can be made about the data in Table IV: (i) The coupling constants for several complexes with Cr···Cr distances of or below 2.8 Å are significantly higher in magnitude than those for complexes with Cr···Cr distances greater than 3 Å, for a given Cr–O(s) value. This is consistent with the existence of a direct exchange pathway. Note that the Fe···Fe distances were greater than 3 Å for all complexes used in the Fe(III) correlation.[4] (ii) Linear oxo-bridged complexes show much stronger coupling than complexes with bent bridges of similar Cr–O(s). Interestingly, the Fe(III) correlation applies to doubly and triply bridged complexes and excludes linear complexes.[4] (iii) Apart from these cases, the data do show an increase in the magnitude of J with decreasing Cr–O(s) similar to that found for the Fe(III) complexes. Clearly, there is a need for further work aimed at the isolation of oxo-bridged Cr(III) complexes in particular containing bent Cr–O–Cr units.

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Supplementary Material Available: For **1**, anisotropic displacement coefficients (Table S1) and H atom coordinates and isotropic displacement coefficients (Table S2) (1 page); a listing of structure factors (Table S3) (10 pages). Ordering information is given on any current masthead page.

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Substituent Constant Correlations as Predictors of Spectroscopic, Electrochemical, and Photophysical Properties in Ring-Substituted 2,2′-Bipyridine Complexes of Rhenium(I)

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The synthesis and the spectroscopic, electrochemical and photophysical properties of the homologous series of photosensitizers, *fac*-[4,4′-X_2-5,5′-Y_2-2,2′-bipyridine]Re(CO)$_3$Etpy$^+$ (X = NEt_2, Me, OMe, H, Ph, Cl, CO_2Me, NO_2, Y = H; X = Y = Me; Etpy = 4-ethylpyridine) are described. Both the quasi-reversible or irreversible oxidation of the Re(I) center and the reversible or quasi-reversible, one-electron reduction of the coordinated bipyridyl ligand are observed to vary with the electron donor/acceptor abilities of X, Y as measured by the sum of the Hammett substituent constants $\sigma_m + \sigma_p$. Hammett ($\sigma_T = \sigma_p + \sigma_m$) values for the X, Y groups are observed to correlate linearly with the metal-to-ligand charge-transfer (MLCT) absorption and emission energies and provide a convenient tool for the estimation of excited-state properties of the complexes. The complexes are moderately strong excited-state oxidants ($E_{1/2}(+^*/0)$ = 0.73–1.12 V vs SSCE) and exhibit emission maxima in the range 528 nm (X = NEt_2, Y = H) to 755 nm (X = NO_2, Y = H). MLCT excited-state decay is dominated by nonradiative decay from the ^{3}MLCT state to the ground state and is governed by an "energy gap law". It is shown that excited-state properties such as absorption energy, emission energy, rate of nonradiative decay (k_{nr}), and the rate of radiative decay (k_r) correlate with σ_T. The correlations can be derived from more fundamental considerations. The dependence of ln k_{nr} on emission energy is similar to values obtained in earlier studies with bipyridyl Ru(II) or Os(II) complexes which do not contain coordinated CO and somewhat less than that observed in a previous study for *fac*-(bpy)Re(CO)$_3$(L′)$^+$ complexes (L′ = monodentate, neutral ligands). This behavior is interpreted as an indication that nonradiative decay involves acceptor modes that are predominantly ring-based vibrations of the substituted bipyridine ligand, but that CO modes are also involved.

Introduction

Complexes of 2,2′-bipyridine (bpy) and its derivatives with spin-paired d^6 third-row transition metals such as Os(II),[1-6] Ir(III),[7,8] and Re(I)[9-15] have received increasing attention due, at least in part, to the potential versatility of such compounds as catalysts[2-14,16-19] and as sensitizers in solar energy conversion[9-11,15,20] schemes. One particularly promising class of compounds for these applications are the *fac*-[L]Re(CO)$_3$(L′)$^{n+}$ (L = 2,2′-bipyridine, and 1,10-phenanthroline and its substituted derivatives; L′ = Cl$^-$, n = 0; L′ = PMe_3, pyridine, MeCN, and other neutral monodentate ligands; n = 1) complexes. The L′ = Cl$^-$ complexes have been found to act as catalysts for the reduction of carbon dioxide in homogeneous solution[12-14,16-18] and as catalysts bound to electrode surfaces.[17-19] The importance of the *fac*-[L]Re(CO)$_3$(L′)$^{n+}$ complexes as sensitizers in solar energy storage schemes has long been recognized.[9-11,20] Luminescence originating from the relaxation of the metal-to-ligand charge-transfer (MLCT) excited state to the ground state provides a convenient probe of photophysical decay channels. These properties have been exploited to obtain information concerning the mechanisms of intramolecular electron-transfer reactions.[21-23] In addition, the sensitivity of photophysical properties to the local solution environment has also been exploited[24,25] to determine the nature of intermolecular interactions of *fac*-(bpy)Re(CO)$_3$NC-

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$(CH_2)_nCH_3^+$ (n = 0–17) complexes.

One advantage in the selection of Re(I) complexes for studies such as those described above is the relative ease with which the *fac*-[L]Re(CO)$_3$(L')$^{n+}$ complexes can be synthesized.[9,11,12,14,26,27] In principle, it is possible to vary the identities of both L and L' to prepare complexes exhibiting a wide range of MLCT excited-state properties. In practice, most theoretical and experimental work has been done using two series of complexes, either *fac*-[L]Re(CO)$_3$Cl or *fac*-(bpy)Re(CO)$_3$(L')$^+$ where L is 2,2'-bipyridine or a related polypyridine ligand and L' is PMe$_3$, pyridine, MeCN, or other, neutral, monodentate donors.[11,20,26,27] Recent work[28,29] has greatly increased the number of *fac*-[L]Re(CO)$_3$Cl and *fac*-(bpy)Re(CO)$_3$(L')$^+$ complexes available for use in catalytic or photochemical studies and, notably, for use as models to understand radiationless decay theory as applied to MLCT excited states.[5,11,20,30–34]

These successful applications of *fac*-[L]Re(CO)$_3$Cl and *fac*-(bpy)Re(CO)$_3$(L')$^+$ complexes have prompted us to prepare new Re(I) complexes of the type *fac*-[4,4'-X$_2$-5,5'-Y$_2$-2,2'-bipyridine]Re(CO)$_3$Etpy$^+$ (X = NEt$_2$, Me, OMe, H, Ph, Cl, CO$_2$Me, NO$_2$, Y = H; X = Y = Me; Etpy = 4-ethylpyridine) which are "hybrids" of the previous *fac*-[L]Re(CO)$_3$Cl and *fac*-(bpy)Re(CO)$_3$(L') series. Determination of the spectroscopic, electrochemical, and photophysical properties of the complexes in acetonitrile solution has allowed us to correlate the MLCT excited-state properties to ground-state properties via a substituent parameter approach and to compare our results to those obtained for related systems.[1,11,35–40] Control of MLCT excited-state properties by the X, Y substituents of the coordinated bipyridyl unit is used to provide a further test of the applicability of radiationless decay theory as a model for MLCT excited-state decay for these and related systems.[5,11,31–35] Our results provide a basis for the future use of such complexes as catalysts or photosensitizers.

Experimental Section

Materials. 2,2'-Bipyridine (bpy) from Aldrich was used without further purification. 4,4'-Dimethyl-2,2'-bipyridine (Me$_2$bpy) was obtained from Reilly Tar & Chemicals and was sublimed prior to use. 4,4'-Diphenyl-2,2'-bipyridine (Ph$_2$bpy) from Aldrich was recrystallized once from benzene/petroleum ether prior to use. 4-Ethylpyridine (Etpy) was used as received from Aldrich. The ligands 4,4'-bis(diethylamino)-2,2'-bipyridine [(NEt$_2$)$_2$bpy],[41] 4,4'-dimethoxy-2,2'-bipyridine [(MeO)$_2$bpy],[41,42] 4,4'-dichloro-2,2'-bipyridine [Cl$_2$bpy],[43] 4,4',5,5'-tetramethyl-2,2'-bipyridine [Me$_4$bpy],[44] 4,4'-dinitro-2,2'-bipyridine [(NO$_2$)$_2$bpy][42], and 4,4'-bis(carbomethoxy)-2,2'-bipyridine [(CO$_2$Me)$_2$bpy][41,45] were prepared according to literature procedures.

Petroleum ether, diethyl ether (anhydrous), methylene chloride, and methanol were all Chempure grade from Curtin Matheson Scientific and were used as received. Acetonitrile (Omni-Solv) and acetone (ACS Reagent grade) from E. M. Scientific (Cherry Hill, NJ) were used without further purification. Benzene was ACS Reagent grade from Fisher Scientific and was used as received. Toluene (Baker Analyzed Reagent, HPLC grade) from J. T. Baker Chemicals (Phillipsburg, NJ) was used without further purification. Tetrahydrofuran from J. T. Baker Chemicals was dried using sodium/benzophenone under an Ar atmosphere at reflux for 1 h. The solvent was distilled prior to use. Anhydrous ethanol (200 proof) was obtained from the Warner-Graham Co. (Cockeyesville, MD). Water was deionized using a Millipore Milli-Q system.

Neutral adsorption alumina (Fisher) was used as received. Ottawa sand and glass wool for chromatography were obtained from Aldrich. SP-Sephadex C-25 ion-exchange chromatography resin was purchased from the Sigma Chemical Co. and was activated by stirring in boiling water for 2 h immediately prior to use.

Sodium metal, benzophenone (Gold Label), trifluoromethanesulfonic acid (CF$_3$SO$_3$H, i.e., triflic acid), silver trifluoromethanesulfonate (AgCF$_3$SO$_3$, i.e., silver triflate), and ammonium hexafluorophosphate (NH$_4$PF$_6$) were all used as received from Aldrich. Trifluoromethanesulfonic anhydride [(CF$_3$SO$_2$)$_2$O, i.e., triflic anhydride] from Alfa-Ventron (Danvers, MA) was used without further purification. NaCl and NaClO$_4$ were both ACS Reagent grade from Fisher Scientific and were used as received. Pentacarbonylrhenium(I) chloride was purchased from the Pressure Chemical Co. (Pittsburgh, PA). Indicating Drierite (CaSO$_4$, anhydrous) was obtained from Aldrich. Argon gas from Robert's Oxygen Co., (Rockville, MD) was scrubbed free of trace oxygen and moisture by passage through successive columns (3 in. i.d. × 24 in. height) of activated BTS-1 1 Catalyst and indicating Drierite, respectively, prior to use. Tetrabutylammonium hexafluorophosphate (TBAH) from Alfa was recrystallized twice from HPLC grade ethyl acetate (Aldrich) prior to use. TBAH was stored in the dark in a vacuum desiccator over Drierite until needed for electrochemical studies.

Measurements. Electrochemical data were acquired for the *fac*-[L]-Re(CO)$_3$Etpy$^+$ complexes via cyclic voltammetry using a Princeton Applied Research Model 173 potentiostat driven by a homebuilt "super cycle" sweep generator with an HP 701 5B X-Y recorder. All electrochemical experiments were performed in a Vacuum Atmospheres drybox under argon atmosphere. The metal complex to be examined (ca. 1 mg) was placed in a small single-compartment electrochemical cell, and 2 mL of high-purity acetonitrile (Burdick & Jackson Labs) containing 0.2 M TBAH was added. When the complex had completely dissolved, a Teflon cap fitted with a Pt-bead working electrode, Pt-wire auxiliary electrode and NaCl saturated calomel reference electrode (SSCE) was placed in the cell. A sweep rate of 200 mV/s was used for all scans. Potentials were reported as $E_{1/2}$ values vs SSCE and were determined from the following relation: $E_{1/2} = {}^1/_2(E_{p,a} + E_{p,c})$, where $E_{p,a}$ and $E_{p,c}$ were the anodic and cathodic peak potentials, respectively.

UV–visible spectral data were recorded for the complexes in MeCN solution in the 300–800-nm spectral region. Samples were contained in 1.00-cm quartz cuvettes and were referenced to a solvent blank. The spectra were obtained using a Bausch & Lomb 210 UV spectrophotometer.

Lifetime measurements were obtained using a laser-pulsed system described earlier.[34] Sample solutions (ca. 2–5 μM in complex) were placed in 1.00-cm square quartz cuvettes and Ar bubble degassed for 20 min prior to data acquisition. An Ar gas blanket was maintained over the solution during the measurements to prevent diffusion of oxygen into the solution from the atmosphere. A 337-nm sample excitation wavelength was used and the sample temperature was 22 °C. Sample emission was monitored at the emission maximum for each complex (note Table III). The lifetime, τ, of the MLCT excited state was obtained from the slope of a plot of ln (emission intensity) vs time. Such plots were linear over at least 3 half-lives. Uncertainties in the lifetime values so obtained were typically less than 2%.

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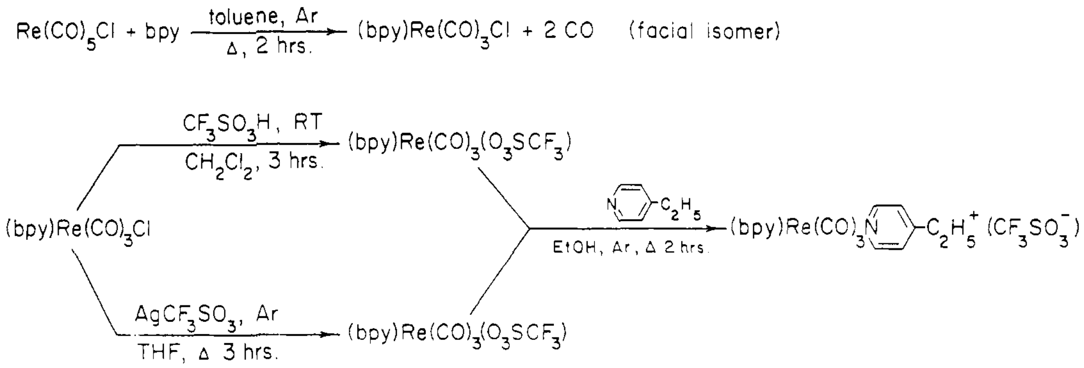

Figure 1. Synthetic scheme for the *fac*-(L)Re(CO)$_3$Etpy$^+$ complexes. The reactions are shown with L = bpy for illustration.

Emission spectra were obtained using a SLM Instruments 8000 photon-counting spectrofluorimeter as a function of wavelength at 22 °C. A 4-nm band-pass was sufficient for all experiments. Data were acquired over the emission wavelength range 500–800 nm. Corrections for the variation of instrument response with wavelength were made with the use of data and programs supplied by the manufacturer.

Emission data were converted to an abscissa linear in energy as described earlier[40,46] for the purposes of our discussion (vide infra) and the determination of quantum yields. Under these conditions, the emission intensities are expressed as emitted quanta per energy interval[47] and the integrated areas are proportional to the radiative quantum yields, ϕ_r. Radiative quantum yields for the *fac*-(L)Re(CO)$_3$Etpy$^+$ complexes in deaerated MeCN solution were measured vs Ru(bpy)$_3$(PF$_6$)$_2$ in deoxygenated MeCN at 22 °C as a standard ($\phi_r = 0.062$).[20] All samples were excited at 355 nm with an integration time of 1 s/nm. Sample absorption at 355 nm was adjusted to the 0.04–0.06 range (measured after degassing) for data acquisition and the appropriate corrections due to slight differences in absorption between samples were made in calculating ϕ_r.[31]

Values of the radiative and nonradiative decay rates of the MLCT excited states of the *fac*-(L)Re(CO)$_3$Etpy$^+$ complexes in MeCN were calculated from values of ϕ_r and τ. The radiative decay rate, k_r, is $k_r = \phi_r\tau^{-1}$ and the nonradiative decay rate, k_{nr}, is $k_{nr} = \tau^{-1}(1 - \phi\tau_r^{-1})$ assuming an intersystem crossing yield of unity.[20,48]

Syntheses. A summary of the synthetic routes to the *fac*-(L)Re(CO)$_3$Etpy$^+$ complexes is shown in Figure 1. The *fac*-(L)Re(CO)$_3$Cl complexes were synthesized from (CO)$_5$ReCl and the appropriate 4,4′-disubstituted 2,2′-bipyridyl ligand, L, using literature methods.[9,11,20,27,39,49–52] In most cases, the desired product precipitated in pure form on cooling to room temperature. For some complexes, e.g., *fac*-[(NO$_2$)$_2$bpy]Re(CO)$_3$Cl, precipitation did not readily occur. Pure complexes were then isolated by dropwise addition of diethyl ether to the reaction mixture. All *fac*-(L)Re(CO)$_3$Cl complexes were isolated in >90% yield based on rhenium. The conversion of *fac*-(L)Re(CO)$_3$Cl to the corresponding *fac*-(L)Re(CO)$_3$Etpy$^+$X$^-$ complexes (X = CF$_3$SO$_3$, PF$_6$) involves the generation of an intermediate triflate species[3,27,49–52] using either triflic acid or silver triflate. The use of triflic acid is illustrated by the following preparation of *fac*-(NEt$_2$)$_2$bpyRe(CO)$_3$Etpy (CF$_3$SO$_3$) from *fac*-[(NEt$_2$)bpy]Re(CO)$_3$Cl via the intermediate *fac*-[(NEt$_2$)$_2$bpy]Re(CO)$_3$(CF$_3$SO$_3$).

Preparation of *fac*-[(NEt$_2$)$_2$bpy]Re(CO)$_3$CF$_3$SO$_3$. *Caution! Trifluoromethanesulfonic acid (triflic acid) and trifluoromethanesulfonic anhydride (triflic anhydride) are exceedingly corrosive and volatile substances. All reactions employing these substances were carried out in a well-ventilated fume hood.* Into a 300-mL boiling flask equipped with Teflon stirbar is added 456 mg (0.75 mmol) of *fac*-[(NEt$_2$)$_2$bpy]Re(CO)$_3$Cl and 30 mL of methylene chloride from a freshly opened bottle. To the stirred yellow suspension are quickly added 1.34 mL (20× required amount) of triflic acid and 3–5 drops of triflic anhydride. The solid immediately dissolves to a muddy yellow solution. The flask is stoppered and the solution is stirred at room temperature for 3 h. The product is precipitated from the solution as a dark yellow solid by dropwise addition of 200 mL of anhydrous diethyl ether to the contents of the flask. The product [(NEt$_2$)$_2$bpy]Re(CO)$_3$(CF$_3$SO$_3$) is collected from suction filtration, washed with 6 × 30 mL of anhydrous diethyl ether to remove excess triflic acid and air suction dried for 15 minutes. Drying is completed in the vacuum desiccator over Drierite overnight. The 529 mg of [(NEt$_2$)$_2$bpy]Re(CO)$_3$(CF$_3$SO$_3$) obtained represents a 98% yield based on starting *fac*-[(NEt$_2$)bpy]Re(CO)$_3$Cl. The product is used without further purification in subsequent reactions.

Preparation of *fac*-[[(NEt$_2$)$_2$bpy]Re(CO)$_3$Etpy](CF$_3$SO$_3$). Into a 250-mL boiling flask equipped with Teflon stirbar and reflux condenser is added 150 mg (0.21 mmol) of *fac*-[(NEt$_2$)$_2$bpy]Re(CO)$_3$(CF$_3$SO$_3$) and 50 mL of ethanol. To this is added 0.24 mL of 4-ethylpyridine (Etpy). The solution is Ar bubble degassed for 15 min and refluxed under an Ar atmosphere with stirring for 2 h. After the solution is cooled to room temperature, the ethanol is removed by evaporation using the rotary evaporator. The sample remaining consists of crude product dissolved in excess Etpy. This is dissolved in a minimum volume (5–15 mL) of 1:2 v/v MeCN/toluene and applied to a neutral alumina column (30 cm height × 3 cm i.d.) for chromatography. Elution with 1:2:1 v/v/v MeCN/toluene/diethyl ether is initiated and continued until excess Etpy has been removed (as judged by the absence of the characteristic Etpy odor in the eluant). Elution with 1:1 v/v MeCN/toluene removes the yellow *fac*-[[(NEt$_2$)$_2$bpy]Re(CO)$_3$Etpy](CF$_3$SO$_3$).

Although some tailing is observed, complete separation of a product band from a small amount of unidentified purple species is achieved. The solvent is removed using the rotary evaporator to yield a yellow solid. This is redissolved in 5 mL of methylene chloride and again evaporated to dryness on the rotary evaporator. Pale yellow flakes (100 mg) of *fac*-[[(NEt$_2$)$_2$bpy]Re(CO)$_3$Etpy](CF$_3$SO$_3$) are obtained in 58% yield (based on starting *fac*-[(NEt$_2$)$_2$bpy]Re(CO)$_3$Cl). The product is analytically pure.

The use of silver triflate in the preparations involves the in situ generation of the intermediate triflate complex and is illustrated by the synthesis of the complex *fac*-[Cl$_2$bpy]Re(CO)$_3$Etpy (CF$_3$SO$_3$). Because silver triflate is light sensitive, all operations are performed in a darkened area of the fume hood under a red safelight.

Preparation of *fac*-[(Cl$_2$bpy)Re(CO)$_3$Etpy](CF$_3$SO$_3$). Into a 250-mL boiling flask equipped with Teflon stirbar and reflux condenser is added 400 mg (0.75 mmol) of *fac*-[Cl$_2$bpy]Re(CO)$_3$Cl and 194 mg (0.75 mmol) of AgCF$_3$SO$_3$. To this is added 100 mL of dry THF. The contents of the flask are Ar bubble degassed for 15 min and refluxed under an Ar atmosphere for 3 h in the dark. The contents of the flask are cooled to room temperature and the AgCl precipitate is removed by filtration through a fine-porosity fritted glass funnel. The AgCl precipitate is washed with 3 × 15 mL of methanol and the washings are combined with the filtrate in a clean 250-mL boiling flask equipped with Teflon stirbar. A 0.75-mL portion of Etpy is added to the flask and the contents are Ar bubble degassed for 15 min. The solution is then refluxed under Ar atmosphere for 2 h. The orange-brown solution is cooled to room temperature and the solvent is removed using the rotary evaporator. Purification of the resulting slurry using alumina chromatography as described for *fac*-[[(NEt$_2$)$_2$bpy]Re(CO)$_3$Etpy](CF$_3$SO$_3$) yields 96 mg (17% based on *fac*-[Cl$_2$bpy]Re(CO)$_3$Cl) of *fac*-[Cl$_2$bpy]Re(CO)$_3$Etpy(CF$_3$SO$_3$) as an analytically pure yellow powder. The chromatographic separation is complicated in this case by the presence of a nonluminescent orange-brown impurity which elutes with an R_f similar to that of the desired product. This behavior probably accounts for the low yield of the complex.

Somewhat improved yields of *fac*-[Cl$_2$bpy]Re(CO)$_3$Etpy(CF$_3$SO$_3$) can be attained by using ion exchange chromatography as a purification procedure. In this procedure, the slurry obtained from the workup was mixed with 5 mL of water and acetone was added dropwise to give a homogeneous solution. A column (30 cm × 2 cm i.d.) of SP-Sephadex

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Table I. Electrochemistry of the Complexes[d]

complex[b]	no.	$E^{ox}_{1/2}$, V[c]	$\Delta E^{ox}_{1/2}$, mV[d]	$E^{red}_{1/2}$, V[e]	$\Delta E^{red}_{1/2}$, mV[f]	$E^*_{1/2}(+/0)$, V
$[(NEt_2)_2bpy]Re(CO)_3Etpy(CF_3SO_3)$	**1**	1.43[g]	*h*	−1.63[i]	*h*	0.72
$[Me_4bpy]Re(CO)_3Etpy(CF_3SO_3)$	**2**	1.70	120	−1.40	60	0.79
$[(MeO)_2bpy]Re(CO)_3Etpy(CF_3SO_3)$	**3**	1.65	120	−1.29	60	0.83
$[Me_2bpy]Re(CO)_3Etpy(CF_3SO_3)$	**4**	1.69	110	−1.25	60	0.88
$[bpy]Re(CO)_3Etpy(CF_3SO_3)$	**5**	1.78	80	−1.26	80	0.83
$[Ph_2bpy]Re(CO)_3Etpy(CF_3SO_3)$	**6**	1.71	100	−1.10	60	0.96
$[Cl_2bpy]Re(CO)_3Etpy(CF_3SO_3)$	**7**	1.80	80	−0.94	70	1.01
$[(CO_2Me)_2bpy]Re(CO)_3Etpy(PF_6)$	**8**	>1.90[j]	*h*	−0.77	60	1.11
				−1.15	80	
				−1.93	60	
$[(NO_2)_2bpy]Re(CO)_3Etpy(PF_6)$	**9**	>1.90[j]	*h*	−0.34[k]	60	1.30
				−0.53	80	

[a] Values obtained in 0.2 M TBAH acetonitrile solution at 22 ± 1 °C. [b] Complexes are facial isomers. [c] Estimated potential from the cyclic voltammogram for the reaction $(L)Re^{II}(CO)_3Etpy^{2+} + e^- \rightleftarrows (L)Re^{I}(CO)_3Etpy^+$ $E^{ox}_{1/2}$ (where L = substituted 2,2-bipyridyl ligand) unless noted otherwise. $E^{ox}_{1/2}$, in V vs SSCE, is given by $E_{1/2} = {}^1/_2(E_{p,a} + E_{plc})$, where $E_{p,a}$ and E_{plc} are the potentials of peak anodic and cathodic current, respectively. Other conditions are given in the Experimental Section. [d] Peak splitting, in mV, for the wave representing the reaction in footnote *c* above. $\Delta E^{ox} = |E_{p,a} - E_{p,c}|$. [e] Estimated potential from the cyclic voltammogram for the reaction: $(L)Re(CO)_3Etpy^+ + e^- \rightleftarrows (L^-)Re(CO)_3Etpy^+$ $E^{red}_{1/2}$ (where L = substituted 2,2′-bipyridyl ligand) unless noted otherwise. $E^{red}_{1/2}$, in V vs SSCE, is defined as for $E^{ox}_{1/2}$ in footnote *c* above. [f] Peak splitting, in mV, for the wave representing the reaction in footnote *e* above: $\Delta E^{red} = |E_{plc} - E_{p,a}|$. [g] $E_{p,a}$ in V vs SSCE for the irreversible oxidation of the NEt_2 group: $NEt_2 - e^- \rightleftarrows NEt_2^+$. The wave for the Re(II/I) couple is obscured by the solvent oxidation wave. [h] Unable to determine. [i] $E_{p,c}$ in V vs SSCE for irreversible wave. [j] Re(II/I) couple obscured by the solvent oxidation wave and is not observed. [k] $E^{red}_{1/2}$ values for the reduction of the NO_2 groups as shown: $[(NO_2)_2bpy]Re(CO)_3Etpy^+ + e^- \rightleftarrows [(NO_2)(NO_2^-)bpy]Re(CO)_3Etpy^+$ $E^{red}_{1/2} = -0.35$ V; $[(NO_2)(NO_2^-)bpy]Re(CO)_3Etpy^+ + e^- \rightleftarrows [(NO_2^-)(NO_2^-)bpy]Re(CO)_3Etpy^+$ $E^{red}_{1/2} = -0.53$ V. [l] Calculated from eq 6 of the text using E_{em} values from Table II. Uncertainty estimate is ±0.1 V.

Table II. Spectral Properties of the Complexes[a]

complex[b]	E_{abs} (ϵ)[c]	E_{em}[e]	σ[f]
1	28.20 ± 0.02 (11400 ± 200)	18.94	−0.53
2	29.05 ± 0.30 (3250 ± 260)[d]	17.70	−0.23
3	28.64 ± 0.20 (4300 ± 200)[d]	17.10	−0.15
4	28.67 ± 0.10 (3490 ± 100)	17.20	−0.12
5	28.70 ± 0.10 (3350 ± 100)	16.84	0.00
6	27.70 ± 0.20 (8350 ± 350)[d]	16.61	0.05
7	27.00 ± 0.05 (4000 ± 80)	15.72	0.24
8	26.33 ± 0.05 (4870 ± 80)	15.15	0.46
9	24.70 ± 0.02 (5260 ± 70)	13.24	0.78

[a] Values determined at 22 ± 1 °C in acetonitrile solution. [b] Numbers for complexes are those used in Table I. [c] E_{abs} is the position of the energy maximum for the lowest energy charge-transfer absorption band from the absorption spectrum. E_{abs} has units of 10^3 cm^{-1}. The value in parentheses, ϵ, is the molar decadic extinction coefficient corresponding to E_{abs}. The units of ϵ are L mol^{-1} cm^{-1}. [d] Low-energy shoulder. Value of E_{abs} given is an estimate from the absorption spectrum. [e] Position of the emission maximum in units of 10^3 cm^{-1} corrected for variations in fluorimeter output as a function of emission wavelength/energy. [f] $\sigma = \sigma_p + \sigma_m$. For complex **2** with X = Y = Me, $\sigma_m \neq 0$. For all remaining complexes with Y = H, $\sigma_m = 1$ and $\sigma = \sigma_p$. Values obtained from: Exner, O. In *Correlation Analysis in Chemistry*; Chapman, H. B., Shorter, J., Eds.; Plenum: New York, 1978.

C-25 ion-exchange resin was prepared according to the manufacturer's instructions. A portion of SP-Sephadex C-25 resin was added to the acetone/water solution of the crude product, and the acetone was removed using the rotary evaporator. The crude product adsorbed onto the resin during the evaporative process. Additional portions of resin were added and the process repeated, if necessary, until adsorption was complete. The resin containing the adsorbed material was carefully loaded onto the column. Elution with water removed Etpy and a small amount of unreacted *fac*-$[Cl_2bpy]Re(CO)_3Cl$. The product was eluted as a Cl^- salt with aqueous 0.25 M NaCl. The numerous side products of the reaction remained on the column. The product was isolated as a PF_6^- salt by dropwise addition of a saturated aqueous NH_4PF_6 solution to the 0.25 M NaCl(aq) solution of the complex. The precipitate was collected by suction filtration and washed with three 15-mL portions of ice cold water. The precipitate then was resuspended in 15 mL of water containing 2 drops of saturated NH_4PF_6 solution and 1 mL of methanol, and sufficient acetone to dissolve the solid was added to the suspension. The complex was reprecipitated in pure form by slow evaporation of the acetone/methanol on the rotary evaporator. The solid was collected by suction filtration and washed successively with 10 mL of ice cold water and 2 × 15 mL of diethyl ether. The complex was air suction dried for 15 min and stored in a vacuum desiccator over Drierite overnight. There were obtained 136 mg (yield of 24% based on *fac*-$[Cl_2bpy]Re(CO)_3Cl$) of bright yellow crystals of analytically pure *fac*-$[Cl_2bpy]Re(CO)_3Etpy(PF_6)$.

Using the triflic acid and silver triflate methods described above, the complexes (described by the compound numbers in the tables) were synthesized in the following yields from the corresponding *fac*-$[L]Re(CO)_3Cl$ derivatives: **1**, 58%; **2**, 33%; **3**, 74%; **4**, 80%; **5**, 90%; **6**, 25%; **7**, 24%; **8**, 18%; **9**, 56%. Complexes **1**, **5**, **6**, and **9** were prepared using triflic acid. The other complexes were prepared using silver triflate.

Results

Synthetic routes[13,27,49-52] to the *fac*-$(bpy)Re(CO)_3Etpy^+(X^-)$ ($X = CF_3SO_3$ or PF_6) complexes using either triflic acid or silver triflate are summarized in Figure 1. Extension of this scheme as described here for the synthesis of other *fac*-$(L)Re(CO)_3Etpy^+(X^-)$ complexes (L = substituted 2,2′-bipyridines) is straightforward though not always facile. Initial reaction of equimolar mixtures of L and $(CO)_5ReCl$ in boiling toluene gives the corresponding analytically pure *fac*-$[L]Re(CO)_3Cl$ species in >90% yield for all L studied. In the conversion of $[L]Re(CO)_3Cl$ to $[L]Re(CO)_3Etpy^+$, the choice of triflic acid vs silver triflate is governed primarily by the nature of L. For example, the use of triflic acid is precluded for L containing groups such as CO_2Me or OMe, which are sensitive to the harsh, acidic conditions. For these complexes the use of silver triflate is preferred.

Reactivity of *fac*-$[L]Re(CO)_3Cl$ with either triflic acid or silver triflate is influenced by the nature of L. For L containing electron-donating groups such as NEt_2, OMe, Me, and H in the 4,4′-positions, the desired *fac*-$(L)Re(CO)_3Etpy^+$ complex is generally formed in moderate to good yield and is readily separated from side products using alumina chromatography. Electron-accepting groups such as Cl, CO_2Me, and NO_2 in the 4,4′-positions produce an opposite effect. The desired *fac*-$[L]Re(CO)_3Etpy^+(X^-)$ complexes are produced in low to moderate yields along with a number of charged side products, which necessitates the use of ion-exchange chromatography for purification of the complexes.[53] In all cases, however, analytically pure *fac*-$[L]Re(CO)_3Etpy^+(X^-)$ complexes can be obtained (see supplemental material).

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(53) The synthesis and purification of **8** ($L = (CO_2Me)_2bpy$) presents an especially difficult problem. Behavior of the crude product during ion-exchange chromatography is consistent with partial hydrolysis of the methyl ester during preparation or product workup. In order to obtain usable quantities of the complex, it is necessary to reesterify the product following initial chromatography. This is done by dissolving the dry solid in anhydrous methanol and saturating the solution with anhydrous HCl gas at ice temperature. The methanol/HCl is removed using the rotary evaporator in the hood, and the resulting solid is subjected to ion-exchange chromatography as before. The purified product is isolated as a PF_6^- salt as described in the Experimental Section.

Electrochemical Properties. Cyclic voltammograms of *fac*-(bpy)Re(CO)$_3$L$'^{n+}$ complexes in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as electrolyte tend to be complicated by rapid chemistry that originates from the initial one-electron reduction or oxidation process. For *fac*-(bpy)Re(CO)$_3$Cl, the one-electron oxidation

$$(bpy)Re(CO)_3Cl \rightarrow [(bpy)Re(CO)_3Cl]^+ + e^- \quad (1)$$

is followed by rapid loss of a formal chlorine radical to form [(bpy)Re(CO)$_3$(CH$_3$CN)]$^+$. For the reduction of (bpy)Re(CO)$_3$Cl, a one-electron bpy-based reduction also leads to chloro ligand loss, which is followed either by solvation (eq 3) or fast dimerization (eq 4).[16]

$$(bpy)Re(CO)_3Cl + e^- \rightarrow [(bpy)Re(CO)_3Cl]^- \quad (2)$$

$$[(bpy)Re(CO)_3Cl]^- + CH_3CN \rightarrow [(bpy)Re(CO)_3(CH_3CN)] + Cl^- \quad (3)$$

$$[(bpy)Re(CO)_3Cl]^- \rightarrow \tfrac{1}{2}[(bpy)Re(CO)_3]_2 + 2Cl^- \quad (4)$$

Although we have not undertaken detailed electrochemical studies on the *fac*-[L]Re(CO)$_3$Etpy]$^+$ complexes, it is likely that the origins of chemical irreversibility are similar. In any event, we have confined ourselves to estimating the reversible potentials for both the oxidative and reductive potentials. Electrochemical data for the *fac*-[L]Re(CO)$_3$Etpy$^+$(X$^-$) complexes are listed in Table I.

The reduction potentials, $E_{1/2}(+/0)$, where the added electron is localized on L in the reduced species, can be rationalized in terms of the electron-donor/acceptor abilities of the 4,4′-substituents of L (eq 5). Reduction is expected to become more difficult when

$$(bpy)Re(CO)_3Etpy^+ + e^- \rightarrow [(bpy)Re(CO)_3Etpy] \quad (5)$$

electron donors (e.g., OMe or Me) are present and, conversely, easier for electron acceptors, e.g., Cl or NO$_2$. This behavior is qualitatively observed in Table I where the most negative values of $E_{1/2}(+/0)$ are associated with L possessing good electron donors. For the *fac*-[L]Re(CO)$_3$Etpy$^+$ complexes in Table I the oxidation probably corresponds to the process

$$(bpy)Re(CO)_3Etpy^+ \rightarrow [(bpy)Re(CO)_3Etpy]^{2+} + e^- \quad (6)$$

(i.e., $E_{1/2}(2+/+)$) followed by a coupled chemical reaction much like that observed the parent complex (bpy)Re(CO)$_3$Cl. In general, oxidation occurs at the metal center to initially generate a Re(II) species. For all complexes, the oxidation is quasi-reversible or irreversible and, with the exceptions of **1**, **8**, and **9** (L = (NEt$_2$)$_2$bpy, (CO$_2$Me)$_2$bpy and (NO$_2$)$_2$bpy, respectively), the estimated $E_{1/2}(2+/+)$ values vary over a narrow potential range (1.6–1.8 V vs SSCE). For **1**, a broad, irreversible peak with E_p of ca. +1.43 V vs SSCE is observed. Preliminary experiments indicate that this wave represents an oxidation of the diethylamino group followed by a rapid chemical process, perhaps polymerization of the product at the electrode surface.[54] We observe no evidence for an additional, metal-based wave in the 1.4–1.9-V range for this complex.[55] For **8** and **9**, no wave corresponding to eq 6 is observed below the onset of solvent oxidation at 1.9 V vs SSCE.

Spectral Properties and Excited-State Potentials. The colors of the complexes vary from red for [L] = 4,4′-(NO$_2$)$_2$bpy to pale yellow for [L] = 4,4′-(NEt$_2$)$_2$bpy due principally to a MLCT transition which is d$_\pi$(Re) → π^*(L) in nature. As for previously investigated polypyridyl–Re(I) complexes, a broad emission band that is predominantly triplet–singlet in character is observed in the range 13 000–19 000 cm^{-1}. Combined with the absorption and emission data, electrochemical data have proven useful as tools for the estimation of MLCT excited state redox potentials of α-diimine complexes of d^6 transition metals such as Ru(II) and Os(II).[36,37,56–59] Knowledge of the ground-state redox potential permits an estimation of the excited-state potential for such cases. Because the *fac*-[L]Re(CO)$_3$Etpy$^+$ complexes discussed here represent a series of structurally and electronically similar species, similar correlations are expected between MLCT spectral properties and ground-state parameters such as $E_{1/2}$ values (vide infra).

Table III. Observed and Calculated Photophysical Parameters for the Complexes[a]

complex[b]	ϕ_r[c]	τ[d]	10^4k_r[e]	10^6k_{nr}[f]	ln k_{nr}[h]
1	0.1102	3400	3.24	0.262	12.48
2	0.0907	1500	6.05	0.606	13.32
3	0.0195	155	12.6	6.33	15.56
4	0.0352	282	12.5	3.42	15.04
5	0.0287	230	12.5	4.05	15.21
6	0.0566	351	16.1	2.69	14.80
7	0.0064	36	17.8	27.6	17.13
8	0.0122	75	16.3	13.2	16.39
9	$\leq 1.7 \times 10^{-4}$[g]	≤ 8[g]	2.12	125	18.64

[a] Values in Ar-degassed acetonitrile solution at 22 ± 1 °C. [b] Numbers for complexes are those used in Table I. [c] Quantum yields determined vs reference solution of Ru(bpy)$_3$(PF$_6$)$_2$ in degassed acetonitrile at 22 ± 1 °C (ϕ_{ref} = 0.062). [d] Luminescence lifetime at 22 ± 1 °C in degassed acetonitrile solution. Units are ns. [e] Radiative rate constant for the relaxation of the MLCT state to the ground state. Units are s^{-1}. [f] Nonradiative rate constant for the relaxation of the MLCT state to the ground state. Units are s^{-1}. [g] Values at or below detection limits of instrument. [h] Units of k_{nr} are s^{-1}.

One such use of the redox potential data from Table I involves the estimation of the oxidizing and reducing strength of the MLCT excited state. For the types of systems considered here, the appropriate equations are

$$E_{1/2}(+^*/0) = E_{1/2}(+/0) + E_{em}/8066 \quad (7)$$

$$E_{1/2}(2+/+^*) = E_{1/2}(2+/+) - E_{em}/8066 \quad (8)$$

where $E_{1/2}(+^*/0)$ (V) measures the strength of the MLCT excited state as an oxidant

$$fac\text{-}\{[L^-]Re^{II}(CO)_3Etpy\}^{+*} + e^- \rightarrow fac\text{-}[L^-]Re^{I}(CO)_3Etpy \quad E_{1/2}(+^*/0) \quad (9)$$

and $E_{1/2}(2+/+^*)$ (V) measures the strength of the MLCT excited state as a reductant

$$fac\text{-}\{[L^-]Re^{II}(CO)_3Etpy\}^{+*} \rightarrow fac\text{-}[L]ReI^{II}(CO)_3Etpy^{2+} + e^- \quad E_{1/2}(2+/+^*) \quad (10)$$

The ground-state redox potentials in eqs 7 and 8 are expressed in volts while E_{em} is the position of the corrected emission maximum in wavenumbers for the complexes (note Table II). For the data in Table II, calculation of $E_{1/2}(2+/+^*)$ is rendered difficult by an absence of data for the complexes anchoring opposite ends of the series (i.e., **1**, **8**, and **9**) and uncertainties in $E_{1/2}(2+/+)$ values due to the quasi-reversible or irreversible nature of the ground-state oxidation process. Because of these problems in determining accurate values of $E_{1/2}(2+/+)$, the calculation of $E_{1/2}(2+/+^*)$ is awkward and none appear in Table I.[60]

Problems with the estimation of the $E_{1/2}(+/0)$ are not serious. Therefore, the $E_{1/2}(+^*/0)$ values calculated from eq 6 and listed in Table I are expected to provide reliable excited-state potentials.

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(55) The polymerization of the NEt$_2$ group via oxidation of **1** produces a polymer film on the electrode surface.[54] The absence of an observable Re(II/I) wave for **1** in solution may be the result of limited accessbility of the solution species to the Pt electrode surface or changes in the permeability of the electrode to interfacial electron transfer caused by the polymer barrier film.

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(60) Work is in progress in our laboratories to measure directly the values of $E_{1/2}(2+/+^*)$ and $E_{1/2}(+^*/0)$ for **1**–**9** by standard techniques.[57]

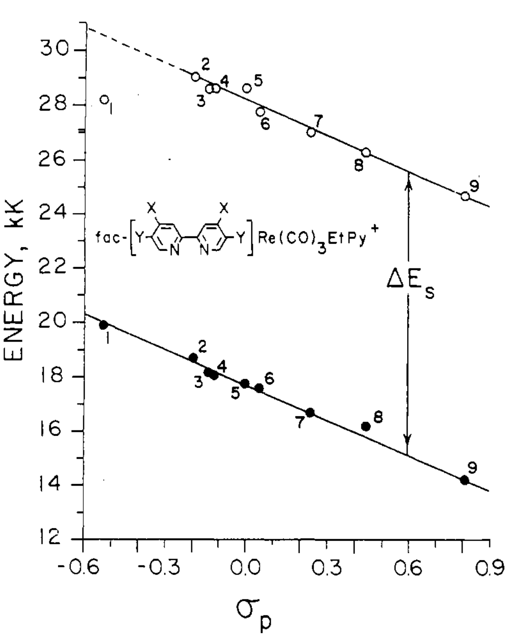

Figure 2. Transition energies vs σ_T correlation plots. Complexes are numbered as indicated in Table I. Open circles indicate absorption energy values, and closed circles represent corrected emission energy values. See text for correlation coefficients and slope and intercept values. Absorption energy for complex **1** is not used in the linear regression analysis (see text).

As will be discussed later, $E_{1/2}(+^*/0)$ values are observed to vary monotonically with $E_{1/2}(+/0)$ in a manner similar to that noted previously for the Os(II)-2,2'-bipyridine chromophores.[36,37,59] The MLCT excited states of the *fac*-[L]Re(CO)$_3$Etpy$^+$ complexes are moderate to good oxidants in solution. $E_{1/2}(+^*/0)$ values range from +0.72 V vs SSCE for **1** to +1.11 V vs SSCE for **8**. For the *fac*-[(NO$_2$)$_2$bpy]Re(CO)$_3$Etpy$^+$ complex (**9**), a value of $E_{1/2}(+^*/0) = +1.30$ V vs SSCE can be calculated using the data in Table I.

Photophysical Parameters. Table III shows the photophysical parameters ϕ_r, the radiative quantum yield of emission, τ, the radiative lifetime of the emitting state, and k_r and k_{nr}, the radiative and nonradiative rate constants, respectively. As is seen in the table all of these properties vary over a wide range when the nature of the substituted bpy ligand is changed. Most dramatic is the change in k_r, and τ, which vary by orders of magnitude.

Discussion

Correlations of Substituent Parameters with Redox Potentials and Excitation Energies. Since thermal population of d–d excited states from the MLCT excited-state manifold, which occurs at room temperature for Ru(bpy)$_3^{2+}$ and its derivatives,[61-70] is less facile for Re(I) complexes,[20] our complexes can be considered two-state systems consisting of MLCT excited and ground states. Absorption and emission are then interrelated processes involving mutually accessible transitions.

For the Re(I) complexes, excited state properties are influenced by the nature of the X, Y substituents of L as indicated qualitatively by the $E_{1/2}(+^*/0)$ values shown in Table I. For reasons of excited-state design, it is desirable to relate ground-state properties such as the $E_{1/2}(2+/+)$ and $E_{1/2}(+/0)$ values and specific MLCT excited-state properties via predictive parameters that are characteristic of X and Y.

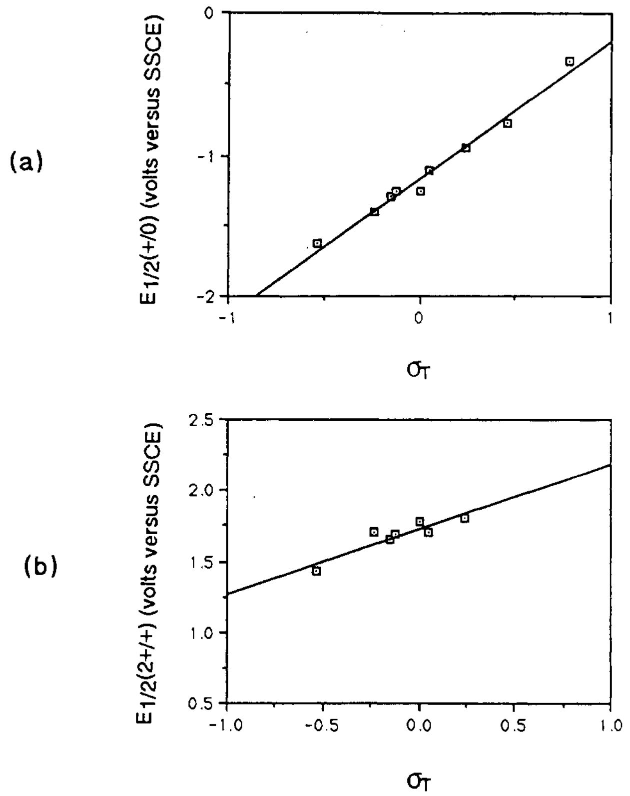

Figure 3. Correlation of $E_{1/2}(+/0)$ (a) and $E_{1/2}(2+/+)$ (b) for the *fac*-(L)Re(CO)$_3$Etpy$^+$ complexes with σ_T. See text for correlation coefficients and slope and intercept values.

Earlier studies[71,72] on Ru(L)$_3^{2+}$ were only partially successful in establishing a predictive relationship between ground- and excited-state properties and Hammett-type parameters. In our series of complexes, however, quite striking correlations do exist. For the *fac*-[L]Re(CO)$_3$Etpy$^+$ complexes, even with the irreversible nature of the redox processes, it is apparent that the energies of both the metal redox orbitals (dπ(Re)) and the ligand-based orbitals vary with the nature of the substituent, although the former are less sensitive. In cases such as this, where the magnitude of an energy quantity is controlled predominantly by an "electronic" factor, it is often possible to describe the behavior of the system using a linear free energy relationship.[73,74] One such relationship, as suggested by the structure of the *fac*-[L]-Re(CO)$_3$Etpy$^+$ complexes, is the Hammett equation[73]

$$-\Delta G = 2.3RT\rho\sigma_T - \Delta G_0 \qquad (11)$$

In eq 11, $-\Delta G$ is a free energy change for the process of interest, i.e. either a redox potential, spectroscopic quantity, or any *kinetic parameter that is determined by these quantities*. ΔG_0 is the free energy change for a reference *fac*-[L]Re(CO)$_3$Etpy$^+$ complex, R is the ideal gas constant and T is the absolute temperature in K. The σ_T values provide a measure of the total electrical effects of the L substituents, and are defined as $\sigma_T = \sigma_p + \sigma_m$, where the σ parameters are those derived for substituent effects at the para

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and meta positions of aromatic substrates. ρ is a measure of the susceptibility of the process under examination to such effects. A negative value of σ_T indicates an electron-donor group and a positive value an electron-acceptor group. The σ values are defined[73-75] such that $\sigma = 0$ for H atom substituents on an aromatic ring system, in our case, polypyridine ligands. For the extended series of *fac*-[4,4′-X_2-5,5′-Y_2-2,2′-bipyridine]Re(CO)$_3$Etpy$^+$ complexes, Y = H for most X so that $\sigma_T = \sigma_p$.[76]

Figure 3 shows the correlations of ground-state redox potentials, $E_{1/2}(2+/+)$ and $E_{1/2}(+/0)$, with σ_T. For the ligand-based reduction all of the data in Table I were used, but for the metal-based oxidation processes complexes **1**, **8**, and **9** were eliminated due to the ligand-based nature of the former and our inability to observe the latter. Linear regression analysis gives the following relationships (in V):

$$E_{1/2}(+/0) = 0.97\sigma_T - 1.16 \qquad r = 0.99 \tag{12}$$

$$E_{1/2}(2+/+) = 0.46\sigma_T + 1.73 \qquad r = 0.91 \tag{13}$$

A standard relation for absorption energy of a MLCT transition, E_{abs}, is[77]

$$E_{abs} = a\Delta E + \chi_T \tag{14}$$

and that for the related emission of the "triplet" associated with initial absorption process, E_{em}, is

$$E_{em} = a'\Delta E - \chi_T - E_{sp} \tag{15}$$

In eqs 14 and 15, ΔE is the difference in orbital energies between the thermally equilibrated HOMO and LUMO immersed in the medium, χ_T is the reorganization energy associated with the transition, and E_{sp} is the spin pairing energy. For the charge-transfer process between Re and L, if it is assumed that the donor dπ(Re) orbital is unmixed with the acceptor π^*(L) orbital, $a = a' = 1$,[78] and the relation in eq 16 holds.

$$\Delta E = E_{1/2}(2+/+) - [E_{1/2}(+/0) - E_{el}] \tag{16}$$

Contributors to eq 15 are the ground-state redox potentials and a constant E_{el} that corrects for the fact that the ligand-localized reduction in the excited state is somewhat different from $E_{1/2}(+/0)$ since it takes place in the presence of a Re^{II} core. Thus

$$\Delta E = -0.51\sigma_T + 2.89 + E_{el} \tag{17}$$

$$E_{abs} = a(-0.51\sigma_T + 2.89 + E_{el}) + \chi_T \tag{18}$$

$$E_{em} = a'(-0.51\sigma_T + 2.89 + E_{el}) - \chi_T - E_{sp} \tag{19}$$

Experimental linear correlations of the energies of the lowest energy MLCT absorption maxima (open circles) and MLCT emission maxima (closed circles) with σ_T are shown in Figure 2. Absorption and emission data in MeCN used in the construction of Figure 2 are listed in Table II. The absorption and emission correlations are found to be[79]

$$E_{abs} = -0.53\sigma_T + 3.49 \qquad r = 0.99 \tag{20}$$

$$E_{em} = -0.51\sigma_T + 2.08 \qquad r = 0.99 \tag{21}$$

From inspection of eqs 18–21 it is apparent that $a = a' = 1$ within the error of the experiments and that the displacement between the emission and absorption correlation lines is a constant, ΔE_s = 1.41 V, which is approximately equal to $2\chi_T + E_{sp}$. Even though estimates of the outer-sphere (solvent) contribution to χ_T can be made for Re^I(bpy) complexes,[80] an accurate estimation of E_{sp} or E_{el} is not possible at this time.

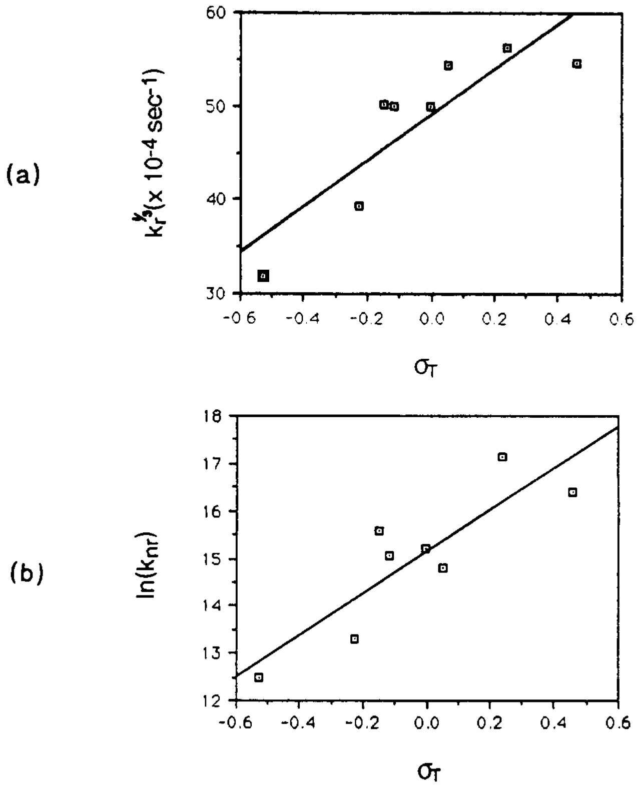

Figure 4. Correlation of ln k_{nr} (a) and $k_r^{1/3}$ (b) for the *fac*-(L)Re(CO)$_3$Etpy$^+$ complexes with σ_T. See text for correlation coefficients and slope and intercept values.

A comment that should be made concerning the redox correlations is that the ρ values found in eqs 12 and 13 demonstrate that the change in the primarily ligand-based LUMO dominates the change in E_{abs} and E_{em} and that the substituent effect is weakly transmitted to the metal.

Correlations with Nonradiative and Radiative Rates. As shown in Table III the excited state lifetimes, τ, generally decrease with increasing σ_T. Similar behavior has been found in studies on MLCT excited states of α-diimine complexes of Ru(II)[20,81,82] and Os(II)[34] as well as the series *fac*-[bpy]Re(CO)$_3$L′$^+$ (L′ = PMe$_3$, pyridine, MeCN, or other monodentate, neutral ligands) complexes.[11,20] A reason for this correlation is found in the "energy gap law" behavior exhibited by the complexes.[34]

In the absence of accessible d–d excited states, MLCT excited-state relaxation to the ground state in 2,2′-bipyridine complexes of low-spin d^6 transition-metal complexes occurs via both radiative and nonradiative paths directly to the ground state. Of the two, the nonradiative decay rate (in the weak coupling limit) for a series of related complexes, k_{nr}, is likely governed by the degree of overlap between specific vibrational wave functions of the MLCT excited-state with isoenergetic ground-state vibrational wave functions. Generally, overlap is increased as the energy difference between the excited and ground electronic states decreases, and this leads to accelerated nonradiative decay. The "energy gap law" in eq 22 provides an approximate, empirical description of this dependence, where the emission energy, E_{em} is taken as an

$$\ln k_{nr} = A - BE_{em} \tag{22}$$

approximation of the energy gap between the lowest vibrational levels of the excited state accessible by thermal population and those appropriate to the ground state. The A term contains

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information regarding the vibrationally induced electronic coupling between states. The B term contains information concerning the nature of the ground-state acceptor vibrations and their role in excited-state deactivation.[20,34,71,81,82]

Substituting the E_{em} relation in eq 21 into eq 22, allows the following to be obtained:

$$\ln k_{nr} = A - B(-0.51\sigma_T + 2.08) \quad (23)$$

The observed relation, as shown in Figure 4a, is described by eq 24.

$$\ln k_{nr} = 4.38\sigma_T + 15.14 \quad (24)$$

When eqs 23 and 24 are combined, A is 29.70 and B is -8.59 V^{-1}. Previous studies have shown two classes of behavior for the constants depending upon complex structure. For complexes not containing a coordinated CO ligand, slopes (B) in the range -7.5 ± 1.5 V^{-1} and intercepts (A) of <31 have been observed.[20,34,71,81,82] For *fac*-[bpy]Re(CO)$_3$L′$^+$ complexes[11] and other complexes containing the coordinated CO ligand,[20,34] slopes of -11.8 to -15 V^{-1} and intercepts >31 have been noted. For complexes without the coordinated CO ligand, the C–C stretching vibrations of the bipyridine skeleton at ca. 1350 cm^{-1} are implicated as key acceptor vibrations in MLCT excited-state deactivation based on vibrational structure analysis of low-temperature emission spectra.[20] For complexes containing coordinated CO, little vibronic structure has been observed in the emission spectra down to 77 K. It has been suggested, however, that CO stretching vibrations at ca. 2000 cm^{-1} replace the C–C vibrations as the primary acceptor vibrations for such complexes.[20] In our work, the slope of -8.59 V^{-1} is close to that noted previously for complexes without coordinated CO ligands.[83] The intercept of 29.70, though near the upper level of the region associated with the C–C vibrations, is still sufficiently large that some CO character could be inferred. It is possible that the C–C- and CO-based acceptor vibrations *both* play a role in radiationless decay with the former being dominant.

Radiative rates, as shown in Table III, are also expected to be correlated with σ_T according to the Einstein formula for spontaneous emission, which varies approximately as the cube of the emission energy

$$k_r = CE_{em}^3 \quad (25)$$

and experimentally can be expected to be

$$k_r^{1/3}C^{-1/3} = -0.51\sigma_T + 2.08 \quad (26)$$

The actual fit is

$$k_r^{1/3} = 24.40\sigma_T + 49.18 \qquad r = 0.87 \quad (27)$$

Equation 27 and Figure 4, which shows the experimental correlation, indicate that the coefficient C, which should be positive, has a negative value. Since both the Einstein or Strickler–Berg formulation of spontaneous emission involve the total overlap of excited-state and ground-state wave functions which is measured by the integrated overlap of the transition, one possible explanation is that the complexes exhibit a large systematic decrease in the bandwidth as the emission energy moves to lower values. Spectral fitting analysis for the related complexes *fac*-[4,4′-X$_2$-5,5′-Y$_2$-2,2′-bipyridine]Re(CO)$_3$Cl[35] supports this trend. In passing, it should be noted that whether or not Hammett parameters are used to express the emission energy or the value of E_{em} (which is assumed to be directly proportional to the overlap) the correlation has a negative slope. Additional work on this problem in underway.[84]

Conclusions

The new Re(I) compounds presented here are an extended series of related complexes exhibiting observable, room-temperature, MLCT excited-state emission in which the excited-state properties are systematically and precisely controlled by the substitution pattern of the diimine chelating ligand.[35,36] The range of excited-state properties spanned by the complexes is comparable to that observed for the related *fac*-[bpy]Re(CO)$_3$L′$^+$ (L′ = PMe$_3$, pyridine, MeCN, and other monodentate, neutral ligands) complexes[11,20] as well as previously described diimine Os(II) complexes.[34,36,37,85] In addition, the complexes are readily synthesized by straightforward extensions of literature techniques.[9,11,20,27,39,49–52] These properties provide a basis for the use of the *fac*-[L]Re(CO)$_3$Etpy$^+$ complexes as potential photosensitizers in micellar environments[33,85] and nonaqueous solar energy storage schemes.[86,87] In contrast to earlier studies using RuL$_3$$^{2+}$ derivatives,[71,72,88] both excited-state and ground-state properties including ground-state redox potentials, excited-state redox potentials, emission maxima, radiative and nonradiative rate constants, and radiative lifetimes for the *fac*-[L]Re(CO)$_3$Etpy$^+$ complexes correlate linearly with the electron-donor/acceptor strength of the L. The substituent effect is measured by the sum of the Hammett parameters σ_p and σ_m on the bipyridine nucleus. The origin of the substituent correlations in our series for both thermodynamic and kinetic quantities can be traced directly to the ability of ring substitution to systematically modify both the ground-state redox potential of the coordinated bipyridine ligand and the ground-state redox potential of the Re center, with the former being the dominant effect. Thus, the individual redox potentials or the quantity $\Delta E_{1/2} = E_{1/2}(2+/+) - E_{1/2}(+/0)$ can be related directly to all of the thermodynamic and kinetic quantities within the series.

The difficulty in obtaining extensive correlations of some of the photophysical parameters with σ_p in the case of the RuL$_3$$^{2+}$ complexes[88] may be attributed to competitive deactivation of the MLCT excited-state by neighboring d–d states in these compounds. The successful correlation of such a wide variety of MLCT excited-state properties in the *fac*-[L]Re(CO)$_3$Etpy$^+$ series with substituent constants represents the most extensive correlation of this type known to us.[36] It permits the quantitative prediction of excited-state properties directly from the single ground-state Hammett σ_T value. For the *fac*-[L]Re(CO)$_3$Etpy$^+$ complexes, an energy gap law is obeyed so that a plot of ln k_{nr} vs E_{em} is linear as expected. Participation of both CO-based and bipyridyl C–C-based acceptor vibrations as acceptor modes in excited-state MLCT deactivation is apparently involved given the structure of the complexes. The role of the CO-based acceptor vibrations in radiationless decay appears important, although relatively constant within the series of complexes, so that variations in k_{nr} arise primarily from variations in the C–C acceptor vibrations. This behavior contrasts with that of *fac*-[bpy]Re(CO)$_3$L′$^+$ complexes in which CO-based modes appear to dominate the decay process.[11,20] Consequently, the *fac*-(bpy)Re(CO)$_3$L′$^+$ and *fac*-[L]-Re(CO)$_3$Etpy$^+$ complexes taken together represent a unique system in which structural variations may be used to factor the nonradiative components of MLCT excited-state decay for observation and study.

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Registry No. **1**, 126183-72-0; **2**, 138518-54-4; **3**, 138518-55-5; **4**, 138518-56-6; **5**, 138518-57-7; **6**, 138518-58-8; **7**, 126205-14-9; **8**, 138518-59-9; **9**, 138518-60-2; *fac*-[(NEt$_2$)$_2$bpy]Re(CO)$_3$CF$_3$SO$_3$, 126183-69-5; *fac*-[Cl$_2$bpy]Re(CO)$_3$Etpy(PF$_6$), 126183-74-2; *fac*-[(NEt$_2$)$_2$bpy]Re(CO)$_3$Cl, 126183-70-8; *fac*-[Me$_4$Nbpy]Re(CO)$_3$Cl, 138518-61-3; *fac*-[(MeO)$_2$bpy]Re(CO)$_3$Cl, 134438-70-3; *fac*-

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Supplementary Material Available: A table containing all elemental analyses for the complexes described in the Experimental Section (1 page). Ordering information is given on any current masthead page.

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and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Kinetic and Structural Studies on the Oxotetracyanotechnetate(V) Core: Protonation and Ligation of Dioxotetracyanotechnetate(V) Ions and Crystal Structure of 2,2′-Bipyridinium *trans*-Oxothiocyanatotetracyanotechnetate(V)

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The tetracyanodioxotechnetate(V) ion undergoes protonation reactions in acidic aqueous solutions, forming the $[TcO(OH)(CN)_4]^{2-}$ (**1**) and $[TcO(OH_2)(CN)_4]^-$ (**2**) complexes. A dimeric species, $[Tc_2O_3(CN)_8]^{4-}$ (**3**), is rapidly formed from the hydroxo oxo complex, and it is therefore impossible to isolate complex **1**. The coordinated water of $[TcO(H_2O)(CN)_4]^-$ can be displaced by monodentate ligands such as thiocyanate. The reaction with thiocyanate ions gives $[TcO(NCS)(CN)_4]^{2-}$ (**4**), the composition and structure of which was confirmed by means of an X-ray crystal structure determination. 2,2′-Bipyridinium oxothiocyanatotetracyanotechnetate(V) ($C_{25}H_{18}N_9OSTc$) crystallizes in the monoclinic space group, $C2/c$, with a = 18.210 (4) Å, b = 19.473 (1) Å, c = 15.501 (3) Å, β = 107.501 (14)°, Z = 8, ρ_{calc} = 1.490 g cm^{-3}. A final R value of 6.4% resulted from refinement of 1868 observed reflections. The first acid dissociation constant of **2** (at 15.0 °C), the forward and reverse rate constants, and the equilibrium quotient for the reaction (at 25.0 °C)

$$\mathit{trans}\text{-}[TcO(H_2O)(CN)_4]^- + NCS^- \underset{k_{-1}}{\overset{k_1,\,K_1}{\rightleftharpoons}} \mathit{trans}\text{-}[TcO(NCS)(CN)_4]^{2-} + H_2O$$

have been determined in 1.0 M (KNO_3) ionic strength aqueous medium as $10^{-2.90\,(5)}$, 22.2 (3) $M^{-1}\,s^{-1}$, 0.43 (4) s^{-1}, and 54 (2) M^{-1}, respectively.

Introduction

Technetium-99m agents are widely used in diagnostic nuclear medicine, while rhenium-186 and rhenium-188 agents are being actively investigated for radiotherapy.[5] In some cases the proposed use of radiorhenium for therapy is predicted on the chemistry and biodistribution of the analogous technetium agent. Since one can qualitatively predict that aspects of the chemistries of technetium and rhenium will not exactly be analogous,[5,6] it becomes important for the use of radiorhenium in nuclear medicine to quantitively assess the extent to which the solution chemistries of technetium and rhenium differ. Many diagnostic technetium agents contain the radioactive metal in the +5 oxidation state. Thus, in this paper we focus our attention on the comparative aqueous solution chemistry of analogous Tc(V) and Re(V) centers.

It was shown previously that the $[MO_2(CN)_4]^{n-}$ ions of Mo(IV), W(IV), and Re(V) may undergo successive protonation reactions to form the corresponding hydroxo oxo and aqua oxo species.[7] It was further shown that the aqua ligand in the $[MO(H_2O)(CN)_4]^{m-}$ ions may be substituted by mono- and bidentate (for the Mo(IV) and W(IV) systems only) ligands.[7,8] These studies lead to predictions regarding other known dioxo tetracyano complexes, that of Tc(V) and Os(VI).[9] It was recently shown that the $[OsO(H_2O)(CN)_4]$ complex is a too strong acid and $[OsO_2(CN)_4]^{2-}$ can therefore not be protonated.[9] In the case of Tc(V), however, the periodicity and the known chemistry of the neighboring metals suggested that protonation and subsequent ligand substitution should be possible. The investigation of these phenomena in the Tc(V) system is described herein.

Experimental Section

General Considerations. Technetium-99 emits a low-energy (0.292 MeV) β-particle with a half-life of 2.12 × 10^5 years. When this material is handled in milligram amounts, it does not present any serious health hazard since ordinary laboratory glassware and other materials provide adequate shielding. Brehmstralung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times, especially when solid samples are handled, to prevent contamination and inadvertent inhalation.

Unless otherwise noted, all chemicals were of reagent grade. $NH_4{}^{99}TcO_4$ was purchased from Oak Ridge National Laboratory and was purified as described previously.[10] (n-Bu_4N)[$TcOCl_4$] was prepared by the method of Davison.[11] All experiments were performed aerobically

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