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Photochemical Behavior of *trans*-$[Ru(NH_3)_4P(OEt)_3L]^{2+}$ Complex Ions (L = $P(OEt)_3$, CO, H_2O)

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trans-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$, *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$, and *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ were photolyzed with light of 313 nm on the lowest energy ligand field excited state. Photoaquation of the thermally substitution inert ammonia is observed for all three complexes with $\phi \cong 0.30$ mol/einstein. *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ undergoes $P(OEt)_3$ photoaquation with $\phi \cong 0.12$ mol/einstein, while *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ displays CO photoaquation with $\phi = 0.07$ mol/einstein. The results suggest that the electronic configuration of the lowest energy excited state of these complexes have contributions from E and A_2 states. Furthermore, in *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ the photoaquation of CO is explained by depopulation of a bonding $d\pi$ orbital and population of a σ^* orbital.

Introduction

The photoaquation of ruthenium(II) and rhodium(III) ammines has been subject of several studies.[1-3] These isoelectronic systems have d^6 low-spin electronic configuration and are kinetically inert with respect to thermal ligand substitution.

Phosphite molecules, when coordinated to Ru(II), strongly labilize the ligand on the trans position and delabilize the cis ligands.[4-6] Phosphite is a good π-acceptor and a moderate σ-donor ligand whereas CO is a good π-acceptor and a weak σ-donor ligand. In addition, both have LF strengths higher than NH_3 or H_2O.

The photosubstitution behavior of the ruthenium(II), as well as rhodium(III), ammine complexes has been assigned to a ligand field (LF) excited state of lowest energy.[1,7-10] The ruthenium(II) ammines that have been studied[1,7-11] involve H_2O, N_2, and azines which have LF strengths similar to that of ammonia where back-bonding is absent. In addition, the weaker back-bonding ligand in the *cis*-$[Ru(NH_3)_4(isn)L]^{2+}$ systems is the preferentially labilized ligand.[10] Thus, it is interesting to investigate the influence of higher ligand field and back-bonding ligands on the photosubstitution properties of ruthenium(II) ammines.

In this paper are described the photosubstitution reactions of the *trans*-tetraammineruthenium(II) complexes *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$, *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$, and *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ ($P(OEt)_3$ = triethyl phosphite).

Experimental Section

Chemicals and Reagents. Triethyl phosphite (Aldrich) was purified by treatment with metallic sodium followed by distillation under reduced pressure before use. Ether, ethanol, and acetone were distilled before use. Carbon monoxide (CO) was generated using the reaction between formic acid and sulfuric acid and was purified by bubbling through alkaline pyrogallol solution. All other materials were reagent grade and were used without further purification. "Ruthenium trichloride" ($RuCl_3 \cdot 3H_2O$) was the starting material for the synthesis of the ruthenium complexes. Doubly distilled water was used throughout this work.

Synthesis. $[Ru(NH_3)_5Cl]Cl_2$,[12] $[Ru(NH_3)_5H_2O](PF_6)_2$,[13] *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$,[4] *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$[14] were prepared and characterized as described in the literature. *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O](PF_6)_2$ was generated in solution from the corresponding *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](PF_6)_2$ salt by dissolving a known amount of the solid in 1×10^{-3} M trifluoroacetic acid solution. The reaction flask was kept protected from light, under argon bubbling and at room temperature (25-27 °C), for a period of 60 h. The electronic spectrum and cyclic voltammogram of the resulting solution are the same as those reported in the literature.[4]

Spectra. Electronic spectra were recorded at room temperature with a Varian 634-S recording spectrophotometer using quartz cells.

Cyclic Voltammetry. The cyclic voltammograms of the complexes were taken with a CV-1B cyclic voltammograph from Bio-Analytical Systems and a Houston Instruments Omnigraph 100 X-Y recorder; and 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 a reference electrode and a platinum wire as an auxiliary electrode; the working electrode was a glassy-carbon electrode.

Photolysis Procedures. Irradiation at 313 nm was carried out by using an Osram 150 xenon lamp in an Oriel Model 8500 Universal arc lamp source with a Oriel interference filter for monochromatization ($\cong$10 nm bandpass), an infrared filter, and a thermostated cell holder. Photolysis reactions were carried out in aqueous trifluoroacetic acid solutions containing 1.0×10^{-3} M concentrations of the desired Ru complex. Ferrioxalate actinometry was used for light intensity measurements. Solutions for photolysis and dark reactions were prepared with purified argon in a Zwickel flask and transferred to the 1.0-cm-pathlength quartz cell (V = 4.0 mL) using an all-glass apparatus. During photolysis, the solution was kept stirred by a small magnetic bar in the cell. All photolysis were carried out at 25.0 ± 0.1 °C. For spectroscopic quantum yield determinations, the reactions under photolysis were monitored periodically by recording the UV-vis spectra. Digital Micronal B375 and Analion PM 600 pH meters were employed to evaluate pH changes as the result of photolysis.

Photoaquation of Ammonia. 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. Solutions used for determination of ammonia photoaquation had an initial pH $\cong$ 4.0.

Photoaquation of Phosphite in *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ and Photoaquation of CO in *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$. These reactions were followed by measuring the aquo complex *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ formed upon photolysis. The aquo complex was evaluated from spectrophotometric measurements at 364 nm where the complex ion *trans*-$[Ru(NH_3)_4P(OEt)_3(pz)]^{2+}$ absorbs[14] (Table I). The pyrazine derivative was generated by adding a weighed amount of pyrazine to the photolyzed Ru(II) complex solutions. Initial pHs of the solutions for

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Table I. Spectral and Voltammetric Data for Selected Ruthenium Ammine Complexes

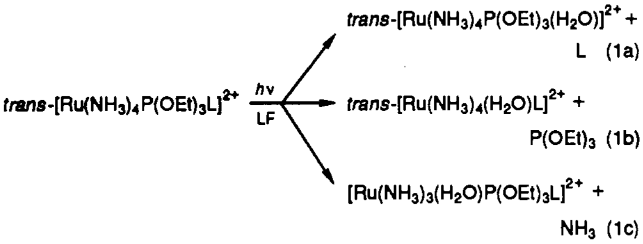
ion complex	λ_{max}, nm	ϵ, $M^{-1}\ cm^{-1}$	$E°_{Ru(III)/Ru(II)}$,[a] V	suggested assignt
trans-$[Ru(NH_3)_4P(OEt)_3H_2O]^{3+}$	285	8.1×10^2	0.52	MLCT
trans-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$	316	6.5×10^2	0.52	LF
trans-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$	262	4.4×10^2	0.65	
	294	2.4×10^2		LF
trans-$[Ru(NH_3)_4(H_2O)_2]^{2+}$	272	499	−0.14	LF
trans-$[Ru(NH_3)_4P(OEt)_3(isn)]^{2+}$	350	4.8×10^3	0.56	MLCT
trans-$[Ru(NH_3)_4P(OEt)_3(pz)]^{2+}$	366	4.2×10^3	0.50	MLCT
trans-$[Ru(NH_3)_4(isn)_2]^{2+}$	474	$\sim 10^4$		MLCT
trans-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$	284	4.7×10^2	1.11	LF
trans-$[Ru(NH_3)_4(H_2O)CO]^{2+}$	281	440	0.90	
			1.16[b]	LF

[a] Versus SCE. [b] i_{pa} irreversible.

phosphite quantum yield measurements were adjusted to ≅2.0 and ≅3.0 for *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$, respectively. Initial pHs for CO quantum yield measurements were adjusted to pH ≅ 3.0 and 4.0. Corrections were made to take into account thermal reactions. For such purpose, analogous reactions were allowed to react in the dark, under the same conditions as the photolyzed solutions. Photolysis runs did not exceed 10% for phosphite and CO photoaquation and 20% for ammonia photoaquation. Quantum yields were calculated by plotting quantum yield versus percent reaction and extrapolation back to 0%. Reported quantum yields are the average of at least three independent determinations.

Results and Discussion

The photoreactions described in this paper are all photosubstitution reactions. All three complexes studied displays a ligand field (LF) state as the lowest energy excited state (LEES). Each one of these transitions involves depopulation of a Ru 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. The possible photosubstitution reactions are depicted in the eq 1.



Reaction 1a occurs both thermally and photochemically for L = $P(OEt)_3$ or CO; the reactions for L = H_2O were not investigated. Reaction 1b was not observed either thermally or photochemically for L = H_2O or CO. Reaction 1c does not occur thermally[4] on the time scale of the experiments, but occurs photochemically for all three complexes studied.

$[Ru(NH_3)_3(H_2O)P(OEt)_3L]^{2+}$ spectra are not known and thus spectrophotometric monitoring of the photolysis is uninformative regarding ammonia photoaquation. However, since only reaction 1c displays a change in pH, ammonia photoaquation was determined potentiometrically by pH changes.

Phosphite in the studied complexes has a strong trans effect and trans influence,[14-16] leading to a thermal labilization of the trans position and a delabilization of the cis positions occupied by the coordinated ammonia. The thermal reaction of *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ in aqueous solutions generates *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ and $P(OEt)_3$ (eq 2). This system

$$trans\text{-}[Ru(NH_3)_4(P(OEt)_3)_2]^{2+} \underset{pH \geq 4.0}{\rightleftharpoons} trans\text{-}[Ru(NH_3)_4P(OEt)_3H_2O]^{2+} + P(OEt)_3$$

$$P(OEt)_3 \rightarrow P(OH)(OEt)_2 + EtOH \qquad (2)$$

$$P(OH)(OEt)_2 \rightleftharpoons P(O)(H)(OEt)_2$$

shows a thermal back-reaction at pHs ≥ 4.0. At lower pHs, the triethyl phosphite hydrolyzes to diethyl phosphonate.[16] The diethyl phosphonate and diethyl phosphite, in equilibrium in solution, are not able[6] to coordinate to the *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ species.

The thermal reaction of *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ in aqueous solution was not detected under the described conditions because the reaction involved is the exchange of water with water. No loss of ammonia was observed from the *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ complex in a 1×10^{-2} M aqueous CF_3COOH solution, after a 1-week period.[4]

trans-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ undergoes thermal CO aquation in aqueous solution (eq 3) forming *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ and CO. The thermal aquation of the cis ammonia was not observed.[14]

$$trans\text{-}[Ru(NH_3)_4P(OEt)_3CO]^{2+} \rightleftharpoons trans\text{-}[Ru(NH_3)_4P(OEt)_3H_2O]^{2+} + CO \qquad (3)$$

Given the above considerations, in order to measure ammonia photoaquation, solutions were adjusted to pH ≅ 4.0, since at this pH and under the ruthenium complex concentrations used, small changes in the H^+ concentration could be detected potentiometrically. Solutions made up to measure phosphite photoaquation were adjusted to lower pHs where there is no thermal back-reaction of phosphite.[17]

Photolysis of *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$. This complex displays an aqueous solution LF absorption band at 316 nm (Table I) as the lowest energy absorption band. Continuous photolysis with 313-nm light of aqueous solutions (pH ≅ 4.0) of *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ shows exclusive ammonia photoaquation (eq 1c), as indicated by the pH changes in the photolysis solutions. The absence of absorption at 285 nm, which is the λ_{max} for *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{3+}$, in a spectral region of low absorption for *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ indicated that no photooxidation to the Ru(III) complex occurred during photolysis. Under the studied conditions, water photoexchange could not be detected and determined.

Reaction 1b, corresponding to phosphite photoaquation, would generate *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$, which absorbs at 277 nm (Table I) and is electroactive at −0.14 V (vs SCE).[18] The photolyzed solutions of *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ do not show any detectable absorbance increase at 277 nm nor do they show any electrochemical process attributable to the *trans*-$[Ru(NH_3)_4(H_2O)_2]^{3+/2+}$ couple. Furthermore, the addition of excess isonicotinamide (isn) ligand to the photolyzed solution did not lead to any absorption at 474 nm (Table I), indicative of the presence of *trans*-$[Ru(NH_3)_4(isn)_2]^{2+}$,[18] which would be formed under these conditions.

Irradiations of solutions containing the *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ complex at pH = 2.0 lead to similar results. However under these conditions, since the aquated ammonia corresponds to a low percentage of the hydrogen ion concentration

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Table II. Quantum Yields for Photoaquation Reactions of Ruthenium Tetraamine Complexes

complex	λ_{max}, nm	λ_{irr}, nm	ϕ_{NH_3}, mol/einstein	$\phi_{P(OEt)_3}$, mol/einstein	ϕ_{CO}, mol/einstein
trans-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$	316	313	0.34 ± 0.06		
trans-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$	294 262	313	0.30 ± 0.02	0.12 ± 0.02	
trans-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$	284	313	0.27 ± 0.03		0.07 ± 0.01

it is not experimentally detected under these conditions.

Only *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ could be detected by spectrophotometric and cyclic voltammetric methods; therefore, reaction 1c was the only observed photoreaction.

Photolysis of *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$. This bis(phosphite) complex displays, in aqueous solutions, two LF bands[15] at 294 and 262 nm (Table I), corresponding to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}, {}^1E_g$ and $^1A_{1g} \rightarrow {}^1B_{2g}, {}^1E_g$, as the lowest energy absorption bands.[19] Continuous photolysis of acidic solutions (pH ≅ 4.0) of this complex with 313-nm light shows a behavior similar to that of the *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$. At this pH, there is also exclusive ammonia photoaquation (eq 1c). The observed marked changes in pH can only be due to ammonia aquation. There are only negligible changes in the spectra upon photolysis. Since *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ has a maximum at 316 nm, the lack of any absorbance increase at this wavelength indicates that no detectable phosphite aquation occurs during the experiments. Although this reaction is less favorable than in the case of the aquo monophosphite complex, the negligible changes in spectra also indicate that no Ru(III) was formed and, thus, that no photooxidation was occurring.

At pH ≅ 2.0 this process displays an observable photoaquation of phosphite. As pointed out for the *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ system, ammonia photoaquation was not experimentally detected at this pH. The phosphite photoaquation was determined by measuring the formation of *trans*-$[Ru(NH_3)_4P(OEt)_3(pz)]^{2+}$,[4] λ_{max} = 366 nm (Table I), which is formed quantitatively by the reactions of *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ with the pyrazine added in excess to the photolyzed solution. The dark reaction, used as a blank, was also treated in the same way, and the difference in absorbance for the two solutions was used for quantum yield calculations. The cyclic voltammograms of the photolyzed solutions showed larger peak currents corresponding to *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{3+/2+}$ than the dark reactions.

Since the released phosphite does not undergo hydrolysis at pH ≥ 4.0, there is no phosphite photoaquation observed at pH 4.0, whereas it does occur at pH = 2.0 where phosphite hydrolysis occurs and it is no longer able to back-react.

Photolysis of *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$. This complex displays, in aqueous solutions, one LF band at 284 nm (Table I) as the lowest energy absorption band. In water the complex *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ slowly undergoes aquation of the coordinated carbon monoxide quantitatively yielding[14] *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$ ($k_{-1} = 2.6 \times 10^{-5}$ s^{-1}, 25 °C, μ = 0.10 M ($NaCF_3COO$), $C_{H^+} = 1.0 \times 10^{-3}$ M). Therefore, the thermal loss of carbon monoxide from *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ is negligible during the photochemical experiments. Continuous photolysis with 313-nm light in acidic solution (pH ≅ 4.0) leads to ammonia and CO photoaquation. Ammonia photoaquation was detected and determined by measuring the pH changes in the photolyzed solutions. The cyclic voltammograms of the photolyzed solutions did not show any peaks characteristic of *trans*-$[Ru(NH_3)_4(H_2O)CO]^{2+}$ (Table I), suggesting that no phosphite aquation was occurring. Therefore, the CO photoaquatioin leads to *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$. Since, spectral changes between the reactant and the product are negligible, CO photoaquation was detected and determined as in the case of the photoaquation of phosphite in *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$, by measuring the formation of *trans*-$[Ru(NH_3)_4P(OEt)_3(pz)]^{2+}$ upon addition of excess pz to the photolyzed solution. Electrochemical oxidation[14] of *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ to the Ru(III) complex leads to a three-electron change process yielding CO_2 and *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O)]^{3+}$, which absorbs at 285 nm (Table I) essentially coincident with the absorption maximum of the parent complex (eq 4).

$$trans\text{-}[Ru(NH_3)_4P(OEt)_3CO]^{2-} \xrightarrow[\text{fast}]{-3e^-} trans\text{-}[Ru(NH_3)_4P(OEt)_3H_2O]^{3+} + CO_2 \quad (4)$$

As a consequence oxidation of the complex would not be detected by the techniques employed in this work. However, reaction 4 is unlikely to have occurred, since the reactions were not run under oxidative conditions.

Photolysis of this complex at pH ≅ 3.0 leads only to CO photoaquation. Ammonia photoaquation, which may also be occurring, is experimentally undetected due to low extents of photoreaction at this pH. Cyclic voltammograms of the photolyzed solutions did not show peaks due to *trans*-$[Ru(NH_3)_4H_2OCO]^{2+}$, and, thus, at pH ≅ 3.0, CO photoaquation was detected and determined in the same manner that it was at pH ≅ 4.0. Similar to the experiment at pH ≅ 4.0, no oxidation could be detected.

Quantum Yields and Excited States. Table II shows the quantum yields for the photosubstitution reactions studied. The three complexes display essentially the same quantum yields of ammonia photoaquation, which is the main reaction for these complexes, neglecting the unaccounted water photoaquation in *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$. As a matter of fact, $[Ru(NH_3)_5L]^{2+}$,[8] *trans*-$[Ru(NH_3)_4LL']^{2+}$, and *cis*-$[Ru(NH_3)_4(isn)L]^{2+}$ [10] (L, L′ = azine) also show ammonia photoaquation as the major photochemical process.

In the ammineruthenium(II) complexes with azine ligands[9,10] the ligand field bands are enveloped by the strongly absorbing MLCT bands, but the photosubstitution reactions were assigned for the lowest energy ligand field excited state (LF*). In the present complexes, however, there are no MLCT bands enveloping the LF bands, and, therefore, the observed photochemistry undoubtedly comes from a ^{3}LF*.

The lowest energy LF band represents the $^1A_{1g} \rightarrow {}^1A_{2g}, {}^1E_g$ transition, which is not resolved in the spectrum. The E component involves a transition from (xz, yz) to z^2, while the A_2 component involves an xy to $x^2 - y^2$ transition or, in other words, contributions from either $d_{x^2-y^2}$ or d_{z^2} orbitals or from both orbitals.

Considering the Ru–phosphite bond coincident with the z axis, the ammonia photoaquation must come from labilization of the x and/or y axis, in all three cases. Population of the A_2 state will photolabilize only the ligands on the xy plane, and therefore only the NH_3 photoaquation should be observed as a result of the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. Labilization of phosphite in the bis(phosphite) complex and of CO in the phosphite CO complex indicates that the z axis is also being labilized. As a consequence of the $^1A_{1g} \rightarrow {}^1E_g$ transition, the E state will become populated, with the consequent photolabilization of the ligands $P(OEt)_3$ and CO.

Since water photoexchange was not investigated in *trans*-$[Ru(NH_3)_4P(OEt)_3H_2O]^{2+}$, nothing can be said about involvement of the E state in the LEES of this complex. However, in the two former complexes at least, the LEES must have some contributions from both the A_2 and E state.

The $^1A_1 \rightarrow {}^1E$ component of the lowest energy LF band involves a transition from (xz, yz) to z^2. However a distortion is expected to occur[20] on both the xz and yz planes in the E state. This would lead to a labilization of all the ligands, implying that $h\nu$ could be explained by the E state alone. However, depopulation of xz and yz should affect mostly π-back-bonding to CO and phosphite

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(19) These transitions might, alternatively, be assigned to the $^1A_2$ and ^1E components of the $^1T_{1g}(O_h)$ parent, but this assignemnts would be harder to reconcile with the photochemical observations.

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ligands and should have little impact on the NH_3 metal bonding.

Thus, as pointed out before, E and A_2 should be very close in energy (or mixed) and very hard to distinguish insofar as our experiments are concerned.

During the photolysis of *trans*-[Ru$(NH_3)_4$P$(OEt)_3$CO]$^{2+}$, CO is exclusively labilized on the *z* axis. During the photolysis of the *cis*-[Ru$(NH_3)_4$(isn)L]$^{2+}$ complex ions, the ligand preferentially labilized is the weaker π-acceptor ligand.[14]

The $E^{\circ\prime}$ for the Ru(III)/Ru(II) couple in the complex *trans*-[Ru$(NH_3)_4$P$(OEt)_3H_2O$]$^{3+/2+}$ is 0.46 V.[4] Since the oxidation of *trans*-[Ru$(NH_3)_5$CO]$^{2+}$ is only observed[21] at potentials higher than +1.0 V, one infers that CO stabilizes Ru(II) through the back-bonding interaction more than P$(OEt)_3$ does.[22]

Triethyl phosphite is a moderate σ base.[6] Therefore for the P$(OEt)_3$ system a synergism is possible between the σ and π components strengthening the Ru(II) → P(III) bond. In fact, the activation enthalpies for the thermal reaction

$$trans\text{-}[\mathrm{Ru(NH_3)_4P(OEt)_3L}]^{2+} + \mathrm{H_2O} \xrightarrow{k_{-1}} trans\text{-}[\mathrm{Ru(NH_3)_4P(OEt)_3H_2O}]^{2+} + \mathrm{L}$$

are 18 and 29 kcal/mol for L = CO and P$(OEt)_3$, respectively.[4,14]

On excitation from the ground state to the LEES, one electron is promoted from a dπ orbital to a σ^* orbital. This electron transfer would destabilize the Ru(II)–P$(OEt)_3$ and Ru(II)–CO bonds in two different ways: first, weakening the σ bonds Ru(II)–P$(OEt)_3$ and Ru(II)–CO as a consequence of the electron density increase on the *z* axis and, second, weakening the π bonds Ru(II)–CO and Ru(II)–P$(OEt)_3$. Since the Ru(II)–CO bond is almost only π in character,[14] this bond will be more sensitive than Ru(II)–P$(OEt)_3$ to the depopulation of t_{2g} orbitals and therefore more easily broken.

The relevance of σ and π components in the Ru(III)/Ru(II)–L bond is well illustrated in the chemistry of the systems[4,22–24] *trans*-[Ru$(NH_3)_4$(P$(OEt)_3)_2$]$^{2+}$ and *trans*-[Ru$(NH_3)_4$P$(OEt)_3H_2O$)]$^{3+}$, [Ru$(NH_3)_5$CO]$^{2+}$ and [Ru$(NH_3)_5N_2$]$^{2+}$. The last two systems, where the Ru(II)–L bond is mainly due the back-bonding Ru(II) → L, easy loss of N_2 and CO upon oxidation occurs since these ligands are not able to donate σ electrons to the Ru(III) center. However due to the P$(OEt)_3$ biphilicity,[6,7] the complex ions *trans*-[Ru$(NH_3)_4$(P$(OEt)_3)_2$]$^{3+}$ and *trans*-[Ru$(NH_3)_4$P$(OEt)_3H_2O$]$^{3+}$, which display only σ-bonding Ru(III)–L are stable.[4,23]

Taking into consideration the fact that CO is a stronger π-acceptor than triethyl phosphite,[14] the photoaquation of CO rather than phosphite along the *z* axis is an apparent contradiction with the observations made on the *cis*-[Ru$(NH_3)_4$(isn)L]$^{2+}$[8–10] systems where the weaker π-back-bonding ligand is preferentially labilized. In the [Rh$(NH_3)_5$py-X]$^{3+}$ systems[25] in which there is no back-bonding, the exclusive aquation of py–X, which is a weaker σ-donor than NH_3, must come from depopulation of a nonbonding dπ orbital to a σ^* orbital along the *z* axis. For *cis*-[Ru$(NH_3)_4$(isn)L]$^{2+}$, the depopulation of a nonbonding dπ orbital and population of a σ^* orbital would not affect back-bonding;[8–10] thus, the weaker π-back-bonding ligand will be the one more easily labilized.

The photochemical behavior of the *trans*-[Ru$(NH_3)_4$P$(OEt)_3$CO]$^{2+}$ complex illustrates well that all molecular orbitals in the valence shell should be taken into account in order to explain photochemical reactivity.

Investigations on related systems are in course and will be reported soon.

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Registry No. pz, 290-37-9; *trans*-[Ru$(NH_3)_4$P$(OEt)_3H_2O$]$^{2+}$, 64939-03-3; *trans*-[Ru$(NH_3)_4$(P$(OEt)_3)_2$]$^{2+}$, 64939-00-0; *trans*-[Ru$(NH_3)_4$P$(OEt)_3$CO]$^{2+}$, 112786-14-8; P$(OEt)_3$, 122-52-1; CO, 630-08-0; NH_3, 7664-41-7; *trans*-[Ru$(NH_3)_4$P$(OEt)_3$(pz)]$^{2+}$, 64939-09-9.

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Notes

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Convenient Synthesis, Structure, and Properties of [(HB$(pz)_3$)FeCl_3]$^-$ [1]

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Introduction

Modeling of active sites of non-heme iron proteins has been one of the active research topics in bioinorganic chemistry in recent years.[2] Tripodal nitrogen ligands HB$(pz)_3^-$ and 1,4,7-triazacyclononane (TACN) (or 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3TACN)) have been successfully employed in the synthesis of the structural models of methemerythrin, [$Fe_2O(O_2CCH_3)_2L_2$] (where L = HB$(pz)_3^-$,[3] TACN, or Me_3TACN[4]). While mononuclear complexes LFeCl_3 where L = TACN or Me_3TACN were known to be good starting materials for the syntheses of various oxo/hydroxo-bridged multinuclear iron complexes,[4,5] the corre-

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