

Ground and Excited State Electron Transfer Processes Involving *fac*-Tricarbonylchloro(1,10-phenanthroline)-rhenium(I). Electrogenenerated Chemiluminescence and Electron Transfer Quenching of the Lowest Excited State

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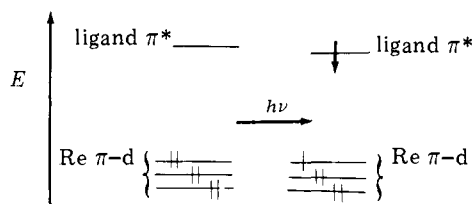
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Abstract: Electron transfer processes of the ground and excited state of *fac*-ClRe(CO)₃L (L = 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline) have been studied at 298 K in CH₃CN solution containing 0.1 M (*n*-Bu₄N)ClO₄. Cyclic voltammetry reveals nearly reversible oxidation and reduction waves at $\sim +1.3$ and ~ -1.3 V vs. an aqueous SCE for both complexes using a Pt electrode. Electrogenenerated chemiluminescence is detectable if the Pt electrode is cycled from $+1.3$ to -1.3 V vs. SCE in a potential step fashion. The electrogenerated luminescence is identical in spectra distribution with that generated by optical excitation of *fac*-ClRe(CO)₃L in the same medium. The low-lying emissive state (Re \rightarrow LCT in absorption) of *fac*-ClRe(CO)₃L is quenchable with electron acceptors. The *N,N'*-dibenzyl-4,4'-bipyridinium and *N,N'*-dimethyl-4,4'-bipyridinium dications quench the excited *fac*-ClRe(CO)₃L complexes at essentially diffusion-controlled rates, but in continuous 436-nm irradiation experiments there is little net chemical reaction. Flash photolysis reveals transient radical cations which back react at an essentially diffusion-controlled rate with [*fac*-ClRe(CO)₃L]⁺. Electron donors can also quench the excited state without net chemical change. Quenching rate constants for a number of electron donors and acceptors are correlated with their $E_{1/2}$ values and the excited state potentials for the *fac*-ClRe(CO)₃L species. The excited species is found to be ~ 2.3 V more oxidizing and reducing than the ground state.

Organometallic molecules have been little studied with respect to bimolecular excited state processes. Many organometallics, and metal carbonyls in particular,^{3,4} undergo very rapid excited-state decay via dissociative type processes which lead to coordinatively unsaturated ground-state intermediates. Such rapid decay precludes efficient bimolecular quenching processes. However, during the last several years it has been determined that organometallics having lowest metal to ligand charge transfer (MLCT) excited states are relatively photo-substitution inert. A number of complexes having lowest MLCT excited states are now known to be luminescent, including W(CO)₅L,⁵ *fac*-XRe(CO)₃L⁶ and *fac*-XRe(CO)₃L₂,⁷ M(CO)₄L,⁸ and *cis*-M(CO)₄L₂⁸ and ML'₆⁹ (L = certain substituted pyridines or 1,10-phenanthroline and related ligands; L' = aryl isocyanide; M = Cr, Mo, or W). Indeed, there are now examples of organometallics which luminesce in room temperature, fluid solution: ML'₆⁹ and *fac*-XRe(CO)₃L⁶ and *fac*-XRe(CO)₃L₂.⁷ The observation of emission reveals that the excited state persists in solution for a period long enough to undergo measurable radiative decay, and this can be generally regarded as an indicator that the lifetime is long enough to allow bimolecular processes to occur with significant efficiency. Some preliminary studies in this connection have already been reported for ML'₆.⁹ And though [Ru(2,2'-bpy)₃]²⁺ and related substances do not meet the strict condition of being organometallics, there has developed a fairly rich literature on their bimolecular excited state processes including energy transfer,^{10,11} proton transfer,^{12,13} and electron transfer.¹⁴⁻²⁰

In this paper we report our findings on the ground- and excited-state charge transfer processes in *fac*-ClRe(CO)₃L (L = 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline). The lowest excited state is Re \rightarrow LCT in absorption and the complexes are emissive in fluid solution at room temperature.⁶ Previously, it has been shown that the excited *fac*-ClRe(CO)₃L complexes are capable of being effectively quenched by triplet quenchers, and quenching by *trans*-stilbene revealed that excitation of the *fac*-ClRe(CO)₃L results in the production of a lowest excited state which can produce the stilbene triplet state with $\sim 100\%$ efficiency.⁶ The *fac*-ClRe(CO)₃(1,10-phenanthroline) in dimethoxyethane solvent has been shown

Scheme I



to be reducible at a dropping Hg electrode with $E_{1/2} \approx -1.2$ V vs. SCE.²¹

With reference to Scheme I, it is readily appreciated that the electronic excited species is simultaneously a more powerful reductant and a more powerful oxidant than the ground-state species. The aim of the present work is to characterize the ground- and excited-state potentials and establish electron transfer as a viable excited-state reaction for *fac*-ClRe(CO)₃L species.

Results and Discussion

A. Quenching by *N,N'*-Dimethyl-4,4'-bipyridinium (MV²⁺) and *N,N'*-Dibenzyl-4,4'-bipyridinium (BV²⁺). Direct Detection of Transients by Flash Photolysis. Initial results concern the quenching activity of MV²⁺ with respect to deactivation of the *fac*-ClRe(CO)₃L excited state. In fact, both MV²⁺ and BV²⁺ quench the excited state, and a linear Stern-Volmer plot²² obtains (Figure 1). The quenching was carried out in degassed CH₃CN solutions of 0.1 M (*n*-Bu₄N)ClO₄ where the lifetime, τ , of *fac*-ClRe(CO)₃L in the absence of quencher was determined to be 0.50×10^{-6} and 0.45×10^{-6} s for L = 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline, respectively. Thus, from the slope ($k_q\tau$) of the Stern-Volmer plot we determine a bimolecular quenching constant, k_q , of $\sim 3 \times 10^9$; quenching by MV²⁺ or BV²⁺ is roughly diffusion controlled.

Since the MV²⁺ triplet energy (~ 71.5 kcal/mol)²³ is above the available excitation energy from the *fac*-ClRe(CO)₃L (~ 50 – 53 kcal/mol),⁶ electronic energy transfer is likely not²² the mechanism of MV²⁺ quenching. To gain positive evidence

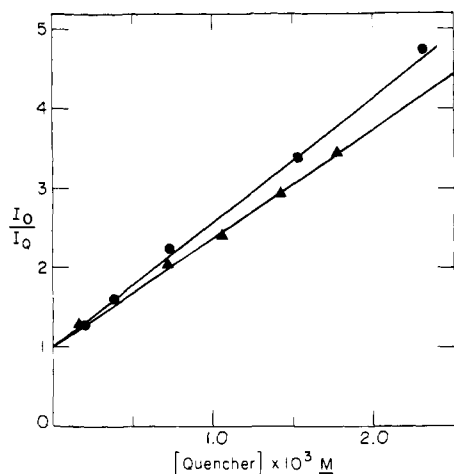
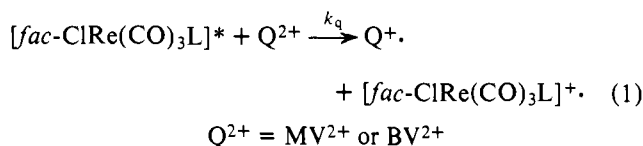


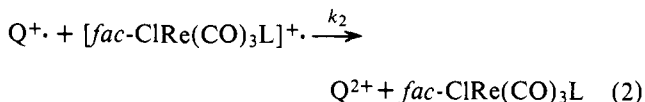
Figure 1. Stern-Volmer plots for quenching of *fac*-ClRe(CO)₃-(1,10-phenanthroline) by *N,N'*-dimethyl-4,4'-bipyridinium (●) and *N,N'*-dibenzyl-4,4'-bipyridinium (▲) both as the PF₆⁻ salts. Quenching is in CH₃CN solution of 0.1 M (*n*-Bu₄N)ClO₄ at 298 K. Excitation wavelength for the emission is 420 nm.

that the quenching corresponds to the reaction



we carried out a flash photolysis study aimed at the detection of MV⁺ and BV⁺, which are the result of electron transfer quenching. These substances are intensely colored with absorption maxima in the vicinity of 600 nm.²⁴ Such species must be transients, since continuous, prolonged 436-nm irradiation of *fac*-ClRe(CO)₃L, where the emission is totally quenched by Q²⁺, leads to no net chemical change ($\Phi_{436nm} \ll 10^{-4}$).

Since excited [Ru(2,2'-bpy)₃]²⁺ is known to be able to reduce both MV²⁺ and BV²⁺, we have compared the transient (MV⁺ or BV⁺) absorption from flash photolysis of *fac*-ClRe(CO)₃L and the Ru system. The point by point, low-resolution spectra for the four systems are shown in Figure 2. Transient spectra for MV⁺ and BV⁺ are in accord with literature data.²⁴ For our Re system we have been unable to directly observe any transient absorption due to the [fac-ClRe(CO)₃L]⁺. The transient absorptions in the vicinity of 600 nm bleach on the time scale of a few milliseconds, and well-degassed solutions can be flashed a number of times without obvious deterioration of the sample. These facts, along with the absence of net photochemistry upon continuous excitation of *fac*-ClRe(CO)₃L, suggest that the reaction



the thermal back electron transfer, occurs efficiently and with a large rate constant k_2 . From the decay of the transient absorption and the reported absorptivity for MV⁺ or BV⁺, we have determined that k_2 is essentially diffusion controlled, as in the [Ru(2,2'-bpy)₃]^{3+/2+} system.

B. Correlation of Quenching Rate and Ease of Reduction of Quencher. Whether quenching by reaction 1 occurs at a fast rate depends on the reducing power of the excited complex with respect to the Q²⁺/Q⁺ couple. Thus, the more easily reduced quenchers should quench at or near the diffusion limit, and as the quencher becomes more difficult to reduce, the rate should fall off and/or other quenching mechanisms may become important. Table I shows a set of quenchers and their associ-

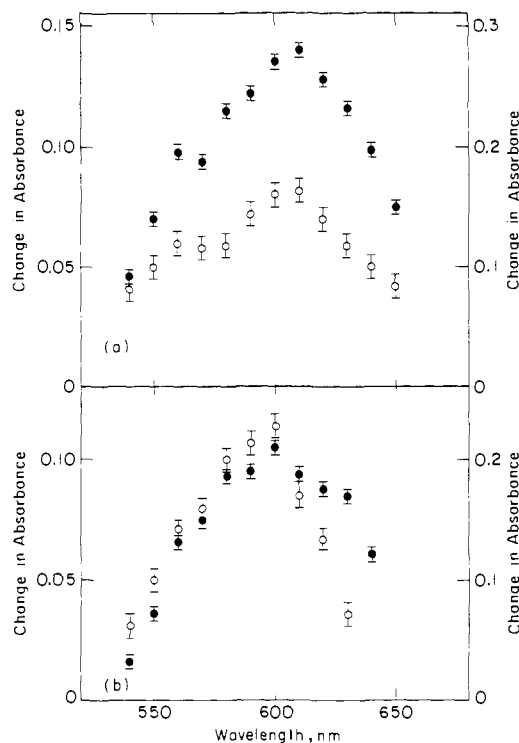


Figure 2. Point by point transient absorption spectra following flash excitation of a 0.1 M (*n*-Bu₄N)ClO₄ CH₃CN solution containing *fac*-ClRe(CO)₃(1,10-phenanthroline) (○ and left scale) and [Ru(2,2'-bpy)₃]²⁺ (● and right scale) in the presence of *N,N'*-dimethyl-4,4'-bipyridinium (a) and *N,N'*-dibenzyl-4,4'-bipyridinium (b) both at $\sim 10^{-3}$ M as the PF₆⁻ salt.

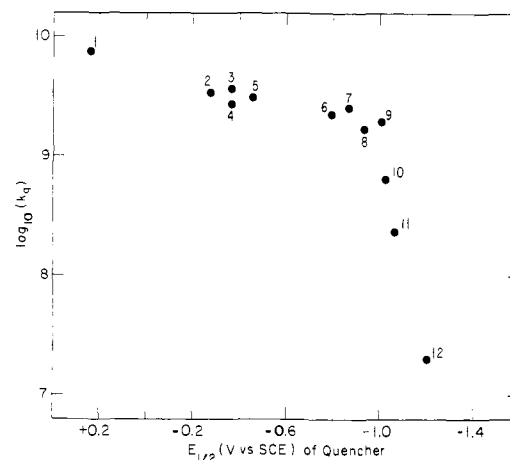
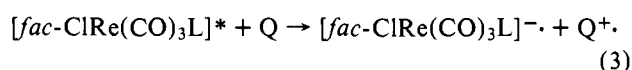


Figure 3. Correlation of quenching rate constant and ease of reduction of quencher. Data are for quenching of excited *fac*-ClRe(CO)₃(1,10-phenanthroline) and are listed in Table I which identifies the quenchers.

ated k_q values determined from Stern-Volmer plots; a plot of $\log(k_q)$ against the $E_{1/2}$ values for the quenchers is given in Figure 3. There is a clear fall-off in quenching rate at $E_{1/2} \approx -1.1$ V vs. SCE.

C. Correlation of Quenching Rate and Ease of Oxidation of Quencher. Since an excited species can be both a more powerful oxidant and reductant than the ground state, we have also considered the possibility of electron transfer quenching according to the equation



A series of quenchers of varying reducing power was studied,

Table I. Electron Transfer Quenchers of Excited *fac*-ClRe(CO)₃L^a

quencher (number) ^b	L ^c	E _{1/2} , V vs. SCE ^d	k _q , L mol ⁻¹ s ⁻¹ ^e
A. Electron Acceptors (cf. Figure 3)			
tetracyanoethylene (1)	A	+0.24	7.43 × 10 ⁹
1,1'-propylene-1,10-phenanthroline hexafluorophosphate (2)	A	-0.27	3.29 × 10 ⁹
1,1'-ethylene-2,2'-bipyridinium hexafluorophosphate (3)	A	-0.36	3.62 × 10 ⁹
<i>N,N'</i> -dibenzyl-4,4'-bipyridinium hexafluorophosphate (4)	A	-0.36	2.67 × 10 ⁹
<i>N,N'</i> -dimethyl-4,4'-bipyridinium hexafluorophosphate (5)	B		3.28 × 10 ⁹
	A	-0.45	3.08 × 10 ⁹
<i>N</i> -methyl-4-cyanopyridinium hexafluorophosphate (6)	B		3.53 × 10 ⁹
	A	-0.45	3.08 × 10 ⁹
<i>p</i> -nitrobenzaldehyde (7)	A	-0.79	2.25 × 10 ⁹
<i>N</i> -methyl-4-carbomethoxy-pyridinium hexafluorophosphate (8)	A	-0.86	2.58 × 10 ⁹
4,4'-dinitrophenyl (9)	A	-0.93	1.70 × 10 ⁹
<i>m</i> -nitrobenzaldehyde (10)	A	-1.00	1.94 × 10 ⁹
4-chloronitrobenzene (11)	A	-1.02	6.4 × 10 ⁸
4-methylnitrobenzene (12)	A	-1.06	2.4 × 10 ⁸
	A	-1.20	<2 × 10 ⁷
B. Electron Donors (cf. Figure 4)			
<i>N,N,N',N'</i> -tetramethyl- <i>p</i> -phenylenediamine (13)	A	+0.24	5.67 × 10 ⁹
	B		8.72 × 10 ⁹
<i>N,N'</i> -diphenyl- <i>p</i> -phenylenediamine (14)	A	+0.35	3.73 × 10 ⁹
<i>N,N</i> -dimethyl- <i>p</i> -toluidine (15)	A	+0.65	2.09 × 10 ⁹
	B		3.91 × 10 ⁹
10-methylphenothiazine (16)	A	+0.83	1.7 × 10 ⁹
<i>N,N</i> -dimethylaniline (17)	A	+0.78	9.8 × 10 ⁸
diphenylamine (18)	A	+0.83	4.0 × 10 ⁸
triphenylamine (19)	A	+0.86	3.3 × 10 ⁸
aniline (20)	A	+0.98	5.8 × 10 ⁷
	B		2.0 × 10 ⁸
<i>p</i> -bromoaniline (21)	A	+0.97	5.4 × 10 ⁷
<i>N,N</i> -dimethylbenzylamine (22)	A	+1.01	<2 × 10 ⁶
<i>p</i> -dimethoxybenzene (23)	A	+1.34	<2 × 10 ⁶
	B		<2 × 10 ⁶

^a Measurements in degassed CH₃CN solutions of 0.1 M (*n*-Bu₄N)ClO₄ at 298 K. ^b These numbers identify the quenchers in Figures 3 and 4. ^c A ≡ 1,10-phenanthroline; B ≡ 4,7-diphenyl-1,10-phenanthroline. ^d The redox potentials of the quenchers are taken from the following sources: (1) ref 28; (2) E. Steckhan and T. Kuwana, *Ber. Bunsenges. Phys. Chem.*, **78**, 253 (1974); (3) ref 30; (4) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970; (5) N. L. Weinberg, Ed., "Techniques of Chemistry", Vol. 5, Part 2, Wiley, New York, N.Y., 1975; (6) P. A. Kohl and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 7531 (1977). ^e Bimolecular quenching constant (±10%) from slope of Stern-Volmer plots.

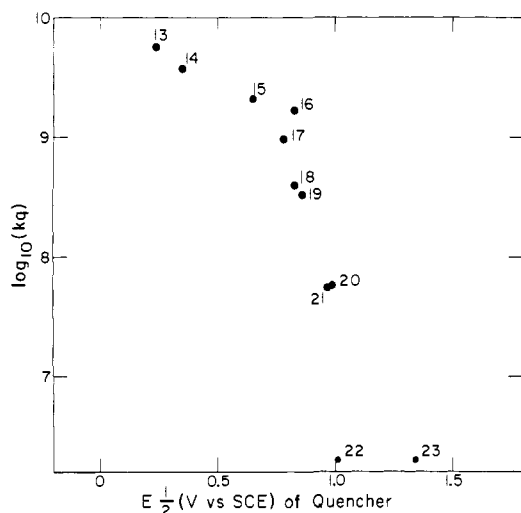


Figure 4. Correlation of quenching rate constant and ease of oxidation of quencher. Data are for quenching of excited *fac*-ClRe(CO)₃(1,10-phenanthroline) and are listed in Table I which identifies the quenchers.

and a plot of log (*k_q*) against the *E*_{1/2} values is given in Figure 4. Quenching becomes slow for *E*_{1/2} more positive than ~+1.0 V vs. SCE. The data are included in Table I. Prolonged 436-nm irradiation of *fac*-ClRe(CO)₃L in the presence of sufficient concentrations of either *N,N,N',N'*-tetramethyl-*p*-phenyl-

enediamine or *N,N*-dimethyl-*p*-toluidine to quench all of the emission resulted in no infrared-detectable net chemical change ($\Phi_{436\text{nm}} \ll 10^{-4}$). This suggests that the back electron transfer reaction is fast and completely efficient.

D. Cyclic Voltammetry for *fac*-ClRe(CO)₃L. The fact that we observe photoinduced electron transfer from *fac*-ClRe(CO)₃L suggests that there are long-lived, one-electron electron-transfer, ground-state products. That the resulting species persist for some time is evidenced by the lack of net chemical change upon continuous irradiation of *fac*-ClRe(CO)₃L in the presence of good electron transfer quenchers. Consequently, we set out to characterize some of the electrochemical properties of the Re complexes by cyclic voltammetry.

Cyclic voltammetry of *fac*-ClRe(CO)₃L has been carried out in the same electrolyte/solvent system as in the quenching and flash photolysis studies. The complex exhibits both an oxidation and a reduction wave which are nearly reversible, Figures 5-7. The two waves are at ~+1.3 and ~-1.3 V vs. aqueous SCE, Table II. Integration of the peak corresponding to the oxidation of the *fac*-ClRe(CO)₃L shows it to have nearly the same area (and peak current) as the peak corresponding to the reduction of the complex. Further, cyclic voltammetry of ferrocene at the same concentration as the *fac*-ClRe(CO)₃L in the electrolyte solution gives an oxidation wave of nearly equal area (and peak current) as found for the *fac*-ClRe(CO)₃L. Assuming that the diffusion coefficient of ferrocene and *fac*-ClRe(CO)₃L are the same, and knowing that the oxidation of ferrocene is a one-electron process,²⁵ we can

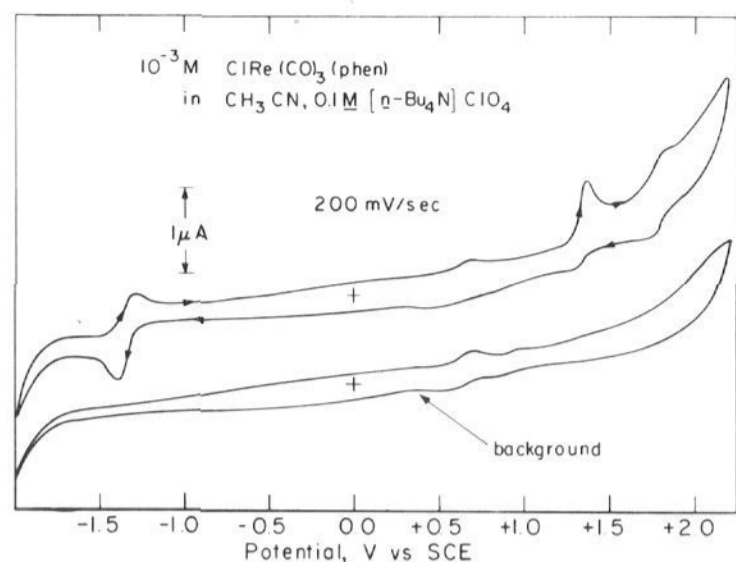


Figure 5. Cyclic voltammetric scans for *fac*-ClRe(CO)₃(1,10-phenanthroline) in solution at 298 K under Ar.

Table II. Electrochemical Data for Ground and Excited State of *fac*-ClRe(CO)₃L^a (cf. Scheme II)

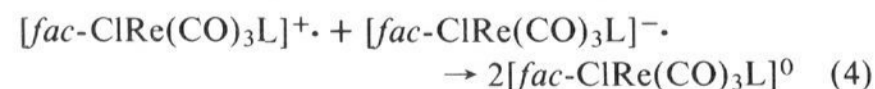
redox couple	L ^b	E ⁰ , V vs. SCE
[<i>fac</i> -ClRe(CO) ₃ L] ⁰ /[<i>fac</i> -ClRe(CO) ₃ L] ^{-•}	A	-1.34
[<i>fac</i> -ClRe(CO) ₃ L] ^{-•} /[<i>fac</i> -ClRe(CO) ₃ L] ⁰	B	-1.30
[<i>fac</i> -ClRe(CO) ₃ L] ^{+•} /[<i>fac</i> -ClRe(CO) ₃ L] ⁰	A	+1.33
[<i>fac</i> -ClRe(CO) ₃ L] ⁰ /[<i>fac</i> -ClRe(CO) ₃ L] ^{+•}	B	+1.32
[<i>fac</i> -ClRe(CO) ₃ L] ^{+•} /[<i>fac</i> -ClRe(CO) ₃ L] ⁰	A	-1.1; ^c -1.0 ^d
[<i>fac</i> -ClRe(CO) ₃ L] ⁰ /[<i>fac</i> -ClRe(CO) ₃ L] ^{+•}	B	-1.0 ^d
[<i>fac</i> -ClRe(CO) ₃ L] ^{*•} /[<i>fac</i> -ClRe(CO) ₃ L] ^{-•}	A	+1.0; ^e +1.0 ^d
[<i>fac</i> -ClRe(CO) ₃ L] ^{-•} /[<i>fac</i> -ClRe(CO) ₃ L] ^{*•}	B	+1.0 ^d

^a All measurements were made in 0.1 M (*n*-Bu₄N)ClO₄, CH₃CN solution at 298 °C. ^b A ≡ 1,10-phenanthroline; B ≡ 4,7-diphenyl-1,10-phenanthroline. ^c Approximated from Figure 3. ^d Approximated from E⁰'s of ground state and an excited-state energy of ~2.3 eV. ^e Approximated from Figure 4.

conclude that the waves at -1.3 and +1.3 V vs. SCE correspond to one-electron processes.

The oxidation and reduction of *fac*-ClRe(CO)₃L is only partially reversible, as evidenced by the lack of return peaks at slow cyclic scan rates. Even at the very high scan rates the return wave is not exactly equal in area to the oxidation or reduction wave for *fac*-ClRe(CO)₃L. Since a return peak is seen at slower scan rates for the reduction than for the oxidation of *fac*-ClRe(CO)₃L, the one-electron reduced species is longer lived than the one-electron oxidized species. Further studies of the kinetics of the decomposition of the radical anion and cation of the complex are underway; from the present work we have established that the electrochemical oxidation and reduction at Pt are at least partially reversible one-electron transfer processes.

E. Electrogenerated Chemiluminescence for *fac*-ClRe(CO)₃L. An additional fact that we obtain from the cyclic voltammetry is that the E⁰'s for [*fac*-ClRe(CO)₃L]⁰/[*fac*-ClRe(CO)₃L]^{-•} and [*fac*-ClRe(CO)₃L]^{+•}/[*fac*-ClRe(CO)₃L]⁰ differ by ~2.6 V. Consequently, the reaction



involves the release of energy to an extent that one of the neutral product complexes may be electronically excited. This follows from the fact that the emission maximum from *fac*-ClRe(CO)₃L is observed at ~2.0 eV in the electrolyte solution.⁶

Using procedures outlined by Faulkner and Bard,²⁶ we have determined that electrogenerated chemiluminescence is possible for the *fac*-ClRe(CO)₃L systems. Cyclic stepping of the

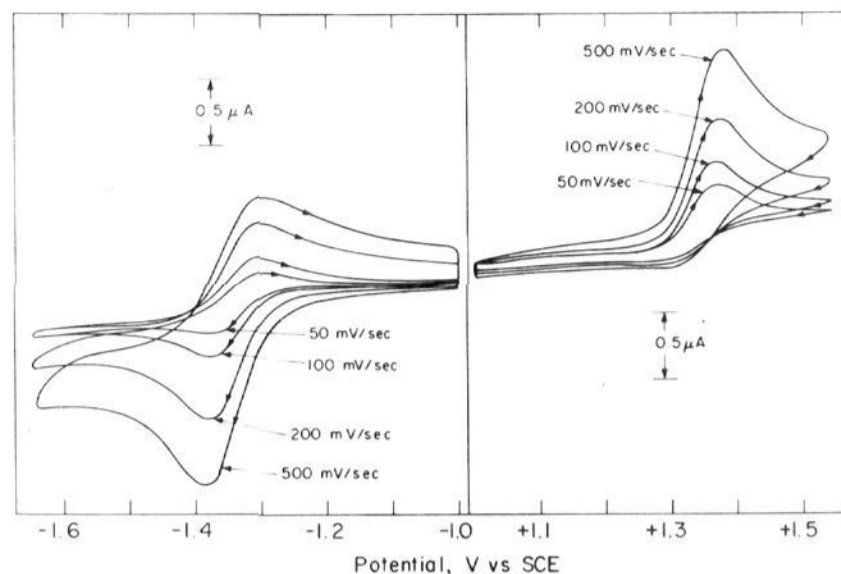


Figure 6. Cyclic voltammetric waves as a function of scan rate for reduction (left portion) and oxidation (right portion) of *fac*-ClRe(CO)₃(1,10-phenanthroline). The conditions are as in Figure 5. Note that even at 500 mV/s the oxidation is not reversible; cf. Figure 7.

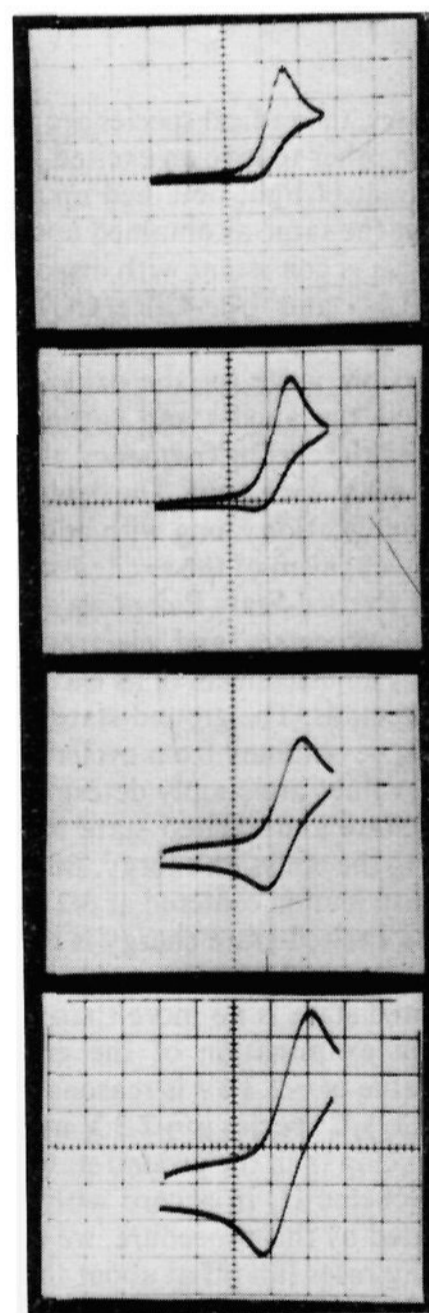


Figure 7. Cyclic voltammetric scans for the oxidation of *fac*-ClRe(CO)₃(1,10-phenanthroline) as a function of scan rate; from the top, 1.0, 2.0, 20.0, and 50.0 V/s. Conditions are as in Figure 5 except that the data are displayed on an oscilloscope. The scans all begin at +1.0 V vs. SCE and the anodic limit at the right is +1.6 V vs. SCE.

potential of a Pt electrode from -1.3 to +1.3 V vs. SCE produces flashes of light in the vicinity of the electrode in the electrolyte solution containing the Re species. The spectral distribution of the electrogenerated chemiluminescence is the same as that obtained by optical excitation of *fac*-ClRe(CO)₃L in the same medium (Figures 8 and 9). Thus, even though the cyclic voltammetry reveals only partially reversible one-electron

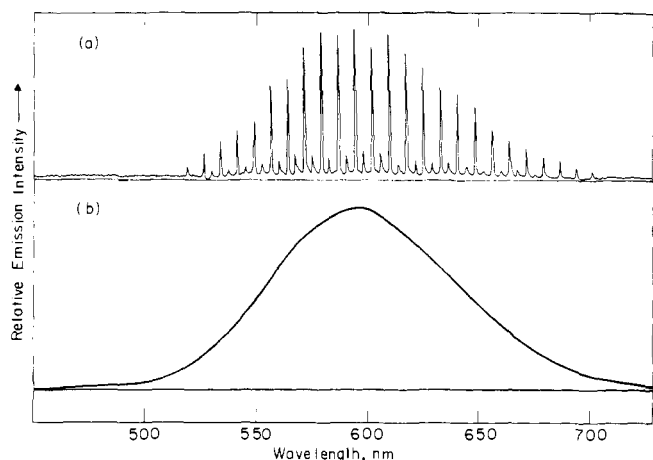


Figure 8. (a) Electrogenerated chemiluminescence from a 0.1 M (*n*-Bu₄N)ClO₄ CH₃CN solution of *fac*-ClRe(CO)₃(1,10-phenanthroline). The potential of the working Pt electrode was stepped from +1.6 to -1.6 V (vs. Ag wire) at a frequency of 0.2 Hz. (b) Optically (420 nm) excited luminescence from solution in (a).

tron redox processes, the radical species are long lived enough to react with each other to give an excited *fac*-ClRe(CO)₃L species. The amount of light obtained upon stepping to the anodic limit is not the same as obtained upon stepping to the cathodic limit. This is consistent with disparate lifetimes for [*fac*-ClRe(CO)₃L]^{-•} and [*fac*-ClRe(CO)₃L]^{+•} which are reflected in the faster scan rates in cyclic voltammetry needed to obtain a reversible wave for the oxidation. The relative amount of light at the anodic and cathodic limits can be changed by varying the cycling frequency, the potential limits, and the holding time at each limit. The details will be included in a subsequent publication along with addition information concerning the mechanism of the excited-state generation.

F. Ground- and Excited-State Potentials of *fac*-ClRe(CO)₃L.

The excited-state processes and electrochemistry of *fac*-ClRe(CO)₃L allow an assessment of its excited-state oxidation and reduction potentials. The ground-state *E*⁰'s for oxidation and reduction can be obtained from cyclic voltammetry, and the excited-state values are simply determined by assuming that the ground state and excited state have a free-energy difference equal to the emission energy. But the emission has a large spectral distribution centered at ~2.0 eV and an exact assignment of the excited-state energy is not possible. From the fact that we observe electrogenerated luminescence, we can say that the excited state is no more than 2.6 eV above the ground state. An examination of the emission spectrum suggests that a value of ~2.3 eV is reasonable. Thus, the excited *fac*-ClRe(CO)₃L species is ~2.3 V more oxidizing and ~2.3 V more reducing than the ground state. The situation is summarized in Scheme II. In accord with the excited-state potentials estimated by this procedure, we note that electron transfer quenching rates fall off at about the *E*_{1/2} values expected (Figures 3 and 4). Table II includes the excited-state potentials estimated from the quenching data and from the emission energy.

Summary

The first excited-state electron transfer studies of metal carbonyl complexes have been carried out using excited *fac*-ClRe(CO)₃L (L = 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline). The lowest lying excited state is quenchable at fast rates by reductants having *E*_{1/2} more negative than ~+1.0 V vs. SCE or by oxidants having *E*_{1/2} more positive than ~-1.1 V vs. SCE. Cyclic voltammetry establishes ground-state *E*⁰'s for oxidation and reduction at ~+1.3 and ~-1.3 V vs. SCE, respectively. With a lowest ex-

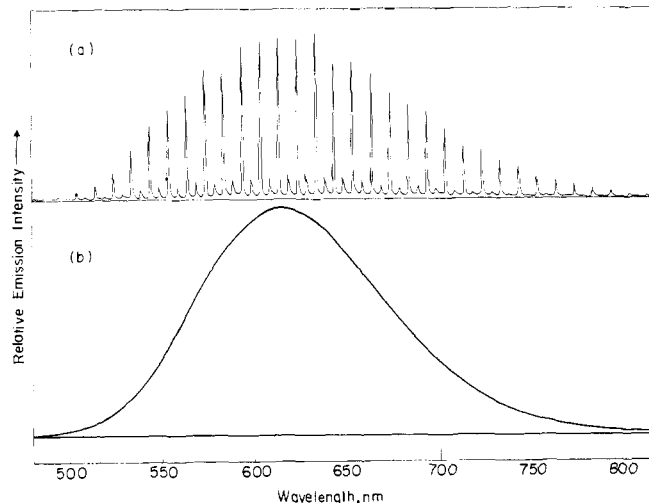
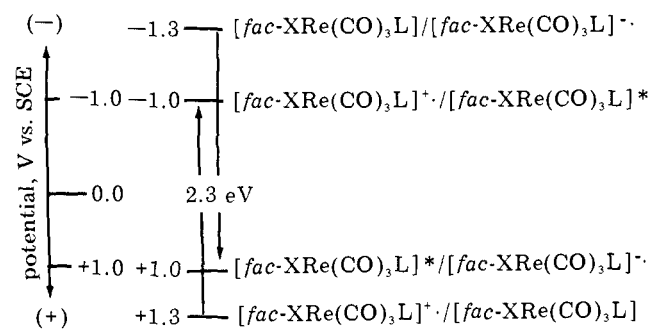


Figure 9. As in Figure 8 except for *fac*-ClRe(CO)₃(4,7-diphenyl-1,10-phenanthroline).

Scheme II



cited state energy of ~2.3 eV, the excited state is ~2.3 V more oxidizing and reducing than the ground state in accord with the dependence of electron transfer quenching rates on the *E*_{1/2} of the quenchers. Electrogenerated chemiluminescence has been observed from *fac*-ClRe(CO)₃L at a Pt electrode by cycling the electrode between the oxidation and the reduction potential in a potential step fashion. The electrogenerated chemiluminescence is produced by generation of one excited (~2.3 eV) *fac*-ClRe(CO)₃L species in the annihilation reaction of the ground-state radical anion and cation which has an exoergicity of ~2.6 eV.

Experimental Section

Instruments. UV-vis spectra were recorded using a Cary 17 spectrophotometer; infrared spectra were recorded using a Perkin-Elmer 180 spectrometer; kinetic flash experiments were carried out using a Xenon Corp. 710 apparatus; emission spectra for Stern-Volmer plots were recorded using an Aminco-Bowman SPF or Perkin-Elmer MPF 44; and the emission lifetimes were determined using an apparatus previously described.²⁷ Cyclic voltammetry and electrogenerated luminescence experiments were carried out using a PAR 173 potentiostat with a 175 Universal Programmer.

Chemicals. *fac*-ClRe(CO)₃L (L = 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline) complexes were prepared according to the literature procedure.⁶ Re(CO)₅Cl (Pressure Chemical Co.) and an excess of L (Aldrich Chemical Co.) were dissolved in spectroquality isooctane (Matheson Coleman and Bell) and heated to ~60 °C; *fac*-Re(CO)₃L precipitates from solution as a yellow solid as it forms; separation by filtration and washing with the spectroquality isooctane removes any unreacted Re(CO)₅Cl and the excess L. Final purification is by addition of isooctane to a concentrated CH₂Cl₂ solution of *fac*-Re(CO)₃L to precipitate the solid. Collection by filtration and washing with isooctane yields a pure yellow solid free (spectrally by

IR and UV-vis) of $\text{Re}(\text{CO})_5\text{Cl}$ and L. Infrared bands (CH₂Cl₂, 298 °C) in the CO stretching region are characteristic: L = 1,10-phenanthroline, 2023 (s), 1916 (m), and 1899 cm⁻¹ (m); L = 4,7-diphenyl-1,10-phenanthroline, 2022 (s), 1916 (m), and 1898 cm⁻¹ (m).

CH₃CN was fresh, dry, spectroquality grade obtained commercially from Eastman Chemical Co. The (*n*-Bu₄N)ClO₄ used was prepared by precipitation from reaction of (*n*-Bu₄N)Br (Pfaltz and Bauer Co.) with NaClO₄ (Fisher) in H₂O. The (*n*-Bu₄N)ClO₄ was then recrystallized from CH₃OH/H₂O, washed with anhydrous (C₂H₅)₂O, and dried in an oven at 80 °C for at least 24 h prior to use.

All *N*-alkylpyridinium derivatives used as quenchers were prepared according to literature methods: *N,N'*-dimethyl-4,4'-bipyridinium dications (MV²⁺);²⁸ *N,N'*-dibenzyl-4,4'-bipyridinium dications (BV²⁺);²⁸ *N*-methyl-4-cyanopyridinium cations;²⁸ *N*-methyl-4-carbomethoxy-pyridinium cations;²⁸ 1,1'-ethylene-2,2'-bipyridinium²⁹ dications; 1,1'-propylene-1,10-phenanthroline dications.³⁰ Typically the iodide or bromide salts after alkylation with the corresponding alkyl halides were converted to the PF₆⁻ salts by metathesis with NH₄PF₆ (Alfa Ventron), followed by recrystallization from C₂H₅OH/H₂O. All nitro compounds and other quenchers used are commercially available, and were purified by appropriate methods.²⁸

Quenching Measurements. Attenuation of 420-nm excited emission from $\sim 3 \times 10^{-4}$ M *fac*-ClRe(CO)₃L in 0.1 M (*n*-Bu₄N)ClO₄ degassed CH₃CN solution by various quenchers was carried out using the emission spectrophotometers. None of the quenchers used absorbs at 420 nm. Linear Stern-Volmer plots²² were obtained in all cases. The quenching constant, *k*_q, was obtained from the slope and emission lifetime at zero quencher concentration; $\tau = 0.50 \times 10^{-6}$ s for L = 1,10-phenanthroline and $\tau = 0.45 \times 10^{-6}$ s for L = 4,7-diphenyl-1,10-phenanthroline.

Flash Photolysis. Typically a solution containing $\sim 5 \times 10^{-4}$ M ClRe(CO)₃L and 3×10^{-3} M quencher was Ar purged for 10 min in a cylindrical Pyrex cell 10 cm long (analyzing beam path) and 1 cm in diameter (flash path) before flash. A near-UV cutoff filter was used to avoid near-UV irradiation of the quencher from the xenon lamp analyzing beam. The transient absorption signals were detected by an RCA 1P21 photomultiplier tube powered by a Kepco Model ABS 1500 power supply and recorded on a Tektronix 564B storage oscilloscope, and then photographed for permanent record. In obtaining back-reaction rate data, a He-Ne laser (633 nm) source was used as the analyzing beam. Typically, flashes were at 500 J and the flash time was ~ 20 μs, allowing observation of transients of longer life than ~ 75 μs. Infrared analysis of solutions before and after flashing showed little (<10%) reaction of the *fac*-ClRe(CO)₃L.

Cyclic Voltammetry. Cyclic voltammetric scans were either displayed on a Houston 2000 *x-y* recorder or on a Tektronix 503 oscilloscope with *x-y* inputs. The working electrode was a small Pt bead modified from a Polarographic Heyrovsky electrode obtained from Sargent Welch. A saturated calomel electrode (SCE) (Fischer) was the reference electrode and Pt gauze was the counterelectrode. All cyclics were recorded on $\sim 10^{-4}$ – 10^{-3} M *fac*-ClRe(CO)₃L in CH₃CN solutions of 0.1 M (*n*-Bu₄N)ClO₄ under Ar after purging with Ar for several minutes.

Electrogenerated Chemiluminescence. A three-electrode, two-compartment cell was used for most of the electrogenerated chemiluminescence experiments. The working Pt electrode and an Ag wire pseudoreference were in one compartment and the counterelectrode was in the other compartment. The cell was positioned in the sample compartment of the Perkin-Elmer emission spectrometer in such a way that the luminescence intensity striking the collection optics was maximized. The emission spectrum could be optically excited under the same conditions. Initial experiments to determine the appropriate potential limits, step time, and other parameters were carried out in a one-compartment cell with an SCE reference electrode. All electrogenerated chemiluminescence experiments were carried out under Ar after having Ar purge the solution.

Continuous Irradiation Experiments. Irradiation (436 nm) of *fac*-ClRe(CO)₃L was carried out in CH₃CN solutions of 0.1 M (*n*-Bu₄N)ClO₄ and 10^{-3} M MV²⁺, BV²⁺, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, or *N,N'*-dimethyl-*p*-toluidine. Samples (3.0 mL) in 13 × 100 mm test tubes were freeze-pump-thaw degassed and

hermetically sealed prior to irradiation. Irradiation was carried out in a merry-go-round.³¹ The 436-nm source was a 550- or 450-W medium-pressure Hanovia lamp filtered with Corning glass filters to isolate the 436-nm Hg emission. The light intensity was determined by ferrioxalate actinometry³² and was typically 10⁻⁷ einstein/min. Analyses of samples for *fac*-ClRe(CO)₃L disappearance was by infrared spectroscopy in the CO stretching region. No net chemical changes were detectable after prolonged irradiation.

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References and Notes

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