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Spectroscopic and Electrochemical Studies of Rhenium(I) Bimetallic Complexes with Asymmetric Polypyridyl Bridging Ligands

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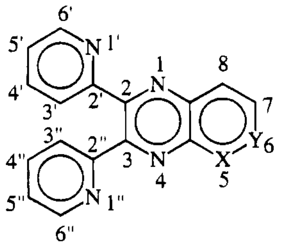
The synthesis and electrochemical and spectroscopic properties of a number of binuclear rhenium(I) ligand-bridged complexes are reported. The ligands are as follows: 2,3-di(2-pyridyl)quinoxaline; 2,3-di(2-pyridyl)-6-methyl quinoxaline; 2,3-di(2-pyridyl)pyrido[2,3-*b*]pyrazine; 2,3-di(2-pyridyl)pyrido[3,4-*b*]pyrazine. Complexes with these ligands show different electrochemical and spectroscopic properties. The pyridopyrazine ring systems show longer wavelength MLCT transitions and are easier to reduce. However, spectroelectrochemical studies reveal that the reduction products for this series of complexes are spectroscopically similar. Raman measurements on the reduced species suggest that the redox orbital for the first reduction resides in an orbital that is localized at the dipyridyl section of each ligand. This is surprising in view of the fact that the larger ring system would be expected to localize the charge. It suggests that the rhenium centers modify the nature of the redox MO to a greater extent than the pyridopyrazine ring system.

Introduction

Polynuclear metal complexes with bridging ligands are of considerable interest because they possess photophysical and redox properties which make them useful as light-harvesting complexes and photonic molecular devices.[1] With bimetallic polypyridine ligand-bridged complexes based on 2,3-di(2-pyridyl)quinoxaline (dpq, Figure 1), the photochemical and redox properties are strongly dependent on the bridging ligand.[2] An important property of such bimetallic complexes is how they localize charge when either photoexcited into a charge-transfer excited state or when electrochemically oxidized or reduced. The charge localization is an important property in the ability of a complex to store energy.[3]

With complexes containing Ru(II), Re(I), or Cu(I), the redox-active excited state is a metal-to-ligand charge-transfer (MLCT) state in which the metal is formally oxidized and the ligand formally reduced to a radical anion.[4−6] Charge localization may occur at the electron donor (metal $d\pi$) orbital or the electron acceptor (ligand π^*) orbital. The redox molecular orbital of reduced complexes has been shown to mimic the behavior of the electron acceptor orbital in the MLCT excited state.[7] Thus, it is possible using spectroelectrochemical techniques to model the MLCT state without resorting to time-resolved techniques.



dpq: X = Y = CH
BL1: X = N; Y = CH
BL2: X = CH; Y = C-CH_3
BL4: X = CH; Y = N

Figure 1. Structures and numbering system for ligands used in this study.

Studies of tris(4-methyl 2, 2′-bipyridine)ruthenium(II)[8] reveal that in the MLCT excited state the excited electron is localized on a single ligand and polarized toward the pyridine end of that ligand. Studies on electrochemically reduced metal complexes also reveal electron localization of the electron acceptor orbital. Wertz *et al.*[9] have shown that the first reduction product of tris[2-(2′-pyridyl)quinoline]ruthenium(II) has the redox electron localized on the quinoline part of one of the 2-(2′-pyridyl)-quinoline ligands.

In almost all studies of polypyridyl bimetallic complexes, the bridging ligands studied have been symmetrical, placing the metal centers in equivalent environments. In order to direct energy or electron transfer in the excited state of a complex, it is necessary to confer asymmetry on the system. This has normally been accomplished by using different metals or metals with different spectator ligands.[10] However, it is possible to develop asymmetry on a ligand-bridged polpyridyl complex by introducing asymmetry into the bridging ligand. This has three effects. First, it creates inequivalence in the redox properties

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of the metal sites. The energy inequivalence of the metal sites is an important parameter in their ability to couple strongly. Systems with strongly coupling bridging ligands such as CN can still show localized mixed-valent properties for this reason.[11] Complexes with asymmetric bridging ligands may therefore be useful in furthering understanding into metal coupling. Second, such ligands should provide a method of conferring directed energy/electron-transfer properties to a complex in which the metal sites have equivalent spectator ligands; i.e., both are $Ru(bpy)_2^{2+}$ or $Re(CO)_3Cl$. Third, the substitution of groups on to the dpq structure permits tuning of the redox and absorption properties of the bimetallic complexes.

We have investigated the spectroscopic and electrochemical properties of a series of ligand-bridged bimetallic rhenium(I) complexes. The ligands are shown in Figure 1. They represent simple perturbations of the quinoxaline ring found in dpq. They are 2,3-di(2-pyridyl)pyrido[2,3-*b*]pyrazine (BL1), 2,3-di(2-pyridyl)-6-methylquinoxaline (BL2), and 2,3-di(2-pyridyl)pyrido-[3,4-*b*]pyrazine (BL4). The $Re(CO)_3Cl$ moiety was chosen because it has spectator ligands that are not redox active or possess visible chromophores, hence simplifying the interpretation of experimental results. Furthermore rhenium(I) polypyridyl complexes are important catalysts for the reduction of CO_2 to CO.[12]

We are interested in the nature of the reduced species of the bimetallic systems in that they mimic part of the MLCT excited-state process. If these complexes are to act as electron donors photocatalytically, the most reactive electron will be found on the radical anion and its properties will be determined by the electron distribution rather than the ground-state functionality.[13] The nature of electron distribution on ligand species may be determined by vibrational[14] or electron spin resonance spectroscopies.[15] We have employed resonance Raman spectroscopy to probe the nature of electron reorganization within the complexes after electrochemical reduction.

Experimental Section

Materials. 2,2′-Pyridil, 2,3-diaminopyridine, 3,4-diaminopyridine, and 3,4-diaminotoluene were purchased commercially and used without further purification. $Re(CO)_5Cl$ was prepared from $Re_2(CO)_{10}$ by reaction with gaseous chlorine.[16] Solvents used for electrochemistry and spectroscopy were spectroscopic grade. These were further purified by distillation and stored over 5 Å molecular sieves prior to use. The electrolyte tetrabutylammonium perchlorate (TBAP) was purified by standard methods.[17]

Ligand Synthesis. Ligands were prepared by Schiff base condensation of 2,2′-pyridil with the appropriate diamino compound following the method of Goodwin and Lyons.[18]

2,3-Di(2-pyridyl)pyrido[2,3-*b*]pyrazine (BL1). ^{1}H-NMR ($CDCl_3$): δ 7.25 (m, 2H, 5′, 5″); 7.76 (dd, 1H, 7); 7.9 (m, 3H, 3′, 4′, 4″); 8.33 (m, 3H, 6′, 6″, 3); 8.57 (dd, 1H, 8); 9.21 (dd, 1H, 6). ^{13}C-NMR ($CDCl_3$): δ 156.6 (6); 150.5, 150.1 (6′, 6″); 140 (8); 138.8, 138.7 (4′, 4″); 127.7 (7); 126.7, 126.1 (3′, 3″); 125.5, 125.2 (5′, 5″). Anal. Calcd: C, 71.57; H, 3.89; N, 24.55. Found: C,71.76; H, 3.81; N, 24.86. Yield 64%.

Table 1. Infrared Spectral Data for Rhenium(I) Complexes in Dichloromethane Solution in the Carbonyl Region

compound	$\tilde{\nu}$/cm^{-1}			
$[Re(CO)_3Cl]_2dpq$	2031$^{w a}$	2024	1937	1916
$[Re(CO)_3Cl]_2BL1$	2032^{w}	2023	1940	1916
$[Re(CO)_3Cl]_2BL2$	2031^{w}	2023	1936	1915
$[Re(CO)_3Cl]_2BL4$	2034^{w}	2024	1942	1920

[a] w, denotes weak feature only observable as a shoulder with measurement at 2 cm^{-1} resolution.

2,3-Di(2-pyridyl)-6-methyl-quinoxaline (BL2). ^{1}H-NMR ($CDCl_3$): δ 7.23 (m, 2H, 5′, 5″); 7.66 (dd, 1H, 7); 7.81 (tt, 2H, 4′, 4″); 8.00 (m, 3H, 5, 3′, 3″); 8.12 (d, 1H, 8); 8.38 (d, 2H, 6′, 6″); 2.62 (s, 3H, 9). ^{13}C-NMR ($CDCl_3$): δ 150.6 (6′, 6″); 138.6 (4′, 4″); 134.9 (7); 130.9 (8); 130.2 (5); 126.2 (3′, 3″); 124.9, 124.8 (5′, 5″); 23.96 (9). Anal. Calcd for BL1·¼MeOH: C, 75.47; H, 4.94; N, 18.29. Found: C, 75.66; H, 4.99; N, 18.77. Yield 75%.

2,3-Di(2-pyridyl)pyrido[3,4-*b*]pyrazine (BL4). ^{1}H-NMR ($CDCl_3$): δ 7.28 (m, 2H, 5′, 5″); 7.87 (tt, 2H, 4′, 4″); 8.0 (m, 3H, 3′, 3″, 8); 8.35 (m, 2H, 6′, 6″); 8.89 (d, 1H, 7); 9.66 (d, 1H, 5). ^{13}C-NMR ($CDCl_3$): δ 156.4 (5); 150.5, 150.4 (6′, 6″); 149.7 (7); 138.7 (4′, 4″); 126.2, 126.1 (3′, 3″); 125.5, 125.3 (5′, 5″); 123.4 (8). Anal. Calcd: C, 71.57; H, 3.89; N, 24.55. Found: C, 71.51; H, 3.71; N, 24.66. Yield 73%.

Complex Synthesis. A typical preparation was as follows: To a degassed, refluxing solution of ligands (0.5 mmol) in methanol (200 mL) was added a suspension of $Re(CO)_5Cl$ (1 mmol, 0.362 g) in methanol (20 mL). After ~30 min under reflux the gold colored solution had darkened to red-brown. Refluxing was continued for 24 h, after which the solution was filtered while still hot. The product precipitated upon cooling.

$[Re(CO)_3Cl]_2dpq$. ^{1}H-NMR ($CDCl_3$): δ 7.63 (m, 2H, 5′, 5″); 7.97 (td, 2H, 4′, 4″); 8.19 (dd, 2H, 6, 7); 8.48 (d, 2H, 3′, 3″); 9.17 (d, 2H, 5, 8). Anal. Calcd: C, 32.18; H, 1.35; N, 6.26. Found: C, 32.35; H, 1.23; N, 6.27. Yield 63%.

$[Re(CO)_3Cl]_2BL1$. ^{1}H-NMR ($CDCl_3$): δ 7.64 (t, 2H, 5′, 5″); 7.99 (m, 2H, 4′, 4″); 8.11 (dd, 1H, 7); 8.43, 8.55 (d, d, 1H, 1H, 3′, 3″); 8.98 (dd, 1H, 8); 9.19 (q, 2H, 6′, 6″); 9.39 (dd, 1H, 6). Anal. Calcd: C, 30.81; H, 1.24; N, 7.81. Found: C, 30.56; H, 1.10; N, 7.66. Yield 77%.

$[Re(CO)_3Cl]_2BL2$. ^{1}H-NMR ($CDCl_3$): δ 2.77 (s, 3H, 9); 7.60 (m, 2H, 5′, 5″); 7.97 (m, 3H, 7, 4′, 4″); 8.43 (m, 3H, 5, 3′, 3″); 8.61 (d, 1H, 8); 9.15 (m, 2H, 6′, 6″). Anal. Calcd: C, 33.01; H, 1.55; N, 6.16. Found: C, 33.03; H, 1.41; N, 6.04. Yield 85%.

$[Re(CO)_3Cl]_2BL4$. ^{1}H-NMR ($CDCl_3$): δ 7.68 (m, 2H, 5′, 5″); 8.01 (tt, 2H, 4′, 4″); 8.4 (d, 1H, 8); 8.54 (t, 2H, 3′, 3″); 9.19 (m, 3H, 7, 6′, 6″); 10.05 (s, 1H, 5). Anal. Calcd: C, 30.81; H, 1.24; N, 7.81. Found: C, 30.92; H, 1.13; N, 7.94. Yield 70%.

Physical Measurements. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda-19 spectrophotometer. Cyclic voltammograms were obtained from nitrogen-degassed dichloromethane solutions containing 0.1 M TBAP as supporting electrolyte and complex at 1 mM concentration. The measurements were carried out using an EG&G PAR 273A potentiostat, with Model 270 software, referenced to a saturated calomel electrode. NMR spectra were recorded using a Varian 200 MHz NMR. Resonance Raman measurements used a Spectra-Physics Model 166 argon ion laser to generate Raman scattering. Scattering was collected in a 135° backscattering geometry and imaged using a two-lens arrangement[19] into a Spex 750M spectrograph. Raman photons were detected using a Princeton Instruments liquid nitrogen-cooled 1152-EUV charge-coupled device. Rayleigh and Mie scattering from the sample was attenuated using a Notch filter (Kaiser Optical Systems Inc.) of appropriate wavelength. Spectroelectrochemical Raman and electronic absorption measurements were facilitated with a thin-layer electrochemical cell.[20]

Results

The complexes are thermally stable. However, they decompose in solution if exposed to sunlight over a period of days. For this reason, measurements were carried out on fresh

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Table 2. Electronic Absorption Data for Rhenium(I) Complexes and Their Free Ligands at 298 K in Dichloromethane

compound	λ/nm (ϵ, M^{-1} cm^{-1})			
dpq		334 (9 500)	271 (18 700)	246 (33 000)
BL1		335 (25 000)	266 (21 000)	234 (45 000)
BL2		335 (15 000)	276 (35 000)	238 (42 000)
BL4		340 (15 000)	270 (35 000)	240 (42 000)
$[Re(CO)_3Cl]_2dpq$	526 (7 400)	397 (12 000)	317 (22 600)	
$[Re(CO)_3Cl]_2BL1$	569 (8 900)	400 (18 000)		
$[Re(CO)_3Cl]_2BL2$	511 (8 650)	401 (14 800)	322 (27 600)	
$[Re(CO)_3Cl]_2BL4$	569 (8 700)	397 (12 400)	307 (25 300)	

solutions and the electronic spectra of these samples were monitored, before and after use, to rule out decomposition within the time frame of the experiment.

Infrared Spectra. The infrared spectra of the binuclear complexes in the carbonyl region are presented in Table 1. All complexes have spectra which when measured with 8 cm^{-1} resolution are dominated by three carbonyl bands, of which the lower two frequencies are only IR active with the higher frequency being both IR and Raman active (symmetric stretch of *equatorial* CO).[21] This is consistent with the IR spectral signature of a $Re(CO)_3Cl$ moiety with the carbonyl units adopting a facial isomer.[22] However, when data are collected at 2 cm^{-1} resolution, the higher frequency CO band splits. For BL1, BL2, and BL4 complexes, the $Re(CO)_3Cl$ units are in slightly different environments and a splitting of the carbonyl frequencies might be expected. This would be clearer for the high-frequency CO band because of its narrow bandwidth (~6 cm^{-1} as opposed to >15 cm^{-1} for the other CO bands). The dpq ligand is not asymmetric and the binuclear complex has both $Re(CO)_3Cl$ units in equivalent environments, yet the high-resolution IR spectrum shows two symmetric stretch *equatorial* CO bands. This splitting may be caused by impurities present in the sample or may be due to cis/trans isomers possible in the binuclear complexes.[15] The presence of an impurity is unlikely for a number of reasons. First, the NMR data show signals from the binuclear complexes only. Second, dpq impurities, such as starting material $Re(CO)_5Cl$,[24] or other products, such as $Re(CO)_3Cl(dpq)$,[23] have IR spectra which do not conform to either of the observed high-frequency CO bands in the binuclear complex. The microanalysis of all four binuclear complexes is consistent with the proposed structures. Finally, the resonance Raman spectra show resonance enhancement of both symmetric stretch *equatorial* CO vibrations with visible excitation wavelengths. This further precludes $Re(CO)_5Cl$ as an impurity and suggests the species pertaining to the higher frequency CO band is visible absorbing. The most plausible explanation of this result is that cis and trans isomers are formed each of which has a separate IR signature.

Electronic Spectra. Electronic absorption spectra were measured for ligands and complexes in dichloromethane solution. The data are presented in Table 2.

The bimetallic ligand-bridged complexes show similar spectral features. The lowest energy transition occurs in the 510–570 nm region for each. This is assigned as a $Re(I)(d\pi) \rightarrow BL(\pi^*)$ metal-to-ligand charge-transfer transition on the basis of literature assignments[24,25] for similar complexes and resonance Raman data, *vide infra*. Each complex shows a band at 400 nm. In binuclear rhenium(I) complexes with the related 2,3(2-pyridyl)pyrazine, two MLCT bands are assigned occurring at 454 and 342 nm.[27] In view of the lower transition energy of the lowest MLCT band for the complexes studied in this work and the fact that ligand-centered transitions rarely move upon binding[26] to a metal, the most plausible assignment for the 400 nm band is MLCT. Absorption features to the blue of this region are dominated by ligand-centered (π, π^*) transitions. The electronic spectra of the complexes show that the substitution of a methyl group onto the quinoxaline ring shifts the MLCT transition to the blue from 526 to 512 nm. The methyl group destabilizes the bridging ligand radical anion as indicated by the negative shift for the bridging ligand reduction on going from $[Re(CO)_3Cl]_2dpq$ to $[Re(CO)_3Cl]_2BL2$.

Table 3. Electrochemical Results for Rhenium(I) Complexes and Free Ligands in Dichloromethane at 298 K[a,b]

$E_{1/2}$/V compound	oxidation	reduction
dpq		−1.56
BL1		−1.32
BL2		−1.60
BL4		−1.29
$[Re(CO)_3Cl]_2dpq$		−0.25
$[Re(CO)_3Cl]_2BL1$	1.71 (irr)	−0.16, −0.98, −1.26 (irr)
$[Re(CO)_3Cl]_2BL2$	1.73 (irr)	−0.36, −1.2(irr)
$[Re(CO)_3Cl]_2BL4$	1.71 (irr)	−0.07, −0.94 (irr)

[a] Potentials vs SCE, ± 0.02 V. [b] Supporting electrolyte 0.1 M TBAP. Irreversible processes indicated by irr.

NMR Spectra. Assignments of the ^{1}H-NMR spectra of the complexes and the ligands were based on the COSY spectra and previous literature assignments.[27] ^{13}C-NMR data were assigned on the basis of literature spectra and HETCOR experiments. Substituents that asymmetrize the BL affect the NMR spectra by making the pyridyl resonances inequivalent. This effect shows up most clearly in the ^{13}C-NMR spectra of the ligands in which the pyridine resonances appear as pairs, within 0.2 ppm of one another.

The shifting of the proton resonances downfield for the bimetallic complexes due to the deshielding effect of the metals has been observed in other binuclear rhenium(I) complexes[27] and W(0), Cr(0), and Mo(0) complexes with similar ligands.[28,29]

Electrochemistry. Electrochemical data for complexes and ligands are presented in Table 3.

The irreversible oxidation processes observed at +1.7 V vs SCE are assigned to metal-based Re(I) oxidation.[30] The ligands show reversible first reductions at −1.3 to −1.6 V vs SCE. The substitution of the third heteroatom into the quinoxaline ring in BL1 and BL4 shifts the reduction to more positive potentials. It is noteworthy that the reduction potentials of BL1 and BL4 are very similar. The bimetallic ligand-bridged complexes show reversible reductions at modest negative potentials vs SCE.

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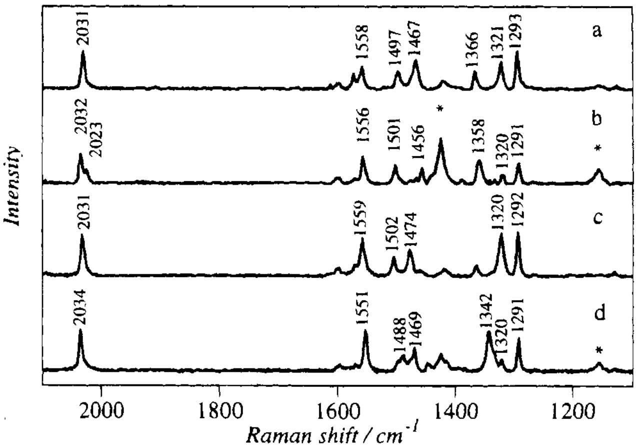

Figure 2. Resonance Raman spectra of binuclear complexes in dichloromethane solution at ~1 mM concentrations. Excitation wavelength 514.5 nm, 40 mW. * denotes solvent feature: (a) $[Re(CO)_3Cl]_2dpq$; (b) $[Re(CO)_3Cl]_2BL1$; (c) $[Re(CO)_3Cl]_2BL2$; (d) $[Re(CO)_3Cl]_2BL4$.

Previous work[29] on similar systems assigns such reductions as ligand based. The effect of the binding of the two $Re(CO)_3Cl$ units to each bridging ligand is to shift the first reduction by ~1.2 V to more positive potentials relative to the free ligand.[31]

Raman Spectra. Resonance Raman spectra generated using 514.5 nm excitation are shown in Figure 2. This excitation wavelength is in resonance with the lowest energy transition for each of the complexes. The resonance Raman effect preferentially enhances scattering from vibrational modes that mimic the electronic excitation.[32] For each of the bimetallic complexes, enhancements of the ligand and metal carbonyl modes are observed. This enhancement pattern is consistent with an MLCT transition.[22] The ligand modes are enhanced by virtue of the fact that the optical electron from the Re(I) center resides in a π^* antibonding orbital. The metal carbonyl stretch enhancements occur because the MLCT transition leads to formal oxidation of the metal center. The CO modes are sensitive to oxidation state, hence the stretching vibration is enhanced.[21,33]

Spectra generated at 488 and 457.9 nm do not show dramatic relative intensity changes of ligand-based modes, although at 457.9 nm all of the bands are less intense by virtue of the excitation wavelength being off-resonance with the MLCT transition.

Normal Raman spectra of the free ligands dpq, BL1, and BL4 were generated using 632.8 nm excitation. The strong emission from BL2 precluded collection of its Raman spectrum. The Raman spectra of the ligands show a number of features. For dpq these lie at 1591, 1441, 1398, and 1324 cm^{-1}. For BL1, features are observed at 1587, 1475, and 1389 cm^{-1}. For BL4, bands occur at 1589, 1478 and 1387 cm^{-1}. For all three samples, the strongest Raman band is at 1398−1387 cm^{-1}.

The bridging ligand vibrational frequencies are similar in each of the bimetallic complexes. The strongest bands in the 1200−1600 cm^{-1} region are presented in Table 4. All of the observed bands are polarized. On substitution at the quinoxaline ring, distinct changes in relative band intensities and band frequencies of the Raman spectra are observed.

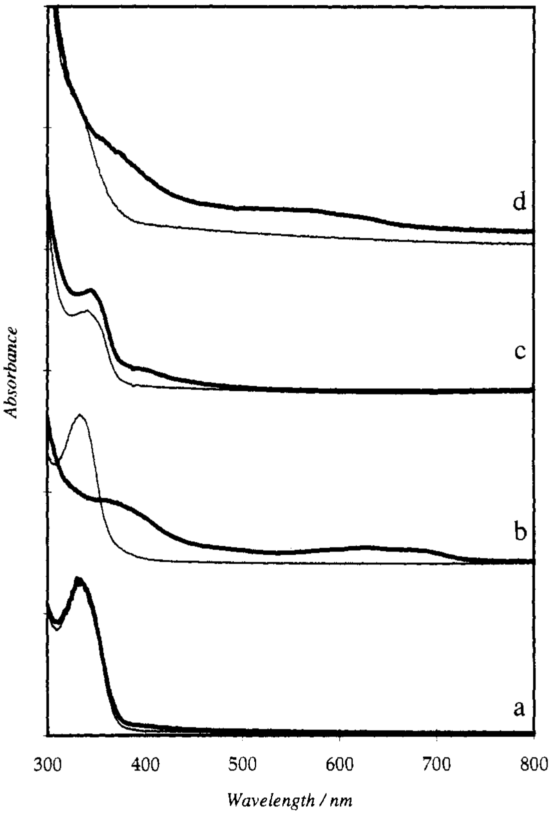

Figure 3. Electronic absorption spectra of ligands and their electrochemical reduction products in dichloromethane at ~1 mM concentration. Supporting electrolyte TBAP. Measurements carried out in an Ottle cell. Thin lines represent electronic absorption spectra of neutral ligand species; heavy lines represent spectra of reduced ligand species: (a) dpq; (b) BL2; (c) BL1; (d) BL4.

Table 4. Resonance Raman Bands Observed for Bimetallic Rhenium(I) Complexes in Dichloromethane with 514.5 nm Excitation

compound	$\tilde{\nu}$/cm^{-1}					
$[Re(CO)_3Cl]_2dpq$	1293	1321	1366	1467	1497	1558
$[Re(CO)_3Cl]_2BL1$	1291	1320	1358	1456	1501	1556
$[Re(CO)_3Cl]_2BL2$	1292	1320	1362	1474	1502	1559
$[Re(CO)_3Cl]_2BL4$	1290	1320	1340	1468	1496	1551

For $[Re(CO)_3Cl]_2BL1$ and $[Re(CO)_3Cl]_2BL4$, which have pyridopyrazine ring systems, the intensity of the 1320 cm^{-1} band drops with respect to other features, i.e., the 1290 cm^{-1} band, which is common to all spectra. However, $[Re(CO)_3Cl]_2dpq$ and $[Re(CO)_3Cl]_2BL2$, which possess a quinoxaline ring in their bridging ligands, have strong 1320 cm^{-1} bands. Features in the 1340−1366 and 1456−1474 cm^{-1} region are frequency sensitive to substitutions at the 5 and 6 positions of the quinoxaline ring. Bands are observed at ~1290 and 1500 cm^{-1} which are common to all four complexes.

Spectroelectrochemistry. All compounds show reversible changes in electronic absorption spectra as they are electrochemically reduced in solution. As the Ottle cell is set at a series of potentials, through the reduction wave, smooth changes are observed. These changes have well-defined isosbestic points indicating the conversion of one species to another with no significant decomposition pathways present.

Electronic absorption spectra of the ligands and their reduction products are shown in Figure 3. BL1 and BL4 show strong visible absorptions when reduced while the methyl-substituted BL2 and dpq absorb in the near-UV/visible. The electronic spectra of the parent and reduced complexes are shown in Figure 4.

Electronic spectra of dpq and dpq$^{\bullet-}$ (Figure 3a) show an isosbestic point at 355 nm. The reduced ligand absorbs at 400 nm (ϵ ~1900 M^{-1} cm^{-1}).

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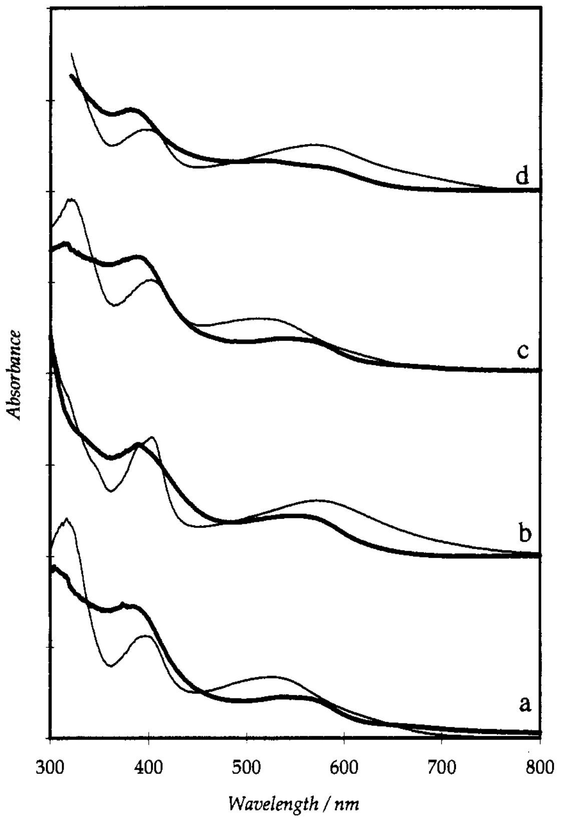

Figure 4. Electronic absorption spectra of complexes and their electrochemical reduction products in dichloromethane at ~1 mM concentration. Supporting electrolyte TBAP. Measurements carried out in an Ottle cell. Thin lines represent electronic absorption spectra of neutral ligand species; heavy lines represent spectra of reduced ligand species: (a) $[Re(CO)_3Cl]_2dpq$; (b) $[Re(CO)_3Cl]_2BL1$; (c) $[Re(CO)_3Cl]_2$-BL2; (d) $[Re(CO)_3Cl]_2BL4$.

Electronic spectra of the BL1 and $BL1^{\bullet -}$ (Figure 3b) show that the reduced species has absorption bands at 670 and 610 nm with ϵ of ~2700 M^{-1} cm^{-1}. The (π, π^*) transition at 340 nm in the parent species has reduced intensity upon reduction, and an absorption feature at 400 nm grows in.

The electronic spectra of BL2 and $BL2^{\bullet -}$ (Figure 3c) show different changes. For this ligand, reduction results in increased absorption throughout the visible region with bands at 340 and 410 nm (ϵ ~3500 M^{-1} cm^{-1}) growing in.

Reduction of BL4 to $BL4^{\bullet -}$ (Figure 3d) results in growth of absorption bands at 375 and 600 nm (ϵ ~3000 M^{-1} cm^{-1}).

The electronic absorption spectral changes resulting from reduction of the complexes are also reversible, showing well-defined isosbestic points. The spectra of $[Re(CO)_3Cl]_2dpq$ and its reduced product (Figure 4a) show that upon reduction the MLCT absorption at 526 nm is reduced in intensity. Isosbestic points may be observed at 450 and 645 nm, with the reduced species showing absorption peaks at 380 and 550 nm (ϵ ~4950 M^{-1} cm^{-1}).

The spectra of $[Re(CO)_3Cl]_2BL1$ and its reduced product (Figure 4b) reveal that reduction causes a depletion of the intensity of the MLCT band at 569 nm. A new band, blue-shifted to 550 nm (ϵ ~6000 M^{-1} cm^{-1}) grows in. Four distinct isosbestic points are observed at 330, 390, 410, and 490 nm, with the reduced species absorbing more than the parent between 410 and 490 and 330 and 390 nm. A peak is discernable at 390 nm and a shoulder at 335 nm.

Reduction of $[Re(CO)_3Cl]_2BL2$ (Figure 4c) results in a depletion of the MLCT band at 511 nm and a new feature at 550 nm appears (ϵ ~5000 M^{-1} cm^{-1}). Isosbestic points occur at 340 and 420 nm with the reduced species absorbing more than the parent between these wavelengths. Other peaks in the reduced spectrum lie at 401 and 322 nm.

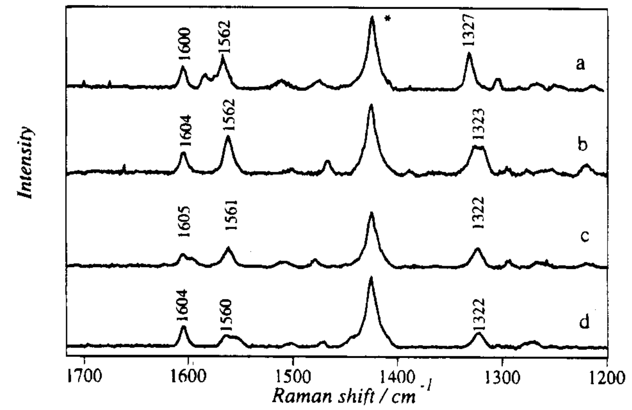

Figure 5. Resonance Raman spectra of electrochemically reduced metal complexes in dichloromethane with TBAP as supporting electrolyte. Excitation wavelength 514.5 nm, 15 mW. Concentration ~1 mM. * denotes solvent feature: (a) $[Re(CO)_3Cl]_2dpq$; (b) $[Re(CO)_3Cl]_2BL1$; (c) $[Re(CO)_3Cl]_2BL2$; (d) $[Re(CO)_3Cl]_2BL4$.

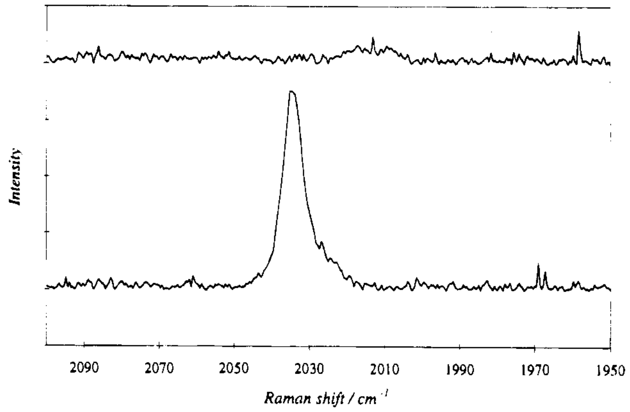

Figure 6. Raman spectra of $[Re(CO)_3Cl]_2BL4$ (lower trace) and its reduction product (upper trace) in the carbonyl region.

Table 5. Resonance Raman Bands Observed for Reduced Bimetallic Complexes in Dichloromethane (Excitation Wavelength 514.5 nm)

compound	$\bar{\nu}$/cm^{-1}						
$[Re(CO)_3Cl]_2dpq$	1300	1327	$1472^{w,a}$	1507^{w}	1562	1580	1600
$[Re(CO)_3Cl]_2BL1$		1323	1466^{w}		1562		1604
$[Re(CO)_3Cl]_2BL2$	1293^{w}	1322	1479^{w}	1507^{w}	1561		1605
$[Re(CO)_3Cl]_2BL4$	1274^{w}	1322	1471^{w}	1502^{w}	1560		1604

[a] w, weak features.

The reduction of $[Re(CO)_3Cl]_2BL4$ (Figure 4d) results in new bands at 550 nm with ϵ ~4000 M^{-1} cm^{-1}. Isosbestic points are observed at 330, 390, and 485 nm.

Raman Spectroelectrochemistry. Raman spectra of the reduction products of the complexes are shown in Figure 5. For each sample, complete reduction of the probed volume is confirmed by bleaching of the $\nu(C{\equiv}O)$ stretch (Figure 6). This band is enhanced through the MLCT transition of the parent complex but absent in the reduction product. The absorption in resonance for the reduction product is a ligand-centered (π^*,π^*) transition which does not enhance carbonyl modes. The increased intensity of the solvent features are also consistent with electronic absorption spectroelectrochemical data which indicate that, in the region 515−540 nm, the wavelength of the observed Raman photons, the reduced species absorbs less than the parent species for each complex. The bands observed in the reduced spectra are presented in Table 5. For each sample, three strong Raman bands are observed. These lie at 1324 ±

3, 1561 ± 1, and 1604 ± 1 cm^{-1}. Other features are also observed, but these three bands dominate the spectrum of each sample.

Discussion

The NMR spectra are informative as to the extent of communication within the bridging ligands and the affect of binding to the Re(CO)$_3$Cl units. The ligand ^{1}H-NMR spectra show that the pyridine protons are only slightly affected by the substituent changes made at the quinoxaline ring system. This is not the case for the quinoxaline proton resonances where large shifts (>0.6 ppm) are observed. Recent crystal structure[34] data for dpq shows that the pyridine rings are 30.3° out of the plane of the quinoxaline. Such a disposition of pyridine and quinoxaline rings would reduce inter-ring conjugation, which is consistent with the NMR data which show that substituent changes at the quinoxaline ring have very little effect on the pyridine ^{13}C resonances.

The proton resonances are shifted downfield when Re(CO)$_3$Cl units are bound to the bridging ligand. The largest shifts are observed at protons α to the chelating nitrogen on the pyridine rings, i.e., 6′, 6″ protons. These shift 0.8 ppm downfield upon chelation to 2Re(CO)$_3$Cl units. Those protons β to the nitrogen 5′,5″ shift 0.4 ppm downfield. These downfield shifts are not isolated to the pyridine protons. Quinoxaline protons, i.e., 5, 6, 7, 8, also shift significantly upon binding to Re(CO)$_3$Cl units. The NMR spectra suggest that the pyridine and quinoxaline parts of the bridging ligand are not strongly interacting and that the binding of 2Re(CO)$_3$Cl units to these ligands perturbs both the pyridine and quinoxaline parts of the ligand.

Tentative vibrational assignments for the bridging ligands may be made by comparison with literature spectra and observation of differences between the complexes. It is unlikely that the ligand will be planar in the bimetallic complex for steric reasons.[24,35] The X-ray crystal structure of dpq bound to rhodium(III) has a nonplanar structure.[34] One might therefore expect the vibrations of the molecule to be localized on the different ring moieties. Our empirical vibrational assignments make this assumption.

The 1291 ± 1 cm^{-1} band is common to all four complexes. Bands in this frequency region are observed in biphenyl systems and are assigned as the C−C stretch for the bond connecting the phenyl rings.[36] Detailed studies[37] of metal polypyridyl systems also suggest that vibrations in the 1300 cm^{-1} region are predominantly C−C bond stretch in character. The fact that the 1290 cm^{-1} band is common to all four complexes suggests it is associated with a part of the ligand unperturbed by the substituent changes at the quinoxaline ring. For these reasons we assign this band as being C3−C2″ and C2−C2′ stretch. The mode at 1320 cm^{-1} observed in [Re(CO)$_3$Cl]$_2$dpq is unshifted on going to the other complexes although its relative intensity of enhancement is altered. The resonance Raman data of the parent complexes show that the introduction of a third nitrogen to the quinoxaline ring to give a pyridopyrazine system, as in [Re(CO)$_3$Cl]$_2$BL1 and [Re(CO)$_3$Cl]$_2$BL4, reduces the intensity of the 1320 cm^{-1} band while causing frequency shifts of the other features. The MLCT transitions for both of these complexes are red-shifted with respect to dpq, suggesting a greater charge localization on the modified quinoxaline ring in the MLCT state. The resonance Raman effect enhances modes that mimic the electronic excitation and would therefore increase the intensity of modes associated with the quinoxaline framework while diminishing the intensity of other modes such as the pyridine ring modes. This would suggest the 1320 cm^{-1} band is associated with the pyridine rings. The NMR spectra indicate that the pyridine ring systems' ^{13}C resonances are barely affected by changes in the quinoxaline ring. Hence the bonding characteristics should also be unaffected. The fact that the vibrational band at 1320 cm^{-1} does not frequency shift with substitution is consistent with it being a pyridine-based mode and we assign it as such. The band at 1366 cm^{-1} for [Re(CO)$_3$Cl]$_2$dpq shifts significantly on substitution at the quinoxaline ring. The complexes with pyridopyrazine ring systems , [Re(CO)$_3$Cl]$_2$BL1 and [Re(CO)$_3$Cl]$_2$BL4, show lower frequencies of vibration. The Raman spectra of the ligands show that the most intense is at 1398 cm^{-1} for dpq and at lower frequencies for BL1 (1389 cm^{-1}) and BL4 (1387 cm^{-1}). The Raman spectrum of quinoxaline[38] shows a strong Raman band at 1369 cm^{-1} which is assigned as a ν_8[39] ring stretching mode.[40] We assign the bands at 1340−1366 cm^{-1} as ring stretching modes of the quinoxaline ring. The mode at 1467 cm^{-1} for [Re(CO)$_3$Cl]$_2$dpq behaves in analogous fashion to the ν_8 mode. It is assigned as the quinoxaline ring stretch ν_5 mode. The band at 1497 cm^{-1} for [Re(CO)$_3$Cl]$_2$dpq is barely shifted on going to the other complexes, indicating less quinoxaline character for this mode. Finally, the feature at 1558 cm^{-1} for [Re(CO)$_3$Cl]$_2$dpq shifts to slightly lower frequencies on going to [Re(CO)$_3$Cl]$_2$BL1 and [Re(CO)$_3$Cl]$_2$BL4, 1556 and 1551 cm^{-1}, respectively. A similar pattern is observed in the normal Raman spectra of the ligands. The strongest feature in this region is at 1591 cm^{-1} for dpq, 1587 cm^{-1} for BL1, and 1589 cm^{-1} for BL4. The frequency shifts for the complexes are similar to those observed for the ν_3 quinoxaline ring stretch mode in the infrared spectrum of quinoxaline, pyrido[3,4-*b*]pyrazine and pyrido[2,3-*b*]pyrazine.[39] We assign these bands as being predominantly quinoxaline ring stretches for these reasons. In summary, the Raman spectra of the complexes are characterized by bands of two distinct types: bands associated with modes of predominantly quinoxaline character and those of pyridyl ring character. These assignments, although empirical in nature, do provide marker bands for each part of the ligand and may be used to determine the nature of the redox orbital for the reduced complexes.

The electronic spectra of the ligands are dominated by (π, π^*) bands. (n, π^*) transitions have low ϵ and are not observed in our spectra.[41] In all cases, the reduced ligand is more absorbing than the parent in the visible spectrum. It is common for polypyridyl ligands to absorb further into the red upon reduction.[42] The methylated ligand, BL2, shows the smallest red shift with BL1 and BL4 having the largest. Reduced BL1 and BL4 absorb appreciably at 600 nm. One could interpret the spectral data as indicating that the π^* MO extends across the fused ring system to a greater extent for BL1 and BL4 than for BL2.

When the spectra of the complexes are considered, it is important to realize that the disposition of the ligand is altered.

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X-ray data for dpq show that the pyridine rings are out of plane with the quinoxaline and the pyridine N atoms are turned toward each other.[34] This arrangement is not possible in the bimetallic complexes. Furthermore, these ligands are known to hydrogen bond in solution.[43] Hence the spectra of the reduced complexes and ligands may not correlate well.

In considering the spectra of the reduced complexes, it is clear that the electronic spectra are very similar for each system despite the different structures of the ligands and their different reduction potentials. A possible explanation for this behavior is that the first reduction of the complexes is not bridging ligand based at all. However, this is not consistent with two facts: (i) The reductions shift with bridging ligand present; (ii) the Raman spectra of the reduced species show enhanced modes which lie at frequencies that can only be attributed to the bridging ligand. Furthermore, if reduction is not bridging ligand based it must be $Re(CO)_3Cl$ based. The resonance Raman data do not show enhancement of carbonyl modes, and this is not consistent with the reduced species absorption having metal character, i.e., being a LMCT or MLCT transition. Alternatively, the redox MO for the bimetallic systems is similar for each of the complexes and different from that of the free ligands. The redox MO is not disposed in the same way as in the free ligand. In fact, the similarity of the electronic spectra suggests that the redox MO is not significantly extended over the quinoxaline ring but has greater density at the pyridine rings which are common to all four ligands. This would be unusual as the pyridine rings would not be anticipated to stabilize the redox π^* orbital as effectively as quinoxaline or pyridopyrazine ring systems. The strong features at 1605 and 1560 cm^{-1} are common to all the reduced spectra. The similarity within the series of ligands is at the pyridyl ring. Hence, these modes are assigned as pyridyl in character. The third feature common to all of the reduced spectra is at ca. 1320 cm^{-1}. This is tentatively assigned as predominantly C−C stretch for the C2−C2′ and C3−C2″ linkages between the ring systems. Hence, reduction shifts this band to higher frequency from 1290 to 1320 cm^{-1}. In TR^3 studies of Ru(II) polypyridyl systems, a shift to higher frequency has been observed for modes containing significant contributions from the C−C stretch connecting pyridyl ring systems.[36]

One might expect that the resonance Raman spectra of the parent species and the Raman spectra of the reduced species would probe the same MO, that is the π^* LUMO of the ligand. The resonance effect in the parent spectrum enhances modes that mimic the MLCT electronic excitation, which formally reduces the ligand. This should provide an indication of where the electron is going if excited, i.e. undergoing electron transfer from metal to ligand.[44] The Raman spectrum of the reduced species reveals the nature of the π^* MO through the frequencies of the observed bands. However, the bands enhanced depend on the resonant chromophore, which in this case is a ligand-based (π^*, π^*). It is interesting to note that the resonance Raman spectra of the complexes show differing enhancement patterns that suggest that for $[Re(CO)_3Cl]_2BL1$ and $[Re(CO)_3Cl]_2BL4$ the π^* LUMO orbital is extended over the pyridopyrazine ring, more so than for $[Re(CO)_3Cl]_2BL2$ and $[Re(CO)_3Cl]_2dpq$. The Raman spectra of the reduced complexes are strikingly similar, suggesting a uniformity in the nature of the redox MOs for these systems. There are two possibilities that may give rise to such findings. One possibility is that the observed bands in the Raman spectra of the reduced species are modes that extend over the entire ligand but the LUMO is such to even out the bonding of each bridging ligand so that all vibrations are coincident. This seems unlikely to occur for all four complexes.

The possibility that the techniques are probing different MOs is more plausible. The resonance Raman spectra of the parent species are probing the optical π^* MO of the bridging ligand. This provides information on where the electron goes initially upon excitation, but it is mute to subsequent reorganization of electrons. In this regard, the redox MO may be more like the ligand MO of the MLCT THEXI[45] state. The redox MO probed by the Raman spectra of the reduced species may be quite localized as are THEXI state orbitals.[8,46] However, our results differ from those of Kincaid[8,45] and Wertz[9] in that they indicate similar electron localization in a series of different bridged ligand systems. This localization is toward the pyridine rings rather than the larger quinoxaline or pyridopyrazine ring systems, i.e., away from the more electron-accepting/-stabilizing ring system. This localization explains the similarity of the electronic spectra of the reduced species but is at odds with the fact that the reduction potentials vary significantly. $[Re(CO)_3Cl]_2BL1$ and $[Re(CO)_3Cl]_2BL4$ are easier to reduce and have MLCT transitions to the red of the $[Re(CO)_3Cl]_2dpq$ and $[Re(CO)_3Cl]_2BL2$. This implies that the bridging ligand π^* LUMO is tuned by the substituents. The most obvious mechanism for varying the π^* MO energy in these systems is if the MO extends on to the fused framework for the pyridopyrazine bridging ligands. This in turn suggests that redox orbital should be polarized toward the fused ring to a greater extent for $[Re(CO)_3Cl]_2BL1$ and $[Re(CO)_3Cl]_2BL4$ than for $[Re(CO)_3Cl]_2dpq$ and $[Re(CO)_3Cl]_2BL2$. However, for the different ligands, the first reduction potential varies from −1.3 to −1.6 V. For the complexes, the variation is between −0.4 and −0.08 V. The differing substituents clearly change the potential of reduction, but the greatest perturbation occurs on going from free ligand to bimetallic complex. The presence of the two Re units causes a +1.2 V shift in the reductions relative to the free ligand. This large stabilization in the redox orbital may wash out the more subtle changes caused by the quinoxaline substituent, to the extent that the redox MO is polarized toward the pyridine rings and away from the quinoxaline or pyridopyrazine units, i.e., toward the metal centers. Electron spin resonance has been used to ascertain such localization processes and would offer further evidence for the localization hypothesis suggested by the Raman data.[15,47]

The redox MO is important in intermetal communication through the bridging ligand unit.[48] We are investigating the issue of metal−metal communication directly by examining Ru(II) complexes of these ligands in which one metal may be oxidized reversibly to create a mixed-valent species which may then be studied spectroscopically.[49]

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Supporting Information Available: UV/visible spectra of each complex at a series of reduction potentials as they are reduced in the Ottle cell. Raman spectra of free ligands: dpq; BL1; BL4 (7 pages). Ordering information is given on any current masthead page.

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