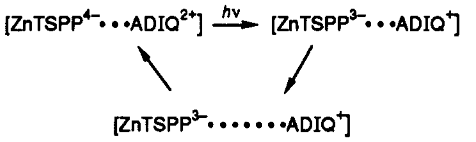
J. Phys. Chem. 1992, 96, 257-264

(ΔG°_{cr})[17] (Table I). There is no indication that the radical ion pairs dissociate into separated radical ions, and excitation of the ion pairs with a 10-ns laser pulse at 532 nm gives no detectable transient species.

Similar experiments made with the ZnTSPP^{4-}/ADIQ^{2+} ion pair indicated that the radical ion pair was present immediately after the laser pulse (Figure 4). This species decayed by first-order kinetics with a lifetime of 90 ± 10 ps (Figure 4). Most of the radical ion pairs were observed to decay to the ground-state ion pair by reverse electron transfer, but approximately 10% persisted on much longer timescales and decayed by first-order kinetics with a lifetime of 70 ± 20 ns (Figure 5). The long- and short-lived radical ion pairs exhibited similar, if not identical, transient differential absorption spectra while the retention of first-order kinetics indicates that the radical ion pair does not dissociate into separated radical ions.

The lifetime of the longer lived radical ion pair was observed to remain constant (±10%) during the application of an external magnetic field of up to 1 kG.[20] This indicates that the species is not a triplet radical ion pair formed by spin realignment via hyperfine interaction. Instead, the longer lived species is assigned to a singlet radical ion pair in which the rate of reverse electron transfer is decreased due to a larger separation of the reactants.



Mataga and co-workers[21] have observed similar behavior with ion pairs formed between 1,2,4,5-tetracyanobenzene and aryl hydrocarbons and have described them as "loose" or "solvent-separated" radical ion pairs. An alternative explanation could involve radical ion pairs in which the reactants are held in different orientations.[22,23]

The lifetimes of the various radical ion pairs (τ_{cr}) depend on the nature of the quaternary salt but do not correlate with the reaction exothermicity (Table I). This behavior is seen clearly when data for *N,N'*-dibenzyl-4,4'-dipyridine BV^{2+} are included in the series. There appears, however, to be a relationship between k_{cr} and the size of the quaternary salt; this latter term is best exemplified by the total number of double bonds present in the π-radical cation (n). Similar behavior has been reported previously by Gould et al.[7] and also can be seen in the results of Ojima et al.[8] In each case, increasing the size of the aromatic nucleus results in a decrease in k_{cr}. Most likely, this effect indicates that the orbital overlap integral decreases as the degree of delocalization of the quaternary salt increases.[22,23] This suggests, in turn, that there is a correlation between the electron-coupling matrix element and the resonance energy of the radical ions. Studies in progress are aimed at extending this series of polycyclic quaternary salts in order to further explore this effect.

Acknowledgment. The Center for Fast Kinetics Research is supported jointly by the Biotechnology Resources Program of the National Institutes of Health (Grant RR00886) and by the University of Texas at Austin. This work was supported by the National Science Foundation (Grant CHE 9102657). We are grateful to Dr. S. J. Atherton for help with the single-photon-counting studies and to P. T. Snowden for providing computer software.

Registry No. ZnTSPP^{4-}·4Na$^+$, 42712-11-8; MV^{2+}·2Cl$^-$, 1910-42-5; BV^{2+}·2Cl$^-$, 1102-19-8; DAP^{2+}·2BF$_4^-$, 21178-14-3; ADIQ^{2+}·2Cl$^-$, 118891-86-4.

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[20] This lifetime was measured after excitation of the ion pair with a 10-ns laser pulse at 532 nm. The sample cell was held between the poles of an electromagnet, and the lifetime was measured as a function of the applied magnetic field. The lifetime was observed to remain independent of magnetic field, at least up to 1 kG.

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Primary Photochemical Processes in *fac*-ClRe(CO)$_3$L$_2$ (L = 4-Phenylpyridine and 4-Cyanopyridine): A Steady-State and Flash Photochemical Study of Reaction Products and Intermediates

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The photochemistry of *fac*-ClRe(CO)$_3$L$_2$, L = 4-phenylpyridine and 4-cyanopyridine, has been investigated by monochromatic steady-state and flash photolyses between 400 and 229 nm. Two parallel photoprocesses, the photogeneration of the emissive MLCT state and the photoredox dissociation in {ClRe(CO)$_3$L$^+$, L$^{\bullet-}$} products, have been observed with both compounds. A third photoprocess, namely, the photogeneration of a Re(I)–ligand biradical, has been observed only in photolyses of the 4-phenylpyridine complex. While this Re(I)–ligand biradical reduces Cu^{II}(TIM)$^{2+}$ to the corresponding Cu(I) species, no such reaction is undergone by the MLCT state. Differences between the electronic structures of these complexes, shown by extended Hückel MO calculations, were related to their intrinsic photochemical behavior.

Introduction

A large number of Re(I) complexes have been the subject of studies concerned with these compounds' thermal and photochemical reactions.[1-23] Some interest in their chemical properties is derived from their potential applications to the catalysis of thermally and/or photochemically driven processes.[11,14-23] Ex-

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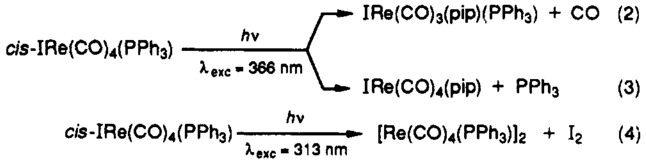
amples in the literature show that some photoprocesses are initiated when metal-to-ligand charge-transfer states, MLCT, undergo electron transfers with reducing molecules such as triethanolamine (eq 1).[11,14-19,24,25] The Re(I) complexes can be excited to other

$$fac\text{-BrRe(CO)}_3\text{bipy} \overset{h\nu}{\rightleftharpoons} \text{MLCT} \xrightarrow{\text{TEOA}} fac\text{-BrRe(CO)}_3\text{bipy}^- + \text{TEOA}^{\bullet +} \quad (1)$$

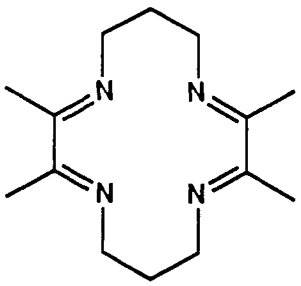
electronic states, i.e., MLCT, LMCT, LLCT, and LC states, by the absorption of photons with energies between 596 and 238 kJ/mol (UV–vis light).[6,8,10,19,23] Excitation with different photonic energies is followed by degradation of the electronic energy through various photophysical and photochemical paths. For example, photoredox and photosubstitution processes have recently been reported for cis-IRe(CO)$_4$(PPh$_3$) in irradiations at 313 and 366 nm respectively (eqs 2–4).[6] Chemical properties of the metal-to-ligand and ligand-to-ligand charge-transfer states have been investigated as a function of the ligand structure and conformational changes.[24] Results of these studies suggest that LLCT and/or MLCT may be convenient reactants for the generation of unstable species where charge separation is long lived. The photoreversible reduction of Cu^{II}(TIM)$^{2+}$ (I) by one of such intermediates has been previously observed in photolyses of the fac-ClRe(CO)$_2$(4-phenylpyridine)$_2$.[19] Such a reaction evolves in parallel to the decay of the MLCT state. In this work, we have investigated the nature of the primary photoreactions of fac-ClRe(CO)$_3$L$_2$, L = 4-phenylpyridine and 4-cyanopyridine, induced by continuous and flash irradiations at various wavelengths.



$$cis\text{-IRe(CO)}_4\text{(PPh}_3) \xrightarrow[\lambda_{exc} = 366\ \text{nm}]{h\nu} \text{IRe(CO)}_3\text{(pip)(PPh}_3) + \text{CO} \quad (2)$$

$$\phantom{cis\text{-IRe(CO)}_4\text{(PPh}_3)} \longrightarrow \text{IRe(CO)}_4\text{(pip)} + \text{PPh}_3 \quad (3)$$

$$cis\text{-IRe(CO)}_4\text{(PPh}_3) \xrightarrow[\lambda_{exc} = 313\ \text{nm}]{h\nu} [\text{Re(CO)}_4\text{(PPh}_3)]_2 + \text{I}_2 \quad (4)$$



(I) TIM

Experimental Section

Flash-Photochemical Procedures. The flash photolysis apparatus for the study of reaction kinetics and the measurement of transient absorption or emission spectra in a nanosecond to second time domain have been described elsewhere.[26-28] In these experiments, 10-ns flashes of monochromatic light were respectively generated with a Nd:YAG (Quanta Ray), an excimer (Lambda Physik), or a N$_2$ laser (Laser Photonics, PRA/Model UV-24). In conventional flash photolysis, two FP-8-100C (Xenon Corp.) flash lamps were used as sources of 30-μs polychromatic light pulses. Solutions were irradiated at selected wavelengths by using appropriate cutoff filters.

The calculation of the number of photons absorbed by the photolyte in a flash-photolysis experiment was based on the actinometry with Co(NH$_3$)$_5$Br^{2+}.[29] Irradiations of the Co(III) complex in aqueous acidic solutions, pH 3, of NaBr generated Br$_2^-$ whose concentrations, [Br$_2^-$]$_0$, were determined from the spectral changes measured 0.2 μs after the flash. Published values of the extinction coefficients for Br$_2^-$ and quantum yields for the photogeneration of the radical ion were used for the calculations.[29-31] Concentrations of the Co(III) complex were selected under the condition that solutions of the actinometer and a given photolyte have the same optical density at the wavelength, λ_{exc}, chosen for the irradiation.

Solutions were deaerated with O$_2$-free nitrogen in a gas-tight apparatus. The solution in the reaction cell was refreshed after each irradiation.

Steady-State Irradiations. Steady-state 350-, 300-, and 254-nm photolyses for the investigation of reaction products were carried out in an irradiator with appropriate Rayonet lamps. A resonance Cd lamp was used for continuous wave irradiations at 229 nm. The concentration of the photolytes were adjusted for absorbing more than 99.99% of the incident light and magnetic bars were used for stirring the solutions while they were irradiated. The deaeration of the liquids was accomplished by using three freeze–pump–thaw cycles or streams of O$_2$-free nitrogen. The Co(NH$_3$)$_5$Br^{2+} was used for the measurement of light intensities.[31]

The luminescence of the Re(I) complexes was investigated in an SLM 8000/8000S spectrofluorimeter with instrument response corrections. Quantum yields of emission were calculated relative to rhodamine B. In keeping with a literature procedure,[32,33] the emission intensity was graphically integrated with respect to the wavelength and subjected to corrections for various inner filter effects.

Analytical Procedures. Gas chromatography was used for the analysis of CO. The gas was removed under vacuum from the photolyzed solution. An ion-selective electrode was used for the measurement of Cl$^-$ concentrations. A calibration curve for the response of the electrode was constructed with standardized solutions of tetraethylammonium chloride in acetonitrile.

Materials. The complexes fac-ClRe(CO)$_3$L$_2$, L = pyridine, 4-cyanopyridine, and 4-phenylpyridine, were prepared and purified by published procedures.[12,34,35] The materials were regarded as pure compounds when their elemental analyses and spectral properties (absorption and emission spectra) agreed with those in the literature. Purified [Cu(TIM)](ClO$_4$)$_2$ was available from a previous work.[36]

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(25) Abbreviations used in this work: 2,2′,2″-nitrilotriethanol, TEOA; 2,3,9,10-tetramethyl-[14]-1,4,8,11-tetraene-N$_4$, TIM; pyridine, py; 4-phenylpyridine, 4-Phpy; 4-cyanopyridine, 4-CNpy; ligand-to-ligand charge-transfer state, LLCT; ligand-to-metal charge-transfer state, LMCT; metal-to-ligand charge transfer state, MLCT; ligand-centered state, LC; metal-centered (ligand field) state, LF.

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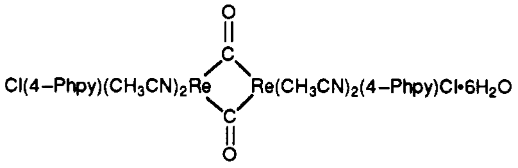
TABLE I: Quantum Yields from Steady-State and Laser Flash Irradiations of *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$[a]

λ_{exc}, nm	$10^5 n_{h\nu}$,[b] einstein dm^{-3} pulse^{-1}	$10^6 I_0$, einstein dm^3 s^{-1}	$\phi \times 10^2$				$[Cu^{II}(TIM)^{2+}]$,[c] M
			Cu(I)	CO	Cl^-	PP	
353.3	3.6 ± 0.2		1.5 ± 0.2			0.20 ± 0.05	6.1×10^{-4}
351	15 ± 1			0.40 ± 0.04			
	25 ± 1				0.025 ± 0.005		
337	6.0 ± 0.2		4.0 ± 0.3			0.18 ± 0.02	1.0×10^{-4}
			4.4 ± 0.3				6.4×10^{-5}
			3.4 ± 0.2				5.2×10^{-5}
			3.0 ± 0.1				2.1×10^{-5}
308	15 ± 1		15 ± 1			0.65 ± 0.02	
			13 ± 1				
300		1.6 ± 0.2		0.85 ± 0.05			
265	35 ± 3 to 3.0 ± 0.2[d]		5.0 ± 0.3			0.70 ± 0.09	3.0×10^{-4}
			4.1 ± 0.3				1.0×10^{-4}
			3.9 ± 0.2				5.2×10^{-5}
			2.8 ± 0.1				2.1×10^{-5}
253.7		5.1 ± 0.2		1.9 ± 0.3			
		8.4 ± 0.4			0.037 ± 0.009		
229		0.33 ± 0.04		8.0 ± 0.3	0.023 ± 0.009		

[a] Solutions of the Re(I) complex in CH_3CN were deaerated by vacuum or with streams of N_2. [b] All the intensities, I_0, in steady-state photolysis and photonic densities, $n_{h\nu}$, in flash photolysis were measured with $Co(NH_3)_5Br^{2+}$. [c] Concentrations of $Cu^{II}(TIM)^{2+}$ used in flash photolysis experiments for the scavenging of a reaction intermediate. The yield of $Cu^I(TIM)$ associated with a given concentration of the scavenger $Cu^{II}(TIM)^{2+}$ is shown in the table's third column. [d] Each quantum yield was measured at several light intensities between the values shown for I_0. The quantum yields exhibited less than a 10% dependence on the light intensity, provided that experimental conditions prevented a secondary photolysis.

The photolysis product $Cl_2Re_2(CO)_2(CH_3CN)_4(4\text{-phenylpyridine})_2 \cdot 6H_2O$ was synthesized by following a photochemical procedure. A 200 cm^3 volume of 2.0×10^{-3} M *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ in deaerated CH_3CN was irradiated at 254 nm, $I \sim 5 \times 10^{-7}$ einstein dm^{-3} s^{-1}, for 15 h. A stream of O_2-free nitrogen was passed through the liquid during the photolyses. The progress of the reaction can be followed by the bleaching of the 300-nm band and the appearance of new bands at 255 and 410 nm in the spectrum of the solution. The product of the photolysis was separated by column chromatography on silica gel previously equilibrated with 1:1 M Cl_2CH_2 in CH_3CN. The adsorbed products were eluted in succession with 200 cm^3 of CH_3CN and with a 1:3 M solution of CH_3OH in CH_3CN until removal of a yellow adsorbate from the column. This fraction was collected and rotoevaporated to dryness. The dark solid material was recrystallized from a saturated solution in CH_2Cl_2 by the addition of isooctane. The UV-vis spectrum of the compound exhibits an absorption band with $\lambda_{max} = 375$ nm, $\epsilon = 1.14 \times 10^4$ M^{-1} cm^{-1}, and the IR spectrum an absorption, $\bar{\nu} = 1828$ cm^{-1}, characteristic of the bridging CO. The compound's elemental analysis (found Cl, 6.1; O, 10.8; N, 7.3; H, 3.9; C, 36.5) is in accord with stoichiometric relationship $Re:Cl:CO:2CH_3CN:4\text{-}Phpy:3H_2O$ (calcd Cl, 6.5; O, 11.7; N, 7.7; H, 3.9; C, 35.3). It is possible to assign to this compound a structure (II) by comparison of such properties to those of related Re dimers.



II

Spectroquality acetonitrile was dried over molecular sieves. Other materials were reagent grade and used without further purification.

Results

The photochemical reactions of the *fac*-$ClRe(CO)_3L_2$, where L = 4-phenylpyridine or 4-cyanopyridine, have been investigated using monochromatic irradiations within the 229–400-nm spectral region. Experimental observations on the photochemical behavior of the Re(I) complexes in flash and continuous photolyses are described below.

Product Quantum Yields. Continuous photolyses, $\lambda_{exc} = 229$, 254, 300, and 350 nm, of *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ in deaerated CH_3CN induce the disappearance of the 320-nm band and the appearance of two new features, $\lambda_{max} = 255$ and 420 nm, in the spectrum of the solution, Figure 1. The rates of these spectral changes, followed at 420 nm and normalized with respect to the light intensity, increased with decreasing λ_{exc}.

The nature of the major photolysis product was investigated by scanning the IR spectrum of 5.0×10^{-3} M Re(I) solutions irradiated, $\lambda_{exc} = 254$ nm and $I_0 = 5.1 \times 10^{-7}$ einstein dm^{-3} s^{-1}, 80 and 160 min.[37] In the region of the CO absorptions, the spectra showed that the intensities of the peaks assigned to *fac*-$ClRe(CO)_3L_2$, $\bar{\nu}_{max} = 2024$, 1892, and 1818 cm^{-1}, decreased and a new band grew at $\bar{\nu}_{max} = 1828$ cm^{-1} with progressively longer irradiations, Figure 1. The position of the emerging band was related to the formation of a product with bridging CO ligands. Moreover, a product whose IR and UV-vis spectra respectively exhibited the characteristiic absorption of the bridging CO ligand, $\bar{\nu}_{max} = 1828$ cm^{-1}, and the band at 375 nm, $\epsilon = 1.14 \times 10^4$ M^{-1} cm^{-1}, was chromatographically separated from the reaction mixture.[38] On the basis of the spectral properties and elemental analysis, the isolated complex was characterized as a Re(I) dimer, $[ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2$ (II).

The quantum yields of Cl^- and CO in photolysis of *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ were measured as a function of the irradiation wavelength, i.e., $\lambda_{exc} = 229$, 254, 300, and 351 nm, Table I.[19] In accordance with the composition of the dimeric product, the quantum yield of Cl^- is very small, $\phi < 10^{-4}$, at all these wavelengths when photolyses are restricted to less than 10% decomposition of the Re(I) complex. Photolabilization and photoredox reactions of the Cl^- ligand must be, therefore, insignificant by comparison to other photoprocesses. Moreover, the dependence of the CO quantum yield on λ_{exc} and the rate of the spectral changes described above exhibited a similar trend, namely, they increased with photonic energy.

Although photochemical transformations of *fac*-$ClRe(CO)_3(4\text{-}CNpy)_2$ in deaerated CH_2Cl_2 were qualitatively similar to those reported above for *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$, in our hands the 4-cyanopyridine complex was too unstable for product analysis and quantum yield measurement.

Transient Emission and Absorption Spectra. Monochromatic flash irradiations, $\lambda_{exc} = 337$ or 353.3 nm, of *fac*-$ClRe(CO)_3(4\text{-}$

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(37) Conversions of 5% and 10% of the Re(I) complex to products.

(38) The chromatographic separation of the dimeric Re(I) complex was not quantitative and could not be used for the measurement of the product quantum yields. Free ligand, 4-Phpy, was also detected as a reaction product, but its concentration could not be determined with the accuracy required for quantum yield calculations.

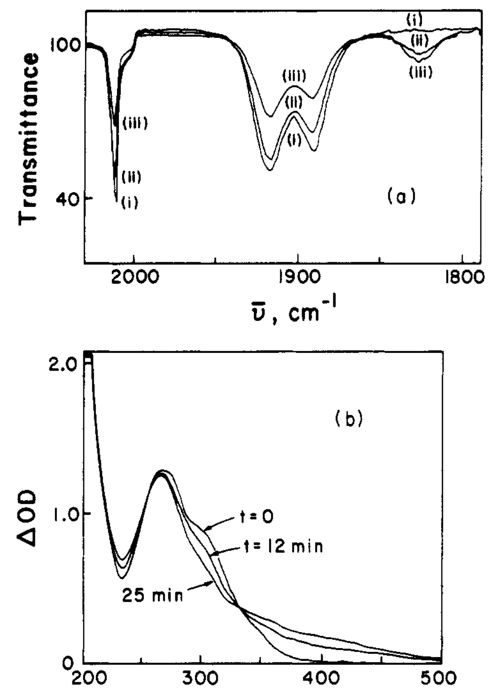

Figure 1. Spectral changes induced in 254-nm photolyses of *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ in deaerated CH_3CN. The IR spectra in (a) were recorded with a 5.0×10^{-3} M solution irradiated 0 min (i), 80 min (ii), and 160 min (iii). The UV-vis spectra in (b) were recorded with a 1.0×10^{-4} M solution in a cell with 0.2-cm optical path after successive intervals of irradiations. Isosbestic points remain undisturbed until secondary photolysis becomes significant.

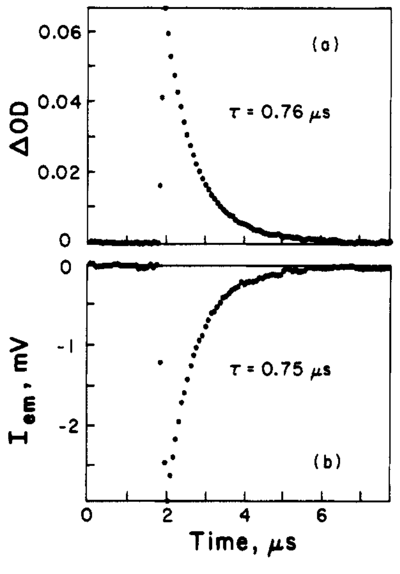

Figure 2. Typical traces for the decay of the 560-nm optical density (a) and the 540-nm emission intensity (b) in 353.3-nm flash irradi8ations of 2.0×10^{-4} M *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ in deaerated CH_3CN. The lifetimes τ measured in each case are indicated on the figure.

Phpy)$_2$ in deaerated CH_3CN and *fac*-ClRe(CO)$_3$(4-CNpy)$_2$ in deaerated CH_2Cl_2 were used for a time-resolved study of the respective MLCT-originated luminescence. The corresponding decay of the emissions, followed respectively at 540 and 560 nm, could be fitted without appreciable deviations to a single exponential:

$$I_{em} = I_0 \exp(-t/\tau)$$

where τ is the emission lifetime, Figure 2. Time-resolved emission spectra and lifetimes calculated for the 4-phenylpyridine complex from these measurements were in good agreement with literature reports.[12]

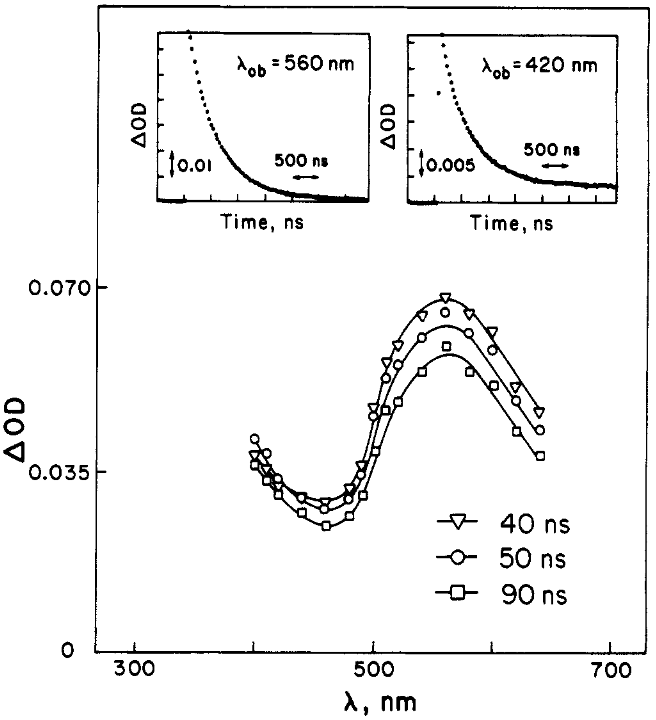

Figure 3. Transient spectra recorded in 266-nm flash irradiations of 10^{-4} M *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ in deaerated CH_3CN. The inserts show two traces for the decay of the optical density at 560 and 420 nm, respectively.

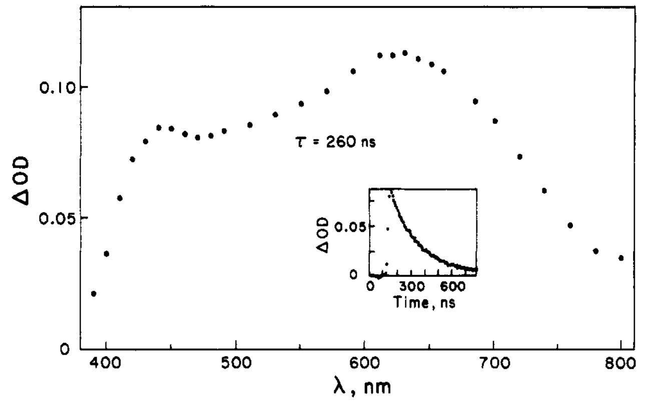

Figure 4. Transient spectrum recorded in 337-nm flash irradiations of 10^{-4} M ClRe(CO)$_3$(4-CNpy)$_2$ in deaerated CH_2Cl_2. The spectrum was measured 30 ns after the laser flash irradiation, and the insert shows a typical trace, λ_{ob} = 530 nm, for the decay of the optical density.

Transient absorption spectra, Figures 3 and 4, were recorded in flash photolysis under experimental conditions similar to those used in the investigation of the luminescence, Figure 2.[19] Irradiations at wavelengths of the first absorption band, i.e., λ_{exc} = 337 or 353.3 nm for the 4-cyanopyridine complex and λ_{exc} = 353.3 nm for the 4-phenylpyridine complex, generated transient spectra that partially disappeared via first-order reactions. Since the lifetimes of these reactions were the same as the luminescence, the new absorptions were associated with MLCT excited states undergoing radiative and radiationless relaxations.

Although the decay of the transient spectra corresponds to an almost complete recovery of the parent complexes of 4-phenylpyridine and 4-cyanopyridine, comparatively small and longer lived absorptions were recorded in a microsecond to second time domain; see insert to Figure 3. These long-lived absorptions, detected after the decay of the MLCT states, must be associated with primary products of photoreactions proceeding in parallel to the formation and decay of the MLCT states. Typically, flash photolyses of the ClRe(CO)$_3$(4-Phpy)$_2$ at 265, 308, or 337 nm generated a long-lived transient spectrum, determined 7 μs after the irradiation,

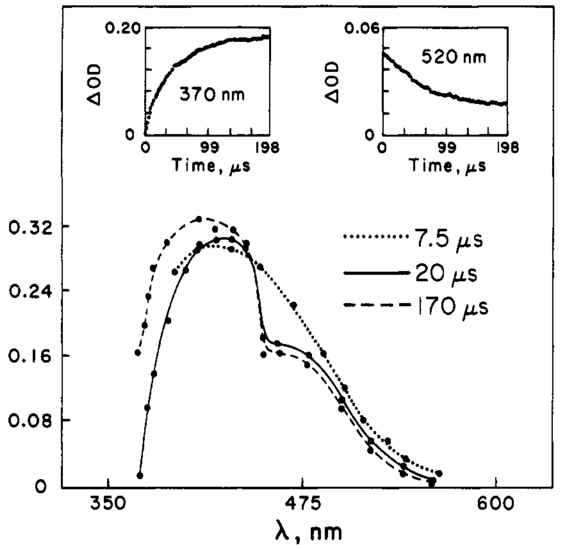

Figure 5. Time-resolved spectral changes associated with chemical reactions of the primary product, PP. Spectra recorded at given times in 266-nm flash irradiations of *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ in deaerated CH_3CN. Inserts show typical traces for a growth, $\lambda_{ob} = 370$ nm, and a decay, $\lambda_{ob} = 520$ nm, of the optical density.

with a maximum at 430 nm. Values of the 560- and 430-nm optical density changes after the respective delays of 15 ns and 15 µs were regarded as measures of the photogenerated MLCT and photolysis product concentrations. The value of ΔOD at 430 nm increases relatively to the one at 560 nm with decreasing λ_{exc} with the same tendency that was found (see above) for the formation of the Re(I) dimer and the quantum yield of CO. The absorption band with $\lambda_{max} = 430$ nm can be, therefore, assigned to a primary product, PP, which precedes the formation of the dimeric Re(I) complex. In addition, the decay of the 560-nm optical density is kinetically of a first order and the rate constant is independent of the excitation wavelength in the 265–337-nm spectral region. Since the value of this rate constant, $k = 1.5 \times 10^6$ s^{-1}, is the same that has been determined from luminescence measurements, such spectral changes must be associated with the radiative and radiationless relaxation of the MLCT state.

The photochemical behavior of the *fac*-$ClRe(CO)_3(4\text{-}CNpy)_2$ in flash irradiations, $\lambda_{exc} = 265$, 308, 337, and 353.3 nm, was similar to that exhibited by the 4-phenylpyridine complex. A short-lived transient with the same lifetime of the luminescence, $k = 3.8 \times 10^6$ s^{-1}, was assigned to the relaxation of the MLCT state, Figure 4. In addition, the transient spectra of the primary photoproduct were recorded at times longer than those required for a complete decay of the MLCT state.

Although spectral transformations described above are principally caused b the disappearance of MLCT states, those detected at times longer than 1 µs must be associated with the conversion of flash-generated metastable products into the stable ones. The spectrum of the primary product, PP with $\lambda_{max} = 430$ nm, observed in 266-nm flash irradiations of *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ undergoes, for example, changes between 10 and 100 µs after the flash, Figure 5. Since the rate of the optical density change is independent of the flash intensity and *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ concentration, it is kinetically of a first order with a rate constant $k = 1.1 \times 10^4$ s^{-1}. Two additional processes, namely, two successive and partial decays of the 430-nm optical density, were observed at times longer than 0.1 s, Figure 6. The half-lifetime of the first process exhibited a linear dependence on the reciprocal of the flash intensity that could be expected of second-order reactions. In agreement with this experimental observation, plots of the reciprocal of the 450-nm optical density change, ΔOD^{-1}, vs time were linear with slopes $k/\epsilon = 2.8$ cm s^{-1} and $k/\epsilon = 2.2 \times 10^{-2}$ cm s^{-1}. Plots of ΔOD^{-1} vs time for the second process were almost linear but deviated from linearity when it had progressed beyond the 80% completion.[39]

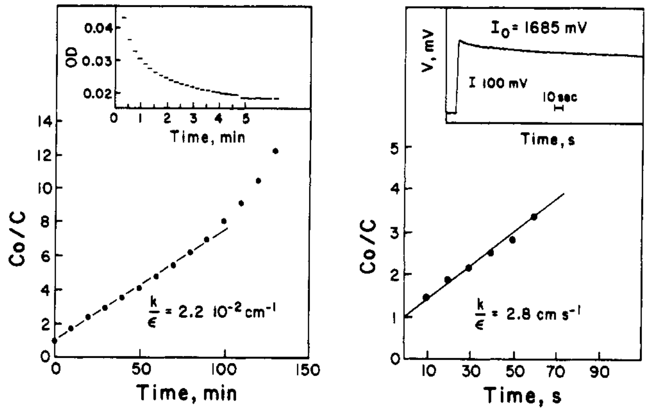

Figure 6. Traces (inserts) and second-order kinetic treatments for the 450-nm optical density changes at times longer than 1 s. Experimental observations were made in 266-nm flash irradiations of 2.7×10^{-5} M *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ in deaerated CH_3CN. Calculated values of k/ϵ are given on the figure.

Observations in a picosecond to nanosecond time domain by a technique reported elsewhere[27] have shown that the photogeneration of the emission MLCT states and primary product PP must have lifetimes, $\tau \le 6$ ps, shorter than the resolution, $t \sim 20$ ps, of the apparatus.

Redox Reactions of MLCT States and Photogenerated Intermediates. To establish if flash-induced spectral changes (see above) were related to processes associated with photooxidations of the solvent CH_3CN, reactions of the primary photoproducts and MLCT states with TEOA were investigated by 308-nm flash photolyses of *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$. The transient spectra, $\lambda_{max} = 390$ and 590 nm, recorded in 308-nm flash irradiations of 2.0×10^{-4} M *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ and 7.5×10^{-1} M TEOA in deaerated CH_3CN, can be assigned to the one-electron reduction product, $ClRe(CO)_3(4\text{-}Phpy)_2^-$.[17] The 308-nm yield of the product formation relative to the 353.3-nm yield was determined by using the corresponding optical density changes and number of photons absorbed by the photolyte. These quantum yields are in the relationship $3.9 = \phi_{353}/\phi_{308}$, which is close to the relationship between corresponding quantum yields of the emissive state, $4.0 = \phi_{353}/\phi_{308}$, calculated from the excitation spectrum; see below. The $ClRe(CO)_3(4\text{-}Phpy)_2^-$ must be generated, therefore, in a reaction between such an excited state and TEOA. It must be noted that a partial decay of the 430-nm optical density was observed after the generation of $ClRe(CO)_3(4\text{-}Phpy)_2^-$ and it was assigned to a reaction between PP and TEOA. In addition, these experimental observations show that the primary product, PP, is not related to a photoinduced oxidation of the solvent since such processes generate a different species, i.e., $ClRe(CO)_3(4\text{-}Phpy)_2^-$.

The photogeneration of other reaction intermediates, in addition to the primary photoproduct, PP, were investigated by using $Cu^{II}(TIM)^{2+}$ in the role of scavenger. Flash irradiations, $\lambda_{exc} = 265$, 308, 337, and 353.3 nm, of the 4-phenylpyridine complex were carried out in solutions where concentrations of *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$, 1.5×10^{-4}–1.0×10^{-4} M, and $Cu^{II}(TIM)^{2+}$, $[Cu^{II}(TIM)^{2+}] \le 2.0 \times 10^{-4}$ M, ensured that 80% or more of the light was absorbed by the Re complex.[40] Although $Cu^{I}(TIM)^+$ was not detected as a product in flash irradiations of blanks prepared with $Cu^{II}(TIM)^{2+}$ alone, significant concentrations of the Cu(I) complex were generated in flash photolysis of solutions containing *fac*-$ClRe(CO)_3(4\text{-}Phpy)_2$ in addition to $Cu^{II}(TIM)^{2+}$.

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(39) The fraction of intermediate concentration reacted at a given time is the ratio of the instantaneous concentration to the initial concentration, c/c_0. It was expressed in terms of the relationship $(\Delta OD - \Delta OD_0)/(\Delta OD_\infty - \Delta OD_0)$ between the instantaneous optical density change, ΔOD, and the optical density changes at the beginning, ΔOD_0, and at the end, ΔOD_∞, of the reaction.

(40) In experimental conditions where absorption of the light by $Cu^{II}(TIM)^{2+}$ was significant, the intensity of the light absorbed by the Re(I) complex was calculated by applying appropriate Beer's law based corrections to the actinometry.[32]

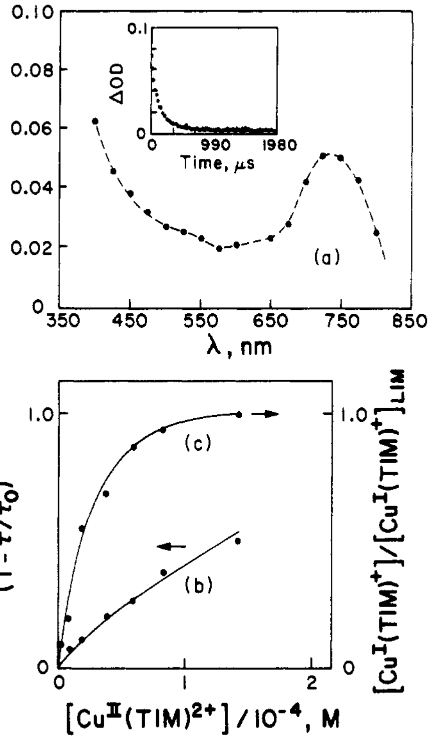

Figure 7. Experimental observations on the scavenging of a reaction intermediate, I, with Cu(TIM)$^{2+}$ in deaerated CH$_3$CN. Spectrum of Cu^I(TIM)$^+$ (a) generated in 353.3-nm flash irradiations of 2.0 × 10^{-4} M *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ in a 5.2 × 10^{-4} M Cu^{II}(TIM)$^{2+}$ solution. The insert shows a trace of the 700-nm optical density change when Cu^I(TIM)$^+$ undergoes a back-electron-transfer reaction. The percentage of the luminescence quenched by a given concentration of Cu^{II}(TIM)$^{2+}$ and the fraction of Cu^I(TIM)$^+$ generated under similar conditions are respectively shown in (b) and (c). Lifetimes, τ, of emission and Cu^I complex concentrations were measured in 353.3-nm flash irradiations of 2.0 × 10^{-4} M Re(I) complex in deaerated CH$_3$CN.

This process is also a source of the species identified in this work as a primary product, i.e., PP with λ_{max} = 430 nm. The disappearance of the Cu(I) complex was followed at λ_{ob} = 750 nm and the decrease of the primary product concentration at λ_{ob} = 450 nm in solutions of identical composition, i.e., 1.0 × 10^{-4} ≥ [Re(I)] ≥ 0.2 × 10^{-4} M, Figure 7A. The dependence of the decay lifetime on the Cu(I) product concentration and least-squares fitting of the traces have shown that such processes are kinetically of second order with a ratio of the rate constant to the extinction coefficient $k/\epsilon = 2.5 \times 10^5$ cm s^{-1} at λ_{ob} = 450 nm and $k/\epsilon = 5.5 \times 10^5$ cm s^{-1} at λ_{ob} = 750 nm. An extinction coefficient of $\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1} for the primary product's absorption at 450 nm was calculated from the k/ϵ values given above and the reported extinction coefficient of Cu^I(TIM)$^+$.

In the preceding experiments, the additional formation of primary product can be related to a reaction of the MLCT state and/or a chemical intermediate with Cu^{II}(TIM)$^{2+}$. These processes were investigated by comparing the respective functional dependences (on Cu(II) concentration) of the luminescence quenching and of the Cu^I(TIM)$^+$ formation, Figure 7b,c. Indeed, the luminescence of *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ is quenched by the Cu^{II}(TIM)$^{2+}$, and the lifetime of the MLCT excited state decreases with increasing quencher concentration. A comparison of the efficiencies of emission quenching and Cu^I(TIM)$^+$ formation reveals that they have a different functional dependence on the Cu(II) concentration. For example, the efficiency of Cu(I) product formation is almost 100% at concentrations of Cu^{II}(TIM)$^{2+}$ where only 30% of the emission is quenched. One cannot equate, therefore, the formation of Cu^I(TIM)$^+$ and an additional concentration of primary product, PP, with reactions of the MLCT states. It must be proposed that an intermediate I, i.e., an unstable Re complex, reacts with Cu^{II}(TIM)$^{2+}$. The efficiency of the reaction between I and Cu^{II}(TIM)$^{2+}$, Figure 7c, suggests that I could regenerate *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ with a lifetime of 1 μs ≤ τ ≤ 100 μs. Moreover, the absorptions of PP and MLCT limit the spectral resolution of flash photochemical observations; values of the extinction coefficients, $\epsilon \leq 2 \times 10^3$ M^{-1} cm^{-1}, for I will make this species undetectable in such experiments.

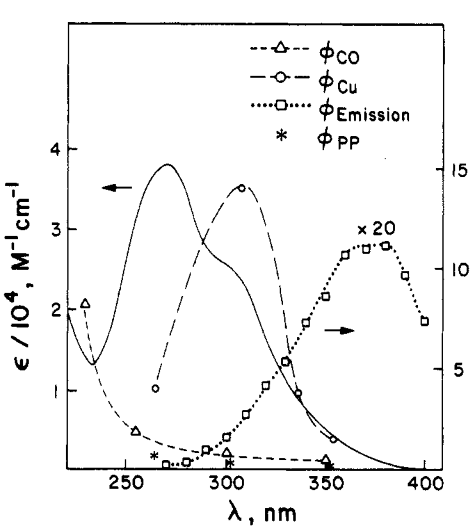

Figure 8. Action and excitation spectra based on product (ϕ_{CO} for CO, ϕ_{Cu} for Cu^I(TIM)$^+$, and ϕ_{PP} for PP) and emission ($\phi_{emission}$) quantum yields from *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ photolyses. The absorption spectrum of the Re(I) complex is shown for comparison.

Action and Excitation Spectra. The observations in flash photolysis described in the previous paragraphs provided us with ways to measure the respective quantum yields of the primary product, PP, and precursor, I, of the Cu^I(TIM)$^+$. Quantum yields, ϕ_I, for the photogeneration of I, were calculated according to eq 5, where [Cu^I(TIM)$^+$]$_0$ represents the flash-generated concentration of the Cu(I) complex produced in a 100% scavenging of I, i.e., for [Cu^{II}(TIM)$^{2+}$] ≥ 1.0 × 10^{-4} M, in flash-photolysis experiments.[19] The flash-generated concentration of radical anion, [Br$_2^-$]$_0$, and the Br$_2^-$ quantum yield, ϕ_{Br}, from the corresponding actinometry with Co(NH$_3$)$_5$Br^{2+} were used in eq 5. Primary product quantum yields, ϕ_{PP}, were calculated (eq 6) in terms of

$$\phi_I = \phi_{Br}[Cu^I(TIM)^+]_0/[Br_2^-]_0 \qquad (5)$$

$$\phi_{PP} = [PP]_0/I_{ab} = \Delta OD_0\phi_{Br}/\epsilon_{PP}[Br_2^-]_0 \qquad (6)$$

the concentration of primary product, [PP]$_0$. Values of [PP]$_0$ were obtained from the optical density changes, Δ_{OD_0}, measured after the decay of the MLCT state, the appropriate primary product extinction coefficient, ϵ_{PP}. The intensity of the light, I_{ab}, absorbed by the Re(I) complex was determined by using the Co(NH$_3$)$_5$Br^{2+} actinometer. The action spectra in Figure 8 were recorded with quantum yields measured in laser-flash irradiations of *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ in suitable concentrations, i.e., 10^{-3}–10^{-5} M in CH$_3$CN, at given wavelengths. In addition, the excitation spectrum was recorded with emission quantum yields, λ_{exc}, measured in continuous-wave monochromatic irradiations of *fac*-ClRe(CO)$_3$(4-Phpy)$_2$ in deaerated CH$_3$CN. These spectra, i.e., excitation and action, have maxima at different wavelengths over the 200–400-nm spectral region and must be regarded as evidence about the kinetic independence of the various photoprocesses undergone by the Re complex.

Molecular Orbital Calculations. Literature reports about the crystallographic structure[23] and electronic structure[41] of Re complexes have provided bond distances and atomic orbital energies useful for these MO calculations. To optimize the value

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(41) Kersting, M.; Hoffmann, R. *Inorg. Chem.* **1990**, *279*, 84.

(42) The method followed for these MO calculations has been described elsewhere.[43,44]

(43) Kraut, B.; Ferraudi, G. *J. Chem. Soc., Dalton Trans.* **1991**, 2063.

(44) Van Vlierberge, B.; Ronco, S.; Ferraudi, G. *Inorg. Chem.* **1988**, *27*, 3453.

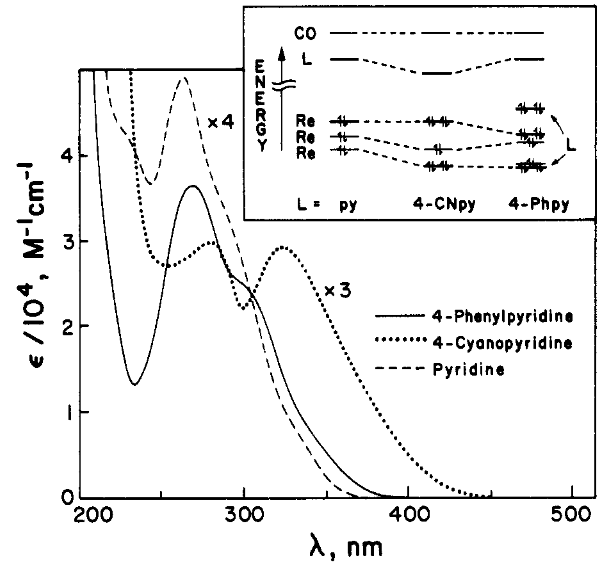


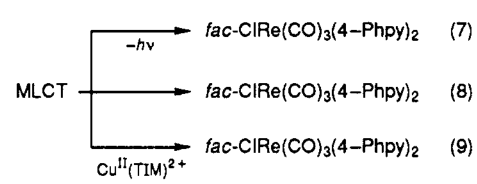
Figure 9. Absorption spectra and energy diagram with relevant molecular orbitals of the pyridine, 4-cyanopyridine, and 4-phenylpyridine complexes. The extinction coefficients of the former two complexes have been respectively multiplied by 4 and 3 for scaling purposes. Molecular orbitals are labeled by the metal or by the ligand making the larger contribution.

of the constant in the Wolfsberg and Helmholtz approximation and zero-order VOIE energies, the MO method was applied to $Re(CO)_5X$, where X = CO, Cl, and Br. In this series of complexes, the differences between calculated and literature-reported energies for electronic transitions[45] were less than 10%. For example, optical transitions for $^1E \leftarrow {}^1A_1$, $E = 347$ kJ; $LF_1 \leftarrow {}^1A_1$, $E = 395$ kJ; and $LF_2 \leftarrow {}^1A_1$, $E = 434$ kJ have been reported for $ClRe(CO)_5$;[45] the corresponding calculated energies are 338, 424, and 473 kJ. Similar agreements between values of the transitions energies deduced respectively from MO calculations and the absorption spectra were sought when such calculations were carried out with pyridine, 4-phenylpyridine, and 4-cyanopyridine complexes. While some high-energy occupied molecular orbitals are linear combinations constructed with even contributions of the Re, Cl, CO, and pyridine orbitals, low-energy unoccupied molecular orbitals are mainly localized in the pyridines, Figure 9. It is possible to identify, therefore, electronic transitions with a significant Re-to-pyridine charge displacement, transitions which should also affect the Re–CO bond in accord with literature reports about the resonance Raman spectra.[46] Vacant molecular orbitals with a large localization on the carbonyls are found at higher energies, i.e., $E > 473$ kJ. These values compare well with those found for $ClRe(CO)_5$. The 4-phenylpyridine complex is unique because there are two occupied orbitals centered only in the pyridine that are placed above those orbitals with partial localization on the Re. This order of orbitals suggests that electronic transitions populating ligand-centered, $\pi\pi^*$, and MLCT excited states should be in close proximity at energies below 290 kJ.[47,48] A direct consequence of these molecular orbital energies is that the separation of charge between pyridines to form a biradical, i.e., $(4\text{-Phpy}^{\bullet+})Re^I(4\text{-Phpy}^{\bullet-})$, must be less endoergonic than that required in the generation of a Re(II)–ligand radical, $Re^{II}(4\text{-Phpy}^{\bullet-})$. Although all the necessary redox potentials for these compounds are not yet available, electrochemical information in literature reports[4-15,20-24] for other Re(I) compounds leads to a similar conclusion.

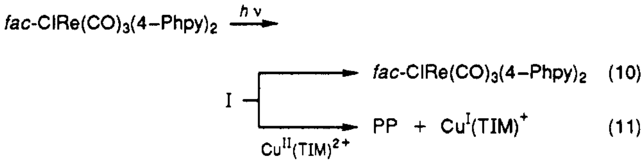
Discussion

The results of time-resolved emission and optical absorption experiments show that, in the absence of suitable quenchers, the MLCT states of the Re(I) complexes are unreactive under the medium conditions of this work, i.e., the population of these states is followed by competitive radiationless and radiative relaxations. Irradiations of the *fac*-$ClRe(CO)_3(4\text{-Phpy})_2$ between 400 and 270 nm generate the MLCT state and an intermediate, I, which reduces $Cu^{II}(TIM)^{2+}$. No such intermediate was detected, however, in photolyses of *fac*-$ClRe(CO)_3(4\text{-CNpy})_2$. A photoinduced dimerization reaction is more efficiently driven when irradiations are carried out at $\lambda_{exc} < 260$ nm and the process is mediated by a microsecond-living primary product PP. Experimental observations on the photoreactions of the *fac*-$ClRe(CO)_3L_2$, L = 4-phenylpyridine and 4-cyanopyridine, will be firstly analyzed from the standpoint of the overall mechanism of the light-induced reactions, and the photochemical properties of the Re(I) complexes will be secondly related to the nature of various populated excited states.

Mechanistic Considerations. The relaxations, radiative and nonradiative, of the MLCT state and the luminescence quenching by $Cu^{II}(TIM)^{2+}$ are respectively represented in eqs 7–9.



An intermediate I, photogenerated in irradiations of the Re(I) complex between 360 and 260 nm, is shown undergoing transformations by competitive processes; a back transformation to *fac*-$ClRe(CO)_3(4\text{-Phpy})_2$, eq 10, and an electron-transfer reaction



$$Cu^I(TIM)^+ + PP \longrightarrow Cu^{II}(TIM)^+ + fac\text{-}ClRe(CO)_3(4\text{-Phpy})_2 \quad (12)$$

between I and $Cu^{II}(TIM)^{2+}$, eq 11. Equation 12 accounts for the oxidation of $Cu^I(TIM)^+$ by PP. Competition between these reactions, eqs 10 and 11, accounts for the lack of products in the absence of the Cu(II) scavenger and the appearance of them, i.e., $Cu^I(TIM)^+$ and excess PP, with a scavenger-concentration-dependent efficiency.

Since the reactions of I do not lead to products of the *fac*-$ClRe(CO)_3(4\text{-Phpy})_2$ decomposition, they suggest possible structures for this intermediate. Charge separation may lead to a Re(II)–ligand radical or a Re(I)–biradical configuration, respectively. MO calculations reveal that the generation of a biradical species, *fac*-$ClRe(CO)_3(4\text{-Phpy}^{\bullet+})(4\text{-Phpy}^{\bullet-})$, requires less energy than the generation of *fac*-$ClRe^{II}(CO)_3(4\text{-Phpy})(4\text{-Phpy}^{\bullet-})$. It must also be noted that a MLCT state can be formally related to a Re(II)–ligand radical intermediate; the tendency of such an excited state to transfer energy and not an electron to $Cu^{II}(TIM)^{2+}$ weighs, therefore, in favor of assigning a biradical-like structure to I. Similar arguments can be used to explain why no intermediate I has been detected in the photolyses of the 4-cyanopyridine complex. Indeed, the separation of charge required in *fac*-$ClRe(CO)_3(4\text{-CNpy}^{\bullet-})(4\text{-CNpy}^{\bullet+})$ is precluded by the order of electronic levels found in MO calculations for *fac*-$ClRe(CO)_3(4\text{-CNpy})_2$; the electronic structure of *fac*-$ClRe^{II}(CO)_3(4\text{-CNpy})(4\text{-CNpy}^{\bullet-})$ being in excess of 30 kJ/mol more stable than the corresponding biradical.

Flash photolysis experiments have shown that the formation of the dimeric complex, $[ClRe(CO)(CH_3CN)_2(4\text{-Phpy})]_2$, involves

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[45] Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ottesen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111.

[46] Stufkens, D. J. *J. Mol. Struct.* **1982**, *79*, 67.

[47] This observation is in agreement with literature reports about the spectroscopic properties of the free pyrazine ligand and the Re(I) complex.[12,48] The ligand-centered state is expected to be less than 38.5 kJ/mol above the MLCT.

[48] Hotchandani, S.; Testa, A. C. *J. Photochem. Photobiol. A: Chem.* **1991**, *55*, 323.

several reactions following the photogeneration of the primary product, PP. Such a primary product must be assigned as $ClRe(CO)_3(4\text{-}Phpy)^{\bullet+}$ in order to rationalize experimental observations, namely, the kinetics and nature of the spectral transformations in the formation of the dimeric product and the oxidation of $Cu^I(TIM)^+$ by PP. The presence of a new absorption band, i.e., $\lambda_{max} = 430$ nm in Figure 5, at longer wavelengths than those in the parent Re(I) complex is expected for a Re(II) complex.[49,50] That this is a mononuclear species results from the 1:2 relationship between quantum yields of primary product and CO. A photoredox dissociation in $ClRe(CO)_3(4\text{-}Phpy)^{\bullet+}$ and pyridine anion radicals,[51–53] eq 13, must be proposed, therefore, to be an

$$fac\text{-}ClRe(CO)_3(4\text{-}Phpy)_2 \xrightarrow{h\nu} ClRe(CO)_3(4\text{-}Phpy)^+ + Phpy^{\bullet-} \quad (13)$$

additional photoprocess induced in irradiations at wavelengths shorter than 330 nm.

In these regards, the spectral transformations, observed in a 10–100-μs time domain, i.e., after the primary process in eq 13, can be related to the loss of CO by the primary product, eqs 14 and 15. Since flash photolysis experiments demonstrated that

$$ClRe(CO)_3(4\text{-}Phpy)^+ \xrightarrow[CH_3CN]{} ClRe(CO)_2(CH_3CN)(4\text{-}Phpy)^+ + CO \quad (14)$$

$$ClRe(CO)_2(CH_3CN)(4\text{-}Phpy)^+ \xrightarrow[CH_3CN]{} ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)^+ + CO \quad (15)$$

the overall process is kinetically of a first order, $k = 1.1 \times 10^4$ s^{-1}, restrictions must be imposed on the respective rates of these reactions, eqs 14 and 15. For example, one of them must be the rate-determining step or their corresponding rate constants must be nearly equal, i.e., less than 10% difference between rate constants. It can be also argued that the loss of CO is followed by a dimerization reaction, eq 16, in order to produce an intermediate,

$$2ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)^+ \rightarrow [ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2^{2+} \quad (16)$$

$[ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2^{2+}$, with a composition close to that in the final product, $[ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2$. Ligand lability in these formally d^5 complexes (larger than in formally d^6 metal ion complexes of Re(I)) and the tendency of Re(II) to form dimers must synergetically provide the required driving force for the sequential substitution and dimerization in eqs 14–16. The first second-order reaction followed by means of the spectral changes at times longer than 0.1 s, i.e., $k/\epsilon = 2.8$ cm s^{-1} at 430 nm, can be associated with the dimerization described in eq 16. The conversion of $[ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2^{2+}$ to the final product requires the addition of two electrons. Our observations on the kinetics of the optical changes at times longer than 0.1 s show that more than one reaction is involved in the reduction of the complex, and a minimal representation of the process is given in eqs 17 and 18, where Red is one the pyridine anion radical, $Phpy^{\bullet-}$ in eq 13, or its dimerization product.[51–53]

$$[ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2^{2+} \xrightarrow[Red]{} [ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2^{+} \quad (17)$$

$$[ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2^{+} \xrightarrow[Red]{} [ClRe(CO)(CH_3CN)_2(4\text{-}Phpy)]_2 \quad (18)$$

Primary Processes and Excited States. The most evident difference between the order of the electronic levels in the 4-phenylpyridine complex and those in the respective 4-cyanopyridine and pyridine complexes of Re(I) is the smaller energy gap between occupied and empty ligand-centered orbitals in the former compound, Figure 9. Such a particular distribution of molecular orbitals in $fac\text{-}ClRe(CO)_3(4\text{-}Phpy)_2$ is indicative of the close vicinage of ligand-centered, $\pi\pi^*$, and $MLCT_{[Re\rightarrow Phpy]}$ states. Although a shoulder in the absorption spectrum ($\lambda \sim 300$ nm) has been assigned to a Re → Phpy transition, at least one additional shoulder is present at longer wavelengths ($\lambda \sim 330$ nm), a position that is conspicuously near the maximum of the excitation spectrum. The energy gap for the two highest occupied orbitals centered in the Re suggests that two Re → Phpy electronic transitions could be almost 33 kJ apart, a value in agreement with a 38-kJ separation of the spectral features. Therefore, a charge-transfer transition to the $^1MLCT_{[(79,80)Re\rightarrow Phpy]}$ states must be responsible for the 330-nm shoulder in the spectrum of the $fac\text{-}ClRe(CO)_3(4\text{-}Phpy)_2$ and the population of the $^3MLCT_{[(79,80)Re\rightarrow Phpy]}$ state associated with the emission.[54] This $^3MLCT_{[(79,80)Re\rightarrow Phpy]}$ state appears to be less efficiently populated, according to the excitation spectrum, when photonic energies approach those of the second charge-transfer transition at 303 nm, i.e., a transition to the $^1MLCT_{[(83,84)Re\rightarrow Phpy]}$, and a $\pi\pi^*$ ligand-centered state at 289 nm. Since the action spectrum for the intermediate I, eqs 10 and 11, reaches a maximum at ca. 300 nm, there must be an efficient conversion of the $^1MLCT_{[(83,84)Re\rightarrow Phpy]}$ and/or $\pi\pi^*$ states to I. It must be noted in the action spectra, Figure 8, that threshold energies, E_{th}, for the photodissociation of the 4-phenylpyridine complex, eq 13, and the generation of the intermediate *I*, eqs 10 and 11, have very close values, namely, $E_{th} = 330$ kJ/mol and $E_{th} = 340$ kJ/mol, for the respective photoprocesses. In addition, the quantum yield for photodissociation remains lower than the quantum yield of I on a broad range of photonic energies, and the demise of the intermediate photogeneration is required, i.e., at $\lambda < 260$ nm, before the onset of the former process. An electronic transition to a ligand-centered $\pi\pi^*$ state, $E_{max} = 449$ kJ/mol, accounts for the absorption band at 260 nm in the spectrum of the complex and is very close to a similar transition in the free ligand.[48]

The increase of the photodissociation quantum yield at wavelengths shorter than 250 nm can be related to the population of several excited states with a strong Re to CO and/or Re → Phpy charge-transfer character. Indeed, our MO calculations place two other MLCT states, $E_{max} > 470$ kJ/mol, at the onset of the photodissociation.

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Registry No. II, 136881-98-6; TEOA, 102-71-6; $fac\text{-}ClRe(CO)_3(4\text{-}Phpy)_2$, 70805-99-1; $fac\text{-}ClRe(CO)_3(4\text{-}CNpy)_2$, 70806-03-0; Cl^-, 16887-00-6; CO, 630-08-0; $ClRe(CO)_3(4\text{-}Phpy)_2^-$, 136881-99-7; $Cu^{II}(TIM)^{2+}$, 71170-97-3.

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