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Photophysical Properties of Rhenium(I) Tricarbonyl Complexes Containing Alkyl- and Aryl-Substituted Phenanthrolines as Ligands

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A number of complexes of the type Re(L-L)(CO)$_3$py$^+$ have been prepared, where L-L is 1,10-phenanthroline or a phenanthroline derivative containing methyl or phenyl groups and py is pyridine. All of the complexes are highly emissive at room temperature in solution or at 77 K in a glass, and the room-temperature luminescence data are consistent with emission from a ^{3}MLCT state. The emission maximum ranges from 510 to 548 nm in CH$_2$Cl$_2$, depending on L-L, and a linear relationship between λ_{max} and the electrode potentials for oxidation and reduction is evident. Lifetimes in acetonitrile are of the order of several microseconds at room temperature (1.6–13 μs), and emission quantum yields are very high (0.17–0.29). Results of photophysical measurements performed at low temperature indicate the presence of two unequilibrated emitting states, a ^{3}MLCT and a ^{3}LC (ligand-centered) state. Time-resolved spectra have established that the ^{3}LC state is the longer-lived of the two and gives a structured spectrum similar to that of the uncoordinated ligand L-L. Both states show a dependence on the substitution pattern, and the contribution of each is determined by the particular L-L. Trends in the room-temperature data may also be accounted for by invoking a multistate model: however, the states are in thermal equilibrium under these conditions.

Introduction

Rhenium(I) tricarbonyl complexes containing bidentate heterocyclic ligands have been a source of much interest for several years,[1–12] largely due to their potential for use in solar energy conversion.[1a,13,14] These complexes are ideally suited for such an application, as they display intense luminescence in the visible region of the spectrum and are stable to photodecomposition.

Several recent studies have examined the effect of different ligand substituents on the luminescence of the complex.[4,11,12] In general, rhenium(I) tricarbonyl complexes are MLCT emitters, typified by a broad, structureless emission band which is sensitive to changes in the nature of the environment, such as temperature, solvent, and pH.[1b,2,11b] Thus, variations in the structure of the non-carbonyl ligands can produce considerable effects on luminescence energies, lifetimes, and quantum yields. For a species Re(L-L)(CO)$_3$X^{n+}, introduction of substituents to either the chromophoric ligand L-L[2a,4,12] or the "spectator" ligand X[11a] has been found to produce measurable changes in the luminescence energy and lifetime without significantly altering the fundamental electronic structure of the complex. In some cases, these effects have been found to be quantifiable by using known theoretical models, such as the Hammett equation.[11a,12] Substituent effects thus provide a useful means by which luminescence can be "fine-tuned", a fact which has been recognized for related complexes of Ru(II) and Ir(III).[12b,15,16]

While a number of studies have been concerned with varying the identity of substituents on a given ligand (L-L or X), the effect of the position a substituent occupies within the chromophoric ligand has not, to our knowledge, been systematically determined. In our earlier work we have examined the excited-state properties of the bimetallic complex (bpy)$_2$Ru(bb)Re(CO)$_3$py^{3+}, where bb is 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane and py is pyridine, and found enhanced emission from the "(bpy)$_2$Ru(bb)$^{2+}$" unit upon excitation at 355 nm, which was attributed to energy transfer from (bb)Re(CO)$_3$py^{+*} to (bpy)$_2$Ru(bb)$^{2+}$.[17] A comparison of the emission lifetime (τ) and quantum yield (ϕ_{em}) of (phen)Re(CO)$_3$py$^+$ (τ = 1.6 μs, ϕ_{em} = 0.180, CH$_3$CN, 298 K) to those of (bpy)Re(CO)$_3$py$^+$ (τ = 0.66 μs, ϕ_{em} = 0.059, CH$_3$CN, 298 K)[11a] revealed that the energy-transfer process in the bimetallic system could potentially be enhanced for a similar bimetallic complex based on a dimeric phenanthroline ligand. Since phenanthroline ligands contain a

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(1) (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (b) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

(2) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2257. (c) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888. (d) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415. (e) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067.

(3) Vogler, A.; Kisslinger, J. *Inorg. Chim. Acta* **1986**, *115*, 193.

(4) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J. M.; Zeissel, R. *Inorg. Chem.* **1988**, *27*, 4007.

(5) (a) Van Wallendael, S.; Shaver, R. J.; Rillema, D. P.; Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 1761. (b) Sahai, R.; Rillema, D. P.; Shaver, R. J.; Van Wallendael, S.; Jackman, D. C.; Boldaji, M. *Inorg. Chem.* **1989**, *28*, 1022.

(6) Ruminski, R.; Cambron, R. T. *Inorg. Chem.* **1990**, *29*, 1574.

(7) Baiano, J. A.; Carlson, D. L.; Wolosh, G. M.; DeJesus, D. E.; Knowles, C. F.; Szabo, E. G.; Murphy, W. R., Jr. *Inorg. Chem.* **1990**, *29*, 2327.

(8) (a) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 2885. (b) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Inorg. Chem.* **1990**, *29*, 2285.

(9) (a) Lin, R.; Guarr, T. F. *Inorg. Chim. Acta* **1990**, *167*, 149. (b) Lin, R.; Guarr, T. F.; Duesing, R. *Inorg. Chem.* **1990**, *29*, 4169.

(10) Kalyasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401.

(11) (a) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335. (b) Leasure, R. M.; Sacksteder, L.; Nesselrodt, D.; Reitz, G. A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1991**, *30*, 3722.

(12) (a) Hino, J. K.; Della Ciana, L.; Dressick, W. J.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1072. (b) Della Ciana, L.; Dressick, W. J.; Sandrini, D.; Maestri, M.; Ciano, M. *Inorg. Chem.* **1990**, *29*, 2792.

(13) (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (b) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098 (c) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755. (d) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

(14) Zipp, A. P. *Coord. Chem. Rev.* **1988**, *84*, 47.

(15) (a) Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3184. (b) Watts, R. J.; Crosby, G. A.; Sansregret, J. L. *Inorg. Chem.* **1972**, *11*, 1474. (c) Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 2606. (d) Watts, R. J. *Inorg. Chem.* **1981**, *20*, 2302.

(16) (a) Pankuch, B. J.; Lackey, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2061. (b) Lackey, D. E.; Pankuch, B. J.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2068.

(17) Van Wallendael, S.; Rillema, D. P. *Coord. Chem. Rev.* **1991**, *111*, 297.

0020-1669/93/1332-3836$04.00/0

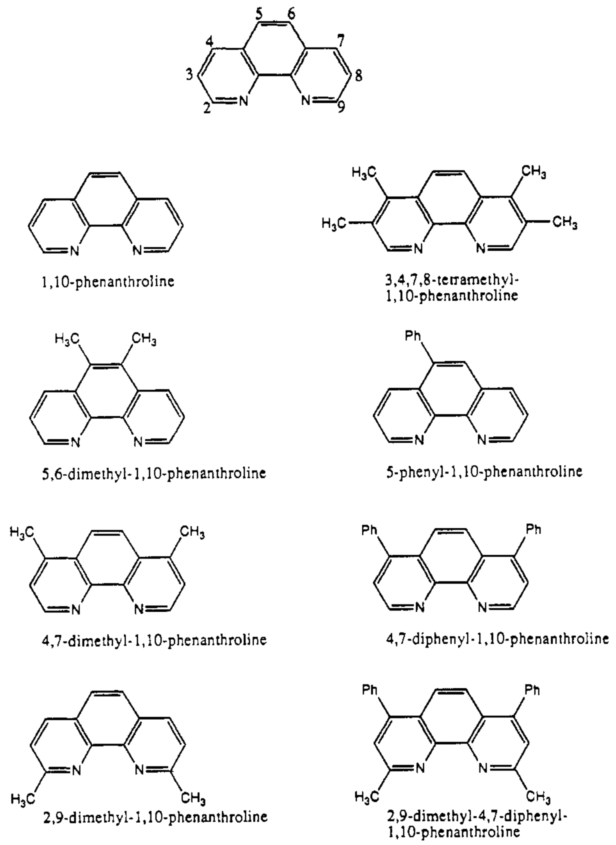

Figure 1. Structures of substituted phenanthroline ligands (L-L).

number of possible bridging sites, we have examined the photophysics of a series of monometallic Re(I) tricarbonyl complexes containing various methyl- and phenyl-substituted phenanthroline ligands (Figure 1) with the goal of linking two ligands at the substituent location giving rise to the optimum photophysical properties. In our study we also found it necessary to experimentally examine the excited-state properties of the free ligands in order to gain insight into the behavior of the complexes.

Experimental Section

Materials. 1,10-Phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline (neocuproine), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline were purchased from Aldrich Chemical Co., Inc. 5,6-Dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline), and 5-phenyl-1,10-phenanthroline were purchased from G. F. Smith Chemicals. Acetonitrile, hexane, methanol, and methylene chloride were HPLC grade. Ethanol and pyridine were reagent grade. All reagents were used as supplied. Tetrabutylammonium perchlorate (TBAP) for electrochemical experiments was obtained from Eastman Kodak Co. and was used without further purification.

Preparation of [Re(L-L)(CO)$_3$py]CF$_3$SO$_3$. All reactions were performed under a blanket of argon and in the dark. The preparation of Re(CO)$_5$CF$_3$SO$_3$ was described previously.[18]

In a typical procedure, Re(CO)$_5$CF$_3$SO$_3$ (0.1 g, 2.1 mmol) was dissolved in methanol (5 mL) and the solution was heated at reflux for 1 h. The cool product solution was then added to a solution of the appropriate ligand L-L (2.4 mmol) in CH$_2$Cl$_2$, and the mixture was heated at reflux overnight (16 h). Solvent was then removed using a rotary evaporator, and pyridine (5 mL) was added to the residue. The resulting yellow solution was heated to ca. 60 °C for 4 h, after which time the pyridine was removed by heating gently under a stream of argon. The remaining solids were dissolved in CH$_2$Cl$_2$ (ca. 5 mL) and purified by column chromatography on neutral alumina (column dimensions 10 × 1 cm) using CH$_2$Cl$_2$ as eluent. A narrow yellow band with orange luminescence eluted first, while the desired product, which had green/yellow luminescence, remained at the top of the column. The eluent was then changed to CH$_3$CN, whereupon the desired product eluted quickly and was collected as a fraction. The solvent was removed by rotary evaporation, and the solid product was precipitated from CH$_2$Cl$_2$ by dropwise addition of hexane. This gave a yellow powder, which was collected by filtration, washed with hexane, and dried in vacuo at room temperature for 8–10 h. The average yield was 65%. Elemental analyses were carried out by Atlantic Microlabs, Norcross, GA, and the results are listed in Table I.

Table I. Elemental Analyses of [Re(L-L)(CO)$_3$py]·CF$_3$SO$_3$·xH$_2$O Complexes

L-L	element	% theory	% found
phen·H$_2$O	C	36.21	36.39
	H	2.17	2.02
	N	6.03	6.04
4,7-Me$_2$phen·2H$_2$O	C	37.19	37.14
	H	2.85	2.42
	N	5.67	5.56
2,9-Me$_2$phen	C	39.08	39.09
	H	2.42	2.49
	N	5.94	5.97
5,6-Me$_2$phen	C	39.08	39.18
	H	2.42	2.46
	N	5.94	5.90
3,4,7,8-Me$_4$phen	C	40.87	40.71
	H	2.88	2.89
	N	5.72	5.63
5-Phphen	C	42.97	42.73
	H	2.27	2.35
	N	5.57	5.42
4,7-Ph$_2$phen	C	47.71	47.79
	H	2.79	2.80
	N	5.06	4.99
2,9-Me$_2$-4,7-Ph$_2$phen	C	48.95	49.12
	H	2.93	2.97
	N	4.89	4.80

Instrumentation. Electronic absorption spectra were recorded using a Perkin Elmer Model 3840 diode array spectrophotometer. Extinction coefficients were determined using Beer's law serial dilution methods.

Corrected emission and excitation spectra were recorded on a Spex Fluorolog 212 spectrophotometer, for which the excitation source was a xenon lamp. For emission lifetime measurements, samples were excited using a Photochemical Research Associate Model LN1000 pulsed N$_2$-pumped PRA LN102 dye laser. Data were collected with a LeCroy TR8828C transient digitizer and an IBM PS/2 Model 60 computer, and the lifetimes were calculated using the On-Line Instrument Systems KINFIT program. All samples for photophysical measurements were prepared with an absorbance of 0.1 at the excitation wavelength and were freeze–pump–thaw-degassed three times. The excitation wavelength was 355 nm unless otherwise specified. Excitation spectra were monitored at the emission maximum unless otherwise specified. Lifetimes were measured at various wavelengths (see text). Emission quantum yields were measured relative to Ru(bpy)$_3^{2+}$ (ϕ_{em}(Ru) = 0.062 in CH$_3$CN at 22 °C, with λ_{ex} = 436 nm[19]). Quantum yields were calculated according to the equation

$$\phi_{em}(\mathrm{Re}) = (A_{\mathrm{Ru}}/A_{\mathrm{Re}})(I_{\mathrm{Re}}/I_{\mathrm{Ru}})\,\phi_{em}(\mathrm{Ru})$$

where I is the integral of the emission spectrum and A is the absorbance of the sampler or standard at the excitation wavelength.

Electrochemical measurements were performed in HPLC grade acetonitrile containing 0.1 M TBAP as the supporting electrolyte. Electrode potentials were determined versus a saturated sodium calomel reference electrode (SSCE), with a platinum disk working electrode and a platinum wire auxiliary electrode. Cyclic voltammograms were generated using a Princeton Applied Research Model 173 potentiostat coupled to a PAR 175 programmer and an IBM 7424 X-Y recorder. Time-resolved emission spectra at 77 K were measured at Wayne State University in the laboratories of John F. Endicott. Briefly, freeze–pump–thaw-degassed samples in 10-mm round Supracil quartz tubes were excited with the 10-ns fwhm pulse from a Molectron UV 1010 N$_2$-pumped DL 14 dye laser at 355 nm. The luminescence was observed using a Princeton Instruments IRY512 gated diode array interfaced to a Jerall Ash spectrograph with an ST120 controller and a FG100 gate pulser. Delay times were set with a Stanford Research DG535 digital delay generator. Gate pulse width and delays were monitored throughout the experiment.

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(18) Shaver, R. J.; Rillema, D. P. *Inorg. Chem.* **1992**, *31*, 1401.

(19) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

Table II. Half-Wave Potentials[a] of the Re(L-L)(CO)$_3$py$^+$ Complexes in Acetonitrile[b]

L-L	oxidation	reductions		
3,4,7,8-Me$_4$phen	+1.60 (130)	−158 (irr)	−1.705 (70)	−1.87 (75)
4,7-Me$_2$phen	+1.64 (110)	−1.38 (80)	−1.58 (65)	−1.76 (80)
5,6-Me$_2$phen	+1.66 (75)	−1.27 (irr)	−1.49 (80)	−1.69 (100)
2,9-Me$_2$phen	+1.70 (130)	−1.30 (irr)	−1.52 (60)	−1.71 (85)
phen	+1.69 (200)	−1.22 (irr)	−1.66 (70)	−1.82 (95)
5-Phphen	+1.69 (80)	−1.19 (irr)	−1.60 (80)	−1.80 (130)
2,9-Me$_2$-4,7-Ph$_2$phen	+1.67 (70)	−1.27 (80)	−1.47 (70)	−1.59 (90)
4,7-Ph$_2$phen	+1.66 (80)	−1.20 (70)	−1.51 (80)	−1.70 (90)

[a] Potentials in V vs SSCE, estimated as $^1/_2(E_p(\mathrm{ox}) + E_p(\mathrm{red}))$; errors ± 0.02 V; scan rate = 200 mV/s; ΔE_p, where $\Delta E_p = E_p(\mathrm{ox}) - E_p(\mathrm{red})$, in parentheses. [b] Acetonitrile solutions containing 0.1 M TEAP as electrolyte; room temperature.

Table III. UV/Visible Maxima[a] of Re(L-L)(CO)$_3$py$^+$ Complexes in Methylene Chloride at Room Temperature

L-L	dπ–π^*, nm[a] (ϵ)[b]	π–π^*, nm[a] (ϵ)[c]
3,4,7,8-Me$_4$phen	375 (3.7)	282 (3.0), 252 (2.7), 240 (2.9)
4,7-Me$_2$phen	375 (5.7), 326 (10)	276 (3.6), 260 (3.3), 236 (3.0)
5,6-Me$_2$phen	387 (3.7)	290 (2.5), 244 (2.8)
2,9-Me$_2$phen	377 (2.4)	285 (2.1), 258 (2.0), 237 (2.2)
phen	384 (3.6)	278 (2.4), 263 (2.8), 234 (2.2)
5-Phphen	384 (4.3), 327 (9.5)	293 (2.5), 246 (3.5)
2,9-Me$_2$-4,7-Ph$_2$phen	387 (5.3), 336 (sh)	300 (4.0), 264 (2.7), 234 (3.0)
4,7-Ph$_2$phen	398 (8.1), 342 (16)	295 (3.8), 269 (2.8), 237 (3.8)

[a] Error ±2 nm. [b] $\epsilon \times 10^{-3}$ M^{-1} cm^{-1}; error ±1 in last digit. [c] $\epsilon \times 10^{-4}$ M^{-1} cm^{-1}; error ±1 in last digit.

Table IV. Corrected Emission Maxima, Lifetimes, and Quantum Yields at Room Temperature in Methylene Chloride and Acetonitrile Measured with 355-nm Excitation

	CH$_2$Cl$_2$		CH$_3$CN		
L-L	λ_{max}, nm[a]	τ, μs[b]	λ_{max}, nm[a]	τ, μs[b]	ϕ_{em}[c]
3,4,7,8-Me$_4$phen	517[d]	12.0	524	13.0	
4,7-Me$_2$phen	528[d]	7.0	548	4.5	0.29
5,6-Me$_2$phen	538	6.4	560	4.1	0.22
2,9-Me$_2$phen	532	4.3	550	2.1	0.17
phen	544	3.0	567	1.6	0.18
5-Phphen	544	9.3	567	4.8	0.17
2,9-Me$_2$-4,7-Ph$_2$phen	553	12.5	565	10.1	0.17
4,7-Ph$_2$phen	558	8.7	576	4.8	0.23

[a] λ_{max} ± 1 nm. [b] Error ±10%; average for three values measured at different detection wavelengths of about 500, 550, and 600 nm. [c] Error ±10%. [d] High-energy shoulder also present.

Results

Carbonyl Stretching Frequency. Infrared spectra were recorded in CH$_2$Cl$_2$. In the carbonyl region, a pattern of three peaks typical of *fac*-Re(L-L)(CO)$_3$X complexes[20] was observed. The highest energy peak was found at 2035 ± 2 cm^{-1}. The two lower energy peaks were poorly resolved and appeared as a broad band at ca. 1930 ± 4 cm^{-1}.

Redox Properties. Half-wave potentials were determined by cyclic voltammetry and are listed in Table II. Each of the complexes displayed an irreversible oxidation in the +1.6 to +1.7 V range (vs SSCE) and a series of three or four reductions between −1.2 and −2.0 V. The oxidation wave was assigned to the metal-centered process, Re$^{2+/+}$, and the first reduction to the ligand-centered L-L$^{0/-}$ process. In every case, the first reduction was not fully reversible at room temperature. However, the complexes with L-L = 4,7-Me$_2$phen, 4,7-Ph$_2$phen, and 2,9-Me$_2$-4,7-Ph$_2$phen did show a return wave if the potential ramp was reversed directly after the first reduction peak; its reversibility was improved for most species, except for the complexes with L-L = 5-Phphen and phen, on cooling the electrolytic solution to −40 °C, and in all cases, the subsequent reduction peaks were suppressed. This implies that the subsequent cathodic processes can be attributed to reduction of daughter products, formed on decomposition of Re(L-L$^-$)(CO)$_3$py^0. The oxidations remained irreversible, even at scan rates up to 1.0 V/s. Half-wave potentials listed in Table II were estimated from the voltammograms, as described in footnote *a*.

For the purpose of this study, it is useful to compare the redox potentials of the substituted complexes to those of the corresponding processes in Re(phen)(CO)$_3$py$^+$. Systematic changes are noted in the first reduction potential, $E_{red}(1)$. Methyl groups attached to phen shift the potential to more negative values whereas phenyl groups have the opposite effect. For example, $E_{red}(1)$ for Re(4,7-Me$_2$phen)(CO)$_3$py$^+$ is shifted 160 mV negatively and $E_{red}(1)$ for Re(4,7-Ph$_2$phen)(CO)$_3$py$^+$ is shifted 20 mV in the positive direction. Methyl groups also shift E_{ox} negatively (50 mV for Re(4,7-Me$_2$phen)(CO)$_3$py$^+$); however phenyl groups have little effect. Complexes with methyl or phenyl groups in equivalent sites (L-L = 4,7-Me$_2$phen, 4,7-Ph$_2$phen) result in greater shifts for methyl-containing species than for phenyl-substituted phenanthroline ligands, as noted above. Further, substituents appear to have a greater potential shift effect when occupying a position in the N-containing ring than when occupying the 5- and/or 6-positions. For example, the two methyl groups in the 5,6-positions result in only a 50-mV shift compared to the 160-mV shift in $E_{red}(1)$ when the two methyl groups are in the 4,7-positions.

Electronic Absorption Spectra. Absorption spectra for the complexes were obtained in methylene chloride, and the results are shown in Table III. Spectra were very similar to those of analogous Re(I) tricarbonyl complexes,[1,2,11] and the assignments have been made accordingly. A typical spectrum consisted of several strong UV bands, assigned as ligand-centered transitions. One or two broad shoulders were observed at lower energy in every case, and the lowest energy feature is assigned as an MLCT transition, dπ(Re(I)) → π^*(L-L).

Since the MCLT band occurs as a broad shoulder, the exact position of the band and the extinction coefficient were subject to error. However, it was possible to assess qualitatively the way in which λ_{max} and its extinction coefficient varied with the different phenanthroline derivatives. Replacement of hydrogen substituents with methyl groups shifted λ_{max} to higher energy; substitution with phenyl groups in the 4,7-positions shifted λ_{max} in the opposite direction to lower energy. Methyl or phenyl groups in the 5- and/or 6-positions had a negligible effect on λ_{max}. For complexes containing phenanthroline with methyl and/or phenyl groups, the extinction coefficient of the MLCT transition tended to increase compared to that for Re(phen)(CO)$_3$py$^+$ (ϵ = 3600 M^{-1} cm^{-1}). The extent of this effect was dependent on the position which the relevant substituent occupied: the most intense MLCT bands were observed for Re(4,7-Ph$_2$phen)(CO)$_3$py$^+$ (ϵ = 8100 M^{-1} cm^{-1}) and Re(4,7-Me$_2$phen)(CO)$_3$py$^+$ (ϵ = 5700 M^{-1} cm^{-1}), while smaller enhancements occurred for Re(5,6-Me$_2$phen)(CO)$_3$py$^+$ (ϵ = 3700 M^{-1} cm^{-1}) and Re(5-Phphen(CO)$_3$py$^+$ (ϵ = 4300 M^{-1} cm^{-1}). An exception occurred for Re(2,9-Me$_2$phen)(CO)$_3$py$^+$. In this case, the lowest energy band is less intense (ϵ = 2400 M^{-1} cm^{-1}) than that observed for Re(phen)(CO)$_3$py$^+$.

Luminescence Properties. (a) Room Temperature. The results of the room-temperature experiments are summarized in Table IV.

The complexes displayed broad emission spectra (Figure 2) which have been assigned as MLCT-based luminescence, typical of this type of complex.[2,11,12] Apart from a high-energy shoulder for the complexes with L-L = 3,4,7,8-Me$_4$phen and 4,7-Me$_2$phen, the spectra were entirely unstructured, with λ_{max} varying from 510 to 548 nm in methylene chloride.

Trends for emission energy maxima of the various substituted phenanthroline complexes followed those outlined above for MLCT absorption maxima and $E_{red}(1)$. Phenyl substituents

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(20) Shaver, R. J. M.Sc. Thesis, The University of North Carolina at Charlotte, 1991.

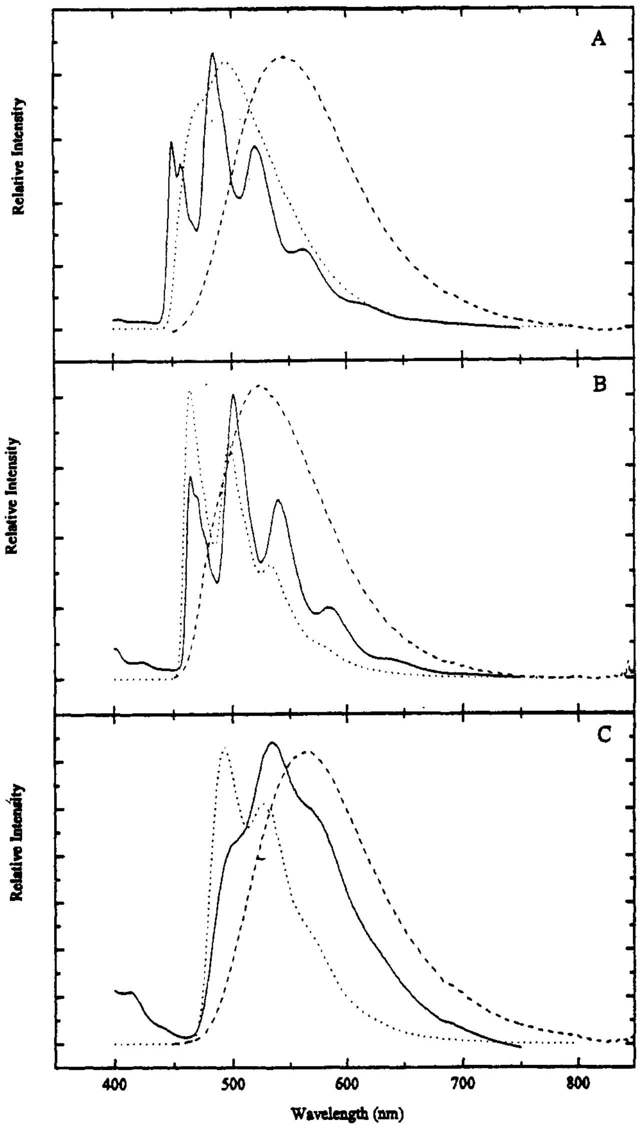

Figure 2. Emission spectra recorded in ethanol–methanol (4:1): (- - -) Re(L-L)(CO)$_3$py$^+$, 298 K; (···) Re(L-L)(CO)$_3$py$^+$, 77 K; (—) L-L free ligand, 77 K. λ_{ex}: 355 nm for the complexes; 320 nm for the ligands. L-L: (A) 2,9-Me$_2$phen; (B) 3,4,7,8-Me$_4$phen; (C) 5-Phphen.

located on the phenanthroline ligands resulted in an emission energy shift to lower energy for the complexes compared to Re(phen)(CO)$_3$py$^+$ (λ_{max} = 544 nm). Methyl substituents, on the other hand, caused a shift to higher energy. Consistent with this, λ_{max} for Re(2,9-Me$_2$-4,7-Ph$_2$phen)(CO)$_3$py$^+$ occurred at somewhat higher energy (540 nm) than that for Re(4,7-Ph$_2$phen)(CO)$_3$py$^+$ (548 nm). Substituents located in the 5- and/or 6-positions had less effect on λ_{max} than substituents that occupied a position on the N-containing ring. Compared to that for Re(phen)(CO)$_3$py$^+$, for example, λ_{max} for Re(5,6-Me$_2$phen)(CO)$_3$py$^+$ was located at 538 nm, while the one for Re(4,7-Me$_2$phen)(CO)$_3$py$^+$ was located at 528 nm.

Emission lifetimes ranged from 3 to 13 μs in ambient methylene chloride and followed first-order decay kinetics. Interestingly, no correlation was evident between the emission energy and the emission lifetime at room temperature. The shortest lifetime found was for Re(phen)(CO)$_3$py$^+$ (τ = 3.0 μs).

Emission maxima were solvent dependent, which is a characteristic of MLCT emission. In acetonitrile, λ_{max} is red-shifted by ca. 20 nm compared to results in methylene chloride and lifetimes were approximately 50% shorter in the more polar solvent. Two complexes with L-L = 3,4,7,8-Me$_4$phen and 2,9-Me$_2$-4,7-Ph$_2$phen showed a much smaller solvent dependence. Emission maxima shifted by only 7 and 12 nm, respectively, and lifetimes were only slightly affected.

Table V. Corrected Emission Maxima of Group A Re(L-L)(CO)$_3$py$^+$ Complexes in Ethanol–Methanol (4:1) at 77 K

L-L	λ_{max}, nm[a]	τ, μs[b]
phen[c]	(474) 497	11.7 ± 1.3
2,9-Me$_2$phen[d]	(474) 495	15.3 ± 1.4
2,9-Me$_2$-4,7-Ph$_2$phen[e]	508 537	22.1 ± 1.3
4,7-Ph$_2$phen[f]	508 536	34.8 ± 0.7

[a] λ_{ex} = 355 nm, error ± 1 nm. [b] λ_{ex} = 355 nm, single-exponential fits. [c] The phen ligand has emission maxima at 450, 485, 522, 564, and 617 nm; λ_{ex} = 320 nm. [d] The 2,9-Me$_2$phen ligand has emission maxima at 450, 485, 521, 562, and 614 nm; λ_{ex} = 320 nm. [e] The 4,7-Ph$_2$phen ligand has emission maxima at 475, 511, 551, 594, and 652 nm; λ_{ex} = 320 nm. [f] The 2,9-Me$_2$-4,7-Ph$_2$phen ligand has emission maxima at 475, 510, 549, 591, and 651 nm; λ_{ex} = 320 nm.

Consistent with the long lifetimes, emission quantum yields were very high, ranging from 0.17 (Re(2,9-Me$_2$phen)(CO)$_3$py$^+$) to 0.28 (Re(4,7-Me$_2$phen)(CO)$_3$py$^+$) for the complexes in acetonitrile. No correlation between emission lifetime and quantum yield in acetonitrile was observed. A reproducible value for the emission quantum yield of Re(Me$_4$phen)(CO)$_3$py$^+$ could not be obtained, as this complex had a tendency to decompose when irradiated in acetonitrile. The decomposiiton was manifested in a gradual collapse of emission intensity when successive spectra were collected on the same sample. In the absence of light the complex was stable indefinitely in the same solvent. None of the other complexes showed this behavior (ϕ_{em} was measured in triplicate for each complex on at least three different occasions, giving values well within experimental error of each other). Lifetime measurements were, however, reproducible for Re(Me$_4$phen)(CO)$_3$py$^+$, as they were for all the other complexes.

(b) Low Temperature. The complexes can be broadly classified into two groups (group A and group B) in terms of thier photophysical characteristics at 77 K in frozen glasses. The emission spectra for the complexes in group A (L-L = phen, 2,9-Me$_2$phen, 4,7-Ph$_2$phen, 2,9-Me$_2$-4,7-Ph$_2$phen) were nearly structureless (Figure 2a), and first-order emission decay was found (Table V). Their emission maxima were shifted by ca. 50–70 nm from their room-temperature values (measured in the same solvent). The spectra of the complexes with L-L = phen and 2,9-Me$_2$phen had emission maxima at 496 nm and a shoulder at 473 nm. The emission spectrum of Re(phen)(CO)$_3$py$^+$ had an additional shoulder at 459 nm. Likewise, the spectra of complexes with L-L = 4,7-Ph$_2$phen and 2,9-Me$_2$-4,7-Ph$_2$phen had coincident maxima at 508 nm and a lower energy peak at about 537 nm. Compared to those at room temperature, lifetimes for the complexes increased 2–3-fold at low temperature. While the decay curves remained exponential, a wavelength dependence was found. For each of the four complexes, the emission lifetime became shorter as the detection wavelength was increased. The effect was slight but significant, as the variation was beyond experimental error (±10%).

The emission spectra of the group B complexes (L-L = Me$_4$phen, 4,7-Me$_2$phen, 5,6-Me$_2$phen, 5-Phphen) showed structure comparable to that of the corresponding free ligands (Figure 2B,C). The major emission peaks are compared in Table VI. As noted in the table, the peaks for complex and free ligand were very close in energy (within 300 cm^{-1}). However, the emission spectra of the complexes were much more intense than those of the ligands when measured under identical conditions.

The trend observed for emission energies of the free ligands at 77 K is different from the trend found for the emission energies of the corresponding complexes at 298 K. Both methyl and phenyl substituents shifted the emission of the free ligand to lower energy compared to the emission of 1,10-phenanthroline, whereas methyl groups of coordinated ligands shifted the emission to higher energy and phenyl groups of coordinated ligands shifted the emission to

Table VI. Corrected Emission Maxima of Group B Re(L-L)(CO)$_3$py$^+$ Complexes and Ligands L-L in Ethanol–Methanol (4:1) at 77 K

L-L	λ_{max}, nm^a				
Re/3,4,7,8-Me$_4$phen	464	497	533	579	
3,4,7,8-Me$_4$phen	464	501	540	584	640
Re/4,7-Me$_2$phen	463	496	530	574	
4,7-Me$_2$phen	461	498	536	580	634
Re/5,6-Me$_2$phen	483	518	555	610	
5,6-Me$_2$phen	476	514	555	605	665
Re/5-Phphen	492	527	569	627	
5-Phphen	499	534	575	632	693

[a] λ_{ex} = 320 nm; error ±1 nm.

Table VII. Emission Lifetimes of Group B Re(L-L)(CO)$_3$py$^+$ Complexes in Ethanol–Methanol (4:1) at 77 K^a

	λ_{obs}, nm^b				
L-L	460	500	550	600	τ, μs
3,4,7,8-Me$_4$phen	29.4 (54)	21.6 (52)	21.5 (71)	20.0 (74)	23 ± 3
	121 (46)	106 (38)	99 (29)	93 (26)	105 ± 9
4,7-Me$_2$phen	27.6 (46)	20.9 (61)	20.8 (72)	18.7 (76)	23 ± 3
	139 (54)	125 (39)	110 (28)	103 (24)	119 ± 13
5,6-Me$_2$phen	36.9 (42)^c	22.7 (58)	18.0 (63)	15.9 (70)	23 ± 7
	286 (58)^c	263 (42)	252 (37)	240 (30)	260 ± 14
5-Phphen		21.5 (61)	15.8 (71)	14.3 (77)	17 ± 3
		357 (39)	331 (29)	310 (23)	333 ± 16

[a] λ_{ex} = 355 nm, unless noted otherwise. [b] Position of observation, unless noted otherwise. Numbers are luminescence lifetimes in microseconds obtained from a biexponential fit of the emission decay; numbers in parentheses compare onset intensity amplitudes in percent contribution from each decay component. [c] 480-nm excitation.

lower energy relative to the emission energy of the complex containing the unsubstituted phenanthroline ligand. The lowest-energy spectra among the free ligands were found for 5-Phphen and 5,6-Me$_2$phen. Interestingly, 5-Phphen shows poorly resolved peaks and its emission spectrum is actually broader than that of its rhenium complex.

The emission decay curves of the group B complexes were evaluated in terms of two exponential components, the lifetimes of which are shown in Table VII. The shorter-lived component, which had the larger associated amplitude, was proportionately more significant at shorter detection wavelengths, accounting for 50–60% of the intensity at the highest-energy emission peak. This component had a lifetime between 15 and 35 μs, and the lifetime of the longer-lived component ranged between 100 and 350 μs, depending on the ligand.

For all of the complexes studied, the appearance of the emission spectrum was dependent to some degree on the excitation wavelength used. Spectra were collected using 320- and 410-nm excitation light, and these were then normalized to the same *maximum* intensity. Excitation at 410 nm resulted in relatively more intensity in the tail of the emission spectrum. For complexes with L-L = 3,4,7,8-Me$_4$phen and 4,7-Me$_2$phen a 20% increase was noted; for the complexes with L-L = phen, 2,9-Me$_2$phen, and 4,7-Ph$_2$phen less than 5% increase was noted. In addition, group A complexes exhibited a small red shift in λ_{max} of about 5 nm with 410-nm excitation.

Excitation Spectra. Excitation spectra were collected in methylene chloride at room temperature and in ethanol–methanol (4:1) at 77 K. The excitation spectra of the present complexes resembled the absorption spectra in the 320–450-nm region, but some features were sharper at 77 K than at room temperature. In the excitation spectra obtained at 77 K, detection toward the red end of the emission envelope produced slight intensity enhancements in the lowest energy shoulder, which corresponds to the MLCT manifold in absorption. This effect was observed for all of the complexes except Re(5-Phphen)(CO)$_3$py$^+$, which showed negligible wavelength dependence.

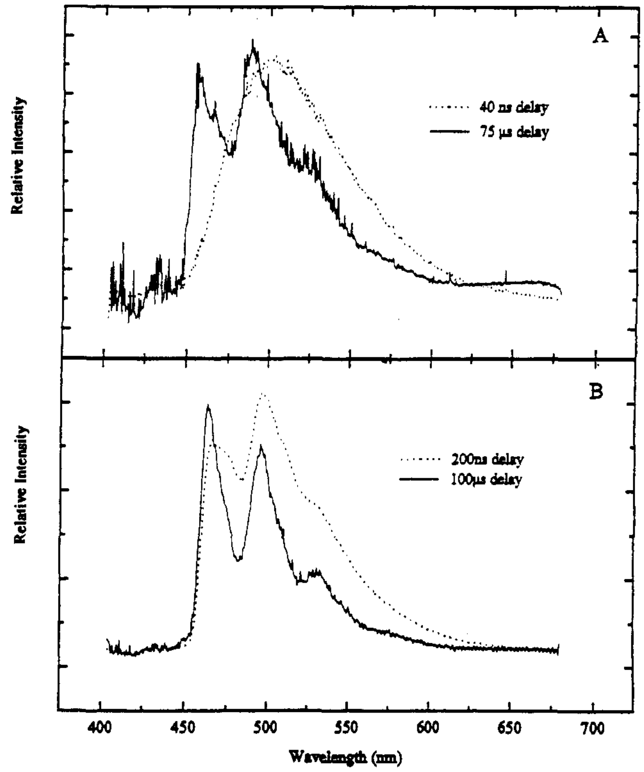

Figure 3. Time-resolved emission spectra recorded in ethanol–methanol (4:1) at 77 K: (A) Re(phen)(CO)$_3$py$^+$, (- - -) 40-ns delay, (—) 75-μs delay; (B) Re(4,7-Me$_2$phen)(CO)$_3$py$^+$, (- - -) 40-ns delay, (—) 75-μs delay.

Time-Resolved Emission Spectra. Low-temperature emission spectra were obtained in 4:1 ethanol–methanol glasses at various delay times after the laser pulse, were normalized to the same maximum intensity, and then were compared at short (<1 μs) and long (>1 μs) delay times (Figure 3). The long delay times were normally 2–3 times longer than the half-life of the slower-decaying component.

Emission spectra for most complexes showed substantial time dependence, particularly for those in group B, which gave structured spectra using CW excitation. These species displayed much more relative intensity at longer wavelengths when short delay times were employed. This was accompanied by a broadening of the existing peaks, although structure was largely retained (Figure 3B). Use of longer delays produced an increase in the relative intensity of the higher energy portion of the spectrum and enhanced the structure of the emission envelope. The energy of the onset of the emission, however, was unaffected by varying the delay.

Group A complexes, which gave broader spectra at 77 K (Re(L-L)(CO)$_3$py$^+$, L-L = 2,9-Me$_2$phen, 4,7-Ph$_2$phen, 2,9-Me$_2$-4,7-Ph$_2$phen), tended to show much less of an effect. Longer delay times resulted in λ_{max} shifting to higher energy by 100–250 cm^{-1} and a slight increase in the relative intensity at shorter wavelengths. In the case of Re(2,9-Me$_2$phen)(CO)$_3$py$^+$, emission spectra collected at very long delay times (100 μs) displayed some structure on the higher energy side of the emission band. A more substantial time dependence was exhibited by Re(phen)(CO)$_3$py$^+$. The spectrum consisted of a broad, structureless band (λ_{max} = 502 nm) when short delays were used, but a structured emission spectrum, with a peak maximum comparable to that of the free ligand but shifted slightly to lower energy (Figure 3A), was obtained at very long delay times (75 μs).

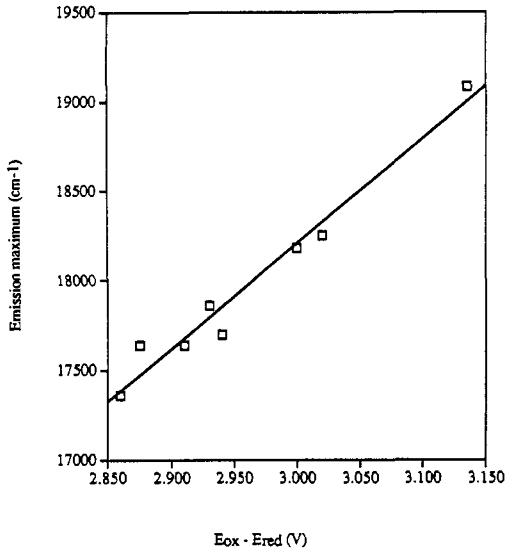

Figure 4. Correlation of emission energy with redox potentials for Re(L-L)(CO)$_3$py$^+$, measured in acetonitrile at 298 K. Slope = 5870 cm^{-1}/V or 0.73 eV/V. Correlation coefficient (R) = 0.98.

Discussion

The infrared, visible/UV, and room-temperature emission spectra were characteristic of Re(L-L)(CO)$_3$X$^+$ complexes having facial geometry, where L-L = a derivative of bipyridine or phenanthroline and X = a monodentate ligand.[2,4,11-13] The infrared spectra in the carbonyl region consisted of a single peak at 2035 cm^{-1} along with a broader envelope containing two absorptions near 1930 cm^{-1}. The visible/UV spectra contained absorptions in the 200–300-nm region associated with intraligand absorptions and a shoulder at lower energy (300–350 nm) attributed to metal-to-ligand charge transfer. The room-temperature emission spectra were broad and nearly structureless, consistent with ^{3}MLCT processes. Emission from Re(phen)(CO)$_3$py$^+$ and Re(5-Phphen)(CO)$_3$py$^+$ was reported earlier and was also attributed to a ^{3}MLCT state.[11a]

Electrochemistry. The redox potentials of relevance to the discussion are the ones derived from the processes involving the HOMO and LUMO. The HOMO consists of the dπ orbitals located on Re(I); the LUMO is predominantly the π^* orbital located on the phenanthroline ligand. Thus oxidation involves removal of an electron from the dπ orbital on Re(I); reduction involves addition of an electron to the π^* orbital on the phenanthroline ligand.

Relative to Re(phen)(CO)$_3$py$^+$, the effects of methyl and phenyl substituents bonded to the phenanthroline ligand followed the Hammett concept in a general way. Methyl groups, which are electron-donating substituents, shifted redox potentials in the negative direction; phenyl groups, which are weak electron-withdrawing substituents, had the opposite effect. Regardless of whether the substituents were methyl or phenyl groups, the first ligand reduction was shifted more than the metal oxidation. As a result, the separation of the dπ and π^* orbitals increases for the complexes containing attached methyl groups on the phenanthroline ligand and it decreases for complexes with phenanthroline ligands containing attached phenyl groups. The dπ–π^* separation, as determined by the difference $E_{ox} - E_{red}$, is largest for Re(3,4,7,8-Me$_4$phen)(CO)$_3$py$^+$ and smallest for Re(4,7-Ph$_2$phen)(CO)$_3$py$^+$. The potential differences (E_{ox} - E_{red}) correlate with the room-temperature emission maxima expressed in cm^{-1}, as illustrated in Figure 4. Similar trends have been reported previously[4,12b] and indicate that the thermodynamic energy gap and the electronic energy gap parallel one another. The fact that Re(4,7-Me$_2$phen)(CO)$_3$py$^+$ has a larger energy gap than Re(5,6-Me$_2$phen)(CO)$_3$py$^+$ demonstrates the stronger influence of substituents in the 4,7-positions of the phenanthroline ligands.

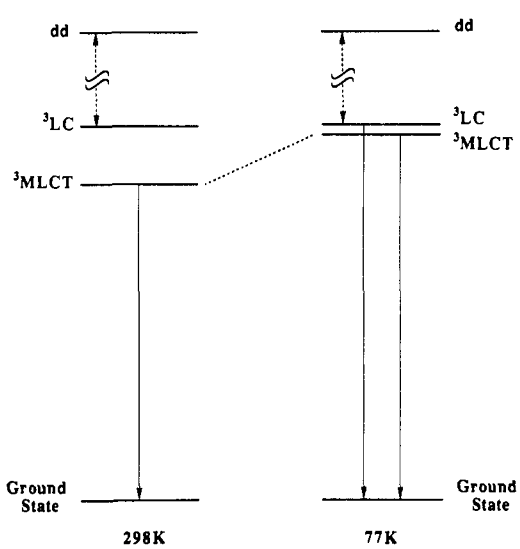

Figure 5. Energy-level diagram for the emitting state of Re(L-L)(CO)$_3$py$^+$.

Emission. The model that will be used in the subsequent discussion concerning the observed photophysical processes is illustrated in Figure 5. The model consists of three excited states: a triplet metal-to-ligand-charge-transfer state, ^{3}MLCT, a triplet ligand-centered state ($\pi\pi^*$), ^{3}LC, and a metal-centered dd state. The ^{3}LC state is taken to be essentially temperature-independent, so the energy gap between it and the ^{3}MLCT state is smaller at 77 K because the ^{3}MLCT state is shifted to higher energy. The energy gap between the ^{3}LC and dd states is unknown. In general, Re(L-L)(CO)$_3$py$^+$ complexes are photostable, although, as will be described below, the Re(3,4,7,8-Me$_4$-phen)(CO)$_3$py$^+$ complex showed photodecomposition ascribed to population of the dd state.

Room-Temperature Emission. At room temperature, emission occurs primarily from the MLCT state, which is equilibrated with respect to the solvent environment and geometry of the complex, since the reorientation of the solvent cage is fast compared to the rate of deactivation of the emitting state. The trend in emission energy follows the thermodynamic energy gap. However, trends in emission lifetime and quantum yield are less straightforward to interpret. It has been shown that, for a series of complexes based on a common chromophoric unit, the energy gap law will generally be obeyed.[21] That is, a linear relationship between ν_{max} and ln k_{nr} holds (where k_{nr} is the nonradiative decay rate), the lower-energy emissions being shorter-lived. This has been demonstrated for the related Re(I) tricarbonyl complexes Re(bpy)(CO)$_3$py-X$^+$ [11a] and Re(4,4′-X$_2$-5,5′-Y$_2$bpy)(CO)$_3$Etpy$^+$ where X = NEt$_2$, OMe, H, Cl and Y = Me, H.[12a] No such linear relationship holds for the phenanthroline complexes studied here: while methyl and phenyl groups have opposite effects on the emission energy, all of the derivatized ligands produce complexes longer-lived than Re(phen)(CO)$_3$py$^+$. (The overall decay rate ($k = k_r + k_{nr}$) was employed as an approximation for k_{nr}. Variations in the observed lifetime are assumed to arise largely from changes in k_{nr} for low-quantum-yield species).

Similarly, the lifetimes do not appear to be related to the emission quantum yields. These observations are unusual for MLCT emitters. The predominant influence over the emission lifetime appears to be the number of substituents occupying the phen ligand, as the two tetrasubstituted species, Re(3,4,7,8-Me$_4$-phen)(CO)$_3$py$^+$ and Re(2,9-Me$_2$-4,7-Ph$_2$phen)(CO)$_3$py$^+$, give the longest lifetimes in either solvent. A further distinction for these

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[21] (a) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (b) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444. (c) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.

complexes lies in the lesser solvent dependency observed in the lifetime. While other complexes undergo a 40–60% reduction in lifetime in the more polar solvent, CH$_3$CN, this effect is greatly reduced in the tetrasubstituted complexes, and in fact the values measured for Re(Me$_4$phen)(CO)$_3$py$^+$ in the two solvents are within experimental error (±10%). This behavior is more in keeping with ^{3}LC emission than with ^{3}MLCT emission. However, the redox properties and emission energies of these complexes follow the trends observed among the shorter-lived complexes, so there is no reason to suppose that their emissions have a different origin.

In the case of Re(3,4,7,8-Me$_4$phen)(CO)$_3$py$^+$, the emission lifetime measurements were reproducible, but the complex underwent slow photodecomposition. This may be attributed to population of the dd state lying a higher energy than the ^{3}MLCT state. Within a set of closely-related complexes having the same donor-atom set, the energy of the dd excited state is unlikely to be affected by substituents attached to the phenanthroline ligand, so the dd energy is likely to remain roughly constant throughout the series except, perhaps, for some small nephelauxetic effects. Since the emission energy of Re(3,4,7,8-Me$_4$phen)(CO)$_3$py$^+$ is the highest in the series of complexes, the energy difference between the ^{3}MLCT and dd states might be the smallest, accounting for the population of the dd state and the observed photodecomposition.

Low-Temperature Emission. The complexes exhibiting broad emission spectra at 77 K (group A) behaved for the most part like typical ^{3}MLCT emitters; the structured emission spectra at 77 K (group B) were more typical of ^{3}LC emission. At low temperture, emission occurs from a ^{3}MLCT state which is not fully equilibrated with respect to the solvent environment and the geometry of the complex, since the reorientation of the solvent cage is slow compared to the rate of deactivation of the emitting state. Thus we see a blue shift in the emission spectrum in low-temperature glasses compared to room-temperature fluid solution. Emissions arising from ligand-centered states, on the other hand, are relatively insensitive to solvent and temperature effects, as these transitions involve minimal redistribution of electron density with respect to the solvent dielectric. In group B complexes, the ^{3}MLCT state has been shifted to sufficiently higher energy that it lies at similar energy or above the energy of the ^{3}LC state. As noted in Table VI, the similarity in appearance and energy of the structured emission spectra of the group B complexes to the emission spectra of the corresponding free ligands at 77 K suggests that under these conditions emission occurs from a state which has substantial ligand-centered character.

The energy of the ^{3}MLCT state relative to the ^{3}LC state is influenced by the substitution pattern of the phenanthroline ligand. The emission energy of the free ligands provides a good approximation for the energy of the ^{3}LC state in group B complexes (Table VI) and is assumed also to do so for the group A complexes. To illustrate this point, Re(phen)(CO)$_3$py$^+$ and Re(5-Phphen)(CO)$_3$py$^+$, which have identical room-temperature ^{3}MLCT emission energies, can be compared. The free phenanthroline ligand has a higher energy ^{3}LC state than its 5-Phphen analog, and hence, a larger energy gap between the ^{3}LC and ^{3}MLCT states is expected in Re(phen)(CO)$_3$py$^+$ than in Re(5-Phphen)(CO)$_3$py$^+$. Indeed, the Re(phen)(CO)$_3$py$^+$ complex exhibits predominantly ^{3}MLCT emission at 77 K, whereas structured emission characteristic of the ^{3}LC state is observed for Re(5-Phphen)(CO)$_3$py$^+$.

Multiple Emission. To date there have been many examples of transition metal complexes which apparently display multiple emission in low-temperature glasses, including complexes of Ir(III), Rh(III), and Cu(II).[22-25] Re(I) tricarbonyl complexes have also figured prominently in this regard, with a number of examples of multiexponential decay kinetics being reported in the last 20 years.[2b,d,11,26] The observation of multiexponential decay indicates that at least two states or chromophores are contributing to the emission[27] and that these are not thermally equilibrated. The decay profiles of the group B complexes fit well to a dual exponential, and the lifetime of the shorter-lived component compares favorably with the 77 K lifetimes of the group A complexes (10–35 μs). Although the spectra of group B complexes imply a ^{3}LC assignment, time-resolved spectra lead one to postulate coincident emission from a ^{3}MLCT state along with emission from a ^{3}LC state. Time-resolved spectra show that long-lived component is responsible for the structured spectra and that short-lived component is responsible for the broader spectra, in each case.

A similar conclusion is reached for group A and/or group B complexes when the emission profile is examined as a function of excitation energy and the emission lifetimes and excitation spectra are examined as a function of emission wavelength. When lower energy excitation is used, relatively more spectral intensity is observed at longer wavelengths, suggesting greater population of the ^{3}MLCT state. Similarly, detection of the emission at lower energy results in enhancement of the lower energy absorption bands, attributed to MLCT transitions, in the excitation spectra. Finally, the measurable decrease in emission lifetime at 77 K for the group A complexes as the emission wavelength decreases implies that there is some ^{3}LC character in these emissions, although the broad spectra and single-exponential decays require that this contribution be relatively small.

The room-temperature behavior of the complexes can be rationalized on the basis of the 77 K emission experiments. The lack of a discernible correlation between emission energy and lifetime becomes more understandable if more than one emitting state exists. The lifetime of the ^{3}MLCT state at 298 K appears dependent on the degree of ^{3}LC character which contributes to the emission, either by radiative decay of the ^{3}LC state itself or by mixing of ^{3}LC character into the ^{3}MLCT state. It might be expected, though, that mixing of ^{3}LC character into the ^{3}MLCT state would be reflected in the absorption spectra of the complexes, so that the intensity of the MLCT shoulder would be enhanced for those complexes in which the two states are closest together. In fact, the evidence suggests the contrary; relative to the extinction coefficient for Re(phen)(CO)$_3$py$^+$, lower extinction coefficients were obtained for Re(5,6-Me$_2$phen)(CO)$_3$py$^+$ and Re(5-Phphen)(CO)$_3$py$^+$. This implies that radiative decay of the ^{3}LC state itself occurs at room temperature. If this is so, the amount of emission contributed from the ^{3}LC state would depend on the energy gap between the ^{3}LC and ^{3}MLCT states. Since the ^{3}LC

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(22) DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.

(23) (a) Wallace, L.; Heath, G. A.; Krausz, E.; Moran, G. *Inorg. Chem.* **1991**, *30*, 347. (b) Wilde, A. P.; King, K. A.; Watts, R. J. *J. Phys. Chem.* **1991**, *95*, 629. (c) King, K. A.; Watts, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 1589. (d) Watts, R. J.; Efrima, S.; Metiu, H. *J. Am. Chem. Soc.* **1979**, *101*, 2742. (e) Watts, R. J.; Missimer, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 5350. (f) Watts, R. J.; Brown, M. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 6029.

(24) (a) Merrill, J. T.; DeArmond, M. K. *J. Am. Chem. Soc.* **1979**, *101*, 2045. (b) Watts, R. J.; Van Houten, J. *J. Am. Chem. Soc.* **1978**, *100*, 1718. (c) Crosby, G. A.; Elfring, W. H. *J. Phys. Chem.* **1976**, *80*, 2206. (d) Halper, W.; DeArmond, M. K. *J. Lumin.* **1972**, *5*, 225.

(25) (a) Vitale, M.; Palke, W. E.; Ford, P. C. *J. Phys. Chem.* **1992**, *96*, 8329. (b) Casadonte, D. J., Jr.; McMillin, D. R. *Inorg. Chem.* **1987**, *26*, 3950. (c) Buckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillin, D. R. *J. Am. Chem. Soc.* 1979, *101*, 5846.

(26) Shaw, J. R.; Schmehl, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 389.

(27) We are well aware that many cases of apparently "multiple" emission have subsequently been shown to be caused by impurity, and we have naturally been careful to exclude this possibility in the present systems. Lifetime measurements performed on different batches of the same complex, synthesized by different methods, gave identical decay profiles. This was true whether the complexes were isolated as their perchlorate salts or as the usual triflates. Two complexes, with L-L = 4,7-Me$_2$phen and 5-Phphen, were also subjected to chromatography several times in succession, with no difference in behavior found between the fractions from the various columns (either alumina or silica; eluent methylene chloride followed by acetonitrile). Attempts to use ion-exchange methods failed due to solvent incompatibility.

state of the rhenium complexes is assumed to follow the trend discerned for ^{3}LC energies of the free ligands, the proportion of ^{3}LC emission should be least for Re(phen)$(CO)_3py^+$ and it should have the shortest lifetimes, as unsubstituted phenanthroline gives the highest-energy emission. Indeed this is the case. In addition, a variable contribution of the ^{3}LC state to the emission of each complex within the series studied here may account for the lack of a correlation between the emisson energy and the emission lifetime. Thus, the emission lifetime seems to depend on both the energy of the ^{3}MLCT state and the energy gap between the ^{3}MLCT state and the ^{3}LC state.

The cause of the multiexponential decay kinetics seen for the group B complexes is not certain. Three possibilities seem most likely in the light of the observed photophysical behavior. The first is the emission from two nonequilibrated states within the same complex occurs. Second, the degeneracy of the triplet states within the same complex is lifted, resulting in additional emitting states. Third, the low-temperature glass provides a heterogeneous matrix and since the ^{3}MLCT state is sensitive to the solvent environment, a range of species exists, some of which have lower-energy ^{3}MLCT states and others in which the ^{3}LC state lies lower. In this case, either two lifetimes, characteristic of the two possible lowest-energy states, might be observed, or a range of lifetimes could result from the variable degree of ^{3}LC characer in the emission. The existence of a range of exponential decays may not be distinguishable from the case involving only two, in terms of mathematical curve-fitting. Other workers in this field have favored matrix heterogeneity as an explanation for the emission characteristics described above.[11] Our experiments could not distinguish between the existence of two spatially separated emitting species and the presence of two emitting states within the same molecule. However, since the room-temperature emission appears to originate from more than one state, it could be argued that the same is true at low temperature when the states are closer in energy. Although the energy gap is of the order of the energy of molecular vibrations (500–5000 cm^{-1}), which should facilitate internal conversion, the frozen matrix may prevent this from occurring. In this case nonequilibrated emission from the two states may be observed. In any case, the facts remain that the two states are very close in energy and that both contribute to emission at room temperature and 77 K.

Conclusions

We have shown that, in addition to varying the nature of ligand substituents, one can also achieve fine-tuning by judicious positioning of ligand substituents. In this way, the energy gap between ^{3}MLCT and ^{3}LC states can be varied, affecting the degree of ligand-centered character in the emission and thus altering the photophysical properties of the complex. Since the states are affected differently by a given substitution pattern, it may not be possible to predetermine the behavior of a desired complex prior to its synthesis. Nevertheless, it is clear that the 4,7-sites are more influential toward altering the energy of the ^{3}MLCT state at room temperature than substituents in the other positions. At 77 K some complexes display characteristics of multiple emission, where the enegy gap between ^{3}MLCT and ^{3}LC states is sufficiently small. This might be a single-molecule phenomenon, if the rigid matrix prevents internal conversion via molecular vibrations, but could also be attributed to matrix inhomogeneity.

From the point of view of preparing a dimeric phenanthroline ligand which would confer optimal photophysical properties on a Re(I) complex, we can draw some conclusions from these results. Re(4,7-Me$_2$phen)$(CO)_3py^+$ gave the highest quantum yield of 0.28 and was also long-lived (τ = 4.5 μs in CH_3CN at room temperature). Linking two phenanthroline ligands via an ethylene bridge attached at the 4,7-positions should therefore give a Re(I) tricarbonyl moiety with higher quantum efficiency than a dimer linked via the alternative positions. This may accentuate the energy/electron-transfer process in the mixed-metal Re–Ru system.

Current experiments in our laboratory are concentrated on elucidating the photophysical behavior of the complexes at room temperature, where the emitting system is in thermal equilibrium. The temperature dependence of the emission lifetimes and quantum yields ought to provide valuable information regarding the identity and proximity of the emitting states; in particular, the location of the dd state should be made clear.

Acknowledgment. We thank the office of Basic Energy Sciences of the Department of Energy for support, Professor John Endicott of Wayne State University for the generous use of his laser facilities, and Marc Perkovic for collecting the TA spectra.