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Ground-State and Excited-State Properties of Monometallic and Bimetallic Complexes Based on Rhenium(I) Tricarbonyl Chloride: Effect of an Insulating vs a Conducting Bridge

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The preparation and properties of monometallic and bimetallic complexes of rhenium(I) tricarbonyl chloride coordinated to 4,4′-dimethyl-2,2′-bipyridine ($(CH_3)_2$bpy), 2,2′-bipyrimidine (bpm), 2,3-bis(2-pyridyl)pyrazine (bpp), and 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane (Mebpy-Mebpy) are described. The CO stretching frequencies were in accord with facial geometry for the complexes. The NMR properties revealed that protons on the carbon atoms α to the coordinating nitrogen atoms of coordinated heterocycles were deshielded and shifted downfield. Electrochemically, one or two irreversible oxidations, a reversible reduction assignable to reduction of the heterocyclic ligand, and a second reduction (irreversible) at a potential more negative than that of the first were observed. The monometallic complexes displayed $d\pi \rightarrow \pi^*$ transitions in the 360–380-nm region. The transition red-shifted to 454 nm for [(bpp)(Re(CO)$_3$Cl)$_2$] and to 480 nm for [(bpm)(Re(CO)$_3$Cl)$_2$] but remained at 366 nm for [(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$]. Emission was observed at room temperature for [($(CH_3)_2$bpy)Re(CO)$_3$Cl], [(Mebpy-Mebpy)Re(CO)$_3$Cl], [(bpp)Re(CO)$_3$Cl], and [(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$]. Their emission maxima were located near 600 nm except for [(bpp)Re(CO)$_3$Cl]. Its emission maximum was observed at 700 nm.

Introduction

There has been a recent resurgence in the studies of rhenium(I) polypyridyl–carbonyl complexes.[1-6] The resurgence is the result of interest in the photophysical properties, which are similar to those of ruthenium(II) polypyridyl complexes. In the case of ruthenium, the excited-state species has been shown to catalyze both oxidation and reduction processes.[7] This same idea carries over to the excited-state behavior of rhenium(I) complexes, where, for example, there are reports of electrochemical and photochemical reduction of CO_2 to CO.[8-10]

In our work, we recently reported[3] the synthesis and properties of a series of multimetallic ruthenium(II)/rhenium(I) complexes bridged by 2,2′-bipyrimidine (bpm). We also reported[4] the structural properties of [Re(bpm)(CO)$_3$MeQ]$^{2+}$, where MeQ is the *N*-methyl-4,4′-bipyridinium ion. We have extended our studies to include complexes bridged by 2,3-bis(2-pyridyl)pyrazine (bpp) and 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl))ethane (Mebpy-Mebpy). In this paper we focus on the nature of the bridging ligand and the effect the bridge has on the electrochemical, spectral, structural, and the photophysical behavior of the complexes. The degree of metal–metal interaction across the bridge was expected to decrease in the order bpm > bpp ≫ Mebpy-Mebpy. These ligands are shown in Figure 1.

Experimental Section

Materials. $RuCl_3$ was a gift from Johnson-Mathey, Inc. Re(CO)$_5$Cl, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 2,3-bis(2-pyridyl)pyrazine, and 2,2′-bipyrimidine were purchased commercially and used without further purification. The ligand 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane (Mebpy-Mebpy) was prepared by of the procedure reported by Elliott and co-workers[11] as modified by Sahai et al.[12] Solvents used for preparations and spectroscopic studies were Fisher HPLC grade. Solvents used in electrochemistry were dried over 4-Å molecular sieves before use. The electrolyte, tetrabutylammonium hexafluorophosphate (TBAH) was electrometric grade from Southwestern Analytical. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Preparation of Compounds. The compounds [(bpm)Re(CO)$_3$Cl] and [(bpm)(Re(CO)$_3$Cl)$_2$] were available from a previous study.[3] The complexes [(bpp)Re(CO)$_3$Cl] and [(bpp)(Re(CO)$_3$Cl)$_2$] were prepared by an analogous procedure.[3]

[($(CH_3)_2$bpy)Re(CO)$_3$Cl]. To a solution of 0.10 g (0.27 mmol) of 4,4′-dimethyl-2,2′-bipyridine in 20 mL of methanol was added 0.10 g (0.27 mmol) of Re(CO)$_5$Cl in 40 mL of methanol. The resulting clear, colorless solution was refluxed for 21 h under N_2. A clear, yellow solution slowly evolved during the reflux. The reaction mixture was cooled to room temperature and evaporated to dryness. The resulting residue was dissolved in a minimum amount of acetone and added to 200 mL of anhydrous ethyl ether. The resulting solution was chilled to −5 °C for 24 h, during which time a fine, bright yellow precipitate formed. The product was collected by vacuum filtration, washed with ether, and dried under vacuum. The yield was 0.10 g (76%). Anal. Calcd for $ReC_{15}H_{12}N_2ClO_3$: C, 36.77; H, 2.47; N, 5.72; Cl, 7.24. Found: C, 36.79; H, 2.51; N, 5.68; Cl, 7.27.

[(Mebpy-Mebpy)Re(CO)$_3$Cl]. A solution of 0.10 g (0.28 mmol) of Re(CO)$_5$Cl in 100 mL of methanol was added over a 4-h period to a refluxing solution of 0.40 g (1.09 mmol) of Mebpy-Mebpy in 300 mL of toluene. After being refluxed an additional 4 h, the solution was evaporated to dryness with a rotary evaporator. The yellow residue was suspended in chloroform and filtered through a fine frit to remove an insoluble brown solid. The filtrate was again evaporated to dryness, the residue was resuspended in acetonitrile, and the solution was filtered to remove excess Mebpy-Mebpy. Again the filtrate was evaporated to dryness and the residue was redissolved in a minimum amount of chloroform. The resulting amber solution was added to approximately 100 mL of *n*-hexane, which caused a fine, yellow solid to precipitate. The solid was collected by vacuum filtration, washed with ether, and dried under vacuum. The yield was 0.17 g (75%). Anal. Calcd for $ReC_{27}H_{22}N_4ClO_3$: C, 48.24; H, 3.31; H, 8.34; Cl, 5.27. Found: C, 48.06; H, 3.32; N, 8.23; Cl, 5.36.

[(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$]. A solution of 0.20 g (0.55 mmol) of Re(CO)$_5$Cl in 50 mL of methanol, prepared by sonicating the suspension for 2 h, was added to a refluxing solution of 0.10 g (0.27 mmol) of Mebpy-Mebpy in 30 mL of methanol. Rapidly a bright yellow solution

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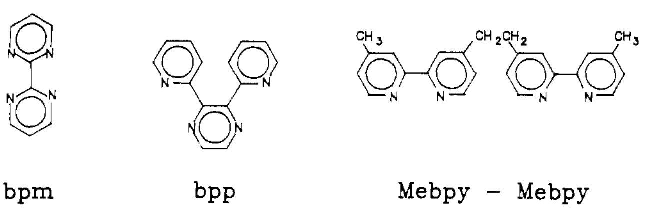

Figure 1. The ligands.

Table I. Carbonyl Stretching Frequencies for Rhenium(I) Complexes

compd	freq, cm^{-1}	ref
Re(CO)$_5$Cl^a	2151, 2044, 2013, 1979	3
[(*o*-phen)Re(CO)$_3$Cl]^b	2015, 1912, 1890	14
[((CH$_3$)$_2$bpy)Re(CO)$_3$Cl]^a	2018, 1932, 1909, 1878	this work
[(Mebpy-Mebpy)Re(CO)$_3$Cl]^a	2019, 1911, 1888	this work
[(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$]^a	2020, 1890	this work
[(bpm)Re(CO)$_3$Cl]^c	2033, 1906 (sh), 1899	3
[(bpm)(Re(CO)$_3$Cl)$_2$]^c	2028, 1908	3
[(bpp)Re(CO)$_3$Cl]^a	2024, 1906, 1896 (sh)	this work
[(bpp)(Re(CO)$_3$Cl)$_2$]^a	2025, 1914	this work

^{a}KBr pellets, ±2 cm^{-1}. ^{b}CH$_2$Cl$_2$. ^{c}Nujol mull, ±2 cm^{-1}.

formed and within 1 h the reaction mixture turned cloudy with suspended yellow solids. The reaction mixture was refluxed for an additional 3 h. Then it was cooled to room temperature and vacuum filtered to collect the precipitate. The precipitate was washed with ether and air-dried. The yield was 0.25 g (94%). Anal. Calcd for Re$_2$C$_{30}$H$_{22}$N$_4$Cl$_2$O$_6$·H$_2$O: C, 36.18; H, 2.43; N, 5.63; Cl, 7.12. Found: C, 36.41; H, 2.49; N, 5.63; Cl, 7.12.

Physical Measurements. Visible–UV spectra were recorded with a Perkin-Elmer Lambda Array 3840 spectrophotometer. Luminescence spectra were recorded with the Perkin-Elmer 650-40 and Spex Fluorolog spectrofluorometers. Cyclic voltammograms were obtained in acetonitrile solutions containing 0.10 M TBAH as the supporting electrolyte. The measurements were made vs the saturated sodium calomel electrode (SSCE). Electrochemistry was carried out with a PAR 173 potentiostat in conjunction with a PAR 175 programmer. Cyclic voltammograms were recorded with a YEW Model 3022 x-y recorder. Luminescence lifetimes were determined with the Molectron nitrogen pumped dye laser system previously described[13] or with a PRA LN1000 pulsed N$_2$ laser, a PRA LN102 dye laser, a LeCroy 6880A transient digitizer, and an IBM PS2 Model 60 microcomputer with a setup similar in design to that of the Molectron system.[13] Infrared spectra were recorded with a Mattson FTIR Model IR 10410 spectrometer. NMR spectra were recorded in acetonitrile-d_3, chloroform-d_1, or DMSO-d_6 with a 300-MHz General Electric QE-300 NMR spectrometer.

Results

Structural Features—Infrared Spectra. The carbonyl stretching frequencies are given in Table I. A comparison of the stretching frequencies of the bpm, bpp, and Mebpy-Mebpy rhenium(I) tricarbonyl complexes to those of Re(CO)$_5$Cl and *fac*-[(*o*-phen)Re(CO)$_3$Cl],[14] where *o*-phen is 1,10-phenanthroline, reveals that the geometry of the tricarbonyl rhenium(I) complexes is also facial. Simplification of the infrared spectrum for the bimetallic complexes compared to their monometallic precursors is observed. Two peaks are present compared to three for the monometallic species. This is due in part to broadening of the bands, which perhaps results from the presence of isomers. A sampling of the bimetallic complex most likely contains a statistical distribution of molecules with Cl$^-$ ligands in two orientations.[3]

There is about a 10 cm^{-1} shift of carbonyl stretching frequencies to higher energy for bpm containing complexes compared to Mebpy-Mebpy systems. This may be due to competition by the polypyridyl and carbonyl ligands for π-electron density from the dπ orbitals of rhenium(I). Since the bpm ligand has lower π* energy levels than bpy analogues,[15] the more favorable π interaction between rhenium and bpm would lead to less electron density available for π bonding of rhenium with the CO π* orbitals, resulting in the observed increase in CO stretching energies for the bpm-based complexes.

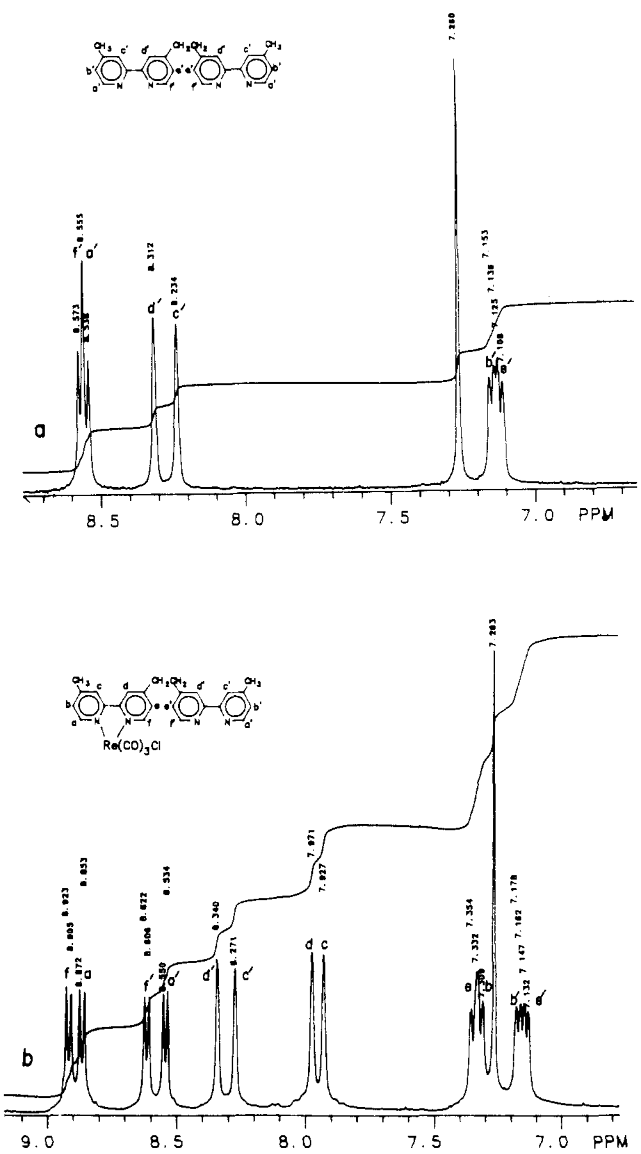

Figure 2. Proton NMR spectra of (a) the Mebpy-Mebpy ligand and (b) the [(Mebpy-Mebpy)Re(CO)$_3$Cl] complex in the aromatic region. The peak at 7.26 ppm is identified as belonging to the solvent.

The IR spectra of the bpp-containing species appear to represent an intermediate case. While the lower energy CO stretches in these complexes are similar in energy to those of the analogous bpm complexes, the high-frequency CO stretch occurs at an energy that is midway between those of the Mebpy-Mebpy and bpm derivatives. However, since the electrochemical and UV–visible data indicate that the π* level of bpp is slightly lower than that of bpm in the mononuclear complexes, one would expect higher carbonyl stretching frequencies for the bpp-containing species on the sole basis of π-acceptor strength. The IR data suggest that σ-donating ability must also be considered and that bpp is a better σ donor than bpm.

Structural Features—NMR Spectra. The proton NMR properties of Mebpy-Mebpy complexes are listed in Table II, and spectra for the Mebpy-Mebpy ligand and the [(Mebpy-Mebpy)Re(CO)$_3$Cl] complex are shown in Figure 2. The bimetallic complex [Re(CO)$_3$Cl(Mebpy-Mebpy)Re(CO)$_3$Cl] was too insoluble to obtain an NMR spectrum. Assignments of proton

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Table II. ^{1}H NMR Properties of Bipyridine Compounds[a]

$(CH_3)_2$bpy[b]	a′, 8.53 (d, 2 H, 6.0 Hz) b′, 7.13 (d, 2 H, 6.0 Hz) c′, 8.22 (s, 2 H)	
[($(CH_3)_2$bpy)-Re$(CO)_3$Cl][c]		a, 8.89 (d, 2 H, 6.0 Hz) b, 7.34 (d, 2 H, 6.0 Hz) c, 7.99 (s, 2 H)
Mebpy-Mebpy[d]	a′, 8.55 (d, 2 H, 4.5 Hz) b′, 7.15 (d, 2 H, 3.0 Hz) c′, 8.23 (s, 2 H) d′, 8.31 (s, 2 H) e′, 7.12 (d, 2 H, 4.5 Hz) f′, 8.56 (d, 2 H, 4.5 Hz)	
[(Mebpy-Mebpy)-Re$(CO)_3$Cl[e]	a′, 8.54 (d, 1 H, 6.0 Hz) b′, 7.17 (dd, 1 H, 6.0 Hz) c′, 8.27 (s, 1 H) d′, 8.34 (s, 1 H) e′, 7.14 (dd, 1 H, 6.0 Hz) f′, 8.61 (d, 1 H, 6.0 Hz)	a, 8.86 (d, 1 H, 6.0 Hz) b, 7.32 (dd, 1 H, 6.0 Hz) c, 7.93 (s, 1 H) d, 7.97 (s, 1 H) e, 7.34 (dd, 1 H, 6.0 Hz) f, 8.91 (d, 1 H, 6.0 Hz)

[a] Shifts are in ppm from TMS, $CDCl_3$-d_1. [b] H_3C, 2.45 ppm, 6 H. [c] H_3C, 2.58 ppm, 6 H. [d] H_3C, 2.46 ppm, 6 H; $-H_2C-CH_2-$, 3.09 ppm, 4 H. [e] H_3C, 2.46 ppm, 3 H; H_3C (Re), 2.53 ppm, 3 H; $-H_2C-CH_2-$, 3.14 ppm, 4 H.

resonances were made by analogy to the model $(CH_3)_2$bpy ligand and the [($(CH_3)_2$bpy)Re$(CO)_3$Cl] complex. The same characteristics found in model compounds carried over to the more complex Mebpy-Mebpy systems. Due to the bridging ethyl group, the protons of the pyridine rings of a given bipyridine unit were no longer equivalent. Thus, the proton pairs, designated as a and f, b and e, and c and d in Figure 2a, resonate at similar, but not necessarily the same, frequencies. On the basis of first-order effects and the fact that recent publications of bipyridine complexes place the resonance of the protons α to the nitrogen farthest downfield,[16,17] the peak positions of proton resonances in the Mebpy-Mebpy ligand were identified as follows: the c′ and d′ proton resonances were singlets and located at 8.23 and 8.31 ppm. The a′ and f′ proton resonances appear as doublets centered at 8.55 and 8.56 ppm with overlapping bands giving rise to the appearance of a virtual triplet. The resonances of the b′ and e′ protons were doublets centered at 7.12 and 7.15 ppm.

More precise assignments required a series of decoupling experiments with particular emphasis on differentiating between a′/f′, b′/e′, and c′/d′ pairs. This was accomplished by decoupling experiments performed for [(Mebpy-Mebpy)Re$(CO)_3$Cl]. As shown in Figure 2b (note: nonprimed labels correspond to protons located on the coordinating ligand), rather marked shifts occur for protons attached to the coordinated ligand. The fact that the resonance frequencies of the protons attached to the uncoordinated ligand remains relatively fixed and that there is little overlap between proton pairs (a/f, etc.) makes assignments relatively straightforward. However, absolute assignments depended upon a very weak, long-range coupling between aliphatic protons of the ethyl bridge and e and e′ aromatic protons. Decoupling at 3.19 ppm resulted in subtle changes to the multiplets located at 7.17 and 7.34 ppm. Decoupling had the effect of sharpening portions of the multiplets, revealing them to be doublets of doublets in the absence of the long-range coupling. The upfield portion of the 7.17 ppm multiplet and the downfield portion of the 7.34 ppm multiplet resolved into a doublet of doublets and were assigned to the e′ and e protons, respectively. All remaining assignments are dependent upon these assignments and are summarized in Figure 3. Further details regarding the decoupling experiments are presented as supplementary information.

The general effect of the Re substituent is to shift proton resonances downfield. The electronic perturbation, however, is limited to all but the c′/b′ pairs. The presence of the Re component also polarizes the ethyl bridge, altering the electron density of each proton such that they no longer are equivalent. The splitting pattern of the ethyl bridge protons is complex and assumed to arise from each proton interacting with three nonequivalent protons of the ethyl group to give a complex multiplet.

The proton shifts can be summarized as follows. Protons on the coordinated ligand: a′ → a, 0.31 ppm; b′ → b, 0.22 ppm; c′ → c, −0.30 ppm; d′ → d, −0.34 ppm; e′ → e, 0.17 ppm; f′ → f, 0.35 ppm. Protons on the uncoordinated ligand: a′ → a′, −0.01 ppm; b′ → b′, 0.02 ppm; c′ → c′, 0.04 ppm; d′ → d′, 0.03 ppm; e′ → e′, 0.02 ppm, f′ → f′, 0.05 ppm. Clearly, the influence of the Re component shifts proton resonances of the coordinated

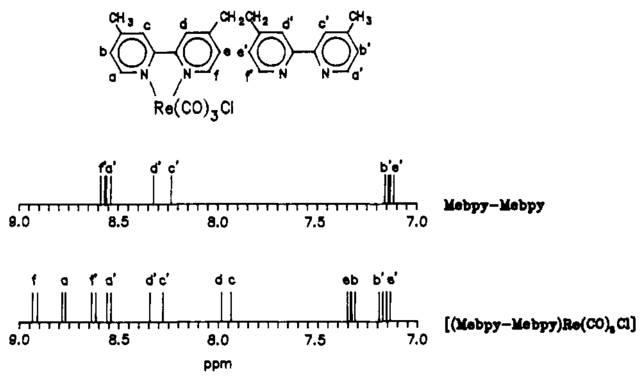

Figure 3. Correlation diagram illustrating the positional shifts of proton resonances from the metal-free ligand to the [(Mebpy-Mebpy)Re$(CO)_3$Cl] complex, which contains one free Mebpy and one metalated Mebpy.

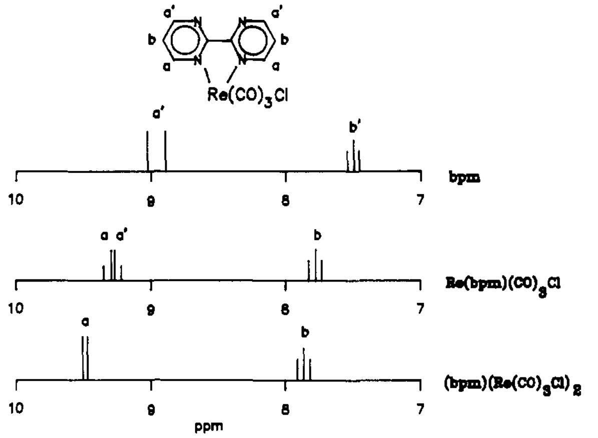

Figure 4. Correlation diagram illustrating the positional shifts of proton resonances in sequence of the bpm ligand, the [bpmRe$(CO)_3$Cl] complex, and the [(bpm)(Re$(CO)_3$Cl$)_2$] complex.

Table III. Proton NMR Properties of Bipyrimidine and 2,3-Bis(2-pyridyl)pyrazine Compounds[a]

bpm[b]	a′, 8.97 (d, 4 H, 6 Hz) b′, 7.52 (t, 2 H, 6 Hz)	
[(bpm)Re$(CO)_3$Cl][b]	a′, 9.23 (d, 2 H, 5 Hz)	a, 9.24 (d, 2 H, 4 Hz) b, 7.81 (t, 2 H, 5 Hz)
[(bpm)-(Re$(CO)_3$Cl$)_2$][c]		a, 9.46 (d, 4 H, 5 Hz) b, 7.95 (t, 2 H, 5 Hz)
bpp[b]	a′, 8.68 (s, 2 H) b′, 8.23 (d, 2 H, 5 Hz) c′, 7.26 (dd, 2 H, 5 Hz, 9 Hz) d′, e′, 7.83 (d, 4 H, 4 Hz)	
[(bpp)Re$(CO)_3$Cl][b]	a′, 8.85 (d, 1 H, 3 Hz) b′, 8.64 (d, 1 H, 4.8 Hz) c′, 7.71 (m, 1 H) d′, 8.21 (td, 1 H, 1.2 Hz, 8 Hz) e′, 8.04 (d, 1 H, 8 Hz)	a, 9.07 (d, 1 H, 3 Hz) b, 9.03 (d, 1 H, 5.4 Hz) c, 7.55 (dd, 1 H) d, 7.79 (td, 1 H, 1.2 Hz, 8 Hz) e, 7.12 (d, 1 H, 9 Hz)
[(bpp)-(Re$(CO)_3$Cl$)_2$][c]		a, 9.21 (s, 2 H) b, 9.14 (s, 2 H) c, 7.84 (t, 2 H, 6 Hz) d, 8.15 (s, 2 H) e, 8.7 (s, 1 H) e″, 8.3 (s, 1 H)

[a] Shifts are in ppm from TMS. [b] Acetonitrile-d_3. [c] DMSO-d_6.

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Table IV. Visible–UV Spectra of Rhenium(I) Complexes and Their Free Ligands in Acetonitrile[a]

compd	$d\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
$(CH_3)_2$bpy		281 (1.3×10^4), 243 (1.0×10^4)
$[((CH_3)_2bpy)Re(CO)_3Cl]$	365 (3.6×10^3), 314 (sh, 8.9×10^3)	290 (1.5×10^4), 236 (sh, 1.3×10^4), 233 (2.0×10^4)
Mebpy-Mebpy		282 (2.8×10^4), 245 (2.2×10^4)
[(Mebpy-Mebpy)Re(CO)$_3$Cl]	366 (3.7×10^3), 315 (sh, 9.1×10^3)	285 (2.7×10^4), 252 (sh, 2.6×10^4), 238 (3.1×10^4)
[(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$]	368 (7.9×10^3), 315 (sh, 1.3×10^4)	291 (3.3×10^4), 256 (sh, 2.2×10^4), 234 (4.5×10^4)
bpm		290 (sh, 7.3×10^2), 238 (1.4×10^4)
[(bpm)Re(CO)$_3$Cl][b]	384 (2.7×10^3), 310 (3.4×10^3)	260 (sh, 1.7×10^3), 232 (2.3×10^4)
[(bpm)(Re(CO)$_3$Cl)$_2$][b]	480 (3.7×10^3),[c] 350 (6.6×10^3)[c]	275 (sh),[d] 232[d]
bpp		304 (1.3×10^4), 269 (1.6×10^4)
[(bpp)Re(CO)$_3$Cl]	406 (3.5×10^3), 330 (sh, 1.1×10^4)	292 (sh), 243 (1.6×10^4)
[(bpp)(Re(CO)$_3$Cl)$_2$]	454 (8.4×10^3), 342 (1.8×10^4)	270 (1.7×10^4)

[a] λ_{max} in nm (±1 nm), ϵ values in M^{-1} cm^{-1} are in parenthesis (±0.1); $T = 25 \pm 2$ °C. [b] From ref 3. [c] In DMF. [d] Due to low solubility, only peak positions were obtained.

bipyridine but leaves the proton resonances of the uncoordinated bipyridine relatively unaffected.

The proton NMR properties of the bpp and bpm complexes are listed in Table III. Due to the symmetry of the bpm ligand, only three protons need be considered, and the sequence of changes that occur upon coordination of the "Re(CO)$_3$Cl" component is illustrated in Figure 4. The a′ protons are equivalent in the free bpm ligand and give rise to a doublet at 8.97 ppm. The proton labeled b′ is split by two equivalent neighbors to give a triplet at 7.52 ppm. Upon coordination of one Re(CO)$_3$Cl unit, the proton resonances shift downfield by approximately 0.3 ppm. The a and a′ protons remain nearly equivalent; two closely spaced doublets located at 9.23 and 9.24 ppm are observed. Addition of the second Re(CO)$_3$Cl results in a further downfield shift of the proton resonances of about 0.2 ppm. In this case a doublet located at 9.46 ppm corresponds to the resonance of the a protons; the one at 7.95 ppm is assigned to protons labeled b on the heterocyclic bpm ring.

The proton NMR spectra of the bpp complexes was considerably more complex, as illustrated in the correlation diagram shown in Figure 5. Decoupling experiments were necessary in order to make the proton assignments. The proton resonance farthest downfield for the free ligand was unaffected by saturation of the other signals. Thus, it was assigned to the isolated protons labeled a′ located on the pyrazine ring. The signal arising from the protons α to the nitrogen atom of the pyridine rings (labeled b′) was assigned to the signal next farthest upfield (8.23 ppm). Decoupling studies revealed that these protons were coupled with the resonance farthest upfield. Therefore, this signal was attributed to the c′ protons leaving the "doublet" at 7.83 ppm assignable to the d′ and e′ protons.

Assignments for the monometallic complex were more difficult, but the proton resonances of the bimetallic complex resimplified to a pattern similar in some respects to that for the free ligand, except the proton resonances were shifted further downfield. The assignments for the monometalated complex required decoupling 10 different signals, and the results are available as supplementary material. Briefly, upon coordination of the first Re(CO)$_3$Cl unit the proton resonances shift as follows: a′ → a, 0.39 ppm; b′ → b, 0.80 ppm; c′ → c, 0.29 ppm; d′ → d, −0.04 ppm; and e′ → e, −0.71 ppm (on the coordinating side); a′ → a′, 0.17 ppm; b′ → b′, 0.41 ppm; c′ → c′, 0.45 ppm; d′ → d′, 0.38 ppm; and e′ → e′, 0.21 ppm (for the uncoordinated components). Similarly for the bimetallic complex, the proton resonances shifted again as follows: a → a, 0.14 ppm; b → b, 0.11 ppm; c → c, 0.29 ppm; d → d, 0.36 ppm; and e → e″, 1.18 ppm; a′ → a, 0.36 ppm; b′ → b, 0.50 ppm; c′ → c, 0.13 ppm; d′ → d, −0.06 ppm; and e′ → e, 0.26 ppm. Two unusual shifts were observed. The shifts of the proton resonance for the b′ proton neighboring coordinated Re was approximately twice as great as normally observed for protons located α to the coordinated nitrogen. This was offset by a rather large negative shift for the e′ proton. The second unusual feature was the nonequivalence of the e protons resonances (labeled e and e″) in the bimetallic complex. In the bimetallic complex these protons appear to be in nonequivalent magnetic environments due to structural constraints. The bimetallic complex is most likely puckered (or twisted) as opposed to planar in order to relieve the steric crowding. The proton lying out of the molecular plane is predicted to shift farthest downfield (labeled e); the other resonance, e″, is predicted for the proton lying in the plane. Upon decoupling at the frequency for e, the peak for e″ disappears, and visa versa. The experiments suggest e and e″ are rapidly interconverting from in-plane to out-of-plane positions at a rate that is slower than the NMR time scale.

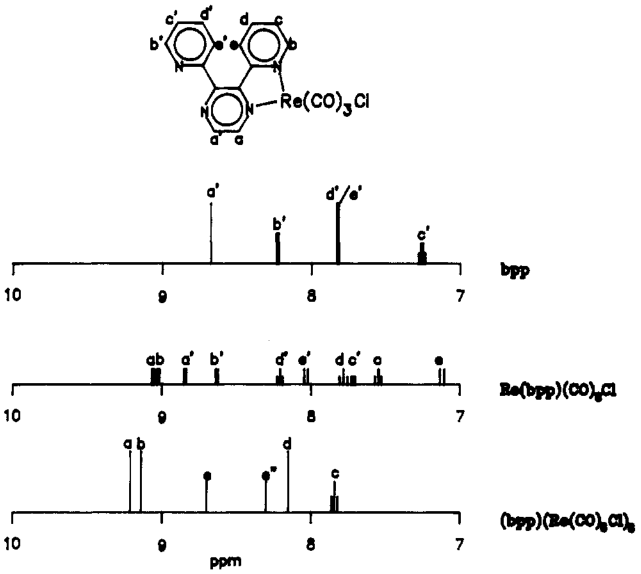

Figure 5. Correlation diagram illustrating the positional shifts of proton resonances in sequence of the bpp ligand, the [bppRe(CO)$_3$Cl] complex, and the [(bpp)(Re(CO)$_3$Cl)$_2$] complex.

Visible–UV Spectra. A summary of the visible–UV spectral properties of the complexes is given in Table IV. Two basic types of transitions were observed. These were $d\pi \rightarrow \pi^*$(bpm), $d\pi \rightarrow \pi^*$(bpp), or $d\pi \rightarrow \pi^*$(bpy) and $\pi \rightarrow \pi^*$(bpm), $\pi \rightarrow \pi^*$(bpp), or $\pi \rightarrow \pi^*$(bpy). While transitions of $d\pi \rightarrow \pi^*$(CO) have been reported for Re(CO)$_5$X, where X = Cl, Br, and I,[18] they are generally 1 order of magnitude less intense. Such transitions are masked by the more intense transition involving the heterocyclic ligand or manifest themselves in more subtle ways (vide infra). In studies of Re(*o*-phen)(CO)$_3$Cl, two transitions in the 300-nm region were assigned as $d\pi \rightarrow \pi^*$(*o*-phen) and others at higher energy to $\pi \rightarrow \pi^*$(*o*-phen).[13]

Certain details in Table IV are of interest. First, the absorption spectra of $(CH_3)_2$bpy and Mebpy-Mebpy are similar except the absorption coefficients of Mebpy-Mebpy are twice as great. Second, the $d\pi \rightarrow \pi^*$ transitions of $[((CH_3)_2bpy)Re(CO)_3Cl]$, [(Mebpy-Mebpy)Re(CO)$_3$Cl], and [(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$] occur at nearly the same energies but the absorption coefficient of the bimetallic species is twice as great as the mo-

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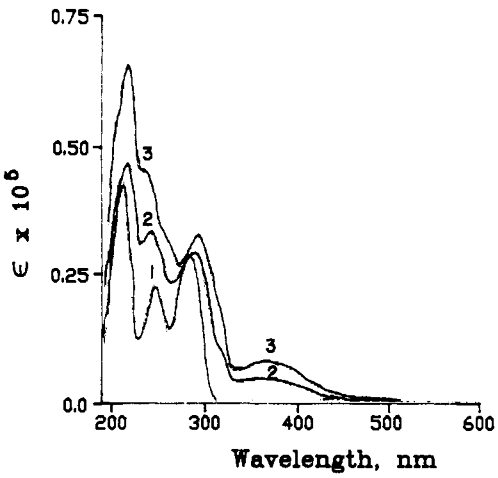

Figure 6. Visible–UV spectral overlay: 1, Mebpy-Mebpy; 2, [(Mebpy-Mebpy)(Re(CO)$_3$Cl)]; 3, [Mebpy-Mebpy(Re(CO)$_3$Cl)$_2$].

nometallic complex. Third, the lower energy $\pi \rightarrow \pi^*$(bpy) transitions of the Mebpy-Mebpy ligand of the [(Mebpy-Mebpy)Re(CO)$_3$Cl] complex and of the [(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$] species remain relatively fixed whereas the higher energy transitions shift toward the blue region and the absorption coefficients increase in a predictable manner. This may be the result of overlapping $\pi \rightarrow \pi^*$(bpy) and d$\pi \rightarrow \pi^*$(CO)[16] transitions. These features are illustrated in Figure 6.

Comparison of the lowest energy d$\pi \rightarrow \pi^*$ transition of the monometallic and bimetallic complexes indicates that little change in energy occurs for the Mebpy-Mebpy complexes whereas there is a shift from 384 to 480 nm for the bpm-based complexes and from 406 to 454 nm for the bpp complexes. A further point of comparison is the lower energy transitions of the bpm- and bpp-based complexes compared to the Mebpy-Mebpy species. This is expected on the basis of the lower π^* energy levels of bpm compared to Mebpy–Mebpy, as indicated by the lower free ligand reduction potential of 1.8 V for bpm[19] compared to 2.26 V for bpy.[20] The shift of the d$\pi \rightarrow \pi^*$(bpm) absorption from 384 nm for [bpmRe(CO)$_3$Cl] to 480 nm for [(bpm)(Re(CO)$_3$Cl)$_2$] is consistent with electrostatic lowering[21] of the bpm π^* energy levels due to the presence of another rhenium(I) chromophore. A similar effect is observed for the bpp complexes, although the shift in the MLCT absorption energy upon attachment of the second metal center is less pronounced than that observed for the bpm-containing species. This may be due to the fact that the metals share only one ring of the bridging ligand and the bimetallic complex is nonplanar for bpp whereas two planar rings are shared for the bpm-based complexes and the π conjugation is uninterrupted.

Electrochemistry. Redox potentials for the complexes were determined in acetonitrile and dimethylformamide and are tabulated in Table V. The bimetallic complexes were only slightly soluble in acetonitrile. Consequently their electrochemical properties were determined in dimethylformamide. The redox processes are relatively straightforward to assign. An electrochemically irreversible oxidation was observed near 1.4 V for the monometallic complexes. This has been assigned to oxidation of the rhenium(I) center.[3] A second oxidation was observed for [((CH$_3$)$_2$bpy)Re(CO)$_3$Cl] and [(Mebpy-Mebpy)Re(CO)$_3$Cl], which is difficult to assign to a given process due to the irreversibility of the initial oxidation at 1.4 V. The similar potentials for oxidation of [(bpm)Re(CO)$_3$Cl], [(bpp)Re(CO)$_3$Cl], and [(Mebpy-Mebpy)Re(CO)$_3$Cl] suggest that the dπ energy levels remain relatively constant in these complexes. Unfortunately, the oxidations for the bimetallic complexes were outside of the working potential range in DMF.[22]

Table V. Polarographic Half-Wave Potentials for Various Rhenium(I) Complexes[a,b]

	$E_{1/2}$, V	
compd	oxidn	redn
[((CH$_3$)$_2$bpy)Re(CO)$_3$Cl]	1.36 (irr), 1.85 (irr)	−1.43, −1.95 (irr)
[(Mebpy-Mebpy)Re(CO)$_3$Cl]	1.37 (irr), 1.66 (irr)	−1.42, −1.89 (irr)
[(Mebpy-Mebpy)-(Re(CO)$_3$Cl)$_2$][c]		−1.29
[(bpm)Re(CO)$_3$Cl][d]	1.43 (irr)	−1.03, −1.65 (irr)
[(bpm)(Re(CO)$_3$Cl)$_2$][c,d]		−0.30, −1.18 (irr)
[(bpp)Re(CO)$_3$Cl]	+1.44 (irr)	−1.01, −1.46 (irr)
[(bpp)(Re(CO)$_3$Cl)$_2$][c]		−0.46, −1.11 (irr)

[a] Potentials are in V vs SSCE, ±0.02 V. [b] Solutions were 0.10 M in TBAH; the solvent was acetonitrile, unless otherwise noted. [c] DMF. [d] Data from ref 3.

The first reduction of the rhenium complexes is reversible with i_c/i_a values near 1 and ΔE_p values ($\Delta E_p = E_p(\mathrm{ox}) - E_p(\mathrm{red})$) that range 60–70 mV, indicative of a one-electron transfer process.[23] The reduction is assigned to the coordinated heterocyclic ligand, as illustrated in eq 1, and is in agreement with the fact that the

$$[(\text{Mebpy-Mebpy})\text{Re(CO)}_3\text{Cl}] + e^- \rightarrow [(\text{Mebpy-Mebpy}^-)\text{Re(CO)}_3\text{Cl}] \quad (1)$$

LUMO is the π^* energy level of the heterocyclic ligand in these complexes.[24] Reduction of [(bpm)Re(CO)$_3$Cl] at −1.03 V and [(bpp)Re(CO)$_3$Cl] at −1.01 V compared to reduction of [((CH$_3$)$_2$bpy)Re(CO)$_3$Cl] at −1.43 V is consistent with the argument referred to previously regarding the lower energy π^* orbitals of bpm and bpp compared to (CH$_3$)$_2$bpy. One important item to note is the change in reduction potential of the monometallic compared to the bimetallic complex. In the case of the saturated –CH$_2$–CH$_2$– linkage reduction of the bimetallic Mebpy-Mebpy complex occurs 130 mV more positive than the monometallic complex. But in the case of the conductive bpm bridge, the shift for [(bpm)(Re(CO)$_3$Cl)$_2$] is 730 mV more positive. Again, the bpp-containing complexes represent an intermediate case, with the reduction of the binuclear species occurring at a potential 550 mV more positive than that of the monometallic complex.

The second reduction is irreversible. It has been assigned as a rhenium-centered process and follows the trends observed for reduction of other rhenium(I) heterocyclic ligand complexes.[3]

Luminescence. The luminescence properties of the complexes are summarized in Table VI. Luminescence at room temperature in acetonitrile was observed for [((CH$_3$)$_2$bpy)Re(CO)$_3$Cl], [(Mebpy-Mebpy)Re(CO)$_3$Cl], [(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$], and [(bpp)Re(CO)$_3$Cl] but not for either of the Re/bpm complexes even out to 1100 nm. Previously, Vogler and Kisslinger reported emission at room temperature from [(bpm)Re(CO)$_3$Cl] in the solid state.[25] In their report, the emission maximum was located at 567 nm whereas we observed a maximum at 595 nm. This difference may be due to different crystalline materials. Recently, Kaim et al. reported luminescence at room temperature for [(bpm)Re(CO)$_3$Cl] in CHCl$_3$. The emission maximum was located at 724 nm but was very weak.[26] The large difference in the positions of emission energy maxima between that observed in the solid state and in chloroform can be attributed to the well-known emission energy matrix dependence observed in rhenium tricarbonyl complexes.[27]

[((CH$_3$)$_2$bpy)Re(CO)$_3$Cl] serves as a good model for the Mebpy-Mebpy complexes as noted by comparing its excitation and emission properties to those of the other two complexes. The

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Table VI. Luminescence Properties of Rhenium Complexes[a]

compd	λ_{ex}(max)[b]	λ_{em}[c] 298 K	λ_{em}[c] 77 K	τ_0,[d] ns	ϕ_{em}[e]
[((CH$_3$)$_2$bpy)Re(CO)$_3$Cl]	370, 311	601	510		1.60×10^{-3}
[(Mebpy-Mebpy)(Re(CO)$_3$Cl)]	373, 312	601	515	35	1.92×10^{-3}
[(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$]	375, 313	603	450, 540	30	1.56×10^{-3}
[(bpm)Re(CO)$_3$Cl]			584, 626		
[(bpp)Re(CO)$_3$Cl]	315, 395	700	580	<20	1.4×10^{-4}

[a] In acetonitrile, unless otherwise noted. [b] Room-temperature excitation maxima determined at emission maxima; λ_{ex} in nm (±2 nm), corrected. [c] λ_{em} in nm (±2 nm); 77 K measurements were in 4:1 ethanol/methanol. [d] τ_0, ±5%; N$_2$ degassed; T = 25 °C. [e] ±10%, relative to rhodamine b (λ_{ex} = 355 nm).

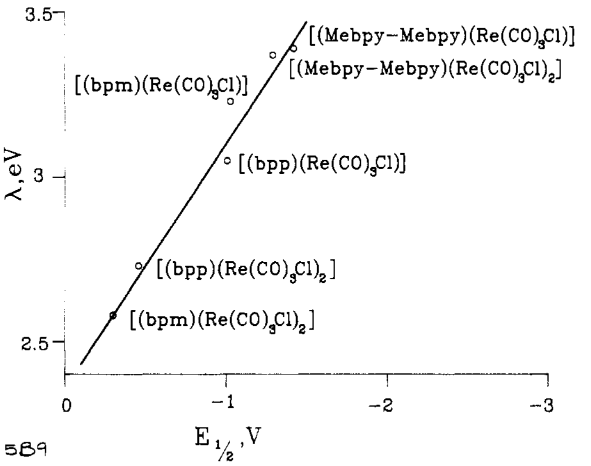

Figure 7. Correlation between the optical and electrochemical reducibility of the heterocyclic ligand of the monometallic and bimetallic complexes. The correlation coefficient is 0.99, the slope is 0.74, and the intercept is 2.38.

luminescence maxima for the Mebpy-Mebpy-based complexes found near 600 nm at room temperature were similar in energy to those found in other rhenium polypyridyl complexes.[28,29] A single blue-shifted maximum was obtained at 77 K. This shift and the lack of vibrational structure are in accord with assignment of these transitions as MLCT in character.[27-29] The changes between the monometallic complex and the bimetallic system are subtle. The excited-state lifetime and radiative quantum yield decrease. Compared to [((CH$_3$)$_2$bpy)Re(CO)$_3$Cl], the tethered "Mebpy" and "MebpyRe(CO)$_3$Cl" components of [(Mebpy-Mebpy)Re(CO)$_3$Cl] and [(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$], respectively, have the effect of lowering the excited-state lifetime from 50 to approximately 30 ns. The 77 K emission spectra exhibit red shifts in the energy sequence [((CH$_3$)$_2$bpy)Re(CO)$_3$Cl] > [(Mebpy-Mebpy)Re(CO)$_3$Cl] > [(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$]; however, at room temperature the trend disappears.

Discussion

The ground-state properties of the rhenium(I) complexes follow those of their ruthenium and rhenium analogues. The low-energy electronic transition correlates with that of the first reduction as shown in Figure 7. The correlation coefficient was 0.99, and the slope was 0.74. The rationale and conditions for observing such trends were discussed previously for ruthenium complexes.[30] The trend is in agreement with addition of an electron either optically or electrochemically to an empty π^* energy level of the ligand.[3,30] The fact that the slope is less than 1 may be due to the changing energy of the dπ levels.

The optical transition occurs from the dπ to the π^* energy level and hence is a metal to ligand charge transfer (MLCT). It follows from excited-state lifetime data that the observed emission occurs from the ^{3}MLCT state, which is populated by intersystem crossing from the ^{1}MLCT state. According to the data in Table IV, whether or not emission is observed depends on the energy of the π^* level. This may be due in part to the energy gap law, where it has been shown for ruthenium analogues that k_{nr}, the nonradiative decay rate constant for energy loss from the ^{3}MLCT state to the ground state, becomes increasingly larger as the energy gap between the excited state and ground state decreases.[31] Another contributor may be the heavy-atom effect resulting from the presence of Cl$^-$, which presumably enhances excited-state decay via the nonradiative route.[32] Thus, the bpm systems with their lower lying π/π^* energy levels have very weak emission, the (CH$_3$)$_2$bpy complexes emit moderately, and the bpp complexes, true to their intermediate structure, emit less strongly than the (CH$_3$)$_2$bpy/Mebpy-Mebpy complexes. Of secondary importance is the role of the tethered "MebpyRe(CO)$_3$Cl" unit in [Cl(CO)$_3$ReMebpy-MebpyRe(CO)$_3$Cl]. Its presence appears to lower the excited-state lifetime from that of the model [(CH$_3$)$_2$bpyRe(CO)$_3$Cl] but does not appear to greatly effect the radiative quantum yield. Possibly, increased emission due to the presence of a second emitting site is offset by the larger number of possible vibronic modes.

Electronic communication by a metal center across a coordinated heterocyclic ring is clearly observed in proton NMR resonances. The effect is confined in general to the coordinated organic ring and does not extend to the uncoordinated heterocycles. In the cases investigated here, the metal center "deshields" the protons such that shifts occur downfield except for protons located next to the carbon-carbon bridge. These protons undergo upfield shifts upon coordination of the first metal center and then undergo downfield shifts when the second metal center is added. These protons are forced to occupy the same region of space for [(bpp)(Re(CO)$_3$Cl)$_2$]. Thus, the protons next to the bridging carbon atoms for [(bpp)(Re(CO)$_3$Cl)]$_2$ are clearly in nonequivalent environments. This is in agreement with an interpretation of electrochemical results, where it was suggested that the structure of [(bpp)(Ru(bpy)$_2$)$_2$]$^{4+}$ was puckered to account for the larger difference in the "Ru(bpy)$_2^{3+/2+}$" potentials of the first and second oxidations than would have been observed if the bimetallic complex were planar.[3]

The rhenium(I) complexes were irreversibly oxidized, but the first reduction was reversible and assigned to reduction of the bridging ligand. In the case of bpp, the pyrazine component has the lower π^* energy level and is expected to be the site of reduction. The reversibility of the reductions suggests that the complexes should behave as photooxidants. The calculated potentials[33] are as follows: [((CH$_3$)$_2$bpyRe(CO)$_3$Cl]$^{0*/-}$, 0.63 V; [(Mebpy-Mebpy)Re(CO)$_3$Cl]$^{0*/-}$, 0.64 V; [(bpp)Re(CO)$_3$Cl]$^{0*/-}$, 0.76 V; [(Mebpy-Mebpy)(Re(CO)$_3$Cl)$_2$]$^{0*/-}$, 0.77 V. Rhenium(I) tricarbonyl complexes have been shown to behave as photoreductants with electron acceptors such as methyl viologen and CO$_2$. When the first irreversible oxidation listed in Table IV is used as an approximation for the Re$^{II/I}$ potential, the excited-state redox potentials are estimated to be as follows: [(CH$_3$)$_2$bpy)Re(CO)$_3$Cl]$^{+/0*}$, −0.70 V; [(Mebpy-Mebpy)(Re(CO)$_3$Cl)]$^{+/0*}$, −0.69 V; [(bpp)Re(CO)$_3$Cl]$^{+/0*}$, −0.33 V. The excited-state potential data indicate that the complexes would be of comparable strength

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as photooxidants or photoreductants.

In summary, NMR and emission data indicate that the role of the insulating bridge in the 4,4′-position of the bipyridine dimer is to both spacially and electronically separate two similar metal centers from substantial communication with one another. It is clear that protons of conjugated ligands are affected by the presence of the metal centers and that the greatest effect is for protons on the coordinating component. The α protons neighboring the coordination site appear to shift downfield about 0.30 ppm for the heterocyclic ligand systems studied here. Further, similar metal centers attached to the *same* heterocyclic rings do interact electronically as noted by differences in their redox and electronic properties compared to the situation where only one metal center is attached. We are currently designing systems where two metal centers will be separated by an insulating spacer but where the metal centers will still be able to contact one another to facilitate electron transport. The bridging ligands currently being synthesized are bipyridine based but contain the bridge in the 6-position as opposed to the 4-position in Mebpy-Mebpy.

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Supplementary Material Available: A listing of decoupling parameters, results, and conclusions for NMR experiments with [(Mebpy-Mebpy)-$Re(CO)_3Cl$], [(bpp)$Re(CO)_3Cl$], and [(bpp)$(Re(CO)_3Cl)_2$] (4 pages). Ordering information is given on any current masthead page.

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Ruthenium(II) Complexes of N,N′-Bridged Derivatives of 2,2′-Biimidazole

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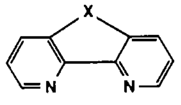
Ruthenium(II) complexes of the type $RuL_3[PF_6]_2$ and $RuL(bpy)_2[PF_6]_2$ have been prepared where L is an N,N′-bridged derivative of 2,2′-biimidazole. Molecular mechanics calculations have been employed to compare the geometries of these ligands to those of analogous 2,2′-bipyridine systems. Analysis of ^1H NMR spectra indicates that in the coordinated state the bridged biimidazoles show greater conformational mobility than their bipyridine counterparts. For the dimethylene-bridged biimidazole, the bite angle is too unfavorable to allow bidentate coordination and NMR evidence points to monodentate coordination in the mixed-ligand complex. The electronic spectra of the RuL_3^{2+} complexes show absorption at about 400 nm, which indicates a high-lying π^* state. This observation is reinforced by low oxidation potentials and high reduction potentials for these systems. The mixed-ligand complexes show an absorption band at even shorter wavelength, which we assign to the biimidazole MLCT state. The redox chemistry of these systems appears to be governed primarily by the bpy ligands.

Introduction

Ligands of the 1,2-diimine type have been widely employed in the complexation of a variety of transition-metal species, especially ruthenium(II).[1] The most commonly employed ligand of this type is 2,2′-bipyridine (bpy), which is readily able to adopt the planar conformation typically required for bidentate coordination. We have recently examined the effect of distorting bpy by the incorporation of a 3,3′-polymethylene bridge as depicted in structure **1**.[2] A series of ruthenium(II) complexes of the types RuL_3^{2+} and $Ru(bpy)_2L^{2+}$ were prepared and studied.[3] In general, it was found that although some flattening of the bridged bpy did occur upon complexation, ruthenium(II) could accommodate surprisingly distorted ligand geometries.



1a X = H,H
b X = CH_2
c X = $(CH_2)_2$
d X = $(CH_2)_3$
e X = $(CH_2)_4$

Other azabiaryl ligands such as 2,2′-bipyrimidine,[4,5] 2,2′-bipyrazine,[5,6] 1,10-phenanthroline,[7] 2,2′-biquinoline,[8,9] and 2,2′-bi[1,8]naphthyridine[9] have also been examined in hopes of tuning the properties of their metal complexes. These systems all share the common feature of chelating through an sp^2 nitrogen incorporated in a six-membered aromatic ring. In the absence of interfering substituents, the geometry of the resulting chelate ring is essentially invariant. If the coordinating nitrogen were instead incorporated into a five-membered heterocycle, however, the bite angle should be substantially diminished and the ligand's ability

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