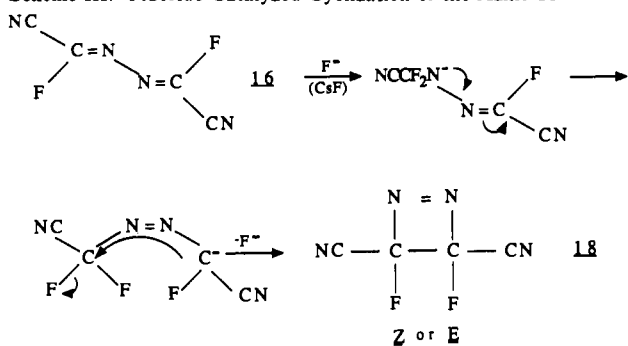


Scheme III. Fluoride-Catalyzed Cyclization of the Azine 16



compounds could be isolated. The results are summarized in Table V. High pressure decreased the yields of coupled products and led to greater formation of nonvolatile liquid and solid residues (presumably polymeric).

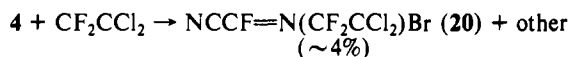
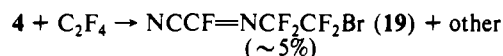
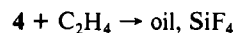
Both **16** and **17** were readily identified by their simple but indicative IR and NMR spectra and large parent ions in their mass spectra. The chemical shifts are reasonable for compounds of this structure, and the single resonance for each indicates only one of two possible geometric isomers is formed in each case, presumably *Z,Z* for **16** and *E* for **17**.¹⁸

Compound **16** is an unusual example of a conjugated system of double and triple C—N bonds. When **16** was condensed onto CsF at $-196\text{ }^{\circ}\text{C}$ and warmed to $22\text{ }^{\circ}\text{C}$, it underwent a rapid reaction (90% of **16** was absorbed by the CsF turning the CsF red-brown) with loss of the $\sqrt{\text{C}=\text{N}}$ at 1658 cm^{-1} in the IR spectra of the volatile product and a shift in the single fluorine resonance from -70.4 to -80.2 ppm. The mass spectrum exhibits a large parent ion in the CI at m/z 143 (MH^+) identical with that of **16**, but the fragmentation pattern is much different. We explain this result on the basis of a fluoride-catalyzed cyclization of **16** to **18**, as shown in Scheme III.^{19,20} **18** can exist as the *E* or *Z* isomer.

- (18) See refs 3 and 9. See also: Perfluorohalogeno-Organic Compounds. *Gmelins Handbuch der Anorganische Chemie*, 8th ed., Springer Verlag: West Berlin, 1980; Part 8.
- (19) The internal nucleophilic displacement of fluoride ion from a saturated carbon is unusual, but precedent for such reactions in cyclizations exists: Chambers, R. D.; Lindley, A. A.; Philpot, P. D.; Fielding, H. C.; Hutchison, J.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 1* 1979, 214.
- (20) The related compound $\text{CF}_2=\text{N}-\text{N}=\text{CF}_2$ also reacts rapidly with CsF to give a brown oil and solid which has not been characterized (Ogden, P. H. *J. Chem. Soc. C* 1971, 2920). The known cyclic compound $\text{CF}_2\text{N}=\text{NCF}_2$ is apparently not formed in the latter reaction but is readily prepared from $(\text{CN})_2$ and AgF_2 which might be mechanistically similar to the formation of **18** from **16** (Emeleus, H. J.; Hurst, G. L. *J. Chem. Soc.* 1962, 3021).

Both isomers should exhibit only a single resonance in the ^{19}F NMR spectrum, and the presence of only one signal in the observed spectrum indicates that only one of the possible isomers is present. However, the configuration cannot be determined from the available data.

Finally, reactions of **4** with alkenes were carried out to see if this compound would undergo addition reactions as observed for other bromoimines.^{3,17} Thermal reactions were carried out with C_2H_4 , C_2F_4 , and CF_2CCl_2 by combining equimolar amounts of the reactants in a 100-mL glass reactor in the dark at $80\text{ }^{\circ}\text{C}$. This procedure gave only traces of molecular adducts, and decomposition and polymer oils were the main products. At $22-25\text{ }^{\circ}\text{C}$ the results were the same for C_2H_4 after 1 day, but C_2F_4 and CF_2CCl_2 showed small amounts of the adducts after 11 and 24 days, respectively.



These products were only identified by IR spectroscopy and MS, and the regioisomer formed in the case of CF_2CCl_2 was not determined. The low yields of these additions compared to previous work with $\text{CF}_2=\text{NX}$ (Cl, Br) and $\text{R}_2\text{CF}=\text{NBr}$ reactions with a variety of alkenes must be due in part to the inherent tendency of **4** to polymerize under radical conditions, as shown by the photolysis of **4**.

Summary

The selective bromo- and chlorofluorination of cyanogen using $\text{CsF}/\text{Cl}_2\text{Br}_2$ has been demonstrated. Bromine forms only the bromoimines, whereas Cl_2 yields predominantly the dichloroamines. By selective control of reaction conditions, the stepwise oxidation of CN groups in cyanogen can be achieved. The substitution of Cl by Br and/or the bromofluorination of $\text{NCCF}_2\text{NCl}_2$ is a complex reaction resulting in 11 identifiable structural isomers of the possible bromo- and chlorofluorination products of cyanogen. Photolysis reactions of selected haloimine and haloamine derivatives of cyanogen provide routes to novel azines and azo compounds which are C-fluorinated derivatives of the dimer of cyanogen.

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Phenyl Substituents and Excited-State Lifetimes in Ruthenium(II) Terpyridyls

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Introducing phenyl substituents in the 4-, 4', and 4''-positions, para to the nitrogens, markedly enhances the excited-state lifetime of $\text{Ru}(\text{trpy})_2^{2+}$, where trpy denotes 2,2':6',2''-terpyridine. The aryl groups conjugate with the low-lying π^* orbital of terpyridine and thereby stabilize the emissive charge-transfer excited state relative to a thermally accessible $^3\text{d-d}$ excited state that provides an efficient means of decay to the ground state. The barriers to deactivation via this channel are estimated to be 1500 cm^{-1} for $\text{Ru}(\text{trpy})_2^{2+}$, 2200 cm^{-1} for $\text{Ru}(4,4'\text{-dpt})_2^{2+}$, and 2300 cm^{-1} for $\text{Ru}(\text{tsite})_2^{2+}$, where 4,4'-dpt denotes 4,4'-diphenyl-2,2':6',2''-terpyridine, and tsite denotes 4,4',4''-triphenyl-2,2':6',2''-terpyridine.

Introduction

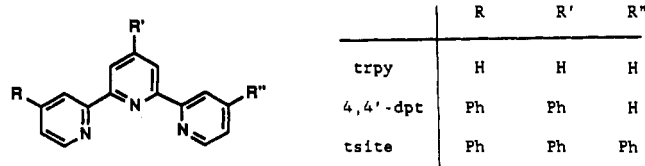
The metal-to-ligand charge-transfer (CT) excited states of polypyridine and polyimine complexes of ruthenium(II) can have

reasonably long lifetimes in fluid solution; hence, they have been the subject of a great deal of experimental work.¹⁻³ We have

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Chart I



been interested in the way in which aryl substituents influence the photochemical and photophysical properties of polyimine complexes of ruthenium(II) as well as copper(I).⁴⁻⁸ When the aryl substituents are introduced α to the imine nitrogens, steric effects dominate. In the case of the copper(I) systems, the aryl substituents inhibit solvent-induced quenching that occurs via exciplex formation, and the CT lifetime is strongly enhanced.^{4,7} In contrast, introduction of phenyl substituents in the 6,6'-positions of trpy (2,2':6',2''-terpyridine) dramatically reduces the lifetime of the ruthenium complex, even at 77 K.⁶ Kirchoff et al.⁶ rationalized this observation in terms of interligand steric interactions, which reduce the effective ligand field strength and destabilize the CT state relative to a comparatively short-lived $3d-d$ state. Excited-state deactivation as well as ligand substitution processes in ruthenium(II) polypyridines are often mediated by $3d-d$ excited states.^{2,3,9-12} This is also true of $Ru(trpy)_2^{2+}$, but the trpy complex is remarkably inert to photosubstitution chemistry because the chelate effect inhibits dissociation of the ligand.⁶ In an interesting paper, Stone and Crosby have reported that the introduction of phenyl substituents at the 4-, 4'-, and 4''-positions of trpy dramatically enhances the excited-state lifetime and the emission quantum yield.¹³ As there is considerable interest in the development of ruthenium(II) sensitizers that have respectable excited-state lifetimes and resist photosubstitution, we have examined the influence of the aryl substituents in more detail. In particular, we have carried out lifetime and emission studies of $Ru(trpy)_2^{2+}$, $Ru(4,4'-dpt)_2^{2+}$, and $Ru(tsit)_2^{2+}$, where 4,4'-dpt denotes 4,4'-diphenyl-2,2':6',2''-terpyridine and tsite denotes 4,4',4''-triphenyl-2,2':6',2''-terpyridine (Chart I). Our findings are described below.

Experimental Section

Materials. 4,4'-Diphenyl-2,2'-bipyridine, trpy, and a small quantity of tsite were purchased from G. F. Smith Chemical Co. and used without further purification. $[Ru(bpy)_3]Cl_2$ was obtained from the same source. 2-Bromopyridine was obtained from Aldrich and purified by a literature method.¹⁴ The 4,4'-dpt ligand was prepared from 4,4'-diphenyl-2,2'-bipyridine and 2-bromopyridine by a variation of the method of Lehn et al.¹⁵ and recrystallized from 1:1 $CHCl_3/C_2H_5OH$ (yield 5%). The identity of the product was established by the parent ion peak in the mass spectrum.

The method of Braddock and Meyer¹⁶ was used to prepare $[Ru(trpy)_2](PF_6)_2$ and $[Ru(4,4'-dpt)_2]PF_6$ from $RuCl_3 \cdot 3H_2O$ (Aldrich). The

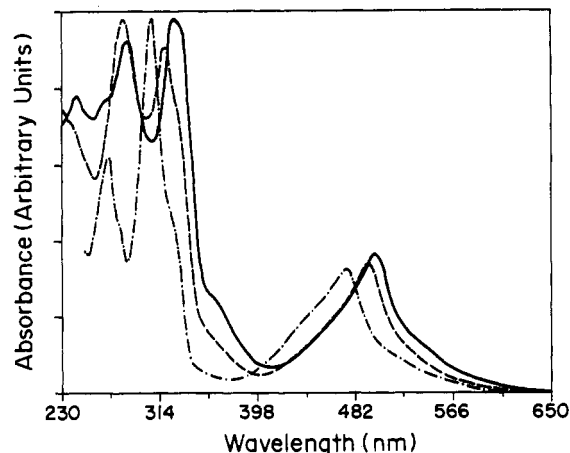


Figure 1. Normalized absorption spectra in 4:1 EtOH/MeOH at room temperature: $Ru(trpy)_2^{2+}$ (---); $Ru(4,4'-dpt)_2^{2+}$ (-.-.); $Ru(tsit)_2^{2+}$ (—).

Table I. Spectral and Photophysical Data

complex	λ_{max} , nm	ϵ , $M^{-1} cm^{-1}$	$10^4 \phi^a$
$Ru(trpy)_2^{2+}$	470	16 100 ^b	
$Ru(4,4'-dpt)_2^{2+}$	495	28 300 (± 300)	1.5
$Ru(tsit)_2^{2+}$	500	38 400 ^b	7.5

^a Emission quantum yield ($\pm 20\%$) in deoxygenated ethanol at 20 °C.

^b Reference 13.

trpy complex gave a satisfactory microanalysis. Since we isolated a very small quantity of the 4,4'-dpt complex, purity was established in the same way as for the tsite complex; vide infra. We prepared $[Ru(tsit)_2](PF_6)_2$ from $Ru(DMSO)_4Cl_2$ ¹⁷ by the following adaptation of the methods described by Davies et al.¹⁸ and Rawle et al.¹⁹ First, we added 2 equiv of $TiBF_4$ to a solution of $Ru(DMSO)_4Cl_2$ in DMSO under a N_2 atmosphere. We then warmed the solution to 60 °C and filtered out the $TiCl_4$ after reducing the volume. We added approximately 2.3 equiv of tsite, refluxed the solution overnight under N_2 , and loaded the resulting solution on a Bio-Rex 70 column (Bio-Rad) equilibrated with MeOH. We eluted a colored fraction with pure MeOH and discarded it. The main red fraction eluted with 0.01 M HCl in MeOH. After removing the solvent, we took up the residue in 1:1 $H_2O/MeOH$ and added aqueous KPF_6 to obtain a maroon solid. Recrystallization from aqueous alcohol gave 12 mg of crude solid. This material was dissolved in acetone/EtOH, and the solution was eluted through a Sephadex LH-20 column (Pharmacia). Finally, we repeatedly recrystallized the compound from H_2O /acetone until the excitation spectrum of the complex in deoxygenated alcohol matched the absorption spectrum. In addition, the absorption spectrum also matched that reported by Stone and Crosby.¹³ As a final confirmation of the identity of the tsite and 4,4'-dpt complexes, parent ion peaks at $m/z = 871.9$ ($[M]^+$) and $m/z = 1023.80$ ($[M]^+$) were observed in the FAB mass spectra of glycerol solutions containing $Ru(4,4'-dpt)_2^{2+}$ and $Ru(tsit)_2^{2+}$, respectively.

Methods. Solutions used for luminescence measurements were deoxygenated by repetitive freeze-pump-thaw cycles. Quantum yields in ethanol solution were calculated by the procedure of Parker and Rees²⁰ with $Ru(bpy)_3^{2+}$ as a reference ($\phi = 0.065$).^{21,22} In the variable-temperature studies all samples were allowed to equilibrate for 1 h after the sensor reached the desired temperature. The samples were dissolved in 4:1 EtOH/MeOH, and the emission was viewed through a $\lambda > 520$ nm long-pass filter. Coumarin 485 was used as the laser dye, and the excitation wavelengths were 490 nm for $[Ru(trpy)_2](PF_6)_2$ and 520 nm for the 4,4'-dpt and the tsite complexes. Luminescence lifetimes were secured from the slopes of standard log plots or by a least-squares fit of an exponential function to the decay trace.

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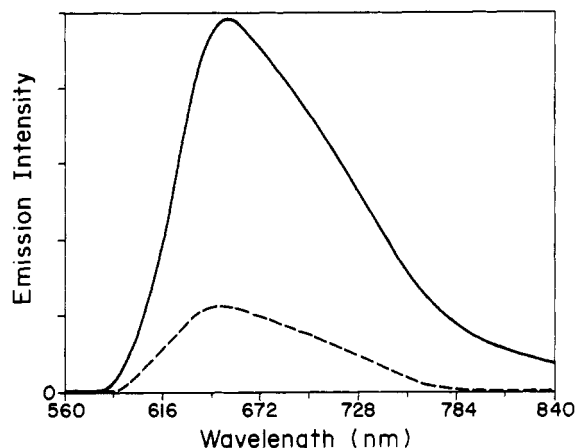


Figure 2. Corrected emission spectra in 4:1 EtOH/MeOH at room temperature: Ru(4,4'-dpt)₂²⁺ (---); Ru(tsitc)₂²⁺ (—).

Table II. Parameters from the Temperature-Dependent Lifetime Data

complex	$10^{-5}k_0$, s ⁻¹	$10^{-13}A_1$, s ⁻¹	ΔE_1 , cm ⁻¹	A_2 , s ⁻¹	ΔE_2 , cm ⁻¹
Ru(trpy) ₂ ²⁺	1.2	1.9	1500		
Ru(4,4'-dpt) ₂ ²⁺	1.1	3.0	2200	2.3×10^6	360
Ru(tsitc) ₂ ²⁺	1.1	1.6	2300	2.9×10^5	110

The temperature-dependent lifetime data were fit by a least-squares technique to the equation

$$1/\tau(T) = k_0 + \sum A_i \exp[-\Delta E_i/(RT)] \quad (1)$$

where parameters are defined below. In the analysis, the ΔE_i were refined by an iterative grid-search process, while, for each set of trial ΔE_i values, the optimum A_i parameters were obtained by a standard linear least-squares algorithm. The calculations were carried out on a micro-computer with the aid of a program written in APL. The weighting scheme for the residuals was based on the assumption that the relative precision of the lifetimes was constant.

Instrumentation. Absorbance measurements were obtained with a Cary 17D or a Perkin-Elmer Lambda 4C spectrophotometer. All emission spectra were run on an SLM Aminco SPF-500C spectrofluorometer. Lifetime data were collected with a N₂-pumped dye laser source and boxcar detector as described previously.²³ Low-temperature measurements were obtained with an Oxford Instruments Model DN 704 liquid-nitrogen cryostat or with the sample immersed in liquid nitrogen within a quartz finger dewar. For the work around ambient temperature the temperature of the sample was controlled with the aid of a Lauda K-2/RD circulating water bath. FAB spectra were run on a Kratos MS 50 mass spectrometer.

Results

The room-temperature absorption spectra of Ru(trpy)₂²⁺, Ru(4,4'-dpt)₂²⁺, and Ru(tsitc)₂²⁺ in 4:1 EtOH/MeOH are reported in Figure 1, and corrected emission spectra of the 4,4'-dpt and the tsitc complexes are reported in Figure 2. Spectral data and quantum yields for the pure compounds are compiled in Table I. Requiring that the excitation spectrum match the absorption spectrum proved to be the critical test of sample purity for Ru(4,4'-dpt)₂²⁺ and Ru(tsitc)₂²⁺. In order to obtain the correct excitation spectrum of the tsitc complex, many successive recrystallization steps were required, even though no detectable changes in the absorption spectrum occurred after the first few iterations.

For all three complexes the emission lifetime increased at lower temperatures. The lifetime data and the fits to eq 1 are presented in Figure 3. Optimum-fit parameters are listed in Table II. Although Stone and Crosby reported a lifetime of 200 ns for Ru(tsitc)₂²⁺ in 4:1 EtOH/MeOH at room temperature,¹³ we calculated a lifetime of 4 ns from an extrapolation based on eq 1. We cannot account for this disparity, but one possibility is that

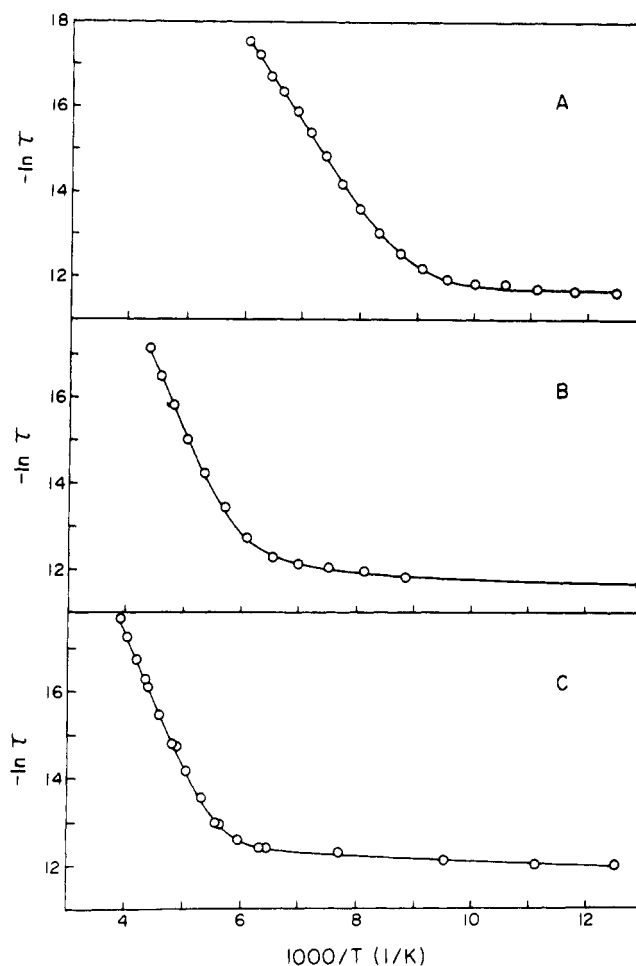


Figure 3. Temperature dependence of the rate of excited-state decay: (A) Ru(trpy)₂²⁺; (B) Ru(4,4'-dpt)₂²⁺; (C) Ru(tsitc)₂²⁺. The solid lines are weighted fits of experimental data to eq 1 with parameters listed in Table II.

a minor impurity, perhaps the one we observed with the blue-shifted excitation spectrum, may have confounded the previous room-temperature studies. The ratio of the quantum yield and our calculated lifetime gives a plausible estimate of 1.9×10^5 s⁻¹ for the radiative rate constant for the excited state of Ru(tsitc)₂²⁺. The fact that this value exceeds the k_0 value in Table II is probably an indication of the error involved in the extrapolation of the lifetime.

Discussion

Several groups have reported that there is no detectable emission from Ru(trpy)₂²⁺ in solution at room temperature.^{6,24,25} The problem is that the ³CT excited state is too short-lived ($\tau = 250$ ps²⁶) due to efficient, thermally activated decay via a proximal ³d-d state.^{6,24} Our results clearly reveal that introduction of phenyl substituents para to the nitrogens inhibits deactivation via the ³d-d excited state. Two effects may be involved. One is that the phenyl substituents may enhance the π -acceptor ability of the ligand²⁷ and thereby destabilize the ³d-d state. The other effect is a lowering of the energy of the ³CT state, as can be seen in the shifts in the absorption and emission maxima.

Some idea of the gaps separating the respective ³d-d and ³CT states can be ascertained from the ΔE_1 values in Table II.

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However, as discussed by Juris et al.,² the ΔE_1 value really defines the effective barrier between two states, not the thermodynamic energy difference. Equations 2 and 3 describe the minimal decay



scheme that allows for deactivation via a ${}^3\text{d-d}$ state, where the k_b step represents decay to the ground state (GS). Since the ${}^3\text{d-d}$ state is a short-lived state that is populated via a thermally activated process, it can be regarded as a steady-state species, in which case the rate constant for decay through this channel can be written as

$$k = k_a \frac{k_b}{k_{-a} + k_b} \quad (4)$$

Limiting cases of eq 4 have been discussed by Juris et al.² Case I behavior obtains when $k_b \gg k_{-a}$. In this limit, the rate constant for the relaxation process in question is effectively k_a . As can be seen from Table II, the ΔE_1 processes all have frequency factors of the order of 10^{13} s^{-1} , which are consistent with a simple barrier crossing (case I) process. Accordingly, ΔE_1 is taken to be the barrier associated with crossing from the ${}^3\text{CT}$ to the short-lived ${}^3\text{d-d}$ state. As with 2,2'-bipyridine complexes,²⁸ this barrier is enhanced by phenyl substituents located para to the donor nitrogens, but in the case of the trpy systems, the bulk of the effect appears to be associated with substitution at the 4'-position.

A second thermally activated decay channel can also be resolved for the 4,4'-dpt and the tsite complexes, where the onset of deactivation via the ${}^3\text{d-d}$ state is displaced to higher energy. A low barrier and a much reduced frequency factor are associated

with this channel. The magnitude of the frequency factor A_2 is consistent with internal conversion between nested energy surfaces, where the Franck-Condon factors for surface crossing are unfavorable. Additional low-lying ${}^3\text{CT}$ states are known to occur in polyimine complexes of ruthenium(II),²⁹ and there is evidence that they, too, facilitate relaxation from the emitting state.^{2,30} Therefore, the ΔE_2 process is attributed to relaxation via a neighboring ${}^3\text{CT}$ state. Equations analogous to eqs 2 and 3 can be written for this process as well, but a somewhat different kinetic model is appropriate. In view of the fact that a series of nested surfaces are involved and in view of the proximity of the two excited states, we assume that repopulation of the emitting ${}^3\text{CT}$ state is more facile than relaxation to the ground state; i.e., $k_{-a} \gg k_b$. In this limit, the two ${}^3\text{CT}$ states are thermally equilibrated, and

$$k_2 \approx k_b k_a / k_{-a} \quad (5)$$

(Note that this is a limiting case of eq 4, but eq 5 may be valid even if the steady-state assumption is inappropriate.) According to this model, the low frequency factor is associated with inter-system crossing from the proximal ${}^3\text{CT}$ state to the ground state. In line with this interpretation, A_2 is of the order of k_0 .

One of the assumptions in our analysis is that direct intersystem crossing from the lowest energy ${}^3\text{CT}$ state to the ground state is a temperature-independent process. The plateau regions in the plots presented in Figure 3 are consistent with this model. Below 20 K, however, Agnew et al. have shown that k_0 is also a temperature-dependent quantity.³¹

Acknowledgment. We wish to acknowledge Jon R. Kirchhoff, who carried out some initial studies of $\text{Ru}(\text{tsite})_2^{2+}$. This research was supported by Grant CHE-8719638.

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Emission and Photochemical Reactivity in Fluorescent Arene Complexes of Cyclopentadienylruthenium(II). Requirements for an Emissive $\text{CpRu}(\text{arene})^+$ Complex

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The syntheses and characterization of five new compounds that contain the CpRu^+ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) moiety bound to a highly fluorescent arene ligand are reported. Nonemissive complexes of the highly emissive laser dyes coumarin-7 (3-(2'-Benzimidazolyl)-7-(*N,N*-diethylamino)coumarin) and coumarin-30 (3-(2'-*N*-methylbenzimidazolyl)-7-(*N,N*-diethylamino)coumarin) in which the CpRu^+ group binds the dye benzimidazolyl arene ring were prepared and are compared to the structurally analogous, emissive complex of coumarin-6. Isomeric complexes of 9-phenylanthracene in which either the end anthracene ring or the substituent phenyl group is bound by the CpRu^+ moiety were prepared for comparison to the structurally analogous complexes of rubrene (5,6,11,12-tetraphenylnaphthacene). Room-temperature emission from fluid solutions of these $[\text{CpRu}(\eta^6\text{-arene})]^+$ complexes is only observed when the metal complex exhibits its lowest energy singlet absorption band at $\lambda_{\text{max}} \geq 480 \text{ nm}$. Reaction and emission quantum yields for the CpRu^+ complexes of coumarin-6, rubrene, and 9-phenylanthracene are reported and used to elucidate the electronic and structural requirements for emission from these compounds.

Introduction

For the past several years, our group has been studying various aspects of the thermal and photochemistry of the arene complexes of iron, ruthenium, and osmium. Most recently, our efforts in this area have turned towards the use of highly fluorescent arenes as the arene ligand in $[\text{CpRu}(\eta^6\text{-arene})]^+$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) com-

plexes. The emission associated with these ligands is very sensitive to changes that result from binding ruthenium to the arene π -system, making it an excellent spectroscopic probe of subtle changes in ruthenium–arene bonding. Consequently, we decided to investigate compounds of this type in the hope that they might yield spectroscopic evidence for reaction intermediates proposed to occur during the thermal¹ and photochemical² displacement

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