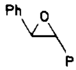
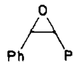
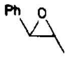
Table II. Relative Reactivities of Metal Triflate Salts and Metalloporphyrins in Reactions of (*Z*)- and (*E*)-Stilbene[a]

(*E*)-Stilbene

catalyst	products, mmol × 10^2	
		PhCHO
$Fe(OTf)_3$	19.5	trace
Fe(TPP)Cl[b]	9.5	0
$Mn(OTf)_2$	3.8	5.1
Mn(TPP)Cl	trace	0

(*Z*)-Stilbene

catalyst	products, mmol × 10^2		
			PhCHO
$Fe(OTf)_3$	11.7	1.3	trace
Fe(TPP)Cl	17.0	0	0
$Mn(OTf)_2$	1.3	1.8	3.6
Mn(TPP)Cl[c]	13.5	7.1	0

[a] These reactions were carried out under conditions such that we could obtain a qualitative comparison of the relative reactivities of the metal triflates and the comparable metalloporphyrins. The reaction conditions are therefore not optimized for any particular system. For these studies, 10^{-2} mmol of the metal salt or metalloporphyrin and 0.5 mmol of (*Z*)- or (*E*)-stilbene was dissolved in 5 mL of acetonitrile (metal triflate) or dichloromethane (metalloporphyrin). Iodosylbenzene, 0.35 mmol, was added slowly over a period of 20 min. The solution was stirred for an additional 10 min. At this point, a 100-μL aliquot was removed, diluted with 2 mL of methanol, and analyzed by HPLC. The metal triflate reactions were carried out in acetonitrile while the metalloporphyrin reactions were carried out in dichloromethane for reasons of solubility. [b] TPP is tetraphenylporphinato. [c] Deoxybenzoin (3.0×10^{-2} mmol) was also detected.

to unfavorable steric interactions between the *E* olefin and the porphyrin.[2] A number of other epoxidation reagents have also been observed to react faster with *Z* olefins.[11] Our preliminary evidence indicates that (*E*)-stilbene is reacting faster than (*Z*)-stilbene in the case of the metal ions. Further mechanistic studies are required in order to explain the preference for (*E*)-stilbene in the metal salt-catalyzed reactions. Nevertheless, we can conclude at this point that the rate of oxygen atom transfer in the metal ion catalyzed reactions is considerably less sensitive to the disposition of the phenyl rings in (*Z*)- and (*E*)-stilbene than are the rates of the iron and manganese porphyrin-catalyzed reactions.

In our future studies we hope to elucidate the mechanisms of these reactions and to extend our studies to other metal ions and complexes and to other oxygen atom donors.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

Registry No. $Cu(NO_3)_2$, 3251-23-8; $Cu(OTf)_2$, 34946-82-2; $Co(NO_3)_2$, 10141-05-6; $Co(OTf)_2$, 58164-61-7; $Mn(OTf)_2$, 55120-76-8; $Fe(OTf)_2$, 59163-91-6; $Fe(OTf)_3$, 63295-48-7; iodosylbenzene, 536-80-1; (*E*)-stilbene, 103-30-0; (*Z*)-stilbene, 645-49-8; 2,3-dimethyl-2-butene, 563-79-1; cyclohexene, 110-83-8; cumene, 98-82-8.

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(11) Miyaura, N.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 2368-2378 and references therein.

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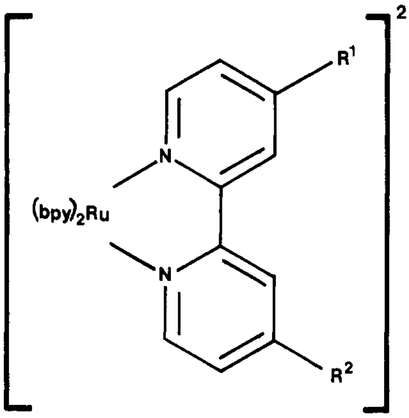
Proton Transfer in the Excited State of Carboxylic Acid Derivatives of Tris(2,2'-bipyridine-*N*,*N*')ruthenium(II)

Sir:

Interest in the bis(2,2'-bipyridine-*N*,*N*')(2,2'-bipyridine-4,4'-dicarboxylic acid-*N*,*N*')ruthenium(II) ion (I) initially arose because it was the first transition-metal complex in which proton transfer was observed in its excited state.[1] We have found that I has two pK_a values (pK_{a1}* = 3.6, pK_{a2}* = 4.5) separated by ~1 pK_a unit. A similar separation has been found for the ground-state pK_a values,[2] where the protons are much more acidic.



Ia: $R^1 = R^2 = CO_2H$
b: $R^1 = CO_2H$, $R^2 = CO_2^-$
c: $R^1 = R^2 = CO_2^-$
IIa: $R^1 = CO_2H$, $R^2 = CH_3$
b: $R^1 = CO_2^-$, $R^2 = CH_3$

The differences in acidities of ground and excited states result in the transfer of none, one, or two protons to the excited state (by control of pH). The results reported here differ greatly from photophysical properties reported previously[1,3] where only one ground-state and one excited-state pK_a value were observed.[1]

Our interest in the dicarboxylic acid complex I arose from the possibility of using the excited state of the neutral, doubly deprotonated species Ic as a sensitizer in the cobalt cage complex mediated photoreduction of water[4-10] (in the hope of reducing the electrostatic work terms involved in excited-state quenching). However, preliminary work on this sensitizer revealed quite different properties[2] to those reported previously.[1] The reported syntheses of the diacid complex[3,11-15] lead

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(13) The problem of impurities in these preparations has also been indicated elsewhere.[14,15]

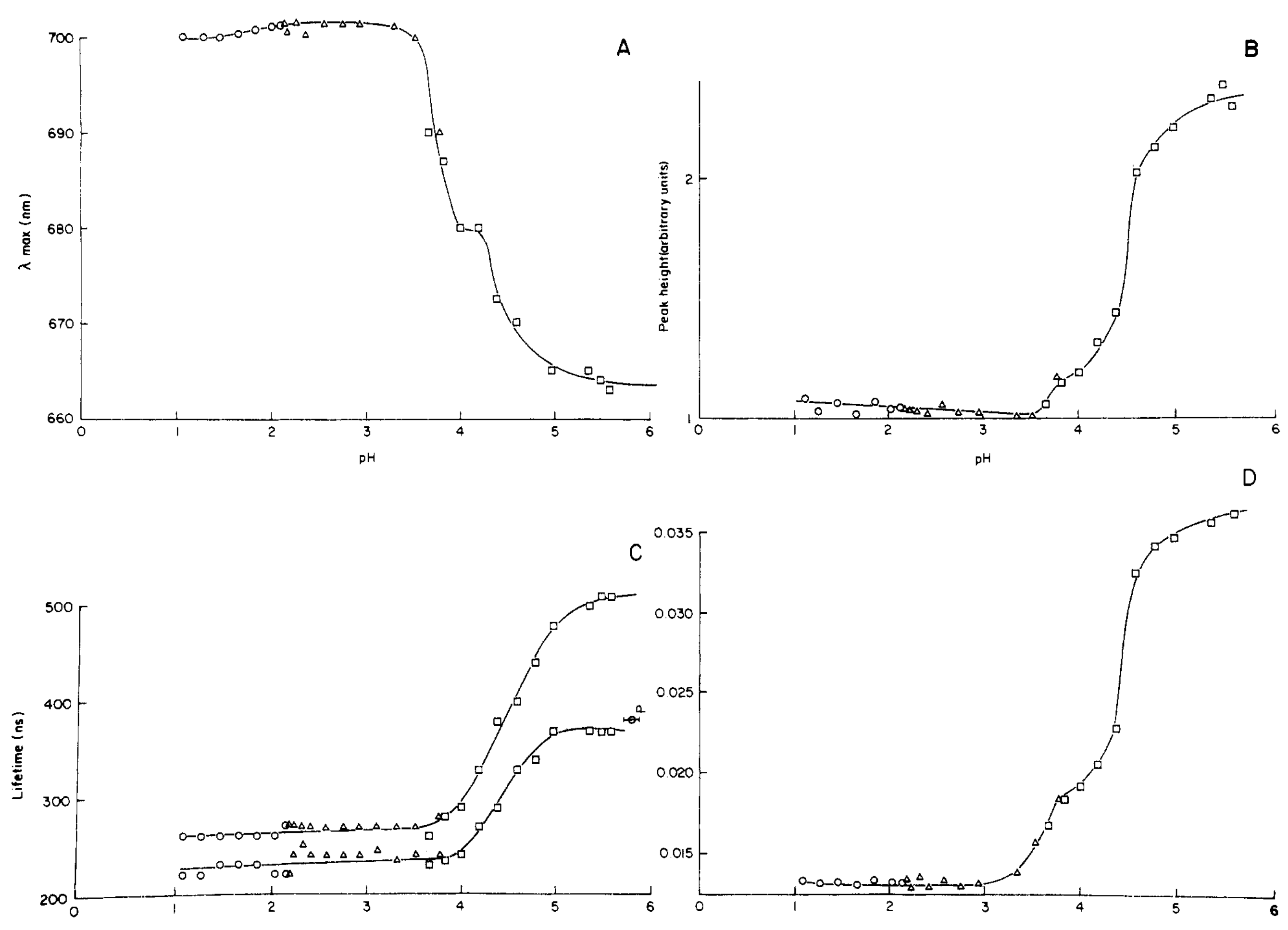

Figure 1. pH dependencies of wavelength maximum of emission (A), emission peak height (B), phosphorescence lifetime in air (O_2) and under nitrogen (N_2) (C), and emission quantum yield (D) for $[Ru(bpy)_2(bpy\text{-}4,4'\text{-}(CO_2H)_2)]^{2+}$. Buffer solutions used were HCl/KCl (○), $ClCH_2CO_2H/NaOH$ (△), and $CH_3CO_2H/NaOH$ (□), all adjusted to an ionic strength of 0.1 M with NaCl.

Table I. Properties of the Excited States of Carboxylic Acid Derivatives of $[Ru(bpy)_3]^{2+}$ [a]

complex	$\tau_{1/2}$, ns	Φ_{em}	λ_{em}, nm	ref
Ia	190	0.013_9	705	*c*
	200 (290)	0.004_7 (0.006)[d]		3
	225 (320)			1
Ib	200[b]	0.019	680	*c*
Ic	385	0.037_4	660	*c*
	420 (620)	0.030_9 (0.038)[d]		3
	270 (390)			1
IIa	82 (120)	~0.006	~720	*c*
IIb	400 (590)	0.040	650	*c*
$[Ru(bpy)_3]^{2+}$	430 (640)	0.044	640	

[a] 20 ± 2 °C. [b] Because of the presence of several emitting species the decay is nonexponential. It is therefore inappropriate to quote values for τ. [c] This work. [d] The reported values for the quantum yields in ref 3 were greater than the actual values because in their calculation incorrect correction were used (see text).

to several side products,[4] including the monoacid complex bis(2,2′-bipyridine-*N*,*N*′)(4′-methyl-2,2′-bipyridine-4-carboxylic acid-*N*,*N*′)ruthenium(II) (II). This prompted us to reinvestigate the pH dependence of the photophysics of complex I, and also of the new complex II.

The syntheses, purification, and identification of the complexes will be reported elsewhere.[4] All measurements were performed in constant ionic strength buffers[16] (μ = 0.1 M) at 20 ± 2 °C. Buffers used were HCl/KCl, CH_3CO_2H/NaOH/NaCl, or $ClCH_2CO_2H$/NaOH/NaCl. The pH values of all solutions were checked with a Radiometer PHM 63 Autocal pH Meter. The ground-state pK_a values of ~1.85 and 2.90 found under these conditions using the spectrophotometric method were in good agreement with our previous measurements[2] (pK_{a1} = 1.75, pK_{a2} = 2.82; cf. pK_a = 5.5 reported elsewhere[1,15]). Phosphorescence spectra were measured over the pH range 1.0–13 (excitation frequency, 478 nm, corresponding to an isosbestic point in the absorption spectra of Ib and Ic) and were corrected for instrument response. Corrections were also made for the change in absorption of Ia at this wavelength. Quantum yields were determined by comparison with the emissin intensity of $[Ru^*(bpy)_3]^{2+}$,[17,18] using the "optically dilute method".[19] The large changes in the corrected emission maximum of I in the pH range 2.5–5.6 (Figure 1) gave pK_{a1}^* ~ 3.7 and pK_{a2}^* ~ 4.5. The peak height intensity of emission does not vary greatly in the pH region 2.5–4.0 but changes dramatically in the pH region 4–5, giving pK_{a2}^* of 4.47. The existence of distinct pK_a^* values

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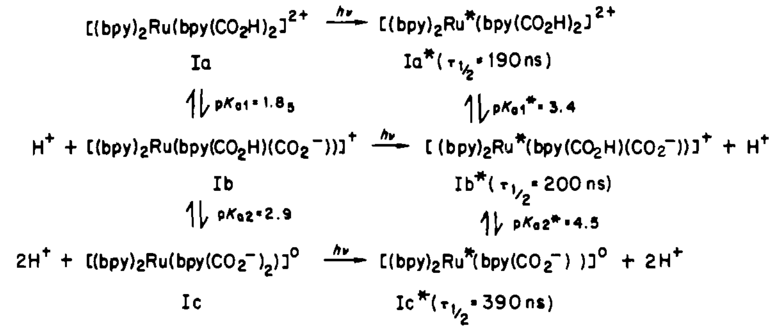
(19) Although the quantum yields reported in ref 3 were similar to ours, they were calculated on incorrect assumptions. The quantum yields for water were extrapolated directly from quantum yields of $[Ru(bpy)_3]^{2+}$ without corrections for solvent effects. Finally, the authors do not refer to the correction of the spectral response of the instrument.

Scheme I



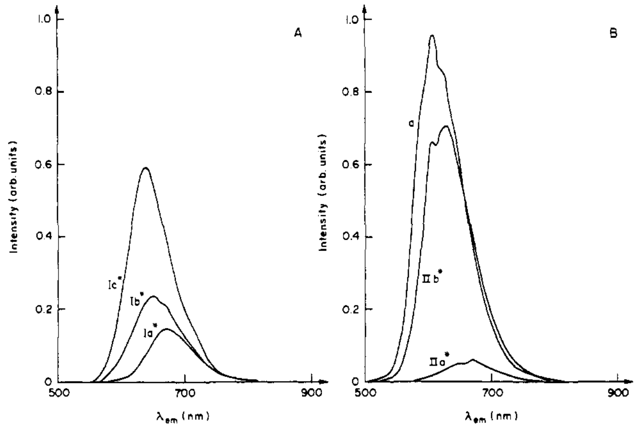


Figure 2. Uncorrected phosphorescence emission spectra: (A) Ia* (pH 1), Ib* (pH 3.95), Ic* (pH 13); (B) $[Ru^*(bpy)_3]^{2+}$ (a), IIa* (pH 1), IIb* (pH 13).

is also demonstrated by the pH dependence of the phosphorescence quantum yields. Two pK_a^* values are evident ($pK_{a1}^* \sim 3.6$, $pK_{a2}^* = 4.5$), the first being manifested mainly in a broadening of the spectrum. The pH dependence of the lifetime of emission only showed the presence of the second pK_a^* value. Figure 1 summarizes these results, giving $pK_{a1}^* = 3.6$ and $pK_{a2}^* = 4.5$ (cf., $pK_a^* = 8.8$ reported previously[1,15]), and Table I compares our results with previously reported data. The uncorrected emission spectra of the three excited states of I, which carry overall 2+ (Ia*), 1+ (Ib*), or no (Ic*) charges are given in Figure 2. While the uncorrected spectra show similar general characteristics to those reported previously,[1,3] they differ considerably in peak heights and emission maxima. Furthermore, large discrepancies in relative quantum yields, pK_a values, and emission lifetimes were observed.[20] To check whether II may have been the source of these discrepancies, we measured its gound- and excited-state properties and obtained pK_a values of comparable magnitude ($pK_a = 3.0$, $pK_a^* = 4.85$) to those observed for the diacid. Uncorrected emission spectra of the deprotonated complex IIb* and its acid form IIa* are shown in Figure 2; their photophysical properties are given in Table I. Probably, both the lack of correction of instrumental response and the presence of impurities account for the discrepancies between the present and earlier reported results.[1,3]

Clearly, the previous notion[1] that proton transfer is observed in the excited states of such molecules is correct; however, contrary to the reported results, we have now found that none, one, or two protons may be transferred, depending on pH. Thus, at pH ~3.1 one proton is transferred, while at pH ~4 two protons are transferred; these processes are summarized in Scheme I. One of the reviewers suggested that the pK_a^* values observed may reflect the kinetics of protonation rather than the equilibrium situation. It was argued that protonation would have to be faster than the diffusion limit. However, proton transfer is not subject to diffusion control because protons can move through a hydrogen-bonded network by exchange, i.e., there is no need for the diffusion of a specific proton over extended distances. Moreover, if kinetic control were operating, one would expect to see changes near the second ground-state pK_a, as transfer of two protons would be required to maintain the same photophysical properties. Earlier work has shown that the electronic excitation energy of Ia* is localized on the $bpy(CO_2H)_2$ ligand[2] and that water effectively quenches the emission from ester derivatives.[20] This is likely to be the reason for the low phosphorescence yield and relatively short lifetimes of Ia*, Ib*, and IIa*, all of which possess one or two CO_2H groups. The large shift in emission maximum of Ib* reflects of the relatively large change in the electron-withdrawing ability of the CO_2H group, which occurs on deprotonation, and the broadness of the spectrum suggests that several well-separated triplet excited states are now contributing to the emission. In contrast, Ic* and IIb* have emission characteristics similar to those of $[Ru^*(bpy)_3]^{2+}$ where the splitting of the triplet excited states is expected to be smaller. In summary, the presence of a $-CO_2R$ substituent (R = alkyl, H) greatly reduces the quantum yields and lifetimes of emission, while the $-CO_2^-$ group has little effect. Details of quenching and hydrogen production experiments using these results will be presented elsewhere.[4]

Acknowledgment. P.A.L. gratefully acknowledges the receipt of a CSIRO Postdoctoral Fellowship. We also thank Dr A. W.-H. Mau for helpful comments on this paper.

Registry No. Ia, 62207-96-9; Ib, 72932-31-1; Ic, 64189-97-5; IIa, 92984-72-0; IIb, 93000-28-3.

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Factors Affecting the Metal-Promoted Head-to-Head Dimerization of CS_2 to C_2S_4. Synthesis, Chemistry, Structure, and MO Analysis of $[(triphos)Rh(\mu\text{-}C_2S_4)Rh(triphos)](BPh_4)_2\cdot CH_2Cl_2$

Sir:

The formation of a C–C bond between two stable molecules represents one of the most attractive goals of organometallic chemistry. Although most desirable would be a metal-promoted dimerization of carbon dioxide to give oxalate, encouraging results have been obtained by using carbon disulfide, a CO_2-like molecule. Indeed two examples of metal-activated head-to-head dimerization to form C_2S_4 species have been reported.[1,2] However, these reports do not provide any useful

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0020-1669/84/1323-4125$01.50/0 © 1984 American Chemical Society