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The Nature of the Lowest Excited State in *fac*-Tricarbonylhalobis(4-phenylpyridine)rhenium(I) and *fac*-Tricarbonylhalobis(4,4′-bipyridine)rhenium(I): Emissive Organometallic Complexes in Fluid Solution[1]

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Received July 17, 1978

Abstract: Electronic absorption and emission spectral studies are reported for *fac*-$XRe(CO)_3L_2$ (X = Cl, Br, I; L = 4-phenylpyridine, 4,4′-bipyridine) complexes in solution at 298 and 77 K. All complexes are emissive at 298 K from a state which is assigned as a Re → LCT state having considerable triplet character, and in every case the emission intensifies, blue shifts, and becomes longer lived at 77 K. For L = 4-phenylpyridine the complexes have a 77 K emissive state which has considerable intraligand (IL) (π–π^*) triplet character, whereas the 4,4′-bipyridine complexes exhibit emission which is dominated by Re → LCT character at any temperature between 77 and 298 K. The temperature dependence, over the range 30–300 K, of the emission lifetime and quantum yield in EPA, 2-propanol, and as a solid for *fac*-$ClRe(CO)_3$(4-phenylpyridine)$_2$ shows that both temperature and medium rigidity significantly influence the emission properties. The temperature dependence of the emission properties shows that both the nonradiative and radiative decay constants change with temperature, in accord with a variable admixture of IL and ReLCT character of the emissive state. Quenching of the excited *fac*-$XRe(CO)_3$(4-phenylpyridine)$_2$ complexes by *trans*-stilbene occurs at a diffusion-controlled rate and produces the spectroscopic *trans*-stilbene triplet which decays to the characteristic ratio of *cis*- and *trans*-stilbene. This result supports the conclusion that the emissive state has considerable triplet character.

Elaboration of the known bimolecular reactions of electronic excited organometallic complexes hinges on the discovery of excited species which persist in fluid solution long enough to suffer some reactive quenching process. Often the lowest excited states of mononuclear organometallics involve orbitals of termination and/or origin which are very consequential with respect to metal–ligand bonding. Lowest lying excited states which are ligand field (d–d) in character are believed to be responsible for the extreme photosensitivity of metal carbonyl complexes with respect to ligand dissociation.[2] Metal–metal bonded complexes often exhibit lowest lying excited states which involve depopulation of the σ_b (with respect to the metal–metal framework) orbital and/or population of the σ^* orbital.[3] Such excited states undergo dissociative-type metal–metal bond homolysis; dinuclear species in particular are efficiently fragmented with optical excitation. To design molecules which have long-lived excited states in solution, one must seemingly avoid introduction of lowest excited states involving transitions which terminate in orbitals which are σ^* in character.

At the present time there are a number of transition-metal complexes which exhibit optically excited luminescence in fluid solution under conditions where photochemistry is possible. Observation of luminescence is an indicator that the excited species is long lived enough to suffer bimolecular reaction in competition with dissociative excited-state reactions. And importantly, the observation of emission allows some key excited-state properties (energy, lifetime, one-electron character) to be determined directly and relatively easily. The solution emission properties of certain Cr(III) complexes are under intense study,[4] in connection to photosubstitution. Detectable luminescence from excited $[Ru(2,2'\text{-bpy})_3]^{2+}$ and related complexes[5] has certainly been a key to the prevailing interest in its solution photochemistry; examples of simple collisional electronic energy transfer,[6] oxidation–reduction,[7] proton transfer,[8] and medium effects such as those resulting from ion pairing[9] and solvent deuteration[10] have been reported. Other examples of low-spin d^6 emitters in fluid solution are Os(II) and Ir(III) complexes of 1,10-phenanthroline[11] and related ligands.

Organometallics $M(CNPh)_6$ (M = Cr, Mo, W) have been found[12] to be luminescent in solution and have been found to undergo bimolecular reactions in the excited state. Recently, the dinuclear system $Rh_2(1,3\text{-diisocyanopropane})_4{}^{2+}$ has been found to be emissive[13] in solution and has been shown to undergo excited-state electron-transfer reactions which yield H_2 from acidic aqueous solutions.[14] The only metal carbonyls known to be emissive in fluid solution are *fac*-$ClRe(CO)_3$(phen) and related complexes.[15] A study of the excited-state electron-transfer properties of this species has recently been completed.[16] A preliminary account[17] describes the emission behavior of *fac*-$XRe(CO)_3$(benzoylpyridine)$_2$ representing a set of metal carbonyl complexes which are emissive in fluid solution but involve no chelating ligand system.

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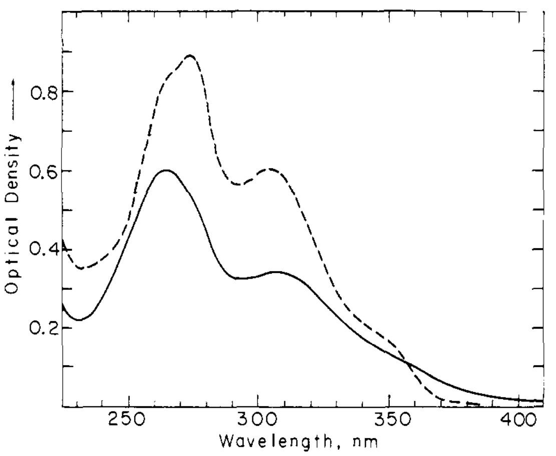


Figure 1. Electronic absorption spectra at 298 (——) and 77 K (- - - -) in EPA for *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$. The spectral changes upon cooling have not been corrected for solvent contraction. Path length is 1.00 cm and concentration of the complex is 1.5 × 10^{-5} M.

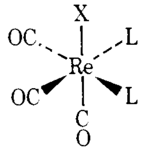
In this article we wish to report the solution emission behavior of *fac*-XRe(CO)$_3$L$_2$ (X = Cl, Br, I; L = 4-phenylpyridine, 4,4′-bipyridine). The data support an assignment of Re → LCT as the lowest (emissive) excited state at 298 K. These complexes are also emissive at low temperature in rigid media, and a comparison of the 298 and 77 K emission properties is made. The low-temperature spectral properties are significantly different and for L = 4-phenylpyridine the emissive state gains considerable intraligand (IL) (π–π^*) character, compared to the 298 K properties.

Results and Discussion

A. Preparation and Characterization of the Compounds. Complexes of the formula *fac*-XRe(CO)$_3$L$_2$ (X = Cl, Br, I; L = pyridine or a substituted pyridine) can generally be prepared according to the equation[15,17,18]

$$\mathrm{XRe(CO)_5} \xrightarrow[\text{isooctane,}\ \text{excess L}]{60\ ^\circ\mathrm{C}} fac\text{-}\mathrm{XRe(CO)_3L_2} + 2\mathrm{CO} \qquad (1)$$

The desired substitution product often precipitates from the alkane solution as it forms and can thus be isolated and purified easily. Representative complexes have been characterized by elemental analyses (cf. Experimental Section). All of the complexes have been characterized by infrared band maxima in the CO stretching region (Table I). The three-band pattern is consistent with the *facial* arrangement of the three COs in the coordination sphere, I. The complexes are, thermally and photochemically, relatively substitution inert; they are not air sensitive and are not volatile. Except for alkanes and H$_2$O, the complexes are soluble in most solvents.



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B. Absorption Spectra. Electronic absorption spectra for two representative *fac*-XRe(CO)$_3$L$_2$ complexes are shown in Figures 1 and 2, and Table II summarizes the absorption positions and absorptivities for a number of complexes. In every case there appear to be two main absorption features in the ultraviolet region. The higher energy features can be associated with an electronic transition localized mainly on the ligand L and will be referred to as the IL(π–π^*) absorption, and the lower energy absorption is attributable to a Re → LCT transition. These assignments are supported by the intensity, position, and solvent dependence of the absorption bands.

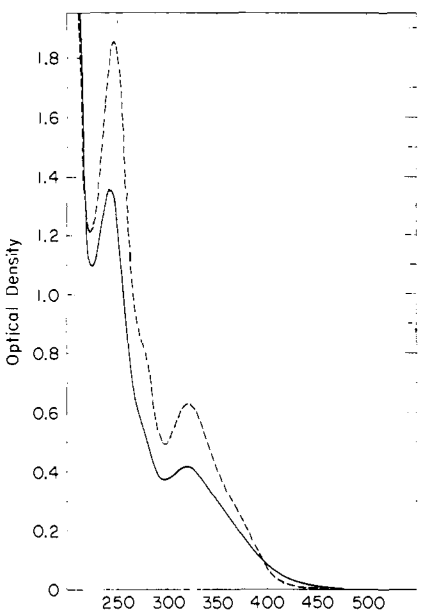


Figure 2. Electronic absorption spectrum of *fac*-ClRe(CO)$_3$(4,4′-bpy)$_2$ in EPA at 298 K (——) and after cooling to 77 K (- - - -). The change in the spectrum upon cooling has not been corrected for solvent contraction.

Table I. Infrared Band Maxima in CO Stretching Region for *fac*-XRe(CO)$_3$L$_2$ Complexes

		bands, cm^{-1} [a]		
X	L	strong	medium	medium
Cl	pyridine	2027	1922	1886
	1,10-phenanthroline = L$_2$	2015	1912	1890
	4-phenylpyridine	2025	1922	1888
	3-cyanopyridine	2035	1935	1898
	3,5-dichloropyridine	2034	1936	1898
	4,4′-bipyridine	2027	1926	1890
	4-cyanopyridine	2032	1936	1898
Br	4-phenylpyridine	2026	1923	1890
	4,4′-bipyridine	2027	1927	1894
I	4-phenylpyridine	2023	1924	1893
	4,4′-bipyridine	2026	1928	1896

[a] CH$_2$Cl$_2$ solutions at 298 K. Data were recorded using a Perkin-Elmer 180 spectrometer.

The higher energy band in each complex falls at a position nearly equal to that found for the free ligand L under the same conditions. Further, the *fac*-XRe(CO)$_3$L$_2$ species exhibit absorptivities for the higher energy absorption which have nearly the same absorptivity per L as L itself. The position of the higher energy band is not too sensitive to solvent or temperature, but does sometimes develop vibrational structure at low temperature as found for the free ligand L. These facts support the IL(π–π^*) assignment for the higher energy absorption in *fac*-XRe(CO)$_3$L$_2$.

The position of the lower energy absorption feature is sensitive to the nature of L, solvent, and temperature, but does not depend on variation in X from Cl to Br to I. Table III gives spectral maxima for the first absorption showing that the more polar solvents yield the higher energy absorption maximum. This solvent dependence parallels that found for other metal carbonyls where an MLCT assignment has been made.[15,19-22] From variation in L, we note that it appears that the more easily reduced[23] L yields complexes exhibiting the lower energy first absorption, consistent with CT character and Re → L

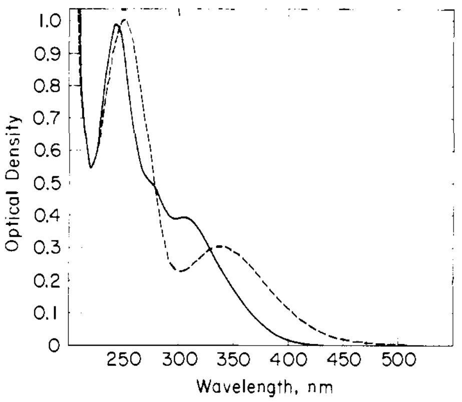


Figure 3. Comparison of electronic absorption spectra of *fac*-ClRe(CO)$_3$(4,4'-bpy)$_2$ (—) and *fac*-[ClRe(CO)$_3$(4,4'-bpyH$^+$)$_2$]$^{2+}$ (- - - -) in CH$_3$CN solution at 298 K at 2.75 × 10^{-5} M in 1.00-cm path length cells.

Table II. Electronic Absorption Band Maxima of *fac*-XRe(CO)$_3$L$_2$ Complexes[a]

X	L	bands, nm (ε, M^{-1} cm^{-1}) Re → LCT	IL(π–π*)
Cl	pyridine	292 (6800)	262 (8700)
	4-phenylpyridine	303 (22 600)	268 (36 500)
	3-cyanopyridine	308 (8900)	253 (15 600)
	3,5-dichloropyridine	310 (6650)	282 (8500)
	4,4'-bipyridine	317 (13 200)	245 (35 900)
	4-cyanopyridine	338 (11 100)	252 (12 500)
Br	4-phenylpyridine	305 (22 500)	268 (37 250)
	4,4'-bipyridine	322 (13 450)	245 (36 250)
I	4-phenylpyridine	305 (21 050)	270 (38 500)
	4,4'-bipyridine	320 (12 500)	238 (35 000)

[a] CH$_2$Cl$_2$ solutions at 298 K; data were recorded using a Cary 17 UV-vis-near-IR spectrophotometer.

Table III. Solvent Dependence on First Absorption Band System in *fac*-XRe(CO)$_3$L$_2$ at 298 K

X	solvent	band max, nm L = 4-phenylpyridine	L = 4,4'-bipyridine
Cl	CH$_3$CN	298	305
Cl	EtOH	300	315
Cl	CH$_2$Cl$_2$	303	317
Cl	THF	305	317
Cl	Et$_2$O	310	
Cl	C$_6$H$_6$	312	325
Cl	4% C$_6$H$_6$/96% isooctane	322	
Br	CH$_3$CN	300	309
Br	CH$_2$Cl$_2$	305	322
Br	Et$_2$O	311	
Br	4% C$_6$H$_6$/96% isooctane	325	
Br	C$_6$H$_6$		328
I	CH$_3$CN	303	308
I	CH$_2$Cl$_2$	305	320
I	Et$_2$O	311	
I	4% C$_6$H$_6$/96% isooctane	328	
I	C$_6$H$_6$		328

Table IV. Absorption Maxima for Protonated and Nonprotonated Form of *fac*-XRe(CO)$_3$(4,4'-bpy)$_2$ at 298 K

solvent	X	band max, nm nonprotonated	protonated
CH$_3$CN	Cl	305	335
	Br	309	332
	I	308	332
MeOH	Cl	315	340
	Br	318	342
	I	320	340
25% EtOH/75% H$_2$O	Cl	305	333
	Br	312	335
	I	315	330

direction. The ordering of the first band as a function of L is as found for the ordering in other d^6 metal carbonyl systems involving a comparable set of ligands L.[19,21] The lack of an effect upon variation in X from Cl to Br to I reflects little change in the charge density on Re in the ground state consistent with the rather modest changes in CO stretching frequency for a given X (Table I). These facts support the assignment of the first absorption band as Re → LCT.

Table IV provides further evidence in support of the Re → LCT assignment for *fac*-XRe(CO)$_3$(4,4'-bpy)$_2$. The nonligated N atom is a site of protonation, and the first absorption maximum red shifts upon protonation consistent with greater base strength in the excited state where L gains negative charge.[8a] Figure 3 shows a comparison of the spectra of a protonated and nonprotonated 4,4'-bipyridine complex.

While the absorption spectra are dominated by the IL(π–π*) and Re → LCT absorptions, it is apparent that ligand field (d-d) absorptions must be in the same energetic region. This follows from the known[24] ligand field band positions in XRe(CO)$_5$ where there are no low-lying Re → LCT bands. The ligand field bands in XRe(CO)$_5$ have molar absorptivities in the ~3000 M^{-1} cm^{-1} range. In the complexes under study here the ligand field bands must be obscured by the other, more intense, absorptions and cannot be directly located.

C. Emission Properties. When optically excited, the 4-phenylpyridine and 4,4'-bipyridine complexes do not appear to undergo efficient dissociative-type reactions. Rather, these and other pyridine complexes undergo detectable optical emission in fluid solution. For all complexes the emission efficiency and its spectral distribution are independent of the excitation wavelength for a given set of conditions. As found for the absorption spectra, the emission properties are only modestly affected by X, but solvent and temperature seem to be very influential with respect to excited-state decay properties. Detailed measurements have been made for the 4-phenylpyridine and 4,4'-bipyridine species (Tables V–VIII and Figures 4–7).

In the same solvent, the emission of the 4,4'-bipyridine complex is significantly to the red of that for the 4-phenylpyridine complex. This is in accord with the notion that the emission originates from the Re → LCT state observed in absorption. If the emission were ligand field in character the emission should be in the same position, since the donor sphere in both systems is the same.[21] Also, though the protonated form of the 4,4'-bipyridine complex unfortunately does not emit in fluid solution at room temperature, both the nonprotonated and protonated species are emissive at 77 K in rigid media (Figure 4); the protonated species emits ~2000 cm^{-1} to the red of the nonprotonated form. Tables V and VI, along with Figure 4, summarize the emission properties of the 4,4'-bipyridines. The 298 K emission lifetimes are in the range 0.3–4.8 μs but go up to 45 μs in rigid media at 77 K, and there is a substantial blue shift in the emission onset and maximum and increase in emission quantum yield, Φ_e, upon cooling solutions of the nonprotonated species from 298 to 77 K. Under no conditions do we find any vibrational structure on the emission spectrum for the 4,4'-bipyridine complexes.

Upon cooling solutions of the 4-phenylpyridine to low temperatures, we find some qualitatively different behavior compared to the 4,4'-bipyridine systems. The lifetime goes from 0.3–2.6 μs at 298 K to 260–450 μs at 77 K. Further, the 77 K emission spectrum exhibits some structure (Figure 5)

Table V. Luminescence Characteristics for *fac*-$XRe(CO)_3(4,4'\text{-bpy})_2$ at 298 K

X	solvent	band max, cm^{-1} [a]	half-width, cm^{-1} [b]	lifetime τ, $\times 10^6$ s ± 15%	quantum yield[c] Φ ± 25%
Cl	CH_3CN	16 500	4000	0.45	0.005
Cl	MeOH	16 500	4000	0.45	0.005
Cl	THF	17 000	4250	0.95	0.018
Cl	H_2CCl_2	17 000	4250	1.30	0.016
Cl	C_6H_6	17 750	4500	4.8	0.055
Br	CH_3CN	16 500	3700	0.40	
Br	MeOH	16 500	3700	0.40	
Br	C_6H_6	17 750	3500	3.0	
I	CH_3CN	16 300	3500	0.30	
I	MeOH	16 200	3600	0.30	
I	C_6H_6	18 000	3300	1.45	

[a] Corrected emission spectra. [b] Half-width is width of correction emission band at half the height at the band maximum. [c] Luminescence quantum yields relative to rhodamine B; data is corrected for difference in refractive index of solvents.

Table VI. Luminescence Characteristics for *fac*-$XRe(CO)_3(4,4'\text{-bpy})_2$ and Protonated Analogue at 77 K

X	solvent	compd	band max, cm^{-1} [a]	half-width[b]	lifetime τ, $\times 10^6$ s ± 15%	quantum yield[c] Φ ± 25%
Cl	EtOH	neutral	19 000	4250	45	0.35
Cl	EtOH	protonated	17 125	5000	3.5	0.02
Cl	EtOH/MeOH (4/1)	neutral	19 100	3900	45	
Cl	EtOH/MeOH (4/1)	protonated	17 100	4750	3.5	
Br	EtOH/MeOH (4/1)	neutral	18 500	4000	40.0	
Br	EtOH/MeOH (4/1)	protonated	17 500	4200	8.0	
I	EtOH/MeOH (4/1)	neutral	18 600	3500	35	
I	EtOH/MeOH (4/1)	protonated	18 000	4500	18	

[a] Corrected emission spectra. [b] Half-width is width of corrected emission band at half the height at the band maximum. [c] Luminescence quantum yields relative to rhodamine B; data is corrected for difference in refractive index of solvents.

Table VII. Luminescence Characteristics for *fac*-$XRe(CO)_3(4\text{-phenylpyridine})_2$ at 298 K

X	solvent	band max, cm^{-1} [a]	half-width[b]	lifetime τ, $\times 10^6$ s	quantum yield[c] Φ
Cl	CH_3CN	18 500	4700	0.85	0.006
Cl	H_2CCl_2	18 700	4500	1.45	0.010
Cl	EtOH	18 800	4500	1.00	0.006
Cl	EPA	18 800	4500	1.50	0.010
Cl	2-propanol	18 800	4500	1.25	0.008
Cl	EtOH/MeOH (4/1)	18 600	4800	1.0	0.005
Cl	Et_2O	18 700	4750	1.75	0.013
Cl	C_6H_6	19 000	4300	1.70	0.017
Cl	4% C_6H_6/96% isooctane	19 000	4300	2.60	0.022
Br	CH_3CN	18 800	4800	0.70	0.006
Br	H_2CCl_2	18 800	4700	1.00	0.008
Br	EtOH/MeOH (4/1)	18 700	4700	0.65	0.004
Br	C_6H_6	19 000	4500	0.95	0.007
Br	4% C_6H_6/96% isooctane	19 000	4500	1.30	0.014
I	CH_3CN	18 600	4600	0.42	0.004
I	H_2CCl_2	18 600	4500	0.48	0.006
I	EtOH/MeOH (4/1)	18 600	4700	0.25	0.003
I	C_6H_6	19 100	4400	0.30	0.005
I	4% C_6H_6/96% isooctane	19 100	4400	0.60	0.010

[a] Corrected emission spectra. [b] Half-width is width of corrected emission band at half the height at the band maximum. [c] Luminescence quantum yields relative to rhodamine B; data is corrected for difference in refractive index of solvents.

which is not found in either the 4,4′-bipyridine or 1,10-phenanthroline[15] complexes under the same conditions. The blue shift and intensification of the emission for these complexes are accompanied by a remarkable increase in emission lifetime. We attribute the increase in lifetime and the appearance of structure on the emission to a substantial contribution from

Table VIII. Luminescence Characteristics for *fac*-XRe(CO)$_3$(4-phenylpyridine)$_2$ at 77 K

X	solvent	band max, cm$^{-1\,a}$	half-width^b	lifetime τ, $\times 10^6$ s	quantum yield^c Φ
Cl	EPA	20 000 (sh) 21 300 22 600 (sh)	3700	450	
Cl	EtOH/MeOH (4/1)	20 000 (sh) 21 300 22 600 (sh)	3900	450	0.8
Br	EPA	19 600 (sh) 21 200 22 250 (sh)	3800	410	
Br	EtOH/MeOH (4/1)	19 500 (sh) 21 000 22 250 (sh)	4000	410	0.8
I	EPA	19 700 (sh) 21 100 22 150 (sh)	3800	260	
I	EtOH/MeOH (4/1)	19 600 (sh) 21 100 22 250 (sh)	3800	260	0.9

[a] Corrected emission spectra. [b] Half-width is width of correction emission band at half the height at the band maxima. [c] Luminescence quantum yields relative to rhodamine B; data is corrected for difference in refractive index of solvents.

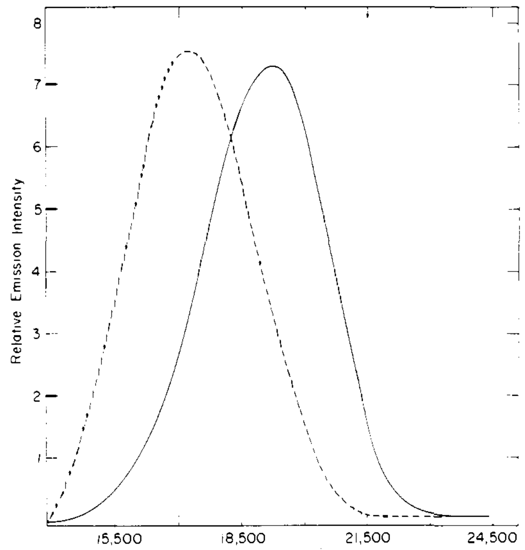


Figure 4. Corrected emission spectral distribution for ~10^{-4} M *fac*-ClRe(CO)$_3$(4,4′-bpy)$_2$ (—) and *fac*-[ClRe(CO)$_3$(4,4′-bpyH$^+$)$_2$]$^{2+}$ (- - - -) in EtOH glass at 77 K. The emission is excited at 350 nm in each case, but the relative sensitivities differ. See Table VI for relative emission quantum yields.

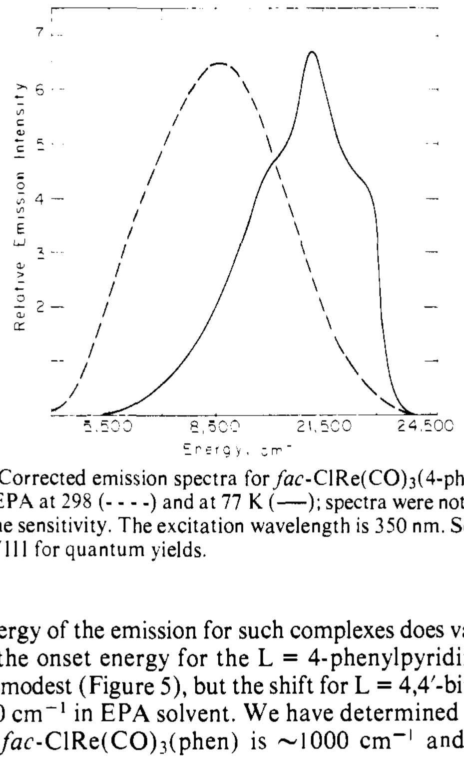
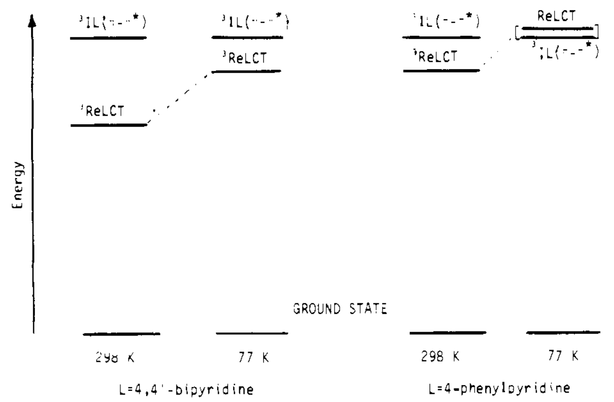


Figure 5. Corrected emission spectra for *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$ in EPA at 298 (- - - -) and at 77 K (——); spectra were not recorded at the same sensitivity. The excitation wavelength is 350 nm. See Tables VII and VIII for quantum yields.

the IL(π–π^*) triplet emission. Though we find only one decay time for the emission, the emission likely does have some considerable admixture of IL and CT character; the free ligand emission at 77 K is at nearly the same position as for the complex. Since the singlet–singlet absorption position of the 4-phenylpyridine is perturbed only slightly by coordination, we do not expect too large a perturbation of the triplet IL excited state energy. The triplet lifetime of 4-phenylpyridine is >1 s; the Re may exert a heavy-atom effect on the IL triplet state which enhances its radiative decay constant.

Scheme I summarizes a comparison of the emission properties of the L = 4,4′-bipyridine and L = 4-phenylpyridine complexes in a common solvent at 298 and 77 K. The scheme shows a qualitative ordering of the Re → LCT and IL triplet excited states relative to the ground state of each system. Changes in the 0–0 energy of the Re → LCT states with temperature and L is seemingly demanded by the fact that the *onset* energy of the emission for such complexes does vary. The shift in the onset energy for the L = 4-phenylpyridine complexes is modest (Figure 5), but the shift for L = 4,4′-bipyridine is ~1100 cm^{-1} in EPA solvent. We have determined that the shift in *fac*-ClRe(CO)$_3$(phen) is ~1000 cm^{-1} and in *fac*-ClRe(CO)$_3$(4-benzoylpyridine)$_2$ the shift is ~500 cm^{-1}. In all three of these cases the emission onset is at higher energy at 77 K than at 298 K and the emission lifetimes at 77 K are of the order of 20 μs. These emission properties, along with a featureless emission band, typify what we will now term "pure" ReLCT excited states for these systems. The L = 4,4′-bipyridine complexes are categorized as pure ReLCT emitters. But for L = 4-phenylpyridine the ReLCT state is higher in energy than for L = 4,4′-bipyridine and even at room temperature the onset of emission is close to that found at low temperature (Figure 5). Assuming that the ReLCT excited states shift to higher energy as they do in the related complexes, the 77 K situation is one where the L = 4-phenylpyridine complexes have considerable IL character in the lowest excited state. Indeed, the L = 4-phenylpyridine complexes exhibit very long emission lifetimes compared to the cases categorized as pure ReLCT, and the L = 4-phenylpyridine complexes also exhibit

Scheme I. State Energies for *fac*-$XRe(CO)_3L_2$[a]



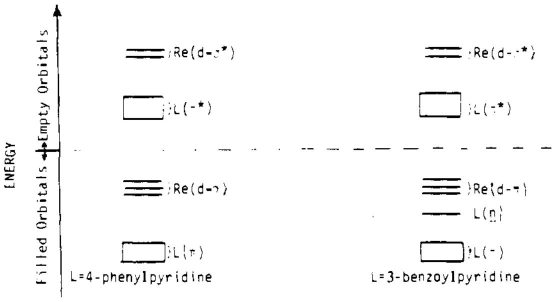
[a] In each energy level diagram the ground state is the reference point at the specified temperature. The state energies have been approximated from emission onset energies and the assumption that the 4-phenylpyridine systems will have a temperature effect similar to that for the 4,4'-bipyridine systems.

vibrational structure on the emission band. The ReLCT and IL states may be nearly isoenergetic at 77 K, but ReLCT emission properties may not be observable owing to lack of sufficient thermal activation to cross to the ReLCT state. At 298 K the emission properties of the L = 4-phenylpyridine systems appear to be dominated by ReLCT characteristics.

A reviewer has suggested the possibility that the 0–0 energies in fact remain invariant with temperature/solvent rigidity and that the variation in emission properties with temperature reflects the differences in the population of two emitting states separated by an energy gap. This interpretation may be viable, but the sensitivity of charge-transfer states to solvent suggests that changes in 0–0 energy could result from the changes in solution that take place with variation in temperature. Further, data presented below show that solvent rigidity, as well as temperature, affects the emission properties. Finally, variation in temperature results in smooth shifts in emission maxima rather than the decline and growth associated with two emitting states. These facts lead us to the general conclusion that ReLCT state energies are very sensitive to molecular environment and to favor the interpretation that the 0–0 energies do change. For L = 4-phenylpyridine we see no reason why its ReLCT state should be any less sensitive to the molecular environment than for other *fac*-$XRe(CO)_3L_2$ or *fac*-$XRe(CO)_3L$ complexes studied.[15,17] But let it be clearly noted that we are assuming that the emission onsets do reflect changes in the 0–0 energies and that the ReLCT state for the 4-phenylpyridine complexes is no less sensitive to environment than its 4,4'-bipyridine analogue.

We recently reported[17] that the ReLCT character of the 298 K emission from *fac*-$XRe(CO)_3$(3-benzoylpyridine)$_2$ (X = Cl, Br, I) changes upon cooling to 77 K in a manner somewhat similar to that indicated in Scheme I for the bis-4-phenylpyridine complexes. However, in the 3-benzoylpyridine complex the 77 K emission actually consists of two emissive states: the short-lived (~10 μs) ReLCT and the long-lived (~1200 μs) triplet IL(n–π*) state. To understand why the 4-phenylpyridine gives only one decay time at low temperature rather than a short ReLCT and a long IL(π–π*), we note the differing ligand orbitals of importance in the IL excited states in the two cases (Scheme II). For L = 4-phenylpyridine each of these orbital types (Re(dπ), L(π), and L(π*)) apparently can mix. However, for L = 3-benzoylpyridine the L(n) orbital, which is localized on the ketone oxygen, is not a π orbital and need not mix with all of the other levels. The point is that the n–π* state need only be perturbed to the extent that the L(π*) orbital interacts with the Re(dπ) levels. Further, the n–π* and ReLCT are likely to have substantially differing geometries and may not interconvert rapidly for this reason. Internal conversion between the IL(π–π*) and ReLCT states in the bis-4-phenylpyridine is likely facilitated by the mixing of the states and possibly by geometrical similarities. It appears likely that for L having an IL(π–π*) triplet the lowest excited states of *fac*-$XRe(CO)_3L_2$ complexes will be an admixture, but an extremely variable one, of ReLCT and IL(π–π*) character.

Scheme II. Orbital Level Diagrams for *fac*-$XRe(CO)_3L_2$ Complexes



Long excited-state lifetimes in fluid solution are often unobservable owing to the presence of impurity quenchers in the solvents. This is a particularly difficult problem for molecules which have fairly high energy excited states capable of being quenched by electronic energy transfer by a wider range of quenchers. Since we have placed considerable emphasis on the changes in lifetime and emission efficiency upon cooling solutions of *fac*-$XRe(CO)_3L_2$, we carried out an experiment which is fairly compelling with respect to showing that the Re complexes are inherently short lived in fluid solution. We showed that benzil (triplet energy ~55 kcal/mol)[25] emits with an emission lifetime of ~0.1 ms under the same conditions (rigorously deoxygenated issoctane/benzene solution) where we found an emission lifetime of ~3 μs for a *fac*-$XRe(CO)_3L_2$ complex. This experiment at least shows that triplet quencher impurities in the solvent are not the source of the short lifetimes for the complexes studied here.

D. Medium and Temperature Effects on Emission Properties. The large changes in emission properties upon cooling solutions of *fac*-$XRe(CO)_3L_2$ to 77 K are a consequence of changes in both the solvent rigidity and the temperature. This was shown to be true in the *fac*-$ClRe(CO)_3$(phen)[15] and related complexes. For L = 4-phenylpyridine and X = Cl we have measured the emission intensity and lifetime as a smooth function of temperature in two different solvents (Figure 6) and for the solid (Figure 7). These data show that the spectral changes are due to both temperature and medium rigidity changes.

First, consider the data for the two solvents EPA and 2-propanol, which have different glass transition temperatures; from Figure 6 we see that major emission spectral changes take place at very different temperatures, consistent with a higher temperature glass point for 2-propanol. But from the data it is clear that substantial additional spectral changes obtain upon lowering the temperature below the glass point. Data for the pure solid are also interesting; the pure solid emission is essentially nondetectable at 298 K but upon cooling the solid the emission efficiency increases by several orders of magnitude. The emission of the pure solid as a function of temperature may be complicated by the fact that there may be traps in the pure solid. But the data from the solutions are unequivocal with respect to an effect from temperature and rigidity.

One additional result from the spectral changes with temperature is noteworthy. We find that there is a smooth change in the spectral distribution of the emission from that associated with the complex at 298 K in solution to that for the 77 K solutions. Further, we find only one decay time at all tempera-

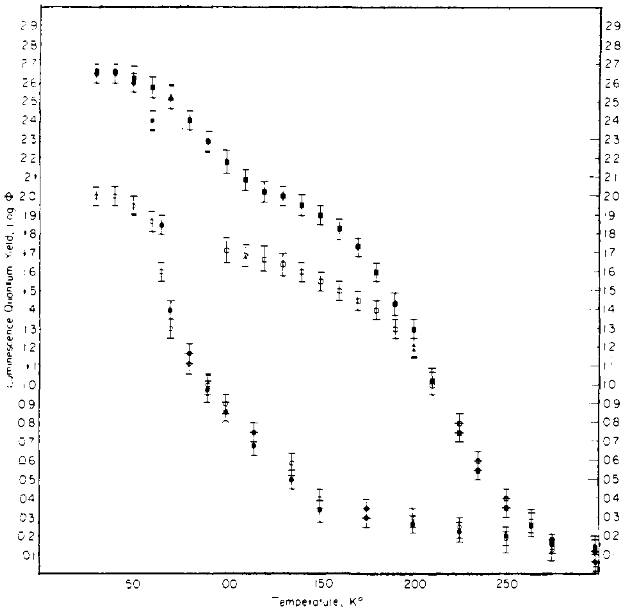


Figure 6. Temperature dependence of relative emission quantum yield (□) and emission lifetime (■) in 2-propanol, emission quantum yield (○), and emission lifetime (●) in EPA for *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$. The excitation wavelength used was 350 nm.

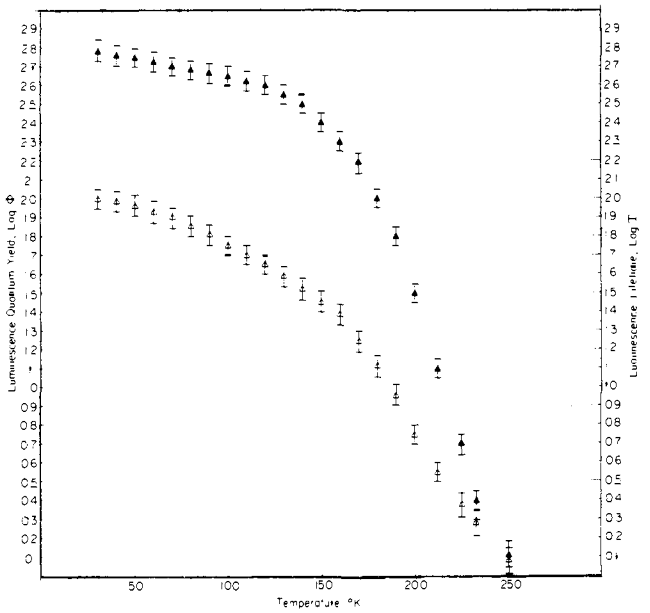


Figure 7. Temperature dependence of relative emission quantum yield (△) and emission lifetime (▲) for solid *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$. The excitation wavelength used was 350 nm.

tures. That is, we do not observe two emission maxima and two lifetimes at some point; rather the emission blue shifts, intensifies, and develops structure smoothly as the temperature is lowered.

Since both the emission lifetime and quantum yield are known from the data given in Figure 6, it is possible to evaluate the values for the radiative (k_r) and nonradiative (k_{nr}) decay constants at each temperature. For example, in EPA k_r varies from 6700 to 2100 s^{-1} from 298 to 50 K, while k_{nr} varies from 6.6×10^5 to 2.1×10^2 s^{-1} over the same range. In contrast to Re(ω)$_5$x,[24a] Ru(η^5-C$_5$H$_5$)$_2$[26] and Ta(CO)$_6^-$,[27] where only k_{nr} varies, we find that both k_r and k_{nr} change for *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$ as the temperature is varied. The changes in both k_r and k_{nr} are consistent with a change in the admixture of IL(π-π^*) and ReLCT character for the emissive state as the temperature varies. For the complexes previously studied no such changes were implicated; a single state having a temperature-independent k_r is reasonable in those systems.[24a,26,27]

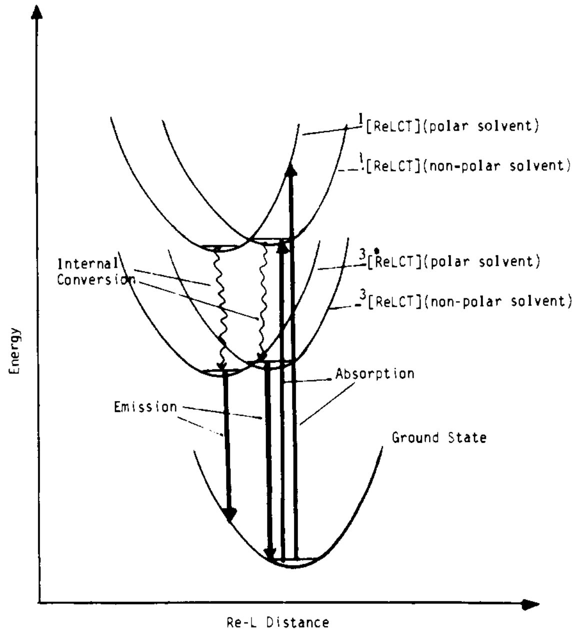
A detailed interpretation of the large solvent rigidity and temperature effects that we find must await further studies. Such would likely include time-resolved emission spectra which are presently outside our instrumental capability. But it is possible that the rigidity effect, at least, is due to structural constraints associated with the Re-L bonding and possibly rotation of the aromatic rings. Such effects have been found in organic molecules.[28a-c] Solvent rigidity effects on the emission properties of coordination complexes other than the *fac*-XRe(CO)$_3$L or these *fac*-XRe(CO)$_3$L$_2$ species have been observed.[28d]

Finally, with respect to medium effects on emission properties, we note that the 298 K emission maximum of the *fac*-XRe(CO)$_3$L$_2$ complexes studied here depends on the solvent in a manner which seems inconsistent with the corresponding changes in the absorption maximum. For L = 4-phenylpyridine the changes in emission maxima are modest, but the emission is ~500 cm^{-1} to the blue in C$_6$H$_6$ compared to CH$_3$CN. For L = 4,4′-bipyridine the emission is >1000 cm^{-1} to the blue in C$_6$H$_6$ compared to CH$_3$CN. For both sets of complexes the ReLCT absorption is >2000 cm^{-1} to the *red* in C$_6$H$_6$ compared to CH$_3$CN. It is logical to attribute the solvent effects mainly to interaction of the ligand orbitals with those of solvent, since the Re(dπ) orbitals should not be solvent accessible. But we must also accommodate the notion that the ReLCT excited state likely has considerable charge redistribution toward a radical anion (L$^-\cdot$) coordinated to a cationic metal center.

Overall solvation effects with respect to the *equilibrium* geometry and energy of the excited state *relative* to ground state can be represented as in Scheme III. In these sketches we choose to illustrate what may be the Re-L distance/energy dependence for the ground and ReLCT excited state. First, note that we *suggest* that the excited-state "distortion" is in fact one which yields a shorter Re-L distance. A lengthened Re-L bond could accord well with solvent effects, but the shorter Re-L bond is consistent with the notion that there will be an electrostatic attraction between the negatively charged L and the oxidized central metal. The contracted Re-L bond is consistent, too, with the substitution inertness of the Re-L bond in the excited state. We prefer the contracted Re-L bond interpretation, since d^5 Ru(III) complexes of nitrogen donors are generally more substitution inert than the d^6 Ru(II) analogues.[29] The ligating atom here is a nitrogen atom and there may well be a stronger bond between the formally d^5 Re(II) and any nitrogen donor ligand interaction on the basis of "hard" and "soft" arguments. The sketches show how it may be *possible* for the absorption and emission to shift in opposite directions with changes in solvent. The scheme should not be taken as reflecting quantitative information but rather as illustrative.

E. *fac*-XRe(CO)$_3$(4-phenylpyridine)$_2$ Sensitized *trans*- → *cis*-Stilbene Isomerization. The lifetimes of the *fac*-XRe(CO)$_3$L$_2$ complexes are in a range which is long enough to allow the observation of fast bimolecular excited-state processes. *trans*-Stilbene, having a triplet energy of ~50 kcal/mol,[30] quenches the excited *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$ complexes at essentially a diffusion-controlled rate (2.4×10^9 L mol^{-1} s^{-1}) as determined by measuring the relative emission quantum yield as a function of *trans*-stilbene concentration. The quenching obeys Stern-Volmer kinetics. Likewise naphthalene (triplet energy ≈ 61 kcal/mol)[25] quenches the bis-4-phenylpyridine complex emission but at a rate which is ~three times slower. Given that the emission energy for the 4-phenylpyridine is ~53 kcal/mol at the *maximum* of the band, it is apparent that there is enough excitation

Scheme III. Representation of Solvent Dependencies of State Geometries and Transition Energies Relative to the Ground State in *fac*-$XRe(CO)_3L_2$ Complexes



energy available to produce the spectroscopic triplet state of naphthalene or *trans*-stilbene by collisional triplet energy transfer.

At least for *trans*-stilbene the mechanism for the quenching does appear to be collisional triplet energy transfer. This result follows from the observation that the *trans*-stilbene quenching of excited *fac*-$XRe(CO)_3$(4-phenylpyridine)$_2$ is accompanied by formation of *cis*-stilbene. The sensitized 366-nm *trans*- → *cis*-stilbene quantum yields (±10%) are 0.58, 0.60, and 0.62 for X = Cl, Br, and I, respectively. The yields were measured at a *trans*-stilbene concentration high enough to quench all of the emission. Further, for X = Cl a photostationary state of 66 ± 2% *cis*-stilbene and 34 ± 2% *trans*-stilbene is achieved beginning with either pure *trans*- or *cis*-stilbene. The photostationary state is near that found[30] for organic triplet sensitizers having a triplet energy similar to that for the *fac*-$XRe(CO)_3$(4-phenylpyridine)$_2$ complexes. The initial *trans*- → *cis*-stilbene quantum yields are the same as those found for benzophenone sensitization,[30] where it is assumed that every photon absorbed actually results in a *trans*-stilbene triplet state. The conclusion is that the excited *fac*-XRe-$(CO)_3$(4-phenylpyridine)$_2$ complexes also completely efficiently produce the *trans*-stilbene triplet excited state in the quenching process.

From the *trans*-stilbene quenching studies it is apparent that the lowest excited state of *fac*-$XRe(CO)_3L_2$ species has enough triplet character to suffer quenching by triplet energy transfer at a diffusion-controlled rate. There is not enough excitation energy from the complexes for the quenching to proceed via singlet–singlet transfer. Owing to the heavy Re atom in the complex[31] it is probable that a pure triplet assignment is inappropriate for the lowest *fac*-$XRe(CO)_3L_2$ excited state. But the energy transfer and emission lifetime measurements are in accord with a lowest excited state having substantial triplet character, and we adopt such an assignment with the understanding that Re might exert an extraordinary spin–orbit perturbation in the system.

F. Proton-Transfer Equilibria of *fac*-$XRe(CO)_3$(4,4′-bpy)$_2$ Complexes. Protonation of the 4,4′-bipyridine complexes is reversible in the pH range ~1–7 in 25% MeOH/75% H_2O. A plot of change in optical density at any wavelength where there is a change gives a curve showing only one inflection point, revealing that $pK_{a(1)} \approx pK_{a(2)} = 4.0$ for X = Cl. The overall pK_a for the equation

$$fac\text{-}[ClRe(CO)_3(4,4'\text{-bpyH}^+)_2]^{2+} \rightleftharpoons fac\text{-}[ClRe(CO)_3(4,4'\text{-bpy})_2] + 2H^+ \quad (2)$$

is 8.0. The difference in absorption maxima for the non- and fully protonated species is ~2750 cm^{-1}, indicating that the overall excited state acid dissociation constant, pK_a^*, is ~13.7,[32] i.e., the excited nonprotonated form is a stronger base than the ground state, in accord with the increased electron density on the ligand in the excited state.

Unfortunately, the protonated form of the complexes is not emissive in fluid solution at room temperature. This precludes the use of an emission titration to directly evaluate the value of pK_a^* in solution at room temperature. The protonated complex does emit at low temperature, though, and the differences in the emission maxima for the protonated and nonprotonated forms of the 4,4′-bipyridine complexes are somewhat smaller than the differences in the ReLCT absorption maxima. Consequently, the calculated value of the overall pK_a^* is somewhat smaller than the ~13.7 calculated from the absorption data. This difference may be due to the fact that the absorption is principally singlet to singlet in character, whereas the emissive excited state has considerable triplet character. Differences in pK_a^* for singlet and triplet excited states are well documented[33] and may well be found[8] in metal complexes also.

The lack of solution emission from the protonated species is interesting and may be due to a number of factors including the lower energy emission having lower probability. The loss of emission may also reflect extensive electron transfer to the attached proton. Such might be important in the evolution of H_2 by electron transfer from an excited molecule,[12b,14] and this possibility is being actively pursued in this laboratory.

Experimental Section

Spectra. All infrared spectra were recorded using a Perkin-Elmer 180 instrument with either 0.1-mm or 1.0-mm path length matched cells. All electronic spectra were recorded using a Cary 17 and low-temperature spectra were obtained using an all-quartz liquid N_2 Dewar equipped with optical quality flats for windows. All luminescence studies were obtained using an Aminco-Bowman spectrophotofluorometer set up for emission measurements in the 300–900-nm range and equipped with a grating blazed at 750 nm. The detectors used were either a Hamamatsu R136 PMT operated at 760 V and 25 °C or an RCA 7102 PMT operated at 1200–1500 V and cooled with a dry ice/2-propanol bath. Both the emission and excitation monochromators were calibrated using a low-pressure Hg lamp. The relative sensitivity of the entire detection system (also for both PMT detectors) has been calibrated in the range 300–600 nm using the rhodamine B quantum counter.[34] Calibration of the entire 300–900-nm range was done using a standard lamp obtained from and calibrated by E, G, & G, Inc., Salem, Mass. The standard lamp is a 200-W tungsten–halogen lamp operated at 6.50 A having serial no. B115 A and was calibrated from NBS standards Qm 197, Qm 198, and Qm 199. Variable-temperature studies were done using a Cryogenic Technology, Inc., Spectrim II sample conditioner. In all cases spectroquality solvents were used as obtained commercially.

Luminescence Lifetimes. Luminescence lifetimes, τ, were measured using a TRW Model 75A decay time fluorometer equipped with a Xenon Corp. Nanopulser excitation source. The Hamamatsu R446UR PMT detector was powered by a Kepco Model 2500 ABC regulated high-voltage supply. Output from the PMT following the ~50-ns excitation pulse was monitored by a Tektronix 453 oscilloscope and recorded with a Polaroid camera. Plots of log (emission intensity) against time were linear in every case over at least two lifetimes. The value of τ is taken as the time required for the luminescence intensity to decay to $1/e$ of its original intensity.

Luminescence Quantum Yields. Luminescence yields of the complexes at 298 and 77 K in various solvents were determined relative to rhodamine B ($\Phi_0 = 0.69$)[35] in EtOH using the following procedure.

The absorbance of the organometallic complex whose quantum yield is to be measured is set equal to that of rhodamine B in EtOH (OD < 0.5 in 1.00-cm cell). The exciting line for both reference and standard was set at 350 nm using the Aminco-Bowman spectrometer. The relative luminescence quantum yield of the complex is then the integrated area under the corrected emission spectrum divided by that for the rhodamine B standard, after correction for differences in the index of refraction of the solvents.[36]

Variable-Temperature Measurements. Variable-temperature measurements were carried out using the Spectrim II, interfaced with either the Aminco-Bowman or the lifetime apparatus. For studies on solid *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$, the powder was diluted with KBr and mixed by grinding. The KBr/*fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$ powder was then placed on the copper cold tip coated with a thin layer of silicone grease used for thermal conduction and adhesion. Direction of the diffuse sample reflectance into the emission monochromator with subsequent cooling to 30 K results in the easy detection of the emission from *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$. A total emission spectrum was recorded at a selected temperature within the range 300-30 K. In a similar fashion the luminescence lifetime was recorded at various temperatures on the TRW setup placing the head of the Spectrim II in the sample compartment and directing the emission into the PMT housing.

Variable-temperature measurements on *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$ in EPA and 2-propanol were carried out in 5-mm tubes which had been previously freeze-pump-thaw degassed at least five times and hermetically sealed. The small sample tube was then loaded into an all-copper sample container designed for the Spectrim II. Thermal conduction was provided by silicone grease. For both the solid and solution experiments, the sample container of the Spectrim II was masked with black electrical tape to reduce reflections and scattering.

Quenching Studies. Quenching of the emission of *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$ was found to obey the Stern-Volmer expression:[25]

$$\Phi_0/\Phi = 1 + k_q\tau_0[Q]$$

where Φ_0 = emission quantum yield in absence of quencher, Φ = emission quantum yield with quencher at [Q] concentration, k_q = bimolecular quenching constant, and τ_0 = emission lifetime in absence of quencher.

CH_2Cl_2 solutions of the complex of interest at a constant concentration and the quencher at various concentrations were placed in 13 × 100 mm test tubes with constrictions, freeze-pump-thaw degassed in at least three cycles, and hermetically sealed. Generally, 375 nm was used as the excitation wavelength for studies using *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$. The luminescence spectrum of each such sample was then measured, and the relative emission was determined as a function of quencher concentration. Plots of the ratio Φ_0/Φ against quencher concentration are linear and the line passes through $\Phi_0/\Phi = 1.0$ at zero quencher concentration. From the slope ($k_q\tau_0$) of this plot the quenching constant, k_q, can be calculated, after determination of the donor lifetime in the absence of quencher, τ_0 = 1.45 μs (Table VII).

Determination of the quantum yields for the *fac*-XRe(CO)$_3$(4-phenylpyridine)$_2$ sensitized isomerization of *trans* → *cis*-stilbene was done using samples for which all of the *fac*-XRe(CO)$_3$(4-phenylpyridine)$_2$ luminescence was quenched. These tubes were irradiated in parallel with actinometry tubes containing benzophenone (0.05 M) and *trans*-stilbene (0.05 M) using a 550-W Hanovia lamp filtered with a no. 7-83 Corning filter pack (to isolate the 366-nm line) and equipped with a merry-go-round. Assuming that the benzophenone-sensitized *trans*- → *cis*-stilbene reaction occurs with a quantum efficiency of 0.60,[30] the values for *fac*-XRe(CO)$_3$(4-phenylpyridine)$_2$ were determined by direct comparison of the amount of *cis*-stilbene formed in parallel irradiations. The stilbenes were analyzed by gas chromatography using a Varian 1400 with a flame ionization detector with a 6 ft × 1/8 in. 3% SE-30 column operated at 160 °C.

Synthesis of *fac*-XRe(CO)$_3$L$_2$ Complexes. The complexes studied were all prepared by the route indicated in eq 1 of the text. All ligands, L, are commercially available and were used as received. The starting Re(CO)$_5$X (X = Cl, Br, I) were obtained from Pressure Chemical Co. and used as received. Heating Re(CO)$_5$X with excess L in isooctane solution leads to the formation of *fac*-XRe(CO)$_3$L$_2$ which precipitates from solution. The solid is then collected by filtration and washed with isooctane to remove any unreacted starting material. The complexes are then analytically pure. A number of the complexes for X = Cl were analyzed by Alfred Bernhardt, West Germany. Anal. Calcd for *fac*-ClRe(CO)$_3$(4-phenylpyridine)$_2$: C, 48.72; H, 2.92; N, 4.55. Found: C, 48.77; H, 3.02; N, 4.44. Calcd for *fac*-ClRe(CO)$_3$(4,4′-bpy)$_2$: C, 44.68; H, 2.59; N, 9.06. Found: C, 44.46; H, 2.71; N, 8.97. Calcd for *fac*-ClRe(CO)$_3$(3,5-diClpy)$_2$: C, 25.93; H, 1.00; N, 4.65. Found: C, 25.86; H, 1.03; N, 4.68. Calcd for *fac*-ClRe(CO)$_3$(3-CNpy)$_2$: C, 35.04; H, 1.56; N, 10.90. Found: C, 35.23; H, 1.69; N, 11.04. Calcd for *fac*-ClRe(CO)$_3$(4-CNpy)$_2$: C, 35.04; H, 1.56; N, 10.90. Found: C, 35.05; H, 1.62; N, 10.98. The protonated form of the 4,4′-bpy complexes was prepared in solution by protonation with HCl.

Acknowledgments. We thank the National Science Foundation for support of this research. M.S.W. acknowledges support as a Dreyfus Teacher-Scholar grant recipient, 1975-1980, and thanks Professor E. I. Solomon for valuable discussion concerning the interpretation of the emission spectral changes with solvent and temperature. The authors also acknowledge some helpful comments from the reviewers of this manuscript.

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Quantitative Studies of Chemical Reactivity of Tetra-μ-butyrato-dirhodium(II) Complexes

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Received August 28, 1978

Abstract: We have studied the thermodynamics of adduct formation for 1:1 and 2:1 adducts formed by Lewis bases with $Rh_2(C_4H_7O_2)_4$ in benzene solutions. Electrochemical studies of these adducts were also carried out in CH_2Cl_2. Corrections for a benzene-acid interaction were necessary to obtain solvent minimized enthalpies of acid-base adduct formation. The thermodynamic data clearly demonstrates substantial changes in the acidic and redox properties of the second metal as a result of base coordination to the first. The metal–metal bonding in the system causes this dimer to be a most unusual Lewis acid, as evidenced by deviations of the E and C predicted enthalpies from those observed. The unusual Lewis acid properties are attributed to the enhanced π-back-bonding capability of the rhodium(II) center as a result of extensive mixing of orbitals with π symmetry on the two metal centers. This causes the rhodium(II) center to be very effective in π-back-bonding to the axial ligands. The reduction potentials of $Rh_2(C_4H_7O_2)^+$, $Rh_2(C_4H_7O_2)_4B^+$, and $Rh_2(C_4H_7O_2)_4B_2{}^+$ are analyzed, and provide further support for the extensive π-back-bonding capabilities of this metal cluster.

Introduction

In recent years, considerable interest has been generated in the area of metal cluster chemistry. Clusters are found in a variety of important biological systems such as the ferredoxins,[1] nitrogenase,[1] cytochrome oxidase, and copper type 3 proteins.[2] In both heterogeneous and homogeneous catalytic systems, metal clusters are reported to effect some intriguing, industrially important reactions. Different mechanisms have been suggested to account for the synergistic ways in which one metal can influence the chemistry at a second metal site.[3]

In various systems, considerable variation exists in the extent of metal–metal interaction. In some, strong metal–metal bonds exist;[4] in others, the metals are interacting in a magnetic sense, but a direct metal–metal bond is absent; in still others, the metals are far enough removed to be noninteracting even in a magnetic sense. A continuum of systems exists which spans the classifications given above. Thus, there are a very large number of variables that can influence a very large number of different synergistic reaction mechanisms. A more complete understanding of this area leading to a full appreciation of the potential of metallomers for novel reaction types will require extensive investigation of many different types of systems. In addition to structural investigations, quantitative studies of chemical reactivity (kinetic and thermodynamic) must be carried out to determine ways and extents to which a second, third, etc., metal atom in a molecule can influence the coordination chemistry and redox chemistry at the first metal site.

Our initial selection of a system for investigation involved the dimeric metal carboxylates because of the extensive structural information available on them.[5] For stability reasons and because of the interest in the metal in catalytic systems, dimeric rhodium(II) acetate was selected. Its synthesis was reported[6] in 1963, and adducts with Lewis bases having both 1:1 and 2:1 stoichiometries were isolated. The crystal structure of the diaquo adduct[5] showed that this complex is isostructural with copper acetate, with each rhodium bound to one oxygen of each of the four acetate groups. The water molecules were found to lie along the fourfold axis defined by the rhodium–rhodium bond. The published metal–metal separation is 2.3855 Å. The analogous butyrate system is illustrated in Figure 1. Kitchens and Bear isolated 1:1 dimethyl sulfoxide and dimethyl sulfide base adducts of rhodium(II) acetate by thermally generating them from the 2:1 adducts.[7]

Molecular orbital calculations of various[8-10] types have been carried out to aid in the elucidation of the electronic structure of the metal dimers. A self-consistent charge and configuration molecular orbital calculation predicted a net single bond between the rhodium atoms.[9] More recently, Norman and Kolari have performed SCF-Xα scattered wave calculations on the diaquo adduct of rhodium(II) acetate.[10] They found a net bond

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