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Selective Photolabilization in *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ Complexes ($P(III) = P(OR)_3$, $P(R)_3$)

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Irradiation in the LF bands $^1A_1 \rightarrow {}^1E(1)$ and $^1A_{1g} \rightarrow {}^1A_{2g}$, ^1E_g leads to NH_3 photolabilization of *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ complexes and to NH_3 and P(III) photolabilization of *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ species. For both series of complexes Φ_{NH_3} has essentially the same experimental value of 0.34 ± 0.03 mol/einstein. The $\Phi_{P(III)}$ values for the bis(phosphane) complexes *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ are in the 0.034−0.070 range for $P(III) = P(OCH_3)_3$ and $P(OC_2H_4Cl)_3$. No clear relationship could be established between the cone angle θ of the phosphane or the formal potential $E^{\circ\prime}{}_{Ru(III)/Ru(II)}$ and the corresponding Φ_{NH_3} and $\Phi_{P(III)}$ data for the complexes studied. The NH_3 ligand is selectively photolabilized when the *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ and the *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ species are irradiated with energies corresponding to the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_1 \rightarrow {}^1A_2$ transitions.

Introduction

Most photochemical work concerning ruthenium complexes is related to charge transfer absorptions.[1−10] The ligand field bands (LF) in ruthenium complexes with unsaturated ligands are usually obscured by the more intense charge transfer bands and therefore are less accessible for photosubstitution studies.[1−10] In studies of ruthenium complexes having only saturated ligands,[7−11] photoredox reactions occur from higher energy charge transfer from the complex to the solvent (CTTS) states.[12,13] In some instances, CTTS and LF states are close in energy and both photoredox and photosubstitution can therefore be observed.[12,13] However, photooxidation has also been observed at high energies for $[Ru(NH_3)_5py]^{2+}$ and $[Ru(NH_3)_5CH_3CN]^{2+}$ species.[12−14]

The electronic spectra in solution of the *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ complexes, P(III) = $P(OR)_3$, $P(R)_3$, exhibit well-defined[15,16] ligand field bands (LF), without the interference of intraligand (IL) or metal-to-ligand charge transfer (MLCT) absorption.

Although inert with respect to substitution reactions, owing to the strong Ru(II)→P(III) back-bonding[15−19] interaction in such complexes, the Ru(II) center is also quite resistant to oxidation, making the internal conversion from LF states to CTTS states more difficult. Therefore, this class of compounds offers a unique opportunity to study the ligand field excited state photochemistry without complications due to redox or secondary thermal reactions.

An additional incentive to undertake this work is the versatility of the phosphanes (phosphites and phosphines) with respect to their σ-donor and π-acceptor properties and steric hindrance, which can be controlled by changing the substituents on the phosphane ligand. This paper describes in extensive photoreactivity study of the Ru(II) center in a controlled environment, with particular emphasis on the role of steric and electronic effects.

Experimental Section

Chemicals and Reagents. Ether, ethanol, and acetone were distilled under reduced pressure before use. All other materials were reagent grade and were used without further purification. Ruthenium trichloride

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($RuCl_3 \cdot 3H_2O$) was the starting material for the synthesis of the ruthenium complexes. Doubly distilled water was used throughout this work.

Syntheses. $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_5H_2O](PF_6)_2$, and *trans*-$[Ru(NH_3)_4(P(OR)_3)_2](PF_6)_2$ ($R = CH_3$, C_2H_5, ${}^iC_3H_7$, C_4H_9, ${}^tC_4H_9$, C_2H_4Cl, $C_6H_{12}N_3$) were synthesized and characterized according to literature procedures.[15−19] *trans*-$[Ru(NH_3)_4(P(III))H_2O](PF_6)_2$ were generated in solution from the corresponding *trans*-$[Ru(NH_3)_4(P(III))_2])PF_6)_2$ salt by dissolving a known amount of the solid in 1.0×10^{-3} M trifluoroacetic acid solution.

trans-$[Ru(NH_3)_5P(C_6H_4\text{-}m\text{-}CH_3)_3](PF_6)_2$ and *trans*-$[Ru(NH_3)_4(P(C_6H_4\text{-}p\text{-}CH_3)_3)_2](PF_6)_2$ were synthesized by the following procedure: A 0.5 g sample of ligand was dissolved in 150 mL of dry deaerated acetone under continuous argon bubbling, in the dark. After 20 min, 200 mg of $[Ru(NH_3)_5H_2O](PF_6)_2$ was added, and after 4 h of reaction, the excess solvent was eliminated by rotoevaporation. A precipitate formed upon addition of 100 mL of ether and was collected under inert atmosphere, washed with copious quantities of ether, dried, and stored in a vacuum desiccator in the absence of light. The yields were 40% and 60%, respectively. Anal. Calc for *trans*-$[Ru(NH_3)_5P(C_6H_4\text{-}m\text{-}CH_3)_3](PF_6)_2$: C, 32.32; N, 8.97; H, 4.65. Found: C, 31.81; N, 8.78; H, 4.59. Found for *trans*-$[Ru(NH_3)_4(P(C_6H_4\text{-}p\text{-}CH_3)_3)_2](PF_6)_2$: C, 31.93; N, 8.88; H, 4.61. The aquo species *trans*-$[Ru(NH_3)_4P(C_6H_4\text{-}m\text{-}CH_3)_3H_2O](PF_6)_2$ and *trans*-$[Ru(NH_3)_4P(C_6H_4\text{-}p\text{-}CH_3)_3H_2O](PF_6)_2$ were generated in solution from aquation of the corresponding species $[Ru(NH_3)_5P(C_6H_4\text{-}m\text{-}CH_3)_3](PF_6)_2$ and *trans*-$[Ru(NH_3)_4(P(C_6H_4\text{-}p\text{-}CH_3)_3)_2](PF_6)_2$.

trans-$[Ru(NH_3)_4P(OC_5H_{11})_3H_2O](PF_6)_2$ was obtained dissolving 0.5 g of the ligand $P(OC_5H_{11})_3$ in 80 mL of previously deaerated acetone. After 20 min, 200 mg of $[Ru(NH_3)_5H_2O](PF_6)_2$ was added to the solution with continuous argon bubbling in the dark. After 3 h, 20 mL of neopentyl alcohol was added for precipitation. After 24 h, the precipitate was collected and washed with ether, dried, and stored in a vacuum desiccator in the absence of light. Yield: better than 60%. Anal. Calc: C, 24.39; N, 7.59; H, 6.42. Found: C, 23.24; N, 7.36; H, 6.25. All the complexes were characterized by UV−visible spectroscopy and cyclic voltammetry.

Spectra. Electronic spectra were recorded at room temperature using quartz cells. Spectral deconvolution was performed using the Gaussian deconvolution routine of the HP 8451-A system software. The EPR spectra were recorded at liquid nitrogen temperature, using a Bruker ESP 300E spectrometer.

Cyclic Voltammetry. The cyclic voltammograms of the complexes were taken with a Model 170 PARC electrochemical system consisting of a Model 175 Universal programmer, a Model 173 potentiostat−galvanostat, a Model 376 voltage−current conversor, and a Model Re 0074 X-Y recorder. The electrochemical cells were of the three-electrode type with a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode; the working electrode was a glassy-carbon electrode.

Photolysis Procedures. Irradiations at 313, 330, 370, and 390 nm were carried out by using an Osram 200 W Hg−xenon lamp in an Oriel Model 6292 Universal arc lamp source with an Oriel interference filter for monochromatization (≈10 nm band-pass), an infrared filter, and a thermostated cell holder. Photolysis reactions were carried out in aqueous trifluoroacetic acid solutions containing 1.0×10^{-3} to 1.5×10^{-3} M of the desired Ru complex. Ferrioxalate actinometry was used for light intensity measurements.[9,10] Solutions for photolysis and dark reactions were prepared and deaerated with purified argon in a Zwickel flask and transferred to 1.0 cm path length quartz cuvettes ($V = 4.0$ mL). During photolysis, the solution was continuously stirred by a small magnetic bar in the cell. All photolyses were carried out at 25.0 ± 0.1 °C. Corrections were made for thermal reactions during photolysis by using a dark unirradiated sample prepared in a manner similar to that for the photolyzed sample. For spectroscopic quantum yield determinations, the samples subjected to photolysis were periodically monitored by recording the UV−vis spectra. Digital Micronal B375 and Analion PM600 pH meters were employed to evaluate pH changes as the result of photolysis.

Photolysis conversions did not exceed 10% for phosphite photoaquation and 20% for ammonia photoaquation. Quantum yields were calculated by plotting quantum yields versus percent reaction and extrapolating back to 0%. Reported quantum yields are the average of at least three independent determinations.

Table 1. Spectral Characteristics, $E°'_{Ru(III)/Ru(II)}$, and Rates of Aquation for Ruthenium(II) Ammine Complexes[19] in Aqueous Solution (CF_3COOH, 1.0×10^{-3} M)[a]

trans-$[Ru(NH_3)_4LY]^{2+}$					
L	Y	λ_{max}, nm	10^2, M^{-1} cm^{-1}	$E°'$, V vs ECS	$k_{-P(OR)_3}$, $s^{-1} \times 10^5$
$P(OCH_3)_3$	H_2O	317	5.7	0.50	
		392	0.29[e]		
$P(OC_2H_5)_3$	H_2O	316	6.4	0.50	
		390	0.30[e]		
$P(O^iC_3H_7)_3$	H_2O	316	5.6	0.48	
$P(OC_4H_9)_3$	H_2O	315	6.4	0.44	
		388	0.32[e]		
$P(O^tC_4H_9)_3$	H_2O	316	5.5	0.48	
$P(OC_2H_4Cl)_3$	H_2O	313	6.3	0.61	
		387	0.15[e]		
$P(C_6H_{12}N_3)$	H_2O	329	3.4	0.59	
		379	0.32[e]		
$P(C_6H_4\text{-}m\text{-}CH_3)_3$	H_2O[f]	380	8.2	0.50	
$P(C_6H_4\text{-}p\text{-}CH_3)_3$	H_2O[f]	370	7.9	0.50	
$P(OC_6H_5)_3$	H_2O	316	7.8	0.66	
$P(OC_5H_{11})_3$	H_2O[f]	298	10.5	0.49	
$P(OCH_3)_3$	$P(OCH_3)_3$	262	5.1	0.68	2.40
		294	3.5		
		360	0.45[e]		
$P(OC_2H_5)_3$	$P(OC_2H_5)_3$	260	4.3	0.65	2.20
		297	2.6		
		359	0.44[e]		
$P(O^iC_3H_7)_3$	$P(O^iC_3H_7)_3$	262	4.8	0.63	8.40
		294	3.1		
$P(OC_4H_9)_3$	$P(OC_4H_9)_3$	262	4.1	0.64	1.90[b]
		294	2.3		
$P(O^tC_4H_9)_3$	$P(O^tC_4H_9)_3$	262	4.1	0.60	1.30[c]
		294	2.3		
$P(OC_2H_4Cl)_3$	$P(OC_2H_4Cl)_3$	226	36	0.96[d]	4.50
		264	4.7		
		294	3.7		

[a] Uncertainties: $\lambda_{max} \pm 2$ nm; $\epsilon \pm 10\%$; $E°' \pm 0.02$ V; $C_{H^+} = 10^{-2}-10^{-4}$; 25.0 ± 0.2 °C. [b] Ethanol/water, 1:1; $C_{Ru} = 1.0 \times 10^{-5}$ M. [c] Ethanol/water, 1:1; $C_{Ru} = 1$ mM. [d] Calculated on the basis of E_{pa}. [e] Obtained through deconvolution technique. [f] This work.

Photoaquation of Ammonia. Since electronic spectra of *trans*-$[Ru(NH_3)_3(P(OR)_3)_2H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ should be very similar and since the use of an ancillary ligand to substitute the equatorial NH_3 ligand is precluded by the sluggishness of this thermal reaction, we decided to quantify the NH_3 produced from pH measurements at pH ≅ 4.0. The pH changes were used to evaluate the release of ammonia from the Ru(II) coordination sphere. After photolysis, the pH values of the dark and irradiated solutions were determined. The quantum yields were calculated from differences in the hydrogen ion concentration of these solutions.

Photoaquation of P(III). These reactions were followed by measuring the aquo complex *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ formed upon photolysis. The aquo complex was evaluated from spectrophotometric measurements of the complex ion *trans*-$[Ru(NH_3)_4(P(III))(pz)]^{2+}$.[15,19] The pyrazine derivative ($\lambda_{max} = 352-370$ nm interval, $\epsilon = (31-57) \times 10^2$ M^{-1} cm^{-1}) was generated by adding a weighed amount of pyrazine to the photolyzed Ru(II) complex solutions. Initial pH values of the solutions for P(III) quantum yield measurements were adjusted to ≅2.0 and ≅3.0.

Results and Discussion

In aqueous solution, *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ undergoes thermal aquation, yielding the *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ complex ions, eq 1 (see Table 1). The half-lives for these reactions in acidic media ($C_{H^+} > 10^{-4}$ M), where the free

$$H_2O + trans\text{-}[Ru(NH_3)_4(P(OR)_3)]^{2+} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4P(OR)_3H_2O]^{2+} + P(OR)_3 \quad (1)$$

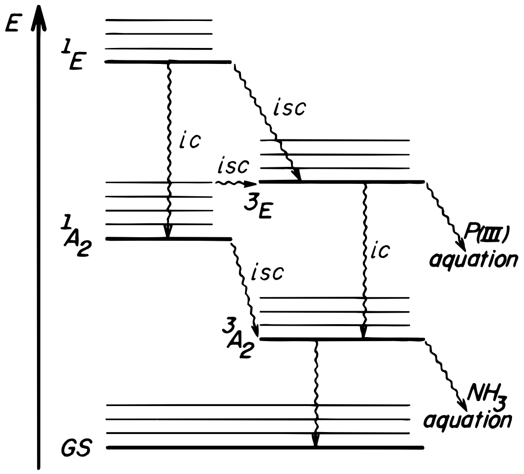

Figure 1. Qualitative Jablonski diagram for *trans*-$[Ru(NH_3)_4(P(III))]^{2+}$ and $[Ru(NH_3)_4(P(III))(H_2O)]^{2+}$ type complexes.

phosphite ligand is quickly hydrolyzed, are on the scale of hours[17−19] (see Table 1). The hydrolysis of the free phosphite is acid catalyzed[15−21] and therefore does not produce any change in the solution hydrogen ion concentration.

In the complexes studied, phosphanes lead to a thermal labilization of the trans position and a delabilization[15−20,22] of the cis positions occupied by the ammonia ligands. These systems show a thermal back-reaction at pH ≥ 4.0. At $C_{H^+} > 10^{-3.5}$ M, the phosphite quickly hydrolyzes to phosphonate:[15−19,21]

$$H_2O + P(OR)_3 \rightarrow P(OH)(OR)_2 + ROH \qquad (2)$$

The phosphonate and the phosphite, in equilibrium in solution, are not able[15−19,22,23] to coordinate to the *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ species.

$$P(OH)(OR)_2 \Leftrightarrow P(O)(H)(OR)_2 \qquad (3)$$

Therefore, the solutions employed to measure phosphite photoaquation were adjusted to $C_{H^+} \geq 10^{-3}$ M to avoid the thermal back-reaction of phosphite. As judged from the electronic and voltammetric spectra, in acidic solutions ($C_{H^+} > 10^{-4}$ M) protected from light, the *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ complex ions do not exhibit any evidence of decomposition on a time scale of weeks.[15−19,22,23]

Regarding the phosphines, the aquated P(III) ligand lives sufficiently long to possibly recombine with the *trans*-$[Ru(NH_3)_4PR_3(H_2O)]^{2+}$ species formed.[16] However, since $C_{P(III)} < 10^{-5}$ M, under our experimental conditions, the recombination reaction has been neglected on the time scale of the experiments. Table 1 also summarizes the voltammetric and electronic characteristics of the complex ions dealt with in this work, and Figure 1 illustrates the general electronic spectral features of these species.

The voltammetric curves for *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ in aqueous solutions exhibit, in each case, only an electrochemically reversible[15−20,23] one-electron process. For the bis(phosphane) species, the $E^{\circ\prime}_{Ru(III)/Ru(II)}$ values are usually in the range 0.63−0.96 V, whereas for the mono(phosphane) complex ions, the redox formal potentials are in the 0.44−0.66 V interval. Therefore, as judged from the $E^{\circ\prime}_{Ru(III)/Ru(II)}$ data (see Table 1), both classes of compounds are not very air sensitive.

For the phosphane complexes $E^{\circ\prime}_{Ru(III)/Ru(II)}$ is at least 0.5 V more positive than those for the hexaammine (−0.17 V) and aquo pentaammine (−0.18 V) species.[23] As a consequence, and in analogy with the behavior of the acetonitrile complexes,[14] the charge transfers from the complex to the solvent bands (CTTS) for the *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ species are expected[14] to occur at energies higher than 35.7 × 10^3 cm^{-1} (280 nm) and out of the energy range of the irradiation used in the present study.

The electronic spectra of solutions containing *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ species are quite different.[19] For *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ complex ions, two absorptions can be easily identified[15,19] around $\lambda = 260-264$ nm and $\lambda = 294-297$ nm, which, according the to expected values for a d^6 low-spin ion of D_{4h} symmetry, have been initially attributed[16,17] to $^1A_{1g} \rightarrow {}^1B_{2g}$, ^1E_g and $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{2g}$ LF transitions, respectively (Table 1). A more careful analysis of the electronic spectra, using deconvolution techniques, allows the identification of a weak band around 360 nm ($\epsilon \cong 45$ M^{-1} cm^{-1}). Considering P(III) to be a strong-field ligand, the higher energy band (294−297 nm) should be assigned to an $^1A_{1g} \rightarrow {}^1E_g$ transition, corresponding to an $xz, yz \rightarrow z^2$ electronic promotion. The lower energy band (359 nm) would be a $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, corresponding to an $xy \rightarrow x^2 - y^2$ promotion.

For the C_{4v} *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ complex ions, the observed[16] absorption in the range $\lambda = 298-380$ nm (see Table 1) has been attributed[16,17] to the symmetry and spin-allowed $^1A_1 \rightarrow {}^1E(1)$ LF transition. Again, a more detailed analysis of the electronic spectra, using deconvolution procedures, allows identification of a weak absorption at $\lambda = 379-392$ nm ($\epsilon = 15-32$ M^{-1} cm^{-1}). In these cases, H_2O replaces a $P(OR)_3$ of higher LF strength. Using the same reasoning as in the D_{4h} cases, the higher energy band can be assigned to an $^1A_1 \rightarrow {}^1E$ transition (an $xz, yz \rightarrow z^2$ promotion) and the lower energy band to an $^1A_1 \rightarrow {}^1A_2$ transition, (an $xy \rightarrow x^2 - y^2$ promotion).

Usually, the $^1A_1 \rightarrow {}^1A_2$ transition is reported to be obscured[24−26] by the stronger $^1A_1 \rightarrow {}^1E(1)$ transition at higher energy. The existence of a lower energy weak band ($^1A_1 \rightarrow {}^1A_2$) in d^6 low-spin systems with C_{4v} symmetry has been described[24] for other d^6 low-spin complexes containing ligands with O, N, S, and P donor atoms.

The possibility of these low-energy bands being assigned to spin-forbidden transitions must also be considered. Since the low-energy bands for both series of complexes reported here (D_{4h} and C_{4v}) are associated with an $xy \rightarrow x^2 - y^2$ excitation and the equatorial ligands for all the cases are NH_3, their energies are expected to be nearly the same. However, the $^1A_1 \rightarrow {}^1A_2$ transitions for the C_{4v} species lies at energies lower than the observed $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions for the D_{4h} complexes. Therefore, considering the observed low molar absorptivities and the spin−orbit coupling effects in the case of ruthenium complexes, it is conceivable that an alternative assignment for the low-energy bands of both series of complexes can be made attributing them to the spin-forbidden transitions $^1A_1 \rightarrow {}^3A_2$ and $^1A_{1g} \rightarrow {}^3A_{2g}$. However, this last assignment has same inconsistencies. If the weak band is assigned to the spin-forbidden transitions, the absorptions at 313 and 297 nm must to be credited to the $^1A_1 \rightarrow {}^2A_1$ and $^1A_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively. Nevertheless the molar absorptivities for these transitions are too high for these symmetry-forbidden transi-

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tions.[25,26] Furthermore, we observed recently in our laboratory that the luminescence of $TbCl_3$, at 545 nm, is suppressed by the compounds dealt with in this work.

The possible photosubstitution reactions for these complexes are depicted in eq 4. Reaction 4 occurs both thermally and

$$\textit{trans}\text{-}[Ru(NH_3)_4(P(III))L]^{2+} + H_2O \xrightarrow[LF]{h\nu} \textit{trans}\text{-}[Ru(NH_3)_4(P(III))(H_2O)]^{2+} + L \quad (4)$$

photochemically for L + P(III); the reactions for L = H_2O were not investigated. Reaction 5 does not occur thermally[15−20] on

$$\textit{trans}\text{-}[Ru(NH_3)_4(P(III))L]^{2+} + H_2O \xrightarrow[LF]{h\nu} [Ru(NH_3)_3(H_2O)(P(III))L]^{2+} + NH_3 \quad (5)$$

the time scale of the experiments but occurs photochemically for all the complexes studied. Reaction 6 is not observed either

$$\textit{trans}\text{-}[Ru(NH_3)_4(P(III))L]^{2+} + H_2O \xrightarrow[LF]{h\nu} \textit{trans}\text{-}[Ru(NH_3)_4(H_2O)L]^{2+} + P(III) \quad (6)$$

thermally or photochemically for L = H_2O but is observed for L = P(III).

The observed photoreactions are all photosubstitutions and are consistent with transitions involving depopulation of a Ru(II) orbital of t_{2g} parentage and population of a σ^* orbital of e_g parentage, leading to an excited state with a $t_{2g}5e_g{}^1$ electronic configuration capable of undergoing substitution reactions.

Photolysis of *trans*-[Ru(NH$_3$)$_4$(P(III))$_2$]$^{2+}$. Table 2 summarizes the quantum yield data for the photoaquation reactions studied for these complexes.

Continuous photolysis of acidic solutions (ph ≅ 4.0) with monochromatic light leads to the photoaquation of NH_3 and $P(OR)_3$. Upon $P(OR)_3$ aquation, the *trans*-$[Ru(NH_3)_4P(OR)_3H_2O)]^{2+}$ species, which absorbs in the $\lambda = 313-317$ nm interval (see Table 1), will be formed.

The characteristic absorptions[27] of the *trans*-$[Ru(NH_3)_4P(OR)_3H_2O]^{3+}$ (for R = Et, $\lambda_{max} = 285$ nm, $\epsilon = 8.1 \times 10^2$ M^{-1}) and *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{3+}$ species[28] (for R = Et, $\lambda_{max} = 292$ nm, $\epsilon = 5.9 \times 10^2$ M^{-1} cm^{-1}) are absent in the electronic spectra of the photolyzed solutions. Furthermore, photolyzed solutions of *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ are EPR silent. Therefore, it is reasonable to conclude, as expected on the basis of the electrochemical data, that no photooxidation reactions take place during the photolysis process.

The photochemically or thermally formed *trans*-$[Ru(NH_3)_4P(OR)_3H_2O)]^{2+}$ by itself does not affect the solution hydrogen ion concentration. The acid *trans*-$[Ru(NH_3)_4P(OR)_3H_2O]^{2+}$ has a pK_a higher[15,18,19] than 10^{10}, and the phosphite−phosphonate equilibrium does not involve[15,18,21] proton release or uptake. Furthermore,[19] these thermal and photochemical aquation reactions are partially suppressed by the phosphane back-coordination if the reaction is carried out at $C_{H^+} < 10^{-4}$ M (for $P(OR)_3 = P(OEt)_3$, $k_{-1} = 75$ M^{-1} s^{-1}, $K_{eq} = 3.3 \times 10^4$ M^{-1}). Therefore, the pH changes at $C_{H^+} \leq 10^{-4}$ M are determined only by the photolyzed NH_3 ligand.

Table 2. Quantum Yields for Photoaquation Reactions of Ruthenium(II) Tetraammine Complexes

trans-$[Ru(NH_3)_4LY]^{2+}$		θ,[a] deg	λ_{irr},[d] nm	Φ_{NH_3}, mol/einstein	$\Phi_{P(OR)_3}$, mol/einstein
L	Y				
$P(OCH_3)_3$	$P(OCH_3)_3$	107	313	0.30 ± 0.02	0.034 ± 0.002
			370	0.32 ± 0.04[c]	$<10^{-3}$
$P(OC_2H_5)_3$	$P(OC_2H_5)_3$[c]	109	313	0.30 ± 0.02	0.040 ± 0.003
			370	0.27 ± 0.04[c]	$<10^{-3}$
$P(O^iC_3H_7)_3$	$P(O^iC_3H_7)_3$	130	313	0.31 ± 0.02	0.044 ± 0.003
$P(OC_4H_9)_3$	$P(OC_4H_9)_3$	112	313	0.35 ± 0.03	0.060 ± 0.003
$P(O^tC_4H_9)_3$	$P(O^tC_4H_9)_3$	172	313	0.34 ± 0.03	0.067 ± 0.004
$P(OC_2H_4Cl)^3$	$P(OC_2H_4Cl)_3$	110	313	0.33 ± 0.02	0.070 ± 0.003
$P(OC_2H_5)_3$	CO[c]	109	313	0.27 ± 0.03	
$P(OCH_3)_3$	H_2O	107	313	0.36 ± 0.03	
			390	0.34 ± 0.05	
$P(OC_2H_5)_3$	H_2O	109	313	0.34 ± 0.06	
			390	0.30 ± 0.04	
$P(O^iC_3H_7)_3$	H_2O	130	313	0.35 ± 0.02	
$P(OC_4H_9)_3$	H_2O	112	313	0.36 ± 0.04	
			390	0.32 ± 0.06	
$P(O^tC_4H_9)_3$	H_2O	172	313	0.36 ± 0.03	
$P(OC_2H_4Cl)_3$	H_2O	110	313	0.36 ± 0.02	
$P(OC_6H_5)_3$	H_2O	128	313	0.36 ± 0.03	
$P(C_6H_{12}N_3)$[b]	H_2O	102	330	0.32 ± 0.04	
			370	0.30 ± 0.05	
$P(C_6H_4\text{-}m\text{-}CH_3)_3$	H_2O	170	330	0.40 ± 0.03	
			370	0.40 ± 0.03	
$P(C_6H_4\text{-}p\text{-}CH_3)_3$	H_2O	145	330	0.36 ± 0.04	
			370	0.36 ± 0.04	
$P(OC_5H_{11})_3$	H_2O	170	313	0.35 ± 0.02	

[a] Cone angle; ref 30. [b] Reference 20. [c] Reference 31; the previous value of $\Phi_{P(OEt)_3} = 0.12$ was misreported. [d] 313 nm for $^1A_{1g} \rightarrow {}^1E_g(1)$ transition; 370 nm for $^1A_{1g} \rightarrow {}^1A_{2g}$ transition.

Photolysis of *trans*-[Ru(NH$_3$)$_4$(P(III))H$_2$O]$^{2+}$. Table 2 shows the quantum yields for the photoaquation reactions of this complex. Continuous photolysis with monochromatic light of aqueous solutions results in ammonia photoaquation (eq 5). The experimental results indicate that no photooxidation of the Ru(II) complex occurred during photolysis. Under the experimental conditions, phosphane photoaquation was not observed and water photoexchange was not investigated. The exchange of the water ligand with the solvent was spectrally undetectable and the thermal lability of the water ligand, due to the high trans effect and trans influence of P(III) ligands, precluded isotopic labeling studies.

Reaction 6, corresponding to phosphite photoaquation, would generate *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$, which absorbs[29] at $\lambda = 277$ nm ($\epsilon = 499$ M^{-1} cm^{-1}) and is electroactive at −0.14 V (vs SCE). The photolyzed solutions of *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ do not show any detectable absorbance increase at 277 nm or any electrochemical process attributable to the *trans*-$[Ru(NH_3)_4(H_2O)_2]^{3+/2+}$ couple. Furthermore, the addition of excess isonicotinamide (isn, 0.50 M) ligand to the photolyzed solution did not produce any absorption at $\lambda = 474$ nm ($\epsilon \approx 10^4$ M^{-1} cm^{-1}) indicative[29] of the presence of *trans*-$[Ru(NH_3)_4(isn)_2]^{2+}$, which would be formed under these conditions. Reaction 5 was accordingly the only photoreaction observed by spectrophotometric, potentiometric, and differential pulse polarographic measurements in the photolyzed solutions.

Quantum Yields. All complexes studied in this work display essentially the same quantum yield values for ammonia photoaquation. This is the main measured reaction for these

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complexes. An attempt to correlate the photochemical behaviors of *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ and *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ complex ions has been carried out by selecting phosphane ligands that present significant differences in steric and electronic effects.

No clear correaltion could be established between θ (phosphane cone angle) and Φ_{NH_3} for the *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ complex ions. Neither could a trend be observed by comparing $E^{\circ\prime}_{Ru(III)/Ru(II)}$ for such species and their respective $\Phi_{P(III)}$.

Similar results were obtained for the *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$ complex ions. High-θ ligands inhibit thermal bis complex formation, leading only to *trans*-$[Ru(NH_3)_4(P(III))H_2O]^{2+}$. However, the observed similarity of the Φ values for ligands with quite different θ values suggests that steric effects can be neglected in these photosubstitution reactions.

Considering the Ru(II)−P(III) bond to be coincident with the *z* axis, ammonia photolabilization must have arisen in all cases from labilization on the *x* and/or *y* axes, whereas phosphite photoaquation must have arisen from labilization on the *z* axis.

For C_{4v} *trans*-$[Ru(NH_3)_4(P(III))(H_2O)]^{+}$ complexes, no phosphite photolabilization was observed, and since water photoexchange was not investigated for these complexes, the experimental quantum yield results for the photochemical process could not be explained by population of the d_{z^2} orbital alone, since NH_3 photolabilization was also observed. Continuous photolysis of these complexes shows essentially the same ammonia photoaquation quantum yields (Table 2).

Taking into account the fact that NH_3 photolabilization occurs for all complexes and that it comes from labilization on the *x* and/or *y* axes, then the electronic configuration of the LEES should have a contribution from the $d_{x^2-y^2}$ orbital.

Examination of Table 2 shows a striking feature for the *trans*-$[Ru(NH_3)_4(P(III))_2]^{2+}$ species. Whereas Φ_{NH_3} is irradiation wavelength independent, P(III) photolabilization is not. It is noteworthy, that the $P(OMe)_3$ and $P(OEt)_3$ complexes show P(III) photolabilization when irradiated with light of 313 nm but exclusive NH_3 photoaquation when $\lambda_{irr} = 370$ nm.

The $\Phi_{P(III)}$ wavelength dependence has some interesting implications. The absence of P(III) labilization upon irradiation at 370 nm implies that, in this case, the z^2 orbital is not contributing to the LEES. The observed labilization of P(III) with light of 313 nm should then arise from reactions of upper energy excited states competitive with other deactivation pathways.

Taking these features into account, the observed quantum yields can be explained on the basis of the following reasoning. Initial excitation to a $^1A_2$ state is followed by efficient intersystem crossing to a $^3A_2$, LEES, since NH_3 is exclusively photoaquated. Irradiation with light of 313 nm is followed by intersystem crossing to lower energy excited states, the lowest of which is $^3A_2$. The P(III) labilization should arise from a ^3E state lying between ^1E and $^3A_2$. Since irradiation at 370 nm does not lead to P(III) labilization, the ^3E state which leads to P(III) labilization should lie above or near $^1A_2$ as illustrated in Figure 2.

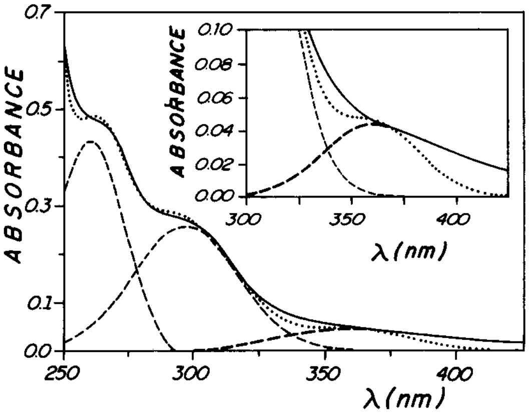

Figure 2. Electronic spectra in aqueous solution (CF_3COOH, 1.0 × 10^{-3} M) of the *trans*-$[Ru(NH_3)_4(P(OC_2H_5)_3)_2]^{2+}$ complex (—) and the result of deconvolution (- - -) for this complex.

Taken together, our results suggest that equatorial ligands could be selectively photoaquated through the appropriate choice of experimental conditions. With appropriate wavelength selection, it could be possible, through deactivation, to populate only the excited triplet state of lowest energy and consequently achieve the desired effect of selective ligand photosubstitution.

As far as we know, this work describes the first example of selective ligand photolabilization[1−11] in Ru(II) complexes. The synthesis of species involving ligand substitution in the equatorial position, laborious because of the inertia of the thermal reaction, could possibly be achieved through photosubstitution reactions. Experiments in this direction are underway in our laboratory and will be reported later.

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