Available online at www.sciencedirect.com

SCIENCE DIRECT®

Coordination Chemistry Reviews 249 (2005) 419–431

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

# Mutual effects in the chemical properties of the ruthenium metal center and ancillary ligands upon coordination

José Carlos Toledo, Benedito dos Santos Lima Neto, Douglas Wagner Franco*

*Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trabalhador Sãocarlense 400, São Carlos, SP 13560-970, Brazil*

Received 12 March 2004; accepted 22 September 2004
Available online 5 November 2004

## Contents

## Abstract

The mutual changes induced in both metal center and selected ligands kinetics and thermodynamic properties, as a consequence of the coordination, are discussed in terms of σ- and π-bonding. Ruthenium penta and tetraammines are used as models, focusing the attention on phosphines, phosphites, nitrosyl, sulfite and sulfate as ancillary ligands.

*Keywords:* Ruthenium ammines; Nitrosyl; Phosphite; Sulfite

## 1. Introduction

Ruthenium(II) and (III) ammines, in particular penta and tetraammines, are a class of compounds with very interesting and, why not say, unique properties conferred by their electronic configurations ($d^5$ and $d^6$ low spin) and the energy and the radial extension of the 4d orbitals [1–4]. The thermal substitution inertness of these complexes contrasts with their high reactivity in electron transfer reactions [1–5]. The interconversion Ru(III)/Ru(II) is fast and generally accomplished without changes in the geometry and in the coordination sphere composition. The Ru(II) center is a good π-donor and weak Lewis acid whereas Ru(III) is a moderate π-acceptor and a strong Lewis acid. Therefore, $[Ru(NH_3)_5L_1]^{3+/2+}$ and *trans*-$[Ru(NH_3)_4L_1L_2]^{3+/2+}$ are very useful models to study the mutual influence of the ligands ($L_1$ and $L_2$) and the metal center with the metal in different oxidation states.

The development of well defined and reproducible synthetic route [1–7] for ruthenium–ammine derivatives was a key issue for tailoring complexes to a desired target. The pentaammine and tetraammine complexes, where $L_{1,2}$: *N*-heterocyclic, have been quite valuable to understand the nature of the bonds between the ligands and Ru(II) and Ru(III)

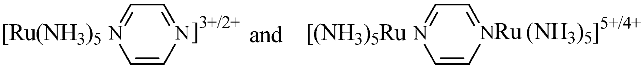
---

* Corresponding author. Tel.: +55 1 6273 9970; fax: +55 1 6273 9976.
*E-mail address:* douglas@iqsc.usp.br (D.W. Franco).

0010-8545/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2004.09.016

centers, and to establish the bases of the charge transfer spectra understanding on coordination compounds [8,9]. In this aspect, the *N*-heterocyclic molecules py, pyrazine (pz), isonicotinamide (isn) and their derivatives [7–10] yielding intensive colorful compounds have proved to be very useful acting as either a probe in kinetic studies or as [1,8–10] ancillary ligand and in tuning the reducing power of Ru(II) [11].

The seminal studies [8,9a], with



describing the nature of both Ru–pz bond and the charge transfer and intervalence bands are well recognized [5,12,13].

There are other classes of ligands that, upon the coordination to Ru(II) promote dramatic changes in the kinetic and thermodynamic properties of the metal center [1–6,14–18]. These so-called “ancillary ligands”, which are precious in the coordination compounds tailoring art, also undergo changes in their properties upon the coordination to the metal center. The present paper deals with the mutual changes induced in both ruthenium center and selected ancillary ligands as a consequence of the coordination. In this scope, the subject will be limited in ruthenium penta and tetraammines complexes, focusing on Ru(II) complexes, phosphines, phosphites, nitrosyl, sulfite and sulfate ligands.

## 2. Phosphane as ligands

### 2.1. General aspects of phosphanes ruthenium complexes chemistry

Phosphites and phosphines, also called phosphanes P(III), are quite interesting and useful ligands. This class of ligands exhibits a characteristic electronic property of being simultaneously strong π-acceptor and moderate to strong σ-donors [13c,16,19]. This biphilic characteristic of $P(OR)_3$ and $P(R)_3$ ligands can be modulated exploring the donor/acceptor electronic capabilities of group R [16]. Also steric effects [20] and solubility can be tuned through of a judicious choice of the size of R [13c,21]. As a consequence, thermal [16] and photochemical reactivities [22] of the complexes can be modulated tailoring the P(III) ligand.

The bond formed between $d^6$ low spin metal center and P(III) ligand is usually strong as a consequence of its multiple character [13b,c,16]. This M(II)=P(III) bond, composed of σ P(III) → M(II) and π M(II) → P(III) components, induces changes in both metal and ligand properties, which could be rationalized in terms of the metal → ligand backbonding model. Similarly to what is observed for other good π-acceptor molecules, when coordinated to $[Fe^{II}(CN)_5]^{3-}$, $Ru^{II}(NH_3)_5]^{2+}$ and $[Os^{II}(NH_3)_5]^{2+}$, phosphite species would accept electron density from the metal *nd*π orbitals stabilizing the metal center in the oxidation state (II) versus the oxidation state (III) by some tenths of volt (Table 1) [16,23,24]. This potential shift to more positive values has been used to expresses the relative metal centers stabilization to oxidation by the P(III) ligands and can be clearly seen comparing the redox potential of the $Ru^{III}/Ru^{II}$ couple in selected species (Table 1). On average, the difference of the $E^{0'}_{Ru(III)/Ru(II)}$ for *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ complex ions is nearly 0.6 V higher than the one for *trans*-$[Ru(NH_3)_5(H_2O)]^{2+}$. This could be attributed on great part to the *nd*π orbitals stabilization through metal → ligand backbonding, by analogy to other systems [2–4,6–10], and it is also noticed by the increase in the energy of MLCT M(II) → L absorption bands for $[M^{II}(NH_3)_5L]^{2+}$ in relation to *trans*-$[M^{II}(NH_3)_4P(III)L]^{2+}$ species (L: pyrazine and isocotinamide), as shown in Table 1.

Table 1
Formal reduction potentials and $\lambda_{max}$ for MLCT transitions ($4d_\pi \rightarrow \pi$) for selected compounds[a]

| Complex | $E^{0'}_{M(III)/M(II)}$ vs. NHE | MLCT $\lambda_{max}$ (eV) |
|---|---|---|
| $[Ru(NH_3)_5(H_2O)]^{2+}$ | +0.06[b] | |
| $[Fe(CN)_5(H_2O)]^{2+}$ | +0.46[c] | |
| *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ | +0.70 | |
| *trans*-$[Ru(NH_3)_4P(OIsp)_3(H_2O)]^{2+}$ | +0.69 | |
| *trans*-$[Ru(NH_3)_4P(OBut)_3(H_2O)]^{2+}$ | +0.68 | |
| *trans*-$[Ru(NH_3)_4P(O^iIsp)_3(H_2O)]^{2+}$ | +0.68 | |
| *trans*-$[Ru(NH_3)_4P(OMe)_3(H_2O)]^{2+}$ | +0.74 | |
| *trans*-$[Ru(NH_3)_4P(O^tBut)_3(H_2O)]^{2+}$ | +0.68 | |
| *trans*-$[Ru(NH_3)_4P(OEtCl)_3(H_2O)]^{2+}$ | +0.85 | |
| *trans*-$[Ru(NH_3)_4Sb(Ph)_3(H_2O)]^{2+}$ | +0.60 | |
| *trans*-$[Ru(NH_3)_4As(Ph)_3(H_2O)]^{2+}$ | +0.61 | |
| $[Fe(CN)_5P(OEt)_3]^{3-}$ | +0.64 | |
| $[Ru(NH_3)_5(pz)]^{2+}$ | | 2.63 |
| *trans*-$[Ru(NH_3)_4P(OEt)_3(pz)]^{2+}$ | +0.78 | 3.39 |
| *trans*-$[Ru(NH_3)_4P(OMe)_3(pz)]^{2+}$ | | 3.40 |
| *trans*-$[Ru(NH_3)_4P(O^iIsp)_3(pz)]^{2+}$ | | 3.35 |
| *trans*-$[Ru(NH_3)_4P(OBut)_3(pz)]^{2+}$ | | 3.40 |
| *trans*-$[Ru(NH_3)_4P(O^tBut)_3(pz)]^{2+}$ | | 3.39 |
| *trans*-$[Ru(NH_3)_4Sb(Ph)_3(pz)]^{2+}$ | 0.83 | 2.92 |
| *trans*-$[Ru(NH_3)_4As(Ph)_3(pz)]^{2+}$ | +0.85 | 2.94 |
| *trans*-$[Ru(NH_3)_4P(Ph)_3(H_2O)]^{2+}$ | 0.77 | |
| *trans*-$[Ru(NH_3)_4P(OPh)_3(H_2O)]^{2+}$ | 0.90 | |
| *trans*-$[Ru(NH_3)_4P(Ph)_3(pz)]^{2+}$ | | 3.16 |
| *trans*-$[Ru(NH_3)_4P(OPh)_3(pz)]^{2+}$ | 1.01 | 3.92 |

[a] Ref. [16].
[b] Refs. [1,2].
[c] Ref. [24].

A π-acidity strength series has been proposed for phosphanes [15,16] based on the $E^{0'}_{Ru(III)/Ru(II)}$ couple of *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ as for example: $P(OPh)_3 > P(OC_2H_4Cl)_3 >$ PTA > ETPB > $P(OMe)_3 \sim$ dppe > $PPh_3 > P(OEt)_3 >$ DMPP $\sim P(O^tBut)_3 \sim P(O^iPr)_3 > P(OH)_3 > P(O^nBut)_3 > P(OH)(OEt)_2 > PEt_3 > P(^nBut)_3 > P(OH)_2O^- > P(OEt)_2O^-$. This series has been extended [6b,7,10b, 15,16] to other ligands ($NO^+ > N_2 > CO > P(OPh)_3 > PPh_3 > P(OMe)_3 > P(OEt)_3 \sim Mepz^+ > AsPh_3 > SbPh_3 \sim SO_2 > P(OH)_3 > P(OH)(OEt)_2 > NCCH_3 > NCCH_2CH_3 > P(OEt)_2O^- > P(OH)_2O^- >$ py $> SO_3^{2-} >$ imN $> H_2O$. A small series exhibiting similar trends have been deduced based on $\lambda_{max}$ of M(II) → L absorption bands for *trans*-$[Ru^{II}(NH_3)_4P(III)L]^{2+}$ (L: isn, pz) species [16,25]. The

$P(R)_3$ phosphines would exhibit similar effects to $P(OR)_3$, but as they are stronger σ bases and weaker π acids than the corresponding phosphites, their effect on the $E^{0'}_{M(III)/M(II)}$ and MLCT energy is lighter. This can be observed comparing the positions of $P(OPh)_3/P(Ph)_3$ and $P(OEt)_3/P(Et)_3$ in the above series.

The correlation of Ru(II) → P(III) backbonding strength with $^{31}P$ chemical shift in *trans*-$[Ru(NH_3)_4P(OEt)_3(L)]^{n+}$, where L: $H_2O$, $P(OEt)_3$, CO, NO (147, 130, 116 and 80 ppm, respectively) seemed to be promising in principle, i.e., the higher the π-acidity of the *trans*-positioned ligand, the higher the $^{31}P$ chemical shift. However, it has been observed that as the π acid ability of the ligand *trans*-positioned to $P(OEt)_3$ increases, the $^{31}P$ chemical shift decreases, suggesting that the correlation is not straightforward.

The strength of the M(II) → P(III) backbonding is such that, as long as P(III) remains coordinated, it becomes quite resistant to hydrolyses and oxidation [14,16,26–29]. The free esters $P(OR)_3$ are well known to undergo acid catalyzed hydrolysis yielding $P(OR)_2(OH)$ species and being very easily oxidized ($H_2O_2$, $I_2$) to the corresponding phosphates [30]. However, as long as $P(OEt)_3$ remains bonded to the metal center (examples being *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$, *trans*-$[Ru(NH_3)_4(P(OEt)_3(H_2O)]^{2+}$ and $[Fe(CN)_5(P(OEt)_3]^{3-}$ ions) [24], it is not hydrolyzed for a period of days [14,16,23,31] even in $C_{H^+} \geq 0.01$ M. This is well documented for a series of *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ ions [14,16].

A similar stability gain relative to oxidation is also observed when $P(OR)_3$ ligand is coordinated to Ru(II) and Fe(II) species [14,16,28]. As long as $C_{H^+} \geq 0.1$ M, phosphites in both *trans*-$[Ru(NH_3)_4(P(OR)_3(H_2O)]^{2+}$, and *trans*-$[Ru(Cl)_2(P(OEt)_3)_4]$ [28] are resistant to oxidation by $H_2O_2$ and Ce(IV) [14,16]. This stability was also observed for $P(OR)_3$ coordinated to Ru(III) and Fe(III) in *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{3+}$, *trans*-$[Ru(Cl)_2(P(OEt)_3)_4]^+$ [29] *trans*-$[Ru(NH_3)_4(P(OEt)_3(H_2O)]^{3+}$ and $[Fe(CN)_5P(OEt)_3]^{2-}$. As long as $C_{H^+} \geq 0.01$ M, these M(III) species are stable for a period of hours in solution. However, as the hydrogen ion concentration decreases, their stability also decreases due to a series of reactions probably starting by:

$$2[Ru(III)P(III) \rightarrow [Ru(IV)(P(III)] + [Ru(II)P(III)] \qquad (1)$$

The *trans*-$[Ru(Cl)_2(P(OEt)_3)_4]^+$ [29] and *trans*-$[Ru(NH_3)_4(P(OEt)_3(H_2O)]^{3+}$, for example [26], have been isolated as the hexafluorphophate salt and are stable for days when stored in vacuum and in the absence of light. The corresponding phosphine *trans*-$[Ru(NH_3)_4(P(R_3)_2)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(R)_3(H_2O)]^{2+}$ complexes, where $P(R)_3$: Et, But and Ph, proved to be less stable regarding oxidation than the corresponding phosphites [16].

Similarly to the sulfite ion $SO_3^{2-}$ [6b,32a], the phosphites and phosphines strongly labilize the ligand in the *trans* position and delabilize the *cis* position regarding the substitution reactions [6b]. As an example, *cis*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$ is detected in $[Ru(NH_3)_5(H_2O)]^{2+}$ 0.1 M HCl solution after 1 h at room temperature. This $NH_3$ dissociation is not observed [6b] in *trans*-$[Ru(NH_3)_4(SO_2)(H_2O)]^{2+}$, *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ solutions under the same experimental conditions even after a four day period [14,16].

The product of the reaction of P(III) or $SO_3^{2-}$ with *trans*-$[Ru(NH_3)_5(H_2O)]^{2+}$ is invariably the *trans*-$[Ru(NH_3)_4(HSO_3)_2]$ and *trans*-$[Ru(NH_3)_4(P(III)_2]^{2+}$ bis species, independently of the P(III)/Ru concentration ratio. Even in excess of Ru(II), the bis species is formed, with the excess of *trans*-$[Ru(NH_3)_5(H_2O)]^{2+}$ metal complex remaining unreacted. It is interesting to highlight that P(III) [16] and $SO_3^{2-}$ [32b] are not able to displace either the *trans*-$NH_3$ ligand in $[Os(NH_3)_5(H_2O)]^{3+}$ [16] or $CN^-$ in $[Ru(CN)_5(H_2O)]^{3-}$ [16] and $[Fe(CN)_5(H_2O)]^{3-}$ [24]. Thus, the $[Fe(CN)_5P(OEt)_3]^{3-}$, $[Ru(CN)_5P(OEt)_3]^{3-}$ and $[Os(NH_3)_5P(OEt)_3]^{2+}$ are the final products independent of whether the entering ligand used is in excess.

The phosphane complexes are more stable to oxidation than are the corresponding sulfite complexes. Whereas the white solid *trans*-$[Ru(NH_3)_4(HSO_3)_2]$ has to be utilized [6b] with dispatch, the *trans*-$[Ru(NH_3)_4P(OR_1)_3(P(OR_2)_3)]^{2+}$ can be manipulated [14,16,23] in the air and kept under vacuum and in the dark for weeks. Again the phosphine complexes are less stable than the phosphite analogues.

In general, *trans*-$[Ru(NH_3)_4(P(OR)_3P(OR)_2]X_2$ (X: $PF_6^-$, $CF_3\ SO_3^-$, $BF_4^-$), $R_1$, $R_2$, $R_1 \neq R_2$ complexes in $[H^+] = 10^{-6}$ to $10^{-7}$ M solution exhibit the reversible equilibrium [14,16,23]:

$$\begin{aligned} &trans\text{-}[Ru(NH_3)_4(P(OR_1)_3P(OR_2)_3]^{2+} \\ &\quad + H_2O \rightleftarrows trans\text{-}[Ru(NH_3)_4(P(OR_1)_3H_2O]^{2+} + P(OR_2)_3 \end{aligned} \qquad (2)$$

However, when the hydrogen ion is higher than $10^{-4}$ M, the *trans*-$[Ru(NH_3)_4(P(OR_1)_3H_2O]^{2+}$ monophosphite species are quantitatively formed [16], since the free $P(OR_2)_3$ is hydrolyzed and the $P(O)(H)(OR_1)_2$ [30] and $P(OH)(OR_1)_2$ do not coordinate to Ru(II) *trans* to $P(OR_1)_3$. Similar behavior was also observed for the *trans*-$[Ru(H_2O)_2(P(OEt)_3)_4]^{2+}$ ion [28a]:

$$\begin{aligned} &trans\text{-}[Ru(H_2O)_2(P(OEt)_3)_4]^{2+} \\ &\quad + 2H_2O \rightleftarrows trans\text{-}[Ru(H_2O)_4(P(OEt)_3)_2]^{2+} + 2P(OEt)_3 \end{aligned} \qquad (3)$$

and for the symmetric binuclear species of ruthenium(II) where the bridging ligand is tetraethylpyrophosphite [28b]:

$$\begin{aligned} &[P(OEt)_3Ru(NH_3)_4P(OEt)_2OP(OEt)_2Ru(NH_3)_4P(OEt)_3]^{4+} \\ &\quad + H_2O \rightarrow 2trans\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} \\ &\quad + H(O)P(OEt)_3 \end{aligned} \qquad (4)$$

Table 2
p$K_a$ values for some acids

| Complex | p$K_a$[a] |
|---|---|
| $H_3PO_4$ | 2.1 |
| $H_3PO_3$ | 1.3 |
| $P(OEt)_2(OH)$ | 6.1 |
| $P(OH)_3$ | 7.4 |
| $[Ru(NH_3)_4(P(OEt)_2(OH))(H_2O)]^{2+}$ | 3.7 |
| $[Ru(NH_3)_4(P(OEt)_2(OH))(pz)]^{2+}$ | 3.7 |
| $[Ru(NH_3)_4(P(OEt)_2(OH))(H_2O)]^{3+}$ | 1.5 |
| $[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$ | 4.7 |
| $[Ru(NH_3)_4P(OH)_3(H_2O)]^{3+}$ | 1.0 |
| $[Fe(CN)_5P(OEt)_2(OH)]^{2-}$ | 5.1[b] |

[a] Ref. [18].
[b] Ref. [24].

It is interesting to highlight that even the P–O–P bond of tetraethylpyrophosphite ligand became resistant to hydrolysis after the coordination.

A good example of the π-bonding M(II)–P(III) relevance has been provided by the reactions of $[Fe(CN)_5(H_2O)]^{3+}$ [24] and $[Ru(NH_3)_5(H_2O)]^{2+}$ [18] with diethyl phosphite. Diethyl phosphite $P(OH)(OEt)_2$ (5%) exists in equilibrium with diethyl phosphonate $P(O)(OEt)_2(H)$ (95%) [30]. However, only the $P(OH)(OEt)_2$, formally P(III), is able to coordinated to Ru(II) [18], shifting the equilibrium phosphonate → diethylphosphite, and thus suggesting that the M(II) → P(III) π-bond is stronger than the O → P(III) one. The manifestation of the π-bonding in the $M–P(OH)(OEt)_2$ fragment is easily observed comparing the p$K_a$ values for the complexes of Table 2. The presence of the metal in the oxidation state (II) in both complexes turns the proton of the *trans*-$[Ru(NH_3)_4(P(OEt)_2(OH)]^{2+}$ species considerably less acid than in the corresponding *trans*-$[Ru(NH_3)_4(P(OEt)_2(OH))]^{3+}$, where the metal center in the oxidation state (III) is not able to engage in backbonding with P(III). Indeed a similar reaction with phosphorus acid $(H)(O)P(OH)_2$ with *trans*-$[Ru(NH_3)_5(H_2O)]^{2+}$ and $[Fe(CN)_5(H_2O)]^{3-}$ led to the formation of *trans*-$[Ru(NH_3)_4(H_2O)P(OH)_3]^{2+}$ and $[Fe(CN)_5P(OH)_3]^{3-}$. As far as we know, these species were the first examples of a phosphorus acid complex in which the binding atom was phosphorus. Notably, As(III) and Sb(III) ligands also show a tendency [16,33] to engage in backbonding as observed for the $E^{0'}_{M(III)/M(II)}$ and $\lambda_{max}$ for MLCT metal → ligand of Table 1.

### 2.2. *trans-effect and trans-influence of phosphanes on ruthenium(II) tetraammines*

Phosphanes are frequently used as ancillary ligands in several reactivity studies, tuning the *trans*-substitution lability of metal complexes via a systematic variation of their steric and electronic properties, as already commented. The choice of a desired phophane is usually guided adjusting the Tolman's cone angle [21], the σ-donor nature of the phosphane and the nucleophilicity of the entering ligand judged by its p$K_a$ value. A more realistic approach of the dependence of the substitution rate on the ligand *trans*-positioned to the leaving group has not been examined separately from the other factors that affect the substitution process.

Assuming that bond breaking is generally more relevant than bond making for octahedral complexes substitution reactions, the *trans*-effect could be defined as the effect of a coordinated ligand on the substitution rate of the ligand *trans* to itself and *trans*-influence is the influence of a coordinated ligand on the bond weakening of the ligand *trans* to itself [34a,b], see Eq. (5):

$$\begin{aligned} &trans\text{-}[Ru(NH_3)_4L_1(H_2O)]^{2+}\\ &\quad +L_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4L_1L_2]^{2+} + H_2O \end{aligned} \tag{5}$$

$L_1$ being the ligand whose *trans*-effect would be evaluated and $L_2$ the probe ligand; $K_{eq}$: $k_1/k_{-1}$.

The *trans*-effect is kinetic in its nature while *trans*-influence is a thermodynamic parameter. For small ligands, where steric hindrance is not very important, both *trans*-influence and *trans*-effect can be rationalized based on electronic properties [15,16].

The *trans*-$[Ru(NH_3)_4L_1(H_2O)]^{2+}$ complex ion represents a good starting model for the evaluation of *trans*-effect and *trans*-influence once the equatorial $NH_3$ molecules are electronic and sterically innocent ligands [1–3,16]. This model allows evaluating the influence of the phosphane ligands ($L_1$: P(III)) towards the substitution of the water molecule.

Thus, the kinetics and the mechanism of the reactions between *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ with the entering ligands pyrazine (pz; p$K_a = 0.5$), isonicotinamide (isn; p$K_a = 3.5$) and imidazole (imN; p$K_a = 6.9$) in water were investigated by either conventional or stopped-flow spectrophotometry [14,15,35–37]. The entering ligands were chosen according to their p$K_a$ values and because the aspects of substitution reactions of *N*-heterocyclic ligands in ruthenium chemistry have been extensively studied [1–4,5,7,10,11,14].

The accumulated data strongly suggest that the reaction occurs via dissociative pathway mechanism [14,15,35–38], most probably $I_d$. The evidence is based on plots of $k_{obs}$ versus entering ligand ($L_2$) concentration and activation parameters ($\Delta S^{\#}$, $\Delta G^{\#}$ and $\Delta V^{\#}$). Plots of $k_{obs}$ versus $C_L$, $L_2$: entering ligand exhibit different trends depending on the nucleophilic character of $L_1$. For instance, for $P(III) = P(OEt)_3$ and considering a number of entering ligands covering a wide range of σ-donor/π-acceptor electronic character, the tendency for rate constant saturation was only observed for electrophilic species, such as pyrazine, pyridine, isonicotinamide, nicotinamide, 4-cyano-pyridine and 4-methyl-*N*-pyrazinium ion, at $[C_{L_2}] > 0.1\ mol\ L^{-1}$ [14], thus suggesting a dissociative pathway mechanism. However, for nucleophilic species such as histidine, glycine, $NH_3$, imidazole, 1-methyl-imidazole, $N_3^-$, $SCN^-$, $CN^-$, $SO_3^{2-}$, $S_2O_3^{2-}$ and $CS_2N_3^-$, straight lines were always observed [14,37,39]; in some cases for

Table 3
Second order rate and equilibrium constants for water exchange with entering ligands $L_2$ pyrazine (pz), isonicotinamide (isn) and imidazole (imN) for *trans*-$[Ru(NH_3)_4(P(III)(H_2O)]^{2+}$ complexes, at 25.0 °C in water

| *trans*-$[Ru(NH_3)_4(P(III)(H_2O)]^{2+}$ | | | | | $L_2$: pz[a] | | $L_2$: isn[b] | | $L_2$: imN[c] | |
|---|---|---|---|---|---|---|---|---|---|---|
| P(III) | p$K_a$[d] | $T$ (°C)[e] | $E^0$ (V vs. SCE)[f] | $\lambda_{max}$ (nm)[f] | $k_1$ ($mol^{-1}$ L $s^{-1}$) | $K_{eq}$ ($mol^{-1}$ L) | $k_1$ ($mol^{-1}$ L $s^{-1}$) | $K_{eq}$ ($mol^{-1}$ L) | $k_1$ ($mol^{-1}$ L $s^{-1}$) | $K_{eq}$ ($mol^{-1}$ L) |
| $P(OEt)_2O^-$ | | | 0.20 | 316 | 560 | 51 | | | | |
| $P(OH)_2O^-$ | | | 0.18 | 316 | 500 | 45 | | | | |
| $P(Et)_3$ | 8.7 | 132 | 0.33 | 344 | 51 | 110 | | | | |
| $P(^nBu)_3$ | 8.4 | 132 | 0.30 | 355 | 35 | 69 | 21 | 95 | 0.28 | 73 |
| $P(OH)_3$ | | | 0.40 | 316 | 15 | 18 | | | | |
| $P(OEt)_2(OH)$ | | | 0.36 | 316 | 15 | 17 | | | | |
| $P(O^nBu)_3$ | | 115 | 0.40 | 316 | 9.8 | 30 | 8.1 | 40 | 20 | 1200 |
| $P(O^iPr)_3$ | 4.1 | 130 | 0.43 | 316 | 8.5 | 20 | 7.4 | 21 | 39 | 1500 |
| $P(O^tBu)_3$ | 11.4 | 172 | 0.45 | 314 | 8.3 | 21 | 6.0 | 20 | | |
| dmpp | | | 0.44 | 410 | 4.1 | 80 | | | | |
| $P(OPr)_3$ | 4.1 | | 0.47 | 316 | | | 2.3 | 39 | | |
| $P(OEt)_3$ | 3.3 | 109 | 0.46 | 316 | 3.8 | 19 | 2.2 | 34 | 15 | 1500 |
| $P(OMe)_3$ | 2.6 | 107 | 0.50 | 316 | 2.3 | 16 | 1.2 | 23 | 9.8 | 660 |
| P $CyH_2$ | | 115 | 0.45 | 354 | 1.8 | 69 | | | | |
| $Ph_2PC_2H_4PPh_2$ | | 125 | 0.54 | 362 | 1.9 | 320 | 1.7 | 86 | 3.5 | 4.7 |
| $PPh_3$ | 2.7 | 145 | 0.48 | 386 | 1.2 | 30 | 1.2 | 75 | 3.9 | 110 |
| $P(OC_2H_4Cl)_3$ | | 110 | 0.61 | 314 | 1.1 | 9.0 | | | | |
| $P(OPh)_3$ | −2.0 | 128 | 0.66 | 316 | 0.15 | 3.6 | 0.08 | 14 | | |
| $P(OCH_2)_3CEt$ | 1.7 | 101 | 0.57 | 314 | 0.15 | 6.5 | | | | |
| $AsPh_3$ | | 141 | 0.43 | 404 | 0.06 | 610 | 0.06 | 1400 | 0.14 | 29 |
| $SbPh_3$ | | | 0.44 | 420 | 0.05 | 960 | 0.04 | 1800 | 0.03 | 6.6 |

[a] In 0.10 mol $L^{-1}$ $NaCF_3CO_2$, pH 3.0 ($CF_3CO_2H$); refs. [14,15].
[b] In 0.10 mol $L^{-1}$ $NaCF_3CO_2$, pH 5.0 ($CF_3CO_2H$); refs. [14,35,36].
[c] In 0.10 mol $L^{-1}$ $NaCF_3CO_2/NaHCO_3$, pH 9.0 (NaOH); refs. [14,37].
[d] P(III) p$K_a$ values; ref. [40].
[e] Tolman's cone angles; ref. [21].
[f] In 0.10 mol $L^{-1}$ $NaCF_3CO_2$, pH 3.0 ($CF_3CO_2H$); values are in the range of 5 to 7.3 × $10^2$ cm $mol^{-1}$ $L^{-1}$; refs. [14,15,35–37].

$[C_{L_2}]$ up to 0.4 mol $L^{-1}$. This seems to be a general behavior for all the phosphorus complexes studied. Meanwhile, an isokinetic plot $\Delta H^{\#}$ versus $\Delta S^{\#}$ is well defined for all the *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ complex substitution reactions, where the entering ligands are pyrazine, isonicotinamide and imidazole. This would suggest that a similar mechanism is operative for all cases, independently of the entering ligand properties.

In order to learn more about the intimate nature of the mechanism, the activation volumes were measured [38] for $P(III) = P(OEt)_3$. The complex-formation reactions of *trans*-$[Ru(NH_3)_4(P(OEt)_3)(H_2O)]^{2+}$ with $L_2$: imidazole (imN), isonicotinamide (isn) and pyrazine (pz) were studied in aqueous solution as a function of entering ligand concentration and pressure up to 100 MPa, at 25.0 ± 0.1 °C. The volumes of activation for the complex-formation reaction were +4.2 ± 0.2 (pH 8.6), +1.9 ± 0.3 (pH 5.3) and +2.0 ± 0.3 $cm^3$ $mol^{-1}$ (pH 5.0), for L: imN, isn and pz, respectively. In the case of isn and pz as entering ligands, the volumes of activation for the reverse aquation reactions were found to be +7.5 ± 0.4 and +10.4 ± 0.3 $cm^3$ $mol^{-1}$, respectively. Based on the volume of activation data and the constructed volume profiles a dissociative interchange mechanism was proposed [38].

Once the results enable a reliable assignment of the underlying mechanism, the second order specific rate constants ($k_1$) for the substitution of the coordinated water molecule by $L_2$ were proposed as a relative measurement of the lability of the water ligand and therefore as a parameter for the evaluation of the relative *trans*-effect of phosphanes [35].

Thus, from the data of Table 3, the following relative series of *trans*-effect can be written [14–16,35–37]:

For $L_2$: pyrazine: $P(OEt)_2O^- \sim P(OH)_2O^- \gg P(Et)_3 > P(^nBu)_3 > P(OH)_3 \sim P(OEt)_2(OH) > P(O^nBu)_3 > P(O^iPr)_3 \sim P(O^tBu)_3 >$ dmpp $\sim P(OEt)_3 > P(OMe)_3 \sim PH_2Cy \sim Ph_2PC_2H_4PPh_2 > PPh_3 \sim P(OC_2H_4Cl)_3 \gg P(OPh)_3 \sim P(OCH_2)_3CEt$.
For $L_2$: isonicotinamide: $P(^nBu)_3 > P(O^nBu)_3 > P(O^iPr)_3 > P(O^tBu)_3 > P(O^nPr)_3 \sim P(OEt)_3 > P(OMe)_3 > Ph_2PC_2H_4PPh_2 \sim PPh_3 \gg P(OPh)_3$.
For $L_2$: imidazole: $P(O^iPr)_3 > P(O^nBu)_3 > P(OMe)_3 > Ph_2PC_2H_4PPh_2 \sim PPh_3 \gg P(^nBu)_3$.

The same tendency is observed roughly independent of the nature of the incoming. This is quite interesting since pyrazine is basically a π-acceptor ligand, the isonicotinamide has a moderate σ-donor and π-acceptor character and imidazole is basically a σ-donor ligand.

Again, this is what would be expected for a strict dissociative mechanism. However, in addition to bond breaking, bond making may also occur on some extension in the transition state, suggesting a possible influence of the nature of the entering ligand on the reaction mechanism. This is clearly observed in the ligand dependence in the $k_{obs}$ plots versus $C_{L_2}$ [14–16]. The fact that the $k_{obs}$ versus $C_{L_2}$ plots with imidazole (and other nucleophiles) do not show linear deviation above 0.1 mol L$^{-1}$, while there is evidence for that with pyrazine and isonicotinamide (and other electrophiles) usually occurring around 0.1 mol L$^{-1}$, suggests some influence of the nature of the entering ligand. Furthermore, the higher the nucleophilic character of the entering ligand, the higher the second order specific rate constant value ($k_1$). Conversely the higher the electrophilic character, the lower this ligand concentration for which the deviation from linearity in plots $k_1$ versus $C_{L_2}$, is observed. However, a direct relationship between $k_1$ and the nature of the entering ligand cannot be so far inferred.

Although all the phosphane complex substitution reactions are reversible, the rate of the back reaction is also quite sensitive to the nucleophilicity of the entering ligand $L_2$. For example, the aquation specific rate constant for Mepz$^+$ from *trans*-[Ru(NH$_3$)$_4$(P(OEt)$_3$)(Mepz)]$^{3+}$ is 6.1 s$^{-1}$, but if $L_2$: SO$_3$$^{2-}$, $k_{-1} = 7.5 \times 10^{-3}$ s$^{-1}$, at 25.0 °C (μ = 0.1 in NaCF$_3$CO$_2$) [14]. This can be observed from $K_{eq}$ values in Table 3 for the triad pz, isn and imN, in all cases.

If the *trans*-influence of the phosphane is related to the weakening of the Ru(II)–L bond in terms of $\Delta G_{eq}$, the following order of increasing *trans*-influence on the basis of $1/K_{eq}$, where $K_{eq} = k_1/k_{-1}$, can be written [14,35–37]:

For $L_2$: pyrazine, the *trans*-influence follows the order: $P(OPh)_3 > P(OCH_2)_3CEt > P(OC_2H_4Cl)_3 > P(OMe)_3 \sim P(OEt)_2(OH) \sim P(OH)_3 \sim P(OEt)_3 \sim P(O^iPr)_3 \sim P(O^tBu)_3 > PPh_3 \sim P(O^nBu)_3 \quad P(OH)_2O^- > P(OEt)_2O^- > PH_2Cy \sim P(^nBu)_3 > dmpp > P(Et)_3$.
For $L_2$: isonicotinamide: $P(OPh)_3 > P(OMe)_3 \sim P(O^tBu)_3 \sim P(O^iPr)_3 > P(OEt)_3 > P(O^nPr)_3 \sim P(O^nBu)_3 > PPh_3 > Ph_2PC_2H_4PPh_2 > P(^nBu)_3$.
For $L_2$: imidazole: $Ph_2PC_2H_4PPh_2 \gg P(^nBu)_3 > PPh_3 > P(OMe)_3 \gg P(O^nBu)_3 > P(OEt)_3 \sim P(O^iPr)_3$.

The positions of the phosphanes in the *trans*-effect and *trans*-influence series are not the same. In general, phosphanes that exhibit low *trans*-effect exhibit high *trans*-influence.

All series can be rationalized concerning the electronic arrangement in the P–Ru–Y bond axis (Y: H$_2$O or L), rather than steric factors. The main evidence for this is the linear free-energy relationship between the log($k_1$) or log($1/K_{eq}$) and $E^{0'}_{Ru(III)/Ru(II)}$ for the aquo species (Fig. 1), where more positive $E^{0'}_{Ru(III)/Ru(II)}$ values indicate stronger Ru(II) → P(III) π-backbonding. Hence, the more positive $E^{0'}_{Ru(III)/Ru(II)}$ the more the metal center exhibits Ru(III) character, which is more inert than Ru(II) [1–3]. Therefore, the metal center would prefer electrophilic ligands rather than nucleophilic ones. This argument would explain why phosphites always exhibit a weaker *trans*-effect than the corresponding phosphine (equal R), since the phosphites are better π-acceptors.

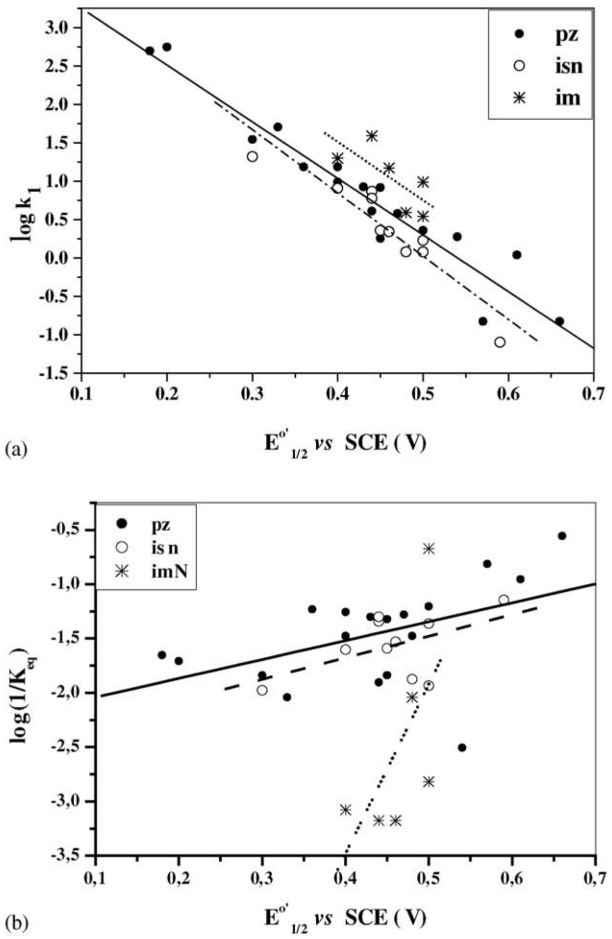


Fig. 1. Linear free-energy relationship for the reaction *trans*-[Ru(NH$_3$)$_4$P(III)(H$_2$O)]$^{2+}$ + $L_2$ ⇄ *trans*-[Ru(NH$_3$)$_4$P(III)($L_2$)]$^{2+}$ + H$_2$O. (a) Second order specific rate constant $k_1$ vs. $E^{0'}$; (b) reciprocal of $K_{eq}$ ($k_1/k_{-1}$) vs. $E^{0'}$. ($L_2$: pz, isn or imN, with the $E^{0'}$ for the aqua reagent species).

The reverse trend can be noted in the phosphane *trans*-influence series written for $L_2$: pz and isn, i.e., the higher the P(III) π-acceptor capacity, the more positive are the $E^{0'}_{Ru(III)/Ru(II)}$ values, leading to low $K_{eq}$ as the competition for the 4dπ electron density in the metal center decreases in the ground state. Thus, plots of log($1/K_{eq}$) as a function of $E^{0'}$ exhibit positive slopes (Fig. 1). In the case of $L_2$: imN, the points seem more scattered. However, the data in Table 3 suggest a relationship between the $K_{eq}$ values with the σ-donor nature of the phosphane. Therefore, the same tendency for the *trans*-effect and *trans*-influence series is obtained.

On the other hand, a decrease in the P(III) π-acceptor contribution is associated with an increase in its σ-donor character, weakening the Ru–$L_2$ bond ($L_2$: H$_2$O or imN) which is σ in character in the ground state. It also would explain why the phosphines show stronger *trans*-labilizing effects, but weaker *trans*-influence than phosphites. Indeed, the aquation of *trans*-[Ru(NH$_3$)$_4$(P(OEt)$_3$)(P(Et)$_3$)]$^{2+}$, yields quantitatively *trans*-[Ru(NH$_3$)$_4$(P(OEt)$_3$)(H$_2$O)]$^{2+}$ as the final product [31].

Despite the difference in the nature of the entering ligand, the slopes in the plots of log($k_1$) versus $E^{0'}_{\mathrm{Ru(III)/Ru(II)}}$ are approximately the same. This could be interpreted as a consequence of a smooth change in the reaction mechanism, when the entering ligand changes from pz to isn to imN. This change, which would suggest a mechanistic continuum type behavior [41], has not been evaluated from the experimental data since the $k_1$ and $k_{-1}$ values are calculated using just the linear portion of the $k_{\mathrm{obs}}$ versus $C_L$ plots. The experimental points under this condition reflect situations where the existence of outer sphere associations is negligible and therefore not detected.

The positions of the phosphanes in the above series can also be rationalized using ligand field arguments. The more the P(III) ligand stabilizes the Ru(II) 4dπ orbitals through Ru(II) → P(III) π-backbonding interaction, the larger the $10\,D_q$ value, and therefore the less reactive the metal center would be regarding substitution. The increase in the $10\,D_q$ value correlates with an increasing energy of the d–d absorption band $\lambda_{\max}$ for the phosphite complexes with regard to the phosphines in the aquo species (Table 3).

In general, phosphane steric hindrance was not expected in this reaction in view of the well defined equatorial plane occupied by the ammines. Only very large P(III) molecules will force the equatorial plane in the opposite direction, thereby affecting the *trans*-positioned water or $L_2$ molecule. Even when changing the $PR_3$ cone angle by 40°, there is no correlation between $k_1$ or $K_{\mathrm{eq}}$ data and the size of phosphanes (Table 3). Once again, the electronic effects seem to be the main factor governing the reaction, which would be consistent with the difference in the $pK_a$ values for phosphites and phosphines.

These studies have also been extended to the ancillary ligands $SbPh_3$ and $AsPh_3$ [33,37]. A $k_1$ data examination shows that these two ligands do not exhibit a substantial *trans*-effect. An increasing *trans*-labilizing ability series can be written as: $SbPh_3 < AsPh_3 \ll P(III)$, when $L_2$: imN, and $SbPh_3 \approx AsPh_3 \ll P(III)$, when $L_2$: isn or pz. Besides the low *trans*-effect, $SbPh_3$ and $AsPh_3$ differ dramatically from the P(III) ligands in their electronic effects upon the metal. In the $E^{0'}$ versus $\log k_1$ plot for the analogous $PPh_3$, $AsPh_3$ and $SbPh_3$, the slope is contrary to the slope observed for the phosphanes [37]. The more positive are the $E^{0'}$ values, the higher the *trans*-effect. Even in such cases, no correlation between the rates and cone angle parameters was found. A comparison of the reciprocal of $K_{\mathrm{eq}}$ data would suggest that the strong *trans*-influence of the former ligands would be mainly due to their σ-donor character and that $SbPh_3$ and $AsPh_3$ labilize the *trans*-imN ligand by weakening the Ru–imN σ-bond in the ground state. The opposite behavior is observed when the ligand is electrophilic in nature, i.e., a very weak *trans*-influence when L: pz or isn.

Finally, the position of the phosphanes in the series of ligands arranged in order of increasing *trans*-labilizing [7,10b,14,32a] effect in *trans*-$[\mathrm{Ru(NH_3)_4L_1(H_2O)}]^{2+}$, considering the second-order specific rate constant of the replacement of water by isn, is: $CO \le N_2 <$ isn < py < $AsPh_3 < SbPh_3 < P(OPh)_3 < NH_3 \le$ imN < $OH^- <$ $PPh_3 \sim P(OMe)_3 <$ dppe < $P(OEt) \sim P(O^n pr)_3 < P(O^i Pr)_3 \sim$ $CN^- \sim P(O^t But)_3 \sim P(But)_3 < SO_3{}^{2-} <$ imC. Unfortunately, there are not sufficient data available in the literature to write a similar *trans*-influence series for $L_2$: pz or imN.

## 3. Nitrosyl and nitric oxide as ligands

### 3.1. Nitrosyl

Additionally to the σ-bond between nitric oxide and transition metal, $NO^+$ has two degenerate unfilled $\pi^*$ orbitals ($\pi^*_y$ and $\pi^*_z$) symmetrically able to engage in π-bonding with the filled *n*dπ orbitals of metal ions. The energy of these two $\pi^*$ orbitals is such that their interaction with filled metals 3dπ, 4dπ and 5dπ orbitals induces remarkable changes in the chemical properties of the metal center, the *trans*-positioned ligand and the NO ligand itself [17,42]. As a consequence the nitrosyl ligand ($NO^+$) is considered perhaps the strongest π-acceptor nitrogen ligand known.

The DFT computation for *trans*-$[\mathrm{Ru^{II}(NH_3)_4(L)(NO^+)}]^{3+/2+}$ complex ions (L: $NH_3$, $Cl^-$, $OH^-$, py and pz) indicates that their LUMO is always composed predominantly of the $\pi^*$ orbitals of NO (68–70%). Thus, the one-electron reduction of these complexes is expected to generate $[\mathrm{Ru^{II}NO^0}]$ species [43,44]. Indeed, the coordinated NO radical has been detected through electron paramagnetic resonance spectroscopy [45] for the reduced form of the *trans*-$[\mathrm{Ru(NH_3)_4(H_2O)(NO)}]^{3+}$ ion and another one electron reduced species as *trans*-$[\mathrm{RuPP(Cl)(NO)}]^{2+}$ PP: $(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2$ or $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$, [45a] *trans*-$[\mathrm{Ru(cyclam)(Cl)(NO)}]^{2+}$ [45b] and $[\mathrm{Ru(bipy)_2(Cl)(NO)}]^{2+}$ [46]. As a consequence of the coordination, the redox potential of coordinated nitrosyl, $\mathrm{Ru^{II}NO^+/Ru^{II}NO^0}$, becomes much less positive than in the free ion ($E^0_{\mathrm{NO^+/NO^0}}$ = +1.042 V versus NHE) [42].

Ruthenium nitrosyl complexes, in particular, exhibit linear Ru–N–O bond angles, NO stretching frequency higher than 1870 $\mathrm{cm^{-1}}$ and are in general susceptible to nucleophilic attack ($OH^-$, $RNH_2$, $RS^-$) [42a,d]. Therefore, they are better described as $[\mathrm{Ru^{II}NO^+}]^6$ [47,43]. The *trans*-$[\mathrm{Ru(NH_3)_4(NO)(L)}]^{3+}$ reaction with hydroxide ions always yields the corresponding nitro compound *trans*-$[\mathrm{Ru(NH_3)_4(L)(NO_2)}]^+$ [44], which in turn can be isolated as a $PF_6{}^-$ salt, confirming the nitrosonium character of the NO ligand in such species. Similarly to other nitrosyl complexes [42,47], the formation of *trans*-$[\mathrm{Ru(NH_3)_4(L)(NO_2)}]^+$ ions from the nitrosyl complexes is assumed to occur in three steps [48]. First, there is a fast ion pair formation between the nitrosyl complexes and $OH^-$ ion, followed by the $OH^-$ addition, leading to the *trans*-$[\mathrm{Ru(NH_3)_4(L)(NO_2H)}]^+$ formation. The *trans*-$[\mathrm{Ru(NH_3)_4(L)(NO_2H)}]$ ion rapidly reacts with a second $OH^-$ ion, producing the nitro compound [48].

Table 4
Data for $K_{OH^-}$ for selected nitrosyl complexes

| Complex | $K_{OH^-}$ $(L^2 mol^{-2})$[a,b] | $k_{OH}$ $(s^{-1} \times 10)$[c,d] | $k_{-NO}$ $(s^{-1})$[e,f] |
|---|---|---|---|
| *trans*-$[Ru(NO)(NH_3)_4(P(OEt)_3](PF_6)_3$ | $3.4 \times 10^5$ | – | 0.980 |
| *trans*-$[Ru(NO)(NH_3)_4(isn)](BF_4)_3$ | $2.5 \times 10^8$ | – | 0.043 |
| *trans*-$[Ru(NO)(NH_3)_4(nic)](BF_4)_3$ | $5.9 \times 10^7$ | 3.300 | 0.025 |
| *trans*-$[Ru(NO)(NH_3)_4(L\text{-}hist)](BF_4)$ | $4.6 \times 10^{13}$ | 0.076 | 0.140 |
| *trans*-$[Ru(NO)(NH_3)_4(py)](BF_4)_{3)}$ | $2.2 \times 10^5$ | 1.450 | 0.060 |
| *trans*-$[Ru(NO)(NH_3)_4(4\text{-}pic)](BF_4)_3$ | $7.7 \times 10^5$ | 0.950 | 0.070 |
| *trans*-$[Ru(NO)(NH_3)_4imN](BF_4)_3$ | $9.7 \times 10^{10}$ | – | 0.160 |
| *trans*-$[Ru(NO)(NH_3)_4imC]Cl_3$ | [g] | – | 4.000 |
| *trans*-$[Ru[(NO)(NH_3)_4(pz)](BF_4)_3$ | $6.0 \times 10^8$ | 17.70 | 0.070 |
| *trans*-$[Ru(NO)(NH_3)_4(4\text{-}Clpy)](BF_4)_3$ | $6.0 \times 10^6$ | 0.260 | 0.030 |
| *trans*-$[Ru[(NO)(NH_3)_4Cl](BF_4)_3$ | [h] | – | – |
| *trans*-$[Ru(NO)(NH_3)_4(H_2O)](BF_4)_3$ | [e] | – | 0.040 |
| *trans*-$[Ru(NO)(cyclam)](PF_6)_2$ | [e] | – | |
| $[Ru(NO)(hedta)]$ | $1.4 \times 10^{13}$ | – | |

[a] *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+} + 2OH^- \overset{K_{OH}}{\rightleftharpoons}$ *trans*-$[Ru(NO_2)(NH_3)_4(L)]^+ + H_2O$.
[b] Ref. [44a,b].
[c] *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+} + OH^- \xrightarrow{k_{OH}}$ *trans*-$[Ru(NO_2H)(NH_3)_4(L)]^{2+}$.
[d] Ref. [48].
[e] *trans*-$[Ru^{II}(NO^0)(NH_3)_4(L)]^{2+} + H_2O \xrightarrow{k_{-NO}}$ *trans*-$[Ru(NH_3)_4(L)(H_2O)]^{2+} + NO$.
[f] Ref. [49].
[g] Non-observable reaction up to $C_{OH^-} \cong 10^{-3}$ M.
[h] Non-reversible reaction.

A wide range of rate constants for $OH^-$ ion attack to $NO^+$ has been reported (Table 4) [48] for a series of *trans*-$[Ru(NH_3)_4(L)(NO)]^{3+}$ nitrosyl complexes, with $k_{OH}$ changing from $7.6 \times 10^{-1}\,M^{-1}\,s^{-1}$ (L: L-Hist) to $8.0 \times 10^2\,M^{-1}\,s^{-1}$ (L: pz). A good linear correlation between $k_{OH}$ with $E^{0'}_{NO^+/NO^0}$ which varies from −0.108 V versus NHE (L: L-Hist) to +0.112 V versus NHE (L: pz) [17,44] was observed. This was expected since, similarly to $\nu_{NO}$, the $E^{0'}_{NO^+/NO^0}$ redox potential reflects the electron density of the NO ligand [44] and, therefore, would be directly related to the susceptibility of the $NO^+$ ligand to nucleophilic attack. Thus, it was demonstrated [48] that for the series of complexes reported, the $E^{0'}_{Ru(III)/Ru(II)}$ redox potential values, similar to $\nu_{NO}$ [42d], are very convenient to predict nucleophilic attack to coordinated $NO^+$ [42a,47a].

According to activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$), see Table 5, the attack of the $OH^-$ ion to the coordinated NO nitrogen atom is likely to proceed by means of an associative mechanism, which would be consistent with an increase in the coordination number of the N atom in nitrosyl ligand and seems to be entropically driven [48].

The stabilization of Ru(II) with respect to the Ru(III) center in *trans*-$[Ru(NH_3)_4(NO)(L)]^{n+}$ complexes (L: *N*-heterocyclic ligand) is quite remarkable due to $NO^+$ coordination and, as far as we know, it is not surpassed by any other ligand [5,42a,d]. The $E^{0'}_{Ru(III)/Ru(II)}$ for the *trans*-$[Ru(NH_3)_4(H_2O)(L)]^{n+}$ aqua complexes (L: *N*-heterocyclic) is in the range of −0.062 V (L: L-Hist) to +0.631 V versus NHE (L: pz) [51]. However, as judged by EPR experiments, in the *trans*-$[Ru(NH_3)_4(NO)(L)]^{3+}$ species no oxidation of the metal center is observed up to 1.2 V [48,51].

Table 5
Activation parameters for nitrosyl-nitro conversion in *trans*-$[Ru(NH_3)_4(L)(NO)]^{3+}$[a]

| Complex | $\Delta H^\ddagger$ (kJ/mol) | $\Delta S^\ddagger$ (J/K mol) |
|---|---|---|
| *trans*-$[Ru[(NO)(NH_3)_4(pz)](BF_4)_3$ | 76 ± 2 | 54 ± 6 |
| *trans*-$[Ru(NO)(NH_3)_4(nic)](BF_4)_3$ | 78 ± 1 | 44 ± 4 |
| *trans*-$[Ru(NO)(NH_3)_4(4pic)](BF_4)_3$ | 75 ± 1 | 26 ± 4 |

[a] Ref. [48].

The changes in the $E^0_{Ru(III)/Ru(II)}$ are also reflected in the electronic spectra. The MLCT bands that occur in the visible region of the spectrum in the $[Ru(NH_3)_5L]^{2+}$ ions [9a] are blue-shifted in *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ below 370 nm upon substitution of the *trans*-$NH_3$ ligand by $NO^+$ [44]. For example, the $\lambda_{max}$ for the MLCT band for the $[Ru(NH_3)_5(pz)]^{2+}$ is 472 nm while for the *trans*-$[Ru(NH_3)_4(NO)(pz)]^{3+}$ it occurs at 242 nm [44b]. The MLCT ($Ru^{II} \rightarrow L$) is red shifted when $NO^+$ is replaced by $NO_2{}^-$ in *trans*-$[Ru(NH_3)_4(L)(NO)]^{3+}$ (L: *N*-heterocyclic). For example, the $\lambda_{max}$ of the $Ru^{II} \rightarrow L$ MLCT band changes from 262 nm (L: 4-pic), 267 nm (L: py) and 272 nm (L: nic) for the nitrosyl complexes to 378, 380 and 388 nm for the corresponding nitro derivatives. Assuming that the energy of $\pi^*$ L orbitals is not significantly affected by the change of the $NO^+$ to $NO_2{}^-$, this difference could be rationalized as due to the difference in Ru $d\pi$ orbital stabilization as a function of the backbonding $Ru \rightarrow NO^+$ and $Ru \rightarrow NO_2{}^-$, since $NO^+$ is a stronger $\pi$-acceptor than $NO_2{}^-$. The MLCT bands all appear at roughly the same energy which is consistent with the above interpretation.

An interesting example of $NO^+$ ligand *trans*-influence on the reactivity of the *trans*-ligand was reported for the sulfite ligand [44b]. The sulfite ligand and the metal center are promptly oxidized by $H_2O_2/H^+$ in *trans*-$[Ru(NH_3)_4(SO_3)(L)]$ complexes [6b]. However, in the *trans*-$[Ru^{II}(NH_3)_4(NO)(SO_3)]^+$ complex, neither the metal nor the $SO_3^{2-}$ ligand are oxidized even using Ce(IV) ions as an oxidant [44b].

Similar to observations with $[Ru(NH_3)_5(SO_2)]^+$ [52], the reaction of the nitrosyl complex with Eu(II) or Cd(Hg) leads to the reduction of the S(IV) ligand yielding the corresponding binuclear species $[(NO)Ru(NH_3)_4S{-}SRu(NH_3)_4(NO)]^{6+}$, isolated as a reasonably stable green salt [44b]. In the presence of Zn(Hg) the reduction of the NO ligand can proceed to $NH_3$.

Striking examples of changes in the metal center and *trans*-ligand properties due to NO coordination were observed in the interatomic distance and coordinated water molecule $pK_a$ for the *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ ion [53]. The interatomic distances $Ru{-}OH_2$, in both $[Ru(NH_3)_5(H_2O)]^{3+}$ and in *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ complex ions are, respectively, 2.11 Å [54] and 2.035 Å [53]. The $Ru{-}OH_2$ interatomic distance in the ruthenium(II) nitrosyl species is similar to the one observed in the ruthenium(III) pentaammine complex ions.

The $pK_a$ for the *trans*-$[Ru^{II}(NH_3)_4(NO)(H_2O)]^{3+}$ acid is 3.1 [53], i.e., approximately 1.3 and 8.0 $pK_a$ units smaller than the values reported for the $[Ru^{III}(NH_3)_5(H_2O)]^{3+}$ [3] and $[Ru^{II}(NH_3)_5(H_2O)]^{2+}$ [11] acids, respectively.

The higher acidity and the short $Ru{-}OH_2$ interatomic distance of a *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ complex were explained as being a consequence of the intense participation of the water oxygen non-bonding π-electrons in the $Ru{-}OH_2$ bond, which was demonstrated through DFT computation to be induced by the NO ligand [53]. Similar changes in the $pK_a$ of the pyrazinium ion in *trans*-$[Ru(NH_3)_4(NO)pzH]^{4+}$ ($pK_a = -0.8$) [55] regarding $[Ru(NH_3)_5(pzH)]^{3+}$ ($pK_a = 2.5$) [2,3] and $[Ru(NH_3)_5(pzH)]^{4+}$ and also in the coordinated water in *trans*-$[Ru(cyclam)(NO)(H_2O)]^{3+}$ ($pK_a = 3.0$) [56] with respect to *trans*-$[Ru(cyclam)Cl(H_2O)]^+$ ($pK_a = 3.3$) [57] have been reported.

The lability of the water ligand in the *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ and $[Ru^{II}(NH_3)_5(H_2O)]^{2+}$ complexes are remarkably different. The substitution of the coordinated water molecule in *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ ion by $Cl^-$ proceeds approximately 30-fold slower [53] than in the $[Ru(NH_3)_5(H_2O)]^{3+}$ ($3.7 \times 10^{-6}$ and $8.7 \times 10^{-5}\ mol^{-1}\ L\ s^{-1}$, 40 °C, $\mu = 2.0$ NaCl; $[H^+] = 1.0 \times 10^{-2}\ mol\ L^{-1}$, respectively). The reaction of $[Ru(NH_3)_5(H_2O)]^{2+}$ with pyrazine ($0.1\ mol\ L^{-1}$) is completed in a few minutes at room temperature ($k_2 = 5.6 \times 10^{-2}\ mol^{-1}\ L\ s^{-1}$) [1,2], while for the *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ ions ($[pz] = 0.5\ mol\ L^{-1}$) no changes are noticed in the electronic spectra after 48 h under comparable experimental conditions [53]. Another example of the lability decrease of the ligand *trans* in position to NO is provided by $Cl^-$ aquation in the *trans*-$[Ru(NH_3)_4(NO)Cl]^{2+}$ complex ion. The chloride ligand is aquated at specific rate constants of $20.2\ s^{-1}$ [58], $5.4 \times 10^{-6}\ s^{-1}$ [59] and $8.4 \times 10^{-6}\ s^{-1}$ at 40 °C [54], respectively, from the $[Ru^{II}(NH_3)_5Cl]^+$, $[Ru^{III}(NH_3)_5Cl]^{2+}$ and *trans*-$[Ru(NH_3)_4(NO)Cl]^{2+}$ ions.

Another example of changes induced by $NO^+$ in the reactivity of the *trans*-ligand has been recently observed in the *trans*-$[Ru(NH_3)_4(NO)P(OEt)_3]^{3+}$ ion. As previously described in this paper the coordination of $P(OEt)_3$ molecules to the Ru(II) center gives the ester a remarkable resistance to hydrolysis and oxidation. When the *trans*-ligand is nitrosyl, however, an activation of the coordinated ester with respect to nucleophilic attack is observed. In general, in aqueous solution the *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ ions undergo $OH^-$ nucleophilic addition, yielding the respective *trans*-$[Ru(NH_3)_4L(NO_2)]^+$ nitro complexes. According to previous kinetic studies in the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}/NO_2^-$ system [60], we expected to observe the occurrence of only the nitrite ligand aquation at $[OH^-] = 10^{-7}$, as $P(OEt)_3$ has strong *trans*-labilizing and *trans*-influence effects.

$$\begin{aligned} &trans\text{-}[Ru(NH_3)_4P(OEt)_3(NO_2)]^+ + H_2O \\ &\quad \rightarrow trans\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + NO_2^- \end{aligned} \tag{6}$$

However, according to electrochemical and spectroscopic ($^{31}P$ NMR, $^1H$ NMR, IR, UV–vis) measurements, after the dissolution of *trans*-$[Ru(NH_3)_4P(OEt)_3(NO)](PF_6)_3$ salt in an aqueous buffered solution (pH 7.0), comparable concentrations of both *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ ions are formed and accounts for more than 95% of all the ruthenium species initially present in the solution [61]. As the *trans*-$[Ru(NH_3)_4P(OEt)_3(NO)]^{3+}$ species is stable in acid solution ($pH \leq 3.0$), the *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ formation could not be attributed to a $P(OEt)_3$ dissociative process. Furthermore, the presence of ethanol has been detected in solution. Therefore, these results strongly suggest that it is likely an $OH^-$ competitive nucleophilic attack occurs in both $NO^+$ and phosphorus ligand, producing, respectively, *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ ions. Therefore, $NO^+$ ligand is likely to exert such a strong influence over the *trans*-positioned ligand that triethylphosphite becomes susceptible to $OH^-$ nucleophilic attack. This behavior is not observed when the *trans*-ligand is CO [62], pyrazine, $H_2O$ or $P(OEt)_3$ [14,16].

### 3.2. Nitric oxide

In contrast to the inertia of the $Ru^{II}NO^+$ species, the lability of NO seems to be common in $Ru^{II}NO^0$ species. DFT computations for *trans*-$[Ru(NH_3)_4(L)(NO)]^{3+}$ and *trans*-$[Ru(NH_3)_4(L)(NO)]^{2+}$ (L: py) showed that, upon reduction, a pronounced bend from 180° to 139° is observed in the Ru–N–O angle. This bending is accompanied by a considerable reduction in overlap of Ru 4dπ and NO $\pi^*$ orbitals [49a]. Consistent with DFT calculations reported for

$[Ru(NH_3)_5(NO)]^{2+}$, the main changes in bond lengths for $[Ru(NH_3)_4(L)(NO)]^{2+}$ were observed along the L–Ru–N–O axis [49b]. As a consequence, Ru–NO bond weakening is expected and therefore it is understandable that the nitric oxide ligand is much more susceptible to dissociation in the *trans*-$[Ru(NH_3)_4(L)(NO)]^{2+}$ species than in their oxidized analogues.

When ligand L is a π-acceptor, as the *N*-heterocyclic molecules, the reduced species releases $NO^0$ according to reaction [49,50]:

$$trans\text{-}[Ru(NH_3)_4(L)(NO)]^{2+} + H_2O \underset{k_{+NO}}{\overset{k_{-NO}}{\rightleftarrows}} trans\text{-}[Ru(NH_3)_4(L)(H_2O)]^{2+} + NO^0 \tag{7}$$

The rate constants for NO dissociation in *trans*-$[Ru(NH_3)_4(L)(NO)]^{2+}$ ions vary from 0.025 $s^{-1}$ (isn) [49] to 4.00 $s^{-1}$ (imC) [50] at 25 °C. The sequence of $k_{-NO}$ as a function of L increases as follows: pic ∼ nic ∼$H_2O$ ∼ py < L-His ∼ imN < pz < imC, which is the same sequence observed for water [32a] or sulfate [63] lability in *trans*-$[Ru(NH_3)_4L(Y)]^{2+}$ complexes (L: *N*-heterocyclic ligand, Y: $H_2O$ or $SO_4{}^{2-}$).

According to the well accepted [5a,b] dissociative pathway for octahedral complexes reactions, the NO labilization would reflect the affinity of *trans*-$[Ru(NH_3)_4(L)(H_2O)]^{2+}$ fragment for the NO ligand, and be directly related to the effective ruthenium charge in these complexes [32]. Since $E^{0'}_{Ru(III)/Ru(II)}$ is an indication of metal center effective charge, it is expected that the more positive the *trans*-$[Ru(NH_3)_4(L)(H_2O)]^{3+/2+}$ redox potential, the lower the $k_{-NO}$ value. As observed for other leaving ligands, a linear tendency ($k_{-NO}/s^{-1} = -0.7 \times E^0$ *trans*-$[Ru(NH_3)_4(L)(H_2O)]^{3+/2+} + 0.07$; $R = 0.97$) [49] is observed when the $E^{0'}_{Ru(III)/Ru(II)}$ in *trans*-$[Ru(NH_3)_4(L)(H_2O)]^{3+/2+}$ is plotted against $k_{-NO}$ values.

The electrochemical ligand parameters ($E_L$), so called “Lever’s parameter”, are known to be helpful in predicting metal redox potentials [64], therefore we expected a correlation between $k_{-NO}$ values and the sum of $E_L$ ($\Sigma E_L$). This correlation indeed exists ($k_{-NO}/s^{-1} = -0.81 \times \Sigma E_L + 0.48$; $R = 0.997$) [49] suggesting that the kinetic parameter is determined very strongly by a thermodynamic energy. Since $E_L$ values for a large number of *N*-heterocyclic ligands are available in the literature, this correlation could become a very convenient tool to estimate the rate constants for NO dissociation from *trans*-$[Ru(NH_3)_4(L)(NO)]^{2+}$ species.

It is important to stress that in complexes where $Cl^-$ is localized *trans* to NO, as in *trans*-$[Ru(NH_3)_4(Cl)(NO)]^+$, *trans*-$[Ru(cyclam)(Cl)(NO)]^+$ and *trans*-$[Ru(depe)(Cl)(NO)]^+$, chloride is preferentially released before NO [17]. This behavior is attributed to the electronic characteristics of L. Chloride binds tightly to Ru(III) due to its efficient σ- and π-donor ability. On the other hand, since Ru(II) species are not able to accept π-donation and are not good Lewis acid, chloride in general dissociates rapidly from Ru(II) complexes [5a]. The same reasoning could explain why $Cl^-$ dissociation takes place before $NO^0$ displacement. The strongly operative π-donation $Cl^- \rightarrow Ru^{II}NO^+$ in *trans*-$[Ru^{II}L_4(Cl)(NO^+)]^{2+}$ induced by the Ru(II) backbonding to $NO^+$ (as occurs with water ligand in the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$), is considerably less in *trans*-$[Ru^{II}L_4(Cl)(NO^0)]^+$ since $NO^0$ is a π-acceptor notably weaker than $NO^+$. Although, computation data are not available for the *trans*-$[Ru(NH_3)_4(Cl)(NO)]^{2+}$/*trans*-$[Ru(NH_3)_4(Cl)(NO)]^+$ system, DFT calculation [65] performed for the *trans*-$[Ru(NH_3)_5(NO)]^{3+}$/*trans*-$[Ru(NH_3)_5(NO)]^{2+}$ confirms that there is a lengthening of the axial Ru–$NH_3$ bond, consistent with the labilization of the ligand *trans* to NO upon reduction.

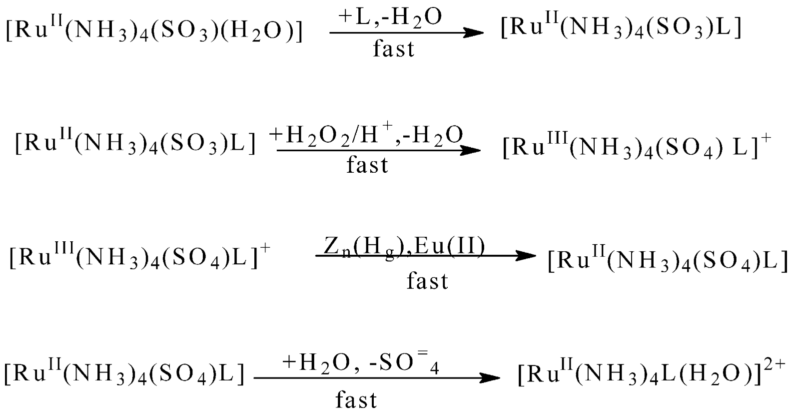
Nitroxyl anion ($NO^-$) has been attracting research interest primarily due to its close relationship to nitric oxide and its biochemistry relevance. The potential of about −0.8 V versus NHE [66] for the reduction $NO/NO^-$ (triplet state) has been recently estimated by quantum mechanic calculation. With such high negative reduction potential, the reduction of NO to $NO^-$ is thermodynamically unfavorable under physiological conditions. The p$K_a$ of its conjugated acid HNO has been recently reevaluated as 11.6 [66] and therefore it exists almost exclusively as HNO at physiological pH.

The voltammograms of nitrosyl complexes in general exhibit the well known reduction wave of $MNO^+/MNO^0$ and a irreversible second wave in a more negative potential region [17,42a,46,53]. This more negative process has been tentatively attributed to the $MNO^0/MNO^-$ couple and its irreversibility may be due to a chemical reaction following the electron transfer ($NO^-$ dissociation or protonation of the coordinated $NO^-$). Indeed, DFT calculations for $[Fe(CN)_5(NO)]^{4-}$ stressed that the $MNO^-$ species is unstable consistent with the irreversibility of the $MNO^0/MNO^-$ redox process [67].

## 4. Sulfite and sulfate ligands

Sulfur(IV) species, such as $SO_2$, $HSO_3{}^-$ and $SO_3{}^{2-}$ have been quite useful as ancillary ligands in ruthenium chemistry [6a,b]. In these forms, they coordinate easily with Ru(II) and exhibit a strong *trans*-effect and *trans*-influence on the coordination sphere. In the form of $SO_2$ it is a strong π-acid and weak σ-base, and as $SO_3{}^{2-}$ they behave as moderate π-acids and good σ-bases. When coordinated to ruthenium tetraammine, these three forms above are interconvertible [6b]:

$$\begin{gathered} trans\text{-}[Ru(NH_3)_4(H_2O)(SO_2)]^{2+} + H_2O \rightleftarrows trans\text{-}[Ru(NH_3)_4(H_2O)(HSO_3)]^+ + H^+ \\ trans\text{-}[Ru(NH_3)_4(H_2O)(HSO_3)]^+ \rightleftarrows trans\text{-}[Ru(NH_3)_4(H_2O)(SO_3)] + H_2O + H^+ \end{gathered} \tag{8}$$



$$[Ru^{II}(NH_3)_4(SO_3)(H_2O)] \xrightarrow[\text{fast}]{+L,-H_2O} [Ru^{II}(NH_3)_4(SO_3)L]$$

$$[Ru^{II}(NH_3)_4(SO_3)L] \xrightarrow[\text{fast}]{+H_2O_2/H^+,-H_2O} [Ru^{III}(NH_3)_4(SO_4)\ L]^+$$

$$[Ru^{III}(NH_3)_4(SO_4)L]^+ \xrightarrow[\text{fast}]{Z_n(H_g),Eu(II)} [Ru^{II}(NH_3)_4(SO_4)L]$$

$$[Ru^{II}(NH_3)_4(SO_4)L] \xrightarrow[\text{fast}]{+H_2O,\ -SO^{=}_4} [Ru^{II}(NH_3)_4L(H_2O)]^{2+}$$

Scheme 1.

The $pK_{a(1)}$ and $pK_{a(2)}$ for *trans*-$[Ru(NH_3)_4(H_2O)(SO_2)]^{2+}$ and *trans*-$[Ru(NH_3)_4(H_2O)(HSO_3)]^+$ acids are, respectively, 2.15 and 5.05 [6,32]. The coordinated sulfite, as previously mentioned, is easily oxidized to sulfate by $H_2O_2$ and the Ru(II) to Ru(III) without alteration in the ruthenium coordination sphere. These Ru(III) complexes are quite robust in solution and in the solid state as their salts (X: $Cl^-$, $CF_3SO_3^-$, $BF_4^-$) are stable in desiccators or vials for years even in the presence of oxygen, but in the absence of light. The same is true for *trans*-$[Ru(NH_3)_4(SO_2)(Cl)]Cl$ and *trans*-$[Ru(NH_3)_4(SO_2)(H_2O)](tfms)_2$. An X-ray study of the *trans*-$[Ru(NH_3)_4(SO_4)$4-pic]Cl shows a bent S–O–Ru bond of 127.5° [63]. The data, together with spectroscopic data (EPR and UV–vis) strongly suggest an extensive σ- and π-bonding interaction between the sulfate oxygen and the Ru(III) ion. The $\lambda_{max}$ for the energy of the LMCT $L \rightarrow 4d\pi$ transition (L: $H_2O$, $SO_4^{2-}$, $Cl^-$) which occurs at 320, 326 and 348 nm for the *trans*-$[Ru(NH_3)_4$4-pic$(H_2O)]^{3+}$, *trans*-$[Ru(NH_3)_4$4-pic$(SO_4)]^+$ and *trans*-$[Ru(NH_3)_4$4-pic$(Cl)]^{2+}$ species, respectively. This sequence would suggest that the π-donor ability of $SO_4^{2-}$ in these complexes would be between the one of $H_2O$ and of $Cl^-$ [68].

The reduction of Ru(III) complex also occurs without any change in the metal center coordination sphere. However, sulfate is a very good leaving group in Ru(II) [6a,b,32,63] and therefore the complex undergoes a fast aquation (ranging from 2.6 $s^{-1}$ for 4-Cl-py to 17 $s^{-1}$ for 4-$NH_2$py) yielding the corresponding *trans*-$[Ru(NH_3)_4(L)(H_2O)]^{2+}$ aqua species.

Inspired by synthetic uses of $SO_4^{2-}$ and $SO_3^{2-}$ as ligands in cobalt chemistry Taube and Isied have developed a very useful synthetic route for ruthenium complexes [6a,b,32]. It takes advantage of the *trans*-effect of the S(IV) species ($SO_3^{2-}$, $HSO_3^-$, $SO_2$) when coordinated to Ru(II), the easy oxidation of S(IV) ligand to S(VI), the stability of the Ru(III)–S(VI) and the lability of the Ru(II)–S(VI) bonds (Scheme 1).

This procedure has also proven to be quite useful for anchoring and modeling supported complexes in functionalized silica gel [69] on organic polymers as 4-polyvinyl-pyridine [70]. A substantial volume of fine synthetic work on electron-transfer studies on homo and heteronuclear binuclear complexes, and synthesis of nitrosyl compounds [17,44] benefitted a lot from the above route [6a,12c,71].

## Acknowledgements

The authors are indebted to FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for the financial support and the José Carlos Toledo Fellowship (99/11252-1), and to Angela Pegnoraro for reading the manuscript.

## References

[1] H. Taube, Surv. Prog. Chem. 6 (1973) 1.

[2] H. Taube, Comments Inorg. Chem. 1 (1981) 17.

[3] P.C. Ford, Coordin. Chem. Rev. 5 (1970) 75.

[4] C.G. Kuehn, S.S. Isied, Prog. Inorg. Chem. 27 (1980) 1048.

[5] (a) E.A. Seddon, K.R. Seddon, The Chemistry of Ruthenium, Elsevier, Amsterdam, 1984;
(b) H. Endres, G. Wilkinson, Comprehensive Coordination Chemistry, vol. 2, Pergamon Press, Oxford, 1987.

[6] (a) S.S. Isied, H. Taube, J. Am. Chem. Soc. 95 (1973) 8198;
(b) S.S. Isied, H. Taube, Inorg. Chem. 13 (1974) 1545.

[7] R.E. Shepherd, H. Taube, Inorg. Chem. 12 (1973) 1392.

[8] P.C. Ford, D.F.P. Rudd, R. Gaunder, H. Taube, J. Am. Chem. Soc. 90 (1968) 1187.

[9] (a) C. Creutz, H. Taube, J. Am. Chem. Soc. 95 (1973) 1086;
(b) C. Creutz, Prog. Inorg. Chem. 30 (1983) 1;
(c) C. Creutz, M.D. Newton, N. Sutin, J. Photochem. Photobiol. A: Chem. 82 (1994) 47.

[10] (a) R.E. Hintze, P.C. Ford, J. Am. Chem. Soc. 97 (1975) 2664;
(b) J.A. Marchant, T. Matsubara, P.C. Ford, Inorg. Chem. 16 (1977) 2160;
(c) A.W. Zanella, P.C. Ford, Inorg. Chem. 14 (1975) 42.

[11] C.G. Kuehn, H. Taube, J. Am. Chem. Soc. 98 (1976) 689.

[12] (a) C.R. Johnson, R. Shepherd, Inorg. Chem. 22 (1983) 2439;
(b) C.R. Johnson, R. Shepherd, Inorg. Chem. 22 (1983) 1117;
(c) A.V. Kameke, G.M. Tom, H. Taube, Inorg. Chem. 17 (1978) 1790.

[13] (a) J.J. Zuckerman, in: C. Creutz, N. Sutin (Eds.), Inorganic Reactions and Methods, VCH Publishers Inc., Deerfield Beach, 1986, p. 5;
(b) G. Wilkinson (Ed.), Electron Transfer Reactions, Comprehensive Coordination Chemistry, The Synthesis, Reactions, Properties & Applications of Coordination Chemistry, Pergamon Press, London, 1987, p. 331;
(c) F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann (Eds.), Advanced Inorganic Chemistry, sixth ed., John Wiley & Sons Inc., New York, 1999;
(d) S.S. Isied (Ed.), Electron Transfer Reactions, American Chemical Society, Washington, 1997.
[14] D.W. Franco, H. Taube, Inorg. Chem. 17 (1978) 571.
[15] J.C. Nascimento Filho, J.B. Lima, B.S. Lima Netto, D.W. Franco, J. Mol. Catal. 90 (1994) 257.
[16] D.W. Franco, Coord. Chem. Rev. 119 (1992) 199.
[17] E. Tfouni, M. Krieger, B.R. McGarvey, D.W. Franco, Coord. Chem. Rev. 236 (2003) 57.
[18] R.L. Sernaglia, D.W. Franco, Inorg. Chem. 28 (1989) 3485.
[19] (a) F.R. Hartley, Chem. Soc. Rev. 2 (1973) 163;
(b) B. Fell, G. Papadogianakis, J. Mol. Catal. 66 (1991) 143.
[20] L. Chen, A.J. Poe, Inorg. Chem. 28 (1989) 3641.
[21] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[22] (a) S.E. Mazzetto, L.M.A. Plicas, E. Tfouni, D.W. Franco, Inorg. Chem. 31 (1992) 516;
(b) S.E. Mazzetto, E. Tfouni, D.W. Franco, Inorg. Chem. 35 (1996) 3509.
[23] D.W. Franco, Inorg. Chim. Acta 32 (1979) 273.
[24] L.C.G. Vasconcellos, K.S.M. Ferreira, L.M.A. Plicas, A.A. Batista, I.S. Moreira, E. Tfouni, D.W. Franco, Inorg. Chim. Acta 214 (1993) 23.
[25] J. Fernandes, Ph.D. thesis, Instituto de Química de São Carlos, 1990.
[26] N.M.S. Rezende, S.C. Martins, L.A. Marinho, J.A.V. Santos, M. Tabak, J.R. Perussi, D.W. Franco, Inorg. Chim. Acta 182 (1991) 87.
[27] S.E. Mazzetto, E. Rodrigues, D.W. Franco, Polyhedron 12 (1993) 971.
[28] (a) S.E. Mazzetto, M.T.P. Gambardella, R.H.A. Santos, L.G.F. Lopes, D.W. Franco, Polyhedron 18 (1999) 979;
(b) M.S. Galhiane, D.W. Franco, J. Coord. Chem. 13 (1984) 315.
[29] J.C. Toledo, D.W. Franco, in preparation.
[30] (a) R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley, New York, 1998, p. 71 ;
(b) W. Gerrad, H.R. Hudson, G.M. Kosolapoff, L. Maier (Eds.), Organic Phosphorus Compounds, vol. 5, Wiley-Interscience, New York, 1975, p. 21.
[31] D.W. Franco, Inorg. Chim. Acta 48 (1981) 1.
[32] (a) S.S. Isied, H. Taube, Inorg. Chem. 15 (1976) 3070;
(b) J. Sen, H. Taube, Acta Chem. Scand. A 33 (1979) 125.
[33] J.M. Rezende, D.W. Franco, Transition Met. Rev. 12 (1987) 267.
[34] (a) T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335;
(b) B.J. Coe, S.J. Glenwright, Coord. Chem. Rev. 203 (2000) 5 (and references therein).
[35] J.C. Nascimento Filho, D.W. Franco, Inorg. Chim. Acta 113 (1986) 55.
[36] J.C. Nascimento Filho, J.M. Rezende, B.S. Lima Neto, D.W. Franco, Inorg. Chim. Acta 145 (1988) 111.
[37] B.S. Lima Neto, J.C. Nascimento Filho, D.W. Franco, Polyhedron 15 (1995) 1965.
[38] B.S. Lima Neto, D.W. Franco, R.V. Eldik, J. Chem. Soc., Dalton Trans. 195 (1995) 463.
[39] S.M. Neiva, L.S. Santos, S.B. Araújo, J.C. Nascimento Filho, D.W. Franco, Can. J. Chem. 65 (1987) 372.
[40] (a) T. Allman, R.G. Goel, Can. J. Chem. 60 (1982) 716;
(b) W.A. Streuli, J. Am. Chem. Soc. 82 (1960) 5791;
(c) C.A. Streuli, Anal. Chem. 32 (1960) 985.
[41] P.A. Lay, Coord. Chem. Rev. 110 (1991) 213.
[42] (a) G.B. Richter-Addo, P. Legzdins, Metal Nytrosyls, Oxford University Press, New York, 1992 (and references therein) ;
(b) J.H. Enemark, R.D. Feltham, Chem. Rev. 13 (1974) 339 (and references therein) ;
(c) J.N. Armor, M.Z. Hoffman, Inorg. Chem. 13 (1974) 339;
(d) F. Bottomley, in: P.S. Braterman (Ed.), Reactions of Coordinated Ligands, vol. 2, Plenum Press, New York, 1989.
[43] S.I. Gorelsky, S.C. Silva, A.B.P. Lever, D.W. Franco, Inorg. Chim. Acta 300 (2000) 698.
[44] (a) S.S.S. Borges, C.V. Davanzo, E.E. Castellano, J.Z. Schpector, S.C. Silva, D.W. Franco, Inorg. Chem. 37 (1998) 2670;
(b) M.G. Gomes, C.V. Davanzo, S.C. da Silva, L.G.F. Lopes, P.S. Santos, D.W. Franco, J. Chem. Soc., Dalton Trans. (1998) 601;
(c) L.G.F. Lopes, M.G. Gomes, S.S.S. Borges, D.W. Franco, Aust. J. Chem. 51 (1998) 865;
(d) R.M. Carlos, D.R. Cardoso, E.E. Castellano, R.Z. Osti, A.J. Camargo, L.G. Macedo, D.W. Franco, J. Am. Chem. Soc. 126 (2004) 2546.
[45] (a) I.A. Bagatin, R.H.A. Santos, D.W. Franco, A. Magalhães, A.G. Ferreira, Inorg. Chim. Acta 333 (2002) 109;
(b) B.R. McGarvey, A.A. Ferro, E. Tfouni, C.W.B. Bezerra, I. Bagatin, D.W. Franco, Inorg. Chem. 39 (2000) 3577.
[46] R.W. Callahan, T.J. Meyer, Inorg. Chem. 16 (1977) 574.
[47] (a) J.H. Enemark, R.D. Felthan, Coord. Chem. Rev. 13 (1974) 339;
(b) R.D. Feltham, J.H. Enemark, Top. Stereochem. 12 (1981) 155.
[48] F. Roncaroli, M.E. Ruggiero, D.W. Franco, G.L. Estiú, J.A. Olabe, Inorg. Chem. 41 (2002) 5760.
[49] (a) J.C. Toledo, H.A.S. Silva, M. Scarpellini, V. Mori, A.J. Camargo, M. Bertotti, D.W. Franco, Eur. J. Inorg. Chem. (2004) 2879;
(b) J.C. Patterson, I.M. Lorkovic, P.C. Ford, Inorg. Chem. 42 (2003) 4902.
[50] L.G.F. Lopes, A. Wieraszko, Y. EL-Sherif, M.J. Clarke, Inorg. Chim. Acta 312 (2001) 15.
[51] H.A.S. Silva, B.R. McGarvey, R.H.A. Santos, M. Bertotti, V. Mori, D.W. Franco, Can. J. Chem. 79 (2001) 679.
[52] C.R. Brulet, S.S. Isied, H. Taube, J. Am. Chem. Soc. 95 (1973) 4758.
[53] C.W.B. Bezerra, S.C. Silva, M.T.P. Gambardella, R.H.A. Santos, E. Tfouni, D.W. Franco, Inorg. Chem. 38 (1999) 5660.
[54] W.C. Silva, E.E. Castellano, D.W. Franco, Polyhedron 23 (2004) 1063.
[55] E.C. Constable, Metals and Ligands Reactivity, Ellis Horwood Limited, Chichester, 1990, p. 33.
[56] D. Lang, L.G.F. Lopes, A.A. Ferro, L.L.G. Vascocellos, J. Davis, A. Prock, D.W. Franco, E. Tfouni, A. Wieraszko, M.J. Clarck, Inorg. Chem. 39 (2000) 2294.
[57] K.Q. Ferreira, F.G. Doro, E. Tfouni, Inorg. Chim. Acta 355 (2003) 205.
[58] G.N. Coleman, J.W. Gesler, F.A. Shirley, J.R. Kuempel Jr., Inorg. Chem. 12 (1973) 1036.
[59] J.A. Broonhead, F. Basolo, R.G. Pearson, Inorg. Chem. 3 (1964) 826.
[60] R.Z. Osti, D.W. Franco, in preparation.
[61] J.C. Toledo, D.W. Franco, in preparation.
[62] L.M.A. Plicas, D.W. Franco, Inorg. Chim. Acta 134 (1987) 265.
[63] H.A.S. Silva, B.R. McGarvey, R.H.A. Santos, M. Bertotti, V. Mori, D.W. Franco, Can. J. Chem. 79 (2001) 679.
[64] A.B.P. Lever, Comprehensive Coordination Chemistry, II, vol. 2, Elsevier Science, 2003, p. 251.
[65] J.C. Patterson, I.M. Lorkovic, P.C. Ford, Inorg. Chem. 42 (2003) 4902.
[66] M.D. Bartberger, W. Liu, E. Ford, K.M. Miranda, D. Switzer, J.M. Fukuto, P.J. Farmer, D.A. Wink, D.N. Houk, Proc. Natl. Acad. Sci. U.S.A. 99 (2002) 10958.

[67] M.C.G. Lebrero, D.A. Scherlis, G.L. Estiú, J.A. Olabe, D.A. Estrin, Inorg. Chem. 40 (2001) 4127.
[68] H.A.S. Silva, R.M. Carlos, A.J. Camargo, C.M.C. Picchi, R.H.A. Santos, B.R. McGarvey, D.W. Franco, Inorg. Chim. Acta 357 (2004) 3147.
[69] S.M.C. Neiva, J.A.V. Santos, J.C. Moreira, Y. Gushikem, H. Vargas, D.W. Franco, Langmuir 9 (1993) 2982.
[70] M.T. Hofmann, B.S. Lima Neto, A.M.G. Massabni, D.W. Franco, J. Inorg. Org. Pol. 3 (1993) 41.
[71] D.E. Richardson, H. Taube, Coord. Chem. Rev. 60 (1984) 107.