range from 86.2 to 88.8°,[12] and the possibility of such an effect has been noted[13] previously. Considerably smaller angles are found in the 16-electron $(CH_3NC)_6Pd_2^{2+}$ and in **2** as well as $K_4[Ni_2(CN)_6]$[14] and $[i\text{-}Pr_4N]_2[Pt_2Cl_4(CO)_2]$[15] which have angles of 76° and 82.7°, respectively. From these values we conclude that semibridging is more important in unsaturated metal–metal bonded species than in their electron-precise counterparts.

Further investigations of these compounds are in progress. Attempts to make longer metal center chains by reactions related to eq 3-5 are in progress. Complexes **1** and **2** are coordinatively unsaturated and preliminary investigations indicate that they are more reactive than the surprisingly robust[4,16] $(CH_3NC)_6Pd_2^{2+}$. For example, recrystallization of **1** and **2** can only be accomplished in the presence of excess ligands.

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Bimolecular Electron Transfer Processes of Electronically Excited Tris(2,2′-bipyridine)chromium(III)

Sir:

Recent reports on the facile electron transfer reactions of the lowest excited state of tris(2,2′-bipyridine)ruthenium(II), $(^3CT)Ru(bpy)_3^{2+}$,[1-10] have focused attention on the general problem of the redox properties of excited states of transition metal complexes.

Tris(2,2′-bipyridine)chromium(III), $Cr(bpy)_3^{3+}$, appears to be an ideal candidate for investigations on bimolecular excited-state processes. The lowest excited state of this complex, i.e., the metal-centered doublet state, $(^2MC)Cr(bpy)_3^{3+}$, is remarkably long lived in fluid solutions ($\tau = 53$ μs in aqueous deaerated solution at 25 °C) and can be conveniently monitored by means of the moderately efficient emission centered at 727 nm.[11] The complex is appreciably photostable in acidic solutions.[12] A recent communication by Bolletta et al.[13] has shown that the doublet state of $Cr(pby)_3^{3+}$ can be efficiently quenched by $Ru(bpy)_3^{2+}$. Since the energies of $(^2MC)Cr(bpy)_3^{3+}$ and $(^3CT)Ru(bpy)_3^{2+}$ are 13 800 and 17 100 cm^{-1}, respectively, energy transfer is forbidden in this system. Thus, the assumption was made that the quenching takes place via the thermodynamically allowed electron transfer from the quencher to the excited state of $Cr(bpy)_3^{3+}$.[13] Here we present the results of some flash photolysis experiments which provide direct evidence for the occurrence of electron transfer in the quenching of the $Cr(bpy)_3^{3+}$ doublet state.

Flash photolysis[14] of aqueous pH 3 solutions of $Cr(bpy)_3^{3+}$ gives rise to a transient absorption with maxima at 390 and 445 nm. The absorption decays by first-order kinetics with a lifetime of 47 μs, a value which compares well with the lifetime of the phosphorescent emission. The transient absorption can be assigned to a transition from the $(^2MC)Cr(bpy)_3^{3+}$ state to upper doublet states.[12]

The $Fe(H_2O)_6^{2+}$ ion is an efficient quencher of the $Cr(bpy)_3^{3+}$ phosphorescence ($k_q = 4.1 \times 10^7$ M^{-1} s^{-1} at $\mu = 1$). When pH 3 solutions containing 5×10^{-5} M $Cr(bpy)_3^{3+}$ and 2×10^{-3} M $FeSO_4$ are flashed, the expected quenching of the doublet absorption is observed and a new transient absorption is formed with maxima at 470 and 560 nm. The spectrum of the new transient absorption matches closely the reported spectrum of $Cr(bpy)_3^{2+}$.[15] The formation of the reduced complex upon quenching of the doublet state is a clear proof of the occurrence of a mechanism involving electron transfer from the quencher to the excited complex (reaction 1).

$$(^2MC)Cr(bpy)_3^{3+} + Fe(H_2O)_6^{2+} \rightarrow Cr(bpy)_3^{2+} + Fe(H_2O)_6^{3+} \quad (1)$$

The $Cr(bpy)_3^{2+}$ absorption disappears after the flash by fast second-order[16] kinetics ($k_2 = 7.3 \times 10^8$ M^{-1} s^{-1} at $\mu = 0.2$) due to the thermal back-electron-transfer reaction (reaction 2), which involves a free energy change of −23.5 kcal/mol.

$$Cr(bpy)_3^{2+} + Fe(H_2O)_6^{3+} \rightarrow Cr(bpy)_3^{3+} + Fe(H_2O)_6^{2+} \quad (2)$$

A similar approach has been used with $Ru(bpy)_3^{2+}$ as a quencher of the $Cr(bpy)_3^{3+}$ doublet state. When solutions containing 1×10^{-4} M $Cr(bpy)_3^{3+}$ and 3.3×10^{-5} M $Ru(bpy)_3^{2+}$ (pH 3, $\mu = 0.2$) are flashed, the characteristic transient absorption of $Cr(bpy)_3^{2+}$ is again observed. In order to interpret this result, however, the peculiar quenching behavior of the system is to be taken into account. Bolletta et al. have shown[13] that $Ru(bpy)_3^{2+}$ is a good quencher of the $Cr(bpy)_3^{3+}$ ^2MC excited state ($k_q = 4.0 \times 10^8$ M^{-1} s^{-1} at $\mu = 0.2$), but that at the same time $Cr(bpy)_3^{3+}$ is an efficient quencher of the ^3CT excited state of $Ru(bpy)_3^{2+}$ ($k_q = 3.3 \times 10^9$ M^{-1} s^{-1} at $\mu = 0.2$). The solutions used in the flash experiment are such that both components absorb a significant fraction of the exciting light and each of the complexes significantly quenches the excited state of the other one. Thus, the observed $Cr(bpy)_3^{2+}$ formation could arise by several pathways, namely, reaction 3 followed by reaction 5, reaction 4 followed by reaction 6, or reaction 4 followed by reaction 7 and reaction 5.

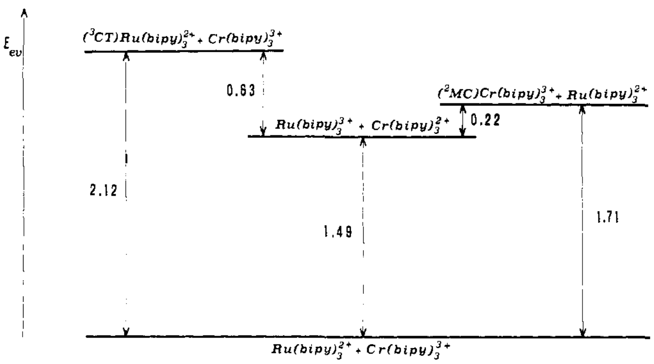

Figure 1. Energetics of the $Cr(bpy)_3{}^{3+}/Ru(pby)_3{}^{2+}$ system. The difference in SRP of the two couples gives the free energy of the redox products, while zero-zero transition energies are used for the two excited states. These excitation energies can be considered as free energies of excitation on the reasonable assumption that entropy changes associated with excitation are small.

$$Cr(bpy)_3{}^{3+} \xrightarrow{h\nu} \rightarrow (^2MC)Cr(bpy)_3{}^{3+} \tag{3}$$

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} \rightarrow (^3CT)Ru(bpy)_3{}^{2+} \tag{4}$$

$$(^2MC)Cr(bpy)_3{}^{3+} + Ru(bpy)_3{}^{2+} \rightarrow Cr(bpy)_3{}^{2+} + Ru(bpy)_3{}^{3+} \tag{5}$$

$$(^3CT)Ru(bpy)_3{}^{2+} + Cr(bpy)_3{}^{3+} \rightarrow Ru(bpy)_3{}^{3+} + Cr(bpy)_3{}^{2+} \tag{6}$$

$$(^3CT)Ru(bpy)_3{}^{2+} + Cr(bpy)_3{}^{3+} \rightarrow Ru(bpy)_3{}^{2+} + (^2MC)Cr(bpy)_3{}^{3+} \tag{7}$$

In order to discriminate between these possible pathways, flash experiments have been carried out using I^- as a selective scavenger of $(^2MC)Cr(bpy)_3{}^{3+}$. A concentration of 5×10^{-3} M I^- is sufficient to completely quench the emission of $Cr(bpy)_3{}^{3+}$. Flash experiments have shown that in these conditions the quenching of $(^2MC)Cr(bpy)_3{}^{3+}$ by I^- is not accompanied by the formation of any observable amounts of $Cr(bpy)_3{}^{2+}$.[17] When solutions containing 1×10^{-4} M $Cr(bpy)_3{}^{3+}$, 3.3×10^{-5} M $Ru(bpy)_3{}^{2+}$, and 5×10^{-3} M I^- are flashed, $Cr(bpy)_3{}^{2+}$ is still observed as a transient product, but in smaller amounts (about one half) than observed in the absence of I^-. Since complete scavenging of $(^2MC)Cr(bpy)_3{}^{3+}$ gives partial disappearance of the $Cr(bpy)_3{}^{2+}$ product, the conclusion is that both electron-transfer pathways, i.e., reactions 3 and 5, and reactions 4 and 6, take place in the $Cr(bpy)_3{}^{3+}/Ru(bpy)_3{}^{2+}$ system. The energetics of this system is shown in Figure 1. The thermal back-electron-transfer reaction (reaction 8),

$$Cr(bpy)_3{}^{2+} + Ru(bpy)_3{}^{3+} \rightarrow Cr(bpy)_3{}^{3+} + Ru(bpy)_3{}^{2+} \tag{8}$$

which involves a free energy change of −34.6 kcal/mol, has a bimolecular rate constant $k_8 = 2.6 \times 10^9$ M^{-1} s^{-1} as determined from the second-order decay of the $Cr(bpy)_3{}^{2+}$ transient.

The results obtained on the $Cr(bpy)_3{}^{3+}/Ru(bpy)_3{}^{2+}$ system demonstrate experimentally the electron-transfer mechanism proposed by Bolletta et al.[13] for the mutual luminescence quenching of these complexes. This system is remarkable in the fact that the same pair of high-energy products is obtained irrespective of the absorbing species. Actually, the reaction uses a wide spectral region of the exciting light and is efficient over a wide range of relative concentrations of the reactants.

The results described here show that the metal-centered doublet state of $Cr(bpy)_3{}^{3+}$ can act as a strong oxidizing agent. The extension of studies on excited-state electron-transfer process of coordination compounds by flash techniques seems to be worthwhile, especially in view of the relevance of these systems as catalysts in solar energy conversion.[18,19] In this regard, it might be pointed out that the $Cr(bpy)_3{}^{3+}/Ru(bpy)_3{}^{2+}$ system is capable of converting a considerable fraction of the absorbed light energy (Figure 1). It might also be interesting to notice that both of the primary photoproducts of this system have been independently found to cause decomposition of water, either by reduction ($Cr(bpy)_3{}^{2+}$)[20] or by oxidation ($Ru(bpy)_3{}^{3+}$).[18]

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Tri-μ_2-carbonyl-tris(η^5-cyclopentadienyl)-*triangulo*-trirhodium. A New, Improved Preparation and Some Observations on Its Dynamic Properties[1]

Sir:

Two isomers of $Cp_3Rh_3(CO)_3$ ($Cp = \eta^5$-C_5H_5), isolated after prolonged photolysis of $CpRh(CO)_2$, were shown by single-crystal x-ray diffraction to have structures **1**[2a] and **2**.[2b] These structures have figured prominently in discussions of trimetallic carbonyl clusters as models for solution structures[3] or for intermediates in carbonyl scrambling processes.[4,5] However, little information has been available concerning whether the rhodium trimers maintain the same structures in solution, whether they are fluxional, or to what extent they interconvert.[4,6,7] We have discovered a new preparation of $Cp_3Rh_3(\mu_2$-$CO)_3$ (isomer **1**) that, in providing **1** in convenient