

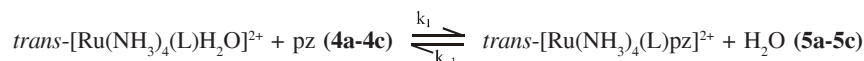
Synthesis and Characterization of New Ammine Ru(II) Complexes Containing P(*m*-tol)₃, P(*p*-CH₃)₃ and P(OC₅H₁₁)₃

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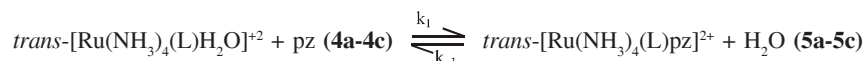
As reações diretas entre [Ru(NH₃)₅(H₂O)](PF₆)₂ (**1**) e P(*m*-tol)₃ (**a**), P(*p*-tol)₃ (**b**) e P(OC₅H₁₁)₃ (**c**) forneceram os complexos [Ru(NH₃)₅P(*m*-tol)₃](PF₆)₂ (**2a**), *trans*-[Ru(NH₃)₄{P(*p*-tol)₃}₂](PF₆)₂ (**3b**) e *trans*-[Ru(NH₃)₄{P(OC₅H₁₁)₃}₂](PF₆)₂ (**3c**), respectivamente. A constante de velocidade específica de substituição da amônia em (**2a**) foi de 4,3 x 10⁻³ s⁻¹ (25 °C, μ = 0,10 mol L⁻¹). Os aquo complexos *trans*-[Ru(NH₃)₄(L)(H₂O)]²⁺ (L = P(*p*-tol)₃, **4b**; L = P(OC₅H₁₁)₃, **4c**) foram gerados pela aquação térmica de uma das moléculas de L, dos respectivos complexos *trans*-[Ru(NH₃)₄L₂]²⁺ (L = P(*p*-tol)₃, **3b**; L = P(OC₅H₁₁)₃, **3c**) e os valores das constantes foram: k₁ = 2,7 x 10⁻³ s⁻¹ e k₋₁ = 3,5 x 10⁻³ s⁻¹, respectivamente. Os valores dos potenciais formais de redução para **3b**, **3c** e **2a** foram 0,50 ± 0,01 V; 0,48 ± 0,01 V e 0,50 ± 0,02 V, respectivamente (vs SCE) [μ = 0,10 mol L⁻¹; NaCF₃COO; C_{H+} = 1,0 x 10⁻³ CF₃COOH]. As reações:



foram estudadas e os valores de k₁, k₋₁ e K_{eq} foram 0,28 mol⁻¹ L s⁻¹, 0,06 s⁻¹, 4,67 mol⁻¹ L [para L = P(*m*-tol)₃, **4a**]; 0,25 mol⁻¹ L s⁻¹, 0,04 s⁻¹, 6,25 mol⁻¹ L [para L = P(*p*-tol)₃, **4b**] e 12,4 mol⁻¹ L s⁻¹, 5,8 x 10⁻¹ s⁻¹, 21 mol⁻¹ L [para L = P(OC₅H₁₁)₃, **4c**] [25°C; μ = 0,10 mol L⁻¹; NaCF₃COO; C_{H+} = 1,0 x 10⁻³ CF₃COOH].

Direct reactions between [Ru(NH₃)₅(H₂O)](PF₆)₂ (**1**) and P(*m*-tol)₃ (**a**), P(*p*-tol)₃ (**b**) and P(OC₅H₁₁)₃ (**c**) lead the complexes [Ru(NH₃)₅P(*m*-tol)₃](PF₆)₂ (**2a**), *trans*-[Ru(NH₃)₄{P(*p*-tol)₃}₂](PF₆)₂ (**3b**) and *trans*-[Ru(NH₃)₄{P(OC₅H₁₁)₃}₂](PF₆)₂ (**3c**) respectively. These complexes have been isolated as hexafluorophosphate salts and characterized by elemental analysis, cyclic voltammetry and UV-VIS spectra measurements. One ammonia ligand in **2a** is displaced at the a specific rate of 4.3 x 10⁻³ s⁻¹ (25 °C, μ = 0.10 mol L⁻¹). The aquo species *trans*-[Ru(NH₃)₄(L)H₂O]²⁺ (L = P(*p*-tol)₃, **4b**; L = P(OC₅H₁₁)₃, **4c**) are generated by the substitution of one L ligand with H₂O, from *trans*-[Ru(NH₃)₄L₂]²⁺ with k₁ = 2.7 x 10⁻³ s⁻¹ [L = P(*p*-tol)₃, **3b**] and 3.5 x 10⁻³ s⁻¹ [L = P(OC₅H₁₁)₃, **3c**] (25 °C, μ = 0.10 mol L⁻¹) (NaCF₃COO/CF₃COOH; C_{H+} = 1.0 x 10⁻³ mol L⁻¹). The formal reduction potentials for the species **3b**, **3c** and **2a** are 0.50 ± 0.01 V, 0.48 ± 0.01 V and 0.50 ± 0.02 V, respectively (vs SCE) [μ = 0.10 mol L⁻¹; NaCF₃COO; C_{H+} = 1.0 x 10⁻³ CF₃COOH].

The following reactions:



[L = P(*m*-tol)₃, P(*p*-tol)₃ and P(OC₅H₁₁)₃] were studied and the calculated values for k₁, k₋₁ and K_{eq} are 0.28 mol⁻¹ L s⁻¹, 0.06 s⁻¹, 4.67 mol⁻¹ L [L = P(*m*-tol)₃, **4a**]; 0.25 mol⁻¹ L s⁻¹, 0.04 s⁻¹, 6.25 mol⁻¹ L [L = P(*p*-tol)₃, **4b**]; 12.4 mol⁻¹ L s⁻¹, 5.8x10⁻¹ s⁻¹, and 21 mol⁻¹ L [L = P(OC₅H₁₁)₃, **4c**], [25.0 ± 0.2 °C; m = 0.10 mol L⁻¹; NaCF₃COO; C_{H+} = 1.0 x 10⁻³ CF₃COOH].

Keywords: ruthenium(II), ammine complexes, phosphine and phosphite ligands

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Introduction

Phosphorus compounds are important ancillary ligands in the art of tailoring catalysts. Their presence in the metal coordination sphere can introduce significant changes in the kinetic and thermodynamic properties of metal complexes containing these ligands.

The chemistry of phosphine and phosphite complexes of Ru(II) and Ru(III) tetraammines has received considerable attention,¹⁻¹¹ efforts being directed to the understanding of the trans effect and trans influence of these ligands in the thermal¹⁻¹¹ and photochemical¹²⁻¹⁷ reactivities of the ruthenium center the complex itself. According to the accumulated data,¹⁻¹¹ for small phosphines and phosphites effect and trans influence are dictated mainly by electronic effects.¹

In this work, the attention was focused on the reactions with the following bulky phosphorus ligands $L = P(m\text{-tol})_3$ ($\theta=170^\circ$), $P(p\text{-tol})_3$ ($\theta=145^\circ$) and $P(OC_5H_{11})_3$ ($\theta=170^\circ$). The basicity of these ligands does not change substantially from one another as do their sizes and therefore the influence of these ligands on the properties of $[Ru(NH_3)_4(L)(H_2O)]^{2+}$ complex ions would be primarily due to steric rather than electronic effects.

Experimental

Chemicals and reagents

The solvents employed were freshly distilled before use. Doubly distilled water was used throughout. All chemicals were of analytical grade purity. The syntheses of the ruthenium compounds, $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_5(H_2O)](PF_6)_2$ followed the procedures already described.^{18,19} Ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) was the starting material for the synthesis of the ruthenium complexes.

Apparatus and techniques

All manipulations were performed under argon due to the known sensitivity of Ru(II) complexes to air oxidation. The complexes were stored under vacuum and protected from light. Their purity was checked by means of elemental analysis, cyclic voltammetry and spectrophotometric measurements. Elemental analyses were performed by the staff of the Microanalytical Laboratory of Instituto de Química-USP.

The UV-VIS spectra were recorded on a HP 8451A-diode array spectrophotometer with 1.0 cm quartz cells at room temperature. Kinetic studies were carried out under

pseudo-first-order conditions and were monitored by following the changes in absorbance at a selected wavelength.

Cyclic voltammetric measurements were performed in a multifunctional PARC system consisting of a model 175 Universal Programmer a model 173 potentiostat-galvanostat, a model 379 digital coulometer, a model 376 voltage-current converter and a model Re 0074 X-Y recorder.

For cyclic voltammetric measurements a glassy carbon electrode, platinum wire and SCE were used as the working, auxiliary and reference electrodes, respectively. Formal reduction potentials for a number of substituted ruthenium ammine complexes were evaluated by cyclic voltammetry. The $E_{1/2}$ values were taken as the average of the anodic and cathodic peak potentials.

Electrochemical reversibility was judged by (a) comparing the ratio of the peak current for the cathodic process relative to the peak current for the anodic process^{20,21} and (b) comparing under the same conditions the peak to peak separation with that of *trans*- $[Ru(NH_3)_4P(OC_2H_5)_3H_2O]^{2+}$ known to be reversible.¹

The electrochemical process in acidic solution is reversible in the sense that the oxidation and reduction wave currents are equal.²⁰⁻²¹ The peak to peak separation, 60 ± 5 mV, is of the same magnitude observed for others ammine Ru(II) complexes systems¹ which are also known to be reversible.

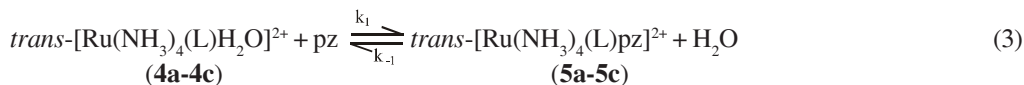
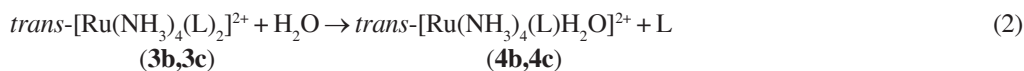
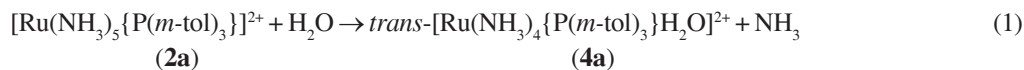
Kinetic measurements

The reaction shown in equation 1 was monitored both by potentiometric (pH) and spectrophotometric ($\lambda_{max} = 380$ nm) measurements.

In the case of the complexes containing two L ligands, equation 2, the substitution reactions were followed spectrophotometrically at $\lambda_{max} = 374$ nm for $L = P(p\text{-tol})_3$ (**3b**) and $\lambda_{max} = 300$ nm for $L = P(OC_5H_{11})_3$ (**3c**). To avoid the back reaction, the complex concentration was kept around 5.0×10^{-5} mol L⁻¹.

The reactions of *trans*- $[Ru(NH_3)_4(L)(H_2O)](PF_6)_2$ ($L = P(m\text{-tol})_3$, **4a**; $P(p\text{-tol})_3$, **4b**; $P(OC_5H_{11})_3$, **4c**) shown in equation 3 were studied under pseudo-first-order conditions with excess pyrazine.

Known volumes of deaerated solutions of pyrazine with pH and ionic strength previously adjusted were prepared in a flask under argon. The solution was transferred rapidly through Teflon tubing by gas pressure to a sealed spectrophotometric cell sealed containing a constant and known volume of deaerated solutions of **4a**, **4b** or **4c**.



The formation of *trans*-[Ru(NH₃)₄(L)pz](PF₆)₂ (L = P(*m*-tol)₃, **5a**; P(*p*-tol)₃, **5b**; P(OC₅H₁₁)₃, **5c**) was monitored following the changes in absorbance at 402 nm, 400 nm and 390 nm for **4a**, **4b** and **4c** respectively. Pyrazine was chosen as auxiliary ligand because the complexes **5a**, **5b** and **5c** exhibit an intense metal-to-ligand charge transfer band (MLCT) in the visible region of the spectra and also because the ligand is very soluble in water and is very good π acceptor. Furthermore there is an extensive volume of data on the trans effect and trans influence of phosphines and phosphates using pyrazine as substituting ligand and *trans*-[Ru(NH₃)₄(L)H₂O]²⁺ type compounds as model.¹⁻¹¹

The observed pseudo-first-order rate constants (*k*_{obs}) were determined graphically from plots of log (*A*_∞ - *A*_t) versus time (where *A*_∞ and *A*_t are the final absorbance value and that at time *t*, respectively). The plots were linear for at least three half-lives. For the substitution reactions, the specific rate constants *k*₁ and *k*₋₁ were determined and the equilibrium constants *K*_{eq} were calculated using the equation *k*_{obs} = *k*₁[pz] + *k*₋₁.

Preparation of the new complexes

trans-[Ru(NH₃)₄{P(*p*-tol)₃}₂](PF₆)₂ (**3b**)

In 100 mL of previously degassed acetone, P(*p*-tol)₃ (0.46 g, 1.5 mmol) was dissolved. After 30 min stirring 0.2 g (0.4 mmol) of recently prepared [Ru(NH₃)₅H₂O](PF₆)₂ (**1**) were added. The solution was stirred for 3 h at room temperature, under argon and in the absence of light. The solution volume was then reduced to 10 mL under vacuum and the complex was precipitated upon the addition of 50 mL of degassed ether (peroxide free). The solid was collected by filtration, washed with ether and dried, producing a yield on the order of 50%. Elemental analysis: Found: C, 47.01; H, 4.90; N, 5.32; Calc. For C₄₂H₅₄N₄P₄F₁₂Ru₁: C, 47.24; H, 5.10; N, 5.25%.

[Ru(NH₃)₅{P(*m*-tol)₃}]₂(PF₆)₂ (**2a**)

The procedure was the same as described for (**3b**). Yield 50%. The composition was confirmed by the analytical

results (Found: C, 31.80; H, 4.60; N, 8.80; Calc. For C₂₁H₃₆N₅P₃F₁₂Ru₁: C, 32.31; H, 4.65; N, 8.97%). The reaction of [Ru(NH₃)₅H₂O](PF₆)₂ with P(*m*-tol)₃ leads to the formation of **2a**. Ammonia trans to P(*m*-tol)₃ is easily aquated, leading to *trans*-[Ru(NH₃)₄{P(*m*-tol)₃}H₂O]²⁺ (**4a**) in 90% yield.

trans-[Ru(NH₃)₄{P(OC₅H₁₁)₃}₂](PF₆)₂ (**3c**)

The procedure was the same as described for (**3b**), except that the phosphite complex **3c** was precipitated by adding a mixture of ethanol-ether (1:2) and produced in approximately 25% yield. Elemental analysis: Found: C, 34.30; H, 8.00; N, 5.60; Calc. For C₃₀H₇₈N₄O₆P₄F₁₂Ru₁: C, 34.52; H, 7.53; N, 5.37%.

Results and Discussion

The product from the reaction of [Ru(NH₃)₅(H₂O)](PF₆)₂ and P(*m*-tol)₃ was isolated in the form of the pentaammine complex, *trans*-[Ru(NH₃)₅{P(*m*-tol)₃}]₂(PF₆)₂, (**2a**). The *trans* complexes containing P(*p*-tol)₃ and P(OC₅H₁₁)₃ were obtained as tetraammine species *trans*-[Ru(NH₃)₄L₂](PF₆)₂, L = P(*p*-tol)₃, **3b**; P(OC₅H₁₁)₃, **3c**. Compounds **3b** and **3c** exhibit a fast L substitution, to form *trans*-[Ru(NH₃)₄(L)H₂O](PF₆)₂, L = P(*p*-tol)₃, **4b**; P(OC₅H₁₁)₃, **4c**. Complex **2a** generates *trans*-[Ru(NH₃)₄{P(*m*-tol)₃}H₂O](PF₆)₂, **4a**, through a fast trans NH₃ ligand substitution.

For **3b** and **3c** the measured rate constants *k*₋₁, for the trans L aquation, are 3.5 × 10⁻³ s⁻¹ and 2.7 × 10⁻³ s⁻¹ respectively. For **2a** the rate constant for ammonia dissociation is 4.3 × 10⁻³ s⁻¹, and is independent of [H⁺] concentration in the 10⁻¹-10⁻⁵ mol L⁻¹ range. In acidic solution, the free phosphite ligand hydrolyzes and the product of the hydrolyses has no affinity²²⁻²⁵ for **4c**.

In aqueous solutions, the UV spectra of **4a**, **4b** and **4c** exhibit absorption bands at λ = 370 nm (ε = 7.9 × 10² mol L⁻¹ cm⁻¹), λ = 300 nm (ε = 10 × 10² mol L⁻¹ cm⁻¹) and λ = 380 nm (ε = 8.2 × 10² mol L⁻¹ cm⁻¹), respectively. The molar absorptivities for these transitions are in the range of those usually observed for the LF (ligand field) transitions in ruthenium(II) ammines.^{1,26-28} Therefore these bands have been attributed to the symmetry and spin allowed

$^1A_1 \rightarrow ^1E(1)$ transition, considering the C_{4v} microsymmetry in spite of the phosphane ligands, Figure 1.

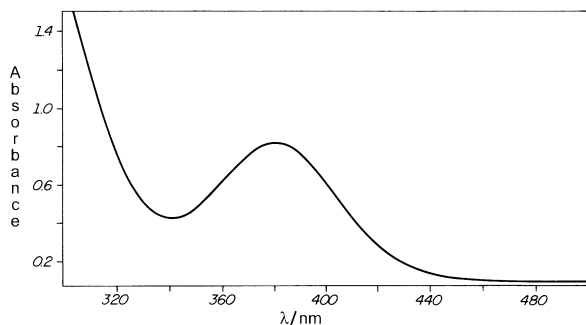


Figure 1. Electronic absorption spectrum of *trans*-[Ru(NH₃)₄{P(*m*-tol)₃}(H₂O)](PF₆)₂, (**4a**) in CF₃COOH; 1.0 × 10⁻³ mol L⁻¹; μ = 0.10 mol L⁻¹; NaCF₃COO; 25 °C.

The colorless aqueous solutions containing the aquo species **4a-4c** rapidly turn pale yellow upon addition of pyrazine. This color is due to the MLCT band, observed in the visible region of the spectrum, 402 nm ($\epsilon = 4.8 \times 10^3 \text{ mol L}^{-1} \text{ cm}^{-1}$), 400 nm ($\epsilon = 5.2 \times 10^3 \text{ mol L}^{-1} \text{ cm}^{-1}$) and 390 nm ($\epsilon = 7.3 \times 10^3 \text{ mol L}^{-1} \text{ cm}^{-1}$) for the P(*m*-tol)₃, (**5a**); P(*p*-tol)₃, (**5b**) and P(OC₅H₁₁)₃ (**5c**) pyrazine complexes, respectively.

The cyclic voltammograms show single, well defined waves for the Ru(III)/Ru(II) couple for all complexes, displaying reversible behavior at sweep rates between 20–200 mV s⁻¹, see Figure 2. The formal reduction potential for the Ru(III)/Ru(II) couple of the **4a**, **4b** and **4c** ions are, respectively, 0.50 ± 0.01V; 0.48 ± 0.01V and 0.50 ± 0.02V (*vs* SCE), [25 °C; μ = 0.10 mol L⁻¹; NaCF₃COO; C_H⁺ = 1.0 × 10⁻³ CF₃COOH]. The small variation in the formal reduction potential data is expected since the electronic properties of these ligands are quite similar.^{1,8,10}

The lability of the coordinated water molecule in **4a-4c** was assessed by measuring the rate at which it is substituted by pyrazine. The plots of k_{obs} as a function of [pz] lead to calculated values of 0.28 mol⁻¹ L s⁻¹, 0.06 s⁻¹, 4.67 mol⁻¹ L for k_1 , k_{-1} and K_{eq} respectively (25.0 ± 0.2 °C) when L = (**4a**); 0.25 mol⁻¹ L s⁻¹, 0.04 s⁻¹, 6.25 mol⁻¹ L = (**4b**) and 12.4 mol⁻¹ L s⁻¹, 5.8 × 10⁻¹ s⁻¹, 21 mol⁻¹ L = (**4c**).

The plots of k_{obs} versus [pz] for the substitution of the water molecule in complexes **4a-4c** have been studied using a number of different phosphines and phosphates L¹⁻¹¹ and exhibit different profiles according to the nature of the entering ligand L. For the complexes reported herein the

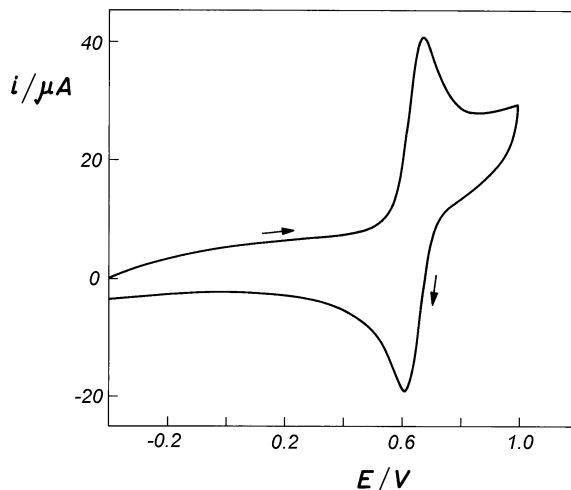


Figure 2. Cyclic voltammogram of *trans*-[Ru(NH₃)₄{P(*m*-tol)₃}(H₂O)](PF₆)₂, (**4a**) in CF₃COOH; 1.0 × 10⁻³ mol L⁻¹; μ = 0.10 mol L⁻¹; NaCF₃COO; 25 °C; scan rate = 200 mV s⁻¹.

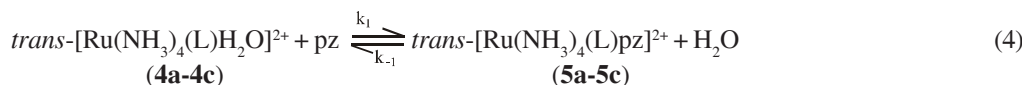
plots of k_{obs} versus [pz], were linear until [pz] < 0.10 mol L⁻¹. However if [pz] > 0.10 mol L⁻¹, the rates become independent of the substituting ligand concentration.

The *trans* effect and *trans* influence of phosphane ligands L have been evaluated¹⁻¹¹ using the kinetic parameters k_1 , k_{-1} and K_{eq} for the reaction shown in equation 4.

Based on this approach, the specific rate constant k_1 , at which the water molecule is substituted by pz, (related to ΔG^\ddagger_1), is proposed as an indicator of the relative *trans* effect of L.¹ The K_{eq} , (related to ΔG_{eq}), was proposed as a relative measure of the *trans* influence of L.¹

According to this approach, the positions of the P(*m*-tol)₃, P(*p*-tol)₃ and P(OC₅H₁₁)₃ ligands in the series of increasing *trans* effect are as follows: P(OPh)₃ ≅ ETPB < P(*p*-tol)₃ ≅ P(*m*-tol)₃ < PTA < P(OC₂H₄Cl)₃ ≤ PPh₃ < dppe ≅ H₂Pcy < P(OMe)₃ < P(OEt)₃ < DMPP < P(^tBu)₃ ≅ P(OⁱPr)₃ < P(OⁿBu)₃ < P(OC₅H₁₁)₃ < P(OH)(OEt)₂ ≅ P(OH)₃ < P(ⁿBu)₃ < P(Et)₃ < P(OH)₂O⁻ < P(OEt)₂O⁻; and the increasing *trans* influence series can be written as: P(Et)₃ ≅ DMPP ≅ H₂Pcy ≅ P(ⁿBu)₃ < P(OEt)₂O⁻ ≅ P(OH)₂O⁻ < dppe < PPh₃ ≅ P(OⁿBu)₃ < P(^tBu)₃ ≅ P(OC₅H₁₁)₃ ≅ P(OⁱPr)₃ ≅ P(OEt)₃ < P(OH)₃ ≅ P(OH)(OEt)₂ < P(OMe)₃ < PTA < P(OC₂H₄Cl)₃ ≅ ETPB < P(*p*-tol)₃ < P(*m*-tol)₃ < P(OPh)₃.

Figure 3 shows the plot of log k_1 versus $E_{\text{Ru(III)/Ru(II)}}^0$ for the *trans*-[Ru(NH₃)₄(L)H₂O]^{3+/2+} species, which displayed a good linear fit. In this figure the trend can be interpreted in the following way: the more positive the $E_{\text{Ru(III)/Ru(II)}}^0$, the more stable is the complex containing the Ru(II) metal



center in comparison with Ru(III) and the slower will be the rate of the water substitution by pz, since the electronic stabilization of the Ru is basically due to the Ru(II)→L back bonding intensity.^{1,2,26,29-31} It is reasonable to assume for the series that the strongest back bonding interaction occurs when L = P(OPh)₃ and the weakest, when L = P(OH)₂O⁻. The plot still exhibits a linear tendency after the inclusion of the new ligands.

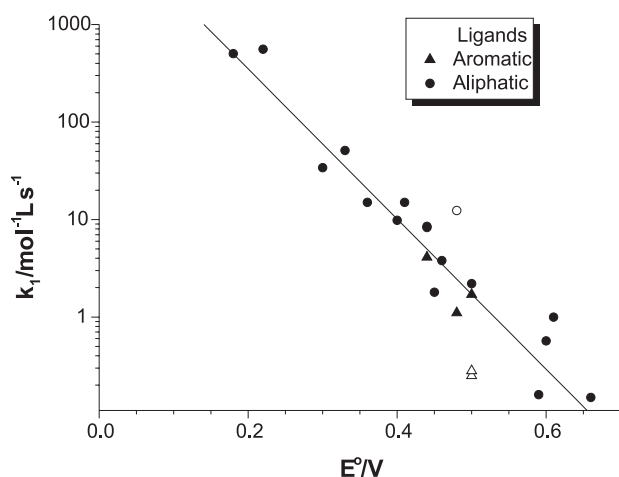
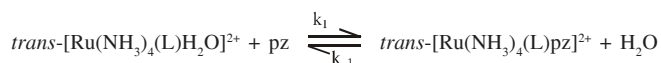


Figure 3. Plot of k_1 versus $E_{\text{Ru(III)/Ru(II)}^\circ}$ the $\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{L})(\text{H}_2\text{O})]^{2+}$ complex ions: (Δ) P(*m*-tol)₃ (**4a**) and P(*p*-tol)₃ (**4b**); (\bullet) P(OC₅H₁₁)₃ (**4c**). The k_1 and E° values of were obtained from Table 1.

Table 1. Electrochemical and kinetic data^(a) for the reaction:



L	$E_{\text{Ru(III)/Ru(II)}^\circ}$	k_{-1} (s ⁻¹)	k_1 (mol ⁻¹ L s ⁻¹)	$1/K_{\text{eq}}$ (mol L ⁻¹)
P(OPh) ₃	0.66	4.2×10^{-2}	0.15	2.8×10^{-1}
PTA	0.60	4.1×10^{-2}	0.57	7.2×10^{-2}
ETPB	0.59	1.9×10^{-2}	0.16	1.2×10^{-1}
P(<i>p</i> -tol) ₃ ^b	0.50	0.4×10^{-1}	0.25	1.6×10^{-1}
P(<i>m</i> -tol) ₃ ^b	0.50	0.6×10^{-1}	0.28	2.1×10^{-1}
P(OC ₂ H ₄ Cl) ₃	0.61	1.1×10^{-1}	1.0	1.1×10^{-1}
PPh ₃	0.48	3.7×10^{-2}	1.1	3.4×10^{-2}
Dppe	0.50	5.3×10^{-2}	1.7	3.1×10^{-2}
H ₂ PCy	0.45	2.5×10^{-2}	1.8	1.4×10^{-2}
P(OMe) ₃	0.50	1.4×10^{-1}	2.2	6.2×10^{-2}
P(OEt) ₃	0.46	1.9×10^{-1}	3.8	4.9×10^{-2}
DMPP	0.44	4.9×10^{-2}	4.1	1.2×10^{-2}
P(OBu ^t) ₃	0.44	4.0×10^{-1}	8.3	4.8×10^{-2}
P(OPr ⁱ) ₃	0.44	4.1×10^{-1}	8.5	4.8×10^{-2}
P(OBu ⁿ) ₃	0.40	3.3×10^{-1}	9.8	3.4×10^{-2}
P(OC ₅ H ₁₁) ₃ ^b	0.48	5.8×10^{-1}	12.4	4.6×10^{-2}
P(OH)(OEt) ₂	0.36	8.4×10^{-1}	15.0	5.6×10^{-2}
P(OH) ₃	0.41	7.9×10^{-1}	15.0	5.3×10^{-2}
P(Bu ⁿ) ₃	0.30	5.1×10^{-1}	34.0	1.5×10^{-2}
PEt ₃	0.33	4.6×10^{-1}	51.0	0.9×10^{-2}
P(OH) ₂ O ⁻	0.18	1.1×10^{-1}	502.0	2.2×10^{-2}

(a) $\mu = 0.10$ mol L⁻¹ (NaCF₃COO/CF₃COOH); 25.0 ± 0.2 °C; (b) this work

These data, except for L = P(*m*-tol)₃, P(*p*-tol)₃ and P(OC₅H₁₁)₃ were taken from reference 2

Abbreviations: dppe = bis(1,2-diphenylphosphino)ethane; DMPP = 1-phenyl-3,4-dimethylphosphole; ETPB = 4-ethyl-2,6,7-trioxo-1-phospha(III)-bicyclo-[2,2,2]octane; PTA=1,3,5-triazo-7-phosphoadamantane.

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