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Thermal and photochemical behavior of *trans*-ruthenium(II) dichloride tetraphosphite complexes

M.A. Esmeraldo [a], N.S. Gonçalves [a], M.A.S. Rios [a], G. Mele [b], L.C.G. Vasconcellos [a], S.E. Mazzetto [a,*]

[a] *Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, C.P. 12 200, 60455-760 Fortaleza, CE, Brazil*
[b] *Dipartimento di Ingegneria dell'Innovazione, Università di Lecce, Via Arnesano, 73100 Lecce, Italy*

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Abstract

trans-$[RuCl_2\{P(OR)_3\}_4]$ complexes were prepared by reaction between $RuCl_3$ and $P(OR)_3$ ligands: $R = CH_3$, C_2H_5, ${}^iC_3H_7$ and ${}^nC_4H_9$. The electronic spectra of freshly prepared solution show similar spectral behavior in two selected pH values: two absorptions bands at 250 nm ($\varepsilon = 10^3$ M^{-1} cm^{-1}) and at 408 nm ($\varepsilon = 10^2$ M^{-1} cm^{-1}) and a shoulder at 280 nm ($\varepsilon \cong 10^2$ M^{-1} cm^{-1}). The complexes exhibit distinct dissociation behavior of ligands as function of the pH (3.0 and 7.0, respectively) with the increase in the size of the alkyl substituent in the phosphorus ligand. The ^{31}P NMR data at the pH 3.0, show only one signal for complexes freshly prepared solutions with $\delta = 131$, 129, 127 and 125 ppm assigned to $R = CH_3$, C_2H_5, ${}^iC_3H_7$ and ${}^nC_4H_9$, respectively. After 24 h reaction, the complexes exhibit ^{31}P NMR signals attributed to new ruthenium compounds formed by chloride and phosphite dissociation, at $\delta = 145$, 143, 140 and 137 ppm for ruthenium complexes, respectively, and signals at $\delta = 11.8$, 9.7, 9.4 and 8.5 ppm, respectively, assigned to free dialkylphosphonate molecules in solution. At pH 7.0, only one ^{31}P NMR signal for each complex was observed with $\delta = 136$, 134, 131 and 130 ppm for $R = CH_3$, C_2H_5, ${}^iC_3H_7$ and ${}^nC_4H_9$, respectively. The complexes were photolyzed with light of $\lambda = 410$ nm centered on the lowest energy of ligand field transition band. Photoaquation generating Cl^- species in solution was observed for all complexes with photoreaction quantum yield ϕ in the range of 0.34–0.35 mol/Einstein at pH 3.0 and in the range of 0.36–0.40 mol/Einstein at pH 7.0. In acidic medium, the irradiation at 408 nm leads to photoaquation of ligands with concomitant stereochemical change, while at neutral conditions only the chloride photolabilization was observed.

Keywords: Synthesis; Trialkylphosphite ligands; Ruthenium(II); ^{31}P NMR; Photoaquation of ligands

1. Introduction

The field of transition metal chemistry is growing rapidly, particularly in the synthesis, reactivity and the connection with their ability to function as homogeneous catalyst in a variety of reactions. Special emphasis has been demonstrated to compounds containing tertiary phosphorus as ligand in ruthenium complexes, due to special properties that those ligands have: stabilize Ru(II) relative to Ru(III); exhibit strong *trans* effect and *trans* influence and delabilize the ligands in the *cis* position [1]. These characteristics were explored using ruthenium ammines as a typical model compound, bearing in mind that the σ-bonding and π-innocent NH_3 ligand are inert toward ligand substitution in the *x* and *y* plane in *trans*-Ru(II) and Ru(III) tetraamines.

Recently, we succeeded in investigating the changes in the ruthenium equatorial ligands [2–5], i.e., substituting the only σ bond characteristics by coordination of different trialkylphosphite ligands capable of σ-donor and π-acceptors bonds. The results showed that altering the alkyl groups at the phosphorus ligand, it is possible investigate the mutual influence between metal and phosphorus ligands upon their reactivities.

Tertiary phosphite esters has also been attracting the attention as ligand in ruthenium metal chemistry [1–17], in particular to the photochemistry/photophysics phenomena [2–5,9,14–17], with emphasis on the application of their properties to solar energy conversion, redox process and electron/energy quenching reactions [15,16]. The rate constants for triplet quenching by coordination complexes have been found to depend critically

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[*] Corresponding author. Tel.: +55 85 8865 4030; fax: +55 85 4008 9978.
E-mail address: selma@ufc.br (S.E. Mazzetto).

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on many parameters like the ligand donor ability, the transition metal identity, the ligands nature, the complex charge, the complex stereochemistry and the solvent [15,16,18,19].

Most of earlier studies have been directed to the tetra and pentaammine ruthenium complexes [1,9,10,14,15,17,20] because the NH_3 are inert with respect to ligand for substitution and the complexes are generally water soluble. As part of a systematic study of the trialkylphosphite ligands and its chemistry within the ruthenium complexes, this work focuses on the chemistry of species where the equatorial NH_3 ligands have been substituted by tertiary phosphorus as ligand, which is a very good π-acceptors. We report the synthesis, characterization, thermal and photochemical reactivity of a series of *trans*-$[RuCl_2\{P(OR)_3\}_4]$ complexes, where R represents CH_3, C_2H_5, $^iC_3H_7$ and $^nC_4H_9$, respectively.

2. Experimental

2.1. Apparatus and materials

Ethanol and acetone (Aldrich) were distilled under reduced pressure before use. Trifluoroacetic acid (Merck, spectroscopic grade) was used as purchased. The aqueous solutions were prepared using doubly distilled water. All other materials were reagent grade (Aldrich/Merck) and were used without further purification. HPLC grade solvents were used. Ruthenium trichloride ($RuCl_3{\cdot}3H_2O$) was the starting material for the synthesis of the complexes and was used as received. Triethyl and trimethyl phosphite (Aldrich) were purified by treatment with metallic sodium followed by distillation under reduced pressure before use. All experiments and manipulations were carried out under argon atmosphere. All-glass connections were used, and routine techniques of air-sensitive material transferring were adapted.

2.2. Synthesis of trans-$[Ru\{P(OR)_3\}_4Cl_2]$; where R = CH_3, C_2H_5, $^iC_3H_7$ and $^nC_4H_9$

The synthesis of *trans*-$[RuCl_2\{P(OCH_3)_3\}_4]$ [4] and *trans*-$[RuCl_2\{P(OC_2H_5)_3\}_4]$ [21] complexes were achieved from direct reaction of the phosphite ligand with ruthenium chloride trihydrate ($RuCl_3{\cdot}3H_2O$) and sodium tetrahydroborate ($NaBH_4$) according to the literature method. Elemental analysis: for *trans*-$[RuCl_2\{P(OCH_3)_3\}_4]$: found: C, 21.52%; H, 5.32%; calc.: C, 21.56%; H, 5.43%; yield ≅ 60% and for *trans*-$[RuCl_2\{P(OC_2H_5)_3\}_4]$: found: C, 34.55%; H, 7.46%; calc.: C, 34.45%; H, 7.25%; yield ≅ 75%. The *trans*-$[RuCl_2\{P(O^iC_3H_7)_3\}_4]$ complex was prepared by dissolving 0.01 mol of ruthenium chloride trihydrate in 45 mL of previously degassed ethanol. After 45 min, 0.14 mol phosphite ligand were added $\{P(O^iC_3H_7)_3\}_4$. The solution was stirred for 24 h at room temperature, under argon atmosphere in absence of light. At this point, 0.07 mol of $NaBH_4$ was added slowly, with the reaction flask siting on ice bath, and the solution was stirred for 5 more hours. After this time, the solution was filtered and reduced to 10 mL by evaporation under low pressure. The yellow solution was kept in freezer for at least for 48 h to allow precipitation. The solid was collected by filtration, washed with ethanol, crystallized twice with *n*-hexane, and dried under low pressure. Elemental analysis: for *trans*-$[RuCl_2\{P(O^iC_3H_7)_3\}_4]$: found: C, 43.07%; H, 8.54%; calc.: C, 43.02%; H, 8.44%; yield ≅ 50%. For *trans*-$[RuCl_2\{P(O^nC_4H_9)_3\}_4]$ complex, several molar ratios were tested in order to find the proper stoichiometry for reaction. The best condition was obtained with 0.01 mol of ruthenium chloride trihydrate, 0.30 mol of phosphite ligand and 0.09 mol of $NaBH_4$. In this case, the solution was stirred for 24 h at room temperature, under argon atmosphere and in absence of light. At this point, the $NaBH_4$ was added slowly (the portion was divided in 4, added, each 2 h), under ice bath, and the solution was stirred for 12 more hours, and a yellow solution was obtained. The solution was kept in freezer for a few days, and the volume was reduced to 25, 10% and finally around 5%, and yellow oil with cloudy aspect was obtained. In this oil, small amounts of hexane were added, and kept in freezer again until complete precipitation (about 30 days). Elemental analysis: for *trans*-$[RuCl_2\{P(O^nC_4H_9)_3\}_4]$: found: C, 49.51%; H, 9.42%; calc.: C, 49.13%; H, 9.30%; yield ≅ 20%.

2.3. Instrumentation and preparation

UV–vis absorption measurements were performed at room temperature with a HP 8453 diode-array spectrophotometer. ^{31}P NMR spectra were measured in acetone-d^6 in a Bruker DRX-500 MHz spectrometer [J values are given in Hz and chemical shifts (δ) are expressed in ppm]. All chemical shifts are reported with respect to 85% H_3PO_4 sealed in a capillary and inserted into a standard 5-mm NMR tube filled with the deutered solvent. The EPR measurements were recorded with a Varian E-109 spectrometer, operation in X band frequency (9000 MHz), with a rectangular cavity, and temperature control system. Acetone was used as solvent. The spectra were carried on at temperature of $-150 \pm 5\,^{\circ}C$, $n = 9068$ MHz ($H = 2000$ G).

2.4. Kinetic and photolysis measurements

The kinetic measurement was performed using degassed solution containing 4.0×10^{-4} M of ruthenium complex that was transferred into the spectrophotometric cell (previously flushed with argon) through Teflon tubing. The reaction rate constants were determinate graphically, assuming pseudo first order condition for either pH, by the line angular coefficient obtained in the plot of $\ln(A_\infty - A_t)$ versus time of reaction at a selected wavelength of 282 nm for at least 5 half life time. The reaction products were characterized in solution by UV–visible and ^{31}P NMR spectroscopy techniques.

The species formed by the dissociation of the *trans*-$[RuCl_2\{P(OR)_3\}_4]$ compounds were also evaluated through volumetric analysis using silver nitrate ($AgNO_3$) as chloride precipitating agent, obeying the stoichiometric ratio of 1:2 (Ru complex:$AgNO_3$). Under stirring, 10 mL of silver nitrate solution (2.4×10^{-3} M) was added in 10 mL of ruthenium complexes solution (1.2×10^{-3} M). The formation of white precipitate was observed and separated by centrifugation and filtration

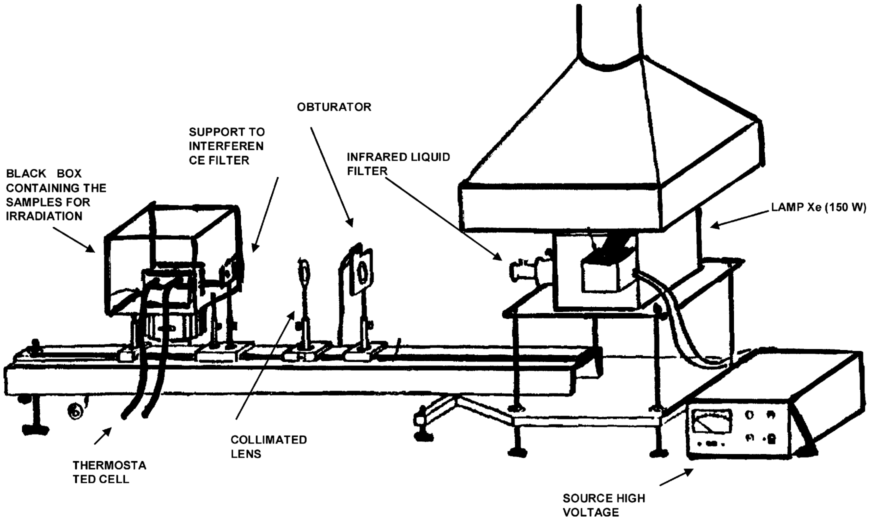

Fig. 1. Design of the photolysis system used in the photochemical experiments.

(3891, black strip, 12.5 cm, gray 0.00009 g). The solution was rotaevaporated until dryness and analyzed by ^{31}P NMR.

The photolysis experiments were carried out with an Osram 150 xenon lamp in an Oriel Model 8500 Universal Arc Lamp source. The irradiation wavelengths were selected with Oriel interference filters for photolysis at the appropriate wavelengths. The interference filter had an average band pass of 10 nm ($\lambda = 410 \pm 10$ nm) and the collimated beam intensities ranged from 4×10^{-8} to 1×10^{-9} Einstein^{-1} cm^{-2} as determined by ferrioxalate actinometry. An infrared liquid filter and a thermostated cell holder were also used in the photolysis of aqueous ethanolic solutions containing the desired ruthenium complex at 1.0×10^{-3} M concentration. Solutions for photolysis and dark reactions were prepared with purified argon in a Zwickel flask, and transferred to the 1.0 cm path length quartz cell ($V = 4.0$ mL) using an all-glass apparatus. During photolysis, the solution was kept under stirring by a small magnetic bar in the cell. All photolysis were carried out at 25.0 ± 0.1 °C. For spectroscopic quantum yield determinations, the reactions under photolysis were monitored periodically by recording the UV–vis and ^{31}P NMR spectra, and by chloride-selective electrode measurements. Photolysis runs did not exceed 10% of phosphite and chloride ion photoaquation. The quantum yields were calculated by plotting quantum yield versus reaction percentage and the extrapolation back to 0%. Fig. 1 shows the exact design of the photolysis system used in the photochemical experiments.

The chloride concentration changes in solution during the photolysis were measured by means of a potentiometric cell composed by the reference electrode (Ag/AgCl, Radelkis OP-0820P) and the working electrode (selective for chloride, Radelkis OP-Cl-0711-P). The solutions pH was determined using a digital Corning pH meter model 440 equipped with a Radelkis OP-274 electrode. The apparatus was used to evaluate the release of chloride from the Ru(II) coordination sphere. The chloride electrode was calibrated before each experiment against sodium chloride solutions of known concentrations. The chloride measurements were performed through calibration curves, in aqueous ethanolic solutions (1:2) containing sodium chloride, in the concentration interval between of 1×10^{-5} to 1×10^{-2} M. After photolysis, values of the dark and irradiated solutions were reported as pCl (pCl = $-\log[\mathrm{Cl}^-]$). The quantum yields were calculated from the differences in the Cl^- ion concentration of these solutions. For these experiments, solutions used for chloride photoaquation determination were set to the chosen pH of 3.0 and 7.0.

3. Results and discussion

3.1. Electronic spectra and kinetic behavior

The electronic absorption of freshly prepared solution ethanol/water (2:1) of *trans*-[$\mathrm{RuCl_2\{P(OR)_3\}_4}$] complexes shown the same profile. The complexes solutions exhibit an

Table 1
Rate constants values for Cl^- aquation in *trans*-[$\mathrm{RuCl_2\{P(OR)_3\}_4}$] at 25 °C

R group	Rate constant (s^{-1})	Rate constant (s^{-1}) pH 3.0	Cone angle[a] pH 7.0
$\mathrm{CH_3}$	1.8×10^{-3}	6.1×10^{-4}	107°
$\mathrm{C_2H_5}$[b]	5.0×10^{-4}	3.2×10^{-5}	109°
$^{n}\mathrm{C_4H_9}$	4.8×10^{-5}	2.4×10^{-5}	112°
$^{i}\mathrm{C_3H_7}$	2.5×10^{-6}	1.1×10^{-6}	130°

[($\mathrm{NaH_2PO_4/Na_2HPO_4}$), pH 7.0, $\mu = 0.10$ M ($\mathrm{CF_3COONa}$) and ethanol/water $\mathrm{CF_3COOH}$ 10^{-2} M, pH 3.0, $\mu = 0.10$ M ($\mathrm{CF_3COONa/CF_3COOH}$)].

[a] Ref. [11,22].

[b] Ref. [2].

absorption band at $\lambda = 250$ nm [$\varepsilon = (3.0–3.4) \times 10^3\ \mathrm{M^{-1}\ cm^{-1}}$], a shoulder at about $\lambda = 280$ nm [$\varepsilon = (9.0–9.7) \times 10^2\ \mathrm{M^{-1}\ cm^{-1}}$], and another band at $\lambda = 408$ nm [$\varepsilon = (1.2–1.7) \times 10^2\ \mathrm{M^{-1}\ cm^{-1}}$]. Similar electronic spectra were observed for these compounds in ethanol/water (2:1) at pH 7.0.

These solutions are not stable by aging, they start exhibit two well defined absorptions at pH 3.0: $\lambda = 282$ nm [$\varepsilon = (2.0–2.2) \times 10^3\ \mathrm{M^{-1}\ cm^{-1}}$] and $\lambda = 394$ nm [$\varepsilon = (5.2–5.6) \times 10^2\ \mathrm{M^{-1}\ cm^{-1}}$]. The same experiment at pH 7.0: $\lambda = 280$ nm [$\varepsilon = (1.1–1.3) \times 10^3\ \mathrm{M^{-1}\ cm^{-1}}$] and $\lambda = 380$ nm [$\varepsilon = (2.0–2.2) \times 10^2\ \mathrm{M^{-1}\ cm^{-1}}$], for 8, 12 and 24 h of reaction in both cases. This behavior is consequence of ligand dissociation in *trans*-[$\mathrm{RuCl_2\{P(OR)_3\}_4}$]. In fact, the complexes in the acidic and neutral solutions underwent a process of thermal aquation. Under these reaction conditions, the values for aquation rate constants (k_{Cl^-}) were calculated, and reported in Table 1.

The observation of the data in Table 1, can lead to an assumption that the presence of bulk ligands coordinated to ruthenium, represented by the increasing cone angle value as consequence of the size of the alkyl substituent, can slow chloride dissociation. The larger the volume of R in $\mathrm{P(OR)_3}$, represented here by their respective cone angles, the slower will be the chlorine dissociation. Several other examples of the effect of ligand size on dissociation process have been reported in literature [1,11,12,15,22–27], as the size of the R group and its steriochemical effect undertakes a very important variable in the phosphite and phosphine chemistry, specially the effect on the rate at which phosphite and/or others ligands dissociate from the metal.

To describe the steric effects of phosphite and other ligands, Tolman [22,24] has defined the cone angle as the apex angle θ of a cone that encompasses the Van der Waals radii of the outermost atoms of a ligand. This factor could contribute to the observed chloride dissociation rate constant differences and could be explained in terms of cone angle of the phosphite ligand. In Table 1, for example, the $\mathrm{P(OCH_3)_3}$ and the $\mathrm{P(OC_2H_5)_3}$ ligands have almost the same cone angle value, therefore, any significant change involving those two compounds cannot be evaluated in terms of this parameter. On the other hand, the $\mathrm{P(O^{\mathit{i}}C_3H_7)_3}$ ligand has the larger cone angle compared to the others three complexes, what certainly should be considered as one of the parameters to explain the lowest values in the rate constants for this complex in both pH investigated. Although the dissociation product is the same, the compound containing $\mathrm{P(O^{\mathit{i}}C_3H_7)_3}$ has the larger steric effect. This affects the reaction into a slower process for ligand release in the axial position. In this case, the steric effect restricts the pathways for solvent attack in axial coordination sites.

In a previous work [26], the rate constant for the aquation of chloride was investigated in *trans*-[$\mathrm{MCl_2L}]^{n+}$ complexes, where M = metal center, L = $\mathrm{(NH_3)_4}$, $\mathrm{(en)_2}$ and cyclam, concerning the influence of the axial ligands upon the chloride dissociation. The presence of bonding interaction [28] between the cyclam nitrogen–hydrogens and chloride ligands was one of the factors used to explain the smaller rate of chloride loss from *trans*-[$\mathrm{RuCl_2(cyclam)}$] ($k_{\mathrm{Cl}^-} = 2.1 \times 10^{-2}\ \mathrm{s^{-1}}$) compared to *trans*-[$\mathrm{RuCl(NH_3)_5]^+}$ ($k_{\mathrm{Cl}^-} = 5\ \mathrm{s^{-1}}$). Therefore, at least for the four compounds listed in Table 1 and also for the examples above, the final product and the reaction rate constant of the dissociation of *trans*-[$\mathrm{RuCl_2\{P(OR)_3\}_4}$] could be dominated by a combination of electronic and steric effects parameters.

A considerable number of studies have been devoted to the quantification of the electronic and stereochemical characteristics of tertiary phosphorus ligands, and several scales of relative σ-donor/π-acceptor strength and stereochemical bulkiness have been reported [1,11,22–24]. These scales have been widely used to define strategies of synthesis and are also important because the M–P bond dissociation enthalpies reflect the electronic and stereo chemical properties of the phosphorus ligands.

The specific rate values for $\mathrm{Cl^-}$ dissociation at the pH 7.0 are always smaller when compared with values in acidic solutions (Table 1). The results are consistent if we consider that under these conditions, the aquation process happens without alteration in the x and y plane configuration of the ruthenium coordination sphere [2–4] during the $\mathrm{Cl^-}$ substitution by the solvent molecules (S). We understand that the x–y plane configuration preservation during the dissociation process at neutral pH solutions is favored energetically by the lack of phosphorus ligand dissociation that occurs in acidic conditions. It is when the large cone angle has its major effect on slowing the chloride aquation reaction.

3.2. The ^{31}P NMR investigation

Investigating with more property the products obtained of the dissociation ligands in the compounds, the reactions were also monitored by ^{31}P NMR technique. The electron-donor ability of the alkyl groups bonded on phosphorus; the coordination to the metal by means of σ- and π-bonding and the cone angle of the ligands are the three most important variables determining ^{31}P chemical shifts. At the pH 3.0, for all *trans*-[$\mathrm{RuCl_2\{P(OR)_3\}_4}$] complexes, the coordinated phosphite ligand presented only one signal for ^{31}P in the freshly prepared solution, Fig. 2, with $\delta = 131$, 129, 127 and 125 ppm for R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $^{i}\mathrm{C_3H_7}$ and $^{n}\mathrm{C_4H_9}$, respectively.

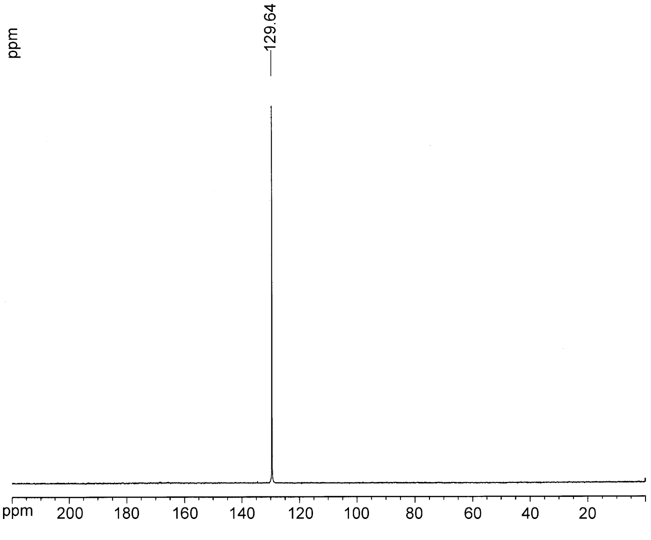

Fig. 2. ^{31}P NMR of the complex *trans*-[$\mathrm{RuCl_2\{P(OC_2H_5)_3\}_4}$], acetone-d^6, freshly prepared solution, at the pH 3.0.

Like in the UV–vis experiments, the ^{31}P NMR signals also change with time due to ligands dissociation. The ^{31}P NMR measures on the *trans*-[RuCl$_2${P(OCH$_3$)$_3$}$_4$] complex, after 12 h reaction in acidic medium, reveals signals at $\delta = 145$ ppm, 131 ppm and 11.8 ppm. The same behavior but with different chemical shift values was observed for each P(OR)$_3$ ligand: ($\delta = 143$, 129 and 9.7 ppm for C_2H_5); ($\delta = 140$, 127 and 9.4 ppm for $^iC_3H_7$) and ($\delta = 137$, 125 and 8.5 ppm for $^nC_4H_9$). The peaks at $\delta = 131$, 129, 127 and 125 ppm have been attributed to the non-dissociated complex in each case, while the peaks at $\delta = 11.8$, 9.7, 9.4 and 8.5 ppm have been assigned to dialkylphosphonite molecules in solution that coexist in equilibrium with dissociated dialkylphosphite [1,10]. The later been the reaction product from dissociated trialkylphosphite where the pH is smaller than 4.0 (Eqs. (1) and (2)) [1,10].

After 24 h, still under acid conditions, the peaks signal attributed to the *trans*-[RuCl$_2${P(OR)$_3$}$_4$] complexes disappeared ($\delta = 131$, 129, 127 and 125 ppm), showing the complete dissociation of the start material, remaining only peaks correspondent to $\delta = 145$, 143, 140 and 137 ppm and $\delta = 11.8$, 9.7, 9.4 and 8.5 ppm, respectively, Fig. 3. Considering UV–vis and NMR behavior and for analogy to previous studies [1,3–5,8,10], the signals corresponding the $\delta = 11.8$, 9.7, 9.4 and 8.5 ppm was attributed to dialkylphosphonate [1,10] molecules [O = PH(OR)$_2$] while the signals in $\delta = 145$, 143, 140 and 137 ppm assigned the *cis*-[Ru{P(OR)$_3$}$_2$S$_4$]$^{2+}$ (S = solvent).

The dialkylphosphonate ^{31}P NMR study has also been reported by Sernaglia and Franco [10,1]. The phosphite complexes have strong *trans* effect and *trans* influence leading to thermal labilization. The dissociated phosphite molecule in aqueous acidic medium (pH < 4.0), hydrolyzes rapidly to the correspondent dialkylphosphite (Eq. (1)), while the dialkylphosphite exhibits the tautomeric equilibrium with the dialkylphosphonate (Eq. (2)) [1,10], which avoids back reaction towards phosphite, which would coordinate ruthenium in the equilibrium presented by the Eq. (1). The P(OR)$_3$ ligand is the only of these phosphorus species that has energetically available 3d orbitals to interact with the t_{2g} orbitals of the Ru(II).

$$\mathrm{P(OR)_3} \overset{\mathrm{H^+}}{\leftrightarrows} \mathrm{P(OH)(OR)_2 + R(OH)} \tag{1}$$

$$\mathrm{P(OH)(OR)_2} \overset{\mathrm{Fast}}{\leftrightarrows} \mathrm{P(O)(H)(OR)_2} \tag{2}$$

At the pHs > 4.0, this system shows the thermal back reaction, Eq. (3) [1,10]:

$$\begin{aligned} &trans\text{-}[\mathrm{Ru(NH_3)_4\{P(OR)_3\}_2}]^{2+} \\ &\leftrightarrows trans\text{-}[\mathrm{Ru(NH_3)_4P(OR)_3H_2O}]^{2+} + \mathrm{P(OR)_3} \end{aligned} \tag{3}$$

The phosphite molecule is bonded to the ruthenium center through the phosphorus atom, with Ru(II)-P(OR)$_3$ bond stronger than Ru(II)-P(OH)(OR)$_2$ or Ru(II)-(O(II)=P(OR)$_3$). Considering the above reactions and previous works, the studies involving Cl$^-$ dissociation reactions were adjusted to the pH values 3.0 and 7.0, respectively.

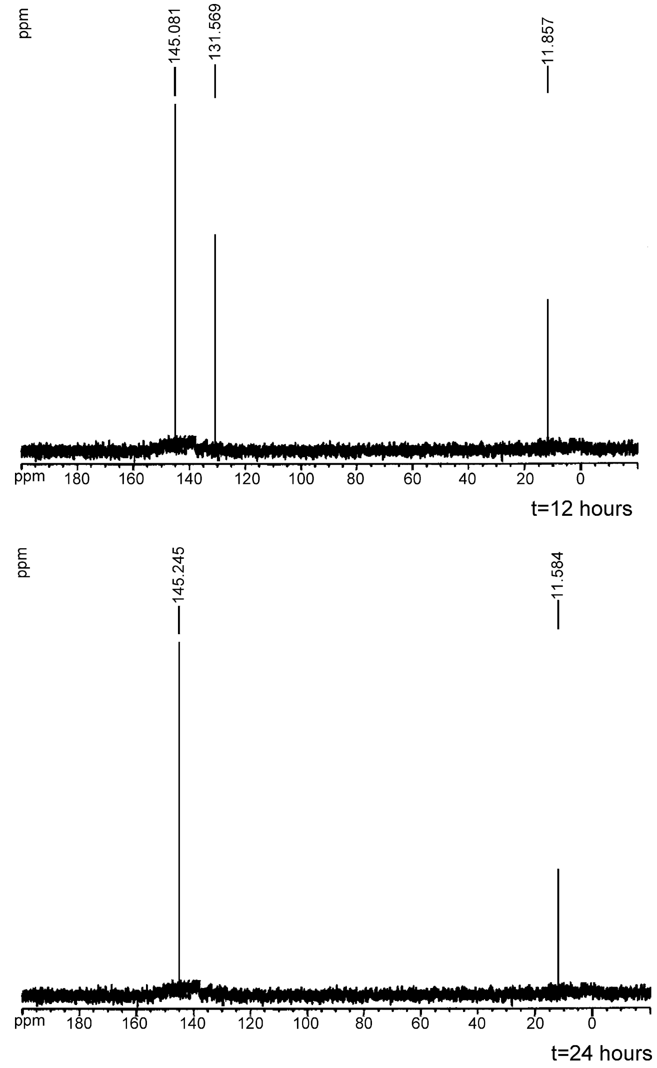

Fig. 3. ^{31}P NMR monitoring of the complex *trans*-[RuCl$_2${P(OCH$_3$)$_3$}$_4$]; acetone-d^6, after 12 and 24 h reaction, pH 3.0.

Taking into account the *trans* influence and the *trans* effect properties of P(III) group coordinated to the Ru(II) center [1,8,10,12,17], it is reasonable to assume that the signals in $\delta = 145$, 143, 140 and 137 ppm corresponds to *cis*-[RuS$_4${P(OR)$_3$}$_2$]$^{2+}$complex, formed after two phosphite dissociation from *trans* position to phosphite in the *trans*-[Ru{P(OR)$_3$}$_4$S$_2$], Eqs. (4)–(7):

$$\begin{aligned} &trans\text{-}[\mathrm{RuCl_2\{P(OR)_3\}_4}]+\mathrm{S} \xrightarrow{k_{-\mathrm{Cl}^-}} trans\text{-}[\mathrm{RuCl\{P(OR)_3\}_4(S)}]^+ \\ &\qquad + \mathrm{Cl^-(fast)} \end{aligned} \tag{4}$$

$$\begin{aligned} &trans\text{-}[\mathrm{RuCl\{P(OR)_3\}_4(S)}]^+ + \mathrm{S} \\ &\xrightarrow{k'_{-\mathrm{Cl}^-}} trans\text{-}[\mathrm{Ru\{P(OR)_3\}_4(S)_2}]^{2+} + 2\mathrm{Cl^-(slow)} \end{aligned} \tag{5}$$

$$\begin{aligned} &trans\text{-}[\mathrm{Ru\{P(OR)_3\}_4(S)_2}]^{2+} + \mathrm{S} \\ &\xrightarrow{k_{-\mathrm{P(III)}}} mer\text{-}[\mathrm{Ru\{P(OR)_3\}_3(S)_3}]^{2+} + \mathrm{P(OR)_3(fast)} \end{aligned} \tag{6}$$

$$mer\text{-}[\mathrm{Ru}\{\mathrm{P(OR)_3}\}_3(\mathrm{S})_3]^{2+} + \mathrm{S} \xrightarrow{k'_{-\mathrm{P(III)}}} cis\text{-}[\mathrm{Ru}\{\mathrm{P(OR)_3}\}_2(\mathrm{S})_4]^{2+} + \mathrm{P(OR)_3(slow)} \qquad (7)$$

The HPLC data [4] corroborate with this assumption. The *trans*-[RuCl$_2${P(OCH$_3$)$_3$}$_4$] complex, under acidic solutions, exhibit a retention time of 5.7 min for freshly prepared solution. After 24 h of reaction, only one peak attributed to *cis*-[Ru{P(OR)$_3$}$_2$(S)$_4$]$^{2+}$ species was observed ($t_R = 4.3$ min). Stephenson [13] also report similar results in a study on the interaction of Ph$_3$P, Ph$_3$As and Ph$_3$Sb with Ru(II) complexes, suggesting easier dissociation of phosphine ligand, confirmed by the fast reaction with carbon monoxide at room temperature (S = solvent) according to:

$$[\mathrm{RuCl_2\{PPh_3\}_4}] + (\mathrm{S}) \rightarrow [\mathrm{RuCl_2\{PPh_3\}_2(S)_2}] + 2\mathrm{PPh_3} \qquad (8)$$

$$[\mathrm{RuCl_2\{PPh_3\}_2(S)_2}] \xrightarrow{\mathrm{CO,fast}} [\mathrm{RuCl_2\{PPh_3\}_2(CO)_2}] \qquad (9)$$

In neutral conditions, the ^{31}P NMR experiments after 8, 12 and 24 h of reaction showed only one ^{31}P NMR signal for each *trans*-[RuCl$_2${P(OR)$_3$}$_4$] compound, with $\delta = 136$ ppm (for CH$_3$), 134 ppm (for C$_2$H$_5$), 131 ppm (for ^{i}C$_3$H$_7$) and 130 ppm (for ^{n}C$_4$H$_9$). These results are also consistent with the unprotected phosphorus atoms due to the electron withdraw effect upon ruthenium coordination among others factors [29]. Conductometric titrations of the resulting solutions with AgNO$_3$, clearly indicate the consumption of two moles of silver ions per mol of complex. This suggests fast discoordination of two chlorides in neutral solution, with stereo retention of the equatorial tetraphosphite ligands, which presents only one δ value for each complex.

Therefore, we assume that in pH 7.0, there is no change in the symmetry configuration of the ruthenium complex during the substitution of the Cl$^-$ ligands by the solvent molecules (S). Assuming that both products: from thermal reaction and volumetric titration reaction are the same, we suggested that the *trans*-[Ru{P(OR)$_3$}$_4$(S)$_2$]$^{2+}$ as the only product of *trans*-[RuCl$_2${P(OR)$_3$}$_4$] dissociation in the neutral conditions, Fig. 4.

$$trans\text{-}[\mathrm{RuCl_2\{P(OR)_3\}_4}] + \mathrm{S} \leftrightharpoons trans\text{-}[\mathrm{RuCl\{P(OR)_3\}_4(S)}]^+ + \mathrm{Cl}^- \quad k_{-\mathrm{Cl}^-}\mathrm{(fast)} \qquad (10)$$

$$trans\text{-}[\mathrm{RuCl\{P(OR)_3\}_4(S)}]^+ + \mathrm{S} \leftrightharpoons trans\text{-}[\mathrm{Ru\{P(OR)_3\}_4(S)_2}]^{2+} + \mathrm{Cl}^- \quad k'_{-\mathrm{Cl}^-}\ \mathrm{(slow)} \qquad (11)$$

Once again, the HPLC data [4] for the *trans*-[RuCl$_2$-{P(OCH$_3$)$_3$}$_4$], recorded to 24 h of reaction, had no retention time changes (only one single peak at $t_R = 4.6$ min), proposing that under these experimental conditions, the dissociation of chloride ions does not change the solvent polarity, and consequently no new peaks should be observed as function of time.

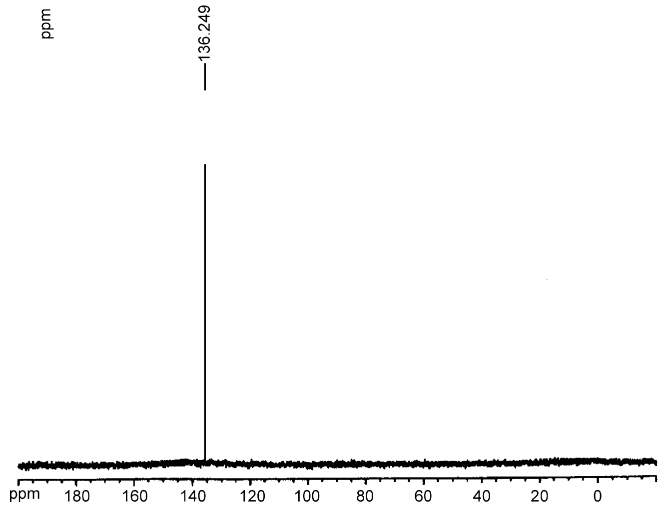

Fig. 4. ^{31}P NMR of the complex *trans*-[Ru(P(OCH$_3$)$_3$)$_4$Cl$_2$]; acetone-d^6; after 24 h of reaction, pH 7.0.

3.3. Photolysis of trans-[RuCl$_2${P(OR)$_3$}$_4$] complexes

The understanding of the thermal reaction behavior for aquation reactions and its experimental conditions with final product characterizations, we may investigate the photochemistry properties of these species. To evaluate the efficiency of irradiation process, it requires direct comparison between the changes in a sample in presence and absence of light.

The photoreactions described in this work are all photosubstitution where the complexes studied display the ligand field state as the lowest energy excited state (LF*). The photoreactions are consistent with transition involving depopulation of a Ru(II) orbital of t_{2g} parentage and population of a σ^* orbital e_g parentage, leading to an excited state with a $t_{2g}{}^{5}e_{g}^{1}$ electronic configuration capable of undergoing substitution reactions, with the chloride labilized photochemically for all complexes in acidic and neutral conditions. Table 2 summarizes the photosubstitution quantum yield and some relevant electronic spectral properties of the *trans*-[RuCl$_2${P(OR)$_3$}$_4$] complexes studied in this work.

According to the UV–vis spectra, the ligand field (LF) and charge-transfer (CT) bands do not overlap. Then, the selective

Table 2
Quantum yields (mol complex/Einstein) for *trans*-[Ru{P(OR)$_3$}$_4$Cl$_2$] complexes[a] photochemical reactivities

R group	λ_{max} (nm)	λ_{irr} (nm) (LF*)	ϕ_{Cl^-} (mol/Einstein)[a]	
			pH 3.0	pH 7.0
CH$_3$	408	410	0.34	0.40
C$_2$H$_5$	408	410	0.35	0.37
^{i}C$_3$H$_7$	406	410	0.35	0.36
C$_4$H$_9$	410	410	0.34	0.38

[Ru complex] = 10^{-3} M; pH 3.0 (adjusted with CF$_3$COOH); pH 7.0 (adjusted with NaH$_2$PO$_4$/Na$_2$HPO$_4$); temperature = 25.0 ± 0.5 °C; cell pathlengths = 1.0 cm.

[a] Average of at least three independent determinations; LF = ligand field; λ_{irr} = irradiation wavelength; ε = molar absorption coefficient.

excitation to form LF* was investigated. Irradiation of deaerated acidic solution (pH 3.0) of *trans*-[RuCl$_2${P(OR)$_3$}$_4$] at $\lambda = 410$ nm, leads to spectral variation, where the absorbance increase at the LF bands while the MLCT band has a small blue shift. These observations are consistent with aquation of the Cl^- ligands, responsible for the changes in the LF band energy. The small blue shift observed in the MLCT band can be explained by stabilization of the bonding energy levels in the complex, due to substitution of chloride by water molecules as ligand, with the later been a better σ-donor (stronger Lewis base) according to the spectrochemical series.

Because of these small changes, the photoaquation of chloride cannot be followed spectrophotometrically in these cases. However, examination on the irradiated and blank solutions with the chloride-selective electrode gave the variation of chloride ions concentration in solution, indicating that chloride is being labilized thermally and photochemically for all complexes. The absence of the absorption bands due to (LMCT) $3p_\pi(Cl^-) \rightarrow 4d_\pi{}^*Ru(III)$ transitions [25,26] indicate that no photooxidation occurs during photolysis. Corroborating with those observations, the EPR spectrum of photolyzed solutions at this pH indicates no presence of paramagnetic products. Thus, taking in consideration the aquation of chloride and absence of ruthenium(III), the molar absortivity increase of the LF band upon irradiation can be assigned solely to the photoaquation of Cl^- and coordination by the solvent.

The analysis of the ^{31}P NMR signal for *trans*-[RuCl$_2${P(OR)$_3$}$_4$] after photolysis shows a similar behavior that in the thermal conditions. Taking for example the *trans*-[RuCl$_2${P(OC$_4$H$_9$)$_3$}$_4$] complex, the signals in 137 and 8.5 ppm it was also observed. Then, it is reasonable to assume that in these experimental conditions the photolabilization of P(OR)$_3$ ligands also occurs. The quantum yields for phosphite labilization were not calculated under these experimental conditions due to the short times of irradiation used (to calculate the quantum yields it is necessary that the photolysis runs did not exceed 10% of phosphite and chloride ion photoaquation).

However, according to the appearance of the phosphonate peaks in the ^{31}P NMR spectra after photolysis, it was possible to observe the photolabilization of P(OR)$_3$ ligands under this experimental conditions. Considering the difficulty of visualizing the ^{31}P NMR signal of dialkylphosphonate [1,10] after small irradiation times, Fig. 5 illustrates the general behavior of the *trans*-[RuCl$_2${P(OR)$_3$}$_4$] complexes that exceeds 10% of reaction.

In neutral conditions, continuous photolysis in the LF band shows only the Cl^- photoaquation indicated by the selective electrode measurements. Under these conditions, the ^{31}P NMR signal assigned to free dimethylphosphonate molecules [1,10] was not observed.

In Table 2, all complexes show small differences in the values of the quantum yield of chloride photoaquation, independently of the increase in size of the phosphite ligands involved. This behavior is not in agreement with the observed to the photochemistry reactions involving different chelate ligands in the *x*- and *y*-axes, like *trans*-[RuL(I)$_2$]$^+$ complexes, with L = (en)$_2$, 2,3,2-tet and cyclam [30], respectively. For these types of complexes, the gradual decrease in quantum yields is closely related to the corresponding increase of the chelate L around the ruthenium. Silva [25] also observed the similar behavior studying the photochemical reactions in *trans*-[Ru(NH$_3$)$_4$ClL′]$^{2+}$ [L = Cl; L′ = pyridine, 4-picoline, isonicotinamide, 4-acetylpyridine], where the substitution of four ammines by cyclam restricted the photosubstitution to the *z*-axis.

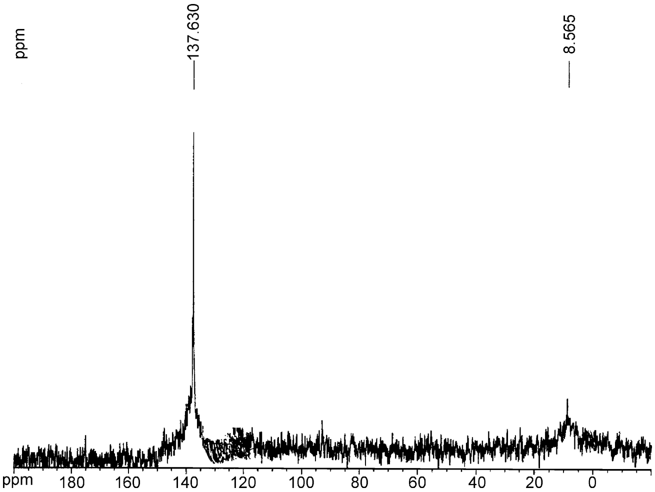

Fig. 5. ^{31}P NMR of the complex *trans*-[Ru(P(OC$_4$H$_9$)$_3$)$_4$Cl$_2$]; acetone-d^6; after photolysis, pH 3.0.

On the other hand, previous studies [31] involving the photoreactivity study of the Ru(II) center with particular emphasis on the role of steric and electronic effects in phosphite complexes *trans*-[Ru(NH$_3$)$_4${P(OR)$_3$}$_2$]$^{2+}$ and *trans*-[Ru(NH$_3$)$_4$(H$_2$O){P(OR)$_3$}]$^{2+}$ complexes with R = CH$_3$, C$_2$H$_5$, ^{i}C$_3$H$_7$, C$_4$H$_9$, ^{t}C$_4$H$_9$, C$_2$H$_4$Cl, C$_5$H$_{11}$, C$_6$H$_5$, C$_6$H$_{12}$N$_3$, have demonstrated that the continuous photolysis with monochromatic light in the LF band excitation leads to the very close values of photoaquation rate constant of NH$_3$ (medium values around 0.35 ± 0.04 mol/Einstein), independently of the increase in the bulk R in P(OR)$_3$ ligands (θ varying between 107 and 172°).

Considering the electronic spectra in solution of the *trans*-[RuCl$_2${P(OR)$_3$}$_4$] exhibit well defined [1–5] ligand field band (LF), without the interference of others bands; the strong Ru(II)-P(III) back-bonding [1,10,20,23,32] interaction and the versatility of the phosphanes (phosphates and phosphines) with respect to their σ-donor and π-acceptor properties and steric hindrance, this new class of compounds offers an opportunity to study the ligand field excited state photochemistry without complications due to redox or secondary thermal reactions. Therefore, the irradiation at 410 nm leads the complexes into the LF* excited state with the metal ion formally in the ruthenium(II) state (t_{2g}^6 configuration).

Considering the photochemistry of this class of compounds and D_{4h} micro-symmetry, the Ru-P(OR)$_3$ bonds are coincident with the *x*- and *y*-axis while the Ru–Cl bond is coincident with the *z*-axis. Photosubstitution reactions of low-spin d^6 complexes follow the Ford's model [1,3–5,9,13,14,17,25,26,31,33] where the photosubstitution reactions came from LF excited state (LF*). The model considers that complexes with MLCT* and LF* are photosubstitution reactive if the LEES (lowest energy excited states) is LF* and unreactive if the LEES is MLCT*.

Therefore, we understand that the lowest energy LF* band represents the component E that involves a transition from (xz,yz) to z^2, while the A_2 component involves xy to x^2–y^2 transitions, or in others words, contributions from either dx^2–y^2 or dz^2 orbitals or from both orbitals [9,14]. Then, the electron population of the $^3A_2$ state will photolabilize ligands on the xy plane, and therefore only $P(OR)_3$ ligands aquation should be observed, while the population of the ^3E state will labilize only the ligands on the z-axis, and only Cl^- ligands should be observed.

Considering that the photochemistry reactions observed in the complexes comes from ^{3}LF, the lowest energy LF* for the chloride it would be a ^3E_g with the LEES d_z^2 in character, leading to photosubstitution of the anion. The similar behavior has been observed in the study of the selective photolabilization of *trans*-$[Ru(NH_3)_4\{P(OR)_3\}_2]^{2+}$ and *trans*-$[Ru(NH_3)_4(H_2O)\{P(OR)_3\}]^{2+}$ complexes [14] in the ligand field lowest energy excited states. The study involving thermal and photochemical properties of others *trans*-$[Ru(NH_3)_4\{P(OR)_3\}_2]^{2+}$ complexes, is in course and will be submitted latter for publication.

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