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Electrogenerated Chemiluminescence. 59. Rhenium Complexes

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Re(L)(CO)$_3$Cl complexes (where L is 1,10-phenanthroline, 2,2′-bipyridine, or a phenanthroline or bipyridine derivative containing methyl groups) are photoluminescent in fluid solution at room temperature. In acetonitrile solutions, these complexes display one chemically reversible one-electron reduction process and one chemically irreversible oxidation process. λ_{max} for the luminescence is dependent on the nature of L, and a linear relationship between λ_{max} and the difference in electrode potentials for oxidation and reduction is evident. Electrogenerated chemiluminescence (ECL) was observed in acetonitrile solutions of these complexes (Bu_4NPF_6 as electrolyte) by stepping the potential of a Pt disk working electrode between potentials sufficient to form the radical anionic and cationic species. The relative amount of light produced during the anodic and cathodic pulses was dependent on the potential limits and pulse duration. ECL was also generated in the presence of coreactants, i.e., with tri-*n*-propylamine upon stepping the potential sufficiently positive to form the deprotonated tri-*n*-propylamine radical and the cationic rhenium(II) species $Re^{II}(L)(CO)_3Cl^+$. When $S_2O_8^{2-}$ was present in solution, ECL was also observed for all of the complexes upon stepping to potentials sufficient to form $(Re^I(L)(CO)_3Cl)^-$ and the strong oxidant $SO_4^{\bullet-}$. In most cases, the ECL spectrum was identical to the photoluminescence spectrum, indicating that the chemical reactions following electrochemical oxidation or reduction form the same metal-to-ligand charge-transfer (MLCT) excited states that are generated in the photoluminescence experiments.

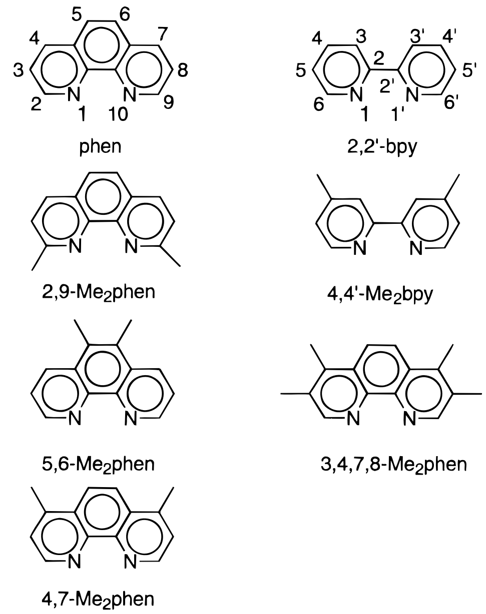

Figure 1. Schematic of the phenanthroline, bipyridine, and methyl-substituted derivatives used in this work (i.e., L in Re(L)(CO)$_3$Cl).

The photophysical properties of rhenium tricarbonyls containing bidentate polypyridyl ligands have been extensively studied.[1−14] Many exhibit strong photoluminescence in solution, suggesting they may be capable of electrogenerated chemiluminescence (ECL). These Re complexes are related to other d^6 transition metal systems such as the Os^{II} and Ru^{II} tris-diimine systems, which themselves are ECL emitting species.[15−22] These considerations and an earlier ECL study of Re phenanthroline complexes[2] prompted us to investigate the electrochemical properties of these complexes in more detail and to examine whether they can be used for the production of ECL.

Complexes of the type Re(L)(CO)$_3$Cl (where L is 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or a methyl-substituted derivative, Figure 1) were chosen for this study in part due to the similarity of Re^I and Ru^{II}. With O_h symmetry, both Re^I and Ru^{II}

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form closed-shell d^6 systems with filled t_{2g} levels. During optical excitation, an electron is promoted from the t_{2g} highest-occupied molecular orbital (HOMO) of the metal to the π^* levels of the L ligand, the lowest-unoccupied molecular orbital (LUMO). As with other transition metal complexes,[23,24] the introduction of substituents to the chromophoric ligand (L) produces changes in the emission energy, in most cases, without changing the fundamental nature of the absorbing and emitting states. The Re^I systems studied here are also of interest as analytical labels and should behave similarly to their Ru^{II} analogues, which have been used as ECL probes in immunoassays and DNA assays.[25,26]

A number of photoluminescence studies have focused on the effect of varying the nature and position of substituents on a given ligand.[4,8−12] Modification of the polypyridyl ligand (L) is a more effective means of altering excited-state behavior (i.e., state types and nonradiative decay pathways) than making changes in the spectator ligands (X, e.g., in $Re(L)(CO)_3X^{n+}$).[8,10] In this work, a series of Re^I tricarbonyl complexes was studied, where the addition of methyl substituents on the phen and bpy cores (Figure 1) allowed systematic control of the MLCT excited-state energies.

In earlier work, the ECL of $Re(phen)(CO)_3Cl$ and $Re(Ph_2phen)(CO)_3Cl$ (Ph_2phen = 4,7-diphenylphenanthroline)[2] was generated via an annihilation reaction sequence. The ECL emission spectrum was similar to that of the optical emission spectrum and was assigned to emission from the lowest energy, ^{3}MLCT, state.[2] The ECL emission maxima were different for L = phen and L = Ph_2-phen, as expected from photophysical studies.[2,6−13] To our knowledge, this has been the only report of ECL of a rhenium complex.

ECL involves the formation of electronically excited states by electron transfer between electrochemically generated species.[15−23,27] In annihilation ECL, the electron-transfer reaction is between an oxidized species and a reduced species, both of which are generated at an electrode surface by alternate pulsing of the electrode potential.[27] ECL can also be generated in a single potential step by utilizing a coreactant, a species that can form energetic oxidants or reductants upon bond cleavage.[20,28−33]

For example, in the previously studied $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system,[30] ECL is produced upon concomitant reduction of $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$:

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} \qquad (1)$$

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+} \qquad (2)$$

$$Ru(bpy)_3^{+} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + SO_4^{\bullet-} + SO_4^{2-} \qquad (3)$$

$$Ru(bpy)_3^{+} + SO_4^{\bullet-} \rightarrow Ru(bpy)_3^{2+*} + SO_4^{2-} \qquad (4)$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \qquad (5)$$

Reaction 3 is probably the main source of $SO_4^{\bullet-}$, since it is a strong oxidant and should be reduced directly at the electrode surface.[30,31] The practical interest in coreactant systems has already been discussed.[33]

In this paper, we describe the electrochemical and ECL behavior of $Re(L)(CO)_3Cl$ complexes under different experimental conditions. A discussion of ECL mechanisms is presented as well as correlations between ECL efficiency and the nature of L. This is the first report of coreactant ECL with a rhenium system.

EXPERIMENTAL SECTION

Materials. $Re(L)(CO)_3Cl$ (L = 1,10-phenanthroline; the methyl-substituted phenanthrolines 4,7-Me_2phen, 2,9-Me_2phen, 5,6-Me_2-phen, and 3,4,7,8-Me_4phen; 2,2′-bipyridine; and 4,4′-Me_2bpy, Figure 1) were available from previous studies.[4] Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6, SACHEM, Austin, TX) was recrystallized twice from 4:1 ethanol/water, dried in vacuo (110 °C), and stored in a vacuum desiccator before use. Acetonitrile (MeCN) was spectroquality (Burdick & Jackson) and was stored in a Vacuum Atmospheres glovebox under a He atmosphere. Tri-*n*-propylamine (98% Aldrich, Milwaukee, WI) was used as received. Deionized water from a Millipore Milli-Q system was used throughout. All other chemicals were reagent grade and were used without further purification.

Methods. Cyclic voltammetric experiments were performed utilizing a Bioanalytical Systems (West Lafayette, IN) Model-100A electrochemical analyzer. ECL experiments employed a Princeton Applied Research 175 universal programmer (PAR, Princeton, NJ), a Model 173 potentiostat/galvanostat, and an Omnigraphic 2000 $x-y$ recorder (Houston Instruments, Austin, TX). A Model CH120 charge-coupled device (CCD) camera (Photometrics, Phoenix, AZ) cooled to −110 °C was used to acquire ECL spectra and to obtain the ECL emission intensities used in the calculation of ECL efficiencies. The CCD camera and the configuration of the experiment have been described in detail elsewhere.[34] Solutions used to obtain ECL spectra and ECL emission intensities incorporated 1 mM rhenium complex, 10 mM $S_2O_8^{2-}$, and 0.1 M Bu_4NPF_6. Light intensities were integrated for 10 min and the solutions stirred throughout. Cyclic voltammetry coupled with photon detection used the PAR electrochemical apparatus described above in conjunction with a Hamamatsu C1230 photon counter (Bridgewater, NJ) equipped with a Hamamatsu R928-P photomultiplier tube cooled to −12 °C. The output was channeled to the y-axis of the $x-y$ recorder to afford ECL vs potential displays.

All electrochemical and ECL experiments employed a conventional three-electrode configuration. The cell was designed to fit in front of the entrance slit to the CCD spectrometer and had a total volume of 4−5 mL. A platinum disk electrode (0.2-cm diameter) was employed as the working electrode with a Pt wire as the auxiliary electrode and a silver wire as the quasi-reference electrode (AgQRE). After a series of experiments, ferrocene was added as an internal reference, and all reported potentials are

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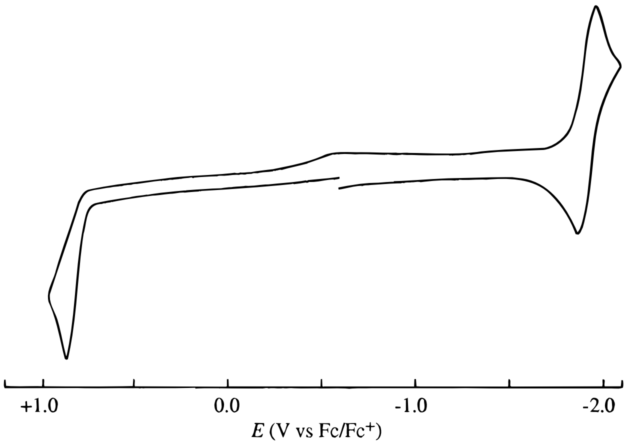

Figure 2. Cyclic voltammograms of 1 mM Re(4,4′-Me$_2$bpy)(CO)$_3$Cl in MeCN and 0.1 M Bu$_4$NPF$_6$ at room temperature; scan rate, 200 mV/s.

Table 1. Electrochemical Data for the Re(L)(CO)$_3$Cl Complexes[a]

L	oxidation (mV) E_{pa}	oxidation (mV) E_{pa}	oxidation (mV) $E_{1/2}$	reduction (mV) E_{pc}	reduction (mV) E_{pc}	reduction (mV) $E_{1/2}$
phen[b]	+980			−1710	−1774	−1742
2,9-Me$_2$phen	+1018	+946	+982	−1798	−1872	−1835
5,6-Me$_2$phen	+962			−1730	−1800	−1765
4,7-Me$_2$phen	+942			−1814	−1880	−1847
3,4,7,8-Me$_4$phen	+948				−2010	
bpy[c]	+983			−1715	−1787	−1751
4,4′-Me$_2$bpy[d]	+930			−1808	−1876	−1842

[a] All potentials were determined at room temperature in MeCN solutions (0.1 M Bu$_4$NPF$_6$) vs Fc/Fc$^+$. E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential. $E_{1/2} = (E_{pa} - E_{pc})/2$. [b] Previously reported in ref 2 in MeCN/Bu$_4$NBF$_4$ vs SCE. [c] Previously reported in ref 36 in MeCN/Bu$_4$NBF$_4$ vs SCE. [d] Previously reported in ref 3 in MeCN/Bu$_4$NBF$_4$ vs SCE.

referenced to the Fc/Fc$^+$ couple. All experiments were carried out in MeCN solutions containing 0.1 M Bu$_4$NPF$_6$. All solutions for ECL intensity measurements were prepared in a drybox under a He atmosphere. Others were prepared in air, purged with Ar for several minutes, and then sealed in an air-tight cell. Before each ECL experiment, a cyclic voltammogram was recorded to establish the exact position of the redox processes vs the quasi-reference electrode.

Absorption spectra were recorded with an Aminco Bowman/Milton Roy Spectronic 3000 array spectrophotometer. Luminescence spectra were measured using an SLM Aminco SPF-500 spectrofluorometer. Relative luminescence quantum yields, ϕ_R, were measured in deaerated (Ar bubbled for 20 min) MeCN solutions at room temperature using the following relationship:[35]

$$\phi_R = \phi_{ref}(I_{sample}A_{ref}/I_{ref}A_{sample})$$

where I is the area under the emission spectrum and A is the absorbance for sample and reference obtained under the same experimental conditions with Ru(bpy)$_3^{2+}$ as the standard, $\phi_{ref} = 0.0682$.[35]

RESULTS AND DISCUSSION

Electrochemistry. Cyclic voltammograms of all the rhenium carbonyl complexes in MeCN/0.1 M Bu$_4$NPF$_6$ showed one reversible reduction wave with half-wave potentials in the range $-1.74 \leq E_{1/2} \leq -1.85$ V ($E_{1/2} = (E_{pa} + E_{pc})/2$). This wave is assigned to reduction of the polypyridyl ligands, L^0/L$^-$.[2,3,10−13]

$$\mathrm{Re^I(L)(CO)_3Cl + e^- \rightarrow Re^I(L^-)(CO)_3Cl^-} \qquad (6)$$

Typical cyclic voltammograms for the Re(L)(CO)$_3$Cl complexes at a Pt disk electrode are shown in Figure 2, and potentials are listed in Table 1. The reduction potentials varied according to the position of the Me groups on the phen and bpy cores. For example, the 4,4′-Me$_2$bpy species ($E_{1/2} = -1.84$ V) lies at more negative potentials than the bpy analogue ($E_{1/2} = -1.75$ V). If the potential is swept more negative, other reductions are seen prior to reduction of MeCN (~-2.8 V). Similar waves have been reported for Re(L)(CO)$_3$py$^+$ systems (py = pyridine) and can probably be attributed to reduction of the metal center, Re$^{I/0}$.[10]

The Re(L)(CO)$_3$Cl systems also display one chemically irreversible oxidation wave at low scan rates (e.g., 200 mV/s) whose potential is dependent upon the nature of the ligand ($E_{pa} = +0.93$ to $+1.02$ V), Table 1. This oxidation has been assigned to the Re$^{I/II}$ redox couple.[1−3,10−13]

$$\mathrm{Re^I(L)(CO)_3Cl - e^- \rightarrow Re^{II}(L)(CO)_3Cl^+} \qquad (7)$$

Only Re(2,9-Me$_2$phen)(CO)$_3$Cl displays a return cathodic peak, but $i_p^c/i_p^a < 1$. At scan rates greater than 5 V/s, the oxidation wave shows a cathodic wave on reversal, and at 50 V/s, the systems appear to be completely chemically reversible.[2] This is indicative of a chemical reaction following electrochemical oxidation, although the nature of the decomposition product was not investigated. However, oxidation of *fac*-Re(bpy)(CO)$_3$Cl is believed to be accompanied by loss of a chlorine radical and subsequent formation of the solvated species, Re(bpy)(CO)$_3$(CH$_3$CN)$^+$.[36] A similar process presumably occurs upon oxidation of the compounds studied here.

Methyl groups attached to the phen and bpy cores make the ligand-based reduction harder and the metal-based oxidation easier (i.e., they shift the peaks to more negative potentials). The positioning of the substituents is important. Substituents that occupy a position in the N-containing ring (the 2, 3, 4, 7, 8, and 9 positions) have a greater influence on Re(phen)(CO)$_3$Cl redox potentials than those on the phenyl ring (5 and 6 positions).[10] For example, the 4,7-Me$_2$phen derivative shows a wave at a potential 105 mV more negative than that of the unsubstituted Re(phen)(CO)$_3$Cl complex, while the 5,6-Me$_2$phen derivative shows only a 23 mV shift. 4,7-Substitution in phen causes a greater shift than 2,9-substitution. As seen in Table 1, the addition of substituents to the phen and bpy cores results in greater shifts in the ligand-based reduction waves than in the metal-based oxidation waves. This results in an increase in the HOMO−LUMO ($d\pi-\pi^*$) gap.

The cyclic voltammogram in Figure 3 shows the reduction of Re(bpy)(CO)$_3$Cl in the absence and presence of (Bu$_4$N)$_2$S$_2$O$_8$. Addition of S$_2$O$_8^{2-}$ (Figure 3B) results in an increase in i_p^c of the first reduction wave, characteristic of a catalytic process (EC′

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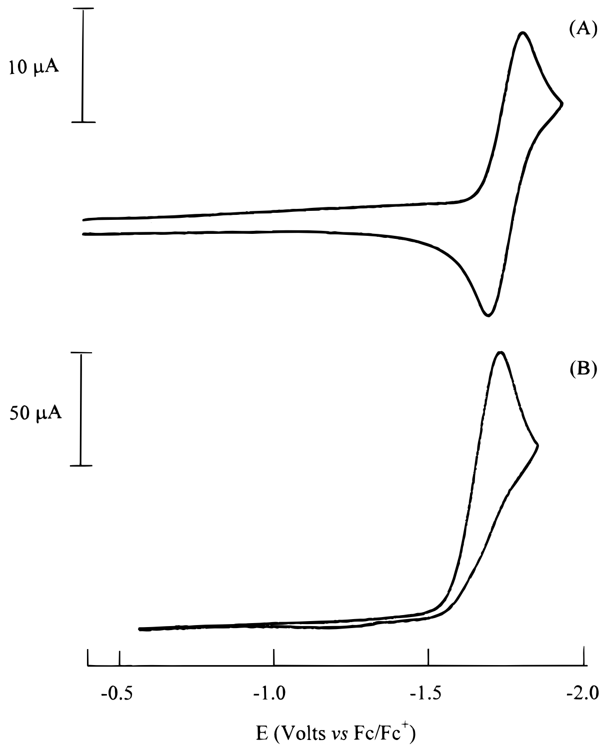

Figure 3. Cyclic voltammograms of (A) 1 mM Re(bpy)(CO)$_3$Cl and (B) 1 mM Re(bpy)(CO)$_3$Cl and 10 mM (Bu$_4$N)$_2$S$_2$O$_8$ in MeCN/0.1 M Bu$_4$NPF$_6$; scan rate, 200 mV/s.

reaction)[37] with regeneration of the Re(bpy)(CO)$_3$Cl at the surface of the electrode. Addition of TPAH (Pr$_3$N) to Re(bpy)(CO)$_3$Cl (Figure 4) does not result in voltammetry characteristic of an EC′ reaction. This may be due to the irreversible nature of the Re oxidation, preventing regeneration of Re(bpy)(CO)$_3$Cl. The first oxidation at about +0.4 V corresponds to the direct oxidation of TPAH, with the second oxidation at +0.98 V being centered on the Re atom.

Spectroscopy. In MeCN solutions at room temperature, the Re(L)(CO)$_3$Cl complexes display overlapping low-energy absorption bands between 300 and 450 nm, previously assigned to MLCT processes [$d\pi(\mathrm{Re^I}) \rightarrow \pi^*(\mathrm{L})$].[1–14] Due to the overlap of these bands, it was difficult to obtain precise absorption energies (E_{abs}) for the MLCT states, as found with other Re(L)(CO)$_3$X^{n+} systems.[8] The Re(L)(CO)$_3$Cl systems also display broad emission spectra, with energy maxima (E_{em}) between 520 and 630 nm (Table 2). The exact energies of the absorption and emission spectra are dependent on the nature of the L−π^* orbitals, as expected for charge-transfer processes. The trend in emission energy maxima follows that found in the reduction potentials (Tables 2 and 1, respectively), with energy maxima ranging from 2.0 to 2.5 eV. Quantum efficiencies for luminescence were found to lie between 0.002 and 0.04 (Table 2), as measured using Ru(bpy)$_3^{2+}$ as a relative standard.

As with the electrochemical results for complexes containing phen ligands, methyl substituents located on the pyridine ring had a greater influence on the emission maxima than those attached to the phenyl moiety. That is, the Re(L)(CO)$_3$Cl complex displays an emission maximum at 599 nm with 5,6-Me$_2$phen, while the py-substituted 4,7-Me$_2$phen and 2,9-Me$_2$phen compounds display maxima of 588 and 595 nm, respectively.

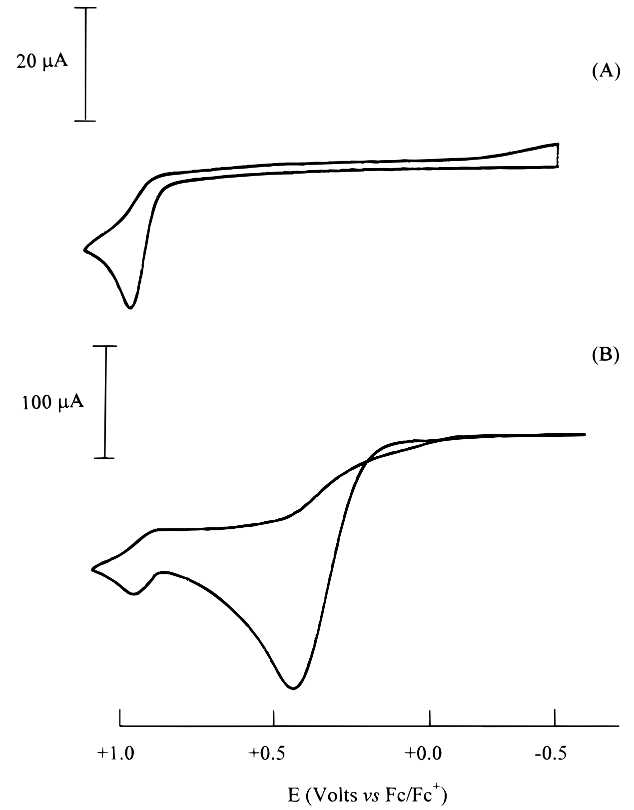

Figure 4. Cyclic voltammograms of (A) 1 mM Re(bpy)(CO)$_3$Cl and (B) 1 mM Re(bpy)(CO) $_3$Cl and 0.1 M TPAH in MeCN/0.1 M Bu$_4$NPF$_6$; scan rate, 200 mV/s.

Table 2. Relative Photoluminescence and ECL Quantum Efficiencies for Re(L)(CO)$_3$(Cl)[a]

L	$\lambda_{\max}$ (nm)[b]	ϕ_{em} (±10%)[c]	ϕ_{ECL} (±20%)[d] (pulsing)	ϕ_{ECL} (±20%)[e] (S$_2$O$_8^{2-}$)	ϕ_{ECL} (±20%)[e] (TPAH)
phen	601	0.0022	6.4×10^{-4}	0.011	0.087
2,9-Me$_2$phen	595	0.010	5.1×10^{-4}	0.0012	0.12
5,6-Me$_2$phen	599	0.018	4.2×10^{-4}	0.0054	0.12
4,7-Me$_2$phen	588	0.037	0.0011	0.030	0.22
3,4,7,8-Me$_4$phen	599	0.0037	3.1×10^{-5}	0.0049	0.0027
bpy	609	0.019	2.9×10^{-4}	0.0031	0.52
4,4′-Me$_2$bpy	599	0.014	6.9×10^{-4}	0.0043	0.40

[a] MeCN solutions at room temperature. [b] $\lambda_{\mathrm{exc}} = 360$ nm. [c] Relative to Ru(bpy)$_3^{2+}$ ($\phi_{\mathrm{em}} = 0.0682$).[35] [d] Relative to Ru(bpy)$_3^{2+}$ ($\phi_{\mathrm{ECL}} = 0.0500$).[20,30] [e] Relative to Ru(bpy)$_3^{2+}$ ($\phi_{\mathrm{ECL}} = 1.0$).

There is a linear correlation between the HOMO−LUMO redox separation and the emission maxima for the Re$^{\mathrm{I}}$ tricarbonyl systems Re(L)(CO)$_3$py$^+$ [7,10,23] and the osmium and ruthenium MLCT emitters.[38–42] Thus, plots of E_{abs} or E_{em} vs $\Delta E_{1/2}$ should produce a linear correlation within the same series of complexes if the same HOMO and LUMO are involved in both the optical and electrochemical processes.[38–42] Plots of E_{em} vs $\Delta E_{1/2}$ [$\Delta E_{1/2} = E_{1/2}(\mathrm{Re^I/Re^{II}}) - E_{1/2}(\mathrm{L^0/L^-})$] display reasonably linear correla-

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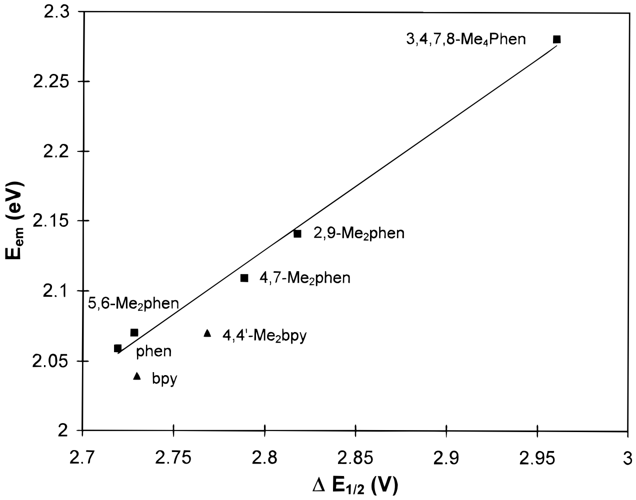

Figure 5. Correlation of emission energy (E_{em}) and difference in redox potentials ($\Delta E_{1/2} = E_{1/2}(Re^{II}/Re^{I}) - E_{1/2}(L/L^-)$) in MeCN at room temperature. The line represents the best fit for the phenanthroline data only and has a correlation coefficient of 0.994.

tions (Figure 5). $E_{1/2}(Re^I/Re^{II})$ values were determined at scan rates of 10 V/s, due to the irreversible nature of this oxidation process at slower scan rates. The linear correlation apparent in Figure 5 indicates that, within this series of complexes, the same $d\pi-\pi^*$ orbitals are involved in both the spectroscopic and electrochemical processes and that the electronic and thermodynamic energy gaps parallel one another.[7,10,23] The lack of discernible grouping patterns and a poor linear correlation in the plot of E_{abs} vs $\Delta E_{1/2}$ may reflect the difficulty in obtaining precise wavelengths for the MLCT transitions from broad, overlapping absorption bands.[8]

Electrogenerated Chemiluminescence. ECL via Annihilation. ECL has been observed for all of the rhenium systems under different experimental conditions. The ECL spectra are similar to the photoluminescence spectra, so the same ^{3}MLCT state is probably formed in both experiments. For solutions containing 1−5 mM $Re(L)(CO)_3Cl$ and 0.1 M Bu_4NPF_6, intense ECL visible to the dark-adapted eye was obtained when the potential of the Pt working electrode was pulsed between the oxidation and reduction waves of the complex (∼+1.2 and −2.0 V). The emission intensity decreased over time, presumably due to the formation of decomposition products during the oxidative pulse. No ECL emission was observed on scanning to potentials less positive or negative than those needed to form the anionic and cationic species, respectively. The generation of luminescence upon pulsing the potential can be explained by analogy to the well-studied $Ru(bpy)_3^{2+}$ system[16] via the following mechanistic process (Figure 6A), eqs 6 and 7 followed by

$$Re^I(L^-)(CO)_3Cl^- + Re^{II}(L)(CO)_3Cl^+ \rightarrow Re^{II}(L^-)(CO)_3Cl^* + Re(L)(CO)_3Cl \quad (8)$$

$$Re^{II}(L^-)(CO)_3Cl^* \rightarrow Re(L)(CO)_3Cl + h\nu \quad (9)$$

ECL with Coreactants. ECL experiments were also carried out on $Re(L)(CO)_3Cl$ solutions containing coreactants. ECL emission spectra were obtained for each of the complexes upon sweeping the potential sufficiently positive to oxidize both the

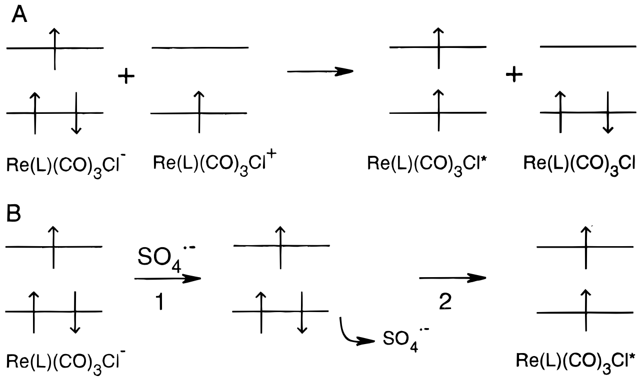

Figure 6. MO diagrams of ECL generation via (A) annihilation and (B) $S_2O_8^{2-}$ reaction sequences. (A) Formation of cationic and anionic species is followed by electron transfer to form the excited-state $Re(L)(CO)_3Cl^*$ and a ground-state $Re(L)(CO)_3Cl$ species. (B) Formation of the reduced $Re(L)(CO)_3Cl^-$ species at the working electrode is followed by interaction with the $SO_4^{\bullet-}$ radical anion (1) and then electron transfer (2) to form the excited-state $Re(L)(CO)_3Cl^*$ species.

complex and Pr_3N[43] and sufficiently negative to reduce both the complex and $S_2O_8^{2-}$. It was necessary to stir the solutions to record the spectra because the light intensities gradually decreased in unstirred solution due to depletion of metal complex at the electrode. The energy maxima from $S_2O_8^{2-}$ ECL are identical to that of the annihilation ECL discussed above, indicating formation of the same excited states in both experiments. However, the $Re(phen)(CO)_3Cl/S_2O_8^{2-}$ system showed a broader emission band and lower intensities at the same concentration of complex. The persulfate system displays a greater width at half-height and also a low-energy shoulder. The identity of the species producing this shoulder was not investigated.

An ECL intensity vs potential scan for $Re(L)(CO)_3Cl$ and $(Bu_4N)_2S_2O_8$ is shown in Figure 7B. ECL is observed only when the potential is sufficiently negative to produce $Re(L)(CO)_3Cl^-$; no ECL results from reducing only the coreactant.[30] $S_2O_8^{2-}$ displays a broad, irreversible reduction with $E° \approx 0.1$ V and has been discussed in detail elsewhere.[30] By analogy with $Ru(bpy)_3^{2+}$ and related systems,[28−31] formation of $Re(L)(CO)_3Cl^*$ can occur by two distinct mechanisms, eqs 1 and 6 followed by

$$Re^I(L^-)(CO)_3Cl^- + SO_4^{\bullet-} \rightarrow Re^{II}(L^-)(CO)_3Cl^* + SO_4^{2-} \quad (10)$$

or

$$Re^I(L)(CO)_3Cl + SO_4^{\bullet-} \rightarrow Re^{II}(L)(CO)_3Cl^+ + SO_4^{2-} \quad (11)$$

followed by eq 8.

Reaction 10 involves direct oxidation of the metal-based t_{2g} orbitals in $Re^I(L^-)(CO)_3Cl^-$ by the strong oxidant $SO_4^{\bullet-}$ (Figure 6B). Reaction 11 involves oxidation of the neutral $Re^I(L)(CO)_3Cl$ by $SO_4^{\bullet-}$, followed by formation of the excited state via an annihilation reaction. In the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system,[30] eq 11 is believed to be responsible for the ECL emission, while in other systems eq 10 has been invoked.[28,31] Reaction 11 followed by eq

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[43] It is believed that, upon oxdiation of TPAH, the strongly reducing intermediate TPA• or $(CH_3CH_2CH_2)_2N(C^{\bullet}HCH_2CH_3)$ is formed, e.g., $N(CH_3CH_2CH_2)_3 - e^- \rightarrow N^{\bullet+}(CH_3CH_2CH_2)_3 \rightarrow (CH_3CH_2CH_2)_2N(C^{\bullet}HCH_2CH_3) + H^+$.

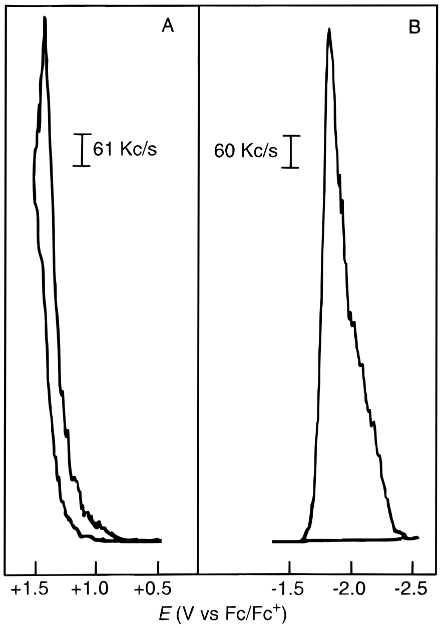

Figure 7. ECL emission intensity vs potential profile of 1 mM Re(bpy)(CO)$_3$Cl with (A) 0.1 M TPAH/0.1 M Bu$_4$NPF$_6$ and (B) 10 mM (Bu$_4$N)$_2$S$_2$O$_8$/1 M Bu$_4$NPF$_6$ in MeCN solutions at room temperature; scan rate, 200 mV/s.

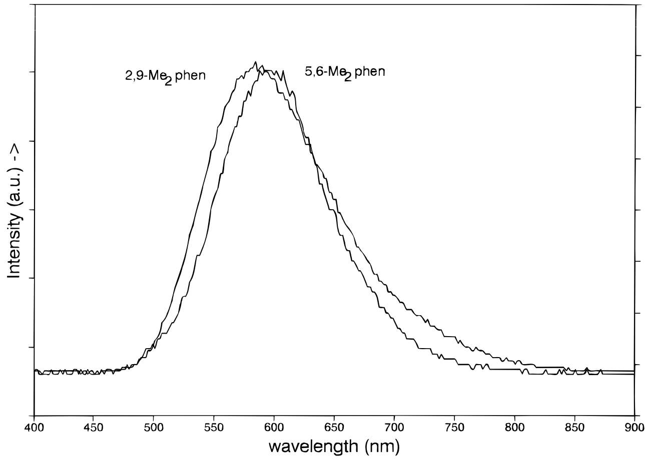

Figure 8. ECL spectra of Re(2,9-Me$_2$phen)(CO)$_3$Cl and Re(5,6-Me$_2$phen)(CO)$_3$Cl. MeCN solutions were 2 mM in complex, 0.1 M in TPAH, and 0.1 M in Bu$_4$NPF$_6$. Spectra were generated by alternate pulsing of electrode potentials between 0.0 and +1.6 V via an oxidative−reductive coreactant reaction sequence. Holding time at each limit was 0.1 s.

8 involves annihilation of the electrogenerated Re^{I}(L^{-})(CO)$_3$Cl^{-} and Re^{II}(L)(CO)$_3$Cl^{+} species but is less likely due to the instability of the cationic species.

ECL emission spectra are shown in Figure 8 for the 2,9-Me$_2$phen and 5,6-Me$_2$phen systems with tri-*n*-propylamine (TPAH) as coreactant. By analogy to the Ru(bpy)$_3^{2+}$ system,[20,32−34] the following reaction sequence has been proposed for the ECL emission observed from these solutions:

$$\mathrm{TPAH} - e^{-} \rightarrow [\mathrm{TPAH}^{+}] \rightarrow \mathrm{TPA}^{\bullet} + \mathrm{H}^{+} \qquad (12)$$

$$\mathrm{TPA}^{\bullet} + \mathrm{Re}^{II}(\mathrm{L})(\mathrm{CO})_3\mathrm{Cl}^{+} \rightarrow \mathrm{Re}^{II}(\mathrm{L}^{-})(\mathrm{CO})_3\mathrm{Cl}^{*} + \mathrm{TPA}^{+} \qquad (13)$$

where the strong reductant TPA$^{\bullet}$ [43] inserts an electron into the ligand-based π^* orbitals. However, due to the instability of the oxidized complex, as can be seen in the cyclic voltammograms (Figure 2), and the short-lived nature of Re^{II}(L)(CO)$_3$Cl^{+}, it is possible that a product of the oxidation takes part in the ECL reaction sequence. As shown in the intensity vs potential plots for Re(bpy)(CO)$_3$Cl (Figure 7A), ECL is observed only when the potentials are sufficiently positive to oxidize the Re center (∼+1.3 V; $E°$(TPAH) ≈ 0.5 V). This has been clearly shown in other rhenium systems, including Re(L)(CO)$_3$Cl (L = bpy, di-2-pyridyl ketone, and 2,2′-dipyridylamine).[44] An alternate mechanism for ECL production is outlined below, eqs 12 and 7 followed by

$$\mathrm{Re}^{I}(\mathrm{L})(\mathrm{CO})_3\mathrm{Cl} + \mathrm{TPA}^{\bullet} \rightarrow \mathrm{Re}^{I}(\mathrm{L}^{-})(\mathrm{CO})_3\mathrm{Cl}^{-} + \mathrm{TPA}^{+} \qquad (14)$$

with emission occurring via annihilation, eq 9. As is the case in the persulfate system, this mechanism seems less likely due to the instability of the cationic Re^{II} species. Thus, direct reaction of Re(L)(CO)$_3$Cl^{+} with TPA$^{\bullet}$ (reaction 13) seems more likely, although no direct evidence exists. Of course, emission from decomposition products of the radical cation is possible. However, one would expect shifts in the emission maxima and this is clearly not seen in these systems.

Comments on ϕ_{ECL}. The relative ECL efficiency, i.e., the number of photons generated per the amount of reactant generated during a pulse (ϕ_{ECL}), was estimated for each of the complexes using Ru(bpy)$_3^{2+}$ as the standard.[20,30,35] The relative efficiency was obtained from the relationship

$$\phi_{\mathrm{ECL}} = \phi°_{\mathrm{ECL}}(IQ°/I°Q)$$

where $\phi°_{\mathrm{ECL}}$ is the ECL efficiency of Ru(bpy)$_3^{2+}$ (taken as 0.05 in MeCN at 25 °C for the annihilation experiments[30]), I and $I°$ are the integrated ECL intensities of the rhenium complexes and Ru(bpy)$_3^{2+}$, and Q and $Q°$ are the charges passed (in coulombs) for the forward sweeps for the complexes and standards, respectively.[35] Since the same experimental setup and concentrations were used for each compound, Q and $Q°$ for each were about the same. For 1 mM Re(L)(CO)$_3$Cl solutions in 0.1 M Bu$_4$NPF$_6$/MeCN and pulse widths of 0.1 s, ϕ_{ECL} was found to be 10^{-2}−10^{-4} (Table 2).

The ϕ_{ECL} values for the Re(L)(CO)$_3$Cl/TPAH and Re(L)(CO)$_3$Cl/S$_2$O$_8^{2-}$ systems were calculated using Ru(bpy)$_3^{2+}$ as the relative standard (taken as 1 in MeCN at 25 °C since the Ru(bpy)$_3^{2+}$/coreactant efficiencies are not known). These values lie between 3×10^{-3} and 0.5 for Re(L)(CO)$_3$Cl/TPAH and between 3×10^{-3} and 3×10^{-2} for Re(L)(CO)$_3$Cl/S$_2$O$_8^{2-}$. During these measurements, light intensities were integrated for 5 min without stirring, thus the reported efficiencies represent an average over this time period. The values of ϕ_{ECL} are much smaller than ϕ_{em} and presumably reflect instability of the redox species and inefficient excited state formation in the annihilation sequence.

There is little correlation between the relative ECL quantum efficiencies (Table 2) and the relative photoluminescence intensities of the Re complexes studied here. This indicates that factors other than luminescence efficiency dictate the ECL efficiency. In all cases, Re(3,4,7,8-Me$_4$phen)(CO)$_3$Cl displays the lowest and Re(4,7-Me$_2$phen)(CO)$_3$Cl the highest ECL efficiencies among the

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(44) Richter, M. M.; Mackenzie, J. M.; Bakir, M.; Bard, A. J., unpublished results.

phenanthroline systems, with the relative ordering of the other complexes dependent on how the ECL excited state is produced.

In the case of 3,4,7,8-Me_4phen, the low efficiency of the ECL may reflect the influence of more than one excited state.[4,10] In a similar Re(I) system, Re(3,4,7,8-Me_4phen)$(CO)_3py^+$, photodecomposition occurred upon irradiation, which was related to the energy of the MLCT state in relation to the metal-centered dd orbitals.[4,10] Within a set of closely related complexes having the same donor atom set, the energy of the dd excited state is unlikely to be affected by substituents attached to the phenanthroline ligand, so the energy of the metal-centered (dd) states probably remains roughly constant throughout the series. Since the ligand-centered reduction of this complex lies at the highest energies (Table 1), the energy difference between the MLCT and the dd states is presumably the smallest,[10] allowing facile population of these higher energy states. In 4,7-Me_2phen, however, the higher relative efficiencies reflect the increased stability conferred on the excited state when electron-donating groups are substituted para to the bonding nitrogens. Just as substitution within the pyridyl ring (3, 4, 7, and 8 positions) results in greater stabilization than substitution on the phenyl ring (5 and 6 positions), substitution within the former is also important.

In the TPAH reaction system, the bpy complexes display higher efficiencies, while for ECL via annihilation and $S_2O_8^{2-}$, ECL quantum efficiencies of the phen- and bpy-substituted systems are comparable (Table 2). This provides evidence for different efficiencies of excited-state formation and underscores the sensitivity of the emitting state to the nature of both the coreactant and the energetic reactants which undergo electron transfer. MLCT states are sensitive to the nature of the environment;[1−14] therefore, the observed differences might be a reflection of both environmental influences and the degree to which the excited state must rearrange (in the ECL experiments) to accommodate the high-energy electron.

Based on the above observations, the design of Re^I tricarbonyl polypyridyl systems with good ECL properties should include substitution in the 4,7 positions for any system incorporating phen ligands, and ECL should be generated via the reductive−oxidative ($S_2O_8^{2-}$) reaction sequence. Unfortunately, in the bpy-based systems, substitution para to the binding sites (4 and 4′ positions) does not appear to confer added stability in either photoluminescence or ECL.

CONCLUSIONS

The electrochemical and spectroscopic behavior in the series of Re(L)$(CO)_3$Cl complexes studied here is similar to the well-studied $Ru^{II}L_3^{2+}$ polypyridine systems. The Re compounds display a chemically reversible ligand-centered reduction and an irreversible metal-centered oxidation. Correlations among the spectroscopic and electrochemical energy gaps show that the MLCT states are similar in both types of complexes. The lowest energy state responsible for luminescence, ^{3}MLCT, can be electrogenerated by annihilation as well as oxidative−reductive (TPAH) and reductive−oxidative ($S_2O_8^{2-}$) coreactant pathways. The ECL properties of these complexes can be systematically changed or tuned by varying both the nature of the chromophoric ligand and the positioning of substituents on this ligand. Methyl substitution resulted in a shift to more negative values of both oxidative and reductive electrochemistry and a shift to higher energies of the photoluminescent and ECL emission maxima. ECL quantum efficiencies were low compared to the $Ru(bpy)_3^{2+}$ system, limiting their use in analytical applications (i.e., immunoassay, DNA probes, and display devices). Comparisons among the phen and bpy complexes showed that the relative efficiency of each is highly dependent on the experimental conditions. Both systems display comparable efficiencies when the excited state is formed via an annihilation sequence, but the bpy systems are more efficient when TPAH is used, and the phen systems are more efficient with $S_2O_8^{2-}$. The relative efficiencies depend on the position of the methyl substituents on the phen ligand. Substitution on the N-containing ring causes an increase in ECL efficiency regardless of the mechanism used to generate ECL.

The poor correlation between the photoluminescence and ECL quantum efficiencies underscores the sensitivity of the electron-transfer reaction and the MLCT state to the surrounding media. The states are also affected by the substitution patterns on the phen and bpy ligands.

This work emphasizes the role orbital energetics play in both the photoluminescent and ECL experiments, since the efficiency of intra- and intermolecular electron transfer is dependent upon the nature of the chromophoric ligand and the precise mechanism by which the excited state is formed.

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