |
| Cl– | 4.93(4.81) | 56.99(57.35) | 3.20(3.18) |
| MeS=O–[b] | 4.66(4.59) | 53.99(54.67) | 3.20(3.19) |
| NO$_2$– | 4.04(4.06) | 54.04(54.67) | 6.41(6.36) |
| RuCl$_2$(dppb)(phen) | 4.95(4.66) | 61.56(61.70) | 3.75(3.60) |

[a] S = 7.60(7.78)%.

[b] S = 7.81(7.57)%.

with a Bruker 400 MHz spectrometer and chemical shifts are reported relative to $H_3PO_4$ 85%. Microanalytical data (C, H and N) were obtained with the use of a Fisons model EA 1108 elemental analyser.

## 3. Procedures

Photolysis experiments were carried out at 298 K in a 10 cm path length quartz cells but some of them were initiated directly in a 3 ml electrochemical cell. The solutions ($10^{-3}$ M of the initial complex concentrations) were deaerated by bubbling argon prior to photolysis and were stirred during irradiation. Solutions protected from light were completely stable on a timescale longer than that of the photochemical experiments. Experiments with different monochromatic lights in different solvents, had, within experimental uncertainties, shown no wavelength dependence and an identical quantum yield was found, as can be seen in Table 2. This behavior indicates that the photochemical reactions are processed through ligand field paths even when the irradiation is in a charge transfer transition region (TC). This procedure was performed for the ruthenium complexes with the 2,2′-bipyridine and the 4,4′-dimethoxy-2,2′-bipyridine ligands and assumed to be the same for the other ligands. Since the quantum yields of the isomerization processes are the same, independent of the irradiation wavelength (Table 2), all the photochemical experiments were performed using white light irradiation. The reported yields are the average of, at least, two independent experiments. Isomerization rate constants for the photoreaction were evaluated from cyclic voltammetry changes (electrochemical $Ru^{III} \rightarrow Ru^{II}$ processes) by using the initial and final differential pulse voltammograms as reactant and as product voltammogram, respectively. As the half-wave potential values for the *trans*- and *cis*-$Ru^{III}/Ru^{II}$ redox processes are easily distinguishable the isomerization from *trans*- to *cis*-[$RuCl_2$(dppb)(4,4′-$X_2$-2,2′-bipy)], complexes were monitored by observing the growth of a new electrochemical wave present in the *cis* isomers. Successive cyclic voltammograms were collected at time intervals from 20 to 180 min.

Table 2
Photoreaction quantum yield for *trans*-[$RuCl_2$(dppb)(bipy)] isomerization for different irradiations and different solvents at 25 °C

| $\lambda_{irr}$ (nm) | Solvent | $\phi$ (mol/einstein)[a] |
|---|---|---|
| 300 | $CH_2Cl_2$ | $0.53 \pm 0.03$ |
| 370 | $CH_2Cl_2$ | $0.54 \pm 0.03$ |
| 500 | $CH_2Cl_2$ | $0.52 \pm 0.03$ |
| 370 | $CH_3CN$ | $0.55 \pm 0.03$ |
| 370 | $CH_3SOCH_3$ | $0.56 \pm 0.03$ |

[a] Determined by UV–Vis experiments.

## 4. Results and discussion

The $^{31}P\{^1H\}$ chemical shifts of the [$RuCl_2$(dppb)(4,4′-$X_2$-2,2′-bipy)] complexes, synthesized in this work, close to 30.0–33.0 ppm, are consistent with a geometry where the nitrogen are *trans* to the phosphorus atoms [12,15].

In $CH_2Cl_2$ solutions, in the UV–Vis region, the complexes show intense bands below 330 nm which are also present in the free ligands and are assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic rings. The two moderately intense bands observed in the complexes between 350 and 550 nm can be assigned to charge transfer transitions (CT) (Ru(II) $d_\pi \rightarrow \pi^*_{(bipy)}$) [16]. The energy of these transitions depend on the substituent group on the bipyridine rings, analogous to those previously reported for other ruthenium(II) complexes [16–19]. Their energies depend on the electron-acceptor properties of the bipyridine ligands, and follow a good linear correlation with the p$K_a$s of the ligands (Fig. 1).

The transitions of the metal ion (d–d transitions) can be obscured by charge transfer transitions at lower energies in these complexes [20]. The UV–Vis spectra of our complexes with bipyridine derivative ligands (see Table 3) are very similar to those described in the literature where two charge transfer transitions were found [21]. As a general tendency, bands for complexes with 1,4-bis(diphenylphosphino)butane are shifted to the infrared region when compared to those for triphenylphosphine complexes with the same bipyridine derivative ligands [15].

As can be seen in Fig. 2, in the visible spectrum of the *trans*-[$RuCl_2$(dppb)(2,2′-bipy)] obtained during the isomerization process, there are three isosbestic points indicating that the final product is only the *cis* form of this complex, which absorbs at 360 nm (shoulder) and 452 nm. Thus, the only photoproducts upon irradiation

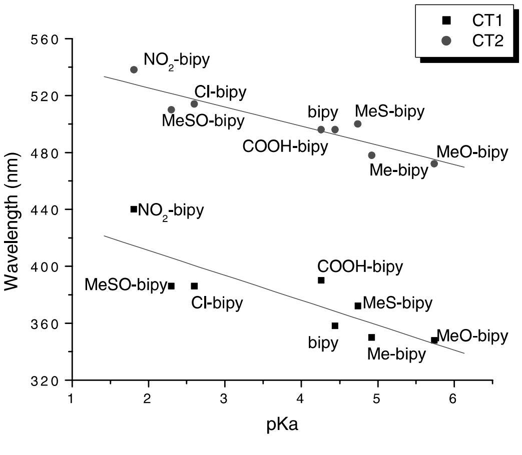

Fig. 1. Correlations between p$K_a$s of the (4,4′-$X_2$-2,2′-bipy)] ligands and energies of the CT transitions of the [$RuCl_2$(dppb)(4,4′-$X_2$-2,2′-bipy)] complexes (■, CT1*; ●, CT2).

Table 3
Charge transfer transitions (TC) for the *trans*-[$RuCl_2$(dppb)(4,4′-$X_2$-2,2′-bipy)] complexes

| [$RuCl_2$(dppb)(X-bipy)] X = | CT1[a] | CT2[a] |
|---|---|---|
| MeO– | 348 (3.56) | 472 (3.25) |
| Me– | 350 (3.49) | 478 (3.32) |
| MeS– | 372 (3.67) | 500 (3.46) |
| H–[b] | 360 (3.52) | 500 (3.37) |
| COOH– | 390 (3.84) | 496 (3.53) |
| Cl– | 386 (3.52) | 514 (3.39) |
| MeSO– | 386 (3.51) | 510 (3.38) |
| $NO_2$– | 438 (3.16) | 538 (3.64) |

[a] Electronic spectral data, in $CH_2Cl_2$ solution. $\lambda$max, nm (log $\varepsilon_{max}$, $M^{-1}$ $cm^{-1}$).

[b] Ref. [12].

of the *trans* isomers for all bipyridine derivative ligands are the respective *cis* isomers. The photochemical reaction products were also quantitatively detected by $^{31}P\{^1H\}$ measurements showing two doublets at about 32.0 ppm (phosphorus *trans* nitrogen) and at about 43.0 ppm (phosphorus *trans* chlorine) what represents a standard AX patterns with $^2J_{AX}$ approximately 32.0 Hz [22,23].

Irradiation of *trans*-isomers in $CH_2Cl_2$ solutions with white light leads to the decrease of their electrochemical currents (Fig. 3) and the appearance of new electrochemical processes at higher potentials, showing the isomerization processes from *trans* to *cis* forms. The isosbestic points at ca. 400 and 480 nm were retained during the conversion, indicating that the photoreaction is not complicated by side or subsequent reactions. The spectral changes observed during the photolysis were essentially independent of the excitation energy, of the complex or of the light intensity. The photoproducts of the reactions (*cis*-isomers) were also identified by CV or DPV measurements (Table 4).

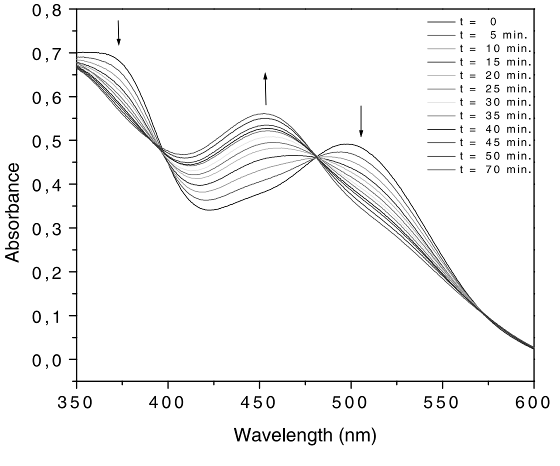

Fig. 2. Photoisomerization process under white light of [$RuCl_2$(dppb)(2,2′-bipy)] in $CH_2Cl_2$ solution ($2.1 \times 10^{-4}$ mol $l^{-1}$), at 298 K.

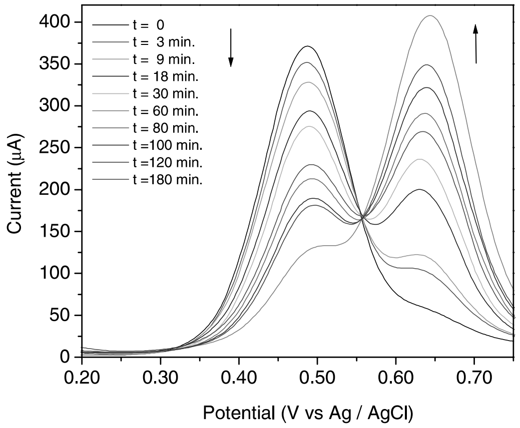

Fig. 3. Changes (isomerization process) in the differential pulse voltammogram resulting from white light photolysis of [$RuCl_2$(dppb)(2,2′-bipy)] $\sim 10^{-3}$ M in $CH_2Cl_2$ (0.1 M PTBA, Pt auxiliary and working electrodes and Ag | AgCl as reference).

The differential pulse voltammogram of an exhaustively photolyzed solution of [$RuCl_2$(dppb)(2,2′-bipy)] with white light $\sim 10^{-3}$ M, 3 ml, at 298 K is shown in Fig. 3.

In cyclic or differential pulse voltammetry in $CH_2Cl_2$, all complexes (*trans* and *cis* isomers) reveal a one-electron ($Ru^{III} \rightarrow Ru^{II}$) process, corresponding to a reversible wave ($i_p^{ox}/i_p^{red}$ values are close to unity at scan rate $v = 10$–$200$ mV $s^{-1}$).

The $E_{1/2}$ values for the complexes depend on the type of isomer present in solution and on the donor properties of the ligands. The *cis*-isomers always show oxidation potentials higher than the corresponding *trans*-isomers; this increase in potential on going from the *trans*- to the *cis*-isomer is well established in Ru(II) chemistry [21,24,25]. The oxidation potential of the complexes reflects the donor property of the substituent group in the X-bipy ligands: electron-withdrawing groups in the 4,4′-positions make the oxidation of the complex more difficult, as expected, while electron-donor groups in these positions make the oxidation easier. This electrochemical behavior was the subject of a very elegant work by Lever's group for an extended series of transition metal complexes [26,27]. The electrochemical redox potentials ($E_{1/2}$) of the *trans*-[$RuCl_2$(dppb)(4,4′-$X_2$-2,2′-bipy)] series can be correlated with the p$K_a$s of the ligands (Fig. 4). This correlation has been also detected for the *cis*-[$RuCl_2(PPh_3)_2$($X_2$-2,2′-bipy)] series where the $PPh_3$ are in *trans* position [15].

Fig. 5 shows the correlation between energies of charge transitions (CT1* and CT2*) of the complexes and their respective electrochemical redox potentials ($E_{1/2}$) where can be observed that complexes with lower energies of transition present lower redox potentials.

The isomerization constant rates for the photoreaction in the [$RuCl_2$(dppb)(X-bipy)] series are given in Table 4 and as can be seen in Fig. 6, there is a good

Table 4
p$K_a$ and cyclic voltammetric ($v = 100$ mV s$^{-1}$) and isomerization rate constant data for the [RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes

| [RuCl$_2$(dppb)(X-bipy)] X = | Ligand's p$K_a$ | $E_{1/2}$ (V) *Trans* | $E_{1/2}$ (V) *Cis* | Isomerisation rate constant $10^5\times$ (s$^{-1}$) |
|---|---|---|---|---|
| MeO– | 5.74 | 0.37 | 0.57 | 86.22 |
| Me– | 4.92 | 0.43 | 0.60 | 85.00 |
| MeS– | 4.74 | 0.45 | 0.62 | 74.50 |
| H– (298 K) | 4.44 | 0.46 | 0.65 | 63.10 |
| H– (293 K) | | | | 35.3 |
| H– (288 K) | | | | 22.8 |
| H– (283 K) | | | | 13.2 |
| COOH– | 4.26[a] | 0.50 | 0.60 | 52.10 |
| Cl– | 2.60 | 0.60 | 0.76 | 35.70 |
| MeS=O– | 2.30 | 0.63 | 0.77 | 13.50 |
| NO$_2$– | 1.81 | 0.70 | 0.86 | 1.98 |
| [RuCl$_2$(dppb)(fen)] | | 0.46 | 0.66 | 84.00 |

[a] Ref. [21].

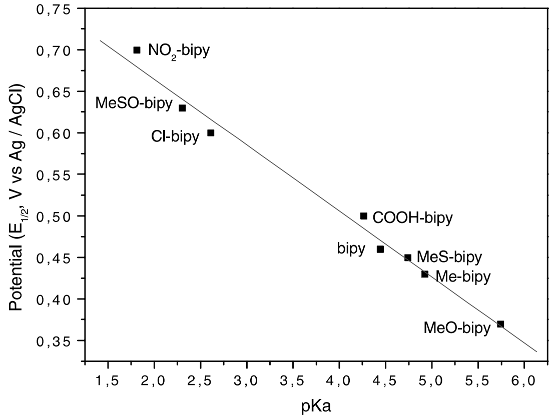

Fig. 4. Correlation of measured values of $E_{1/2}$ for the [RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes with p$K_a$ of free 4,4′-X$_2$-2,2′-bipy ligands.

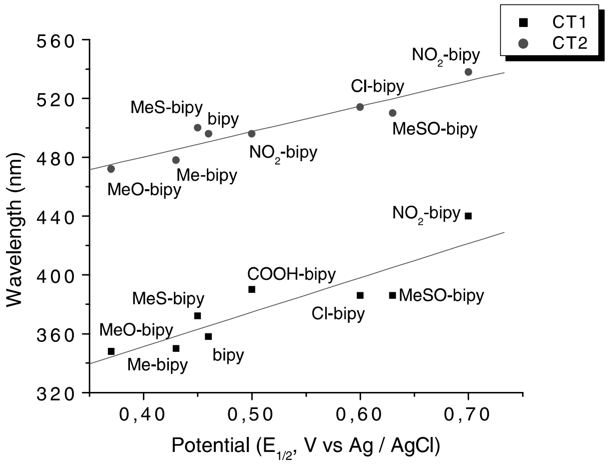

Fig. 5. Correlation between energies of the charge transfer transitions (CT) and potential redox ($E_{1/2}$ V vs. Ag/AgCl) of the [RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes.

correlation between these data and the p$K_a$ of the ligands. The results collected in Table 4 clearly show that the isomerization rate constants depend on the donor properties of the ligands which is a consequence of the electron densities of the metal centers. This in the end is reflected in the Ru–Cl bond character, which is mainly responsible for the isomerization process of the complexes. Thus, as the metal center becomes softer due to its coordination to ligands with high p$K_a$, for instance, lower is the attraction of the metal cation for the chlorine ion. Therefore, the isomerization process is faster.

Fig. 7 shows the correlation between isomerization rate constants and electrochemical redox potentials ($E_{1/2}$) for the series of complexes. To explain the increase of the isomerization rate constant of the complexes with the increase of the p$K_a$ of the coordinate ligand, it is possible to suggest a model where the attraction between the metal center and the chlorine is affected by the donor property of the nitrogen donor atoms of the bipyridine derivative ligands. Thus, as the metal center, in the case coordinated to ligands with high p$K_a$, becomes more electron rich, the faster is the isomerization process.

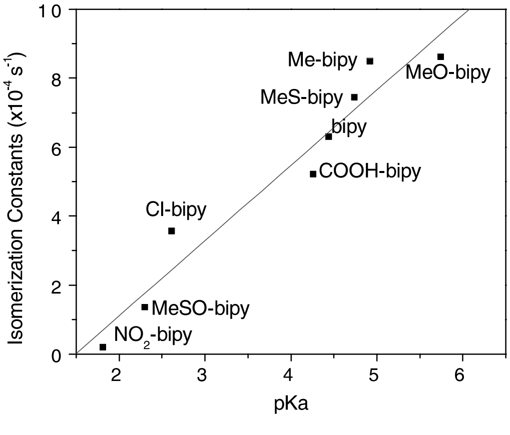

Fig. 6. Correlation between isomerization rate constants of [RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes and p$K_a$ of 4,4′-X$_2$-2,2′-bipy ligands.

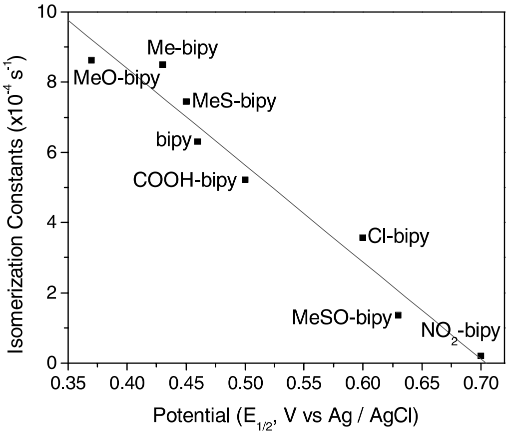

Fig. 7. Correlation between isomerization rate constants of the [RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] and $E_{1/2}$(V vs. Ag/AgCl) of the complexes.

As has been shown, the *trans* complexes can be easily converted into the *cis* isomers in solution, by photolysis at room temperature, under white light. The formation of the *cis*-[RuCl$_2$(dppb)(2,2′-bipy)] complex was nearly quantitative as determined from the relative spectral changes at 450 and 520 nm, after 3 h of reaction. For practical purposes these processes are remarkable because they constitute quantitative synthetic procedures for preparation of the *cis* isomers, which are considerably easier than the original syntheses [25].

The lack of substantial dependence of the quantum yields in the isomerization reactions for the *trans*-[RuCl$_2$(dppb)(2,2′-bipy)] complex (Table 2) on the solvents (coordinating or non-coordinating) suggests a twisting mechanism where no ligand is totally dissociated from the metal center. Since in the *trans*-[RuCl$_2$(dppb)(2,2′-bipy)] series only the chlorine ligand is not quelated probably the mechanism involved in the isomerization process of these complexes is more influenced by the flexibility of the Ru–Cl bond than of the Ru–P or Ru–N bonds. This suggestion finds support in the fact that the chlorine ligand is easily and totally dissociated from the complexes when they are in the presence of coordinating solvent for long period of time.

Variable-temperature data afforded the activation parameters for the isomerization process of the [RuCl$_2$(dppb)(2,2′-bipy)] complex ($\Delta H^{\ddagger} = 69.6$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -73.1$ J K$^{-1}$ mol$^{-1}$). The large, negative entropy factor for this conversion is in agreement with the occurrence of a twist pathway of the isomerization process as suggested above [28–30].

The redox electron in the *cis*/*trans* couples is located in the 4$d\pi$ orbital of the metal. The stronger back-bonding provides greater electrochemical stability for this orbital in the *cis* form. This is a consequence of the competitive effect where the ligands mutually *trans* (phosphorus *trans* nitrogen) compete for the same electron density of the metal [31,32]. Thus, in the *trans* isomers the electron densities are more centered in the metal centers making easier their oxidation processes.

It is interesting to mention that the kinetics of the isomerization process of the compounds can be conveniently followed also by $^{31}$P{$^1$H} NMR spectroscopy (changing from a singlet to two doublets) and that t$_{1/2}$ for the conversion of *trans* to *cis* of the [RuCl$_2$(dppb)(H-bipy)] complex at 298 K is ~18 min, under white light.

## 5. Conclusions

The photoreaction quantum yields for the *trans*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes are independent of both, the wavelength of the irradiation and the solvent used.

The present study demonstrates that the *trans*-[RuCl$_2$(dppb)(4,4′-X$_2$-2,2′-bipy)] complexes are photoisomerized under white light; that the isomerization constant rates are dependent on the p$K_a$ of the ligands and that they follow a twist type mechanism. The electrochemical oxidation potentials of the complexes are also dependent on the p$K_a$ of the ligands, decreasing with the increasing of the donor properties of the X-bipy molecules.

The isomerization rate constants of the complexes increase with the donor properties of the ligands showing that the electron enrichment of the metal center of electrons facilitates the isomerization process. This suggests that in this case, the Ru–Cl bonds become weaker or more relaxed allowing the isomerization process to occur faster. This suggestion finds support in the fact that in presence of coordinating solvent for long periods of time the chlorine ligand dissociates.

The large negative activation entropy of the isomerization is consistent with an intramolecular twist process for the isomerization reaction.

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