Articles

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Ligand-Bridged Rhenium(I) Complexes: An Electrochemical and Photophysical Study

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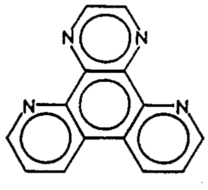
The synthesis and properties of a series of rhenium(I) carbonyls incorporating the bidentate bridging ligands 4′,7′-phenanthrolino-5′,6′:5,6-pyrazine (ppz), 2,3-bis(2-pyridyl)pyrazine (bppz), and 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (ddpq) have been investigated. All mononuclear complexes are emissive in room-temperature fluid solution; the luminescence originates from an MLCT excited state. On the other hand, emission was detected for only one of the binuclear complexes, $[(ppz)(Re(CO)_3(CH_3CN))_2]^{2+}$. The lack of emission from the remaining binuclear species is attributed to the perturbation of the π^* orbital on the bridging ligand that results from the attachment of the second metal center. The magnitude of this effect has been probed by electrochemical and spectroscopic experiments. Lifetime measurements confirm the existence of a correlation between MLCT energy and the nonradiative decay rate, and the observed trend is in at least qualitative agreement with the energy gap law. Variations in the quantum yield for emission between similar complexes possessing different bridging ligands are attributed to changes in ligand rigidity, and complexes of ppz exhibit the largest ϕ_{em} values. Not only are the corresponding bppz and ddpq derivatives much weaker emitters, but steric interactions lead to the thermal decomposition of binuclear complexes based on these ligands.

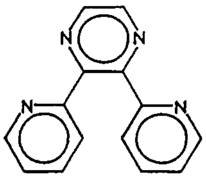
Introduction

Ligand-bridged multinuclear complexes have been extensively explored by several groups in an effort to achieve a more complete understanding of their electronic and photophysical properties.[1-35] Much of the impetus for this work stems from the potential utility of such complexes in photochemical energy storage schemes, as multielectron redox agents, and in fundamental investigations of intramolecular electron- and energy-transfer processes. In particular, group 6 metal carbonyls[16-25] and ruthenium polypyridines[1-13] have been widely studied in this regard. More recently, rhenium polypyridines have begun to receive attention,[26-35] owing to their attractive ground-state properties and high quantum efficiency for emission from the metal-to-ligand charge-transfer (MLCT) excited state.[26-42] The lack of emission from the first binuclear complex of this type, $[Cl(CO)_3Re(bpym)Re(CO)_3Cl]$ (where bpym = 2,2′-bipyrimidine) was attributed to the population of a low-lying nonemissive metal-to-metal charge-transfer (MMCT) state from the initially populated MLCT level.[26] However, given the intrinsic thermodynamic difficulty of both the one-electron oxidation and the one-electron reduction of the rhenium center in related complexes, such an event seems unlikely. Indeed, other reports suggest that the decrease in energy of the π^* orbital on the bridging ligand upon attachment of the second metal is of prime importance and that the observed photophysics are controlled, at least in part, by the energy gap law.[34,35,43-48] In order to gain more insight into the electronic properties of binuclear complexes, we have prepared a series of mononuclear and binuclear species containing the potential bridging ligands 4′,7′-phenanthrolino-5′,6′:5,6-pyrazine (ppz), 2,3-bis(2-pyridyl)pyrazine (bppz), and 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (ddpq) (structures I–III). Specifically, the effects of supporting ligands and secondary metal attachment on the energetics of these systems have been explored. A comparison of the spectroscopic and photophysical properties of such complexes is especially revealing, and the observed behavioral differences can be accounted for in terms of electronic and structural features.



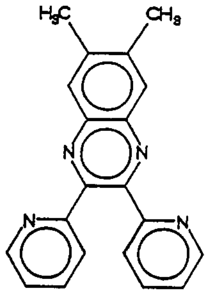
4′,7′-phenanthrolino-5′,6′:
5,6-pyrazine (ppz)

I



2,3-bis (2-pyridyl)
pyrazine (bppz)

II



6,7-dimethyl-2,3-di
(2-pyridyl)-quinoxaline
(ddpq)

III

Experimental Section

Materials. $Re(CO)_5Cl$ was purchased from the Pressure Chemical Co. and was used without further purification. The bridging ligands 2,3-bis(2-pyridyl)pyrazine (bppz) and 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (ddpq) were obtained from Aldrich; bppz was used as received, while ddpq was recrystallized in chloroform before use. 4′,7′-

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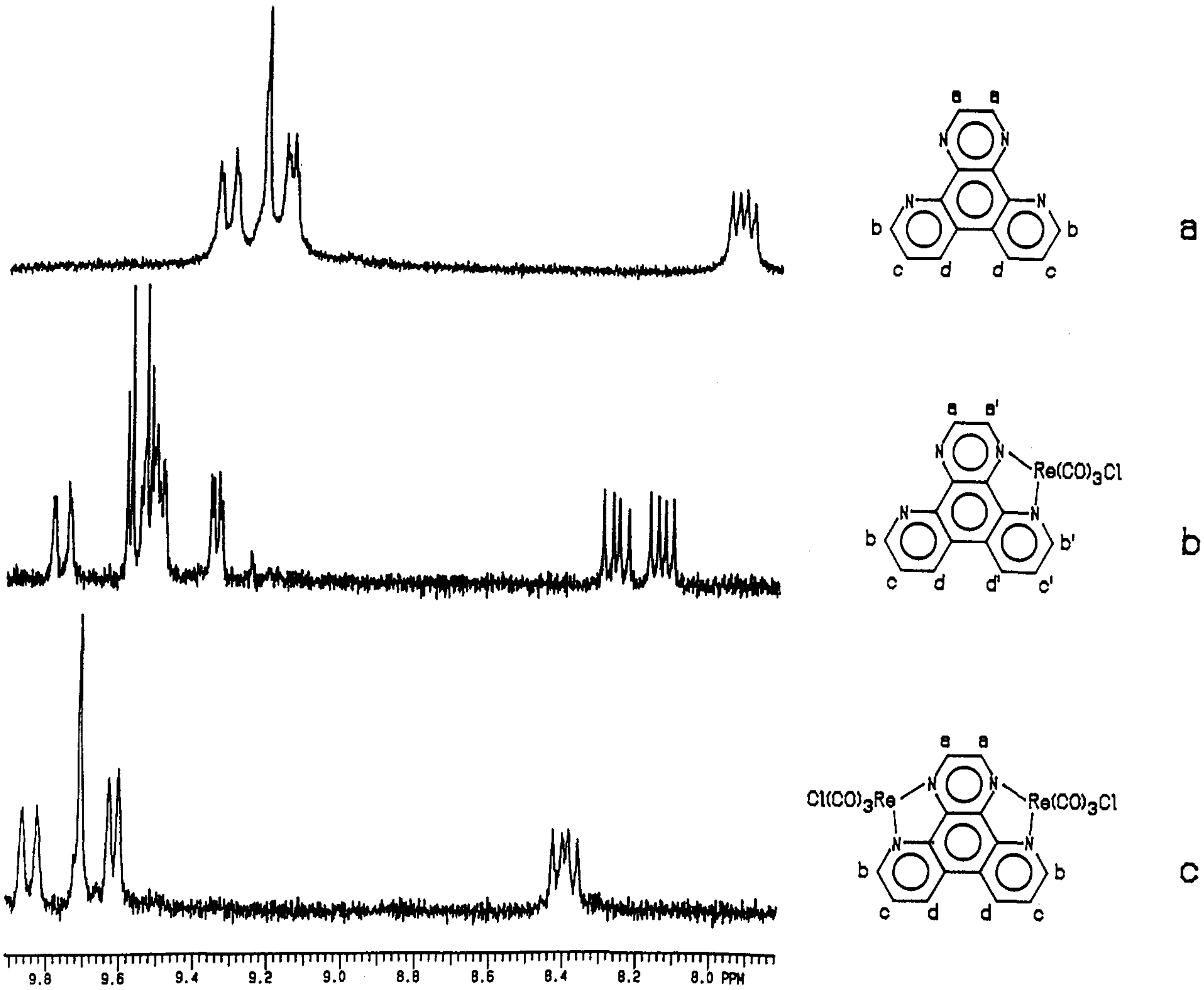

Figure 1. ^1H NMR spectra of (a) ppz free ligand, (b) $(ppz)Re(CO)_3Cl$, and (c) $(ppz)(Re(CO)_3Cl)_2$ in DMSO-d_6.

Phenanthrolino-5',6':5,6-pyrazine (ppz) was prepared by the procedure of Schmidt and Druey.[49] The 4,7-phenanthroline-5,6-dione employed in this synthesis was a generous gift from Ciba-Geigy, Ltd., and was used as received. All solvents used in the spectroscopic and electrochemical studies were spectral grade (Burdick & Jackson); acetonitrile was freshly distilled over calcium hydride. Tetraethylammonium perchlorate (TEAP) (Southwestern Analytical, electrometric grade) was dried overnight in a vacuum oven prior to use. Mononuclear complexes *fac*-$(LL)Re(CO)_3Cl$ and *fac*-$[(LL)Re(CO)_3(CH_3CN)](CF_3SO_3)$ (LL = ppz, bppz, or ddpq) were prepared by literature methods.[38,50] The binuclear species were prepared as described below for the ppz complexes.

$(ppz)(Re(CO)_3Cl)_2$. $Re(CO)_5Cl$ (213 mg, 0.59 mmol) and ppz (67 mg, 0.29 mmol) were dissolved by sonication in 150 mL of methanol. The reaction mixture was refluxed for 18 h under a nitrogen atmosphere

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Table I. ^{1}H NMR Data for ppz Complexes[a]

compd	chem shift, ppm
ppz	H_a: 9.25 (2 H, s)
	H_b: 9.36 (2 H, d, J_{bc} = 8.3 Hz)
	H_c: 7.96 (2 H, dd, J_{cb} = 8.3 Hz, J_{cd} = 4.2 Hz)
	H_d: 9.18 (2 H, d, J_{dc} = 4.2 Hz)
$(ppz)Re(CO)_3Cl$	H_a: 9.52 (1 H, d, $J_{aa'}$ = 2.7 Hz)
	$H_{a'}$: 9.57 (1 H, d, $J_{a'a}$ = 2.7 Hz)
	H_b: 9.54 (1 H, d, J_{bc} = 8.4 Hz)[b]
	$H_{b'}$: 9.76 (1 H, d, $J_{b'c'}$ = 8.6 Hz)
	H_c: 8.13 (1 H, dd, J_{cb} = 8.4 Hz, J_{cd} = 4.4 Hz)
	$H_{c'}$: 8.26 (1 H, dd, $J_{c'b'}$ = 8.5 Hz, $J_{c'd'}$ = 5.2 Hz)
	H_d: 9.34 (1 H, d, J_{dc} = 4.4 Hz)
	$H_{d'}$: 9.49 (1 H, d, $J_{c'd'}$ = 5.2 Hz)
$(ppz)(Re(CO)_3Cl)_2$	H_a: 9.70 (2 H, s)
	H_b: 9.84 (2 H, d, J_{bc} = 8.0 Hz)
	H_c: 8.39 (2 H, dd, J_{cb} = 8.0 Hz, J_{cd} = 5.1 Hz)
	H_d: 9.61 (2 H, d, J_{dc} = 5.1 Hz)

[a] s = singlet, d = doublet, dd = doublet of doublets; DMSO-d_6 as solvent; peak shifts relative to TMS internal standard = 0 ppm. [b] H_b is partially obscured under H_a; coupling constant was not obtained directly.

and then reduced in volume to approximately 10 mL and stored at 5 °C overnight. The resulting dark red precipitate was collected by filtration and washed with methanol, ether, and finally pentane. Yield: 0.2005 g, 81%. Anal. Calcd for $C_{20}H_8Cl_2N_4O_6Re_2$: C, 28.48; H, 0.96; N, 6.64. Found: C, 28.57; H, 0.97; N, 6.57.

$[(ppz)(Re(CO)_3(CH_3CN))_2](CF_3SO_3)_2$. $(ppz)(Re(CO)_3Cl)_2$ (96 mg, 0.11 mmol) and $AgCF_3SO_3$ (89 mg, 0.35 mmol) were dissolved by sonication in 150 mL of freshly distilled CH_3CN. The solution was protected from light and refluxed for 22 h under a nitrogen atmosphere. The solvent was then removed by rotary evaporation, and 5 mL of methylene chloride was added to redissolve the resulting solid. The solution was filtered, and a small amount of diethyl ether was added to the filtrate in order to induce precipitation. The product was collected by filtration. Yield: 0.1176 g, 90%.

Methods. NMR spectra were obtained on a Varian Gemini 200-MHz FT-NMR spectrometer. Electronic absorption spectra were obtained on an AVIV Model 14 DS spectrophotometer, equipped for computerized data acquisition. Steady-state emission maxima were measured using a Perkin-Elmer LS-50 luminescence spectrometer outfitted with a Hamamatsu R955 photomultiplier tube for enhanced red sensitivity. Emission spectra were corrected for instrument response by using a calibrated tungsten lamp. Quantum yields were calculated relative to Ru(2,2′-bipyridine)$_3^{2+}$ in deoxygenated water as a standard (ϕ_{em} = 0.055)[51] and were corrected for changes in the refractive index. Emission lifetime measurements were carried out with a Lumonics HY750 Nd:YAG laser operated at 355 nm (pulse width 7–8 ns), coupled with a Le Croy 3500 transient digitizer. Electrochemistry was performed with an EG & G PAR Model 273 potentiostat/galvanostat using either a glassy-carbon or a platinum working electrode in a conventional three-electrode cell. A saturated sodium calomel electrode (SSCE) was employed as the reference.

Results and Discussion

NMR Spectra. The ^{1}H NMR spectra of the bppz-containing complexes have already been reported,[29] and very similar results are obtained for the corresponding ddpq derivatives. On the other hand, the spectra of the ppz-containing species are significantly different from those of the corresponding bppz and ddpq complexes, as described in detail below. All relevant ^{1}H NMR data for ppz and its complexes are summarized in Table I.

The NMR spectrum of the ppz free ligand (Figure 1a) displays four sets of resonances in the aromatic region, and each is readily assignable to a given pair of equivalent nuclei on the basis of expected splitting patterns. Coordination of the first metal center lowers the symmetry of the ppz moiety and splits the degeneracy of each pair of protons. All peaks are shifted downfield upon metal attachment by 0.18–0.40 ppm, and differences of 0.05–0.22 ppm between the chemical shifts of protons on the coordinated and uncoordinated halves of the ligand are observed. Unlike the spectrum of the corresponding bppz complex,[29] no unusual upfield shifts are observed.

Attachment of the second rhenium site restores the symmetry of the bridging ligand, and the NMR spectrum of $(ppz)(Re(CO)_3Cl)_2$ reverts to a simple splitting pattern similar to that found for the free ligand. In fact, since coupling constants are not significantly changed on going from free ppz to $(ppz)(Re(CO)_3Cl)_2$, the two spectra are nearly identical except for the downfield shift of approximately 0.45 ppm (0.43–0.48 ppm) caused by metal attachment.

Table II. Infrared Carbonyl Stretching Frequencies[a]

complex	freq, cm^{-1}
$(bppz)Re(CO)_3Cl$	2025, 1905
$[(bppz)Re(CO)_3(CH_3CN)]^+$	2038, 1923
$(bppz)(Re(CO)_3Cl)_2$	2025, 1914
$(ddpq)Re(CO)_3Cl$	2017, 1939, 1911
$[(ddpq)Re(CO)_3(CH_3CN)]^+$	2039, 1924
$(ddpq)(Re(CO)_3Cl)_2$	2022, 1917
$(ppz)Re(CO)_3Cl$	2024, 1949 (sh),[b] 1919
$[(ppz)Re(CO)_3(CH_3CN)]^+$	2043, 1934, 1943 (sh)
$(ppz)Re(CO)_3Cl)_2$	2029, 1935, 1900
$[(ppz)(Re(CO)_3(CH_3CN))_2]^{2+}$	2040, 1935

[a] Measurements performed on KBr pellets, ±2 cm^{-1}. [b] sh = shoulder.

In contrast to the ppz results, the binuclear complexes of both bppz and ddpq exhibit broad ^{1}H NMR peaks whose assignment requires extensive decoupling experiments.[29] Several features of these spectra are noteworthy. First, the protons on C-4 of the two pyridine rings were found to be inequivalent, and this result was interpreted in terms of a puckered conformation.[10,29,52-54] Second, the broad peaks observed in the NMR experiments suggest that, in room-temperature DMSO, interconversion between the in-plane (with respect to the pyrazine ring) and the out-of-plane position occurs at a rate comparable to the NMR time scale.

Another consequence of the steric repulsion between the C-4 protons in bppz and ddpq is manifested in the thermal stability of the binuclear species. While $(ppz)(Re(CO)_3Cl)_2$ is indefinitely stable in room-temperature dimethyl sulfoxide, the corresponding bppz and dppq species undergo decomposition to their respective mononuclear complexes in a matter of hours. This process can be conveniently followed by ^{1}H NMR spectroscopy. Apparently, the inability of these ligands to achieve a fully planar conformation results in poor overlap between the nitrogen lone pair and the empty metal d orbitals on one of the rhenium atoms,[54] and the ligand is readily displaced by solvent. In the *mononuclear* complexes of bppz and ddpq, however, the bound pyridine remains coplanar with the pyrazine moiety, and the metal center is quite inert with respect to substitution of the chelating ligand.

IR Spectra. A comparison of the carbonyl stretching frequencies of these complexes with literature data can be used to confirm their geometry as well as to provide insight into the electronic properties of the bridging ligands (Table II). Previous work suggests that a thorough analysis requires consideration of both σ-donating and π-accepting abilities.[29] The C–O stretching frequencies of $(ppz)Re(CO)_3Cl$ and $(bppz)Re(CO)_3Cl$ are similar to reported values for the related 2,2′-bipyridine and 1,10-phenanthroline complexes,[37] consistent with a facial arrangement of the ligands. While $(ddpq)Re(CO)_3Cl$ displays a pattern much like that of $(ppz)Re(CO)_3Cl$, the stretching frequencies are 8–10 cm^{-1} lower, perhaps reflecting increased electron donation from the methyl substituents. In all cases, replacement of the chloro ligand by acetonitrile leads to a substantial increase in C–O stretching frequency.

On the other hand, coordination of a second metal center to the remaining available site of a bppz-, ddpq-, or ppz-containing mononuclear complex results in only minor IR spectral changes. Although a detailed interpretation is made more difficult by the presence of overlapping bands, the C–O stretches *generally* shift to slightly higher energy upon binucleation. This observation might

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Table III. Electrochemical Data (V vs SSCE)[a]

complex	$E_{1/2}^{red}(1)$	$E_{1/2}^{red}(2)$	E_p^{ox}
(bppz)Re(CO)$_3$Cl	−1.00		+1.47 (irr)
[(bppz)Re(CO)$_3$(CH$_3$CN)]$^+$	−0.87		>+1.75
(bppz)(Re(CO)$_3$Cl)$_2$	−0.55	−1.13 (irr)	+1.50 (irr)
(ddpq)Re(CO)$_3$Cl	−0.77		+1.52 (irr)
[(ddpq)Re(CO)$_3$(CH$_3$CN)]$^+$	−0.68	−1.18	>1.75
(ddpq)(Re(CO)$_3$Cl)$_2$	−0.37	−0.69 (irr) −0.82 (irr)	+1.59 (irr)
(ppz)Re(CO)$_3$Cl	−0.90 (irr)		+1.46 (irr)
[(ppz)Re(CO)$_3$(CH$_3$CN)]$^+$	−0.84 (irr)		>1.75
(ppz)(Re(CO)$_3$Cl)$_2$	−0.39	−1.14	+1.53 (irr)
[(ppz)(Re(CO)$_3$(CH$_3$CN))$_2$]$^{2+}$	−0.23	−0.98	>+1.75

[a] Measurements were performed at room temperature in freshly distilled CH$_3$CN with 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

be explained either by decreased σ-donation, by increased π-acceptance from the bridging ligand, or by some combination thereof. In any event, the observed shifts are small, indicating that the electron density at Re is relatively insensitive to the attachment of a second metal center.

Electrochemistry. Oxidation and reduction potentials of all complexes are given in Table III. On the basis of earlier literature reports,[28-30,32-36] the chemically irreversible oxidation observed near +1.5 V vs SSCE for the chloro complexes can be confidently assigned as a metal-centered one-electron (per Re) process. The electrochemical data for the binuclear complexes indicate that the metal oxidations are strongly overlapping; no evidence for a distinct second wave is ever observed, and peak currents (though difficult to measure because of the proximity of the Re$^{II/I}$ couple to the anodic solvent limit) correspond to a net two-electron oxidation. The small shift (30–70 mV) to more positive potentials which occurs upon binucleation is consistent with the IR results, which reveal only minor differences in electron density at the metal center. On the other hand, no anodic waves are seen for any of the acetonitrile complexes, suggesting that rhenium oxidation is shifted past the anodic solvent limit for such cationic species.

Each of the mononuclear complexes also displays a one-electron reduction which can be attributed to a ligand-centered process.[27-30,32-42] This initial reduction occurs at moderate potentials (−0.68 to −1.00 V vs SSCE) and is both chemically and electrochemically reversible for all compounds except (ppz)Re(CO)$_3$Cl and [(ppz)Re(CO)$_3$(CH$_3$CN)]$^+$. The available cyclic voltammetric data suggest that the lack of reversibility for these two complexes may be caused by an increased tendency for adsorption owing to the large planar aromatic character of the ppz ligand. The measured half-wave potentials for all other complexes shift only slightly upon changing the nature of the other ligands attached to the metal center, in accord with the assignment as a ligand-centered reduction. Thus, replacement of Cl$^-$ by CH$_3$CN induces a small (60–130 mV) shift of the first reduction to more positive potentials. The magnitude of this change in the potential for ligand-centered reduction decreases as the size of the aromatic system increases: bppz > ddpq > ppz.[10]

In contrast, coordination of the second rhenium results in a substantial decrease in the energy of the LUMO, as evidenced by the 400–520-mV shift of the first reduction to more positive potentials which accompanies binucleation. Our observations correlate well with electrochemical measurements on the analogous binuclear complexes incorporating −Ru(bpy)$_2^{2+}$ (bpy = 2,2′-bipyridine),[5,6,10] where differences between the first reduction potentials of the mononuclear and binuclear complexes were found to be 430 and 440 mV for bppz and ppz, respectively. However, the ppz complexes of rhenium examined here display a slightly larger effect than either the Re/bppz or Ru/ppz systems.

Many of the complexes, particularly the bimetallic derivatives, undergo further reduction. For example, (bppz)(Re(CO)$_3$Cl)$_2$ exhibits a cathodic wave at -1.13 V; the corresponding anodic peak is not apparent at any accessible scan rate. The cathodic peak potential is about 300 mV more positive than expected for a metal-centered reduction,[27-30,32-42] suggesting that this second reduction, like the first, is centered on the polypyridine ligand. This assignment is consistent with the expected 400-800-mV difference between the first and second reduction potentials of such ligands.[10,30,55] Resonance Raman and ESR data on the related [(bppz)(Ru(bpy)$_2$)$_2$]$^{4+}$ complex also support this conclusion.[10]

Table IV. Absorption Data[a]

complex	MLCT max, nm	ϵ, M^{-1} cm^{-1}
(bppz)Re(CO)$_3$Cl	417	3970
[(bppz)Re(CO)$_3$(CH$_3$CN)]$^+$	~396[b]	*c*
(bppz)(Re(CO)$_3$Cl)$_2$	484	9750
(ddpq)Re(CO)$_3$Cl	~435[b]	4940[b]
[(ddpq)Re(CO)$_3$(CH$_3$CN)]$^+$	390[d]	*b*
(ddpq)(Re(CO)$_3$Cl)$_2$	~500[b]	4770[b]
(ppz)Re(CO)$_3$Cl	435	5450
[(ppz)Re(CO)$_3$(CH$_3$CN)]$^+$	385	5060
(ppz)(Re(CO)$_3$Cl)$_2$	562	7070
[(ppz)(Re(CO)$_3$(CH$_3$CN))$_2$]$^{2+}$	485	8140

[a] All measurements were carried out in spectroscopic grade CH$_2$Cl$_2$ at 25 °C. [b] Due to the close proximity of a π–π* transition, peak maximum could only be estimated. [c] Solubility problems preclude precise measurement of extinction coefficients. [d] MLCT maximum obtained from excitation spectrum.

In the case of (ddpq)(Re(CO)$_3$Cl)$_2$, scanning to potentials more negative than that of the first reduction reveals two closely spaced chemically irreversible processes, centered at ca. −0.69 and −0.82 V. These waves do not appear to either coalesce or separate appreciably over the range of accessible scan rates. Further, the cathodic currents for each of these processes measured individually are roughly half that of the first reduction. Finally, two additional chemically irreversible reductions, at ca. −1.23 and −1.65 V, are also observed at a freshly polished glassy-carbon electrode; however, these waves disappear on subsequent scans owing to passivating adsorption. The cathodic currents associated with these latter processes are generally equal to 80–90% of the peak current for the first reduction, but the waves are considerably broader, possibly indicating the presence of two unresolved components. Unfortunately, the low solubility of this complex, as well as the complications introduced by adsorption, precludes a complete analysis of its electrochemical behavior.

The binuclear complexes containing ppz exhibit equally unusual and interesting voltammetry. On the basis of arguments similar to those presented above, the second reduction, which is located at −1.14 V for (ppz)(Re(CO)$_3$Cl)$_2$ and at −0.98 V for [(ppz)(Re(CO)$_3$(CH$_3$CN))$_2$]$^{2+}$, presumably corresponds to a ligand-centered process.[10,30,42,56] As with the bppz and ddpq binuclear complexes, this reduction proceeds via an EC mechanism[57] and hence is chemically irreversible. However, in the case of the ppz derivatives, the formation and electrochemical reactivity of the species which results from the coupled chemical process can be cleanly followed. Cyclic voltammograms for each complex display a set of two reversible or quasireversible couples at potentials more negative than that of the second reduction; peak currents for these waves decrease with increasing scan rate. Peak potentials for [(ppz)(Re(CO)$_3$(CH$_3$CN))$_2$]$^{2+}$ are −1.30 and −1.73 V, while those for (ppz)(Re(CO)$_3$Cl)$_2$ are observed at −1.35 and −1.75 V. The nature of the chemical reaction which follows the addition of the second electron is currently being probed by spectroelectrochemical methods, but a full spectroscopic, kinetic, and mechanistic investigation is beyond the scope of this work.

Electronic Absorption Spectra. By analogy to previously reported systems, the lowest energy transition in these complexes is assigned as a dπ → π*(LL) (where LL represents the polypyridine ligand) metal-to-ligand charge-transfer (MLCT) process.[26-30,32-40] Absorption maxima and molar absorptivities are

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Table V. Emission Data[a]

complex	ϕ_{em}[b]	τ_0, s	k_r,[c] s^{-1}	k_{nr},[c] s^{-1}	λ_{max},[d] nm
(bppz)Re(CO)$_3$Cl	0.0012	<2.0 × 10^{-8}	>6.0 × 10^4	4.99 × 10^7	693
[(bppz)Re(CO)$_3$(CH$_3$CN)]$^+$	0.0070	9.8 × 10^{-8}	7.1 × 10^4	1.01 × 10^7	640
(ddpq)Re(CO)$_3$Cl	0.00008	*e*			773
[(ddpq)Re(CO)$_3$(CH$_3$CN)]$^+$	0.0339	8.63 × 10^{-7}	3.9 × 10^4	1.12 × 10^6	667
(ppz)Re(CO)$_3$Cl	0.0021	3.15 × 10^{-8}[f]	6.6 × 10^4	3.17 × 10^7	695
[(ppz)Re(CO)$_3$(CH$_3$CN)]$^+$	0.1195	1.241 × 10^{-6}	9.6 × 10^4	7.10 × 10^5	591
[(ppz)(Re(CO)$_3$(CH$_3$CN))$_2$]$^{2+}$	0.0007	*e*			741

[a] All measurements performed in room-temperature deoxygenated CH_2Cl_2. [b] All compounds are referenced to Ru(bpy)$_3^{2+}$ in degassed H_2O (ϕ_{em} = 0.055)[51] and are corrected for refractive index. [c] k_r and k_{nr} were calculated from ϕ_{em} and τ_0 according to ref 60. [d] Emission spectra are corrected for excitation lamp intensity and PMT response. [e] Emission too weak and lifetime too short for accurate measurement. [f] Lifetime obtained using a single-photon-counting system at the University of Florida, Gainesville, FL.

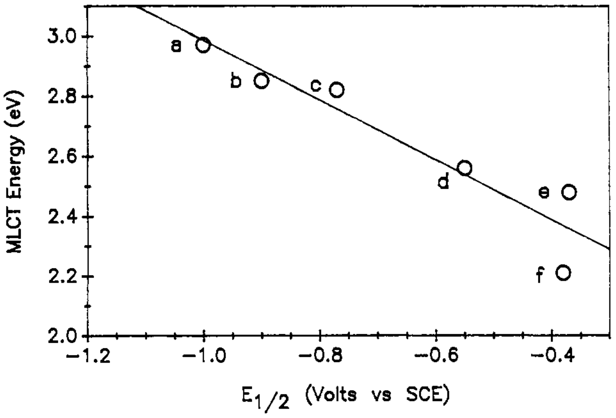

Figure 2. Correlation of MLCT energy vs first reduction potential: (a) (bppz)Re(CO)$_3$Cl; (b) (ppz)Re(CO)$_3$Cl; (c) (ddpq)Re(CO)$_3$Cl; (d) (bppz)(Re(CO)$_3$Cl)$_2$; (e) (ddpq)(Re(CO)$_3$Cl)$_2$; (f) (ppz)(Re(CO)$_3$Cl)$_2$.

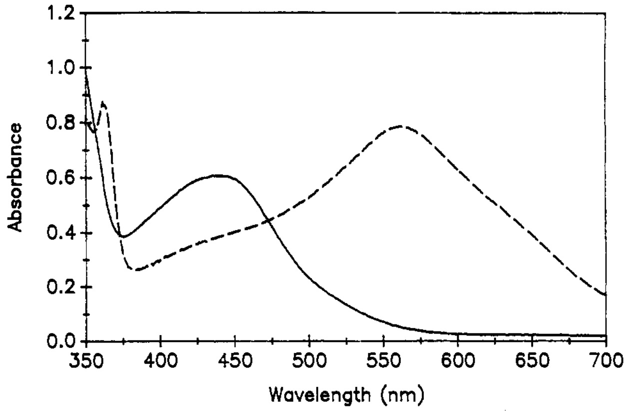

Figure 3. Absorption spectra of (ppz)Re(CO)$_3$Cl (—) and (ppz)(Re(CO)$_3$Cl)$_2$ (---) in room-temperature CH_2Cl_2.

collected in Table IV. Consistent with an MLCT assignment, a plot of absorption energy vs reduction potential of the ligand yields a linear correlation (Figure 2).[7,30,39] Transition energies are also sensitive to the nature of the supporting ligand bound to the metal center, owing to changes in the ease of metal oxidation.

The absorption data reveal that a substantial red shift occurs upon attachment of the second metal center (Figure 3). Similar shifts have been noted for related bimetallic complexes,[5,6,21-30,34] and the effect has been attributed to the stabilization of the π^* orbital on the bridging ligand,[5-7,10,21-25,34] as confirmed by the electrochemical data. This stabilization is the direct result of the electropositive character of the metal center and is sensitive to the nature of the supporting ligands. Interestingly, at least in the case of the ppz bridging ligand, the –Re(CO)$_3$Cl group appears to cause a somewhat larger perturbation of the π^* orbital energy than does –Ru(bpy)$_2^{2+}$ (5200 cm^{-1} vs 3650 cm^{-1}), despite the larger electrostatic effect of the ruthenium-containing fragment.[5,6] The differences between the two systems may reflect the greater relative importance of π-back-bonding to the bridging ligand in the ruthenium case, owing to the strong π-acid character of the competing carbonyl ligands on the rhenium center. Such effects are likely to be less pronounced for the bppz and ddpq ligands, since the lack of planarity in these systems allows for only a small degree of back-bonding with either metal.

Emission Spectroscopy. All emission data are presented in Table V. The mononuclear chloro complexes of bppz and ppz display relatively weak emission bands near 700 nm under these conditions, while the emission from (ddpq)Re(CO)$_3$Cl is much weaker and appears at substantially lower energy. The luminescence maxima for these three complexes occur at significantly longer wavelengths than those reported for the analogous (bpy)Re(CO)$_3$Cl[43] and (1,10-phenanthroline)Re(CO)$_3$Cl[36,39] complexes. Moreover, the radiative quantum yields are lower[36,43] and their excited-state lifetimes are also somewhat shorter.[39,43] The observed differences in excited-state energy can be readily attributed to differences in the nature of the aromatic ligand. For example, (ddpq)Re(CO)$_3$Cl displays the least negative first reduction potential and lowest energy MLCT absorption among the mononuclear chloro complexes examined here; hence its long-wavelength emission is not at all surprising. On the other hand, despite the obvious distinctions between the bppz and ppz free ligands, the photophysical properties of (bppz)Re(CO)$_3$Cl and (ppz)Re(CO)$_3$Cl are strikingly similar.

Replacement of the chloro ligand by acetonitrile in these species has a number of interesting consequences. In all cases, increases in emission energy, quantum yield, and excited-state lifetime are observed; however, these changes are much more dramatic for the ppz and ddpq derivatives than for bppz. Although the blue shift of the emission maximum which occurs upon chloride replacement is most easily explained by changes in the Re$^{II/I}$ oxidation potential, shifts in ligand reduction potential must also be considered. Thus, since both the Re$^{II/I}$ couple and the bppz$^{0/-}$ couple in [(bppz)Re(CO)$_3$X^{n+}] shift to more positive values upon changing X from Cl$^-$ to CH$_3$CN, the net change in the energy of the MLCT excited state corresponds to the sum of these two competing effects. While the ppz and ddpq complexes behave similarly, the first reduction potential is less sensitive to the nature of X, so that the change in metal oxidation potential clearly dominates. As a result, the magnitude of the blue shift in the bppz case (ca. 0.15 eV) is much smaller than that observed with the ppz (ca. 0.31 eV) or ddpq (ca. 0.26 eV) derivatives. The short wavelength, high quantum yield, and long lifetime of the emission from [(ppz)Re(CO)$_3$(CH$_3$CN)]$^+$ are particularly intriguing in view of the presence of a large aromatic system. Indeed, the behavior of this complex is remarkably similar to that of the much smaller complex [(bpy)Re(CO)$_3$(CH$_3$CN)]$^+$.[43] For example, despite slightly different emission energies, the lifetimes of the two complexes are virtually identical (1241 ns vs 1201 ns[43]) and radiative quantum yields agree within a factor of 2.[58]

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(58) The quantum yield for emission from [(2,2′-bipyridine)Re(CO)$_3$(CH$_3$CN)]$^+$ under these conditions is reported as 0.41 in ref 43. However, subsequent measurements in our laboratory and elsewhere[59] indicate that the correct value is 0.22.

(59) Schanze, K. Personal communication.

In the current study, the increases in emission quantum yield and excited-state lifetime which occur upon replacement of the chloride ligand by acetonitrile can be explained by the energy gap law.[34,35,43-48] It has been previously established that the energy gap relationship is applicable to the photophysical behavior of many transition-metal complexes,[43-48] including rhenium polypyridines.[43,48] Thus, for a given polypyridyl ligand, the measured nonradiative decay rates decrease with increasing excited-state energy as expected (Table V). Unfortunately, quantitative correlations between ln k_{nr} and excited-state energy are not possible here, since structural parameters of the chelating ligands also induce substantial variation in k_{nr} values. Such variations have been demonstrated by comparing results from a series of osmium complexes incorporating two different bidentate ligands (2,2′-bipyridine and 1,10-phenanthroline).[45,46]

Analogous effects have also been noted for mononuclear and binuclear complexes of bppz and ppz with $-Ru(bpy)_2^{2+}$.[5,6] Fuchs et al.[6] have interpreted their results in terms of differences in vibronic coupling. In other words, the more flexible nature of the bppz ligand introduces additional vibrational modes which are capable of dissipating excited-state energy nonradiatively.[5,6,58] As a result, despite more extensive conjugation in the bridging ligand, $[(ppz)(Ru(bpy)_2)_2]^{4+}$ possesses a much greater radiative quantum yield than $[(bppz)(Ru(bpy)_2)_2]^{4+}$ owing to the more rapid nonradiative decay of the latter species. The mononuclear rhenium complexes described herein fit a similar pattern, as evidenced by a comparison of the nonradiative decay rates of the ppz complexes with those of the corresponding bppz derivatives.

One result of the greater propensity of ppz-containing complexes for radiative decay is the observation of room-temperature emission from $[(ppz)(Re(CO)_3(CH_3CN))_2]^{2+}$. In spite of its exceptionally facile first reduction, this complex displays a weak but easily detectable emission at very low energy, even with excitation wavelengths >500 nm. In fact, long-wavelength excitation was preferred, since extensive photodecomposition was observed with higher energy irradiation. This photodecomposition process was accompanied by the growth of a new emission band near 590 nm, suggesting the formation of $[(ppz)Re(CO)_3(CH_3CN)]^+$. Nonetheless, the original ppz-bridged bimetallic species represents, to our knowledge, the first example of a binuclear Re(I) complex incorporating a completely planar aromatic bridging ligand which is luminescent in room-temperature fluid solution.[26,27]

A final feature of this results which may be worth noting is that the measured excited-state lifetime of $[(ddpq)Re(CO)_3(CH_3CN)]^+$ is significantly longer (863 ns) than would be anticipated from a simple consideration of its structural features and excited-state energy. In fact, the measured nonradiative decay rate is an order of magnitude lower than expected. Given the structural similarity between bppz and ddpq, it seems unlikely that the aforementioned explanation of Fuchs et al.[6] could account for such behavior. The unusually low radiative decay rate for this complex is equally puzzling. However, the electronic properties of the ddpq ligand may offer a suitable explanation. In the electronic absorption spectrum of free ddpq, the $\pi \rightarrow \pi^*$ transition is observed at 350 nm, compared to 310 and 298 nm in free ppz and bppz, respectively. Similarly, the $\pi \rightarrow \pi^*$ intraligand bands in the Re complexes of ddpq occur at lower energy than in the analogous ppz and bppz derivatives. Since the proximity of the $d\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states in rhenium polypyridine tricarbonyls is well-established,[36-40,50] it seems conceivable that the lowest excited state of this particular complex may possess significant $\pi \rightarrow \pi^*$ character. Transient absorption experiments designed to probe the nature of the lowest excited state in this complex are currently in progress.

Conclusion

The spectroscopic and photophysical behavior of this series of ligand-bridged bimetallic rhenium complexes differs significantly from that of their monometallic counterparts. As with the analogous ruthenium systems, much of the difference results from the perturbation of the π^*-orbital energy on the bridging ligand by attachment of the second metal center. However, unlike the ruthenium polypyridines, the rhenium-based system allows for further variation in the coordination environment. Changing the nature of the sixth ligand provides a second method for "fine-tuning" the electronic properties of the rhenium complexes. This added synthetic freedom may aid in the design of suitable photooxidants and/or photoreductants for a variety of purposes. Since the formation of bimetallic Re^I complexes through the use of doubly monodentate bridging ligands has already been demonstrated,[25,32-35] numerous examples of ligand-bridged clusters possessing higher nuclearity can be envisioned, including potentially luminescent polymeric species.

The behavior of the ppz-containing complexes is especially noteworthy. In particular, $[(ppz)Re(CO)_3(CH_3CN)]^+$ is very strongly luminescent in room-temperature fluid solution and may provide an important building block for the preparation of novel multinuclear photoredox agents. This investigation clearly illustrates that both electronic and structural features of the ligand contribute to the attractive photophysical properties of ppz-containing complexes. The rigidity of ppz also permits the preparation of thermally stable homobinuclear species and is responsible, at least in part, for the observation of room-temperature emission from $[(ppz)(Re(CO)_3(CH_3CN))_2]^{2+}$. In contrast, the bimetallic complexes of bppz and ddpq exhibit limited thermal stability in coordinating solvents, and ^1H NMR spectroscopy reveals that these molecules are highly fluxional, even at room temperature. The more flexible nature of the latter ligands is also responsible for the increased vibrational coupling between electronic states, resulting in rapid nonradiative decay rates.

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