the dithiane moieties, furnishing the γ-lactone XII[8] (70%). Compounds IX-XII represent excellent synthetic intermediates for construction of important, biologically active molecules, namely, prostaglandin A_2 and brefeldin A,[17] and investigations directed toward these goals are currently in progress in our laboratories.

The introduction of selenium reagents as initiators to induce ring closures offers promising avenues for forming heterocycles of various sizes. We are currently engaged in examining the mechanistic and stereochemical aspects of this reaction as well as exploring the synthetic utility of this process in the construction of β-lactones[13,18] and macrocyclic lactones.[19,20]

Acknowledgments. We wish to express our deep gratitude and appreciation to Professor Madeleine M. Joullié for helpful discussions and support during this investigation. We are indebted to Dr. Fred L. De Roos for mass spectra. This research was supported by the University of Pennsylvania.

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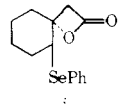
(13) Preliminary observations indicate that the initial product in entry 4 is the spiro β-lactone i (IR, ν_{max} 1820 cm^{-1}) which subsequently rearranges to the γ-lactone (IR, ν_{max} 1765 cm^{-1}).



i

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Excited State Proton Transfer of a Metal Complex: Determination of the Acid Dissociation Constant for a Metal-to-Ligand Charge Transfer State of a Ruthenium(II) Complex

Sir:

We wish to report the first observation of protonation of an electronic excited state of a metal complex without excited state deactivation. This allows the first direct determination of the pK_a of an electronic excited metal complex (pK_a*). Such studies have been carried out for a number of organic molecules,[1] but there is a conspicuous absence of such information for excited transition element complexes. In view of the strong current interest in the chemistry of metal-to-ligand charge transfer (MLCT) excited complexes and the availability of a number of such systems with excited state lifetimes long enough for proton transfer equilibria to be established prior to electronic deactivation,[2-8] pK_a* measurements for these systems deserve particular attention. Values of pK_a* for MLCT states have been estimated[9,10] from absorption measurements but are subject to question for reasons cited below.

One candidate for study is the complex Ru (2,2′-bipyridine)$_2$(2,2′-bipyridine-4,4′-dicarboxylic acid)$^{2+}$, whose diester derivatives have recently been reported to photoassist decomposition of water, presumably be means of photoinduced electron transfer from a MLCT excited state.[11] The parent Ru(2,2′-bpy)$_3^{2+}$ species and a variety of related Ru(II) complexes have been extensively investigated and the results indicate MLCT character for the lowest (luminescent) excited state.[2] The close similarity in the electronic absorption and emission spectra of Ru(2,2′-bpy)$_3^{2+}$, its dicarboxylic acid, and diester derivatives suggests the MLCT assignment for the lowest excited state in the latter complexes.

We have investigated[12] the excited state proton transfer equilibrium involving the carboxylic acid derivative and can now add proton transfer to the known intermolecular processes of excited Ru(II) complexes, which to date have only included electron transfer and energy transfer.[13] The equilibrium measured is indicated in eq 1. The ground state pK_a, pK_a^0, can be determined by spectrophotometric titration, i.e., by measurements of the absorption spectra as a function of pH in aqueous solution, Figure 1. The spectral changes are completely reversible. Isosbestic points are preserved over the entire pH excursion, evidencing that both -COOH groups have ap-

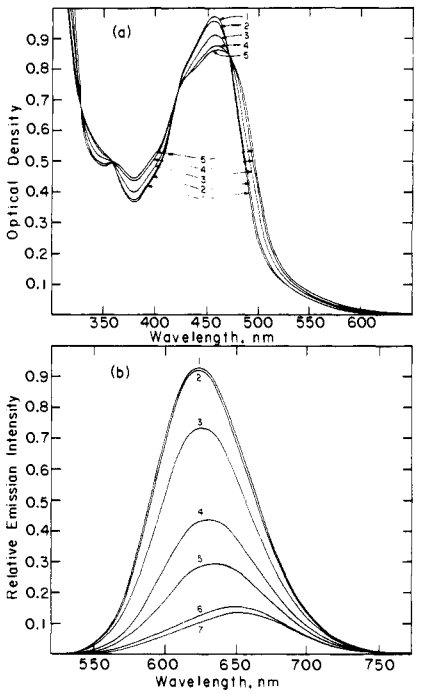
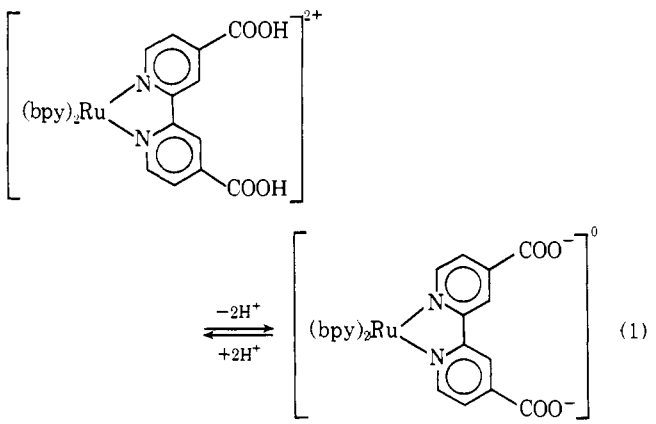


Figure 1. (a) Absorption spectra of $Ru(2,2'\text{-bpy})_2(2,2'\text{-bpy-}4,4'\text{-}(COOH)_2)^{2+}$ in aqueous solution. Curves 1-5 are at pH 10, 3.6, 2.75, 2.05, and 1, respectively. The concentration of the complex is 7.1×10^{-5} M and spectra were recorded in 1.0-cm path length cells. (b) Uncorrected emission spectra of aqueous solutions containing $Ru(2,2'\text{-bpy})_2(2,2'\text{-bpy-}4,4'\text{-}(COOH)_2)^{2+}$. Curves 1-7 are at pH 10, 5.75, 4.5, 4.0, 3.6, 2.75, and 1, respectively. The excitation wavelength is 470 nm and the concentration is 7.1×10^{-5} M. The spectra shown are not corrected for variation in detector sensitivity with wavelength. All spectra were recorded at 25 °C.



(1)

proximately the same pK_a. A plot of optical density vs. pH, Figure 2, at any wavelength where there is a change shows one inflection point at pH 2.75, defining a $pK_a^0 = 5.50 \pm 0.05$ for the two proton equilibrium, eq 1. Though the two acid groups appear to behave independently, we are unable to detect the monoprotonated species in the optical spectra, Figure 1.

Direct measurement of the excited state equilibrium has been accomplished by a luminescence titration; i.e., the luminescence spectrum has been measured as a function of pH, exciting at one of the isosbestic points. Representative raw data (uncorrected emission spectra) are included in Figure 1, and a plot of luminescence intensity vs. pH is shown in Figure 2. *The crucial result is that at ~pH 3.5 one excites, virtually exclusively, the deprotonated form and observes luminescence which is predominantly from the protonated form.* This shows that the excited complex can be protonated without concomitant electronic excited state deactivation. The excited state pK_a, pK_a^*, is given by eq 2,[1]

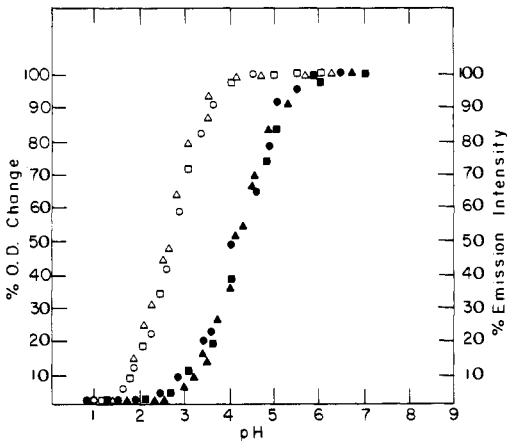


Figure 2. Spectrophotometric and luminescence titrations of $Ru(2,2'\text{-bpy})_2(2,2'\text{-bpy-}4,4'\text{-}(COOH)_2)^{2+}$ in aqueous solution at 25 °C: The symbols ○, □, and △ represent percent change in optical density at 490 nm as a function of pH recorded in three independent experiments. The symbols ●, ■, and ▲ represent the percent change in emission intensity as a function of pH at 625 nm, exciting at the 350, 430, and 470 nm isosbestic points, respectively.

$$2\text{pH} = pK_a^* - \log\left[\frac{\tau(\text{protonated})}{\tau(\text{deprotonated})}\right] \qquad (2)$$

where the pH is taken at the inflection point in the luminescence titration curve, Figure 2, and τ is the luminescence lifetime measured to be 0.39 and 0.32 μs for the deprotonated and protonated forms, respectively. The pK_a^* is found to be 8.50 ± 0.05. These results show that the deprotonated complex is a stronger base in the Ru → L CT excited state than in the ground state. While we can only speculate on the significance of the magnitude of the effect, the direction of the change in pK_a is consistent with the MLCT assignment, in that the intuitive notion is that increased negative charge on the ligand will increase the base strength.

Estimates of pK_a^* can be made from absorption spectra.[1] For the case at hand, there is no well-defined 0-0 transition position, and thus, the difference in absorption maxima of the fully protonated and deprotonated form, $\Delta\nu$, must be used to calculate the value of pK_a^* for the two proton equilibrium. Such a calculation gives $pK_a^* = 5.90$, according to eq 3,[3] where $\Delta\nu$ is in cm^{-1} and R and T have their usual meanings.

$$pK_a^* = pK_a^0 + \frac{2.86\Delta\nu}{2.3RT} \qquad (3)$$

The discrepancy between this value of pK_a^* and that determined from the luminescence titration is significant and reveals the importance of being able to use the luminescence titration. The difference in absorption spectral maxima does not necessarily accurately reflect the difference in free energy of the *relaxed* excited states. The pK_a^* values from such data should be used with reservation, as has been long appreciated.[1,14] The emission spectra are a better predictor of pK_a^*, but the values calculated from the emission maxima still do not exactly match the titration results. This difficulty, again, likely stems from the absence of a well-defined 0-0 transition.

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The Interaction of Isocyanides and $Fe_4S_4L_4$ Clusters

Sir:

Despite the recent, intense interest in the $Fe_4S_4L_4$ system as a model,[1,2] for biological reducing agents of the ferredoxin type, not a great deal is yet known about the chemical reactivity of this inorganic class.[3-5] As results of a study motivated by an enzyme precedent, videlicet the nitrogenase-mediated conversion of isocyanides to amines,[9] we describe herein the preparation as well as the infrared spectral and electrochemical characterization of $Fe_4S_4L_4$–isocyanide derived adducts which markedly promote the α,α-addition of mercaptans to isocyanides, the first observed nonenzymic catalytic reaction of this cluster type.

The reaction of *p*-chlorophenylisocyanide (**1**) with either $\mathbf{2a}^{2-}$ or $\mathbf{2a}^{4-}$ [10] in the presence of excess ethanethiol as the proton source exclusively generated *N*-(*p*-chlorophenyl) ethylthioformimidate (**5a**),[11] readily hydrolyzable to *p*-chloroaniline. For reactions run in tetramethylurea (TMU) for 1 h at 22 °C and with 100 molar equiv of isocyanide **1** and 150 molar equiv of ethanethiol, conversions based on isocyanide were 37% from $\mathbf{2a}^{2-}$ and 73% from $\mathbf{2a}^{4-}$. A control in which cluster was omitted showed a 1% conversion, while a reaction in which metallic sodium was substituted for **2a** gave a 13% conversion. Solutions of decomposed clusters were not catalytically active. Significantly, replacement of mercaptan by *n*-C_4H_9OH, $(C_2H_5)_3SiH$, $CH_3(C_6H_5)PH$, or $(C_2H_5)_2NH$ resulted in no consumption of isocyanide under otherwise identical conditions. In light of previously examined metal mediated[12,13] α,α-additions to isocyanide as well as electrochemical and other information presented below, we postulate the reaction sequence outlined in Scheme I.

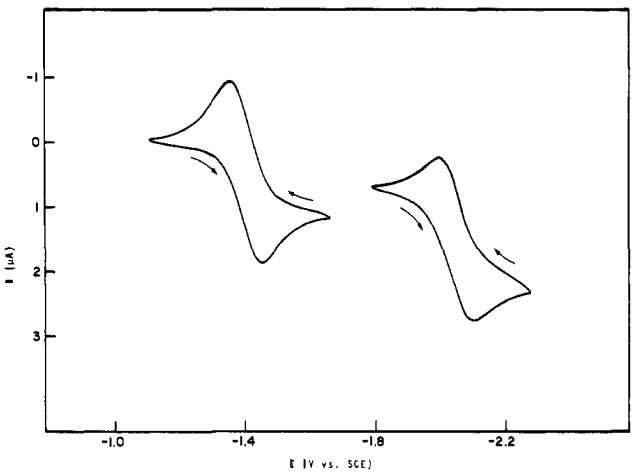
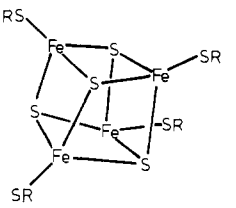


Figure 1. Cyclic voltammograms of 5 mM $\mathbf{2a}^{2-} \rightleftharpoons \mathbf{2a}^{3-}$ and $\mathbf{2a}^{3-} \rightleftharpoons \mathbf{2a}^{4-}$.



2a: R = C_2H_5
b: R = $C_6H_5CH_2$
c: R = C_6H_5, C_6H_5, S

Cyclic voltammetry[14] of 5 mM $(n\text{-}Bu_4N^+)_2\mathbf{2a}^{2-}$ revealed two chemically reversible one-electron couples ($\mathbf{2a}^{2-}/\mathbf{2a}^{3-}$ and $\mathbf{2a}^{3-}/\mathbf{2a}^{4-}$) which could be independently scanned (Figure 1). During cyclic voltammetry monitored titration of the **2a** solution with *n*-$C_9H_{19}NC$, neither the $\mathbf{2a}^{2-}/\mathbf{2a}^{3-}$ couple nor the $\mathbf{2a}^{3-}$ to $\mathbf{2a}^{4-}$ reduction was altered in relative intensity; however, the $\mathbf{2a}^{4-}$ to $\mathbf{2a}^{3-}$ oxidation was progressively attenuated while a new couple appeared at −2.26 V vs. SCE (Figure 2a), ascribed to the catalytically active $\mathbf{2a}^{4-}$-isocyanide adduct.

Confirmation of adduct formation and function was obtained through assay of the catalytic process. TMU solutions of $\mathbf{2a}^{2-}$ or $\mathbf{2a}^{4-}$ with varying numbers of molar equivalents of isocyanide **1** were prepared, and after a few minutes, or as many as 96 h, were introduced into TMU solutions of 100- to 1000-fold excess of **1** and ethanethiol. The most active catalyst preparation resulted from equimolar quantities of $\mathbf{2a}^{4-}$ and isocyanide **1** (98% yield of thioformimidate **5a** after 1 h) and was analyzed by cyclic voltammetry (Figure 2b). The