4346 Inorg. Chem. 1992, 31, 4346–4353

Structural, Spectroscopic, and Electrochemical Investigation of Luminescent Bimetallic Complexes of Rhenium(I)

Rongguang Lin, Yigang Fu, Carolyn P. Brock, and Thomas F. Guarr*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

Received December 10, 1991

The synthesis, electrochemistry, and photophysical properties of a series of homobimetallic Re(I) complexes are described. Such complexes can be represented by the general formula $[(LL)(CO)_3Re(BL)Re(CO)_3(LL)]^{2+}$, where LL is 2,2′-bipyridine (bpy), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me$_4$phen), or 2,2′-biquinoline (bqu) and BL is pyrazine, 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane, or 1,3-bis(4-pyridyl)propane. One of these compounds (LL = 2,2′-bipyridine, BL = 1,2-bis(4-pyridyl)ethane; empirical formula = $[Re_2C_{38}H_{28}N_6O_6][BC_{24}H_{20}]_2\cdot 2C_4H_{10}O$) has been found to crystallize in the monoclinic space group $P2_1/n$ with cell parameters of $a = 14.124$ (3) Å, $b = 15.117$ (2) Å, $c = 19.744$ (4) Å, $\beta = 95.140$ (9)°, and $Z = 2$. Crystallographic data were collected by the $\omega/2\theta$ method, and all non-H atoms were refined anisotropically using 4023 reflections having $I > 3\sigma(I)$. The final R factor was 0.036. The rhenium–nitrogen bond distances are 2.17 Å (average) for Re–N(2,2′-bipyridine) and 2.213 (6) Å for the Re–N(pyridyl) linkage, while the intramolecular Re–Re′ distance is 13.540 (2) Å. Oxidation potentials show a weak dependence on the nature of LL, ranging from +1.66 to +1.84 V vs SSCE. Conversely, reduction potentials are extremely sensitive to variations in both the chelating and bridging ligands. Absorption bands at 280–320 nm are assigned as intraligand $\pi \rightarrow \pi^*$ transitions; Re → LL MLCT bands are found at ca. 340, 347, and 382 nm for the Me$_4$phen, bpy, and bqu complexes, respectively. Additional Re → BL MLCT bands are observed for the bimetallic complexes containing the pyrazine or 4,4′-bipyridine bridges. The availability of low-lying Re → BL MLCT states can have a strong influence on the room-temperature photophysical properties, as demonstrated by comparisons with the corresponding monometallic species. Thus, attachment of the second metal center to $[(Me_4phen)(CO)_3Re(pyrazine)]^+$ results in a dramatic red shift of the emission energy (694 vs 514 nm), as well as a substantial decrease in excited-state lifetime (60 ns vs 7.63 μs). Emission lifetimes for all of the monometallic and bimetallic complexes reported herein are in qualitative agreement with the energy gap law.

Introduction

The recognition of the photoinduced redox activity of numerous d^6 metal complexes has led to an interest in the corresponding multimetallic species. Much of the work to date has involved ruthenium polypyridines bridged by such ligands as 2,2′-bipyrimidine or 2,3-bis(2-pyridyl)pyrazine.[1–8] Only recently have the analogous complexes of rhenium(I) chromophores begun to receive attention,[9–15] and bimetallic complexes of Re(I) which are luminescent in room-temperature fluid solution are still quite rare. On the other hand, there are several reports concerning room-temperature emission from both homobimetallic and heterobimetallic complexes of group VI metal carbonyls bridged by such ligands as pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), and 1,2-bis(4-pyridyl)ethane (bpa).[16–25] The spectroscopy of these compounds has been carefully investigated, and there have been several elegant studies of their photophysical and photochemical behavior. Surprisingly, there are very few reports of bimetallic Re(I) complexes linked in this fashion,[12–15] despite the fact that the parent monometallic species such as $(bpy)Re(CO)_3(py)^+$ (bpy = 2,2′-bipyridine, py = pyridine) possess attractive spectroscopic, photophysical, and electrochemical properties.[26–28] We wish to report the synthesis of a series of homobimetallic rhenium complexes, as well as the results of an investigation of their absorption, emission, and electrochemical behavior. The bridging ligands employed in this study are pyz, 4,4′-bpy, bpa, and 1,3-bis(4-pyridyl)propane (bpp).

In contrast to an earlier report regarding the 2,2′-bipyrimidine-bridged bimetallic species,[9] all of the new complexes except for those containing pyz are highly luminescent in room-temperature fluid solution. Although the lack of emission from $[Cl(CO)_3Re(2,2'\text{-bipyrimidine})Re(CO)_3Cl]$ has been attributed to the presence of a low-lying metal-to-metal charge-transfer state,[9] it has recently been shown that this MMCT level is not energetically accessible from the initially populated MLCT state and hence cannot be responsible for the observed behavior.[11,12] Rather, the similarities and differences in the photophysical properties of all of the various monometallic and bimetallic species

---

(1) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.
(2) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.
(3) Rillema, D. P.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 3849.
(4) Curtis, J. C.; Bernstein, J. S.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 385.
(5) Rillema, D. P.; Taghdiri, D. G.; Jones, D. S.; Keller, C. D.; Worl, L. A.; Meyer, T. J.; Levy, H. A. *Inorg. Chem.* **1987**, *26*, 578.
(6) Sahai, R.; Morgan, L.; Rillema, D. P. *Inorg. Chem.* **1988**, *27*, 3495.
(7) Schmehl, R. H.; Auerbach, R. A.; Wacholtz, W. F. *J. Phys. Chem.* **1988**, *92*, 6202.
(8) Cooper, J. B.; MacQueen, D. B.; Petersen, J. D.; Wertz, D. W. *Inorg. Chem.* **1990**, *29*, 3701.
(9) Vogler, A.; Kisslinger, J. *Inorg. Chim. Acta* **1986**, *115*, 193.
(10) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J. M.; Zeissel, R. *Inorg. Chem.* **1988**, *27*, 4007.
(11) Van Wallendael, S.; Shaver, R. J.; Rillema, D. P.; Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 1761.
(12) Lin, R.; Guarr, T. F. *Inorg. Chim. Acta* **1990**, *167*, 149.
(13) Lin, R.; Guarr, T. F.; Duesing, R. *Inorg. Chem.* **1990**, *29*, 4169.
(14) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885.
(15) Tapolsky, G.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 2285.
(16) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.
(17) Lees, A. J.; Fobare, J. M.; Mattimore, E. F. *Inorg. Chem.* **1984**, *23*, 2709.
(18) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1139.
(19) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 3325.
(20) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365.
(21) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *22*, 1146.
(22) Ernst, S.; Kaim, W. *J. Am. Chem. Soc.* **1986**, *108*, 3578.
(23) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68.
(24) Moore, K. J.; Petersen, J. D. *Polyhedron* **1983**, *2*, 279.
(25) Overton, C.; Connor, J. A. *Polyhedron* **1982**, *1*, 53.
(26) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415.
(27) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.
(28) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335.

0020-1669/92/1331-4346$03.00/0

can be adequately explained in terms of a simple model based on the energy gap law.[12-15,28]

Experimental Section

(A) Materials. Pentacarbonylchlororhenium(I) (Pressure Chemical Co.), 2,2′-bipyridine (bpy) (Aldrich), 2,2′-biquinoline (bqu) (Aldrich), and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen) (GFS Chemicals) were used as received. The bridging ligands pyz, 4,4′-bpy, and bpa were also purchased from Aldrich and used without further purification. bpp used in this study was obtained from Reilly Tar and Chemical and recrystallized twice from methanol/diethyl ether prior to use. NMR spectroscopy was utilized to confirm the purity of all chelating and bridging heterocyclic ligands. The tetraalkylammonium salts (Southwestern Analytical) were dried overnight in a vacuum oven before being employed in the electrochemical measurements. All solvents were reagent or spectral grade and were purified and dried by distillation using established procedures prior to these experiments. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

(B) Methods. NMR spectra were obtained in either d_6-acetone or d_6-DMSO (Cambridge Isotopes) and were performed on a Varian Gemini 200-MHz NMR spectrometer. The crystal structure of $[(CO)_3(bpy)Re(bpa)Re(bpy)(CO)_3][B(C_6H_5)_4]_2$ reported herein was determined on an Enraf-Nonius CAD-4. Infrared spectra were obtained in Nujol mulls, using a Perkin-Elmer Model 1710 FTIR spectrometer. Electronic absorption spectra were recorded on an Aviv Model 14DS spectrophotometer equipped for computerized data acquisition. Steady-state emission spectra were recorded on either a Perkin-Elmer Model LS-50 luminescence spectrometer or a SPEX Fluorolog F111AI. Emission lifetimes (355-nm excitation) were determined using a Lumonics HY750 Nd:YAG pulsed laser system in conjunction with a LeCroy Model 3500SA transient digitizer. The electrochemical experiments were carried out in deoxygenated dimethyl sulfoxide (DMSO, Burdick & Jackson) containing 0.1 M tetraethylammonium hexafluorophosphate (TEAH) as electrolyte. The working electrode was either a glassy-carbon or Pt disk, and the data were collected using an EG&G PAR Model 273 potentiostat/galvanostat which was interfaced to a laboratory computer.

Since several of these compounds were found to undergo decomposition in coordinating solvents (vide infra), all necessary physical measurements were performed within 20 min of the preparation of a fresh sample solution. Under these conditions, the extent of decomposition was kept to <1%, even in the worst case.

(C) Crystallography. The structure was solved by the heavy-atom method. The geometry of the cation is constrained by a crystallographic inversion center, while the anion and solvent molecules are in general positions. The solvent molecules were located in difference Fourier syntheses and either were disordered or exhibited large thermal motion. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in the cation and anion were placed in calculated positions 1.00 Å from the associated carbon atom and were not refined; no hydrogen atom positions were calculated for the solvent molecules. No correction for extinction was necessary. The computer programs used in this work have been described previously;[29] scattering factors, including anomalous terms for the Re atoms, were taken from Cromer and Waber.[30] The largest positive and negative peaks in the final difference Fourier maps were both located near the rhenium atom.

(D) Synthesis. ***fac*-Re(bpy)(CO)$_3$Cl.** This complex was prepared in accord with established literature procedure.[31] $Re(CO)_5Cl$ was dissolved together with a slight excess of 2,2′-bipyridine in spectroquality isooctane, and the solution was heated to 60 °C for 1 h. The product, a bright yellow solid, was isolated by filtration and washed several times with copious amounts of isooctane to remove any unreacted $Re(CO)_5Cl$ and the excess bpy. Final purification was achieved by the slow addition of isooctane to a concentrated solution of the complex in CH_2Cl_2, followed by filtration and washing with isooctane to yield a pure yellow solid. Typical yields were 90–95%.

***fac*-[Re(bpy)(CO)$_3$(CH$_3$CN)]CF$_3$SO$_3$.** This complex was prepared by a modification of the method reported by Fredericks et al.[26] In a typical synthetic procedure, 1.24 g of $Re(bpy)(CO)_3Cl$ (2.68 mmol) and 0.71 g (2.76 mmol) of $AgCF_3SO_3$ were dissolved in 600 mL of acetonitrile, and the solution was heated at reflux for 8 h. The mixture was filtered and the solvent removed from the filtrate by rotary evaporation. The residue was dissolved in CH_2Cl_2, and the solution was filtered, then carefully layered with diethyl ether, and refrigerated. The product was collected as pale yellow needles and dried in vacuo. Yield: 1.52 g, 92%.

Table I. Elemental Analysis Data (%) for (2,2′-Bipyridine)tricarbonylrhenium(I) Complexes

complex	calcd (found)		
	C	H	N
$[(bpy)(CO)_3Re(pyz)]PF_6$	31.34 (31.31)	1.86 (1.86)	8.60 (8.54)
$[(bpy)(CO)_3Re(pyz)Re(CO)_3(bpy)](CF_3SO_3)_2\cdot(CH_3)_2CO$[a]	33.18 (33.79)	2.17 (2.47)	6.45 (6.20)
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)]CF_3SO_3$	39.40 (38.30)	2.20 (2.35)	7.66 (7.27)
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bpy)](CF_3SO_3)_2$	34.92 (34.85)	1.85 (1.88)	6.43 (6.34)
$[(bpy)(CO)_3Re(bpa)Re(CO)_3(bpy)](CF_3SO_3)_2\cdot(CH_3)_2CO$[a]	37.07 (36.60)	2.46 (2.45)	6.03 (5.91)
$[(bpy)(CO)_3Re(bpp)Re(CO)_3(bpy)](CF_3SO_3)_2$	36.50 (36.03)	2.24 (2.45)	6.23 (6.12)

[a] The presence of an included solvent molecule was verified by NMR spectroscopy.

***fac*-[Re(bpy)(CO)$_3$(BL)]CF$_3$SO$_3$ (BL = pyz, 4,4′-bpy, bpa, bpp).** This series of compounds was prepared by the method of Caspar and Meyer,[27] using the direction reaction of an approximately 10-fold excess of the appropriate ligand with *fac*-$[Re(bpy)(CO)_3(CH_3CN)]CF_3SO_3$ in THF solution at reflux for 3 h. After the solution had cooled, ether was added dropwise and the bright yellow solid was isolated by filtration. In a representative preparation, 300 mg (0.487 mmol) of *fac*-$[Re(bpy)(CO)_3(CH_3CN)]CF_3SO_3$ and 900 mg (4.9 mmol) of 1,2-bis(4-pyridyl)ethane were dissolved in THF and heated to reflux for 2 h. After cooling, approximately 120 mL of ether was added slowly to precipitate the product *fac*-$[Re(bpy)(CO)_3(bpa)]CF_3SO_3$ as a yellow solid. The crude product was purified by chromatography on silica gel using a 2:1 (v:v) mixture of CH_2Cl_2 and CH_3CN as eluant. The solid material was obtained by rotary evaporation of the appropriate fraction. Final purification was achieved by reprecipitation from CH_2Cl_2 solution by the slow addition of ether. Yield: 330 mg, 90%. These complexes are soluble in polar organic solvents, such as methanol, acetone, and acetonitrile, but insoluble in solvents of lower polarity (e.g., ether, pentane).

[(bpy)(CO)$_3$Re(BL)Re(CO)$_3$(bpy)](CF$_3$SO$_3$)$_2$ (BL = pyz, 4,4′-bpy, bpa, bpp). These bimetallic complexes were conveniently prepared by refluxing a THF solution containing a 2:1 ratio of *fac*-$[Re(bpy)(CO)_3(CH_3CN)]CF_3SO_3$ and the desired bridging ligand.[12] In a typical experiment, 0.2154 g (0.35 mmol) of *fac*-$[Re(bpy)(CO)_3(CH_3CN)]CF_3SO_3$ was dissolved in 10 mL of THF, and the resultant solution was slowly added to a flask containing 0.322 g (0.175 mmol) of bpa in 5 mL of THF. The mixture was refluxed for 6 h, and the formation of a yellow precipitate was observed during the course of the reaction. After filtration, the solid was washed with THF and ether. The crude product was purified by recrystallization from acetone/ether and dried in vacuo. Yield: 0.20 g, 87%. For L = pyz, some decomposition was observed in coordinating solvents (see text) and the pure product was better obtained by recrystallization from CH_3NO_2/ether. The bimetallic complexes are soluble in strongly polar solvents, such as acetone, DMSO, and CH_3CN, but insoluble in THF, CH_2Cl_2, and ether. Analytical data for all bpy-containing bimetallic complexes are given in Table I.

Results and Discussion

The majority of the preparations described in the Experimental Section utilize *fac*-$[(bpy)(CO)_3Re(CH_3CN)]CF_3SO_3$ (or the bqu- and Me_4phen-containing analogues) in THF as a synthetic intermediate. With appropriate control of experimental conditions, reactions 1 and 2 (where BL represents a potential bridging

$$[(bpy)(CO)_3Re(CH_3CN)]^+ + BL\ (10\times\ \text{excess}) \rightarrow [(bpy)(CO)_3Re(BL)]^+ \quad (1)$$

$$2[(bpy)(CO)_3Re(CH_3CN)]^+ + BL \rightarrow [(bpy)(CO)_3Re(BL)Re(CO)_3(bpy)]^{2+} \quad (2)$$

ligand) can be made to proceed in virtually quantitative fashion. These procedures appear to be quite general, at least for dibasic

---

(29) Brock, C. P.; Webster, D. F. *Acta Crystallogr.* **1976**, *B32*, 2089.

(30) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV. Tables 2.2B and 2.3.1.

(31) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.

N-heterocyclic bridging ligands.[12-15,27] In addition, purification is very straightforward, particularly for the bimetallic species.

While all of the complexes reported herein are stable indefinitely in the solid state, the pyrazine-bridged bimetallic complexes undergo slow decomposition in polar solvents such as CH_3CN, acetone, or dimethyl sulfoxide. The decomposition of these complexes apparently occurs by a thermal process and occurs on a time scale of several hours for the bpy complex. The decomposition reaction can be readily followed by ^1H NMR. The NMR spectra suggest that the mechanism involves replacement of the pyrazine ligand by solvent (S) and/or adventitious water:

$$[(bpy)(CO)_3Re(pyz)Re(CO)_3(bpy)]^{2+} + S \rightarrow [(bpy)(CO)_3Re(S)]^+ + [(bpy)(CO)_3Re(pyz)]^+ \quad (3)$$

The monometallic pyz complex displays similar behavior (eq 4), but the rate of ligand replacement is 5–10 times slower than in the bimetallic case. No such decomposition was observed for either monometallic or bimetallic complexes containing the other bridging ligands employed in this study (4,4′-bpy, bpa, bpp), at least over a period of 10 days.

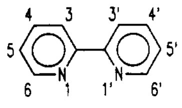
$$[(bpy)(CO)_3Re(pyz)]^+ + S \rightarrow [(bpy)(CO)_3Re(S)]^+ + pyz \quad (4)$$

The ready solvation of the pyz-bridged bimetallic bpy complex suggests that the presence of the first rhenium center dramatically reduces the basicity of the uncoordinated pyz nitrogen. This behavior contrasts sharply with that of $Ru(NH_3)_5(pyz)^{2+}$, which is a much stronger base than pyz itself.[32] The increased Ru–N bond strength in the "dimer" has been attributed to efficient π-back-bonding from the Ru(II) center to the protonated pyrazine ligand.[33,34]

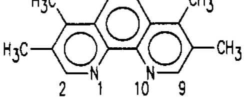
In the present case, π-back-bonding effects are likely to be less dominant, since the carbonyl ligands, as well as the chelating polypyridine, will compete for any excess electron density at Re. Nonetheless, the stability of the pyz-bridged bimetallic rhenium complex can be controlled to some extent by modulating the electron density at the metal through the choice of substituents on the chelating polypyridine ligand. Thus, $[(Me_4phen)(CO)_3Re(pyz)Re(CO)_3(Me_4phen)]^{2+}$ is much more stable than the analogous bpy complex with respect to ligand substitution, and significant decomposition requires several days in room temperature solution. In fact, it proved difficult to obtain samples of $(Me_4phen)(CO)_3Re(pyz)^+$ that were not contaminated with the bimetallic species, even when a very large excess of pyz was employed during the synthetic procedure. By contrast, all attempts to prepare a pyz-bridged bimetallic complex from rhenium tricarbonyl fragments containing the bqu ligand, a relatively poor electron donor compared to bpy, were unsuccessful. Apparently, the increase in metal–nitrogen bond order through back-bonding, though less pronounced here than in the ruthenium case, is still an important determinant of the overall stability of the complex.

In principle, ^1H NMR can be used to probe the π-electron density on the pyridyl-based ligands.[33,34] However, while the chemical shifts of protons in the para position correlate well with calculated π-electron densities,[32] shifts at the ortho and meta positions exhibit a less straightforward dependence and generally provide only qualitative information. In addition, earlier results on the $Ru(NH_3)_5(pyz)^{2+}$ system suggest that, because of paramagnetic anisotropy and solvent effects, proton chemical shift data are not reliable indicators of ligand π-electron density in transition metal complexes. Lavallee et al.[34] conclude that the upfield shift of the pyz H-2/H-6 resonance which occurs upon complexation is the result of the paramagnetic anisotropy of the Ru(II) ion. This effect apparently overrides the expected downfield shift caused by the partial positive charge on the pyz ligand. On the other hand, the coordination of a second Ru(II) results in a larger electrostatic (diamagnetic) contribution and a net downfield shift.[33]

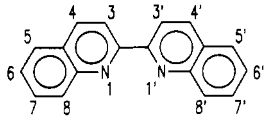
^{1}H NMR Spectra. Each of the desired complexes, as well as the important synthetic intermediates, can be readily characterized by ^1H NMR. Peak positions and their assignments are collected in Table II. All of the resonances can be assigned to either the chelating or the bridging ligand by comparison to the spectra of the free ligands.



bpy



Me_4phen



bqu

bpy Complexes. Only four resonances are observed for uncoordinated bpy: the two doublets located at 8.71 and 8.44 ppm are attributed to the protons on the C-6/C-6′ and C-3/C-3′ carbon atoms, respectively. The triplet at 7.96 ppm is assigned to the C-4/C-4′ protons, while the triplet at 7.46 ppm can be assigned to the protons on C-5/C-5′. All of these resonances shift downfield dramatically (by 0.33–0.41 ppm) upon attachment of an electron-withdrawing $-Re(CO)_3Cl$ group. Replacement of the chlorine ligand in $[(bpy)(CO)_3ReCl]$ by CH_3CN results in a further downfield shift of each resonance by 0.07–0.09 ppm, consistent with the change from a neutral species to a cationic complex.

The bpy ^1H resonances are also affected by the replacement of the CH_3CN ligand by pyz, 4,4′-bpy, bpa, or bpp. For example, the resonance due to the C-6 and C-6′ protons on bpy shifts downfield by 0.2–0.3 ppm, while the resonances of the C-3 and C-3′ protons are shifted upfield by 0.08–0.16 ppm. On the other hand, the positions of the peaks corresponding to the protons on C-4/C-4′ and C-5/C-5′ are virtually unaffected (shifts are less than 0.05 ppm). In the monometallic complexes, much of the symmetry of the N-heterocyclic bridging ligand is lost, and the NMR indicates clearly discernible differences between those protons on the ring attached to the Re center and those on the "dangling" ring. Similar behavior is noted for $[(bpy)(CO)_3Re(pyz)]^+$, where the pyz protons appear as a pair of doublets at 8.71 and 8.51 ppm (d_6-DMSO).

Upon attachment of the second metal, the symmetry of the bridging ligand is restored, and the NMR spectrum is considerably simpler than that of the corresponding monometallic complex. Indeed, although the peaks are shifted somewhat from their uncomplexed positions, the observed splitting pattern closely resembles a superposition of the $[(bpy)(CO)_3Re(CH_3CN)]^+$ and BL NMR spectra. For example, the pyrazine protons collapse to the expected singlet (at 8.44 ppm) in the bimetallic complex. Complexation of the second rhenium center results in a slight upfield shift of the bpy resonances when BL = pyz; these resonances are essentially unchanged upon secondary metal attachment to the other bridging ligands.

bqu Complexes. The bqu chelating ligand in each of these complexes exhibits a characteristic splitting pattern (four doublets and two triplets) which can be readily assigned by comparison

---

[32] Ford, P.; Rudd, De F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1967**, *90*, 1187.

[33] Lavallee, D. K.; Fleischer, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583.

[34] Lavallee, D. K.; Baughman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718.

Table II. ^{1}H NMR Data for Monometallic and Bimetallic (2,2'-Bipyridine)tricarbonylrhenium(I) Complexes

	chemical shift[a] (ppm)									
	bpy				BL					
complexes										
$[(bpy)(CO)_3Re(Cl)]$	9.04 (d, 2 H)	8.79 (d, 2 H)	8.37 (t, 2 H)	7.79 (t, 2 H)						
$[(bpy)(CO)_3Re(CH_3CN)]^+$	9.11 (d, 2 H)	8.87 (d, 2 H)	8.46 (t, 2 H)	7.87 (t, 2 H)						
$[(bpy)(CO)_3Re(pyz)]^+$	9.31 (d, 2 H)	8.77 (d, 2 H)	8.43 (t, 2 H)	7.92 (t, 2 H)		8.71 (d, 2 H)	8.51 (d, 2 H)			
$[(bpy)(CO)_3Re(pyz)Re(CO)_3(bpy)]^{2+}$	9.20 (d, 4 H)	8.76 (d, 4 H)	8.41 (t, 4 H)	7.89 (t, 4 H)		8.44 (s, 4 H)				
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)]^+$	9.39 (d, 2 H)	8.75 (d, 2 H)	8.43 (t, 2 H)	7.92 (t, 2 H)	8.76 (d, 2 H)	8.54 (d, 2 H)	7.85 (d, 2 H)	7.77 (d, 2 H)		
$[(bpy)Re(CO)_3(4,4'\text{-}bpy)Re(CO)_3(bpy)]^{2+}$	9.36 (d, 4 H)	8.71 (d, 4 H)	8.41 (t, 4 H)	7.91 (t, 4 H)		8.54 (d, 4 H)	7.76 (d, 4 H)			
$[(bpy)(CO)_3Re(bpa)]^+$	9.33 (d, 2 H)	8.72 (d, 2 H)	8.42 (t, 2 H)	7.91 (t, 2 H)	8.54 (d, 2 H)	8.28 (d, 2 H)	7.35 (d, 2 H)	7.30 (d, 2 H)	2.91 (b, 4 H)	
$[(bpy)(CO)_3Re(bpa)Re(CO)_3(bpy)]^{2+}$	9.32 (d, 4 H)	8.69 (d, 4 H)	8.38 (t, 4 H)	7.90 (t, 4 H)		8.28 (d, 4 H)	7.25 (d, 4 H)		2.74 (b, 4 H)	
$[(bpy)(CO)_3Re(bpp)]^+$	9.32 (3, 2 H)	8.71 (d, 2 H)	8.41 (t, 2 H)	7.90 (t, 2 H)	8.54 (d, 2 H)	8.27 (d, 2 H)	7.40 (d, 2 H)	7.29 (d, 2 H)	2.59 (m, 4 H)	1.81 (m, 2 H)
$[(bpy)(CO)_3Re(bpp)Re(CO)_3(bpy)]^{2+}$	9.32 (d, 4 H)	8.71 (d, 4 H)	8.40 (t, 4 H)	7.90 (t, 4 H)		8.25 (d, 4 H)	7.24 (d, 4 H)		2.50 (t, 4 H)	1.70 (p, 2 H)

[a] In d^6-DMSO. d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, and b = broad.

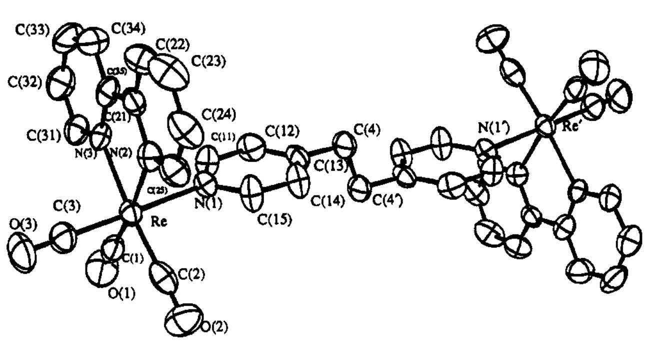


Figure 1. ORTEP drawing of the cation $[(bpy)(CO)_3Re(bpa)Re(CO)_3(bpy)]^{2+}$.

with the NMR spectrum of quinoline.[35] Although some minor differences in bqu chemical shifts among the various monometallic complexes are seen (particularly when the pyz and 4,4'-bpy derivatives are compared), this basic pattern remains unchanged upon variation of BL. However, all of the bqu protons exhibit a small upfield shift upon the formation of bimetallic complexes, even for the longer bridging ligands bpa and bpp.

On the other hand, the resonances due to the BL protons shift dramatically (typically ca. 1 ppm) upon attachment of the rhenium center. As a result, the furthest downfield signal attributed to the bridging ligand in $[(bqu)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bqu)]^{2+}$ is observed at 7.64 ppm. This compares with a chemical shift for the same protons in the free ligand of 8.73 ppm. An examination of molecular models suggests that the chemical shifts of the BL protons in the 2 and 6 positions are probably influenced by the aromatic ring current of the chelating polypyridine. Thus, the large upfield shift of the ortho pyz resonances in the bqu complex can be accounted for by an enhanced ring current effect which results from the larger size of this ligand. Likewise, weak ring current effects may also be responsible for the slight upfield shift of the bpy and Me$_4$phen α-protons upon attachment of the second metal center.

Me$_4$phen Complexes. ^{1}H NMR spectra of the Me$_4$phen complexes are readily interpretable and are entirely analogous to those of the corresponding bpy derivatives.

X-ray Crystallography. Repeated attempts at crystal growth showed that the bimetallic cations tend to crystallize with included solvent, probably as a consequence of their dumbbell-like shape. High-quality crystals of $[(bpy)(CO)_3Re(bpa)Re(CO)_3(bpy)][BPh_4]_2\cdot 2(C_2H_5)_2O$ were grown by slow diffusion of diethyl ether into a nitromethane solution of the compound. Unit cell dimensions for the monoclinic unit cell were obtained by a least-squares fit for 22 reflections ($10.6° < \theta < 12.9°$) under the constraints $\alpha = \gamma = 90°$. The presence of four diethyl ether molecules in the $P2_1/n$ unit cell was first suggested by calculation of the expected unit cell volume and was later confirmed via ^{1}H NMR. Three check reflections collected regularly during about 150 h of data collection revealed a −1.0% variation in intensity. Data were corrected for Lorentz polarization effects and for decay. An empirical absorption correction (μ = 27.8 cm^{-1}; 10 ψ-scans) was applied with Flack's program CAMEL;[36-38] the transmission factors varied by up to ±15%. An ORTEP diagram is presented in Figure 1; relevant crystallographic data and positional parameters for significant atoms are listed in Tables III and IV, respectively. Selected bond length and bond angle information is collected in Table V.

The crystallographic data are consistent with the available NMR and IR spectral data. The rhenium–nitrogen bond lengths (Table V) are typical of this type of complex[39-41] (2.16–2.21 Å),

---

[35] Black, P. J.; Heffernan, M. L. *Aust. J. Chem.* **1964**, *17*, 558.

[36] Flack, H. D. *Acta Crystallogr.* **1974**, *A30*, 569.

[37] Flack, H. D. *Acta Crystallogr.* **1977**, *A33*, 890.

[38] Flack, H. D.; Vincent, M. G. *Acta Crystallogr.* **1978**, *A34*, 489.

[39] Horn, E.; Snow, M. R. *Aust. J. Chem.* **1980**, *33*, 2369.

Table III. Crystallographic Data and Experimental Details of the Structure Determination

formula	$[Re_2C_{38}H_{28}N_6O_6]$-$[BC_{24}H_{20}]_2 \cdot 2C_4H_{10}O$	*Z*	2 (cation has imposed symmetry $\bar{1}$)
molar mass	1823.8 amu	*D*(calcd)	1.443 g/cm^3
space group	$P2_1/n$ (No. 14)	temp	295 (1) K
cell dimens	a = 14.124 (3) Å	radiation	Mo Kα (λ = 0.7107 Å)
	b = 15.117 (2) Å	abs coeff μ	27.8 cm^{-1}
	c = 19.744 (4) Å	R^a	0.036
	β = 95.140 (9)°	$R_w{}^b$	0.035
V	4199 (1) Å^3		

[a] $R = (\sum||F_o| - |F_c|| / \sum|F_o|)$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o{}^2]^{1/2}$, where $w = 4I/(\sigma^2(I) + 0.02I^2)$.

Table IV. Positional Parameters and Equivalent *B* Values for the Significant Atoms of $[Re_2(CO)_6(bpy)_2(bpa)Et][BPh_4]_2 \cdot 2Et_2O$

atom	*x*	*y*	*z*	*B* (Å^2)^a
Re	0.24257 (2)	−0.12291 (3)	−0.04042 (2)	3.038 (8)
O(1)	0.4197 (5)	−0.0391 (4)	−0.0920 (4)	6.5 (2)
O(2)	0.1882 (5)	−0.1904 (5)	−0.1847 (3)	6.0 (2)
O(3)	0.1285 (5)	0.0450 (4)	−0.0789 (4)	6.5 (2)
N(1)	0.3168 (4)	−0.2479 (4)	−0.0111 (3)	3.0 (2)
N(2)	0.1294 (4)	−0.1785 (4)	0.0145 (3)	3.3 (2)
N(3)	0.2776 (4)	−0.0852 (4)	0.0644 (3)	3.1 (2)
C(1)	0.3526 (6)	−0.0707 (6)	−0.0737 (4)	3.8 (3)
C(2)	0.2070 (6)	−0.1653 (6)	−0.1290 (5)	4.3 (3)
C(3)	0.1710 (6)	−0.0168 (6)	−0.0647 (5)	4.1 (3)
C(4)	0.4689 (6)	−0.4919 (6)	−0.0281 (4)	4.3 (2)
C(11)	0.3994 (6)	−0.2500 (5)	0.0261 (5)	4.1 (3)
C(12)	0.4500 (6)	−0.3276 (6)	0.0417 (4)	4.2 (3)
C(13)	0.4142 (6)	−0.4071 (5)	0.0157 (4)	3.3 (2)
C(14)	0.3292 (7)	−0.4038 (5)	−0.0228 (5)	4.5 (3)
C(15)	0.2826 (6)	−0.3254 (6)	−0.0346 (5)	4.4 (3)
C(21)	0.1359 (6)	−0.1642 (5)	0.0824 (4)	3.4 (2)
C(22)	0.0651 (7)	−0.1932 (6)	0.1212 (5)	4.7 (3)
C(23)	−0.0135 (6)	−0.2387 (7)	0.0899 (6)	5.4 (3)
C(24)	−0.0183 (6)	−0.2531 (6)	0.0220 (6)	4.8 (3)
C(25)	0.0536 (6)	−0.2218 (6)	−0.0150 (5)	4.2 (3)
C(31)	0.3528 (6)	−0.0367 (5)	0.0867 (5)	3.8 (3)
C(32)	0.3758 (7)	−0.0168 (7)	0.1528 (6)	4.9 (3)
C(33)	0.3174 (8)	−0.0486 (7)	0.2011 (5)	5.4 (3)
C(34)	0.2380 (7)	−0.0993 (6)	0.1793 (5)	4.8 (3)
C(35)	0.2193 (6)	−0.1144 (6)	0.1107 (4)	3.5 (2)

[a] The equivalent displacement parameter is defined as (4/3)Tr($\beta \cdot G$), where $\beta_{ij} = 2\pi^2 a_i{}^* a_j{}^* U_{ij}$.

Table V. Selected Bond Lengths (Å) and Angles (deg) in $[Re_2(CO)_6(bpy)_2(bpa)Et][BPh_4]_2 \cdot 2Et_2O$

	Distances		
Re–N(1)	2.213 (6)	Re–N(2)	2.178 (6)
Re–N(3)	2.161 (6)	Re–C(1)	1.912 (10)
Re–C(2)	1.889 (10)	Re–C(3)	1.933 (9)
C(1)–O(1)	1.148 (9)	C(2)–O(2)	1.171 (10)
C(3)–O(3)	1.133 (8)	N(1)–C(11)	1.322 (9)
C(4)–C(4)′	1.495 (16)	C(4)–C(13)	1.506 (10)
Re–Re′	13.540 (2)	N(1)–N(1)′	9.201 (12)
	Angles		
N(1)–Re–N(2)	83.8 (2)	N(1)–Re–N(3)	85.0 (2)
N(1)–Re–C(1)	93.5 (3)	N(1)–Re–C(2)	91.9 (3)
N(1)–Re–C(3)	176.7 (3)	N(2)–Re–N(3)	74.9 (2)
N(2)–Re–C(1)	170.3 (3)	N(2)–Re–C(2)	100.6 (3)
N(2)–Re–C(3)	93.0 (3)	N(3)–Re–C(1)	95.6 (3)
N(3)–Re–C(2)	174.8 (3)	N(3)–Re–C(3)	95.1 (3)
C(1)–Re–C(2)	88.8 (4)	C(1)–Re–C(3)	89.8 (4)
C(2)–Re–C(3)	87.8 (4)	O(1)–C(1)–Re	178.2 (8)
O(2)–C(2)–Re	177.4 (8)	O(3)–C(3)–Re	179.6 (8)

Table VI. IR Data for (2,2′-Bipyridine)tricarbonylrhenium(I) Complexes

complex	wavenumber (cm^{-1})		
$[(bpy)(CO)_3Re(pyz)]^+$	2029	1934	1914
$[(bpy)(CO)_3Re(pyz)Re(CO)_3(bpy)]^{2+}$	2038	1953	1930
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)]^+$	2031	1936	1920
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bpy)]^{2+}$	2029	1940	1919
$[(bpy)(CO)_3Re(bpa)]^+$	2031	1938	1918
$[(bpy)(CO)_3Re(bpa)Re(CO)_3(bpy)]^{2+}$	2030	1936	1914
$[(bpy)(CO)_3Re(bpp)]^+$	2030	1934	1918
$[(bpy)(CO)_3Re(bpp)Re(CO)_3(bpy)]^{2+}$	2030	1936	1914

as are the Re–C bond distances (1.89–1.93 Å). Differences in Re–N bond lengths between the two heterocyclic ligands (2.17 Å average for Re–N(bpy), 2.21 Å for Re–N(py)) can probably be attributed to differences in π-back-bonding. Bond angles between adjacent sites in the coordination octahedra are near 90° with two exceptions: the N(2)–Re–N(3) bond angle is 74.9°, while the N(2)–Re–C(2) bond angle is 100.6°. Again, these values are similar to those reported for related tricarbonylrhenium(I) complexes containing polypyridine ligands.[39–41] However, the two adjacent C–Re–N(bpy) angles in the bpy plane (100.6 and 95.6°) differ by a somewhat larger amount as compared to the previously reported $[Re_2(bpy)_2(CO)_6(\mu\text{-}H)]Cl$[41] and [Re(2,2′-bipyrimidine)$(CO)_3$(*N*-methyl-4,4′-bipyridinium)]$^{2+}$ [40] systems.

Unlike (μ-H)[*fac*-(bpy)$(CO)_3$Re]$_2$Cl, which displays a roughly 90° rotation between the pseudo-square-pyramidal coordination spheres around each metal,[41] the structure of $[(bpy)(CO)_3Re(bpa)Re(CO)_3(bpy)]^{2+}$ contains an inversion center. The resultant twist of the molecular backbone allows sufficient room for the incorporation of two diethyl ether molecules. The two $BPh_4{}^-$ ions appear to "cap" the bpy–Re–py portions of the cation.

IR Spectra. The carbonyl stretching frequencies for all complexes are presented in Table VI. Each of these compounds displays three CO stretching bands,[26,42] with the highest energy transition appearing as a very sharp peak at about 2030 cm^{-1}. The two remaining bands are relatively broad and overlap considerably. With the exception of the pyz complexes, no significant differences in CO stretching frequencies were observed between monometallic and bimetallic complexes. In the case of BL = pyz, all three CO stretching bands shift to higher frequencies upon coordination of the second metal center. Such behavior is consistent with increased Re → pyz π-back-bonding in the bimetallic species.

Electrochemistry. bpy Complexes. Cyclic voltammetric data for these complexes are collected in Table VII. Each complex displays two essentially reversible reductions in DMSO, at roughly −1.1 and −1.3 V vs SCE. On the basis of previous literature reports, these waves can be attributed to the reduction of bpy and of Re, respectively.[12–15,27,31] As expected, the measured potentials corresponding to these processes remain relatively constant throughout this series of complexes. For the bimetallic complexes, the reductions near −1.1 and −1.3 V are net two-electron processes, and each is probably best described as originating from two closely spaced one-electron reductions.

Two of the bimetallic complexes, $[(bpy)(CO)_3Re(pyz)Re(CO)_3(bpy)]^{2+}$ and $[(bpy)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bpy)]^{2+}$, exhibit an additional one-electron reversible reduction at less negative potentials. For these complexes, this first reduction is found to be a one-electron process and has been tentatively assigned to the reduction of the bridging ligand.[13] A similar process can be envisioned for the bpa- and bpp-bridged bimetallic complexes, but due to the lack of conjugation, the reduction of those bridging ligands apparently occurs at potentials more negative than the cathodic solvent limit.

bqu Complexes. The reduction of the coordinated bqu ligand occurs at considerably less negative potentials than that of bpy.[43,44]

---

(40) Winslow, L. N.; Rillema, D. P.; Welch, J. H.; Singh, P. *Inorg. Chem.* **1989**, *28*, 1596.
(41) Guilhem, J.; Pascard, C.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Dalton Trans.* **1989**, 1450.
(42) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.
(43) Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675.
(44) Schmehl, R. H.; Auerbach, R. A.; Wacholtz, W. F. *J. Phys. Chem.* **1988**, *92*, 6202.

Table VII. Electrochemical Data[a]

complex	$E_{1/2}$ (V) $LL^{0/-}$	 $LL^{-/2-}$	 $BL^{0/-}$	 $Re^{+/0}$	E_p (V)[b] $Re^{2+/+}$
$[(bpy)(CO)_3Re(pyz)]^+$	−1.11			−1.27	+1.78
$[(bpy)(CO)_3Re(pyz)Re(CO)_3(bpy)]^{2+}$	−1.12		−0.66	−1.28	+1.78
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)]^+$	−1.09			−1.27	+1.75
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bpy)]^{2+}$	−1.10		−0.96	−1.26	+1.78
$[(bpy)(CO)_3Re(bpa)]^+$	−1.09			−1.30	+1.75
$[(bpy)(CO)_3Re(bpa)Re(CO)_3(bpy)]^{2+}$	−1.08			−1.30	+1.73
$[(bpy)(CO)_3Re(bpp)]^+$	−1.09			−1.30	+1.76
$[(bpy)(CO)_3Re(bpp)Re(CO)_3(bpy)]^{2+}$	−1.08			−1.30	+1.73
$[(bqu)(CO)_3Re(pyz)]^+$	−0.59	−1.16			+1.82
$[(bqu)(CO)_3Re(4,4'\text{-}bpy)]^+$	−0.59	−1.16			+1.84
$[(bqu)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bqu)]^{2+}$	−0.59	−1.16			+1.84
$[(bqu)(CO)_3Re(bpa)]^+$	−0.59	−1.16			+1.83
$[(bqu)(CO)_3Re(bpa)Re(CO)_3(bqu)]^{2+}$	−0.59	−1.16			+1.82
$[(bqu)(CO)_3Re(bpp)]^+$	−0.59	−1.16			+1.84
$[(bqu)(CO)_3Re(bpp)Re(CO)_3(bqu)]^{2+}$	−0.59	−1.16			+1.83
$[(Me_4phen)(CO)_3Re(pyz)]^+$				−1.36[c]	+1.69
$[(Me_4phen)(CO)_3Re(pyz)Re(CO)_3(Me_4phen)]^{2+}$			−0.69	−1.35[c]	+1.69
$[(Me_4phen)(CO)_3Re(4,4'\text{-}bpy)]^+$				−1.36[c]	+1.68
$[(Me_4phen)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(Me_4phen)]^{2+}$			−0.99	−1.36[c]	+1.68
$[(Me_4phen)(CO)_3Re(bpa)]^+$				−1.37[c]	+1.67
$[(Me_4phen)(CO)_3Re(bpa)Re(CO)_3(Me_4phen)]^{2+}$				−1.36[c]	+1.66
$[(Me_4phen)(CO)_3Re(bpp)]^+$				−1.37[c]	+1.67
$[(Me_4phen)(CO)_3Re(bpp)Re(CO)_3(Me_4phen)]^{2+}$				−1.36[c]	+1.66

[a] Potential measurements are referred to the saturated calomel electrode in 0.1 M TBAH–CH_3CN at room temperature; scan rate is 25 mV/s. All values are ±0.02 V. [b] The $Re^{2+/+}$ couple is chemically irreversible; E_p values represent anodic peak potentials. [c] Assignment of this process as a metal-centered reduction is not absolutely certain; see text for details.

Accordingly, all bqu complexes examined display a reversible couple near −0.59 V vs SCE which can be confidently assigned as a ligand-centered process. Unlike the bpy derivatives, the initial reduction of all bqu complexes appears to occur at the bqu ligand itself. The second reduction of complexes containing bqu is a nearly reversible process centered at about −1.16 V vs SCE. Although the reduction of binucleated 4,4′-bpy could conceivably occur in this potential region,[12-15] the cyclic voltammograms for $[(bqu)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bqu)]^{2+}$ are virtually identical to those for $[(bqu)(CO)_3Re(bpa)Re(CO)_3(bqu)]^{2+}$, and peak currents for the first and second reductions were nearly equal for both complexes (corresponding to $n = 2$). Such behavior indicates that this second cathodic wave must be associated with either metal-centered reduction or with further reduction of the bqu ligand. However, the reversibility of this reduction, along with its position, argues against a $Re^{I/0}$ assignment,[26,27,31] and assignment of the process to $bqu^{-/2-}$ appears more plausible. Further, this assignment is consistent with the expected 400–800-mV difference between the first and second reduction potentials of such ligands.[8,45,46] Apparently, the π-system of bqu is sufficiently large to support two successive bqu-centered one-electron reductions before bridging ligand reduction occurs, even when BL = 4,4′-bpy. Presumably, the pyz-bridged bimetallic complex would exhibit quite different behavior, but that particular compound could not be prepared by the synthetic route employed in this study.

Me_4phen Complexes. For monometallic complexes of Me_4phen, the first reduction appears as a totally chemically irreversible process with a cathodic peak potential of about −1.35 V vs SCE. Unfortunately, the peak position provides no clues to the origin of the reduction, since the observed value is very close to that predicted for reduction of either the rhenium center itself or of the coordinated Me_4phen ligand. However, the lack of a return wave associated with the initial reduction suggests that it may be a metal-centered rather than a ligand-centered process. In any event, only the bimetallic complexes containing pyz or 4,4′-bpy bridging ligands display voltammetric waves at less negative potentials. For these complexes, one-electron reversible reductions are observed at −0.69 and −0.99 V vs SCE, respectively. As with the bpy analogues discussed above, these processes are attributed to the reduction of the bridging ligands.

Electronic Absorption Spectra. bpy Complexes. The UV–visible spectra of the monometallic complexes $[(bpy)(CO)_3Re(BL)]^+$ are very similar to those reported for analogous Re(I) complexes.[26,27,31,42] One key feature of these spectra is the appearance of a very broad, moderately intense band (ε = 2000–6000 M^{-1} cm^{-1}), which has been attributed to the Re → bpy MLCT absorption in each case (MLCT absorption data are summarized in Table VIII). A second MLCT excited state (Re → BL) is possible, but this transition is expected to occur at higher energies for the ligands utilized in this study and is probably obscured by the more intense intraligand $\pi \rightarrow \pi^*$ (bpy) transitions.

The electronic spectra of the bimetallic complexes exhibit the same characteristic shape, but molar absorptivities are significantly larger (roughly a factor of 2). Further, the bimetallic complexes containing pyz and 4,4′-bpy exhibit an additional low-energy Re → BL MLCT absorption band. The exact position of this peak is rather difficult to determine since it appears as a very broad shoulder on the low-energy side of the Re → bpy MLCT band, but reasonable estimates can be made using deconvolution or difference techniques.

bqu Complexes. Each of these complexes displays a very intense absorption in the UV region, which is assigned as an intraligand transition. In addition, all bqu complexes show broad MLCT bands near 380 nm, corresponding to a 35–40-nm red-shift from the analogous bands in the bpy complexes. The lowest energy absorption band maxima for monometallic and bimetallic complexes are identical and do not vary with bridging ligand.

Me_4phen Complexes. For the monometallic Me_4phen complexes, the lowest energy absorption bands are somewhat blue-shifted compared to those of the corresponding bpy complexes and are assigned to the Re → Me_4phen MLCT transition. For the bimetallic complexes containing Me_4phen, however, the nature and position of the lowest energy band is dependent on the bridging ligand in much the same fashion as previously described for the bpy derivatives.

---

(45) Baiano, J. A.; Carlson, D. L.; Wolosh, G. M.; DeJesus, D. E.; Knowles, C. F.; Szabo, E. G.; Murphy, W. R., Jr. *Inorg. Chem.* **1990**, *29*, 2327.

(46) DeArmond, M. K.; Hanck, K. W.; Wertz, D. W. *Coord. Chem. Rev.* **1985**, *64*, 65.

Table VIII. MLCT Absorption and Emission Data[a,b]

complex	MLCT abs max (nm)	emission max (nm)[c]	τ (ns)	emission quantum yield ϕ_{em}[f]
$[(bpy)(CO)_3Re(pyz)]^+$	346	570	540	0.25
$[(bpy)(CO)_3Re(pyz)Re(CO)_3(bpy)]^{2+}$	380 (347)	703	*d*	$<5 \times 10^{-4}$
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)]^+$	348	578	240	0.14
$[(bpy)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bpy)]^{2+}$	350	578	365	
$[(bpy)(CO)_3Re(bpa)]^+$	345	579	210	
$[(bpy)(CO)_3Re(bpa)Re(CO)_3(bpy)]^{2+}$	347	580	210	0.13
$[(bpy)(CO)_3Re(bpp)]^+$	347	580	175	
$[(bpy)(CO)_3Re(bpp)Re(CO)_3(bpy)]^{2+}$	349	580	170	
$[(bqu)(CO)_3Re(pyz)]^+$	386	682	*d*	4.4×10^{-3}
$[(bqu)(CO)_3Re(4,4'\text{-}bpy)]^+$	384	687	*d*	2.9×10^{-3}
$[(bqu)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bqu)]^{2+}$	382	687	*d*	4.0×10^{-3}
$[(bqu)(CO)_3Re(bpa)]^+$	382	687	*d*	
$[(bqu)(CO)_3Re(bpa)Re(CO)_3(bqu)]^{2+}$	380	687	*d*	2.8×10^{-3}
$[(bqu)(CO)_3Re(bpp)]^+$	382	687	*d*	
$[(bqu)(CO)_3Re(bpp)Re(CO)_3(bqu)]^{2+}$	380	687	*d*	
$[(Me_4phen)(CO)_3Re(pyz)]^+$	332	514	7630	0.25
$[(Me_4phen)(CO)_3Re(pyz)Re(CO)_3(Me_4phen)]^{2+}$	380	694	60[e]	$<5 \times 10^{-4}$
$[(Me_4phen)(CO)_3Re(4,4'\text{-}bpy)]^+$	335	527	15000	0.57
$[(Me_4phen)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(Me_4phen)]^{2+}$	340	630	595[e]	
$[(Me_4phen)(CO)_3Re(bpa)]^+$	340	526	13000	
$[(Me_4phen)(CO)_3Re(bpa)Re(CO)_3(Me_4phen)]^{2+}$	340	529	10550	0.54
$[(Me_4phen)(CO)_3Re(bpp)]^+$	340	524	11500	0.54
$[(Me_4phen)(CO)_3Re(bpp)Re(CO)_3(Me_4phen)]^{2+}$	340	528	10500	

[a] All data obtained in room-temperature CH_3CN; solutions were deoxygenated using at least three freeze–pump–thaw cycles prior to lifetime measurements. [b] All lifetimes at ±10% unless otherwise noted. [c] Corrected for instrument response. [d] Lifetime is too short to measure with available instrumentation (<20 ns). [e] ±10%. [f] All compounds are referenced to $[(bpy)(CO)_3Re(CH_3CN)]^+$ in degassed CH_2Cl_2 ($\phi_{em} = 0.22$[50]).

Photophysical Properties. bpy Complexes. With the exception of $[(bpy)(CO)_3Re(pyz)Re(CO)_3(bpy)]^{2+}$, all of the complexes containing bpy display strong luminescence near 575 nm in room-temperature fluid solution (Table VIII). In contrast, the pyz-bridged bimetallic species displays only weak, short-lived ($\tau <$ 20 ns) emission near 700 nm. Emission bands are broad and featureless in all cases, consistent with an MLCT origin. Excited-state lifetimes of the bimetallic bpa and bpp complexes are almost identical to those of the corresponding monometallic species, while the bimetallic 4,4′-bpy complex is somewhat longer-lived than its monometallic derivative (365 ns vs 240 ns).[12,14,15]

bqu Complexes. Luminescence spectra of the bqu complexes show a large red-shift of the band maxima as compared to the bpy complexes (Table VIII).[26,47] Emission intensities are also much weaker than those of the bpy derivatives, in accord with the energy gap law.[27,28,48,49] Room-temperature excited-state lifetimes of the bqu complexes are too short (<20 ns) to measure with our current instrumentation.

Me$_4$phen Complexes. All monometallic complexes containing Me$_4$phen exhibit intense luminescence in fluid solution upon irradiation into the MLCT absorption band. Such emission is extremely long-lived as compared to most other tricarbonylrhenium(I) polypyridines, with room-temperature lifetimes of 7.6–15 μs (Table VIII).

On the other hand, the luminescence of the bimetallic Me$_4$phen complexes depends strongly on the nature of the bridging ligand. When BL = bpa or bpp, the emission maxima and excited-state lifetimes are very similar to those of the corresponding monometallic species. However, when BL = pyz or 4,4′-bpy, the emission is much weaker and strongly red-shifted as compared to the monometallic complexes. The excited-state lifetimes of the pyz- and 4,4′-bpy-bridged complexes are also considerably shorter than those of the other bimetallic Me$_4$phen derivatives.

All available photophysical data are consistent with the presence of one or more low-lying emissive MLCT states. In all of the monometallic species examined, the Re → LL MLCT level represents the lowest-lying excited state (at room temperature), with intraligand excited states at somewhat higher energy. Moreover, the trend in excited-state lifetimes can be described, at least qualitatively, by the energy gap law.[27,28,48,49] Those bimetallic complexes that contain a nonconjugated bridging ligand such as bpa or bpp behave similarly; the two rhenium centers are nearly independent in these complexes. However, when short, conjugated bridges are employed (e.g., pyz, 4,4′-bpy), the attachment of the two metal centers serves to depress the energy of the π^*-orbital on the bridge[12,13] to such an extent that the Re → BL MLCT state drops below the Re → LL level (except when LL = bqu and BL = 4,4′-bpy). The relative positions of the two important MLCT levels in bimetallic complexes of this type are summarized in Figure 2.

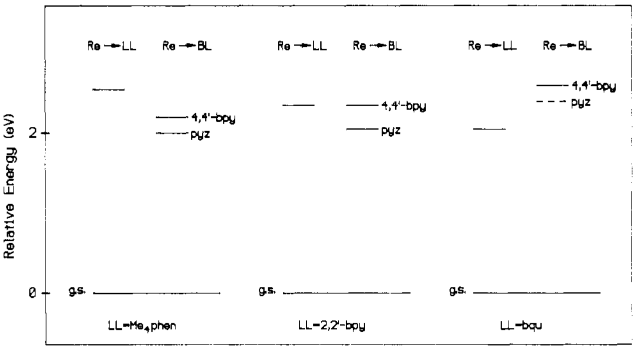


Figure 2. Diagram outlining the relative energies of the two lowest-lying MLCT states (denoted Re → BL and Re → LL) in complexes of the type $[(LL)(CO)_3Re(BL)Re(CO)_3(LL)]^{2+}$, where BL = 4,4′-bpy or pyz. Excited-state energies have been estimated from spectroscopic data except for LL = bqu; Re → BL MLCT energies for the bqu complexes represent rough estimates from electrochemical data.

For all complexes, excitation spectra closely parallel the corresponding absorption spectra. Such behavior suggests that, for those complexes in which the Re → BL MLCT level represents the lowest-lying excited state, population of this level can occur either in a direct manner or via rapid internal conversion from higher-lying (e.g., $\pi \rightarrow \pi^*$ IL, Re → LL MLCT) states. The low energy emission (at ca. 700 nm) from such complexes is ascribed to radiative decay from the Re → BL MLCT state to the ground state.

---

(47) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, 998.
(48) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.
(49) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.
(50) Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1992**, *31*, 5.

As previously demonstrated,[12-15] the energies of the MLCT states are rather well-matched when LL = bpy and BL = 4,4′-bpy. In fact, there is evidence that the two excited states are in equilibrium under some conditions, and "fine-tuning" of the relative energies can be performed simply by changing solvents.[14,15] The incorporation of methyl substituents in the chelating ligand (as in Me_4phen) has two important effects.[13] First, the energy of the Re → LL MLCT state increases by virtue of the more negative ligand reduction potential. Second, since the presence of electron-donating substituents increases the electron density at the metal center slightly, the energy of the Re → BL MLCT level decreases.[13] Indeed, substituent effects have been used to control the ordering of excited states in similar complexes.[13]

Conversely, replacement of the bpy chelate by the electron-poor bqu ligand yields a system in which the Re → bqu MLCT state lies at ca. 2.05 eV. The energy of the Re → 4,4′-bpy state in the 4,4′-bpy-bridged bqu "dimer" can be crudely estimated from electrochemical data as ca. 2.4 eV, so that the Re → bqu level remains the lowest-lying excited state upon complexation of the second metal center.

Conclusions

These results demonstrate that ligand substitution provides an effective means for controlling the nature, energy, and photodynamics of the lowest excited state. Perhaps more importantly, the data show that subtle changes in electron density can have a profound effect on the thermal stability of the ground state in these complexes. By varying the electronic nature of both the chelating and bridging ligand, it is possible to "tune" the ground- and excited-state properties of the resultant bimetallic species over an extremely wide range. It is hoped that such tunability will ultimately lead to the rational design of efficient transition metal-based photocatalysts and multielectron redox agents.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Partial support from the American Philosophical Society is also appreciated. In addition, we gratefully acknowledge the support of the University of Kentucky Major Research Instrumentation Bond Program for the purchase of supplies and equipment used in this study (ID Nos. P-049-8E030, P-053-8E030, and 7E-8E48-25). T.F.G. thanks the administrators of the University of Kentucky Fund for Excellence for a faculty fellowship. We also thank Mr. B. J. Yoblinski for making several of the excited-state lifetime measurements.

Supplementary Material Available: Text describing pertinent experimental details, complete tables of positional parameters, anisotropic displacement parameters, and bond lengths and angles, and ORTEP projections including counterions and solvent molecules (13 pages). Ordering information is given on any current masthead page.