

associated 2T_2 ion state. The large Os 5d contribution to and high binding energy of the 1e molecular orbitals supports the traditional view of strong π -bonding.

Acknowledgment. We wish to thank Dr. N. Edelstein for the

Os spin-orbit coupling calculations, Dr. P. A. Cox and Professor C. K. Jørgensen for helpful discussions, Prof. W. von Niessen for use of this Green's function program, the Johnson Matthey Chemical Co. for a loan of OsO₄, and the SERC for financial support.

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164-4630

Spectroscopic, Electrochemical, and Spectroelectrochemical Investigations of Mixed-Metal Osmium(II)/Ruthenium(II) Bimetallic Complexes Incorporating Polypyridyl Bridging Ligands

Mark M. Richter and Karen J. Brewer*

Received July 30, 1991

The synthesis, electrochemical, spectroscopic, and spectroelectrochemical properties of [(bpy)₂Os(BL)Ru(bpy)₂](PF₆)₄ (where BL = 2,3-bis(2'-pyridyl)pyrazine (dpp), 2,3-bis(2'-pyridyl)quinoxaline (dpq), and 2,3-bis(2'-pyridyl)benzoquinoxaline (dpb) and bpy = 2,2'-bipyridine) are reported. Addition of the Ru(bpy)₂²⁺ moiety to the vacant coordination site on the bridging ligand in the [Os(bpy)₂BL]²⁺ parent compounds results in a shift to lower energies of the metal-to-ligand charge transfer (MLCT) transitions terminating in the bridging-ligand-based π^* orbital as well as a shift to more positive potential of the bridging-ligand-based electrochemical reductions. The lowest energy electronic transitions in these mixed-metal systems have been assigned to overlapping Os(d π) \rightarrow BL(π^*) and Ru(d π) \rightarrow BL(π^*) ¹MLCT transitions with the Os(d π) \rightarrow BL(π^*) transition occurring at slightly lower energies. On the basis of spectroelectrochemical experiments, the first and second reductions of the bimetallic complexes have been assigned to sequential reductions of the bridging ligand.

Introduction

There has been an increased amount of interest recently in multimetallic polypyridyl complexes which incorporate both osmium and ruthenium.^{1,2} Whereas the majority of studies have centered on ruthenium polypyridyl complexes, osmium polypyridyl complexes have also been shown to have interesting spectroscopic and electrochemical properties.³ Also, osmium appears to have several advantages over ruthenium. For example, the excited state chemistry of ruthenium is strongly affected by low-lying dd states which tend to complicate the interpretation of the photophysical and photochemical properties and have been known to lead to photodecomposition.⁴ The dd states in osmium are much higher in energy than in ruthenium and many of the problems associated with ruthenium can be bypassed or avoided.

Within this framework we have synthesized compounds of general form [(bpy)₂Os(BL)Ru(bpy)₂]⁴⁺, where BL = dpp, dpq, and dpb. These ligands are similar to bpy but have the added ability to coordinate additional metal centers through the remote nitrogens, making possible the development of multimetal systems.

- (1) (a) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710. (b) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.
- (2) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2159.
- (3) See, for example: Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *168*, 1. Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. Sabbatini, N.; Balzani, V. *J. Am. Chem. Soc.* **1972**, *94*, 7587. Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1971**, *93*, 1800. Kane-Maguire, N. A. P.; Lagford, C. H. *J. Am. Chem. Soc.* **1971**, *93*, 1800. Balzani, B.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Lawrence, G. A. *Coord. Chem. Rev.* **1975**, *15*, 321. Lin, C. T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97. Brugger, P. A.; Infelta, P. O.; Brown, A. M.; Gratzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 320. Brewer, K. J.; Murphy, R. W., Jr.; Spurlin, S. R.; Petersen, J. D. *Inorg. Chem.* **1986**, *25*, 882. Hage, R.; Haasnoot, J. G.; Niewenhuis, H. A.; Reedijk, J.; de Ridder, D. J. A.; Vos, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9245. Barigelletti, F.; De Cola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* **1991**, *30*, 641 and references therein.
- (4) (a) Lumpkin, R. S.; Kober, E. M.; Worl, L. A.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1990**, *94*, 239. (b) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755 and references therein. (c) Pinnick, D.; Durham, B. *Inorg. Chem.* **1984**, *23*, 1440.

Table I. Cyclic Voltammetric Data for Bimetallic Polypyridyl-Bridged Os(II)/Ru(II) Complexes

complex	solvent	$E_{1/2}$, ^a V		
[(bpy) ₂ Os(dpp)Ru(bpy) ₂] ⁴⁺	CH ₃ CN	+1.56	+1.01	
	DMF	-0.62	-1.03	-1.34
[(bpy) ₂ Os(dpq)Ru(bpy) ₂] ⁴⁺	CH ₃ CN	+1.61	+1.09	
	DMF	-0.33	-0.94	-1.32
[(bpy) ₂ Os(dpb)Ru(bpy) ₂] ⁴⁺	CH ₃ CN	+1.62	+1.09	
	DMF	-0.21	-0.76	-1.34
		-1.42	-1.59	-1.75

^aPotentials were recorded versus a Ag/AgCl reference electrode (0.268 V vs SHE) in 0.1 M Bu₄NPF₆ at a scan rate of 200 mV/s.

These three ligands differ from each other only by the addition of electron-withdrawing benzene groups fused to the side of the pyrazine ring. This results in a net stabilization of the lowest-unoccupied π^* orbital. Also, this series of ligands, like the non-bridging bpy ligand, provide diimine coordination to the metal center. This makes possible the development of a series of compounds in which properties that are not directly related to the BL-based orbital energies are not significantly altered by bridging-ligand substitution.

The mono- and bimetallic complexes reported herein clearly demonstrate how both the ground-state electrochemical and metal-to-ligand charge-transfer (MLCT) excited-state properties of these mixed-metal systems are dependent upon the nature of the bridging polypyridyl ligand.

Experimental Section

Materials. The materials were reagent grade and used without further purification. The ligands dpq and dpb were synthesized according to literature methods.^{5,6} The acetonitrile used in the electrochemical measurements was spectroquality (Burdick and Jackson) and the supporting electrolyte used, tetrabutylammonium hexafluorophosphate

- (5) Goodwin, H. A.; Lions, F. *J. Am. Chem. Soc.* **1959**, *81*, 6415.
- (6) Baiano, A. J.; Carlson, D. L.; Wolosh, G. M.; DeJesus, D. E.; Knowles, C. F.; Szabo, E. G.; Murphy, W. R., Jr. *Inorg. Chem.* **1990**, *29*, 2327.

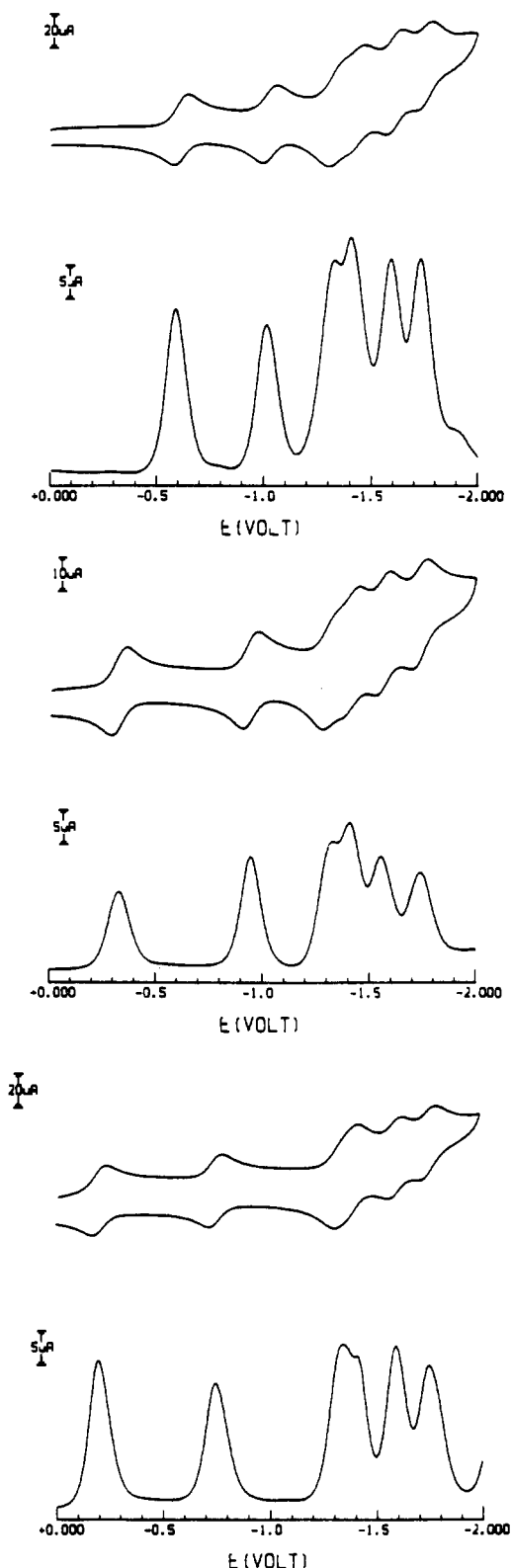


Figure 1. Cyclic and Osteryoung square-wave voltammograms (DMF containing 0.1 M Bu_4NPF_6): (A) $[(\text{bpy})_2\text{Os}(\text{dpp})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$; (B) $[(\text{bpy})_2\text{Os}(\text{dpq})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$; (C) $[(\text{bpy})_2\text{Os}(\text{dpb})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$.

(Bu_4NPF_6)₄ was prepared from tetrabutylammonium bromide (Aldrich) and HPF_6 (Aldrich), recrystallized from ethanol several times, and stored in a vacuum desiccator prior to use. All other chemicals were from Fisher Scientific.

Syntheses. The monometallic $[\text{Os}(\text{bpy})_2(\text{BL})](\text{PF}_6)_2$ (BL = dpp, dpq, and dpb) precursor complexes were prepared as described previously.⁷ $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ was prepared according to the literature.⁸

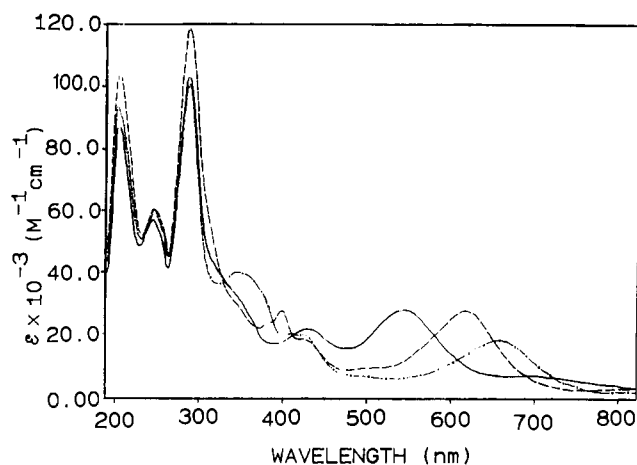


Figure 2. Electronic absorption spectra for a series of Os(II)/Ru(II) polypyridyl complexes in CH_3CN : (—) $[(\text{bpy})_2\text{Os}(\text{dpp})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$; (---) $[(\text{bpy})_2\text{Os}(\text{dpq})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$; (-·-) $[(\text{bpy})_2\text{Os}(\text{dpb})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$.

$[(\text{bpy})_2\text{Os}(\text{dpp})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ was synthesized⁹ by reacting approximately 5 equiv of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ (0.244 g, 0.504 mmol) with 1 equiv of $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$ (0.107 g, 0.104 mmol) in 200 mL of 2:1 (v/v) ethanol/ H_2O and purified by column chromatography on neutral alumina using a 1:1 (v/v) toluene/acetonitrile eluent. Yield: 70%.

$[(\text{bpy})_2\text{Os}(\text{dpq})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4 \cdot 3\text{H}_2\text{O}$ was prepared as above substituting $[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$ (0.123 g, 0.114 mmol) for $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$. Yield: 85%. Anal. Calcd: C, 37.97; H, 2.74; N, 9.16. Found: C, 37.82; H, 2.94; N, 9.46.

$[(\text{bpy})_2\text{Os}(\text{dpb})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ was prepared as above substituting $[\text{Os}(\text{bpy})_2(\text{dpb})](\text{PF}_6)_2$ (0.113 g, 0.100 mmol) for $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$. Yield: 87%. Anal. Calcd: C, 40.28; H, 2.61; N, 9.09. Found: C, 40.25; H, 2.95; N, 9.18.

Measurements. Cyclic and Osteryoung square-wave voltammograms were recorded in acetonitrile or DMF with 0.1 M Bu_4NPF_6 as the supporting electrolyte.⁷ The spectra of acetonitrile solutions at room temperature were recorded.

Spectroelectrochemistry. The apparatus used for the spectroelectrochemical experiments has been described in detail.¹¹ The 1 mM acetonitrile solutions of the bimetallic complexes were electrolyzed at a Pt mesh electrode. Oxidative spectroelectrochemistry results for the monometallic Os(II) complexes have been previously reported.⁷

Results and Discussion

Electrochemistry. The oxidative data for the three mixed-metal complexes in acetonitrile is given in Table I. The complexes display ΔE_p ($\Delta E_p = E_p^a - E_p^c$) values slightly greater than the expected value of 59 mV, similar to the value of 75 mV exhibited by ferrocene under the same conditions.

In acetonitrile, $[(\text{bpy})_2\text{Os}(\text{dpq})\text{Ru}(\text{bpy})_2]^{4+}$ displays two reversible oxidations and six reductions in the potential window from +2.00 to -2.00 V vs Ag/AgCl. The waves corresponding to the third and fourth reductions are not well resolved. The complexes $[(\text{bpy})_2\text{Os}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ and $[(\text{bpy})_2\text{Os}(\text{dpb})\text{Ru}(\text{bpy})_2]^{4+}$ each display two reversible oxidations and four reversible reductions. The fifth and sixth reductions are not well behaved, and following these processes desorption spikes are observed on the reverse scans at scan rates as high as 8 V/s. In DMF, the adsorption and desorption spikes disappear and the bimetallic complexes display six reversible reductions. It was not possible to observe the oxidative waves for the compounds in DMF due to oxidation of the solvent. The reductive electrochemical data for in DMF is given in Table I and shown in Figure 2. The proposed scheme for the oxidative and reductive processes is as follows:

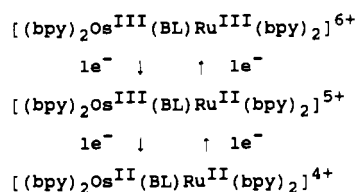
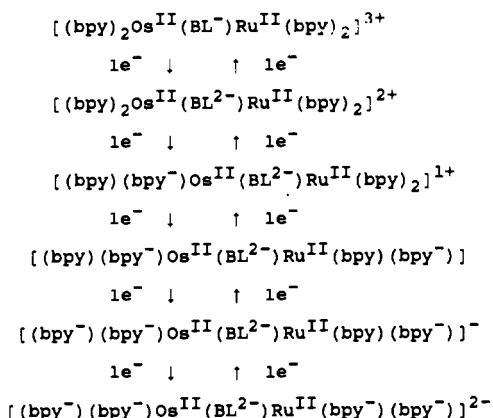
(8) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(9) Kalyanasundaram, K.; Nazeeruddin, Md. K. *Chem. Phys. Lett.* **1989**, *158*, 45.

(10) Rasmussen, S. C.; Richter, M. M.; Yi, E.; Place, H.; Brewer, K. J. *Inorg. Chem.* **1990**, *29*, 3926.

(11) Brewer, K. J.; Lumpkin, R. S.; Ovos, J. W.; Spreer, L. O.; Calvin, M. *Inorg. Chem.* **1989**, *28*, 4446.

Oxidative Processes:

Reductive Processes: $1e^- \downarrow \quad \uparrow 1e^-$ 

The cyclic voltammograms of the bimetallic compounds are consistent with two metal-based oxidations at positive potentials and a series of ligand-based reductions at negative potentials. In all of the bimetallic complexes the first reduction may be assigned as a bridging-ligand-based reduction.^{6,7,9,12-14}

The addition of the $Ru(bpy)_2^{3+}$ fragment through the remote nitrogens on the bridging ligands in the bimetallic complexes results in a net stabilization of the π^* orbitals of the bridging ligands and anodic shifts of the first BL reduction of 334, 368, and 334 mV for $[(bpy)_2Os(dpp)Ru(bpy)_2]^{4+}$, $[(bpy)_2Os(dpq)Ru(bpy)_2]^{4+}$, and $[(bpy)_2Os(dpb)Ru(bpy)_2]^{4+}$, respectively, as compared with the osmium monometallic precursor complexes (in CH_3CN).

Recently, Berger has shown via spectroelectrochemical measurements on $[Ru(bpy)_2(dpp)]^{2+}$ and $[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$ that the second reduction in the bimetallic complex does indeed correspond to the addition of a second electron to the dpp ligand and that in the monometallic complex the second reduction corresponds to a bpy based reduction.¹⁴ The second reductions seen in the bimetallic compounds occur at potentials comparable to the first reduction in the osmium monometallic complexes and are assigned as the second reduction of the bridging ligand.^{9,15} The subsequent four reductions are assigned as sequential reductions of the bpy ligands by analogy to the Os(II) and Ru(II) monometallic precursor complexes.^{6,7,9,12,13}

The oxidative processes involve oxidation of Os(II) to Os(III) and Ru(II) to Ru(III). The Ru(II)/Ru(III) oxidation occurs at a potential approximately 500 mV more positive than that for the corresponding Os(II)/Os(III) oxidation, consistent with the oxidation potentials of the monometallic $[M(bpy)_2(BL)]^{2+}$ complexes ($M = Os$ and Ru ; $BL = dpp, dpq,$ and dpb).^{6,7,9,12,13}

Electronic Absorption Spectra. The ligands used in this study have been characterized in detail elsewhere.^{6,7,9,10} The lowest energy $\pi-\pi^*$ transition shifts to the red as the bridging ligand is

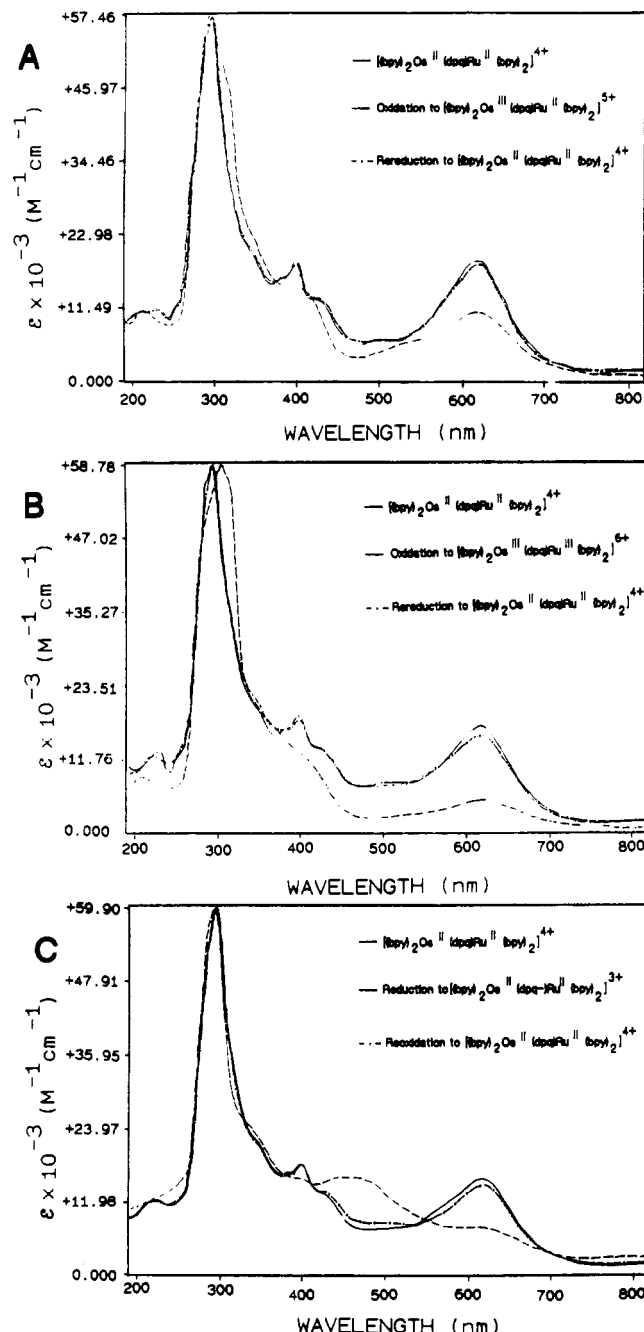


Figure 3. Spectroelectrochemical results for $[(bpy)_2Os(dpq)Ru(bpy)_2](PF_6)_4$ in CH_3CN (0.1 M Bu_4NPF_6): (A) (—) original spectrum, (---) spectrum after oxidation with approximately 1 equiv of charge at +1.350 V (Ag/Ag^+), and (---) spectrum after rereduction with 1.0 equiv at 0.0 V; (b) (—) original spectrum, (---) spectrum after oxidation with approximately 2 equiv of charge at +1.800 V (Ag/Ag^+); and (---) spectrum after rereduction with 2.0 equiv at 0.0 V; (C) (—) original spectrum, (---) spectrum after reduction with approximately 1 equiv of charge at -0.700 V (Ag/Ag^+), (---) spectrum after reoxidation with 1.0 equiv at 0.0 V.

varied from dpp to dpq to dpb.⁷ The UV-vis spectral data for each of the bimetallic complexes studied are shown in Figure 3 and summarized in Table II.

The electronic spectrum of $[(bpy)_2Os(dpp)Ru(bpy)_2]^{4+}$ has been previously reported in DMF at room temperature.⁹ The values reported in the table are those obtained with our system using acetonitrile. The absorption spectra of the bimetallic complexes are similar to those of previously characterized mono- and bimetallic Os(II) and Ru(II) polypyridyl complexes.^{7,9,12,13,15,17-23}

- (12) (a) Braunstein, C. H.; Baker, A. D.; Streckas, T. C.; Gafney, H. D. *Inorg. Chem.* **1984**, *23*, 857. (b) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgan, R.; Streckas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2691.
- (13) (a) Rillema, D. P.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 3849. (b) Rillema, D. P.; Callahan, R. W.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 2589.
- (14) Berger, R. M. *Inorg. Chem.* **1990**, *29*, 1920.
- (15) Murphy, W. R., Jr.; Brewer, K. J.; Gettcliffe, G.; Petersen, J. D. *Inorg. Chem.* **1989**, *28*, 81.
- (16) Murphy, W. R.; Brewer, K. J.; Gettcliffe, G.; Petersen, J. D. *Inorg. Chem.* **1989**, *28*, 81.

- (17) Petersen, J. D.; Murphy, W. R., Jr.; Brewer, K. J.; Ruminski, K. R. *Coord. Chem. Rev.* **1985**, *64*, 261 and references therein.

Table II. Electronic Spectral Data for Polypyridyl-Bridged Bimetallic Os(II)/Ru(II) Complexes^a

complex	abs		assignt
	λ_{\max} , nm	$10^{-3}\epsilon$, $M^{-1} \text{ cm}^{-1}$	
[(bpy) ₂ Os(dpp)Ru(bpy) ₂] ⁴⁺	286	102.7	$\pi-\pi^*$ (bpy)
	348	31.3	$\pi-\pi^*$ (dpp)
	430	22.3	¹ MLCT(bpy)
	542	28.5	¹ MLCT(dpp)
[(bpy) ₂ Os(dpq)Ru(bpy) ₂] ⁴⁺	286	118.6	$\pi-\pi^*$ (bpy)
	398	28.4	$\pi-\pi^*$ (dpq)
	424 (sh)	19.1	¹ MLCT(bpy)
	616	28.5	¹ MLCT(dpq)
[(bpy) ₂ Os(dpb)Ru(bpy) ₂] ⁴⁺	286	100.3	$\pi-\pi^*$ (bpy)
	344	40.7	
	408	20.6	$\pi-\pi^*$ (dpb)
	424	20.5	¹ MLCT(bpy)
	658	18.5	¹ MLCT(dpb)

^aSpectra were recorded in CH₃CN at room temperature.

The complexes are intensely colored and possess complex spectra with overlapping bands stretching well into the near infrared (>750 nm) region of the spectrum. The spectra consist of both bpy and BL based $\pi-\pi^*$ bands in the UV with the bridging ligand centered $\pi-\pi^*$ and $n-\pi^*$ absorptions shifting to the red upon coordination of the second metal fragment.

The lowest energy bands, in the visible region, consist of overlapping $d\pi(\text{Os})$ and $d\pi(\text{Ru}) \rightarrow \pi^*(\text{BL})$ ¹MLCT transitions, with the osmium-based component occurring at lower energy.^{6,7,9,20,25} The lowest energy ¹MLCT band is clearly red-shifted relative to its position in the osmium monometallic complexes upon coordination of the Ru(bpy)₂²⁺ fragment. Shifts such as these have been observed by other authors^{6,13} and can be attributed to stabilization of the π^* levels of the bridging ligand due to interactions with the electronegative Ru(bpy)₂²⁺ moiety. These low-energy bands show a solvent-dependence, shifting to lower energies in solvents with lower dielectric constants, consistent with their MLCT assignment.^{6,7,26-37} The transition energy of the lowest energy MLCT band decreases from dpp to dpq to dpb.

Slightly higher in energy than the Ru($d\pi$) \rightarrow BL(π^*) and Os($d\pi$) \rightarrow BL(π^*) transitions are a series of additional charge-

transfer bands. These transitions also show a solvent dependence, shifting to lower energies in solvents with lower dielectric constants. However, unlike the bridging-ligand-based MLCT bands, the energy of these transitions remains essentially constant as the bridging ligand is varied from dpp to dpq to dpb (430, 424, and 424 nm, respectively). These observations are consistent with metal $d(\pi) \rightarrow \pi^*$ MLCT transitions in which these higher energy transitions terminate in a π^* orbital localized principally on the bpy ligand.^{12,13,38}

Spectroelectrochemistry. Oxidation of [(bpy)₂Os(dpp)Ru(bpy)₂]⁴⁺, [(bpy)₂Os(dpq)Ru(bpy)₂]⁴⁺, and [(bpy)₂Os(dpb)Ru(bpy)₂]⁴⁺ to 1300, 1350, and 1400 mV, respectively, generate the Os(III)/Ru(II) species. After passage of approximately 1 reduction equiv each the original spectra are obtained with greater than 95% regeneration. Oxidative and reductive spectroelectrochemical results for [(bpy)₂Os(dpq)Ru(bpy)₂]⁴⁺ can be found in Figure 3.

Upon oxidation, partial loss of the low-energy transitions (between 450 and 700 nm) is observed. This supports our assignment of these transitions as arising in part from Os($d\pi$) \rightarrow BL(π^*) charge-transfer transitions. As expected, the absorptions arising from ligand-centered transitions ($\pi-\pi^*$ and $n-\pi^*$) appear not to be affected by oxidation of the metal center.

Bulk electrolysis through the second metal-based oxidation to generate the Os(III), Ru(III) complex was not totally reversible (<80% regeneration) probably due to decomposition resulting from the high positive charge density on the electrogenerated 6+ species. Upon oxidation by two electrons in the dpp, dpq, and dpb bimetallic complexes, almost total loss of the lowest energy absorption is observed. This confirms the assignment of the lowest energy absorption as arising from overlapping Os($d\pi$) \rightarrow BL(π^*) and Ru($d\pi$) \rightarrow BL(π^*) charge-transfer transitions. Loss of the higher energy transitions between 450 and 600 nm is also observed and supports their assignment as either Os- or Ru-based higher energy MLCT transitions. Absorptions between 400 and 450 nm are partially lost upon oxidation of both metal centers, suggesting that transitions in this region are both ligand and metal centered.

It was not possible to reversibly reduce and reoxidize the dpp bimetallic complex. One-electron reduction to -700 mV in the dpq bimetallic complex and -500 mV in the dpb complex results in almost complete loss of the lowest energy transition. Upon further reduction to -1200 mV for the dpq complex and -1150 mV for the dpb complex, total loss of the lowest energy transition is observed. This further supports the assignment of the lowest energy acceptor π^* orbitals as BL based. Reoxidation of the singly reduced species gives rise to almost complete regeneration of the original spectra (>95%) while the doubly reduced species gives rise to only partial regeneration (<60%). In both the singly and doubly reduced spectra there is a drastic increase in the 400-550-nm region of the spectrum. The increased absorbance in the visible region of the spectrum could arise from low-energy ligand-based $\pi^*-\pi^*$ transitions made possible upon electrochemical occupation of the BL based π^* orbitals. Higher energy transitions between 320 and 400 nm experience a decrease in intensity upon two-electron reduction of the metal complexes, which indicates that transitions in this region are in part $\pi-\pi^*$ BL-based transitions. The observed changes in the spectra for the doubly reduced species are not consistent with a reduced bipyridine ligand.¹⁴

Correlation of Spectroscopic and Electrochemical Results. It has been observed^{4,22,39-46} that a plot of the energies for lowest

- (18) Dose, E.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.
 (19) Petersen, J. D. In *Supramolecular Photochemistry*; Balzani, V., Ed.; NATO ASI Ser. C214; Reidel: Dordrecht, The Netherlands, 1987; p 135.
 (20) (a) Schanze, K. S.; Neyhart, G. A.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 2182. (b) Goldsby, K. A.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3002.
 (21) Creutz, C.; Chou, M.; Netzel, T. C.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.
 (22) Johnson, S. R.; Westmoreland, D. T.; Caspar, J. V.; Barqawi, K. R.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3195.
 (23) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587.
 (24) (a) Donahue, R. J.; Tait, C. D.; DeArmond, M. K.; Wertz, D. W. *J. Phys. Chem.* **1986**, *90*, 3923. (b) Donahue, R. J.; Tait, C. D.; DeArmond, M. K.; Wertz, D. W. *J. Phys. Chem.* **1986**, *90*, 3927.
 (25) Campagna, S.; Denfi, G.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *J. Chem. Soc., Chem. Commun.* **1989**, 1500.
 (26) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.
 (27) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.
 (28) Ishikawa, T.; Nitta, S.; Kondo, S. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2401.
 (29) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1597.
 (30) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7892.
 (31) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1986**, *91*, 91.
 (32) Sostero, O. T.; Mazzocchin, G. A. *Inorg. Chim. Acta* **1974**, *11*, 237.
 (33) Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098.
 (34) Sugimori, A.; Matsui, M.; Akiyama, T.; Kajitani, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3263.
 (35) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 4, 1261.
 (36) Clark, S. F.; Watts, R. J.; Dubois, D. L.; Connolly, J. S.; Smart, C. C. *Coord. Chem. Rev.* **1985**, *64*, 273.
 (37) Ferguson, J.; Krausz, R. *Chem. Phys. Lett.* **1982**, *93*, 1, 21.

- (38) (a) 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. (b) Rillema, D. P.; Jones, D. S. *J. Chem. Soc., Chem. Commun.* **1979**, 849.
 (39) (a) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7385. (b) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.
 (40) Juris, A.; Belser, P.; Baghelletti, F.; von Zewelsky, A.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 256.
 (41) Dodsworth, E. S.; Lever, A. *Chem. Phys. Lett.* **1985**, *119*, 61.
 (42) Saiji, T.; Aoyagui, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 1.
 (43) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J. M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007.

energy absorptions (E_{abs} (eV)) versus the difference in redox potentials between the metal-based oxidation (Os(II)/(III)) and first bridging-ligand-based reduction (BL/BL^-) ($\Delta E_{1/2} = E_{1/2}(\text{Os}^{\text{II/III}}) - E_{1/2}(\text{BL/BL}^-)$) should be linear if the same $d\pi-\pi^*$ MLCT orbitals are involved in both the optical and electrochemical processes. A plot of E_{abs} (eV) vs $\Delta E_{1/2}$ (V) for the three bimetallic complexes reported herein as well as for the previously reported monometallic complexes⁷ $[\text{Os}(\text{bpy})_3]^{2+}$, $[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$,

$[\text{Os}(\text{bpy})_2(\text{dpq})]^{2+}$, and $[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$ yielded a linear least-squares analysis of

$$E_{\text{abs}} = 1.0395\Delta E_{1/2} + 0.4710 \quad r = 0.995$$

where r is the correlation coefficient. Analysis of the equation shows that the slope is nearly equal to unity, as was to be expected,^{7,39,41,42} and supports our assertion that the lowest energy absorptions are indeed MLCT in character. Continuing study of these complexes and their higher order polymetallic derivatives will be the subject of a forthcoming report.

Acknowledgment. We thank Johnson Matthey for loan of the ruthenium used in this study. This work was supported in part by funds provided by Washington State University and the National Science Foundation (Grant CHE-9108374).

- (44) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104.
 (45) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755.
 (46) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zewelsky, A. *Inorg. Chem.* **1987**, *26*, 4115.

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305

Reduction of $[\text{Os}(\text{NH}_3)_5(\eta^1\text{-CH}_3\text{CN})]^{2+}$ to $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-CH}_3\text{CH}=\text{NH}_2)]^{3+}$

Tai Hasegawa, Keh Shin Kwan, and Henry Taube*

Received October 4, 1991

The reduction of $[\text{Os}(\text{NH}_3)_5(\text{CH}_3\text{CN})(\text{O}_3\text{SCF}_3)_2]$ or of $[\text{Os}(\text{NH}_3)_5(\text{O}_3\text{SCF}_3)](\text{O}_3\text{SCF}_3)_2$ in acetonitrile by zinc amalgam yields a product of composition corresponding to the formula $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-CH}_3\text{CH}=\text{NH}_2)(\text{O}_3\text{SCF}_3)_3]$ (**4**). Proton NMR spectroscopy shows a large splitting between cis and trans amines and for the heteroligand shows a pattern consistent with the structure proposed. In particular three equivalent protons and one other proton are not exchangeable with deuterium in methanol- d_4 while two protons, inequivalent as observed in acetonitrile- d_3 , are. Although some **4** is formed also in dried CH_3CN , the yield is much increased when a small amount of water is added. Compound **4** is quite stable in solution in DME, but when Proton Sponge (1,8-bis(dimethylamino)naphthalene) is added, deprotonation to produce $[\text{Os}(\text{NH}_3)_5(\text{CH}_3\text{CH}=\text{NH})]^{2+}$ takes place, which then disproportionates to yield the acetonitrile complex as one of the products. The value of $\text{p}K_a$ for the corresponding protonation-deprotonation equilibrium quotient, $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-}(\text{CH}_3)_2\text{C}=\text{NH}_2)]^{3+} = [\text{Os}(\text{NH}_3)_5(\eta^1\text{-}(\text{CH}_3)_2\text{C}=\text{NH})]^{2+} + \text{H}^+$, for the more stable analogue derived from acetone in water at room temperature was measured as 10.3 ± 0.2 .

Introduction

Earlier work has shown that when acetone binds to $\text{Os}(\text{NH}_3)_5^{2+}$, the η^2 -mode is strongly favored.^{1,2} Moreover, since it appears that $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-acetone})]^{2+}$ is the most stable η^2 -acetone complex to have been prepared, it is expected that imines would also bind to $\text{Os}(\text{NH}_3)_5^{2+}$ in like fashion. Although other examples of this type of binding have been reported,³ in the few examples from these laboratories, η^1 -binding of imines to $\text{Os}(\text{NH}_3)_5^{2+}$ prevails.⁴ This is also the case for acetonitrile,^{5,6} and again there are several examples of η^2 -binding, to other metal centers, even of unactivated nitriles.⁷

In continuing the investigation of the osmium ammine nitriles, we have discovered conditions under which the reduction of $[\text{Os}(\text{NH}_3)_5(\text{CH}_3\text{CN})]^{3+}$ or of $[\text{Os}(\text{NH}_3)_5(\text{O}_3\text{SCF}_3)]^{2+}$ in the presence of acetonitrile takes a course different from that reported.^{5,6} On the basis of evidence to be presented herein, we infer that an η^2 -iminium adduct of $[\text{Os}(\text{NH}_3)_5]^{2+}$ is produced.

Experimental Section

Materials. Molecular sieve (3 Å) was obtained from Aldrich and activated by heating at 200 °C for 20 h under vacuum before use.

Acetonitrile was purified by refluxing it over P_2O_5 , after which it was distilled from anhydrous K_2CO_3 . For the driest solvent, the resulting liquid was stored over molecular sieve and dispensed as needed.

Zinc amalgam was prepared from the granular form (30 mesh), this being first activated by pretreatment with 3 M HCl for 20 min, after which it was left in contact with saturated $\text{HgCl}_2(\text{aq})$ for 30 min. The solid was washed thoroughly with water, washed with acetone and diethyl ether, and then was dried at 150 °C under vacuum for 20 h. Sodium trifluoromethanesulfonate was purchased from Alfa Chemical and was dried at 150 °C under vacuum. Acetonitrile- d_3 was obtained from Aldrich and dried over activated molecular sieve. No trace of water was observed by ^1H NMR spectroscopy. Acetone was purified by vacuum distillation over B_2O_3 .⁸ Ether was obtained from Aldrich (Sure Seal) and dried over NaH when necessary. All other chemicals were purchased from Aldrich and used as obtained. Buffer solutions were made up according to literature specifications.⁹

All solvents were deoxygenated by purging with dry argon, and reactions were carried out under argon atmosphere in a Vacuum Atmospheres Corp. glovebox.

Instrumentation. ^1H NMR spectra were obtained on Varian XL-400 (400-MHz) and Gemini (200-MHz) spectrometers. Internal references were used when estimating reaction yields. Electrochemical measurements were made under argon; as apparatus a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer was used. Cyclic voltammograms were recorded with a Pt^0 working electrode (1 mm²), a Pt^0 counter electrode, and a reference that was calibrated with the ferrocenium/ferrocene couple (0.545 V vs NHE). All potentials are reported vs this couple. UV-vis spectra were recorded in quartz cells at room temperature on a Hewlett-Packard Model 8452A diode array spectrophotometer.

Preparation of Compounds. $[\text{Os}(\text{NH}_3)_5(\text{O}_3\text{SCF}_3)](\text{O}_3\text{SCF}_3)_2$ (**1**) was prepared as described in the literature.¹⁰

- (1) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8233.
 (2) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.
 (3) An early, perhaps the first, example was reported by: Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3161.
 (4) Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3261.
 (5) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.* **1989**, *28*, 3001.
 (6) Sekine, M.; Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3604.
 (7) The first example for acetonitrile: Thomas, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5943. For CF_3CN : Bland, W. J.; Kemmitt, W.; Moore, R. O. *J. Chem. Soc., Dalton Trans.* **1972**, 1292.

- (8) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43* (20), 3966.
 (9) Perrin, D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988; p 52.