

bonylbis( $\eta^5$ -phenylcyclopentadienyl)diiron (**9**) rests upon its composition (*Anal.* Calcd for  $C_{26}H_{18}O_4Fe_2$ : C, 61.66; H, 3.56. Found: C, 61.44; H, 3.50.), molecular weight (Rast) (calcd, 506; found, 510), and nmr spectrum ( $\delta$ , ppm,  $CDCl_3$ ) [4.63 (t, 2 H, protons 8, 11), 5.19 (t, 2 H, protons 9, 10), 7.49 (m, protons 1, 2, 3, 4, and 5)]. The ir spectra showed bridging carbonyl at 1770 and 1800  $cm^{-1}$ , and terminal carbonyl at 1998, 1970, and 1955  $cm^{-1}$ .

Complex **10**, formed in 75% yield from spiro-[2,4-cyclopentadiene-2',5'-dimethyl-1,7'-norcaradiene] (**5**) had mp 138° dec. The composition (*Anal.* Calcd for  $C_{18}H_{14}O_3Fe$ : C, 61.90; H, 4.52. Found: C, 61.76; H, 4.69.) and nmr spectrum [( $\delta$ , ppm,  $CDCl_3$ ) 1.70 (s, 3 H, protons on 13), 1.88 (s, 3 H, protons on 14), 2.87 (d, 1 H, proton 1), 4.53 (m, 1 H, proton 6), 4.65 (m, 1 H, proton 8), 4.74 (m, 1 H, proton 11), 5.04 (m, 1 H, proton 9), 5.30 (q, 1 H, proton 10), 5.72 (s, 2 H, protons 3 and 4)] are in agreement with expectation. The mass spectrum of **10** showed the parent molecular ion at  $m/e$  310 (27%) and peaks for successive loss of CO, 282 (10%) and 254 (44%), and base peak for  $C_{13}H_{14}Fe$  at 226. The ir spectrum showed strong terminal carbonyl stretching absorptions at 1960–1985 and 2020  $cm^{-1}$  and acyl carbonyl stretching frequency at 1640  $cm^{-1}$ .

The fact that the cyclohexadiene system is uncomplexed in **10** indicates that its complexation is not a necessary prerequisite for the opening of the cyclopropyl ring. In the full paper the mechanism of the reaction of the divinylcyclopropyl system with  $Fe_2(CO)_9$  will be discussed in light of these results.

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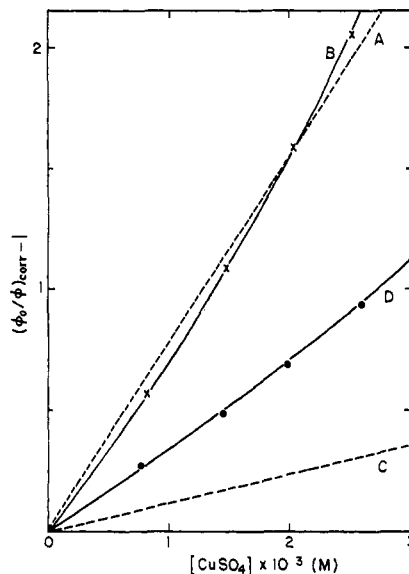
### Luminescence Quenching of Dicyanobis(1,10-phenanthroline)ruthenium(II) by Cupric Ion in Aqueous Solutions. Dynamic and Static Processes

Sir:

We wish to report on the quenching of the charge-transfer (CT) luminescence of  $Ru(phen)_2(CN)_2$  (phen = 1,10-phenanthroline) by  $Cu^{2+}$  ( $H_2O$ ,  $\sim 22^\circ$ ). This system demonstrates what we believe to be the first unequivocal evidence for both static and dynamic quenching of a metal complex exhibiting CT luminescence.<sup>1</sup> Static quenching appears to proceed by coordination of  $Ru(phen)_2(CN)_2$  to the  $Cu^{2+}$  by a CN-bridge, and it was possible to determine the equilibrium constant,  $K_{eq}$ , by luminescence measurements only.

(1) Fujita and Kobayashi<sup>2</sup> have suggested a combinational quenching of  $Ru(bipy)_3^{2+}$  by  $Co(C_2O_4)_3^{4-}$  based only on intensity data. Failure to correct for trivial effects<sup>3</sup> probably accounts for their observations, however.

(2) J. Fujita and H. Kobayashi, *Ber. Bunsenges. Phys. Chem.*, **76**, 115 (1972).



**Figure 1.** Intensity Stern-Volmer quenching plots for deactivation of aqueous  $Ru(phen)_2(CN)_2$  by  $CuSO_4$ . Values obtained in deoxygenated solutions ( $\times$ 's) and in  $O_2$ -saturated solutions ( $\bullet$ 's): A, Stern-Volmer plot with  $K_{SV} = 780 M^{-1}$ ; B, combination static and dynamic quenching with  $K_{SV} = 325 M^{-1}$  and  $\beta K_{eq} = 270 M^{-1}$ ; C, Stern-Volmer plot with  $K_{SV} = 130 M^{-1}$ ; D, combination static and dynamic quenching with  $K_{SV} = 55 M^{-1}$  and  $\beta K_{eq} = 270 M^{-1}$ . See text for details.  $[Ru(phen)_2(CN)_2] \sim 2 \times 10^{-5} M$ .  $\lambda_{exc} = 480 nm$ .

The first indication that quenching was not simply diffusional, as it is with most metal complex quenchers<sup>3-6</sup> and  $O_2$ ,<sup>7</sup> was the apparent slight upward curvature to the intensity,  $\phi$ , Stern-Volmer (SV) quenching plot ( $\phi_0/\phi - 1$  vs.  $[Q]$ ) in deoxygenated solutions. See Figure 1. The effect was not large, however, and the data were fit fairly well by normal SV kinetics with  $K_{SV} \sim 780 M^{-1}$  (curve A). That this simple explanation was incorrect was established by making a decay time,  $\tau$ , SV plot ( $\tau_0/\tau - 1$  vs.  $[Q]$ ) under similar conditions; this procedure yields the true  $K_{SV}$  free of any contribution from static quenching. A linear plot resulted with  $K_{SV}^{N_2} = 335 M^{-1}$  ( $k_2 \sim 5 \times 10^8 M^{-1} sec^{-1}$ ) in considerable disagreement with the  $\phi$ -derived value. Thus, both static and dynamic quenching pathways seemed to be operative.

As an additional test of the inadequacies of the diffusion only model, we measured the  $\phi$ -quenching by  $CuSO_4$  in an  $O_2$ -saturated solution (Figure 1). Under these conditions  $\tau$  of the donor is reduced by a factor of 6.15 by oxygen quenching.<sup>7</sup> Since  $K_{SV} = k_2\tau_0$  and  $k_2$  should be unaffected by oxygen, the  $K_{SV}$  of  $\sim 780 M^{-1}$  for a deoxygenated solution should be reduced by a factor of 6.15 to  $\sim 130 M^{-1}$  for the  $O_2$ -saturated ones if all quenching were diffusional; line C is the required experimental curve. The extreme disagreement between C and the data again argues for a combinational model.

(3) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **95**, 5159 (1973).

(4) H. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, **94**, 8238 (1972).

(5) F. Bolletta, M. Maestri, and F. Moggi, *J. Phys. Chem.*, **77**, 861 (1973).

(6) F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, **95**, 7864 (1973).

(7) J. N. Demas, D. Diemente, and E. W. Harris, *J. Amer. Chem. Soc.*, **95**, 6864 (1973).

For a combinational quenching mechanism, the intensity SV equation is

$$K_{SV}^{app} = [(\phi_0/\phi)_{corr} - 1]/[Q] = (K_{SV} + \beta K_{eq}) + K_{SV}(\beta K_{eq})[Q] \quad (1)$$

where  $K_{SV}^{app}$  is the apparent intensity SV quenching constant and  $K_{SV}$  is the true SV quenching constant.  $\beta$  varies from 1.000 for measurements made under optically dilute conditions to  $(\epsilon_{DQ}/\epsilon_D)$  for optically dense solutions.  $\epsilon$  is the molar extinction coefficient, and the subscript DQ and D represent values for the association pair and donor, respectively, taken at the excitation wavelengths. Equation 1 holds if the donor concentration is much less than  $[Q]$ , which is satisfied in our experiments.

From the limiting value of  $K_{SV}^{app}$  at low concentrations of  $\text{CuSO}_4$  in  $\text{O}_2$ -saturated solutions,  $K_{SV}^{\text{O}_2} + \beta K_{eq} \sim 325 \text{ M}^{-1}$ . Since  $K_{SV}^{\text{O}_2} = K_{SV}^{\text{N}_2}/6.15 = 55 \text{ M}^{-1}$ ,  $\beta K_{eq} \sim 270 \text{ M}^{-1}$ . Solid curve D is calculated from these two values and eq 1. Using  $\beta K_{eq}$  and  $K_{SV}^{\text{N}_2}$ , curve B is obtained. In both cases there is virtually perfect agreement between the  $\text{N}_2$  and  $\text{O}_2$  saturated results and the theoretical curves. It should be stressed that these two curves are computed only from  $K_{SV}^{\text{N}_2}$ ,  $K_{SV}^{app}$  for  $\text{O}_2$  saturated solutions at low concentrations of quencher and the  $\text{O}_2$  dependence of  $\tau$ . It thus seems probable that the combination of diffusional and static mechanisms is the only reasonable one which can successfully account for all data.

Since our solutions were optically dilute ( $A \sim 0.02$ ),  $\beta = 1$ , and  $K_{eq} \sim 270 \text{ M}^{-1}$ . Thus,  $K_{eq}$  was obtained without recourse to any of the conventional techniques for measuring  $K_{eq}$ 's.

As an independent check of the existence of static quenching, we then monitored the absorption spectra of solutions containing both donor and  $\text{CuSO}_4$ . The  $\text{Ru}(\text{phen})_2(\text{CN})_2$  CT band moved  $\sim 10 \text{ nm}$  to higher energy on addition of  $\text{Cu}^{2+}$  ( $1.6\text{--}16 \times 10^{-3} \text{ M}$ ), which demonstrates association. No isosbestic points were observed, however, which suggests formation of both a 1:1 and 2:1 copper-ruthenium adduct.

The most reasonable mechanism of association is coordination of  $\text{Ru}(\text{phen})_2(\text{CN})_2$  to the  $\text{Cu}^{2+}$  through the free end of the CN. Several lines of evidence support this. Only substitutionally labile species ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$ ) statically quench  $\text{Ru}(\text{phen})_2(\text{CN})_2$ .<sup>8</sup> Also other neutral ruthenium(II) complexes without coordinated CN only quench dynamically.<sup>9</sup> Finally, CN's can form bridging ligands between metal ions in solution and the solid state.<sup>10</sup> Since luminescence is certainly terminated by the presence of one bonded  $\text{Cu}^{2+}$ , our measured  $K_{eq}$  represents the first association constant. Our absorption data do not permit us to evaluate the second but suggest its value is not greatly different from that of the first.

The static quenching could be by nearest neighbors rather than by chemical association. The low concentration of quencher, however, makes this at most a minor pathway.<sup>11</sup>

(8) J. N. Demas, J. W. Addington, D. Diemente, and E. Harris, manuscript in preparation.

(9) J. N. Demas, D. Diemente, and J. Bowman, manuscript in preparation.

(10) D. F. Shriver, *Struct. Bonding (Berlin)*, **1**, 32 (1966).

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It should be noted that an expression functionally identical with eq 1 results when quenching occurs from both the emitting state and an upper state which is precursor to the emitting one. We rule this possibility out, since decay time measurements show that any upper state must have a decay at least  $10^2$  times faster than the emitting level. Thus, quenching of the upper level could not be significant under our conditions.

Schilt demonstrated the protonation of  $\text{Fe}(\text{bipy})_2(\text{CN})_2$  and  $\text{Fe}(\text{phen})_2(\text{CN})_2$  in solution.<sup>12</sup> Based on the blue shift of the absorption spectrum on protonation, he argued that  $\text{H}^+$  directly attacks the  $\text{Fe}^{2+}$  rather than the CN. The very similar spectral changes in the  $\text{Ru}(\text{phen})_2(\text{CN})_2\text{-Cu}^{2+}$  system suggest that this argument is incorrect, since the bulky  $\text{Cu}^{2+}$  cannot attach itself to the  $\text{Ru}^{2+}$  directly.

Our results clearly stress the importance of combining both  $\tau$  and  $\phi$  quenching data to obtain a full understanding of the photo and chemical processes in systems involving luminescent metal complexes. Also, these results demonstrate an unusual technique for studying equilibria involving transition metal complexes. We are currently constructing a nanosecond decay time apparatus to determine ion-pairing constants between metal complexes by these methods.

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(12) A. A. Schilt, *J. Amer. Chem. Soc.*, **82**, 3000 (1960).

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## Organic Reactions at High Pressure. Cycloadditions of Enamines and Dienamines<sup>1</sup>

Sir:

The use of very high pressures for preparative organic chemistry has been relatively little explored.<sup>2</sup> The pressure dependence of the rate constant of the reaction is  $\delta \ln k/\delta p = -\Delta V^\ddagger/RT$ . If  $\Delta V^\ddagger$ , the activation volume, is negative, *i.e.*, if the formation of the activated complex from the reactants results in overall contraction, the rate  $k$  will increase with increasing pressure.<sup>2</sup> The effect of pressure on the rate of several Diels-Alder reactions has been determined and found to provide a large acceleration, the  $\Delta V^\ddagger$  being between  $-25$  and  $-38 \text{ cm}^3/\text{mol}$ .<sup>3</sup>

We would like to report our results which show that high pressure (8–20 kbars, 7895–19,738 atm) is a valu-

(1) This research was supported by National Science Foundation Grant No. GP-8700.

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