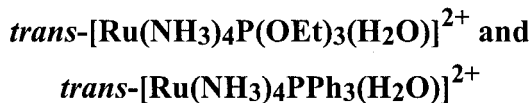


On the Reaction of Nitrite Ion with the Complex Ions



Lucidio de Sousa Santos

Departamento de Química, UNESP - Bauru, C.P. 473, 17033-360 Bauru - SP, Brazil

Sebastião Barros Araujo

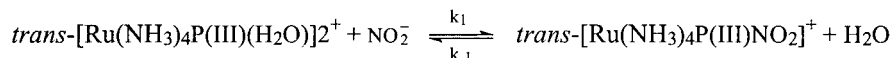
Universidade Federal do Piauí, Teresina - PI, Brazil

Douglas Wagner Franco

Instituto de Química de São Carlos - USP, C.P. 369, 13560-970 São Carlos - SP, Brazil

Received: March 16, 1994; October 27, 1994

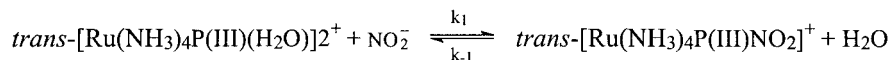
Os complexos *trans*-[Ru(NH₃)₄P(III)NO₂](PF₆), onde P(III) = P(OEt)₃, P(Ph)₃, foram isolados e caracterizados por análise elementar, voltametria cíclica, condutância molar e espectroscopias infravermelho e ultra-violeta visível. O íon complexo *trans*-[Ru(NH₃)₄P(III)NO₂]⁺ forma-se em meio aquoso de acordo com:



Os valores de k_1 e k_{-1} são $3,8 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ e $6,0 \text{ s}^{-1}$ para P(III) = P(OEt)₃ e $28 \text{ M}^{-1}\text{s}^{-1}$ e $0,02 \text{ s}^{-1}$ para P(III) = P(Ph)₃. Os parâmetros de ativação para a reação acima são: $\Delta H^\ddagger_1 = 7,5 \text{ kcal mol}^{-1}$, $\Delta H^\ddagger_{-1} = 10,7 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger_1 = -21,7 \text{ cal deg}^{-1} \text{ mol}^{-1}$ e $\Delta S^\ddagger_{-1} = -19,3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ para P(III) = P(OEt)₃.

Por acidificação as espécies nitrito são convertidas nas correspondentes espécies nitrosilos: *trans*-[Ru(NH₃)₄P(III)(NO₂)]⁺ + 2H⁺ $\xrightarrow{k_1}$ *trans*-[Ru(NH₃)₄P(III)(NO)]³⁺ + H₂O com constantes k_1 , de $5,7 \times 10$ and $3,4 \times 10 \text{ M}^{-1}\text{s}^{-1}$ para P(III) = P(Ph)₃ e P(OEt)₃, respectivamente.

The complexes *trans*-[Ru(NH₃)₄P(III)NO₂](PF₆), (P(III) = P(OEt)₃, PPh₃), have been isolated and characterized by elemental analysis, cyclic voltammetry, molar conductivity, and infrared and ultraviolet-visible spectroscopies. The complex ion *trans*-[Ru(NH₃)₄P(III)NO₂]⁺ is formed in aqueous media according to the reaction:



The k_1 and k_{-1} data are $3.8 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ and 6.0 s^{-1} for P = P(OEt)₃, and $28 \text{ M}^{-1} \text{ s}^{-1}$ and 0.02 s^{-1} for P(III) = PPh₃. The activation parameters for the reaction above are $\Delta H^\ddagger_1 = 7.5 \text{ kcal mol}^{-1}$, $\Delta H^\ddagger_{-1} = 10.7 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger_1 = -21.7 \text{ cal deg}^{-1} \text{ mol}^{-1}$, and $\Delta S^\ddagger_{-1} = -19.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for P(III) = P(OEt)₃.

Upon acidification the nitrite species are converted into the corresponding nitrosyl species: *trans*-[Ru(NH₃)₄P(III)(NO₂)]⁺ + 2H⁺ $\xrightarrow{k_1}$ *trans*-[Ru(NH₃)₄P(III)(NO)]³⁺ + H₂O at the second order specific rate constants k_1 , of 5.7×10 and $3.4 \times 10 \text{ M}^{-1}\text{s}^{-1}$ for P(III) = P(Ph)₃ and P(OEt)₃, respectively.

Keywords: ruthenium tetraammine, nitrite complexes

Introduction

A great number of examples of ruthenium nitrosyl complexes have been described in the literature¹⁻⁵, but only a few ruthenium nitrite species are reported⁶⁻⁹. Nitrite complexes are important as precursors of the corresponding nitrosyl species and relevant as potential oxygen transfer agents^{10, 11}, useful as catalysts for air oxidation of organic substrates¹⁰⁻¹².

Motivated by the stability of the Ru-P(III) bond^{13, 14}, the kinetic inertia of the equatorial amines, and the easy and reversible electron transfer in the *trans*-[Ru(NH₃)₄P(III)(H₂O)]^{3+/2+} system^{15, 16}, we are attempting to design a Ru-P(III) complex which could act as a potential redox catalyst.

The possibility of controlling the properties of the ruthenium center by changing the organic radical linked to the phosphorus atom makes these compounds very attractive from the synthetic point of view.

This paper deals with the kinetic behavior of nitrite as a substituting ligand in *trans*-[Ru(NH₃)₄P(OEt)₃(H₂O)]²⁺ and *trans*-[Ru(NH₃)₄PPh₃(H₂O)]²⁺ complex ions. Also described here is the conversion of the title complexes to the corresponding nitrosyl species in aqueous solutions.

Experimental Details

The solvents employed were distilled before use. Doubly distilled water was used throughout. All chemical reagents were analytical grade.

The synthesis of the ruthenium compounds, [Ru(NH₃)₅Cl]Cl₂, [Ru(NH₃)₅(H₂O)](PF₆)₂, *trans*-[Ru(NH₃)₄(P(OEt)₃)₂](PF₆)₂, and *trans*-[Ru(NH₃)₄P(OEt)₃(H₂O)](PF₆)₂, and [Ru(NH₃)₄P(Ph)₃(H₂O)](PF₆)₂ were performed according to literature procedures^{14, 15, 17-19}.

Preparation of *trans*-[Ru(NH₃)₄P(OEt)₃NO₂](PF₆) (I)

In 30 mL of previously degassed water 0.4 g of *trans*-[Ru(NH₃)₄P(OEt)₃H₂O](PF₆)₂ were dissolved, followed by the addition of solid NaNO₂ (2 g). After 30 min, the solution volume was reduced to 3-5 mL under vacuum. *Trans*-[Ru(NH₃)₄P(OEt)₃(NO₂)](PF₆) precipitated upon the addition of solid NH₄PF₆ (0.3 g), and was collected by filtration and washed with ethanol and ether. Yields were better than 60%. Calcd. %: C, 13.7; N, 13.3; H, 5.10; Found: C, 13.8; N, 13.0; H, 4.80.

Preparation of *trans*-[Ru(NH₃)₄P(Ph)₃(NO₂)](PF₆) (II)

The procedure was the same as described for I, except that the phosphine complex¹⁹ *trans*-[Ru(NH₃)₄P(Ph)₃(H₂O)]²⁺ was dissolved in a water-ethanol mixture (3:2). The red-brown solid was usually obtained in 60% yield. Anal. Calcd. %: C, 34.7; N, 11.2; H, 4.3. Found: C, 33.6; N, 10.8; H, 4.3.

Apparatus and Techniques

All manipulations were carried out under an argon atmosphere due to the known sensitivity of ruthenium(II) complexes to air oxidation.

The UV-VIS spectra were recorded on a HP 8451A diode array spectrophotometer. Reactions were carried out under pseudo-first-order conditions (excess of NO₂⁻ or hydrogen ion), and were monitored by following the changes in absorbance at a selected wavelength in an Aminco-Morrow stopped-flow spectrophotometer.

The observed pseudo-first-order rate constants (*k*_{obs}) were graphically determined from plots of log (*A*_∞ - *A*_{*t*}) vs. time. For the substitution reactions, the specific rate constants *k*₁ and *k*₋₁ and the equilibrium constant *K*_{eq} were calculated¹⁴ from *k*_{obs} = *k*₁ [NO₂⁻] + *k*₋₁ and *K*_{eq} = *k*₁/*k*₋₁. The *k*₁ for the nitrite → nitrosyl conversion has been calculated according to: *k*_{obs} = *k*₁ [H⁺]. Slope as drawn by eye were checked on sample plots against least squares analysis with agreement within 2%.

The conductometric measurements were performed at (25 ± 0.1) °C in nitromethane using a Micronal Conductometer B-331 and a conductometric cell with a constant equal to 0.786 cm⁻¹. Infrared spectra were obtained in KBr pellets or Nujol films using a Nicolet model 5-SXC-FT spectrophotometer.

The electrochemical measurements were performed in a PARC System Model 173 Potentiostat/Galvanostat, a model 175 Universal Programmer and a RE 0074X-Y recorder. The cell for cyclic voltammetric measurements employed carbon paste or vitreous carbon as the working electrode, platinum wire as the auxiliary, and SCE as the reference electrode. For the electrochemical and kinetic experiments the temperature was kept constant within ± 0.2 °C using a Superohm thermostat.

Results and Discussion

The UV spectra of the I and II ions exhibit absorption bands at 334 nm, ε = (1.8 ± 0.2) × 10⁴ M⁻¹ cm⁻¹ and 362 nm, ε = (2.4 ± 0.2) × 10³ M⁻¹ cm⁻¹, respectively. The molar absorptivities for these transitions are higher than those usually observed for the LF transitions in ruthenium(II) amines^{15, 20, 21}, and probably should be MLCT in character.

The infrared spectra of the *trans*-[Ru(NH₃)₄P(OEt)₃NO₂](PF₆) and *trans*-[Ru(NH₃)₄P(Ph)₃NO₂](PF₆) complexes show ν_a (NO₂) at 1470 and 1430 cm⁻¹ and ν_s (NO₂) at 1340 and 1330 cm⁻¹ for I and II, respectively. Based on the ν_(N=O) band for complexes I and II, it is likely that the bonding mode in the title complexes is nitro coordination^{6, 22}.

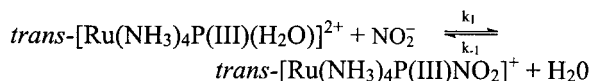
The cyclic voltammograms for complexes I and II obtained in alkaline media exhibit large anodic peak currents corresponding to more than one electron change per metal center, and the absence of the corresponding cathodic

peak. These anodic peaks for both compounds **I** and **II** appear at potentials more positive than + 0.60 V, and the E_{pa} values are dependent upon the hydrogen ion concentration of the medium. This irreversible electrochemical behavior is typical¹⁴⁻¹⁷ of phosphane complexes of ruthenium amines in alkaline media, and is currently under investigation in our laboratory.

Conductometric measurements in nitromethane for complexes **I** and **II** yield $\Lambda_M = 44.8$ and $47.8 \text{ mol}^{-1} \text{ cm}^2 \text{ ohm}^{-1}$, respectively. These Λ_M values are consistent with the 1:1 electrolyte formulation for compounds **I** and **II**, based on the conductivity data for similar ruthenium(II) amines complexes²³.

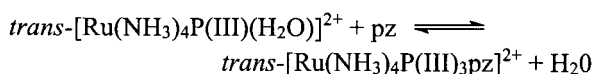
As observed in the substitution reaction of nucleophiles with $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(III)}(\text{H}_2\text{O})]^{2+}$ complexes^{14, 24}, no evidence for rate saturation has been observed in the plots of k_{obs} vs. $C_{\text{NO}_2^-}$.

The substitution reaction,



where P(III) = P(Ph)₃ and P(OEt)₃ respectively, has been studied and the results are summarized in Table 1. At 25°C, the numerical values for k_1 , k_{-1} and K_{eq} for the water substitution reactions in $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(III)}(\text{H}_2\text{O})]^{2+}$ by NO_2^- are $(38 \pm 1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $6.0 \pm 0.5 \text{ s}^{-1}$, $67 \pm 7 \text{ M}^{-1}$ and $28 \pm 1. \text{M}^{-1} \text{ s}^{-1}$, $0.02 \pm 0.01 \text{ s}^{-1}$, $1.4 \times 10^3 \text{ M}^{-1}$ for P(III) = P(OEt)₃ and P(Ph)₃, respectively.

The $E^\circ_{\text{Ru(III)/Ru(II)}}$ values for the $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(OEt)}_3(\text{H}_2\text{O})]^{3+/2+}$ and $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(Ph)}_3(\text{H}_2\text{O})]^{3+/2+}$ systems are¹⁵ respectively + 0.46 and 0.48 V vs. SCE, at 25°C. The values¹⁵ of the formation constant, K_{eq} , for the reaction,



are 20 and 29 M^{-1} for P(III) = P(OEt)₃ and P(Ph)₃, respectively.

Therefore, on the basis of the above data it is reasonable to assume that the effect of π acidity of P(Ph)₃ and P(OEt)₃ ligands over the Ru(II) center is not very different, and according to the affinities of the $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(Ph)}_3(\text{H}_2\text{O})]^{2+}$ and $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(OEt)}_3(\text{H}_2\text{O})]^{2+}$ for NO_2^- , is expected to be similar.

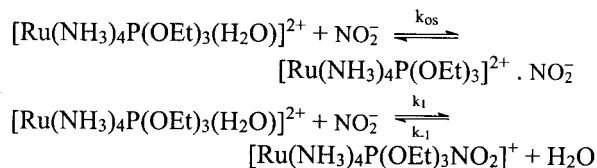
The P(Ph)₃ molecule (cone angle = 145), is more voluminous²⁵ than P(OEt)₃ (cone angle = 109) and, as observed from CPK models, a steric constraint effect is operative¹⁹ in the coordination sphere of $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(Ph)}_3(\text{H}_2\text{O})]^{2+}$ ions. However, in spite of the above arguments, the $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(Ph)}_3\text{NO}_2]^{2+}$ complex ions are found to be about 20 times more stable than the corresponding triethyl phosphite species.

In general the same species exhibit higher stability constant values in a water-ethanol medium than in pure water²⁻²⁸. However, in the $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(Ph)}_3(\text{H}_2\text{O})]^{2+} - \text{NO}_2^-$ system, despite the partial substitution of water for ethanol, the higher value of K_{eq} exhibited by the nitrite species of the phosphine complex, compared to the analogous P(OEt)₃ system, is probably due to the uncertainty in the k_{-1} value. Therefore, for the phosphine complex, the K_{eq} value of $1.4 \times 10^3 \text{ M}^{-1}$ probably would express only the upper limit for the $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(Ph)}_3(\text{H}_2\text{O})]^{2+} - \text{NO}_2^-$ association constant.

The position of NO_2^- in the series of ligands arranged¹⁵ in order of decreasing affinity for $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(OEt)}_3(\text{H}_2\text{O})]^{2+}$ is as follows: $\text{CO} \geq \text{SO}_3^- > \text{P(OEt)}_3 > \text{CN}^- > \text{imN} > \text{NO}_2^- > \text{NH}_3 > \text{L-hist.} > \text{MeimN} > \text{S}_2\text{O}_3^- > \text{L-cys} > \text{isn} > \text{fu} > 4\text{-pic} > \text{pz} > \text{gly} > \text{py} > \text{N}_3^- > \text{en} > \text{Mepyr}^+ > \text{SCN}^-$.

As observed in the substitution reactions of $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(OEt)}_3(\text{H}_2\text{O})]^{2+}$ with nucleophiles^{14, 24}, no evidence for rate saturation was observed in the plots of k_{obs} vs. $C_{\text{NO}_2^-}$ for the systems dealt with in this study. Furthermore, for L = P(OEt)₃ and $C_{\text{NO}_2^-} = 0.075 \text{ M}$, the experimental k_{obs} value exceeds by three times the observed value for the limiting rate¹⁴ for Mepyr⁺ as entering ligand in $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(OEt)}_3(\text{H}_2\text{O})]^{2+}$.

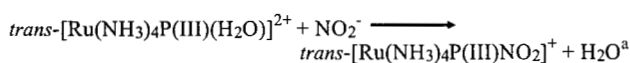
As a consequence, it seems unlikely that the above reaction could be explained by a scheme of the type:



The treatment of the experimental data in Table 1, performed according to the equations^{14, 26-28} leads to a calculated value of K_{os} equal to 0.5 and 0.3 for P(III) = P(Ph)₃ and P(OEt)₃, respectively, suggesting that the formation of the outer sphere complexes is not favorable in such systems.

The activation and equilibrium parameters for the NO_2^- substitution in $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(OEt)}_3(\text{H}_2\text{O})]^{2+}$ are shown in Tables 1 and 2. The replacement of the water ligand by NO_2^- in $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(OEt)}_3(\text{H}_2\text{O})]^{2+}$ is slightly exothermic, ($\Delta H_{\text{eq}} = 3.2 \text{ kcal mol}^{-1}$, $\Delta S_{\text{eq}} = -2.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$).

The activation parameter data calculated from the specific rate constant values of Table 1 fit very well in isokinetic plots²⁶⁻³⁰ of ΔH^\ddagger_1 vs. ΔS^\ddagger and ΔH^\ddagger_{-1} vs. ΔS^\ddagger_{-1} for a series of ligands already studied¹⁵ (Table 2). From these plots it is possible to calculate the average ΔG^\ddagger_1 values as $16 \pm 2 \text{ kcal mol}^{-1}$ for the substitution reactions of the $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P(OEt)}_3(\text{H}_2\text{O})]^{2+}$ ion. For the aquation reactions of the substituted monophosphite complexes, the calculated average ΔG^\ddagger_{-1} is $20 \pm 2 \text{ kcal mol}^{-1}$.

Table 1. Rate constants for the substitution reaction:

T (°C)	P(III)	C _{NO₂⁻} (M)	K _{obsd} × 10 ⁻¹ s ^{-1b}
5	P(OEt) ₃	0.0250	0.53
5	P(OEt) ₃	0.0500	0.84
5	P(OEt) ₃	0.0750	1.15
5	P(OEt) ₃	0.100	1.65
5	P(OEt) ₃	0.150	2.31
15	P(OEt) ₃	0.0250	1.26
15	P(OEt) ₃	0.0500	1.75
15	P(OEt) ₃	0.0750	2.66
15	P(OEt) ₃	0.100	3.30
15	P(OEt) ₃	0.125	4.05
25	P(OEt) ₃	0.0250	1.54
25	P(OEt) ₃	0.0500	2.31
25	P(OEt) ₃	0.0750	3.46
25	P(OEt) ₃	0.100	4.33
25	P(OEt) ₃	0.150	6.30
25	P(Ph) ₃	0.0250	0.070 ^c
25	P(Ph) ₃	0.0500	0.138 ^c
25	P(Ph) ₃	0.0750	0.210 ^c
25	P(Ph) ₃	0.100	0.290 ^c
25	P(Ph) ₃	0.125	0.340 ^c

^aμ = 0.3 (CF₃COOH/CF₃COONa), pH = 11, C_{Ru(II)} = 2 × 10⁻³ M.

^beach value is an average of at least three independent determinations whose agreement is better than 95%.

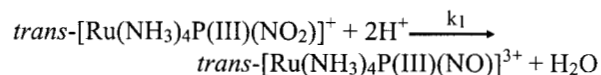
^cμ = 0.3 (CF₃COOH/CF₃COONa), pH = 11, C_{Ru(II)} = 2 × 10⁻³ M, in aqueous/ethanolic (3:2) medium.

It should be mentioned that the k₁ and k₋₁ values for electrophilic ligands have been calculated taking into account only the linear region of the plots of k_{obs} vs. C_{NO₂⁻}. These experimental points correspond to a situation in which any formation of a possible outer sphere association is negligible.

Under this condition, the electrophilic and nucleophilic ligands fit into the same straight line (Figs. 1 and 2), showing that the isokinetic plots for these systems are not very helpful in elucidating these reaction mechanisms. The plots²⁹ of log k₁ vs. log K_{eq} and log k₋₁ vs. log 1/K_{eq} are not very informative, so that in the present system the groups of nucleophilic and electrophilic ligands cannot be clearly separated in the graphs.

However, as proposed earlier^{14,15,24} for nucleophiles as entering ligands, the activated complex for the NO₂⁻ substitution in *trans*-[Ru(NH₃)₄P(OEt)₃(H₂O)]²⁺ would probably involve one metal complex and one ligand with some degree of bond making.

The electronic spectra of the nitrite species as illustrated in Fig. 3 changes as a function of the medium hydrogen ion concentration. Experiments show that the coordinate nitrite, in both nitrite complexes, can be easily converted into the corresponding nitrosyl species upon acidification, according to:



The hyperfine structure due to the HONO acid³⁰ has not been observed in the electronic spectra of the solutions containing *trans*-[Ru(NH₃)₄P(III)NO₂]⁺ complexes after their acidification. Therefore, since no free HONO has been detected³⁰ under these experimental conditions is

Table 2. Activation^a parameters for ligand substitution in *trans*-[Ru(NH₃)₄P(OEt)₃(H₂O)]²⁺.
$$\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P}(\text{OEt})_3\text{H}_2\text{O}]^{2+} + \text{L} \xrightleftharpoons[k_{-1}]{k_1} \text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P}(\text{OEt})_3\text{L}]^{2+} + \text{H}_2\text{O}$$

L	ΔH [‡] ₁ (kcal mol ⁻¹)	ΔH [‡] ₋₁ (kcal mol ⁻¹)	ΔS [‡] ₁ (cal deg ⁻¹ mol ⁻¹)	ΔS [‡] ₋₁ (cal deg ⁻¹ mol ⁻¹)
niC	14	24	-8.6	-18.2
4-cp	12.2	18.3	-16.2	-0.9
4-cpH ^b	6.5	9.1	-32.0	-25.0
NO ₂ ^{-c}	7.5	10.7	-21.7	-19.3
N ₃ ⁻	3.4	6.0	-37	-32
CS ₂ N ₃ ^{-b}	8.7	10.3	-19.4	-26.3
isn	17.5	23.5	1.7	14.6
pyr	19.5	20.8	9.4	0.4
py	8.1	15.4	-31.7	-12.7
imN	16.1	20.7	0.2	-1.7
P(OEt) ₃	—	28.2	—	15.0
CO	—	18	—	-18

^aμ = 0.10, NaCF₃COO/CF₃COOH, ΔS[‡]₁ and ΔS[‡]₋₁ calculated for T = 25 °C; ^bμ = 0.10, NaCF₃COO/CF₃COOH; ^cμ = 0.30, NaCF₃COO/CF₃COOH.

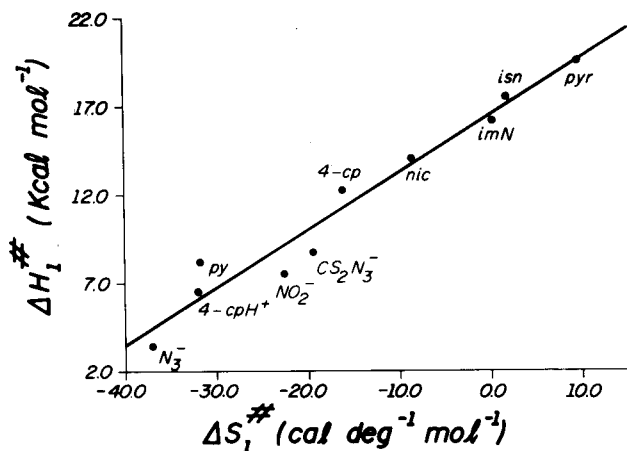


Figure 1. Isokinetic plot for the substitution reaction:

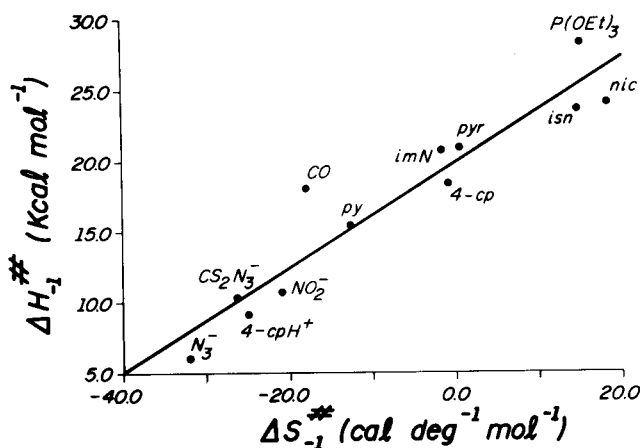
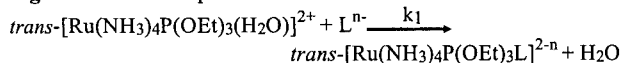


Figure 2. Isokinetic plot for the substitution reaction:

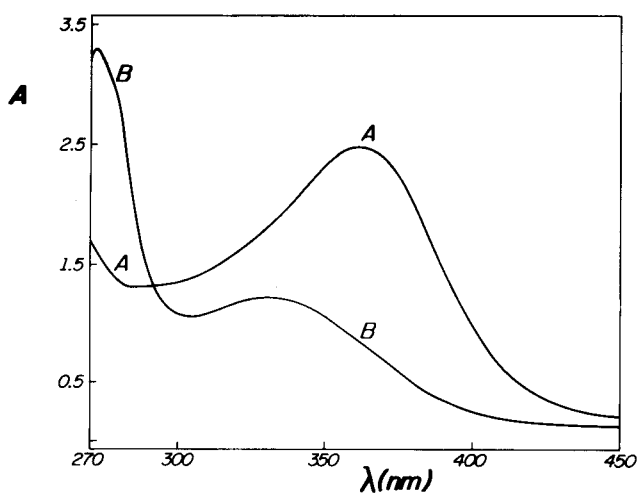
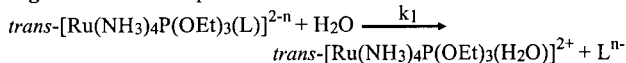


Figure 3. Electronic spectra of aqueous solution containing *trans*- $[\text{Ru}(\text{NH}_3)_4\text{P}(\text{Ph})_3\text{NO}_2](\text{PF}_6)$, ($1.0 \times 10^{-3} \text{ M}$), 25°C as a function of the pH: A, pH = 3.0; B, pH = 11.

Table 3. Kinetic data for the reaction*:

$$\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{P}(\text{III})(\text{NO}_2)]^+ + 2\text{H}^+ \xrightarrow{k_1} \text{trans-}[\text{Ru}(\text{NH}_3)_4\text{PPh}_3\text{NO}]^{3+} + \text{H}_2\text{O}$$

P(III)	$[\text{H}^+]$	$k_{\text{obsd}} (\text{s}^{-1})^{**}$	$k_1, \text{M}^{-1} \text{s}^{-1}$
P(Ph) ₃	0.0300	1.73	57.7
	0.0500	2.89	57.8
	0.100	5.77	57.7
	0.150	8.66	57.7
	0.200	1.50	57.5
	0.250	13.86	55.4
P(OEt) ₃	0.0500	1.72	34.4
	0.100	3.46	34.6
	0.150	5.13	34.2
	0.200	6.93	34.4
	0.250	8.66	34.6

* $\mu = 0.30 \text{ M}$ (CF_3COONa), 25°C ; ** each value is a mean of three independent determinations whose agreement is better than 95%.

likely to suppose that all the nitrite complexes were quantitatively converted into the corresponding nitrosyl species.

This reaction has been studied spectrophotometrically for the complexes as P(III) = P(Ph)₃ and P(OEt)₃, and the data are summarized in Table 3. The above reaction is first order on complex and on hydrogen ion concentration and has been proven to be reversible upon alkalization.

For the experimental conditions specified in Table 3, the second order specific rate constants k_1 for the nitrite-nitrosyl conversion in the title complexes are $(5.7 \pm .1) \times 10 \text{ M}^{-1} \text{ s}^{-1}$ and $(3.4 \pm .1) \times 10 \text{ M}^{-1} \text{ s}^{-1}$ for the phosphine and the phosphite complexes, respectively.

Studies of these systems are in progress in our laboratory and will be reported later.

Acknowledgments

The authors are indebted to Dr. Sebastião Claudino da Silva for helpful discussions and to FAPESP (Proc. 92/3515-3), CNPq and PRONAC-FINEP for financial support.

References

1. J.H. Enermark and D.R. Felthan, *Coord. Chem. Rev.* **13**, 339, 1974.
2. K.G. Cauton, *Coord. Chem. Rev.* **14**, 317 (1975).
3. R. Davis, *Coord. Chem. Rev.* **1**, 1 (1981).
4. K.P. Krishna, *Chem. Rev.* **51**, 69 (1983).
5. G. Wilkinson, R.D. Gillard and J.A. McCleverty, *Comprehensive Coordination Chemistry* (Pergamon Press, Oxford, 1987), vol. 2.
6. a) N.R. Davies and T.L. Mullins, *Aust. J. Chem.* **21**, 915 (1968); b) J.B. Godwin and T.J. Meyer, *Inorg. Chem.* **10**, 2150 (1971); c) S.A. Adeyemi, F.J. Miller and T.J. Meyer, *Inorg. Chem.* **11**, 994 (1972); d) J.L.

- Walsh, R.M. Bullock and T.J. Meyer, *Inorg. Chem.* **19**, 865 (1980); e) F.W. Pipes and T.J. Meyer, *Inorg. Chem.* **23**, 2466 (1984).
7. H. Nagao, M. Mukaida, K. Shimizu, F.S. Howell and H. Kakihana, *Inorg. Chem.* **25**, 4312 (1986).
8. A.K. Deb, P.C. Paul and S. Coswami, *J. Chem. Soc. Dalton Trans.* 2052 (1988).
9. R.A. Leising and K.J. Takeuchi, *J. Am. Chem. Soc.* **110**, 4079 (1988).
10. D.A. Muccigrosso, F. Mares, S.E. Diamond and J.P. Solar, *Inorg. Chem.* **22**, 960 (1983), and references therein.
11. M.A. Andrews and K.P. Kelly, *J. Am. Chem. Soc.* **103**, 2894, (1981).
12. N.G. Jackson, M.L. Randall, A.M. Sargenson and W. Marty, *Inorg. Chem.* **22**, 1013 (1983).
13. H.L.K. Wah, M. Potel, F. Tomi, F. Agbossou, D. Ballivet-Tkatchenko and F. Urso, *Inorg. Chim. Acta* **205**, 113 (1993), and references therein.
14. D.W. Franco and H. Taube, *Inorg. Chem.* **17**, 571 (1978).
- 15 a) D.W. Franco, *Coord. Chem. Rev.* **119**, 199 (1992);
b) abbreviations: imN: imidazol N bounded, MeimN: methylimidazol N bounded; L-hist: L-histidine; L-cys: L-cystine; pyr: pyrazine; gly: glycine; py: pyridine; fu: furane; 4-pic: 4-picoline; Mepz⁺: Methylpyrazinium.
16. J.A.V. Santos, S.C. Martins, L.A. Marinho, M. Tabak, J.R. Perussi and D.W. Franco, *Inorg. Chim. Acta* **182**, 87 (1991).
17. S.E. Mazzetto, E. Rodrigues and D.W. Franco, *Polyhedron* **12**, 971 (1993).
18. S.S. Isied and H. Taube, *Inorg. Chem.* **13**, 1545 (1974).
19. J.M. Rezende and D.W. Franco, *Trans. Met. Chem.* **12**, 267 (1987).
20. H. Taube, *Comments Inorg. Chem.* **17**, 1 (1981), and references therein.
21. A.B.P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 2nd ed., 1984), p. 24.
22. E.E. Mercer, W.A. McAllester and J.R. Durig, *Inorg. Chem.* **11**, 1881 (1966).
23. L.M.A. Plicas and D.W. Franco, *Inorg. Chim. Acta* **134**, 265 (1987).
24. L.S. Santos, S.M.C. Neiva, S.B. Araujo, J.C. Nascimento Filho and D.W. Franco, *Can. J. Chem.* **65**, 372 (1987).
25. C.A. Tolman, *Chem. Rev.* **77**, 313 (1977).
26. R.G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes* (VCH, Publishers, Weinheim, 2nd ed., 1991).
27. R.B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems* (Oxford University Press, New York, 1991).
28. D. Katakis and G. Gordon, *Mechanisms of Inorganic Reactions* (John Willey & Sons, New York, 1987).
29. J.R. Chipperfield, *Advances in Linear Free Energy Relationship* (N.B. Chapman and J. Shorter Eds., Plenum Press, London, 1972), p. 321, and references therein.
30. M.G. Gomes, S.S.S. Borges, L.G.F. Lopes and D.W. Franco, *Anal. Chim. Acta* **282**, 81 (1993).