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Photophysical Studies of $XRe(CO)_4L$ (X = Cl, I; L = CO, pip, PPh_3) Complexes. Examples of Ligand Field Luminescence from Organometallic Complexes in Fluid Solution

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Abstract: A series of *cis*-$XRe(CO)_4L$ [X = Cl, I; L = NC_5H_{11} (pip), PPh_3] complexes have been prepared via photochemical and thermal reactions of the parent $XRe(CO)_5$ species. Electronic absorption spectra have been recorded for these complexes in solution at 293 K and in EPA glasses at 80 K. The lowest lying absorption system is assigned definitively to ligand field (LF) ${}^1A_1(e^4b_2^2) \rightarrow {}^{1,3}E(e^3b_2^2a_1^1)$ transitions; the band energies depend on L and are ordered CO > P donor > N donor, in accordance with the LF strength. Luminescence spectra, lifetimes, quantum yields, and excitation spectra from the *cis*-$XRe(CO)_4L$ (L = pip, PPh_3) derivatives in both 293 K solution and EPA glasses at 80 K are consistent with emission from the lowest energy ^{3}LF state. In contrast, the parent $XRe(CO)_5$ molecules were not found to emit under identical experimental conditions. The photochemistry of these *cis*-$XRe(CO)_4L$ complexes has also been investigated. Irradiations at 313 or 366 nm of *cis*-$XRe(CO)_4L$ in solution at 293 K that contains an excess concentration of entering ligand give rise to ligand-substitution processes involving replacement of both CO and PPh_3 ligands. Irradiation at 313 nm of *cis*-$IRe(CO)_4(PPh_3)$ in solution at 293 K without added scavenging ligands leads to formation of carbonyl-bridged $[Re(CO)_4(PPh_3)]_2$ dimer and I_2 products. These photochemical processes are correlated with the model of lowest lying electronically excited states.

In recent years a great deal has been learned about the electronic structure of transition-metal complexes from their photophysical and photochemical behavior.[1] Luminescence techniques can act as powerful spectroscopic probes, offering valuable insight to the nature of excited states and deactivation mechanisms in these molecules.[2]

A wide variety of transition-metal organometallic complexes have been established to undergo radiative decay in a rigid low-temperature environment, and there are now several examples reported that exhibit observable emission in room-temperature solution conditions. Among mononuclear metal carbonyls, complexes of the general formulas $M(CO)_5L$ (M = Mo, W; L = a substituted pyridine ligand),[3] *cis*-$M(CO)_4L_2$ (M = Cr, Mo, W; L = pyridine or a pyridine derivative),[4] $M(CO)_4L$ (M = Cr, Mo, W; L = an α-diimine ligand),[5] $XW(CO)_2L_2(CPh)$ (X = Cl, Br, I; L = a donor ligand; CPh = alkylidyne ligand),[6] $ClRe(CO)_3L$ [L = bpy (2,2′-bipyridine), phen (1,10-phenanthroline), or a related ligand derivative],[7] *fac*-$[SRe(CO)_3L]^+$ [S = CH_3CN, PhCN, pip (piperidine), py (pyridine), $NC(CH_2)_nCH_3$; L = bpy, phen, or biquin (2,2′-biquinoline)],[8] $XRe(CO)_4L_2$ (X = Cl, Br, I; L = a pyridine derivative),[9] $[Re(CO)_2(bpy)L_2]^+$ (L = a tertiary phosphine),[10] $Ph_3XRe(CO)_3(phen)$ (X = Ge, Sn),[11] $[Ir(CO)L(mnt)]^-$ (L = CO, PPh_3, CN^-; mnt = maleonitriledithiolate),[12] and the radical complex $Re(CO)_4(DTBQ)^\bullet$ (DTBQ = 3,5-di-*tert*-butyl-*o*-benzoquinone)[13] are known to be emissive under fluid conditions. Room-temperature emission has also been reported from a series of ligand-bridged $(OC)_5MLM'(CO)_5$ (M, M′ = Cr, Mo, W; L = a binucleating N-donor ligand) compounds[14] and metal–metal-bonded $[(Cp)M(CO)_3]_2$ (M = Mo, W; Cp = C_5H_5)[15] and $Re_2(CO)_8(phen)$[16] molecules. In all of these cases, however, the room-temperature emission is thought to arise from lowest lying metal to ligand charge-transfer (MLCT) excited states. In contrast, organometallic complexes with low-lying ligand field (LF) excited states are normally highly photoreactive in fluid solution[1d] and, to date, have only been observed to luminesce in rigid low-temperature glasses or matrices.[2]

Recently, while investigating the photochemical properties of a series of *cis*-$XRe(CO)_4L$ [X = Cl, I; L = pip, PPh_3] complexes, we recorded luminescence spectra in room-temperature solution that apparently arise from the low-lying LF states of these molecules.[17] In this article we fully characterize the electronic absorption, emission, excitation, and photochemical properties of these complexes and provide a description of their low-energy excited states and photophysical pathways.

Experimental Section

Materials. All starting materials used in the syntheses are commercially available. Complexes $ClRe(CO)_5$ and $[IRe(CO)_4]_2$ were purified by repeated sublimations under reduced pressure. The ligands pip and PPh_3 were purified by usual distillation and sublimation techniques, respectively. Benzene used in this study was of Photrex grade (Baker Chemical Co.). The solvent mixture EPA (5:5:2 ether/isopentane/ethanol) was made up immediately before use from dried and purified spectral-grade solvent components. Other solvents were obtained at the

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best commercial grade and further purified according to standard laboratory procedures prior to use. All solvents used in the emission experiments were rigorously purified to ensure the removal of emitting or quenching impurities.

Synthesis of IRe(CO)$_5$. The IRe(CO)$_5$ complex was obtained by refluxing [IRe(CO)$_4$]$_2$ in hexane for 6 h while continuously purging with CO.[18] After the solvent was removed, the product was recrystallized from a hexane/dichloromethane mixture.

Synthesis of *cis*-ClRe(CO)$_4$L (L = pip, PPh$_3$) Complexes. The *cis*-ClRe(CO)$_4$(pip) complex was prepared by direct irradiation with a 200-W mercury arc lamp of the parent ClRe(CO)$_5$ complex (10^{-4} M) in deoxygenated benzene (50 mL) containing excess pip (10^{-3} M). The product compound was obtained by evaporating the solvent, and the residue was then purified by chromatography on silica gel. Elution with hexane removed the unreacted starting materials, and subsequent elution with benzene yielded the product. The *cis*-ClRe(CO)$_4$(pip) compound was further purified by recrystallization from a 10:1 hexane/dichloromethane mixture. Analogous procedures were used to prepare the *cis*-ClRe(CO)$_4$(PPh$_3$) complex with carbon tetrachloride as the solvent during photolysis.

Synthesis of *cis*-IRe(CO)$_4$L (L = pip, PPh$_3$) Complexes. The *cis*-IRe(CO)$_4$(pip) complex was prepared and purified by a similar procedure to the above chloro derivative following direct photolysis of the parent [IRe(CO)$_4$]$_2$ complex in deoxygenated carbon tetrachloride. The *cis*-IRe(CO)$_4$(PPh$_3$) species was not, however, readily obtainable photochemically. Instead, it was prepared according to a thermal method[19] where the parent [IRe(CO)$_4$]$_2$ complex (10^{-4} M) was reacted with PPh$_3$ (10^{-4} M) in refluxing chloroform (100 mL) over a 12-h period. This complex was purified according to the procedure described above for the other derivatives.

Equipment and Procedures. Infrared spectra were recorded on a Perkin-Elmer 283B spectrometer from the complexes in carbon tetrachloride solution using a NaCl cell of 1-mm path length. Reported band maxima are considered accurate to ±2 cm^{-1}. Electronic absorption spectra were recorded on either Hewlett-Packard Model 8450A diode array or Perkin-Elmer Model 559A spectrometers, and the reported band maxima are considered accurate to ±2 nm.

Emission and excitation spectra were obtained on a SLM Instruments Model 8000/8000S spectrometer, which incorporates a photomultiplier-based photon-counting detector. The photomultiplier tube used in these measurements was a Hamamatsu R928. Both the emission and excitation spectra were fully corrected for variations in detector response and excitation lamp intensity as a function of wavelength, and the band maxima are considered accurate to ±4 nm. Excitation data were recorded from samples that were optically dilute ($A < 0.1$) throughout the spectral region. Under these conditions excellent agreements were observed between the excitation and absorption spectra for known standards quinine sulfate and 1,2-benzanthracene. Emission quantum yields (ϕ_e) were determined by the Parker–Rees method with dilute quinine sulfate in 0.2 M H$_2$SO$_4$ as a calibrant (ϕ_{em} = 0.55 at 293 K).[20] These values were corrected for the differing refractive indices of the solvents[21] and found to be reproducible to ±15%.

Emission lifetimes (τ_e) were measured with a PRA System 3000 time-correlated pulsed single-photon-counting apparatus. Samples were excited with 330-nm light from a PRA Model 510 nitrogen flash lamp that had been transmitted through an Instruments SA Inc. H-10 monochromator. Emission was detected from the sample at 90° via a second H-10 monochromator and a thermoelectrically cooled Hamamatsu R955 photomultiplier tube. Resulting photon counts were stored on a Tracor Northern Model 7200 microprocessor-based multichannel analyzer, and the instrument response function was then deconvoluted from the luminescence data to obtain an undisturbed decay that was fitted by means of a least-squares procedure on an IBM PC. Each sample gave rise to a single-exponential emission–decay curve; reported errors represent the reproducibility of readings for at least three measurements.

In the emission and excitation experiments the sample solution was deoxygenated and filtered through a 0.22-μm Millipore filter prior to taking measurements. The solution temperature was controlled to ±0.1 K. Low-temperature absorption and emission measurements were performed with an Oxford Instruments DN1704K liquid-nitrogen cryostat that contained a 1-cm path length quartz cell. The temperature of the solution was maintained to ±0.2 K by means of an Oxford Instruments Model 3120 controller.

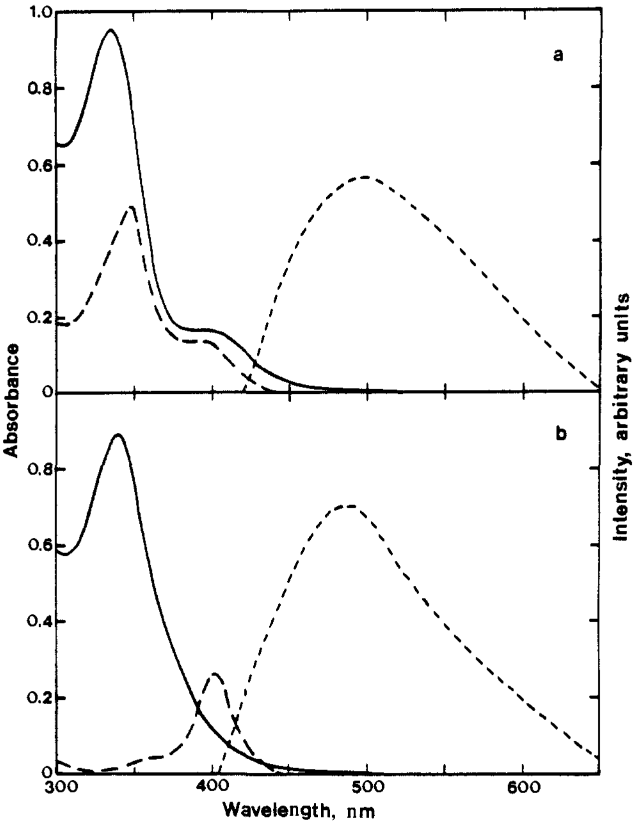

Figure 1. Electronic absorption (—), emission (---), and excitation (--) spectra of (a) *cis*-ClRe(CO)$_4$(pip) and (b) *cis*-IRe(CO)$_4$(pip) complexes in deoxygenated benzene at 293 K. Emission spectra were recorded following excitation at 330 nm, and excitation spectra were recorded by monitoring at emission maxima. Both emission and excitation spectra are fully corrected for variations in instrumental response as a function of wavelength.

Photochemical quantum yields (ϕ_{cr}) were measured following excitation at 313 nm with an Ealing 200-W medium-pressure Hg lamp using a Baird-Atomic Co. interference filter (10-nm band-pass) to isolate the excitation wavelength. Quantum yields were determined from $\sim 10^{-4}$ M deoxygenated solutions of *cis*-XRe(CO)$_4$L with Cr(CO)$_6$ in cyclohexane (ϕ_{cr} = 0.67, λ_{ex} = 313 nm)[22] as a calibrant; typical irradiation light intensities were 10^{-9}–10^{-8} einstein s^{-1}. In these experiments the concentrations of reactants and products were followed by UV-vis spectroscopy. Infrared spectra were also recorded at various intervals during these photolyses to monitor the reaction. Photochemical quantum yields were corrected for the changing degree of light absorption and for inner-filter effects due to product formation as necessary. Measurements were typically made over relatively small (<10%) reaction conversions, and the quantum yields obtained were reproducible to ±15%.

Results

Infrared spectra have been recorded from the XRe(CO)$_4$L (X = Cl, I; L = CO, pip, PPh$_3$) complexes in the carbonyl stretching region, and these results are in excellent agreement with those reported previously for XRe(CO)$_5$ and *cis*-XRe(CO)$_4$(PPh$_3$) (X = Cl, Br, I) compounds.[19,23] Infrared data are available as supplementary material.

Electronic absorption, emission, and excitation spectra have been recorded for each of these complexes in deoxygenated benzene at room temperature, and the results are shown in Figures 1 and 2. For each complex the broad emission spectral distribution was observed to be independent of excitation wavelength in the 300–400-nm region, indicating that the emission apparently arises from a single excited state. Furthermore, the congruent spectral features of the absorption and excitation spectra (see Figures 1 and 2) reveal that the luminescence arises from the lowest lying excited state in each of these compounds. A complete list of all the

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Table I. Electronic Absorption, Excitation, and Emission Spectral Data for $XRe(CO)_5$ and *cis*-$XRe(CO)_4L$ Complexes in Deoxygenated Benzene at 293 K

			emission[b]					
complex	absorption [λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)]	excitation[a]	λ_{max}, nm	half-width (±300), cm^{-1}	ϕ_e[c] × 10^3	τ_e, ns	k_r, s^{-1} × 10^6	k_{nr}, s^{-1} × 10^8
$ClRe(CO)_5$	322 (2010), 345 (670)		*d*					
cis-$ClRe(CO)_4(PPh_3)$	336,[e] 369 (400)	334, 366	402	5440	2.7	1.2 (±0.1)	2.3	8.3
cis-$ClRe(CO)_4$(pip)	336 (1340), 402 (230)	352, 398	498	5460	16	2.0 (±0.1)	8.0	4.9
$IRe(CO)_5$	339 (2130), 377 (200)		*d*					
cis-$IRe(CO)_4(PPh_3)$	335 (2350), 370 (400)	313, 368	397	4320	0.09	<0.5	>0.18	
cis-$IRe(CO)_4$(pip)	342 (4910), ~400[e]	360,[e] 408	494	8550	6.5	1.4 (±0.3)	4.6	7.1

[a] Corrected excitation spectra with emission monitored at the emission maximum. [b] Corrected emission spectra following excitation at 330 nm. [c] Measured relative to the value of 0.55 reported for quinine sulfate in 0.2 M H_2SO_4;[20] estimated error is ±15%. [d] No emission observed. [e] Observed as a shoulder.

Table II. Electronic Absorption and Emission Data for $XRe(CO)_5$ and *cis*-$XRe(CO)_4L$ Complexes in EPA Glasses at 80 K

		emission[a]			
complex	absorption (λ_{max}, nm)	λ_{max}, nm	half-width (±300), cm^{-1}	τ_e, μs	k_r, s^{-1} × 10^5
$ClRe(CO)_5$	320, 344	*b*			
cis-$ClRe(CO)_4(PPh_3)$	327, 360	394	4480	5.3 (±0.1)	1.9
cis-$ClRe(CO)_4$(pip)	320, 374	460	4820	8.9 (±0.4)	1.1
$IRe(CO)_5$	333, 368	*b*			
cis-$IRe(CO)_4(PPh_3)$	326, 365	396	4130	14.7 (±1.4)	0.68
cis-$IRe(CO)_4$(pip)	322, 380[c]	474	6200	11.9 (±0.7)	0.84

[a] Corrected emission spectra following excitation at 330 nm. [b] No emission observed. [c] Observed as a shoulder.

absorption and luminescence spectral data obtained at room temperature, including emission quantum yields (ϕ_e) and lifetimes (τ_e), is shown in Table I. Importantly, no emission was observed from the parent $ClRe(CO)_5$ and $IRe(CO)_5$ complexes under identical experimental conditions used in recording the spectra from the substituted complexes. Radiative (k_r) and nonradiative (k_{nr}) decay constants (see Table I) were calculated from the ϕ_e and τ_e values according to eq 1 and 2. Here, it is explicitly assumed that the emitting state is formed with unit efficiency.[2]

$$k_r = \phi_e/\tau_e \quad (1)$$

$$k_{nr} = (1/\tau_e) - k_r \quad (2)$$

Low-temperature electronic absorption and emission data have also been recorded from these rhenium carbonyl complexes in frozen EPA glasses at 80 K. Spectra recorded from the *cis*-$IRe(CO)_4(PPh_3)$ complex are typical of this series and are depicted in Figure 3; the absorption and emission spectra obtained from this complex in 293 K EPA solution are also shown for comparison. All the low-temperature absorption and emission data obtained, including emission lifetimes, are summarized in Table II. Derived k_r values assumed that ϕ_e is unity at low temperature, and, thus, these parameters should only be regarded as estimates.

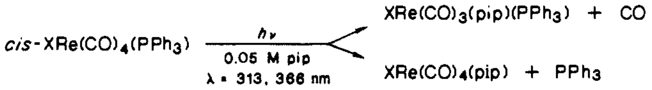
Electronic absorption and emission spectra have been obtained from the *cis*-$XRe(CO)_4L$ complexes in various solvents at room temperature. The data indicate that there is relatively little solvent dependence on either the absorption or emission features; the results obtained for *cis*-$IRe(CO)_4(PPh_3)$ in the following deoxygenated solvents are representative of the series: methanol, λ_{max} = 332, 365 nm and λ_{em} = 388 nm; dichloromethane, λ_{max} = 330, 365 nm and λ_{em} = 392 nm; EPA, λ_{max} = 336, 371 nm and λ_{em} = 398 nm; chloroform, λ_{max} = 332, 365 nm and λ_{em} = 389 nm.

The photochemistry of *cis*-$XRe(CO)_4(PPh_3)$ complexes in deoxygenated methylene chloride solution has been investigated following excitation at 313 and 366 nm. In the presence of an excess of scavenging ligand (e.g., 0.05 M pip), irradiation at either 313 or 366 nm leads to substitution of both CO and PPh_3 ligands (see Scheme I).

Electronic absorption spectral changes accompanying the 313-nm photolysis at 293 K of *cis*-$IRe(CO)_4(PPh_3)$ in deoxygenated methylene chloride containing 0.05 M pip are depicted in Figure 4. Infrared spectra recorded during this photolysis indicate formation of both $IRe(CO)_3(pip)(PPh_3)$ (ν_{CO} = 2025, 1948, 1900 cm^{-1}) and $IRe(CO)_4$(pip) (ν_{CO} = 2100, 2002, 1940 cm^{-1}) products. The analogous reaction was observed to take place for the *cis*-$ClRe(CO)_4(PPh_3)$ complex with the formation of $ClRe(CO)_3(pip)(PPh_3)$ (ν_{CO} = 2020, 1935, 1895 cm^{-1}) and $ClRe(CO)_4$(pip) (ν_{CO} = 2010, 1920 cm^{-1}) products. Quantum yields (ϕ_{cr}) have been determined from the rate of disappearance of reactant *cis*-$XRe(CO)_4(PPh_3)$ and are shown in Table III. The closely related *cis*-$XRe(CO)_4$(pip) complexes appear to undergo similar ligand-substitution processes, but these reactions were not investigated in detail as the photoproducts were observed to decompose rapidly in solution.

Irradiation at 313 nm of *cis*-$IRe(CO)_4(PPh_3)$ in deoxygenated carbon tetrachloride solution containing no added scavenging ligand led to an additional photoprocess involving the dissociation of I atoms and the formation of a carbonyl-bridged dimer species (see Scheme II).

Scheme I



Scheme II

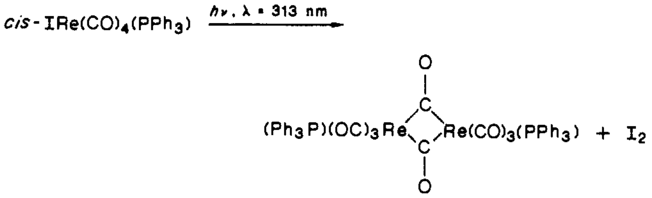


Table III. Photoreaction Quantum Yields (ϕ_{cr}) for 313-nm Photolysis of *cis*-$XRe(CO)_4L$ Complexes in Deoxygenated Solution at 293 K[a]

	ϕ_{cr} (±15%)	
complex	Scheme I[b]	Scheme II[c]
cis-$ClRe(CO)_4(PPh_3)$	0.022	
cis-$IRe(CO)_4(PPh_3)$	0.023	0.008

[a] Quantum yields measured by monitoring disappearance of reactant complex. [b] Measured in deoxygenated methylene chloride solution containing 0.05 M pip. Reaction products are $XRe(CO)_3(pip)(PPh_3)$ and $XRe(CO)_4$(pip). [c] Measured in deoxygenated carbon tetrachloride solution containing no added ligand. When X = I, the reaction products are $[Re(CO)_4(PPh_3)]_2$ and I_2; when X = Cl, no dimerization reaction appears to take place.

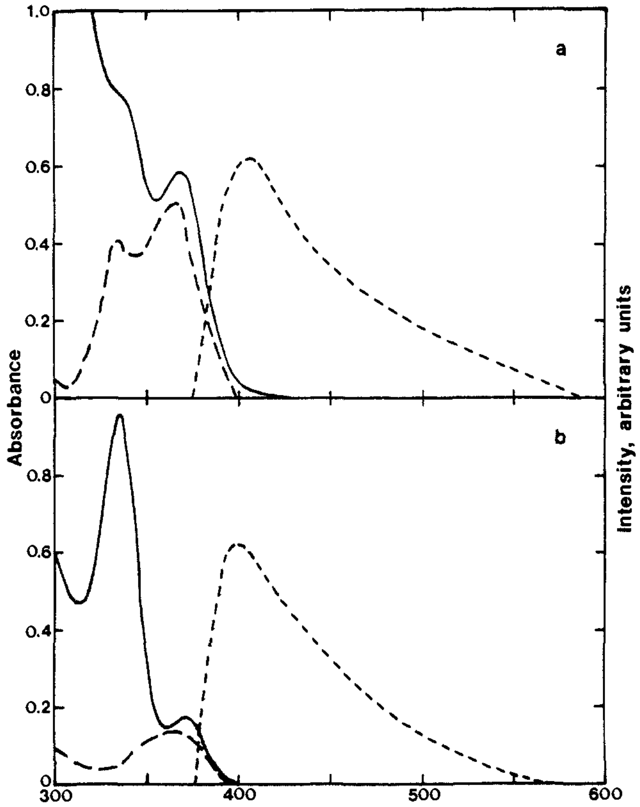


Figure 2. Electronic absorption (—), emission (- - -), and excitation (– –) spectra of (a) *cis*-ClRe(CO)$_4$(PPh$_3$) and (b) *cis*-IRe(CO)$_4$(PPh$_3$) complexes in deoxygenated benzene at 293 K. Emission spectra were recorded following excitation at 330 nm, and excitation spectra were recorded by monitoring at emission maxima. Both emission and excitation spectra are fully corrected for variations in instrumental response as a function of wavelength.

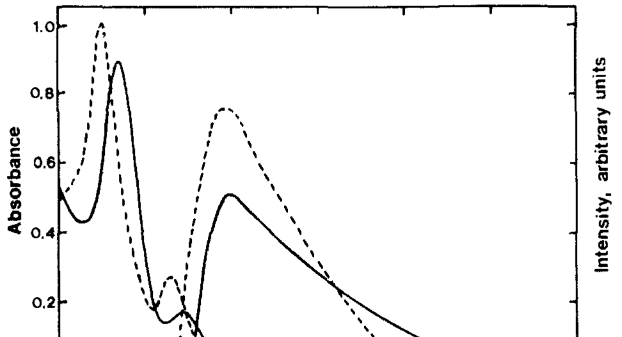


Figure 3. Electronic absorption and emission spectra of *cis*-IRe(CO)$_4$(PPh$_3$) in EPA solution at 293 K (—) and 80 K (- - -). Emission spectra were recorded following excitation at 330 nm and are fully corrected for variations in detector response as a function of excitation wavelength.

Electronic absorption spectral changes accompanying this reaction are shown in Figure 4. The formation of I$_2$ can be observed by the appearance of the characteristic absorption band centered at 516 nm. Infrared spectra recorded during photolysis indicate the formation of the rhenium dimer characterized by a bridging-carbonyl stretch appearing at 1818 cm^{-1}. Importantly, we found no evidence for the formation of bridged-ligand dimers on 313-nm irradiation of the analogous *cis*-ClRe(CO)$_4$(PPh$_3$) complex; in this instance photolysis gave rise to ligand-substitution chemistry that is described in Scheme I, where the entering ligands are believed to be solvent impurity species. Additionally, the photoinitiated dimerization reaction only occurred following irradiation at 313 nm and not at 366 nm; excitation at the longer

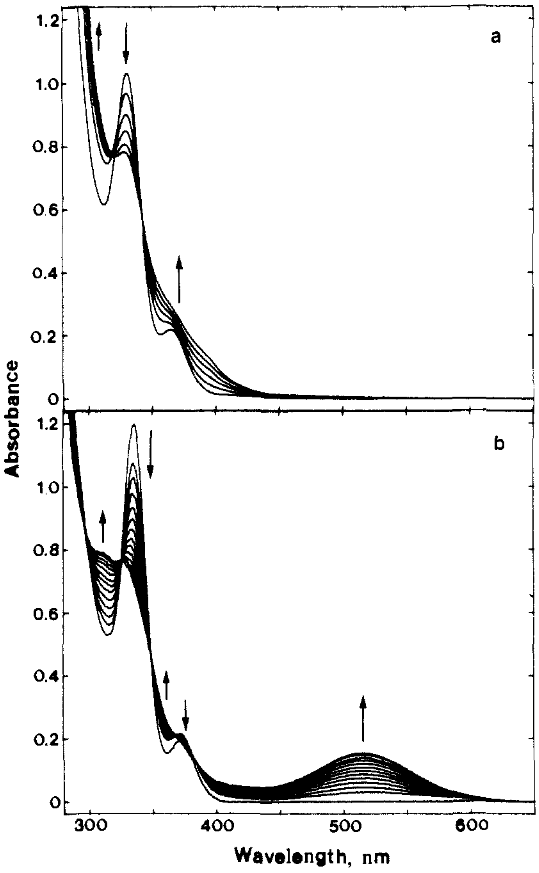


Figure 4. Electronic absorption spectral changes accompanying the 313-nm photolysis (40-min time intervals) of *cis*-IRe(CO)$_4$(PPh$_3$) in deoxygenated solution at 293 K. Solutions are (a) methylene chloride containing 0.05 M pip and (b) carbon tetrachloride with no added ligand.

wavelength again produced the ligand-substitution processes described by Scheme I. The quantum yield determined for the dimerization reaction (Scheme II) of the *cis*-IRe(CO)$_4$(PPh$_3$) complex is shown in Table III.

Discussion

Electronic Absorption Spectra. The electronic structures of XM(CO)$_5$ (X = Cl, Br, I; M = Mn, Re) complexes have been the subject of several investigations. An early study by Gray et al. has provided a molecular orbital description for the bonding in XMn(CO)$_5$ (X = Cl, Br, I) complexes and assigned the first charge-transfer band to a (Mn, d_{xy})$b_2 \rightarrow \pi^*$(CO) type of transition.[24] Further studies of the ultraviolet photoelectron (UPS)[25] and electronic spectra[26] of these XMn(CO)$_5$ complexes have concluded that the HOMO orbital is primarily halogen in character. The energy order of the four highest filled molecular orbitals has been reported to be $X_\pi > X_\sigma > e(d_{xz}, d_{yz}) > b_2(d_{xy})$, where the X_π and X_σ levels have symmetry e and a_1, respectively. An investigation of the UPS spectra of the analogous XRe(CO)$_5$ (X = Cl, Br, I) complexes has revealed that the energy level ordering is $X_\pi > b_2 > e > X_\sigma$,[27] although the extent of metal character in the HOMO orbital is thought to depend substantially on the nature of the halide.[28,29] Consequently, the lowest energy absorption bands in these XM(CO)$_5$ (M = Mn, Re) complexes

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have been regarded as being predominantly of $(X, \pi)e \rightarrow \pi^*(CO)$ charge-transfer character.[26] A study of the absorption and magnetic circular dichroism (MCD) spectra of $BrMn(CO)_5$ has suggested that the lowest band is mainly a charge-transfer $(Br, \pi)e \rightarrow a_1(d_{z^2})$ transition.[30]

More recently the electronic spectra of these $XM(CO)_5$ (X = Cl, Br, I; M = Mn, Re) species have been reinterpreted. Detailed comparisons of the absorption spectra of these complexes with a wide range of other d^6 metal carbonyls have led to a definitive ligand field (LF) $^1A_1(e^4b_2^2) \rightarrow {}^{1,3}E(e^3b_2^2a_1^1)$ assignment for the lowest energy bands.[23,29] Observed photosubstitution chemistry and low-temperature emission behavior of $XRe(CO)_5$ are also in accordance with this LF assignment.[23]

Our electronic absorption data for the $XRe(CO)_4L$ (X = Cl, I; L = CO, pip, PPh_3) complexes are completely in agreement with a $^1A_1 \rightarrow {}^{1,3}E$ LF assignment for the lowest energy states, as the energies follow the order of the ligands CO > P donor > N donor in LF strength (see Tables I and II) and are not solvent dependent. In contrast, the energies of the lowest absorption bands are not markedly affected by the nature of halide, and this does not support either an X → Re or $X \rightarrow \pi^*(CO)$ charge-transfer (CT) assignment. It has been noted in the literature that most metal complexes with low-lying charge-transfer states exhibit at least a 1-eV shift to lower energy on replacing the Cl atom by the I atom,[29,31] although exceptions to this rule have been observed (e.g., $Pt(PR_3)_2X_2$ complexes).[32] However, the *cis*-$XRe(CO)_4L$ complexes studied here would seem unlikely to be such an exception because the photoelectron data available for the parent $XRe(CO)_5$ complexes suggest that the degree of metal character will vary substantially on changing the halide.[28,29] Finally, the observed molar absorptivities of the lowest energy transitions are fairly low (see Table I), consistent with the orbital-forbidden LF assignment and not a CT one.

Luminescence Data. Emission has been observed from each of the *cis*-$XRe(CO)_4L$ (X = Cl, I; L = pip, PPh_3) complexes in deoxygenated benzene at 293 K. In each case a single broad emission band has been obtained and, importantly, the excitation spectra associated with this emission are congruent with the lowest lying absorption features (see Figures 1 and 2). Therefore, these emission and excitation results are indicative of radiative decay from the lowest lying $^1A_1 \rightarrow {}^3E$ LF excited state. This assignment of LF emission is unprecedented for a metal carbonyl complex in room-temperature solution, and LF states from organometallic complexes have been typically characterized by rapid bond dissociation and efficient nonradiative decay when under fluid conditions.[1d,2] As expected for excited states undergoing efficient radiationless processes, the observed emission lifetimes are very short and the emission quantum yields quite low (see Table I). Calculated radiative (k_r) and nonradiative (k_{nr}) rate decay constants are of the order 10^6–10^7 and 10^8–10^9 s^{-1}, respectively (see Table I), and are consistent with emission from ^{3}LF states. Deactivation from MLCT states is generally much less rapid; e.g., $k_r \sim 10^2$–10^3 s^{-1} and $k_{nr} \sim 10^6$–10^8 s^{-1} values have been determined recently from a series of $(CO)_5WLW(CO)_5$ complexes exhibiting MLCT emission at room temperature.[14b,33] Additionally, the emission maxima of these *cis*-$XRe(CO)_4L$ complexes are not appreciably solvent dependent in accordance with the LF assignment, whereas X → Re and Re → L charge-transfer transitions are apt to show much larger solvent sensitivities.[1d,7a,34]

Significantly, no emission was observed from the parent $XRe(CO)_5$ complexes in fluid solution. In light of the above discussion on the nature and energy ordering of the lowest energy excited states, it is suggested that the corresponding $^1A \rightarrow {}^{1,3}E$ LF levels may be effectively quenched internally by the close-lying $(X, \pi)e \rightarrow \pi^*(CO)$ or $(X, \pi)e \rightarrow a_1(d_{z^2})$ states in these $XRe(CO)_5$ complexes (vide infra). However, the $XRe(CO)_5$ compounds have been reported to luminesce from ^{3}LF states as solids at low temperature, and it is that notable that their emission bandwidths are also exceptionally broad (3630–6700 cm^{-1}).[23]

Although excitation spectra recorded from these *cis*-$XRe(CO)_4L$ derivatives exhibit excellent congruence with the lowest energy $^1A \rightarrow {}^3E$ LF absorption features, there is a much poorer agreement in the 300–350-nm region at the high-energy side of the $^1A \rightarrow {}^1E$ LF absorption band (see Figures 1 and 2). These discrepancies are most significant in the spectra of the iodide derivatives (see Figures 1b and 2b). It is concluded that the iodide complexes, in particular, undergo efficient radiationless deactivation from a higher lying state and that this state does not effectively populate the ^{3}LF emitting state. This photophysical behavior strongly suggests the presence of a photoreactive state in the 300–350-nm region (see Photochemistry).

Low-Temperature Measurements. Although there is some sharpening of the absorption and emission features observable as the temperature is lowered to 80 K and the solutions form frozen glasses, overall the bands are not greatly shifted in energy (see Figure 3 and Table II). The lack of energy dependence of band position with temperature is compatible with the model of lowest lying LF states.[2] In contrast, large "rigidochromic" effects have been recognized in the emission spectra of several rhenium and tungsten carbonyl systems that emit from charge-transfer levels.[5a,b,7a]

Emission lifetimes obtained from the *cis*-$XRe(CO)_4L$ complexes in EPA solution at 80 K are entirely consistent with emission arising from ^{3}LF states. Numerous reports have appeared in the literature that have characterized LF emission from organometallic complexes in frozen glasses at liquid-nitrogen temperatures, and typically the observed lifetimes are in the microsecond range.[2] On the other hand,the lifetimes recorded here are considerably shorter than that expected for decay from a $(X, \pi)e \rightarrow a_1(d_{z^2})$ charge-transfer level. Notably, even when the parent $XRe(CO)_5$ complexes are in frozen EPA glasses, they still do not give rise to detectable luminescence, in agreement with a previous report.[23] Observations of emission from these compounds have been confined to those from the solid materials in the 25–80 K range. Interestingly, the emissions of $XRe(CO)_5$ have been shown to be extremely temperature dependent, and a subsequent analysis of the emission quantum yields and lifetimes has revealed that it is the nonradiative rate constant (k_{nr}) and not the radiative rate constant (k_r) that is affected by temperature changes.[23] As noted above, the absence of emission from these $XRe(CO)_5$ complexes is associated with efficient nonradiative population of close-lying CT levels.

Photochemistry. Products formed on light irradiation at 313 or 366 nm of solutions containing an excess concentration of scavenging ligand (see Scheme I) are concordant with the well-known ligand field photosubstitution processes of metal carbonyl complexes.[1d] Disappearance quantum yields (see Table III) indicate that these complexes are fairly photosensitive but much less so than dissociation of CO from the parent $ClRe(CO)_5$ ($\phi_{cr} = 0.76$) and $IRe(CO)_5$ ($\phi_{cr} = 0.67$) molecules,[23] which are not emissive in room-temperature or 80 K solution.

In the absence of scavenging ligand the *cis*-$IRe(CO)_4L$ complex undergoes an additional photoprocess involving the formation of I_2 and a carbonyl-bridged dimer complex (see Scheme II). Significantly, this reaction was only observed to occur for X = I and for the excitation at the shorter wavelength. These results imply that in this molecule another excited state lies above the $^1A_1 \rightarrow {}^{1,3}E$ LF transition and is responsible for this photoreaction. This state may be a second LF level or one of the charge-transfer transitions thought to be present, i.e., $(X, \pi)e \rightarrow \pi^*(CO)$ or $(X, \pi)e \rightarrow a_1(d_{z^2})$.[23,25-30] At this point we favor the notion of this higher lying level being either a photoreactive I → Re or I → CO CT state because the LF states for both of the halide complexes should be approximately isoenergetic,[23,24] and yet the observed dimerization and halide dissocation reaction is limited to X = I. Moreover, the photochemistry observed here bears strong resem-

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blence to the ligand to metal charge-transfer chemistry well established for several classical coordination systems.[35] As stated earlier, X → Re and X → CO CT states often exhibit >1-eV shift to lower energy on replacing the Cl atom by the I atom,[29,31] and, thus, one of these levels may well be reached on excitation of *cis*-$IRe(CO)_4L$ at 313 nm. Nonetheless, this photochemical dimerization reaction of the iodide compounds significantly contributes to the disparities observed in the 300–350-nm regions of the absorption and excitation spectra.

Concluding Remarks

Obtained electronic absorption, emission, excitation, and photochemical data fully support $^1A(e^4b_2^2) \rightarrow {}^{1,3}E(e^3b_2^2a_1^1)$ assignments for the lowest lying excited states of *cis*-$XRe(CO)_4L$ (X = Cl, I; L = pip, PPh_3) complexes. The absence of emission from the $^1A \rightarrow {}^{1,3}E$ LF levels of the parent $XRe(CO)_5$ compounds is thought to be caused by efficient internal quenching processes involving close-lying $(X, \pi)e \rightarrow \pi^*(CO)$ or $(X, \pi)e \rightarrow a_1(d_{z^2})$ charge-transfer levels.

This observation of luminescence from the *cis*-$XRe(CO)_4L$ derivatives is significant in that these are the first demonstrated examples of radiative decay in fluid solution from the LF states of organometallic complexes. Clearly, the lowest lying LF states of organometallic complexes need not necessarily be dominated by radiationless processes. There are a wide range of transition-metal organometallic complexes known to exhibit lowest lying LF levels, and these results suggest that further studies of their photophysical properties may be informative.

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Registry No. *cis*-$ClRe(CO)_4(pip)$, 113975-87-4; $ClRe(CO)_5$, 14099-01-5; *cis*-$ClRe(CO)_4(PPh_3)$, 15189-56-7; *cis*-$IRe(CO)_4(pip)$, 113975-88-5; $[IRe(CO)_4]_2$, 15189-53-4; *cis*-$IRe(CO)_4(PPh_3)$, 15189-55-6; $IRe(CO)_5$, 13821-00-6.

Supplementary Material Available: Table of infrared spectral data in the carbonyl stretching region for $XRe(CO)_5$ and *cis*-$XRe(CO)_4L$ complexes (1 page). Ordering information is given on any current masthead page.

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Rupture and Repair of the Porphyrin Inner Core: Carbon–Nitrogen Bond Breaking and Formation in Ruthenium Complexes of an N,N′-Bridged Porphyrin

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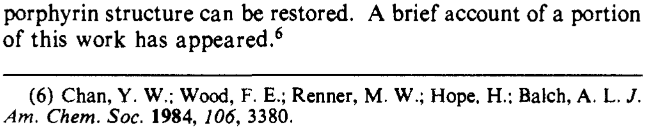
Abstract: Treatment of the *N,N′*-vinyl-bridged porphyrin **1** with $Ru_3(CO)_{12}$ yields three products: the carbene complex $TPPRu\{C{=}C(p\text{-}ClC_6H_4)_2\}$ (**3**) (TPP is the dianion of tetraphenylporphyrin), and two Ru(II) dicarbonyl complexes **4** and **5** in which the N,N′-bridge remains intact, but the ruthenium has inserted into a pyrrole C–N bond. Complexes **4** and **5** differ in that **4** contains the $C{=}C(p\text{-}ClC_6H_4)_2$ N,N′-bridge, while **5** contains a $CHCH(p\text{-}ClC_6H_4)_2$ N,N′-bridge. Spectroscopic data (^1H NMR, UV/vis, infrared) for the three products are reported. Crystals of **4**, $\{TPPCHCH(p\text{-}ClC_6H_4)_2\}Ru(CO)_2 \cdot {}^1/_2CH_2Cl_2$, crystallize in the monoclinic space group $P2_1/c$ with a = 12.633 (7) Å, b = 19.293 (10) Å, c = 19.820 (9) Å, β = 95.59 (3)°, Z = 4 at 130 K. The structure was refined to R = 0.079 for 640 parameters and 4172 reflections. The ruthenium is six-coordinate with two cis carbon monoxide ligands, bonds to two normal pyrrole groups, and bonds to the C and N of the ring-opened pyrrole. The damaged porphyrin is no longer planar. Upon heating, both **4** and **5** undergo C–N bond formation to reform the porphyrin ring.

The stability of the porphyrin macrocycle is one of the causes of its widespread utility in biology. Most chemical attack on porphyrins that alters the nature of the macrocycle involves reactions on the porphyrin periphery.[1,2] Reactions at the interior of the porphyrin are restricted to protonation, metalation,[3] N-akylation or N-arylation,[4] or N-oxidation.[5] These reactions, however, leave the four pyrrole rings intact while adding groups to the pyrrole nitrogen atoms. Here we describe novel reactions which lead to the rupture of the porphyrin inner core through the cleavage of the pyrrole C–N bond by a metal atom (ruthenium). Remarkably, however, this rupture is repairable, and the full porphyrin structure can be restored. A brief account of a portion of this work has appeared.[6]

Scheme I



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