

## Bimetallic Complexes of Rhenium(I). Preparation of $\text{Re}(\text{BL})(\text{CO})_3\text{Cl}$ and $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{BL})$ (BL = 2,3-Bis(2-pyridyl)pyrazine, 2,3-Bis(2-pyridyl)quinoxaline, and 2,3-Bis(2-pyridyl)benzo[g]quinoxaline)

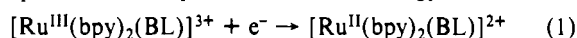
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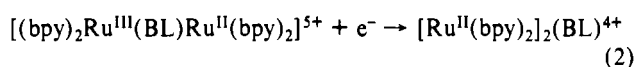
Mono- and bimetallic complexes of  $\text{Re}(\text{CO})_3\text{Cl}$  containing the bidentate, bridging ligands 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq), and 2,3-bis(2-pyridyl)benzo[g]quinoxaline (dpg) have been prepared and characterized. The synthesis and characterization of the new bidentate bridging ligand dpg are reported. The lowest energy electronic absorption band has been assigned as a metal-to-ligand charge-transfer (MLCT) process, where the acceptor state is localized primarily on the bridging ligand. Unlike the analogous Ru bimetallic complexes of dpp and dpq, the bimetallic complexes of Re that contain these ligands do not luminescence. The first reduction of these complexes occurs between -0.12 and -1.00 V (vs a 3 M NaCl Ag/AgCl reference electrode), and is localized on the bridging ligand. With the exception of  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$ , the second reduction of these complexes is also localized on the bridging ligand. Data is presented that shows that the  $\text{Re}(\text{CO})_3\text{Cl}$  moiety is more effective at stabilizing the reduced forms of dpp, dpq, and dpg than  $\text{Ru}(\text{bpy})_2^{2+}$ . This yields a series of five mono- and bimetallic complexes that have two ligand-centered reductions at relatively positive potentials.

### Introduction

The chemistry of ruthenium polypyridyl complexes has rapidly expanded in the past 2 decades, due in part to the variety of ground-state and excited-state redox properties associated with these molecules.<sup>1</sup> A developing area of ruthenium chemistry has been that of ligand-bridged bimetallic complexes,<sup>2-6</sup> such as  $[\text{Ru}(\text{bpy})_2]_2(\text{BL})^{4+}$  (where bpy = 2,2'-bipyridine and BL = 2,3-bis(2-pyridyl)pyrazine (dpp) and 2,3-bis(2-pyridyl)quinoxaline (dpq); see Figure 1). These two ligands are similar to bpy with respect to the coordination around the metal center,<sup>4</sup> so properties that do not directly depend on the energies of the  $\pi$  and  $\pi^*$  orbitals of the BL are not strongly affected. For example, Gafney et al.<sup>3</sup> has shown via electrochemical measurements of the  $\text{Ru}^{\text{III/II}}$  reduction potentials for eqs 1 and 2 that the energy of the metal-



$$E_{1/2} = 1.33 \text{ V}$$



$$E_{1/2} = 1.38 \text{ V}$$

centered  $d\pi$  orbitals are very similar in both the mono- and bimetallic systems. On the other hand, those properties that depend on the lowest energy  $\pi^*$  orbital, such as ligand-centered reductions and MLCT (metal-to-ligand charge-transfer) absorptions, are strongly affected by the identity of the bridging ligand and the nuclearity of the complex.

In order to extend the series of bridging ligands based on dpp, we prepared 2,3-bis(2-pyridyl)benzo[g]quinoxaline (dpg; see Figure 1) via the condensation of 2,2'-pyridil and 2,3-diaminonaphthalene. Preparation of  $[\text{Ru}(\text{bpy})_2]_2(\text{dpg})^{4+}$  showed that dpg is an effective bridging ligand, with the first and second reductions of the complex being localized on the dpg.<sup>7</sup> To further probe the properties of this new bridging ligand, as well as dpp and dpq, we turned to the smaller  $\text{Re}(\text{CO})_3\text{Cl}$  moiety.

As noted by Juris<sup>8</sup> et al., considerably less attention has been paid to polypyridyl derivatives of  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ , which is similar in many respects to  $\text{Ru}(\text{bpy})_3^{2+}$ . Polypyridyl tricarbonyl complexes of this low-spin,  $d^6$  metal ion exhibit MLCT absorptions around 400 nm and are frequently luminescent at room temperature in fluid solution. They also serve as efficient photo- and electrocatalysts for the reduction of  $\text{CO}_2$  to CO and other products.<sup>9-17</sup>

This latter reactivity is based on reduction of polypyridyl-centered  $\pi^*$  orbitals, which is also the acceptor orbital for the MLCT process.

The  $\text{Re}(\text{CO})_3\text{L}$  (L = a monodentate Lewis base) moiety offers a number of advantages for the study of dpp-type bridging ligands. For our purposes, the most important advantages are that there is no change in total complex charge upon binding a second  $\text{Re}(\text{CO})_3\text{Cl}$  moiety to  $\text{Re}(\text{BL})(\text{CO})_3\text{Cl}$  and there are no bpy ligands to complicate the spectroscopy and electrochemistry. The high charge of  $[\text{Ru}(\text{bpy})_2]_2(\text{dpp})^{4+}$  was a major obstacle in its purification.<sup>3a</sup> It is also of interest to observe the effects of adding the second metal center to the bridging ligand in the absence of changes in the overall complex charge. The presence of only one type of polypyridyl acceptor ligand will eliminate the overlap of the  $d\pi(\text{M}) \rightarrow p\pi(\text{BL})$  and  $d\pi(\text{M}) \rightarrow p\pi(\text{bpy})$  absorption bands, as is the case in complexes like  $[\text{Ru}(\text{bpy})_2]_2(\text{dpp})^{4+}$ .

Two ligand-bridged, symmetrically bimetallic complexes containing the  $\text{Re}(\text{CO})_3\text{Cl}$  moiety have been reported, utilizing 2,2'-bipyrimidine (bpm)<sup>18</sup> and 5,5',3'',5'''-tetramethyl-

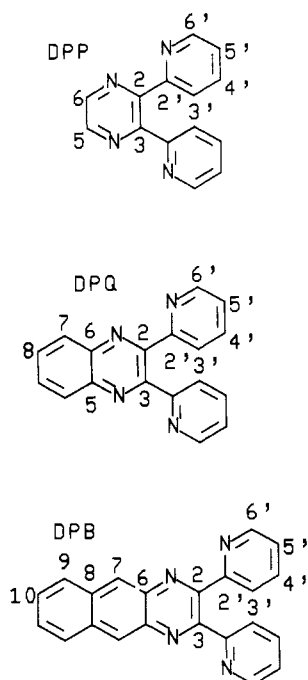
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**Figure 1.** Structures and carbon numbering system used for the bridging ligands dpp, dpq, and dpb.

2,2':6,2'':6'':2'''-quaterpyridine (QP).<sup>8</sup> Bimetallic complexes built around bpm show significant perturbations of what are normally thought of as largely metal-centered properties, according to criteria such as described in eq 1 and 2 above.<sup>2</sup> In the case of  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{bpm})$ , this results in the absence of radiative decay as a relaxation pathway for the excited state of this complex. In contrast,  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{QP})$  exhibits radiative relaxation, which suggests that the properties critical to this process are not significantly perturbed upon addition of the second  $\text{Re}(\text{CO})_3\text{Cl}$  group. Without the monometallic analogue,  $\text{Re}(\text{QP})(\text{CO})_3\text{Cl}$ , further conclusions are difficult to make, since the properties of the monometallic species are critical to the understanding of the changes induced by addition of the second metal fragment. However, given that the absorption and emission energies for  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{QP})$  are in the same range as those for the bpy complex, it is likely that the  $\pi^*$  orbitals of one bpy fragment in this ligand are not affected by coordination of a metal fragment to the other.

The dpp ligand series represents a middle ground between QP and bpm, since the metal-centered properties are generally unaffected by the presence of a metal fragment on the other side of the ligand, but those properties sensitive to the energy of the BL  $\pi^*$  orbital are affected by the number of metals bound to the ligand. Given that three ligands are now available in the dpp series, a unique opportunity exists to study the properties of bimetallic complexes of  $\text{Re}(\text{CO})_3\text{Cl}$  where the only variation is the energy of the bridging ligand's  $\pi$  system. With the intent of developing this series, we report the syntheses and properties of  $\text{Re}(\text{BL})(\text{CO})_3\text{Cl}$  and  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{BL})$ , where BL = dpp, dpq, and dpb.

### Experimental Section

**Materials.** All preparative solvents were of reagent grade and were used without further purification. For electrochemical experiments, Burdick-Jackson high-purity methylene chloride and acetonitrile were used after drying over activated molecular sieves (4 Å, Davidson). The deuterated solvent used for  $^{13}\text{C}$  NMR measurements was supplied by Stohler Isotope Chemicals. The compounds  $\text{Re}(\text{CO})_3\text{Cl}$  (Pressure Chemical Co.), 2,2'-pyridyl (Aldrich), *o*-phenylenediamine (Aldrich), 2,3-diaminonaphthalene (Fluka), and 2,3-bis(2-pyridyl)pyrazine (dpp)

(Aldrich) are commercially available and were used as received. Tetrabutylammonium hexafluorophosphate (TBAH) was prepared from tetrabutylammonium bromide (Fluka) and hexafluorophosphoric acid (Alfa-Ventron). The product was recrystallized from ethanol three times and dried in a vacuum oven at 100 °C for 6 h.

**Chromatography.** Thin-layer chromatography on aluminum oxide 150 F254 Type T plates from EM Science was used to test for purity and formulate the mobile phases for preparative column purification. Gravity-feed liquid chromatography utilizing Ace Glass columns and Fisher A-540-500 alumina was used to purify bulk (100 mg) samples of the metal complexes. The mobile phases were typically prepared from mixtures of acetone, methylene chloride, and acetonitrile.

**Instrumentation.** Electrochemical measurements were carried out in acetonitrile and methylene chloride with 0.1 and 0.2 M TBAH, respectively, as supporting electrolyte. A platinum-disk working electrode, a platinum-wire auxiliary electrode, and a 3 M NaCl Ag/AgCl reference electrode (+0.20 V vs the normal hydrogen electrode) (all from Bioanalytical Systems) were used in the voltammetric experiments. All cyclic (CV) and Osteryoung square-wave voltammograms (OSWV) were obtained on a BAS-100 electrochemical analyzer. The cyclic voltammograms were run at a scan rate of 100 mV/s unless otherwise noted. The conditions for OSWV were as follows: square wave amplitude, 25 mV; sampling points, 256; frequency, 15 Hz; step E, 4 mV.

Infrared spectra were recorded on a Bomem Michelson series 100 FTIR spectrometer.

Elemental analyses were performed by the elemental analysis group at Merck and Co., Rahway, NJ.

Electronic absorption spectra were obtained on an Aviv Model 118DS UV-vis spectrophotometer or a Hewlett-Packard Model 8452A diode array spectrophotometer controlled by an AT&T 6300 microcomputer.

A Spex Model F222A spectrofluorimeter was used to acquire the emission spectra. The photomultiplier tube used to detect the emission was a Hamamatsu R928 side-on tube with an absolute low-energy cutoff of 930 nm.

Proton-decoupled  $^{13}\text{C}$  NMR spectra were obtained on a General Electric QE 300 Fourier transform NMR spectrometer operating at 75.48 MHz. The samples were dissolved in  $\text{CDCl}_3$  containing 1% tetramethylsilane (TMS) and placed in 5 mm NMR tubes for analysis. All chemical shifts were reported vs TMS.

**Syntheses.** **2,3-Bis(2-pyridyl)quinoxaline (dpq).** This ligand was synthesized according to the procedure of Goodwin and Lions.<sup>20</sup> Anal. Calcd: C, 76.04; H, 4.25; N, 19.71. Found: C, 75.77; H, 4.47; N, 19.62.

**2,3-Bis(2-pyridyl)benzo[*g*]quinoxaline (dpb).** A slurry of 2,3-diaminonaphthalene (1.6 g, 0.01 mol) and 2,2'-pyridyl (2.1 g, 0.01 mol) in 70 mL of absolute ethanol was prepared. The resulting mixture was heated at reflux for 5 h. The dark brown-yellow solution was aged overnight at 10 °C. Filtering yielded gold crystals of crude product (3.0 g). Several recrystallizations from ethanol, followed by sublimation, gave pure dpb as a bright yellow solid (2.6 g, 79%). Particular care is needed in the purification of this ligand, since 2,2'-pyridyl is a persistent impurity in this particular synthesis. Anal. Calcd: C, 79.03; H, 4.22; N, 16.76. Found: C, 79.12; H, 3.96; N, 16.50.

**Preparation of Rhenium Complexes.** All rhenium complexes were prepared by the same general method, which is a modification of the  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$  synthesis originally reported by Wrighton and Morse.<sup>21</sup> Any deviations are reported in the specific syntheses below. In the preparation of the monometallic complexes,  $\text{Re}(\text{CO})_3\text{Cl}$  and 3 equiv of the polypyridyl ligand were slurried in toluene. This mixture was refluxed with stirring for 18 h. The darkly colored solution was cooled, and the precipitate that formed was collected by filtration. The bimetallic complexes were prepared in a similar fashion except that the stoichiometry was 2.5 equiv of  $\text{Re}(\text{CO})_3\text{Cl}$  to 1 equiv of the ligand.

**$\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$ .** After a few minutes of reaction, the solution changed from a pale yellow to dark brown-orange. The yellow complex was purified by column chromatography using 100% acetonitrile as the mobile phase. The column cut was concentrated, flash precipitated from diethyl ether, and collected by filtration. Anal. Calcd: C, 37.81; H, 1.87; N, 10.38. Found:<sup>22a</sup> C, 37.68; H, 2.07; N, 10.28.

**$\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$ .** After approximately 10 min at reflux the solution changed from pale yellow to dark red-orange. The red complex was purified by column chromatography using a mobile phase of 98% methylene chloride/2% acetonitrile. The column cut was evaporated to dryness. A saturated solution of the resultant solid was prepared in acetonitrile. The material was then flash precipitated from diethyl ether

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(22) (a) These analyses were corrected for water content, as measured by Karl Fischer titration. (b) This analysis was corrected for water content, as measured by Karl Fischer titration and thermogravimetric analysis.

**Table I.**  $^{13}\text{C}$  Chemical Shifts in ppm and Assignments for dpp, dpq, and dpb

ligand	chem shift								
	C-3'	C-4'	C-5'	C-6'	C-6	C-7	C-8	C-9	C-10
dpp	124.2	136.5	123.0	148.8	142.7				
dpq	124.2	136.6	123.0	148.6	BH <sup>b</sup>	130.5	129.4		
dpb	124.1	136.7	123.0	148.4	BH	a	BH	a	a

<sup>a</sup> Signals at 127.0, 127.9, and 128.6 ppm are observed for this ligand, but are not specifically assignable with the data currently available.  
<sup>b</sup> BH = bridgehead carbon, no proton attached.

**Table II.** Electronic and Infrared Spectra Data<sup>a</sup>

complex	$\lambda_{\text{abs}}$ , nm ( $\epsilon$ , $\text{M}^{-1} \text{cm}^{-1}$ )				$\nu_{\text{CO}}$ , $\text{cm}^{-1}$	footnote
	soln 1	soln 2	soln 3			
Re(dpp)(CO) <sub>3</sub> Cl	400 (3636)	404	416		2024 1921 1915 1905	1
Re(dpq)(CO) <sub>3</sub> Cl	432	438	449 (3407)		2025 370 (10617) 1924 266 (26989) 1905	3
Re(dpb)(CO) <sub>3</sub> Cl	460	462	478 (4179)		2021 408 (11103) 1918 328 (43281) 1893	
[Re(CO) <sub>3</sub> Cl] <sub>2</sub> (dpp)	456 (8523) 335 (18367) 268 (sh)	458	485		2025 1943 1915 1895	
[Re(CO) <sub>3</sub> Cl] <sub>2</sub> (dpq)	505 (7692) 395 (12864) 317 (26427) 287 (sh)	507	526		2025 1925 1897	
[Re(CO) <sub>3</sub> Cl] <sub>2</sub> (dpb)	518	532	542 (7960) 381 (42777) 368 (sh)		2028 1926 1891	3

<sup>a</sup> Infrared spectra run in KBr pellets except as noted: (1) CH<sub>3</sub>CN solution,  $\epsilon(20^\circ\text{C}) = 37.5$ ; (2) (CH<sub>3</sub>)<sub>2</sub>CO solution,  $\epsilon(25^\circ\text{C}) = 20.7$ . (3) CH<sub>2</sub>-Cl<sub>2</sub> solution,  $\epsilon(25^\circ\text{C}) = 8.93$ . Dielectric constants were taken from: *Burdick and Jackson Laboratories Solvent Guide*; Burdick and Jackson: Muskegon, MI, 1980.

and collected on a sintered glass frit. Anal. Calcd: C, 42.75; H, 2.05; N, 9.50. Found: C, 42.70; H, 2.02; N, 9.38.

**Re(dpb)(CO)<sub>3</sub>Cl.** A color change from yellow to deep orange was observed after a few minutes at toluene reflux. After washing sparingly with acetone to remove some excess dpb the material was chromatographed by using a mobile phase of 100% acetone. The column cut was evaporated to dryness and reconstituted in minimal methylene chloride. The dark orange complex was collected by filtration after flash precipitation from pentane. Anal. Calcd: C, 46.91; H, 2.20; N, 8.75. Found:<sup>22a</sup> C, 47.12; H, 2.21; N, 8.56.

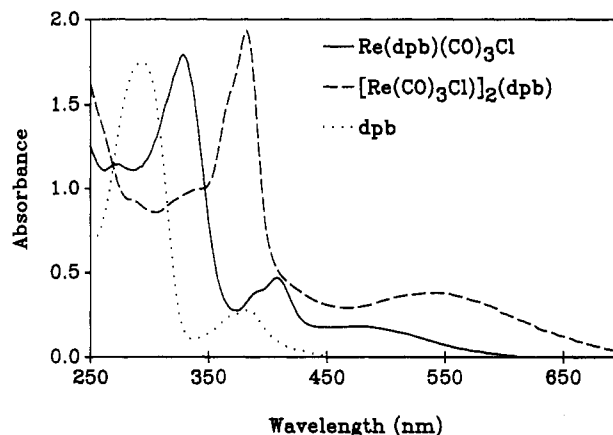
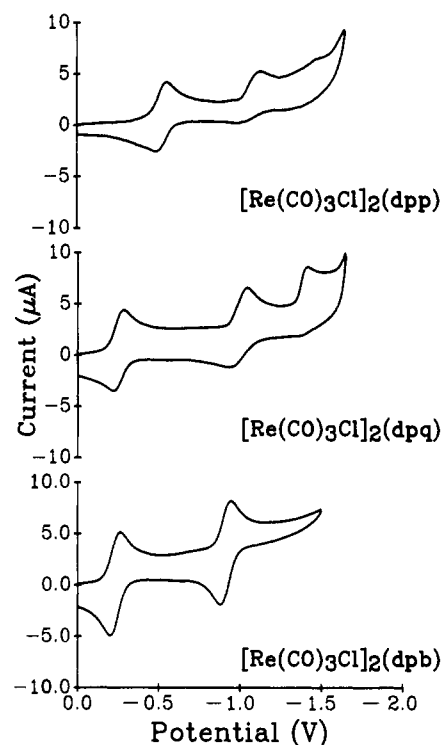
**[Re(CO)<sub>3</sub>Cl]<sub>2</sub>(dpp).** The reaction mixture changed color from pale yellow to deep red after 10 min under toluene reflux. The red complex was purified by column chromatography using a mobile phase of 100% acetonitrile. The column cut was evaporated to dryness, reconstituted in minimal methylene chloride, and flash precipitated from pentane. The resultant solid was collected by filtration. Anal. Calcd: C, 28.41; H, 1.19; N, 6.63. Found:<sup>22b</sup> C, 28.31; H, 1.25; N, 6.24.

**[Re(CO)<sub>3</sub>Cl]<sub>2</sub>(dpq).** A color change from pale yellow to deep burgundy red was observed after approximately 30 min under toluene reflux. The brick red solid was purified by column chromatography using an eluent of 100% methylene chloride. The column cuts were concentrated and flash precipitated by addition to pentane. The precipitate was isolated by filtration. Anal. Calcd: C, 32.18; H, 1.35; N, 6.26. Found: C, 32.23; H, 1.61; N, 5.95.

**[Re(CO)<sub>3</sub>Cl]<sub>2</sub>(dpb).** Rhenium pentacarbonyl chloride (0.20 g, 5.5 × 10<sup>-4</sup> mol) and dpb (0.062 g, 1.9 × 10<sup>-4</sup> mol) were slurried in 2:1 ethanol/methylene chloride. The resulting mixture was heated at reflux for 24 h. Upon cooling, a dark violet product precipitated. This material was purified by column chromatography using a mobile phase of 100% methylene chloride. The column cut was concentrated and flash precipitated from acetonitrile. The solid was collected by filtration. Anal. Calcd: C, 35.56; H, 1.49; N, 5.92. Found: C, 35.83; H, 1.78; N, 5.79.

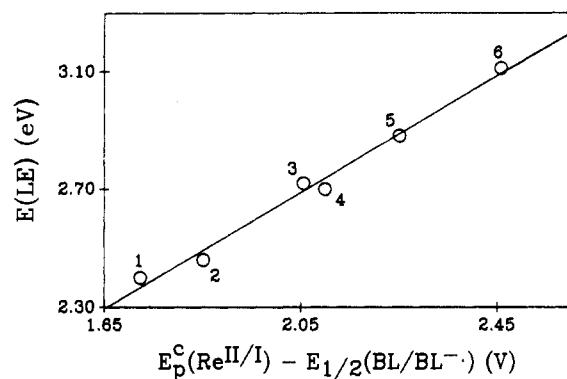
## Results

The results obtained for the six complexes prepared are presented in Tables I–IV and Figures 2–4. All complexes examined

**Figure 2.** Electronic absorption spectra of dpb, Re(dpb)(CO)<sub>3</sub>Cl, and [Re(CO)<sub>3</sub>Cl]<sub>2</sub>(dpb) dissolved in methylene chloride.**Figure 3.** Cyclic voltammograms of [Re(CO)<sub>3</sub>Cl]<sub>2</sub>(dpp) (CH<sub>3</sub>CN/0.1 M TBAH), [Re(CO)<sub>3</sub>Cl]<sub>2</sub>(dpq) (CH<sub>3</sub>CN/0.1 M TBAH), and [Re(CO)<sub>3</sub>Cl]<sub>2</sub>(dpb) (CH<sub>2</sub>Cl<sub>2</sub>/0.2 M TBAH).**Table III.** Reduction Potentials of Re(BL)(CO)<sub>3</sub>Cl and [Re(CO)<sub>3</sub>Cl]<sub>2</sub>(BL) Complexes (in V vs 3 M NaCl Ag/AgCl Reference Electrode)<sup>a</sup>

complex	$E_p^{b,c}$	$E_{1/2}^d$	$E_p^e$	$E_p^f$
Re(dpp)(CO) <sub>3</sub> Cl	+1.48	-0.97		-1.58
Re(dpq)(CO) <sub>3</sub> Cl	+1.55	-0.70		-1.32
Re(dpb)(CO) <sub>3</sub> Cl	+1.56	-0.73 <sup>h</sup>	-1.48 <sup>h</sup>	-1.61 <sup>h</sup>
		-0.54 <sup>b</sup>	-1.08 <sup>b</sup>	
		-0.65 <sup>h</sup>	-1.37 <sup>h</sup>	
[Re(CO) <sub>3</sub> Cl] <sub>2</sub> (dpp)	+1.54	-0.52	-1.13	-1.50
[Re(CO) <sub>3</sub> Cl] <sub>2</sub> (dpq)	+1.60	-0.25	-1.05	-1.42
[Re(CO) <sub>3</sub> Cl] <sub>2</sub> (dpb)	+1.61	-0.12 <sup>b</sup>	-0.82 <sup>b</sup>	
		-0.23 <sup>h</sup>	-0.91 <sup>h</sup>	

<sup>a</sup> Potentials were determined in acetonitrile with 0.1 M TBAH as the supporting electrolyte, except as otherwise noted. <sup>b</sup> Potential is the peak potential from OSWV. <sup>c</sup> Re<sup>II/I</sup> oxidation. <sup>d</sup> BL<sup>-</sup>/BL<sup>-</sup> reduction. <sup>e</sup> BL<sup>-</sup>/BL<sup>2-</sup> reduction; cathodic peak potential; no reoxidation observed. <sup>f</sup> Re<sup>I/0</sup> reduction; no return oxidation observed. <sup>g</sup> Reoxidation observed in the cyclic voltammogram obtained in methylene chloride. <sup>h</sup> Potential from cyclic voltammetry in methylene chloride with 0.2 M TBAH as the supporting electrolyte.



**Figure 4.** Plot of the energies of the lowest energy absorption band (in eV) vs  $E_p^C(\text{Re}^{\text{II/I}}) - E_{1/2}(\text{BL}/\text{BL}^-)$  (in V) of  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{BL})$  (BL = dpb, dpq, dpp; points 1, 2, 3, respectively) and  $\text{Re}(\text{BL})(\text{CO})_3\text{Cl}$  (BL = dpb, dpq, dpp; points 4, 5, 6, respectively) in acetonitrile.

**Table IV.** Comparison of the Potential for the First Bridging Ligand Reduction (in V) for  $\text{Re}(\text{CO})_3\text{Cl}$ - and  $\text{Ru}(\text{bpy})_2^{2+}$ -Containing Systems

		$E_{1/2}(\text{M}(\text{BL})/\text{M}(\text{BL}^-))$			ref
		dpp	dpq	dpb	
A	$[\text{Ru}(\text{bpy})_2(\text{BL})]^{2+}$	-1.06	-0.77	-0.54	<i>b</i>
	$\text{Re}(\text{BL})(\text{CO})_3\text{Cl}$	-0.97	-0.70	-0.54	<i>a</i>
	difference	0.09	0.07	0.00	
B	$[\text{Ru}(\text{bpy})_2]_2(\text{BL})^{4+}$	-0.66	-0.37	-0.20	<i>b</i>
	$[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{BL})$	-0.52	-0.25	-0.12	<i>a</i>
	difference	0.14	0.12	0.08	
C	$\text{Re}(\text{BL})(\text{CO})_3\text{Cl}$	-0.97	-0.70	0.54	<i>a</i>
	$[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{BL})$	-0.52	-0.25	-0.12	<i>a</i>
	difference	0.45	0.45	0.42	
D	$[\text{Ru}(\text{bpy})_2(\text{BL})]^{2+}$	-1.06	-0.77	-0.54	<i>b</i>
	$[\text{Ru}(\text{bpy})_2]_2(\text{BL})^{4+}$	-0.66	-0.37	-0.20	<i>b</i>
	difference	0.40	0.40	0.34	

<sup>a</sup>This work. <sup>b</sup>The data for the ruthenium dpp and dpq complexes was taken from ref 38. The data for the ruthenium dpb complexes was taken from ref 7.

appear to be thermally inert in solution since the absorption spectra exhibit no change over a period of several hours.

Two of the complexes,  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$  and  $\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$ , were found to luminescence at 679 and 750 nm, respectively, in acetonitrile at room temperature.  $\text{Re}(\text{dpb})(\text{CO})_3\text{Cl}$  was initially thought to luminescence at ca. 560 nm in  $\text{CH}_2\text{Cl}_2$ , but it was later discovered to be due to an impurity. Reaction of 2,2'-pyridil with  $\text{Re}(\text{CO})_3\text{Cl}$  yielded a complex mixture. The leading band resulting from column chromatography of this mixture (alumina/acetonitrile) yielded a substance that had a more intense luminescence spectrum with the same emission energy as the impure  $\text{Re}(\text{dpb})(\text{CO})_3\text{Cl}$ . Careful purification of dpb before its use as a starting material or of  $\text{Re}(\text{dpb})(\text{CO})_3\text{Cl}$  that resulted from impure dpb yielded nonluminescent samples of  $\text{Re}(\text{dpb})(\text{CO})_3\text{Cl}$ . Unlike the analogous Ru bimetallic complexes of dpp and dpq, no luminescence was observed for the bimetallic complexes of Re that contain these ligands.

## Discussion

**Characterization of dpb.** The bridging ligand dpb was prepared by a Schiff base condensation between 2,2'-pyridil and 2,3-diaminonaphthalene in ethanol. This synthesis parallels the synthesis of dpq originally reported by Goodwin and Lions.<sup>20</sup> In order to verify the identity of the bright yellow product, the  $^{13}\text{C}$  NMR and electronic spectra of dpb, dpq, and dpp were obtained.

The  $^{13}\text{C}$  NMR chemical shifts for the three ligands and our tentative interpretations of the data are shown in Table I. They were assigned by analogy with pyridine,<sup>23</sup> pyrazine,<sup>23</sup> and bpy.<sup>24,25</sup>

Our results indicate that the peak at 143 ppm is due to the C-6 carbon, not the C-6' carbon as previously reported<sup>26</sup> for dpp. Since the primed carbons should be conserved in all three molecules, it is more appropriate to assign the peak at 148.8 ppm to C-6'. Further NMR experiments are underway to definitively assign the  $^{13}\text{C}$  chemical shifts for these ligands and their complexes with Ru, Fe and Re.

**Electronic Absorption Spectroscopy.** Table II contains the electronic spectral data for each of the molecules examined. Included in this table are the wavelengths for the lowest energy band of each complex in acetonitrile, acetone, and methylene chloride. The spectra for dpb,  $\text{Re}(\text{dpb})(\text{CO})_3\text{Cl}$ , and  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpb})$  are shown in Figure 2.

The free ligand spectra show high-energy, high-intensity bands typical of fully allowed  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. These bands shift to lower energy as the degree of  $\pi$  delocalization increases, which is consistent with expectations.

The lowest energy bands of the monometallic complexes are broad, with maxima in the range from 400 to 500 nm and molar extinction coefficients ranging from  $3 \times 10^3$  to  $5 \times 10^3$   $\text{L mol}^{-1} \text{cm}^{-1}$ . In addition, each complex shows several structured bands at higher energies similar to those in the corresponding free ligands. In  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$ , these bands are not fully resolved from each other. The extinction coefficients for these higher energy transitions are from  $1.0 \times 10^4$  to  $4.5 \times 10^4$   $\text{L mol}^{-1} \text{cm}^{-1}$ . On the basis of the free ligand spectra and the qualitative similarity of the absorption spectra to results previously published<sup>8,21,27</sup> on related complexes, the lowest energy absorption maxima are assigned to  $d\pi(\text{Re}) \rightarrow p\pi^*(\text{BL})$  MLCT.<sup>28</sup> These low-energy bands are solvent dependent, shifting to longer wavelengths in solvents of lower dielectric constant. This effect has been observed by several other authors.<sup>17,21,27,29,30</sup> The positions of the low energy maxima are also sensitive to the nature of the BL, shifting to longer wavelengths as the degree of  $\pi$  delocalization in the acceptor ligand increases. This observation is not surprising since the energy of a quantum-mechanical particle in a "box" is inversely related to the length of the box. If the system is viewed in terms of this crude analogy, it is clear that this trend is consistent with the MLCT assignments.<sup>6,31</sup> The higher energy UV absorptions are attributed to intraligand (IL)  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. Some of these bands show a slight solvent dependence, which is less pronounced than those observed for the MLCT absorptions. This could be indicative of  $n \rightarrow \pi^*$  components in these complex bands.<sup>32,33</sup>

By the use of spectral data available on  $\text{Re}(\text{py})_2(\text{CO})_3\text{Cl}^{21}$  (py = pyridine),  $\text{Re}(\text{CO})_3\text{Cl}$ , empirical *f* and *g* parameters<sup>34</sup> and the "rule of average environment",<sup>34</sup> a system of simultaneous equations (two equations in two unknowns) was set up and solved to yield an *f* value of 1.42 for CO and a *g* value of 23.0 for Re(I). From these results, the lowest energy ligand field (LF) transition for these complexes was estimated to occur at ca. 340 nm. The molar extinction coefficients for LF transitions in organometallic complexes are known to be  $10^3$ – $10^4$   $\text{L mol}^{-1} \text{cm}^{-1}$ , in contrast to those of traditional Werner-type complexes.<sup>35</sup> The LF transitions for  $\text{Re}(\text{CO})_3\text{Cl}$  were determined in this laboratory to be ca. 3200 and 1000  $\text{L mol}^{-1} \text{cm}^{-1}$  at 318 and 342 nm in  $\text{CH}_3\text{CN}$  ( $^1E \leftarrow ^1A_1$ ,  $^3E \leftarrow ^1A_1$ ),<sup>36,37</sup> respectively. On the basis of the above work and

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earlier work,<sup>8,21,27</sup> it is clear that the lower intensity LF absorbances are obscured by the more intense IL bands.

The bimetallic complexes feature several overlapping bands in the region from ca. 230 to 430 nm. Each complex also possesses a solvent-dependent lowest energy absorption band in the range 450–550 nm. The intense higher energy transitions are assigned to  $\pi \rightarrow \pi^*$  ligand-centered processes. The lowest energy bands are assigned to the  $d\pi(\text{Re}) \rightarrow p\pi^*(\text{BL})$  process by analogy with the monometallic complexes. The extinction coefficients of the lowest energy bands in the bimetallic complexes are approximately twice those in the corresponding monometallic complexes, supporting their MLCT assignment. These assignments parallel those made for ligand-bridged bimetallic complexes of Ru(II).<sup>3,4,6,38</sup>

Several trends in the electronic spectra data are evident upon examination of Table II and Figure 2. In each case, the IL absorbances are red-shifted upon coordination of the second  $\text{Re}(\text{CO})_3\text{Cl}$  fragment to the monometallic complex to form the bimetallic complex. For the  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}/[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpp})$  pair, bimetallic formation is also accompanied by a marked increase in the structure of the spectrum. The MLCT band is also clearly shifted to lower energy relative to its position in the monometallic complex upon addition of the second metal fragment. Shifts of this type, particularly with respect to the MLCT band, have been observed by other authors<sup>6,39</sup> and can be attributed to an apparent stabilization of the  $\pi^*$  levels on the bridging ligand due to interaction with the additional electropositive Re(I) center. Since the IL transitions are essentially  $\pi \rightarrow \pi^*$  in nature, their shift to lower energy is also explained. The energy of the MLCT bands of the bimetallic complexes increase in the order  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpb}) < [\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpq}) < [\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpp})$  ( $\lambda_{\text{max}}$  MLCT ( $\text{CH}_3\text{CN}$ , 25 °C)) = 518, 505, 456 nm, respectively). As in the mononuclear complexes, this is consistent with the varying degrees of  $\pi$  delocalization on the bridging ligand.

**Emission Spectroscopy.** The emission maxima for both  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$  and  $\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$  appear to be at the expected wavelengths to support an emitting state of principally MLCT character. This assertion is based on the correlation of the emission energies and redox potentials for similar polypyridyl Re(I) complexes reported by Juris et al.<sup>8</sup> A linear relationship between the first reduction potential and the emission energy of these complexes was observed,<sup>8,40</sup> and used as evidence for the MLCT nature of the emitting state. The fact that the luminescence of  $\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$  is shifted to lower energy from that of the dpp analogue is also consistent with a  $p\pi^*(\text{BL}) \rightarrow d\pi(\text{Re})$  emission. No emission was observed for the three bimetallic complexes  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{BL})$ , (BL = dpp, dpq, dpb). If these complexes were emitting from MLCT excited states, the emission maxima would be predicted, as in the above,<sup>8</sup> to be in the range from ca. 800 to 1100 nm for these complexes. Not only is this range beyond the practical sensitivity of the PMT used in our instrumentation but the radiative quantum yield and hence the luminescent intensities are expected to be very low due to energy gap law considerations.<sup>41</sup>

**Vibrational Spectroscopy.** The infrared spectra of both the monometallic and bimetallic Re(I) complexes in general exhibit three absorption bands in the carbonyl stretching region (from 2100 to 1800  $\text{cm}^{-1}$ ). In the case of  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$  and  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpp})$ , a weaker fourth band at 1915 and 1943  $\text{cm}^{-1}$ , respectively, appears associated with the lower energy pair. These additional bands may be due to the samples containing a mixture of cis and trans isomers.<sup>44</sup> In all cases, a sharp, intense band is

observed at ca. 2025  $\text{cm}^{-1}$  accompanied by two partially resolved bands of approximately equal intensities, at ca. 1922 and 1902  $\text{cm}^{-1}$  (see Table II). Most of the bands for the bimetallic complexes show some degree of structure when examined in the solid state.

The occurrence of three carbonyl stretching bands in tricarbonyl Re(I) complexes of this type has been reported in several other papers.<sup>8,12,28,42–44</sup> In accordance with the work of Stufkens et al.,<sup>28</sup> we interpret the higher energy band at ca. 2025  $\text{cm}^{-1}$  as being due to the carbonyl group cis with respect to the bridging ligand. If the two overlapping lower energy bands represent splitting of two otherwise degenerate transitions, these data are consistent with placing the Re center in a degraded  $C_{3v}$  local environment, which implies that the facial isomers were obtained as major products.

**Electrochemistry.** The three mononuclear Re complexes prepared display two reductions and one oxidation in the potential region from +2.00 to –2.00 V. The cyclic voltammograms in the negative potential region are typical of Re complexes of this type. In each case the oxidative waves show no corresponding reductive wave. These waves are assigned to the Re(II)/Re(I) process.<sup>40</sup> The least cathodic reductive waves are reversible or quasi-reversible ( $E_{\text{pa}} - E_{\text{pc}} = 60 - 90$  mV) (see Table III for reduction potentials). These latter waves are assigned to the first reduction of the bridging ligand (dpp, dpq, dpb).<sup>10,12,40</sup> This is based on the anodic shift of the first reduction in the order of increasing  $\pi$  delocalization and by analogy with the observations of Juris.<sup>8</sup>

The second reduction may be due to a metal centered Re(I)/Re(0) process<sup>10</sup> for  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$ , because of the lack of a return oxidation, the difference in the cathodic peak currents between this and the first reductive waves and the sensitivity of this process to electrode conditions. This assignment may also be true for the third reduction of  $\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$ . Sullivan<sup>10</sup> has shown that the second reduction potential for  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}]^{n+}$  (L = H<sup>-</sup>, Cl<sup>-</sup>, n = 0; L = 4-ethylpyridine, n = 1) varies with changes in L, which is consistent with this reduction being a metal-centered process. Furthermore, Sullivan and O'Toole<sup>10b</sup> have observed relatively small and widely variable heterogeneous electron-transfer rates for the metal-based  $\text{Re}^{I/0}(\text{bpy})(\text{CO})_3\text{X}$  couple, which dramatically affects the appearance of the wave for this process in the cyclic voltammograms. Our observations are consistent with this notion, which probably reflects a large inner-sphere reorganizational energy associated with the population of the  $\sigma^*$  orbitals of the metal.

The second reductions of  $\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$  and  $\text{Re}(\text{dpb})(\text{CO})_3\text{Cl}$  are assigned to a bridging ligand-localized process. This interpretation is based on the insensitivity of the second reduction to variations in the sixth ligand, and the potential difference and qualitative peak current similarities between the first and second reductions. Preliminary data for  $[\text{Re}(\text{dpb})(\text{CO})_3(\text{CH}_3\text{CN})]^+$  and  $[\text{Re}(\text{dpb})(\text{CO})_3(\text{C}_5\text{H}_5\text{N})]^+$  show that these complexes have reductions at –0.42 and –1.05 V for the  $\text{CH}_3\text{CN}$  derivative and –0.39 and –1.01 V for the  $\text{C}_5\text{H}_5\text{N}$  derivative, respectively. In these cases, the second reduction is insensitive to the substitution of pyridine or acetonitrile for chloride, when the anodic shift due to the change in overall complex charge is taken into account. In addition, the differences in the first and second reduction potentials for the Cl<sup>-</sup>,  $\text{CH}_3\text{CN}$ , and  $\text{C}_5\text{H}_5\text{N}$  complexes, as well as for free dpb, are all roughly 700 mV. DeArmond et al.<sup>45,46</sup> and Vlcek<sup>47</sup> have shown that the difference in the first and second reduction potentials of polypyridyl ligands similar to these is 400–700 mV. We therefore conclude that the second reduction in these cases is ligand-based.

Two reductive waves and one oxidative wave are also exhibited in the cyclic voltammograms of the bimetallic complexes. These redox potentials can also be found in Table III, and the cyclic voltammograms in the negative potential region can be found in

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Figure 3. By analogy with the discussion presented above for the dpb monometallic species, the first and second reductions are assigned to bridging ligand localized reductions and the irreversible oxidation to the Re(II)/Re(I) couple.

A third reduction is also observed for  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpp})$  and  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpq})$ . This reduction is assigned to the Re(I)/Re(0) couple for one of the metal centers. As in the mononuclear species, the anodic shift of the first reduction potential with increasing degree of  $\pi$  delocalization on the bridging ligand can be correlated with spectroscopic trends.

**Correlation of Spectroscopic and Electrochemical Results.** Correlations between  $(E_p^c(\text{Re}^{II/I}) - E_{1/2}(\text{BL}/\text{BL}^{*-}))$  and  $E(\text{LE})$  (the lowest energy absorption band) have appeared in several works involving transition-metal chemistry.<sup>8,40,48-50</sup> Analogous correlations have also been applied to  $E_{em}$ , the energy corresponding to the maximum emission. These relationships are useful since they provide a means of estimating the energies of the MLCT transitions from electrochemical data or vice versa. The practical utility of these trends is found in the rational design of complexes with particular properties, such as redox potentials or emission energies.<sup>48</sup>

The quantity  $(E_p^c(\text{Re}^{II/I}) - E_{1/2}(\text{BL}/\text{BL}^{*-}))$  was plotted vs  $E(\text{LE})$  in Figure 4 for the six Re complexes. The  $E_p^c(\text{Re}^{II/I})$  and  $E_{1/2}(\text{BL}/\text{BL}^{*-})$  values were taken from OSWV and were determined simultaneously (data from the same scan) for each complex.  $E(\text{LE})$  was determined from the lowest energy absorption (400–550 nm), converting the wavelength to its energy equivalent in eV ( $1 \text{ eV} = 1.2422 \times 10^3 \text{ nm}^{-1}$ ). Since this type of data consists of two random variables (as opposed to independent, dependent variable pairs) the most appropriate statistical parameter to establish the degree of association between the two variables is the product-moment correlation coefficient.<sup>51</sup> The product-moment correlation coefficient for these data is 0.999. A *t* test for the significance of this correlation showed that the probability of these data being random is less than 1%. The high degree of association between these two variables is consistent with the hypothesis that the same orbitals are involved in both the electrochemical process and in the optical process. Resonance Raman has definitively established the nature of the lowest energy absorption as MLCT ( $d\pi(\text{Re}) \rightarrow p\pi^*(\text{BL})$ ) in related diimine complexes of Re(I).<sup>28</sup> Since the difference between the first-oxidation and first-reduction potentials is a reflection of the energy difference between the HOMO and LUMO in the complexes under study, the combination of the above facts provide strong evidence in support of the MLCT lowest energy absorption assignment as well as the assignment of the first oxidation process as metal-centered  $\text{Re}^{II/I}$  and the first reduction as ligand-centered  $(\text{BL}/\text{BL}^{*-})$ .

Traditionally, linear least-squares regression analysis is used to generate the best-fit line and test the degree of association of the two random variables.<sup>8,48</sup> While such a treatment is not appropriate for the latter purpose, it is convenient to calculate a best-fit line by this method for the prediction of band gap energies from absorption data or vice versa. The experimental data was subjected to a linear least-squares regression analysis and the results are

$$E(\text{LE}) = 0.98(E_p^c(\text{Re}^{II/I}) - E_{1/2}(\text{BL}/\text{BL}^{*-})) + 0.68$$

$$r = 0.993$$

**Comparisons with Ruthenium Analogues.** The first major difference between the Ru and Re complexes of the dpp-type ligands is that adjusting the stoichiometry of the reagents was

sufficient to control the nuclearity of the Re complexes. In the synthesis of  $[\text{Ru}(\text{bpy})_2(\text{BL})]^{2+}$  and  $[\text{Ru}(\text{bpy})_2]_2(\text{BL})^{4+}$ , a mixture of mono- and bimetallic complexes results. The metal-to-ligand molar ratio in these latter cases merely increased the amount of one component over the other. This is probably due to the repulsion between the two dipositively charged metal fragments.

Table IV shows the effect of binding  $\text{Re}(\text{CO})_3\text{Cl}$  or  $\text{Ru}(\text{bpy})_2^{2+}$  groups to the three bridging ligands. As generally observed for complexes of this type,<sup>47</sup> the reduction potentials of the bridging ligands are more positive when bound to the metals than when free.<sup>7</sup> The results in Table IVA,B show that this anodic shift is greater for  $\text{Re}(\text{CO})_3\text{Cl}$  than for  $\text{Ru}(\text{bpy})_2^{2+}$ , except for the dpb-containing monometallics. This greater shift is also observed in Table IVC,D, which compares the effect of binding the second metal fragment. In all cases, an increase in nuclearity for the Re complexes causes at least a 50-mV greater change in the ligand-centered reduction potential than in the related Ru complexes. The anodic shifts of the diimine-centered reductions by bound metal ions have been interpreted as being due to stabilization of the reduced forms of the ligand by the positive field (Lewis acid nature) of the metal fragment.<sup>47</sup> These data show that  $\text{Re}(\text{CO})_3\text{Cl}$  is more effective at stabilizing the reduced form of the ligands than  $\text{Ru}(\text{bpy})_2^{2+}$ .

As the size of the ligands increases, the greater stabilizing ability of  $\text{Re}(\text{CO})_3\text{Cl}$  becomes less pronounced. Furthermore, adding a second metal fragment has a smaller stabilizing effect on dpb<sup>-</sup>, as evidenced by the differences shown in Table IVC,D. This probably reflects the increased delocalization of the added electron over the larger  $\pi$  system of this ligand, which would dilute the effect of the metal ion. It is interesting to note that the anodic shift of the ligand-centered reduction potential upon adding the second metal fragment to dpp and dpq is the same for a given metal ion.

## Conclusions

The preparation and characterization of a series of homologous mono- and bimetallic complexes containing the  $\text{Re}(\text{CO})_3\text{Cl}$  metal fragment built around the dpp series of bridging ligands has been accomplished. Increasing the degree of conjugation beyond dpp by fusing one or two benzene rings to the 5,6-carbons of the pyrazine or binding a second  $\text{Re}(\text{CO})_3\text{Cl}$  moiety to the bridging ligand changes the site of the second reduction from the metal to the ligand in both the bimetallic and monometallic complexes. It has been shown that the lowest energy visible absorbance is MLCT in character. In contrast to the Ru bimetallic complexes containing dpp and dpq, not one of the three Re bimetallic complexes prepared were observed to luminesce at room temperature. The electrochemical data is consistent with the greater ability of the  $\text{Re}(\text{CO})_3\text{Cl}$  group to stabilize the reduced form of the bridging ligands ( $\text{BL}^-$ ) more than  $\text{Ru}(\text{bpy})_2^{2+}$ . Further studies are underway to replace the chloride ligand with stronger field ligands and to develop any electrocatalytic properties toward the reduction of  $\text{CO}_2$  that these complexes may have.

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**Supplementary Material Available:** Figures depicting the electronic absorption spectra of dpp,  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$ ,  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpp})$ , dpq,  $\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$ , and  $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{dpq})$  dissolved in acetonitrile and the cyclic voltammograms of  $\text{Re}(\text{dpp})(\text{CO})_3\text{Cl}$  ( $\text{CH}_3\text{CN}/0.1 \text{ M TBAH}$ ),  $\text{Re}(\text{dpq})(\text{CO})_3\text{Cl}$  ( $\text{CH}_2\text{Cl}_2/0.2 \text{ M TBAH}$ ), and  $\text{Re}(\text{dpb})(\text{CO})_3\text{Cl}$  ( $\text{CH}_2\text{Cl}_2/0.2 \text{ M TBAH}$ ) (3 pages). Ordering information is given on any current masthead page.

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