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Photochemistry and Photophysics of Bis(terpyridyl) Complexes of Ru(II) in Fluid Solution. Evidence for the Formation of an η^2-Diphenylterpyridine Complex

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Abstract: The photochemical and photophysical properties of $Ru(dpt)_2^{2+}$, where dpt denotes 6,6″-diphenyl-2,2′:6′,2″-terpyridine, are described. The absorption maximum occurs at 477 nm in CH_2Cl_2 and is ascribed to a metal-to-ligand charge-transfer band. Excitation at 477 nm yields little or no detectable emission in CH_2Cl_2 at room temperature or in a 4:1 EtOH/MeOH glass at 77 K. Upon irradiation in CH_2Cl_2 at 25 °C with added SCN^-, $Ru(dpt)_2^{2+}$ undergoes photoanation. The quantum yield for the reaction is $(4.0 \pm 0.5) \times 10^{-3}$. Several possible structures for the photoproduct are considered, and on the basis of the available data, it is formulated as $Ru(dpt)(\eta^2\text{-dpt})(NCS)^+$. The photophysical properties of $Ru(dpt)_2^{2+}$ are compared with other Ru(II) bis(terpyridyl) complexes, and we conclude that the extremely short lifetimes of these complexes cannot be explained by solvent interactions with the metal center. A kinetic scheme is proposed in which nonradiative decay occurs via a d–d excited state which is prone to undergo ligand substitution processes. The model is used to explain the disparate behavior of three different complexes of Ru(II) involving terpyridine-based ligands.

The electronic excited states of pseudooctahedral complexes of Ru(II) with heteroaromatic ligands such as 2,2′-bipyridine (bpy) have been extensively studied.[1-3] One question which has yet to be answered satisfactorily is why the excited-state lifetime of $Ru(trpy)_2^{2+}$, the 2,2′:6′2″-terpyridine complex, is so short in fluid solution. Whereas the excited state lifetime of $Ru(bpy)_3^{2+}$ is 600 ns in aqueous solution,[3] the lifetime of $Ru(trpy)_2^{2+}$ is <5 ns under comparable conditions.[4,5] In marked contrast, the trpy complex has the longer lifetime in an alcohol glass at 77 K (10.7 vs 5.2 μs).[6] Evidently a nonradiative decay channel exists in fluid solution which is very effective in the case of the trpy complex. One suggestion has been[4] that $Ru(trpy)_2^{2+}$, like its Cr(III) counterpart,[7] has a relatively "open" structure which renders the excited state very susceptible to solvent interactions. Solvent-induced quenching is well estabilshed in related Cu(I) systems and has been attributed to exciplex formation.[8-10] We have found that in the latter systems, the introduction of bulky substituents adjacent to the nitrogen donors of the heteroaromatic ligands tends to prolong the excited state lifetimes, apparently because the substituents shield the metal center from solvent interactions.[9,10] In order to test whether this effect extends to ruthenium terpyridyls, we have synthesized $Ru(dpt)_2^{2+}$, where dpt denotes 6,6″-diphenyl-2,2′:6′,2″-terpyridine. The photochemical and photophysical properties of the complex are the subject of this report.

Table I. Selected Properties of Ruthenium Terpyridines[a]

complex[b]	λ_{max}^{abs}, nm	ϵ, $M^{-1}\ cm^{-1}$	λ_{max}^{em}, nm	τ, ns	ref
$Ru(trpy)_2^{2+}$	470	16 100		<5	*c*, *h*
$Ru(tro)_2^{2+}$	560	8 200			*c*
	490	24 200			
$Ru(tsite)_2^{2+}$	500	38 400	*g*	200	*c*
$Ru(bpy)(trpy)(PTZ)^{2+}$	450	*g*	608	480	*d*, *e*
$Ru(dpt)_2^{2+}$	477	6 850			*f*

[a] Unless otherwise indicated the measurements are at room temperature in alcohol solution. [b] Ligand abbreviations: tro = 4′-phenyl-2,2′:6′,2″-terpyridine; tsite = 4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine; PTZ = phenothiazine. [c] Stone, M. L.; Crosby, G. A. *Chem. Phys. Lett.* **1981**, *79*, 169–173. [d] Solvent is water. [e] Root, M. J.; Deutsch, E.; Sullivan, J. C.; Meisel, D. *Chem. Phys. Lett.* **1983**, *101*, 353–356. [f] This work. Solvent is CH_2Cl_2. [g] Not reported. [h] References 4 and 5.

Experimental Section

Materials. $RuCl_3{\cdot}3H_2O$, 2,2′:6′,2″-terpyridine, and phenyllithium were purchased from Aldrich. The dpt ligand was synthesized as previously reported.[11] $[Ru(trpy)_2](PF_6)_2$ and $[Ru(dpt)_2](ClO_4)_2$ were prepared by a modification of the method of Braddock and Meyer.[12] $[(n\text{-}Bu)_4N]SCN$ was prepared from the bromide (purchased from Aldrich) by a standard ion-exchange method[13] and was recrystallized from ethyl acetate and ether. Spectroscopic-grade solvents were used in the absorption, luminescence, and photolysis studies.

Methods. The sample was deoxygenated by repeated freeze–pump–thaw cycles, thermostated at 25 °C, and stirred continuously throughout photolysis. The incident light intensity was determined by ferrioxalate actinometry.[14] Since optically dense solutions were used and since we irradiated at an isosbestic wavelength (432 nm), the rate of product formation was described by eq 1, where ϕ is the quantum efficiency of the photoreaction. C_P, C_R, and C_T denote the photoproduct, reactant,

$$dC_P/dt = \phi\ (I_0/V)(C_R/C_T) \qquad (1)$$

and total ruthenium concentrations, respectively, at time t, I_0 is the light flux in einsteins per second, and V is the photolyte volume. The quantum efficiency ϕ was obtained from a plot of the integrated rate expression (eq 2). At time t the formation of product was monitored at 670 nm

$$C_TV[\ln\ (C_T) - \ln\ (C_T - C_P)] = \phi tI \qquad (2)$$

(ϵ = 950 $M^{-1}\ cm^{-1}$), where the parent complex evinced no significant absorbance. The results were in excellent accord with the form of eq 2. Samples used for luminescence measurements were also deoxygenated by repetitive freeze–pump–thaw cycles. Luminescence lifetimes were secured from the slopes of standard log plots.

Instrumentation. Absorption measurements were made with a Cary 17D spectrophotometer, and the luminescence studies were conducted

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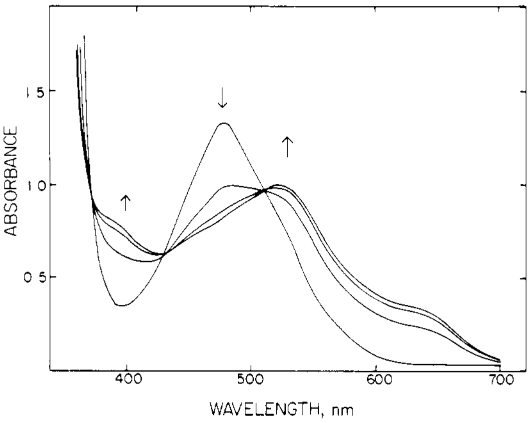

Figure 1. Sequential absorption spectra of $Ru(dpt)_2^{2+}$ upon irradiation in CH_2Cl_2 with excess SCN^-. Time intervals are 0, 10, 20, and 30 min and $[Ru] = 1.68 \times 10^{-4}$ M and $[SCN^-] = 1.51 \times 10^{-3}$ M. The arrows represent the direction of absorbance change for the major peaks.

with a Perkin-Elmer MPF-44B spectrofluorimeter. Temperature control was achieved with a Lauda K-2/RD circulating bath. Lifetimes were determined with a Princeton Applied Research Model 2100 N_2-pumped dye laser. Low-temperature measurements were obtained in a quartz Dewar. The photolysis apparatus has been described previously.[15] The infrared spectra of CH_2Cl_2 solutions were obtained with an IBM IR/32 Fourier transform spectrophotometer. The ^1H NMR spectrum of the photoproduct in CD_3CN was obtained with a Bruker 200-MHz Fourier transform spectrometer.

Results and Discussion

Spectral Properties. $Ru(dpt)_2^{2+}$ exhibits an absorption maximum in CH_2Cl_2 at 477 nm which by analogy with related polypyridine complexes (Table I) can be assigned to a d–π^*, metal-to-ligand charge-transfer transition(s). No significant luminescence could be detected from $Ru(dpt)_2^{2+}$ in CH_2Cl_2 solution at room temperature or in a 4:1 ethanol/methanol glass at 77 K. By comparison, the quantum yield of luminescence from $Ru(dpt)_2^{2+}$ at 77 K must be at least 1000 times smaller than that of $Ru(trpy)_2^{2+}$. For several ruthenium complexes exhibiting significant interligand steric interactions, the luminescence efficiencies have been observed to be quite weak, especially in fluid solution.[16-18] Space-filling models suggest that significant interligand steric repulsions exist in $Ru(dpt)_2^{2+}$ as well. The connection between the steric effects and the luminescence efficiency will be discussed after phtochemical studies of the complex are described.

Photochemistry. $Ru(dpt)_2^{2+}$ is photoreactive in some solvents but is quite stable to light in pure CH_3OH or CH_2Cl_2 when perchlorate is the counterion. In the presence of more nucleophilic anions like Br^- and SCN^-, CH_2Cl_2 solutions of the complex are stable in the dark over extended periods of time, but they are photosensitive. Figure 1 shows the absorbance changes which occur when SCN^- is the anion. The observation of isosbestic points at 373, 432, and 512 nm is consistent with the formation of a single photoproduct which is itself photostable.[19] In a solution with a mole ratio of thiocyanate to $Ru(dpt)_2^{2+}$ of 10:1, the quantum yield of the photoreaction is $(4.0 \pm 0.5) \times 10^{-3}$.

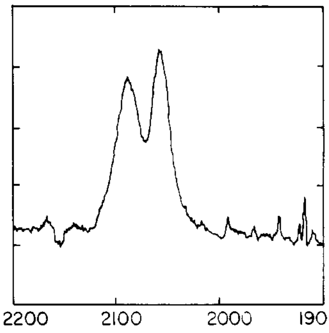

Figure 2. FTIR absorption spectrum of the completely photolyzed sample. The two peaks represent coordinated (2088 cm^{-1}) and uncoordinated SCN^- (2056 cm^{-1}).

Spectral changes qualitatively similar to those in Figure 1 occur upon the photoanation of $Ru(bpy)_3^{2+}$[20] and Ru(2,2′-bipyrazine)$_3^{2+}$.[21] In these systems a stepwise loss of a heteroaromatic ligand occurs, yielding, for example, *cis*-$Ru(bpy)_2X_2$, where X^- is a halide or a pseudohalide such as SCN^-. A related reaction occurs with $Ru(dpt)_2^{2+}$, but the complete dissociation of a dpt ligand does not occur. This is apparent from Figure 1 since a much greater loss of intensity, approximately 50% of the total charge-transfer absorbance, would attend such a reaction.[22] Moreover, infrared studies indicate that only one thiocyanate is bound per ruthenium atom in the photoproduct. Figure 2 shows part of the infrared absorption spectrum of an exhaustively photolyzed solution which originally contained 2 mol of SCN^- per mol of $Ru(dpt)_2^{2+}$. Prior to photolysis, only the band at 2056 cm^{-1} (characteristic of uncoordinated SCN^-) was present. The band at 2088 cm^{-1} grew in during photolysis and is assigned to coordinated SCN^-, most likely the N-bonded form.[23] Analysis of the difference spectrum revealed that 57% ± 5% of the thiocyanate remained unbound.

The obvious possibilities for the photoproduct are $Ru(dpt)_2(NCS)^+$ and $Ru(dpt)(\eta^2\text{-dpt})(NCS)^+$, where η^2 denotes a bidentate dpt group bound to Ru(II) via the 1 and 1′ nitrogens. Other structures consistent with the binding of one anion per ruthenium center are $Ru(\eta^2\text{-dpt})_2(NCS)L^+$, where L is a coordinating impurity such as H_2O, and a binuclear complex with two SCN^- groups bridging $Ru(\eta^2\text{-dpt})_2^{2+}$ units. These structures can be dismissed becaused we observed isosbestic points during photolysis and because identical spectra were obtained when solutions with 2:1 and 10:1 SCN^--to-ruthenium ratios were irradiated. In view of the steric congestion about ruthenium, vide infra, the seven-coordinate structure $Ru(dpt)_2(NCS)^+$ is also implausible. For these various reasons and in light of previous work, $Ru(dpt)(\eta^2\text{-dpt})(NCS)^+$ is the only reasonable product formulation. This structure is also compatible with the ^1H NMR results. While the NMR spectrum of the photoproduct is too complex for detailed analysis, it clearly reveals that the dpt groups are bound in an asymmetric environment. The case for the proposed photoproduct is further bolstered by a recent structure report which establishes a precedent for a bidentate terpyridine linkage to Ru(II).[24] In $RuBr_2(CO)_2(\eta^2\text{-trpy})$, the coordination geometry is pseudooctahedral, with the bromide ligands above and below the equatorial plane defined by the carbonyl ligands and the coordinated nitrogen atoms. For steric reasons the plane of the unbound pyridyl group is rotated appreciably out of the equatorial plane and is approximately parallel to the neighboring CO ligand. The steric requirements of N-bonded SCN^- are no worse than those of CO; hence $Ru(dpt)(\eta^2\text{-dpt})(NCS)^+$ is a viable structure.

Photoanation is at least 100 times less efficient in the case of $Ru(trpy)_2^{2+}$. Small spectral changes are observed upon irradiating

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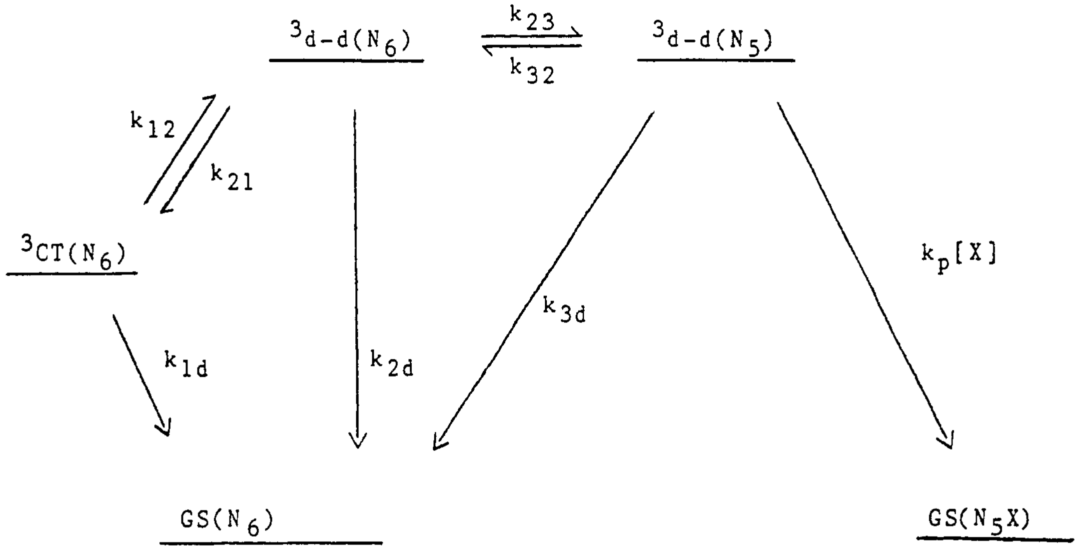
Scheme I



the latter in the presence of Br$^-$ or SCN$^-$, but they occur primarily during the first several minutes of photolysis. Sample impurities are an unlikely explanation for this behavior since independent preparations of Ru(trpy)$_2^{2+}$ gave similar results. Apparently, a photostationary state is achieved after a small amount of Ru(trpy)$_2^{2+}$ has reacted.

Excited-State Considerations. The results discussed above tend to rule out the notion that the open structure of Ru(trpy)$_2^{2+}$ permits solvent interactions which limit the excited-state lifetime. The phenyl substituents of dpt should effectively interfere with solvation in the pockets between ligands; yet, there is no indication of any enhancement of the d–π^* excited-state lifetime. Therefore, alternative explanations for the efficient nonradiative decay must be considered.

Early on, Fink and Ohnesorge suggested that the anomalously weak emission from Ru(trpy)$_2^{2+}$ might be due to the equilibration of the CT state with high-spin d–d states.[25] Rapid intersystem crossing to the ground state was assumed to be an intrinsic property of the paramagnetic d–d states. Another interpretation was offered by Lytle and co-workers based on ^{1}H NMR studies. They inferred that the terminal pyridines of trpy were relatively weakly bound in Ru(trpy)$_2^{2+}$ and subject to photodissociation in solution.[26] Presumably photodissociation could occur directly from the CT state. Reattachment to give the fully chelated form would complete a photochemical route to efficient nonradiative decay. More recently, Meyer and co-workers have suggested that the unfavorable bite angles associated with the trpy ligand result in a relatively weak ligand field in Ru(trpy)$_2^{2+}$ such that low-lying d–d states are available to quench the CT states.[27] Some indication of the deviation from idealized octahedral geometry can be inferred from the structure of Cr(trpy)$_2^{3+}$, where the N–Cr–N angles involving trans nitrogens are $\leq 160°$.[7] Similar angles are observed in a series of cobalt complexes.[28] As we will show, the model which assumes that the ^{3}CT excited state can be quenched by a neighboring ^{3}d–d state is capable of rationalizing a wide body of data involving ruthenium terpyridyls.

By now the quenching of CT emission by neighboring d–d states in Ru(II) complexes is a well-recognized phenomenon.[18,29,30] In Scheme I, we present an energy level scheme which is appropriate for the trpy system and which is analogous to one proposed by Meyer and co-workers for Ru(bpy)$_3^{2+}$.[31] The states are labeled according to the electronic configuration; e.g., GS denotes ground state, as well as the donor set about the ruthenium. One excited state, the dissociated d–d state, is assumed to be pentacoordinate.[32] In the photoanation product a terpyridine nitrogen is displaced by another ligand, e.g., thiocyanate. The k_{3d} step is meant to account for both the direct reattachment of the pyridine nitrogen and the possibility of a two-step pathway via a solvated intermediate. The kinetics of this scheme are quite complex,[33] and we illustrate the possibilities by discussing three specific cases: Ru(trpy)$_2^{2+}$, Ru(dpt)$_2^{2+}$, and Ru(tsite)$_2^{2+}$.

If the unfavorable bite angles of the trpy system moderate the ligand-field strength and cause ^{3}d–d states to be thermally accessible, the k_{12} step becomes important. Conversion to a d–d state involves the population of a σ antibonding orbital and, therefore, changes in the molecular geometry. If the distortions are large, ligand dissociation (the k_{23} step) and/or strong coupling to the ground-state surface[34] can give rise to efficient radiationless decay. Under these conditions, the k_{2d} and k_{3d} processes can compete with the k_{21} step, and quenching of the ^{3}CT emission can occur as in Ru(trpy)$_2^{2+}$. The quenching may be much less important in a low-temperature glass where the k_{12} step may be impaired. Note that there are two distinct contributions to the barrier to the k_{12} step. One is the thermodynamic energy separation between the ^{3}CT and the ^{3}d–d states. This factor alone may explain why the quenching in Ru(trpy)$_2^{2+}$ is less important at low temperatures where the average thermal energy is decreased. In addition there is an activation energy associated with the structural reorganization. This can be substantial in a rigid matrix even if the state-to-state separation is small.

The case of Ru(dpt)$_2^{2+}$ is similar except that the CT emission is negligible even in a low-temperature glass. Space-filling models suggest that the phenyl substituents give rise to interligand steric repulsions which further weaken the ligand field. As a result, the ^{3}d–d state may fall significantly below the ^{3}CT state so that CT emission is quenched at all temperatures. The same repulsions could explain why photoanation is more efficient in the dpt complex. The anation step is important only if it competes with ring closure in the pentacoordinate excited state. This is likely

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[33] In fact the first-order rate constant written k_p[X] is oversimplified. If the reaction proceeds with rate constant k from a simple ion pair with formation constant K, the rate expression is $kK[X]/(1 + K[X])$ and, at high [X], can be independent of X.

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in the case of $Ru(dpt)_2^{2+}$ where steric effects are expected to hinder the k_{32} and k_{3d} steps. Since SCN^- falls high in the spectrochemical series and since the CT bands of the photoproduct are red-shifted, the gap between the ^{3}d–d state and the ^{3}CT state of the photoproduct is likely to be enhanced over that of $Ru(dpt)_2^{2+}$. In line with this reasoning, the isothiocyanate complex is hardly photoreactive; it exhibits an emission at 77 K which maximizes at 767 nm (uncorrected) and has a lifetime of ca. 2 μs.

The case of $Ru(tsite)_2^{2+}$ is interesting because it is a reasonably good emitter in fluid solution at room temperature (Table I). The 4,4′ and 4″ phenyl substituents are unlikely to affect significantly the energy of the ^{3}d–d state, but they undergo mesomeric interactions with the terpy moiety and therefore could influence the energy of the ^{3}CT state. Indeed, from the absorption data in Table I, it appears that the CT maximum occurs at lower energy in the tsite complex. Moreover, the mesomeric effect may be enhanced in the thermally equilibrated excited state where the ligand assumes radical anion character. Stabilization of the ^{3}CT state relative to the ^{3}d–d state would increase the barrier to the k_{12} step and enhance the lifetime of the CT excited state.

Although Scheme I has been applied only qualitatively, it seems capable of explaining all the available results pertaining to $Ru(trpy)_2^{2+}$ derivatives. As an alternative, one might invoke a model which assumes a single excited state of mixed CT and d–d character. Variations in the series would then be attributed to differences in the proportion of d–d character and/or the activation energy associated with the dissociative step. The multiple state model is preferred because of the diverse observations which show that these states often coexist and mutually determine the photochemical and photophysical properties of related d^6 complexes.[35-39]

Acknowledgment. This work has been supported through Grant CHE 81-05003 from the National Science Foundation. The Purdue group would like to thank Charles J. Cameron for assistance in obtaining the photoproduct infrared spectrum.

Registry No. $Ru(dpt)_2^{2+}$, 94619-67-7; $Ru(dpt)(\eta^2\text{-dpt})(NCS)^+$, 94619-68-8; SCN^-, 302-04-5.

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Quenching Studies of $^*Cu(dpp)_2^+$. Evidence for Competitive Electron-Transfer and Energy-Transfer Quenching by $Cr(acac)_3$ Derivatives

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Abstract: The kinetics of quenching $^*Cu(dpp)_2^+$, the ^{3}d–π* excited state of $Cu(dpp)_2^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline), by a series of $Cr(acac)_3$ derivatives and a series of nitroaromatics have been studied in CH_2Cl_2 solution at 20 °C. For the nitroaromatic compounds, the quenching rate falls off as the electrode potential of the quencher ranges below that of $^*Cu(dpp)_2^+$, consistent with an electron-transfer mechanism. The results were analyzed by a variation of the Marcus theory, and the self-exchange rate for the $Cu(dpp)_2^{2+}/^*Cu(dpp)_2^+$ system was estimated to be 8×10^9 M^{-1} s^{-1}. The Cr(III) quenchers span a much wider range of electrode potentials and are also capable of undergoing energy-transfer quenching via the low-lying doublet excited states. As a result the quenching rate constant exhibits a more complex dependence on the free energy of electron-transfer quenching. In the exergonic region, the rate plateaus at the diffusion limit; as electron-transfer quenching becomes endergonic, the rate initially decreases and then levels off again at ca. 10^7 M^{-1} s^{-1}. This behavior is explained as a changeover from electron-transfer to energy-transfer quenching where the latter process occurs at a roughly constant rate throughout the series. When electron-transfer quenching is prominent, the average self-exchange rate for the Cr(III)/Cr(II) couples is estimated to be 2×10^9 M^{-1} s^{-1}, suggesting that the Cr(II) forms are low spin. The utility of $^*Cu(dpp)_2^+$ as a redox reagent and novel aspects of the homologous series of $Cr(acac)_3$ derivatives as quenchers are discussed.

There is continuing interest in the photochemical and photophysical properties of charge-transfer (CT) excited states of transition-metal complexes, partly because such states have been found to be useful in various schemes for energy conversion and fuel formation.[1,2] The long-lived charge-transfer excited state(s) of $Ru(bpy)_3^{2+}$, where bpy denotes 2,2′-bipyridine, has been studied in great detail, especially by the use of quenching methods.[2-6] It is prone to electron-transfer quenching, and the redox properties of the state are well established.[7-9] Defining the scope and the limitations of such excited-state reagents depends upon the characterization of many more systems. One of the aims of the present work has been to characterize the redox properties of the d^{10} complex $Cu(dpp)_2^+$ (dpp denotes 2,9-diphenyl-1,10-phenanthroline), an ion recently found to exhibit a long-lived CT excited state in CH_2Cl_2 solution.[10] Here we report that various

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