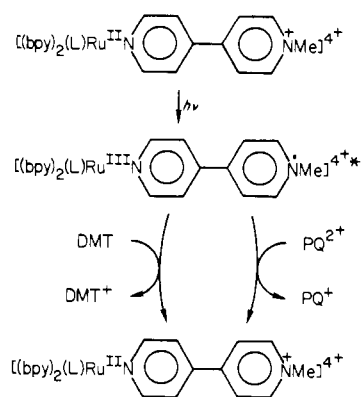


Scheme V



4). As in the case of $\text{Ru}(\text{bpy})_3^{2+}$, a series of one-electron transfer steps leads to net deactivation of the excited state with the production of separated redox products (Scheme V). However, given the properties of the pyridinium CT state, the electron- and electron-hole-loss steps occurs from different parts of the molecule. The directional symmetry of the CT state is transferred to the external redox environment with respect to the internal coordinates of the molecule.

Conclusions and Final Comments

The point of the experiments described here was to show that certain charge-transfer excited states have the innate

properties of an electronic-charge separation and the capability of undergoing facile electron and electron-hole loss which mimics the behavior expected for a photodiode at the molecular level. Further, by adding an external electron acceptor to the basic chromophore, as in the complex $[(\text{bpy})_2\text{Ru}(\text{NC}_5\text{H}_4\text{C}_3\text{H}_4\text{NCH}_3)_2]^{4+}$, it is possible to introduce an element of directed charge transfer to the large, transient intramolecular photopotential inherent in the excited state.

In terms of a device-type application, the systems studied here suffer from the inherent disadvantage of any homogeneous system—the isotropic, nondirectional character of the medium. There is no easy way to carry the directed CT character of the excited state to the redox products which appear following electron and electron-hole loss. In order to maintain the CT asymmetry, it will be necessary to imbed the ground-state precursors of appropriately designed excited states into a matrix array perhaps based on electrode attachment, membranes, or monolayer assemblies.

There is an additional point of fundamental interest that should be made. Based on the type of experiments described here and transient absorption measurements, it may be possible to demonstrate long-range, intramolecular electron transfer following optical excitation in properly designed systems and so to develop useful models for the initial charge-splitting step that occurs in photosynthesis.

Registry No. $\text{Ru}(\text{bpy})_3^{2+}$, 15158-62-0; $[(\text{bpy})_2\text{Ru}(\text{NC}_5\text{H}_4\text{C}_3\text{H}_4\text{NCH}_3)_2]^{4+}$, 69021-46-1; DMT, 99-97-8; PQ^{2+} , 4685-14-7.

Contribution from the Department of Chemistry and Quantum Institute, University of California, Santa Barbara, California 93106

Intramolecular Energy Transfer in a Rhodium(III) Metalloorganic Bichromophore System. Photochemical and Photoluminescence Studies

MICHAEL A. BERGKAMP, RICHARD J. WATTS,* and PETER C. FORD*

Received July 28, 1980

Reported are the photochemical, photoluminescence, and spectral studies of a series of pentaammine(organonitrilo)rhodium(III) compounds, $\text{Rh}(\text{NH}_3)_5(\text{N}\equiv\text{C}-\text{R})^{3+}$ (where R is a phenyl, benzyl, or 2-phenylethyl group or a substituted derivative). The absorption spectroscopy exhibits features attributable to both $\pi\pi^*$ and ligand field transitions. The luminescence spectra, however, exhibit only ligand field (LF) emissions regardless of whether the $\pi\pi^*$ or LF states are initially populated. The luminescence lifetimes at 77 K are also characteristic of LF states. Irradiation of the $\pi\pi^*$ or LF bands in aqueous solutions leads to photosubstitution of the organonitrile ligand with the quantum yields being somewhat smaller for $\lambda_{\text{irr}} = 254 \text{ nm}$ ($\pi\pi^*$) than 313 nm (LF) in most cases. The results are discussed in terms of the efficiency of interconfigurational energy transfer between $\pi\pi^*$ and LF states.

Introduction

Since the early investigations of intramolecular energy transfer by Weber¹⁻³ and by Schnepf and Levy⁴ in bichromophoric molecules, there has been much interest in this area.⁵ Bimetallic chromophores, organic bichromophores, and metalloorganic systems in which the ligand chromophore is coordinated to the metal chromophore have all received considerable spectral, photochemical, and photophysical atten-

tion.⁶⁻¹¹ The present work is concerned with the last type, complexes of a transition metal ion with a phenyl group containing organonitrile ligand $\text{Rh}(\text{NH}_3)_5(\text{N}\equiv\text{C}-\text{R})^{3+}$. The presence of distinctly different chromophores, the π -unsaturated phenyl ring, for which $\pi\pi^*$ transitions dominate the spectroscopy, and the low-spin d^6 Rh(III) center, for which

(1) Weber, G. *Trans. Faraday Soc.* **1950**, *44*, 185.
 (2) Weber, G. *Nature (London)* **1957**, *180*, 1409.
 (3) Weber, G.; Teale, F. W. J. *Trans. Faraday Soc.* **1958**, *54*, 640.
 (4) Schnepf, O.; Levy, M. J. *Am. Chem. Soc.* **1962**, *84*, 172.
 (5) De Schryver, F. C.; Boens, N.; Put, J. *Adv. Photochem.* **1977**, *10*, 359 and references therein.

(6) De Schryver, F. C.; Put, J.; Leenders, L.; Loos, H. *J. Am. Chem. Soc.* **1974**, *96*, 6994.
 (7) Wagner, P. J.; Nokahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8475.
 (8) Carlson, G. B.; Quina, F. H.; Zarnegar, B. N.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 347.
 (9) Adamson, A. W.; Vogler, A.; Lantzke, I. *J. Phys. Chem.* **1969**, *73*, 4183.
 (10) Chaisson, D. A.; Hintze, R. E.; Stuermer, D. H.; Petersen, J. D.; McDonald, D. P.; Ford, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 6665.
 (11) Zarnegar, P. P.; Bock, C. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 2470.

ligand field (d-d) transitions are spectrally predominant, in the same complex provides the opportunity to investigate the energy-transfer processes between the two centers unencumbered by the diffusion and configuration uncertainties which plague bimolecular studies of the same phenomenon. Reported here are spectral, photochemical, and photophysical studies of these compounds.

Experimental Section

Materials and Syntheses. $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ was prepared according to the method in the literature.¹² The organonitrile complexes $[\text{Rh}(\text{NH}_3)_4\text{L}](\text{ClO}_4)_3$, where L = benzonitrile (bzn), *o*-toluonitrile (2-Me-bzn), hydrocinnamitrile (hcn), 3-(*p*-hydroxyphenyl)propionitrile (4-HO-hcn), benzyl cyanide (bzyln), and (*p*-methoxyphenyl)acetonitrile (4-MeO-bzyln), were prepared according to the procedure of Foust and Ford¹³ with the following modifications. $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ (200 mg, 0.4 mmol, was dissolved in a minimum of redistilled *N,N*-dimethylacetamide (5–7 mL) and heated at 110 °C for 45 min. The appropriate organonitrile ligand (1–2 mL) was added, and the solution was heated 9 h at 85 °C. The solution was cooled in ice and added to ice-cold isobutyl alcohol (50 mL) to give a white precipitate which was filtered and washed with $\text{Et}_2\text{O}/\text{EtOH}$. Several recrystallizations of the product from hot (50 °C) 0.01 M HClO_4 were essential for purity (yields 65–85%).

Reagent grade organonitrile compounds (Aldrich) were used without further purification, and water was doubly distilled.

Photolyses Procedures. Photolyses with 313- and 254-nm light were carried out, under thermostated conditions, with optical trains and procedures described previously.^{14,15} In most cases, quantum yields were obtained from spectral changes (monitored on a Cary 118C spectrophotometer) in the wavelength region of the lowest ligand field absorption band. Spectroscopic quantum yields were obtained by plotting interval quantum yields as a function of percent reaction and extrapolating the roughly linear plot to 0%. Aquation of the coordinated ammonia was also determined from the difference between the initial pH of the photolysis solution (pH ~3) and the pH measured after irradiation. Aquation yields of the organonitrile ligands were independently examined by ion-exchange analysis of the free ligands released. After irradiation a sample of the photolysis solution was loaded onto a column (Bio-Rad Ag-50W-X4) and the free organonitrile ligand was eluted with pH 3 HClO_4 . The amount of organonitrile released was determined by monitoring the absorption spectrum of the eluent at the λ_{max} of the organonitrile ligand. Corrections for secondary photolysis of the free organonitrile ligands released in the initial photosubstitution process were unnecessary, as prolonged irradiation of aqueous solutions of the free organonitrile compounds resulted in only minor spectral changes. In general, photolysis experiments were run without deoxygenating the solutions; however, representative photolyses carried out under deoxygenated conditions (argon atmosphere) showed no quantum yield differences from those systems saturated with air. Concurrent dark reactions were monitored in each case to evaluate thermal reactions but were negligible in every case.

Luminescence Procedures. The ambient- and low-temperature (77 K) emission spectra of the free organonitrile compounds were recorded with a Perkin-Elmer Hitachi MPF-3 spectrofluorimeter equipped with a Hamamatsu R-446 multialkali photomultiplier tube and an automatic emission corrector. A phosphorescence adaptor was used in recording time-resolved emission spectra.

The luminescence measurements of the Rh(III) complexes were made on solid perchlorate salts and KBr pellets (2% complex by weight) at 77 K. The excitation source was a Quanta-Ray DCR-1A Nd-YAG laser system equipped with a HG-1 harmonic generator and PHS-1 prism harmonic separator for the generation and isolation of the fourth harmonic wavelength, 266 nm. The laser pulse had a width of ~9 ns, typical power of ~25 mJ/pulse, and a 7-mm beam diameter at the point where it impinged upon the sample at a repetition rate of 10 Hz. The sample emission was monitored at right angles to the excitation and was passed through a Perkin-Elmer Model 98

Table I. Electronic Absorption Spectra of the Free Organonitrile Ligands

ligand ^a	λ_{max} (ϵ) ^b
bzn	277 (822), 270 (890), 263 (650), 258 (405), 230 (1.10×10^3), 226 (1.27×10^3) 222 (1.3×10^4)
bzyln	267 (61), 263 (134), 257 (175), 252 (137), 247 (95)
hcn	267 (110), 263 (172), 257 (239), 252 (220), 247 (189)
2-Me-bzn	284 (1.4×10^3), 276 (1.4×10^3), 270 (1.0×10^3), 233 (9.6×10^3), 227 (1.1×10^4)
4-MeO-bzyln	282 (1.4×10^3), 275 (1.7×10^3), 225 (1.0×10^4)
4-HO-hcn	284 (1.5×10^3), 277 (1.9×10^3), 224 (9.2×10^3)

^a Abbreviations listed in the Experimental Section. ^b Absorption maximum in nm; ϵ in $\text{M}^{-1} \text{cm}^{-1}$.

Table II. Electronic Absorption Spectra of $\text{Rh}(\text{NH}_3)_5\text{L}^{3+}$ Complexes

complex	λ_{max} (ϵ) ^a
$\text{Rh}(\text{NH}_3)_5\text{bzn}^{3+}$	300 (342), 282 (1.5×10^3), 275 (1.7×10^3), 268 (1.7×10^4), 244 (1.7×10^4), 240 (2.0×10^4), 235 (2.1×10^4)
$\text{Rh}(\text{NH}_3)_5\text{bzyln}^{3+}$	299 (221), 266 (294), 262 (368), 256 (422), 251 (389), 246 (350)
$\text{Rh}(\text{NH}_3)_5\text{hcn}^{3+}$	300 (183), 267 (208), 263 (276), 257 (341), 251 (311), 247 (271)
$\text{Rh}(\text{NH}_3)_5(2\text{-Me-bzn})^{3+}$	310 (310), 290 (2.1×10^3), 284 (2.2×10^3), 247 (1.3×10^4), 237 (1.6×10^4)
$\text{Rh}(\text{NH}_3)_5(4\text{-MeO-bzyln})^{3+}$	300 (249), 279 (1.2×10^3), 273 (1.4×10^3), 226 (9.3×10^3)
$\text{Rh}(\text{NH}_3)_5(4\text{-HO-hcn})^{3+}$	307 (143), 280 (460), 274 (520), 223 (2.5×10^3)

^a Absorption maximum in nm; ϵ in $\text{M}^{-1} \text{cm}^{-1}$.

monochromator equipped with a dense flint-glass prism and detected with a red-sensitive photomultiplier tube. For lifetime measurements, the output of the photomultiplier tube (EMI Q9558) was applied to a Tektronix 549 oscilloscope, and decay curves were photographed from oscilloscope traces. For the measurement of emission spectra, the photomultiplier (RCA 7102) output was applied to the input of a PAR Model 164 Gated Integrator Module of a PAR Model 162 boxcar averager. The output of this detection system, which has been described in detail previously,¹⁶ represented the average of at least six intensity measurements for each 1-nm segment of the spectrum. Luminescence spectra were also recorded by utilizing the Hg-Xe lamp for excitation at 313 nm and lock-in signal averaging, details of which may be found elsewhere.^{15,17}

Results

Absorption Spectra. The electronic absorption spectra of the Rh(III) complexes and the free organonitrile ligands are given in Tables I and II. The bands observed for the organonitrile compounds are characteristic of the $\pi\pi^*$ intraligand transitions of the phenyl ring. These absorptions remain relatively unchanged upon coordination to the Rh(III) metal center except for the small red shift in the benzonitrile complexes, which are conjugated between the two chromophore

(12) Bushnell, C. W.; Lalor, G. L.; Moelewyn-Hughes, E. A. *J. Chem. Soc. A* **1966**, 719.

(13) Foust, R. D.; Ford, P. C. *Inorg. Chem.* **1972**, *11*, 899.

(14) Petersen, J. D.; Ford, P. C. *J. Phys. Chem.* **1974**, *78*, 1144–9.

(15) Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4549–54.

(16) Watts, R. J.; Brown, M. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 6029.

(17) Watts, R. J.; Harrington, J. S.; Van Houten, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 2179–87.

(18) Takei, K.; Kanda, Y. *Spectrochim. Acta* **1962**, *18*, 1201–16.

(19) Fratev, F.; Tadjer, A. *J. Mol. Struct.* **1975**, *27*, 185–93.

(20) Bass, A. H. *J. Chem. Phys.* **1950**, *18*, 1403.

(21) Thomas, T. R.; Crosby, G. A. *J. Mol. Spectrosc.* **1971**, *38*, 118.

Table III. Photosubstitution Quantum Yields for $\text{Rh}(\text{NH}_3)_5\text{L}^{3+}$ (L = Organonitrile)^a

complex	λ_{irr}	$\Phi_{\text{L}}^{b,c}$	$\Phi_{\text{NH}_3}^b$
$\text{Rh}(\text{NH}_3)_5\text{bnz}^{3+}$	313	0.31 ± 0.01 (12)	$<10^{-2}$
	254	0.24 ± 0.02 (9)	$<10^{-2}$
$\text{Rh}(\text{NH}_3)_5\text{bzyln}^{3+}$	313	0.49 ± 0.04 (10)	$<10^{-3}$
	254	0.58 ± 0.04 (11)	$<10^{-2}$
$\text{Rh}(\text{NH}_3)_5\text{hcn}^{3+}$	313	0.34 ± 0.06 (13)	$<10^{-3}$
	254	0.27 ± 0.03 (12)	$<10^{-3}$
$\text{Rh}(\text{NH}_3)_5(2\text{-Me-bzn})^{3+}$	313	0.34 ± 0.03 (3)	$<10^{-2}$
	254	0.27 ± 0.02 (3)	$<10^{-2}$
$\text{Rh}(\text{NH}_3)_5(4\text{-MeO-bzyln})^{3+}$	313	0.24 ± 0.02 (8)	$<10^{-2}$
	254	0.12 ± 0.01 (2)	$<10^{-2}$
$\text{Rh}(\text{NH}_3)_5(4\text{-HO-hcn})^{3+}$	313	0.27 ± 0.05 (5)	$<10^{-2}$
	254	<i>d</i>	
$\text{Rh}(\text{NH}_3)_5(\text{N}\equiv\text{CCH}_3)^{3+}$	313 ^e	0.47 ± 0.04	$<2 \times 10^{-3}$
	254 ^e	0.48 ± 0.05	$<7 \times 10^{-2}$

^a Aqueous perchlorate media (pH 3), 25 °C. ^b Mol/einstein. ^c Mean value and average deviation with number of independent determinations in parentheses. ^d Unidentified photoreaction occurs. ^e Reference 22.

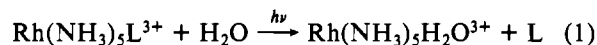
Table IV. Luminescence Spectral Data for the Free Organonitrile Ligands

ligand	$T, ^\circ\text{K}$	$S_0 \leftarrow S_1$		$S_0 \leftarrow T_1$	
		<i>b</i>	<i>c</i>	<i>b</i>	<i>c</i>
bnz	77	34.7	2.6	25.4	3.4
	298	34.7	3.0		
bzyln	77	35.8	3.3	27.0	4.3
	298	35.6	3.1		
hcn	77	34.9	4.5	26.5	4.7
	298	35.6	3.7		
4-Me-bzyln	77	33.6	2.5	25.3	4.6
	298	33.5	2.9		
4-HO-hcn	77	33.9	2.5	25.7	4.4
	298	33.1	3.0		
2-Me-bzn	77	33.8	2.4	25.0	3.7
	298	33.3	3.1		

^a 77 K in MeOH/H₂O (4:1, v/v) glass; 298 K in MeOH/H₂O (4:1, v/v) solution. ^b Energy of emission intensity maximum in 10^3 cm^{-1} . ^c Bandwidth at half-height of emission intensity maximum in 10^3 cm^{-1} .

centers. The spectra of the rhodium complexes exhibit an additional band at about 300 nm due to the $^1E, A \leftarrow ^1A$ ligand field absorption. The second ligand field absorption band usually associated with low-spin d^6 complexes is obscured by the more intense $\pi\pi^*$ intraligand bands.

Photolyses. The irradiation of these complexes in room-temperature aqueous solution at 313 or 254 nm results in substitution of the unique ligand as the only observed photoreaction.



The lack of measurable pH changes during photolysis indicates that the substitution of NH_3 is a minor process at best (upper limit $<10^{-2}$). The photosubstitution quantum yields measured at both irradiation wavelengths are summarized in Table III. With the exceptions of $\text{Rh}(\text{NH}_3)_5(4\text{-HO-hcn})^{3+}$ and $\text{Rh}(\text{NH}_3)_5\text{bzyln}^{3+}$, the quantum yields measured at 254 nm are 20–50% less than those measured at 313 nm. This observation has been made previously for the benzonitrile complex where slightly higher values for eq 1 were reported ($\Phi = 0.35$ and 0.29 for $\lambda_{\text{irr}} = 313$ or 254 nm, respectively);²² however, in that case poorer experimental precision precluded differentiating these two values. For $\text{Rh}(\text{NH}_3)_5\text{bzyln}^{3+}$ a different observation is made and the quantum yield shows a 20% increase on going from 313- to 254-nm excitation. For $\text{Rh}(\text{NH}_3)_5(4\text{-HO-hcn})^{3+}$

Table V. Luminescence Data for $\text{Rh}(\text{NH}_3)_5\text{L}^{3+}$ Complexes (L = Organonitrile)

complex	τ^a	ν_{max}^b	$\nu_{1/2}^c$
$\text{Rh}(\text{NH}_3)_5\text{bnz}^{3+}$	8.0 ± 0.2 (7)	15.8	3.7
$\text{Rh}(\text{NH}_3)_5\text{bzyln}^{3+}$	8.1 ± 0.1 (3)	14.7	3.1
$\text{Rh}(\text{NH}_3)_5\text{hcn}^{3+}$	8.4 ± 0.1 (2)	14.7	2.8
$\text{Rh}(\text{NH}_3)_5(4\text{-MeO-bzyln})^{3+}$	7.9 ± 0.1 (2)	14.7	3.0
$\text{Rh}(\text{NH}_3)_5(4\text{-HO-hcn})^{3+}$	7.6 ± 0.2 (2)	14.7	3.0
$\text{Rh}(\text{NH}_3)_5(2\text{-Me-bzn})^{3+}$	7.5 ± 0.2 (2)	16.0	3.8
$\text{Rh}(\text{NH}_3)_5(\text{N}\equiv\text{CCH}_3)^{3+}$	7.1 ± 1.0^d	15.2 ^d	3.4 ^d

^a Measured lifetime in microseconds; mean value and average deviation with number of determinations in parentheses. All samples were taken as perchlorate salts at 77 K. ^b Energy of emission intensity maximum (corrected) in 10^3 cm^{-1} . ^c Bandwidth at half-height of emission intensity maximum (10^3 cm^{-1}). ^d Reference 22.

254-nm irradiation results in complicated spectral changes, indicating photoreaction(s) other than eq 1, and photoproduct(s) was (were) not identified.

Emission spectral data for the free organonitrile ligands excited at the absorption maximum of the lowest $\pi\pi^*$ band (250–270 nm) are summarized in Table IV. The low-temperature spectra exhibit two structured bands separated by $8\text{--}9 \times 10^3 \text{ cm}^{-1}$, which are assigned as fluorescence and phosphorescence on the basis of energy, structure, and apparent lifetimes. The higher energy band in each case is a mirror image of the lowest energy absorption band seen for that same compound, while the lower energy emission is rather broad and less structured. When recorded with a phosphoroscope, the emission spectra displayed only the low-energy band, indicating that the lifetime of the state responsible for that emission was significantly longer than that of the state leading to the higher energy emission.²³ At ambient temperatures the emission spectra lack the broad low-energy band and show only the higher energy fluorescence band. The energies of the band maxima are relatively unchanged with temperature, but most of the structure disappears as the temperature is increased. The results for benzonitrile are in excellent agreement with the previously published fluorescence and phosphorescence spectra.^{18–20}

Emission Spectra of $[\text{Rh}(\text{NH}_3)_5\text{L}](\text{ClO}_4)_3$. Each complex displays a broad Gaussian emission band similar to those previously assigned²¹ for rhodium(III) complexes as LF emissions and are therefore assigned analogously. The corrected ν_{max} values and the respective bandwidths at half-height, $\Delta\nu_{1/2}$, are reported in Table V. The emission spectra are independent of the excitation wavelength, 313 or 254 nm, and there is no evidence for higher energy emissions such as those reported for the free organonitriles. For those complexes with RCH_2CN ligands the nature of the ring substituents and the number of methylene groups have little effect upon the energy of the emission maxima and the spectral properties are close to those of the acetonitrile complex $[\text{Rh}(\text{NH}_3)_5\text{N}\equiv\text{CC-H}_3](\text{ClO}_4)_3$. However, the two benzonitrile complexes exhibit slightly higher energy emission maxima. The value of $15.8 \times 10^3 \text{ cm}^{-1}$ observed for $[\text{Rh}(\text{NH}_3)_5\text{bnz}](\text{ClO}_4)_3$ is identical with the previously reported value.²²

Luminescence Lifetimes of $[\text{Rh}(\text{NH}_3)_5\text{L}](\text{ClO}_4)_3$. The lifetimes (Table V) of all of the complexes were virtually identical

- (23) Preliminary measurements on emission lifetimes for the organonitrile ligands at 77 K suggest that the blue fluorescence has a lifetime of $<1 \mu\text{s}$, while the green phosphorescence has a lifetime of tens of seconds. These values are consistent with previous measurements on similar compounds.
- (24) Bent, D. V.; Hayon, E. *J. Am. Chem. Soc.* **1975**, *97*, 2606–12.
- (25) Haaland, D. M.; Nieman, G. C. *J. Chem. Phys.* **1973**, *59*, 1013–27.
- (26) Luminescence from $\pi\pi^*$ intraligand states should be at energies of $>25 \times 10^3 \text{ cm}^{-1}$ (see Table IV) and have lifetimes of $<1 \mu\text{s}$ and $\sim 10 \text{ s}$ for the fluorescence and phosphorescence, respectively.
- (27) Luria, M.; Ofran, M.; Stein, G. *J. Phys. Chem.* **1974**, *78*, 1904–9.

and in the microsecond range. There was no evidence for the longer lifetimes that might be expected from a $\pi\pi^*$ -emitting state.²³ The lifetime measured for $[\text{Rh}(\text{NH}_3)_5\text{bzn}](\text{ClO}_4)_3$ agrees with the reported value.

Luminescence Studies of the Isolated Chromophores. The emission spectrum of a 2×10^{-3} M aqueous solution of benzonitrile was recorded before and after the addition of equimolar and then threefold excess amounts of $[\text{Rh}(\text{NH}_3)_5(\text{NC-CH}_3)](\text{ClO}_4)_3$. The energies and intensities of the benzonitrile fluorescence peak at $34.7 \times 10^3 \text{ cm}^{-1}$ were identical for all three spectra.

Discussion

The absorption and emission spectral data suggest that the two chromophore centers are largely unperturbed by coordination, since spectral features can generally be attributed to the isolated chromophores. The exception is that the $\pi\pi^*$ absorption bands of the two benzonitrile ligands exhibit a slight bathochromic shift upon coordination, indicating some perturbation of the ring orbitals perhaps due to the increased electron-withdrawing nature of the coordinated CN group. The low-temperature (77 K) luminescence lifetimes and emission spectra are characteristic of those expected for the lowest energy LF state of a Rh(III) center and are independent of whether the complexes are excited at 313 nm (LF) or at 254 nm ($\pi\pi^*$ plus LF). Given that the excitation of the free ligands leads to both fluorescence and phosphorescence at 77 K and fluorescence at 295 K, one must conclude that coordination to the $\text{Rh}(\text{NH}_3)_5^{3+}$ center provides new pathways for rapid nonradiative deactivation of the fluorescent $\pi\pi^*$ ligand state. That these pathways involve energy transfer to the Rh(III) center is indicated by the observation of significant reaction from the LF excited states, even for those systems where most of the light is absorbed by the organic chromophore (see below).

Since diffusion is slow in low-temperature rigid matrices, it is probable that any energy transfer between chromophores is intramolecular. This conclusion is supported by the emission behavior of model solutions containing mixtures of the two chromophores. The fluorescence of free benzonitrile in 295 K aqueous solution remained unchanged after the addition of a threefold excess of $\text{Rh}(\text{NH}_3)_5(\text{N}\equiv\text{CCH}_3)^{3+}$. This indicates that intermolecular energy transfer between the free organonitrile singlet state and the Rh(III) center is not efficient. (Bimolecular energy transfer between several organic triplet sensitizers and certain rhodium(III) ammine complexes have been reported previously.²²) Whether the intramolecular energy transfer in the complexes occurs by an exchange interaction of the Dexter type²⁸ or a long-range Förster mechanism²⁹ is unclear as the complexes studied are not rigid and may exist in conformations in which the two chromophores are in close proximity to one another.

Absorption of 254-nm light involves excitation of both spin-allowed $\pi\pi^*$ and LF transitions. The relative percentage of light absorbed by each chromophore can be estimated by approximating the extinction coefficient of the higher energy LF band at this wavelength as equal to the ϵ_{max} observed for the ${}^1\text{E}, {}^1\text{A}_2 \leftarrow {}^1\text{A}_1$ band, a reasonable assumption in view of the spectra of other rhodium(III) ammine complexes.³⁰⁻³²

(For example, the two LF bands of aqueous $\text{Rh}(\text{NH}_3)_5(\text{N}\equiv\text{CCH}_3)^{3+}$ occur at $\lambda_{\text{max}} = 301$ and 255 nm with the respective ϵ 's 158 and $126 \text{ M}^{-1} \text{ cm}^{-1}$.) Given that the free-ligand extinction coefficients for $\pi\pi^*$ transitions in this spectral region range from $\sim 10^2$ to $> 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, it is clear that the $\pi\pi^*$ transitions of the ligand chromophore contribute very significantly to the absorption at 254 nm.

The wavelength independence of photosubstitution quantum yields found for the irradiation of LF bands of rhodium(III) amines is generally interpreted as indicating efficient internal conversion/intersystem crossing from high-energy LF states to a common lowest energy triplet LF state from which ligand aquation or deactivation to the ground state principally occurs. Thus, in the present systems, direct excitation of the LF transition contributing to the 254-nm absorption would lead to photosubstitution with an efficiency comparable to that seen for direct excitation of the lower energy LF band with 313-nm light. However, the contribution from such direct LF excitation at 254 nm to the overall quantum yield would be a function of the relative amount of light absorbed by the metal center. Given that the organic chromophores are generally the stronger absorbers in this spectral region, one would expect marked decreases in the photosubstitution yields owing to inner filtering by those chromophores, *unless* energy transfer from $\pi\pi^*$ to LF states is occurring. Although Φ_{254} is somewhat less than Φ_{313} for several of these systems, the differences are far too small to explain the quantum yields solely in terms of the direct excitation of LF bands. Hence, we conclude that photosolvation arises from intramolecular relaxation within the LF excited-state manifold as well as from interconfigurational relaxation from the $\pi\pi^*$ to LF manifold. However, the smaller values of Φ_{254} for several complexes suggest that such energy transfer may not occur with unitary efficiency in every case. If so, the failure to observe ligand $\pi\pi^*$ emissions from the complexes would suggest that other nonradiative deactivation pathways from the fluorescent ligand state are accelerated by coordination to the Rh(III) center.

In summary, the quenching of ligand-centered fluorescence and the observation of metal-center reactions characteristic of ligand field excited states both indicate that initial excitation of the ligand chromophore of the $\text{Rh}(\text{NH}_3)_5(\text{RCN})^{3+}$ complexes is followed by intramolecular energy transfer to the metal center. The quantum yields for the photosubstitution processes suggest that the efficiency of such energy transfer is less than unity in several cases.

Acknowledgment. P.C.F. acknowledges support from the National Science Foundation. R.J.W. acknowledges the Department of Energy, Office of Basic Energy Sciences, for support of this work. M.A.B. is grateful to the University of California for a Regents Fellowship. The rhodium used in these studies was provided on loan from Matthey Bishop, Inc.

Registry No. $[\text{Rh}(\text{NH}_3)_5\text{bzn}](\text{ClO}_4)_3$, 36449-60-2; $[\text{Rh}(\text{NH}_3)_5\text{bzyln}](\text{ClO}_4)_3$, 76793-73-2; $[\text{Rh}(\text{NH}_3)_5\text{hcn}](\text{ClO}_4)_3$, 76793-75-4; $[\text{Rh}(\text{NH}_3)_5(2\text{-Me-bzn})](\text{ClO}_4)_3$, 76793-77-6; $[\text{Rh}(\text{NH}_3)_5(4\text{-MeO-bzyln})](\text{ClO}_4)_3$, 76793-79-8; $[\text{Rh}(\text{NH}_3)_5(4\text{-HO-hcn})](\text{ClO}_4)_3$, 76793-81-2; bzn, 100-47-0; bzyln, 140-29-4; hcn, 645-59-0; 2-Me-bzn, 529-19-1; 4-MeO-bzyln, 104-47-2; 4-HO-hcn, 17362-17-3; $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$, 15611-81-1.

(28) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

(29) (a) Mataga, N.; Kubota, T. "Molecular Interaction and Electronic Spectra"; Marcel Dekker: New York, 1970; Chapter 5. (b) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7-17.

(30) Bergkamp, M. A.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1980**, *102*, 2627-31.

(31) Skibsted, L. H.; Ford, P. C. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 109-13.

(32) Schmidtke, H. H. *Z. Phys. Chem. (Wiesbaden)* **1965**, *45*, 305-16.