

does not contribute appreciably to the dissolution of magnetite (at least at this temperature). This is not totally surprising considering that the rate constant for the homogeneous electron transfer is rather small ( $1.9 \times 10^{-3} \text{ s}^{-1}$  at  $35^\circ \text{C}$ ). On the other hand, the rather high activation enthalpy for electron transfer suggests that the reductive dissolution of magnetite at higher temperatures would proceed at useful rates ( $k_2$  (extrapolated to  $80^\circ \text{C}$ ) =  $1.2 \times 10^{-1} \text{ s}^{-1}$ ). Due to experimental difficulties this aspect was not pursued at the present time.

### Conclusions

There are several important observations resulting from this work:

(1) Until now Cr(II) has been studied mainly for its redox behavior,<sup>9</sup> although some of the other properties (such as hydrolysis in aqueous solutions<sup>24</sup>) have been studied indirectly. We now have a species of Cr(II) that is relatively stable to air oxidation and hence can be used to study its substitution chemistry relatively easily.

(2) This is probably the first instance when significantly high concentrations of a relatively long-lived precursor complex (involving Cr(II)) has been produced by mixing an oxidant and a reductant directly.<sup>25,26</sup> An interesting aspect of this study is that the spectrum of the inner-sphere complex can be obtained at various stages of the reaction. Further studies are being directed toward obtaining the visible and Raman spectra of this intermediate at various stages of the formation and decay by rapid data acquisition using photodiode arrays. We believe that this would give further insight regarding the detailed mechanism of electron transfer by providing information about the structure of the intermediate at various stages of the reaction. Redox reactions involving transition-metal oxidants and tris(picolinato)chromate(II) will probably follow an inner-sphere mechanism similar to this reaction with  $\text{Fe}^{3+}$ , and this system should provide an

excellent experimental model for future studies on intramolecular electron transfer. The unusual stability of tris(picolinato)chromate(II) can be explained by the following two reasons:

(1) The pyridine ring is able to withdraw electrons, which is supported by the fact that the complex of Cr(II) with isonicotinic acid<sup>27</sup> is also stable with respect to oxidation (though not to the same extent as the complex with picolinic acid).

(2) From a skeletal molecular model for tris(picolinato)chromate(II) it can be seen that Cr(II) can form a chelate by using both the carboxyl oxygen and the nitrogen on the pyridine ring to form a sterically stable closed five-membered ring structure. Since the nitrogen and the carboxyl oxygen on picolinic acid are part of a conjugated structure,<sup>25</sup> the complex is extremely stable with respect to oxidation. Even though the nitrogen and the carboxyl oxygen are part of a conjugated system in isonicotinic acid, the complex is not as stable due to the fact that it is not possible for the metal ion to be bonded to both the nitrogen and the oxygen.

Finally, certain guidelines regarding the suitability of a reducing agent for dissolving oxides having a high chromium content can be formulated. In order to prepare a complex of Cr(II) that would have a thermodynamically favorable redox potential for reducing Cr(III), one would have to use a ligand that is not strongly electron withdrawing. A rule of thumb would be to use a ligand that would complex Cr(III) more strongly than Cr(II). It appears that complexes of oxalic acid or ethylenediaminetetraacetic acid (EDTA) with Cr(II) would be suitable for this purpose. Since the dissolution of corrosion products in nuclear reactors is usually carried out at high temperatures, chromium(II) oxalate should be more suitable than the chromium(II) EDTA complex. Further work along these lines should provide definitive answers.

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**Registry No.** Fe, 7439-89-6; Cr(pic)<sub>3</sub><sup>-</sup>, 97352-99-3.

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## Chemistry of Highly Reduced Polypyridyl-Metal Complexes. Anion Substitution Induced by Ligand-Based Reduction

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For a series of complexes of the type *cis*-[M(bpy)<sub>2</sub>(L)Cl]<sup>n+</sup> (bpy = 2,2'-bipyridine), where M is Ru<sup>II</sup> or Os<sup>II</sup> and L is a variety of ligands that range from  $\sigma$  and  $\pi$  donors such as Cl<sup>-</sup> to  $\sigma$  donors and  $\pi$  acceptors such as pyridine or tertiary phosphines to  $\pi$  acceptors such as CO, bpy-based electrochemical reduction causes rapid loss of Cl<sup>-</sup>. Cyclic voltammetric and bulk electrolysis studies in CH<sub>3</sub>CN show that two sequential, one-electron reductions (each bpy based) followed by reoxidation lead to exchange of CH<sub>3</sub>CN for Cl<sup>-</sup> at the metal center. The results of differential-pulse polarographic experiments show that the rate of Cl<sup>-</sup> loss is retarded as the ligand L is made more electron withdrawing. Likewise, using complexes containing the better electron-accepting anions NO<sub>2</sub><sup>-</sup> and CN<sup>-</sup> instead of Cl<sup>-</sup> leads to stabilization of the bpy-reduced product and slower loss of the anionic ligand.

Metal complexes containing polypyridyl ligands such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), or their substituted derivatives show distinctive electrochemical properties that derive from both metal- and ligand-based redox processes. In the majority of cases the complexes show at least one electrochemically reversible, one-electron reduction for each of the polypyridyl ligands present in the coordination sphere. For complexes like [M(bpy)<sub>3</sub>]<sup>2+</sup> (M = Fe, Ru, Os)<sup>1-4</sup> or [Ru(bpy)<sub>2</sub>(PR<sub>3</sub>)Cl]<sup>+</sup><sup>5</sup> the

reduction processes occur at potentials more negative than -1.2 V (vs. SCE) although the exact potential depends upon a number of factors such as the  $\sigma$ -donor and  $\pi$ -acceptor abilities of the ancillary ligands and the overall charge on the complex.<sup>5</sup>

An important aspect of the reactivity of the reduced complexes is their implied ability to act as multiple-electron reservoirs, which may have important applications in chemical reductions. Thus, [Ru<sup>II</sup>(bpy<sup>-</sup>)<sub>2</sub>(bpy)]<sup>0</sup> will produce H<sub>2</sub> from aqueous acetonitrile

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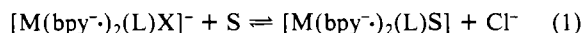
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solution, giving  $[\text{Ru}(\text{bpy})_3]^{2+}$ .<sup>6</sup> The use of reduced polypyridyl complexes of Ru(II) and Os(II) in photochemical energy conversion schemes involving reductive quenching of metal to ligand charge-transfer (MLCT) excited states is also notable although often mechanistically obscure.<sup>7</sup>

In this paper we present evidence for anionic ligand substitution induced by reduction at polypyridine ligands. The net reactions involve exchange of anions such as  $\text{Cl}^-$  for solvent as shown in eq 1 ( $M = \text{Ru}, \text{Os}$ ). One of our interests in processes like that



shown in eq 1 is related to their potential importance in the activation and reduction of small molecules. For example, for a weakly bound solvent molecule, transient binding of  $\text{CO}_2$  to the metal center would result in a situation where two bpy-localized electrons exist at redox potentials that are thermodynamically capable of reducing  $\text{CO}_2$  to formate in a protic medium. In such an intermediate, the possibility clearly exists for reduction and possibly even catalytic reduction of  $\text{CO}_2$ .

## Experimental Section

**Reagents and Metal Complexes.** All of the metal complexes used in this study were prepared according to previously published synthetic procedures. The materials include *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>,<sup>5</sup> *cis*-Os(bpy)<sub>2</sub>Cl<sub>2</sub>,<sup>8</sup> *cis*-[Ru(bpy)<sub>2</sub>(py)Cl](PF<sub>6</sub>),<sup>9</sup> *cis*-[Ru(bpy)<sub>2</sub>(PPh<sub>3</sub>)Cl](PF<sub>6</sub>),<sup>5</sup> *cis*-[Ru(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>),<sup>10,12</sup> *cis*-[Os(bpy)<sub>2</sub>(CH<sub>3</sub>CN)Cl](PF<sub>6</sub>),<sup>11</sup> *cis*-[Os(bpy)<sub>2</sub>(PPh<sub>3</sub>)Cl](PF<sub>6</sub>),<sup>11</sup> *cis*-[Os(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>),<sup>12</sup> *cis*-[Ru(bpy)<sub>2</sub>(py)NO<sub>2</sub>](PF<sub>6</sub>),<sup>9</sup> *cis*-[Ru(bpy)<sub>2</sub>(py)CN]PF<sub>6</sub>,<sup>9</sup> and *cis*-[Os(bpy)<sub>2</sub>(py)Br](PF<sub>6</sub>).<sup>11</sup> The supporting electrolyte used in the electrochemical experiments was tetraethylammonium perchlorate (TEAP) or tetrabutylammonium hexafluorophosphate (TBAH). Reagents for synthesis included reagent grade ethanol, acetonitrile, and toluene all obtained from Aldrich Chemical Co. and, for the electrochemical experiments, spectrograde acetonitrile from the Burdick and Jackson Co.

**Instrumentation.** All electrochemical experiments were performed with a PAR Model 174 potentiostat and a Model 178 digital coulometer in conjunction, for cyclic voltammetry, with a "super-cycle" triangular sweep generator built locally.<sup>13</sup> Although details of the cyclic voltammetry experiments are given in the following section, sweep rates of 50–200 mV/s and a Pt-bead or Pt-button working electrode were generally employed. In all cases a Pt-wire auxiliary electrode and a saturated sodium chloride calomel electrode were used. For the differential-pulse polarography experiments a sweep rate of 10 mV/s was used along with a modulation amplitude setting of 10. All experiments were performed under either N<sub>2</sub> or Ar atmosphere (identical results were obtained) in a one-compartment cell. The reference electrode in most cases was separated from the bulk cell by a fine frit enclosed in a glass tube. Although some coulometry experiments were performed on the bench under an inert atmosphere, a far more reliable method used a Vacuum Atmospheres Model HE-63 glovebox containing a N<sub>2</sub> atmosphere.

## Results and Discussion

**Ligand-Localized Reduction in the Complexes *cis*-[M(bpy)<sub>2</sub>(L)Cl]<sup>+</sup> and *cis*-[M(bpy)<sub>2</sub>L<sub>2</sub>]<sup>2+</sup> ( $M = \text{Ru(II)}, \text{Os(II)}$ ).** Early studies by Aoyagui and co-workers<sup>2</sup> and Bard and co-workers<sup>1</sup> established that the first two reductions for complexes such as  $[\text{M}(\text{bpy})_3]^{2+}$  ( $M = \text{Fe(II)}, \text{Ru(II)}, \text{Os(II)}$ ) are ligand localized.

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**Table I.** Reduction Potentials for 2,2'-Bipyridine Complexes of Ru(II)<sup>a</sup>

complex <sup>b</sup>	$E_{1/2}^{\text{III}}(\text{Ru}^{\text{II}})$	$E_{1/2}^{\text{c}}(\text{r},1)^{\text{c}}$	$E_{1/2}^{\text{c}}(\text{r},2)^{\text{c}}$	$\Delta E_{\text{r}}^{\text{d}}$	ref
[Ru(bpy) <sub>2</sub> Cl <sub>2</sub> ]	0.32	-1.61	-1.86	0.25	e
[Ru(bpy) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	0.92	-1.48	-1.73	0.25	f
[Ru(bpy) <sub>2</sub> (py)Cl] <sup>+</sup>	0.79	-1.51	-1.71	0.20	e
[Ru(bpy) <sub>2</sub> (PPh <sub>3</sub> )Cl] <sup>+</sup>	0.94	-1.46 <sup>g</sup>	-1.66 <sup>g</sup>	0.20	e
[Ru(bpy) <sub>2</sub> (py)CN] <sup>+</sup>	1.04	-1.48	-1.72	0.24	e
[Ru(bpy) <sub>2</sub> (py)NO <sub>2</sub> ] <sup>+</sup>	1.06	-1.46	-1.70	0.24	e
[Ru(bpy) <sub>2</sub> (py) <sub>2</sub> ] <sup>2+</sup>	1.30	-1.35	-1.56	0.21	f
[Ru(bpy) <sub>2</sub> (CO)(O <sub>2</sub> CH)] <sup>+</sup>	1.44	-1.32	-1.51	0.19	h
[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	1.50	-1.32	-1.51	0.19	h
[Ru(bpy) <sub>2</sub> (Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )] <sup>2+</sup>	1.63	-1.29	-1.54	0.25	i
[Ru(bpy) <sub>2</sub> ( <i>cis</i> -Ph <sub>2</sub> PCH=CHPPh <sub>2</sub> )] <sup>2+</sup>	1.75	-1.30	-1.50	0.20	i
[Ru(bpy) <sub>2</sub> (CO)(CH <sub>3</sub> CN)] <sup>2+</sup>	2.14	-1.15	-1.36	0.21	e

<sup>a</sup> Measured by cyclic voltammetry using a Pt-bead electrode in CH<sub>3</sub>CN solution with 0.1 M TEAP ([NEt<sub>4</sub>][ClO<sub>4</sub>]) as the supporting electrolyte. All potentials are vs. SCE and are in V. <sup>b</sup> As PF<sub>6</sub><sup>-</sup> salts for the cations. <sup>c</sup> bpy-localized reductions; see text.  $E_{1/2}(\text{r})$  values either are reversible potentials taken from cyclic voltammetry and calculated as  $E_{1/2} = 1/2(E_{\text{p,c}} + E_{\text{p,a}})$  where  $E_{\text{p,c}}$  and  $E_{\text{p,a}}$  are the peak potentials for the reductive and oxidative waves or in the case of irreversible waves, are derived from differential-pulse polarograms. <sup>d</sup>  $\Delta E_{\text{r}} = E_{1/2}(\text{r},1) - E_{1/2}(\text{r},2)$ ; the difference in potential between the first and second ligand-based reductions. <sup>e</sup> This work. <sup>f</sup> Salmon, D. J. Ph.D. Thesis, The University of North Carolina, Chapel Hill, NC, 1978. <sup>g</sup> Note that the values reported in ref 5 for the reductive potentials are incorrect. <sup>h</sup> Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241. <sup>i</sup> Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

**Table II.** Reduction Potentials for 2,2'-Bipyridine Complexes of Os(II)<sup>a</sup>

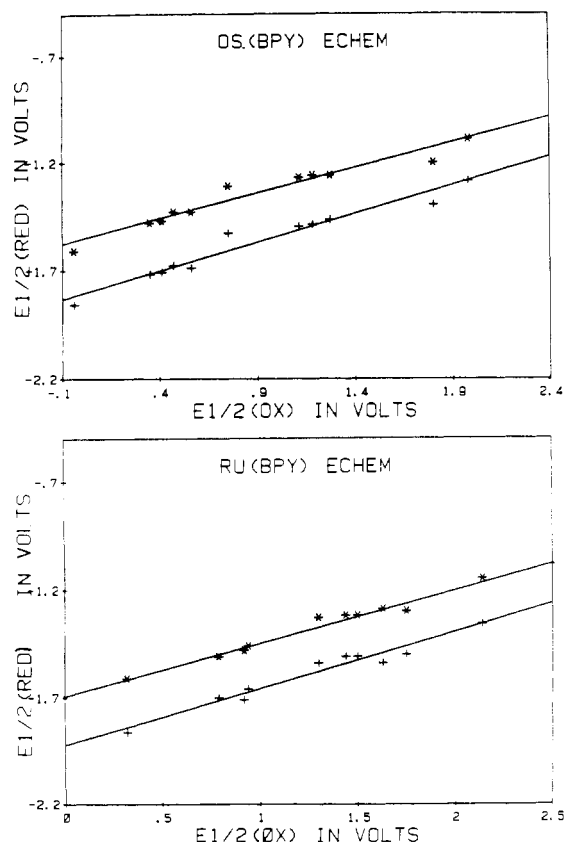
complex <sup>b</sup>	$E_{1/2}^{\text{III}}(\text{Os}^{\text{II}})$	$E_{1/2}^{\text{c}}(\text{r},1)^{\text{c}}$	$E_{1/2}^{\text{c}}(\text{r},2)^{\text{c}}$	$\Delta E_{\text{r}}^{\text{d}}$	ref
[Os(bpy) <sub>2</sub> Cl <sub>2</sub> ]	-0.04	-1.61	-1.86	0.25	e
[Os(bpy) <sub>2</sub> (py)Br] <sup>+</sup>	+0.35	-1.48	-1.72	0.24	e
[Os(bpy) <sub>2</sub> (CH <sub>3</sub> CN)Cl] <sup>+</sup>	+0.41	-1.47	-1.71	0.24	e
[Os(bpy) <sub>2</sub> (NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> )] <sup>2+</sup>	+0.47	-1.43	-1.68	0.25	e
[Os(bpy) <sub>2</sub> (PPh <sub>3</sub> )Cl] <sup>+</sup>	+0.56	-1.43	-1.69	0.26	e
[Os(bpy) <sub>2</sub> (py) <sub>2</sub> ] <sup>2+</sup>	+0.75	-1.31	-1.53	0.22	f
[Os(bpy) <sub>2</sub> (dars)] <sup>2+</sup>	+1.11	-1.27	-1.50	0.23	f
[Os(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	+1.18	-1.26	-1.49	0.26	e
[Os(bpy) <sub>2</sub> (Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )] <sup>2+</sup>	+1.27	-1.26	-1.47	0.21	f
[Os(bpy) <sub>2</sub> (Me <sub>2</sub> SO) <sub>2</sub> ] <sup>2+</sup>	+1.80	-1.20	-1.40	0.20	f
[Os(bpy) <sub>2</sub> (PPh <sub>3</sub> )CO] <sup>2+</sup>	+1.98	-1.09	-1.29	0.20	g

<sup>a</sup> Measured by cyclic voltammetry or differential-pulse polarography using a Pt-bead electrode in CH<sub>3</sub>CN solution with 0.1 M TEAP as supporting electrolyte. All potentials are vs. SCE and are in V. <sup>b</sup> Cations as PF<sub>6</sub><sup>-</sup> salts. <sup>c</sup> bpy-localized reductions; see text.  $E_{1/2}(\text{r})$  values either are reversible potentials taken from cyclic voltammetry and calculated as  $E_{1/2} = 1/2(E_{\text{p,c}} + E_{\text{p,a}})$  or, in the case of irreversible waves, are derived from differential-pulse polarograms. <sup>d</sup>  $\Delta E_{\text{r}} = E_{1/2}(\text{r},1) - E_{1/2}(\text{r},2)$ . <sup>e</sup> This work. <sup>f</sup> Kober, E. M. Ph.D. Thesis, The University of North Carolina, Chapel Hill, NC, 1982. <sup>g</sup> Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241.

DeArmond, Hanck, and co-workers<sup>3</sup> have significantly elaborated on this theme, specifically for  $[\text{Ru}(\text{bpy})_3]^{2+}$  and its substituted derivatives, and recently Morris, Hanck, and DeArmond have used low-temperature electrochemical techniques in conjunction with EPR spectral data to measure the rate of intramolecular electron transfer between bpy ligands in  $[\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3]^+$  (4,4'-Me<sub>2</sub>bpy = 4,4'-dimethylbipyridine).<sup>14</sup>

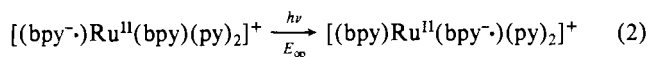
Less attention has been paid to the reductive electrochemistry of the bis complexes *cis*- and *trans*-[M(bpy)<sub>2</sub>L<sub>2</sub>]<sup>2+</sup>, where L is

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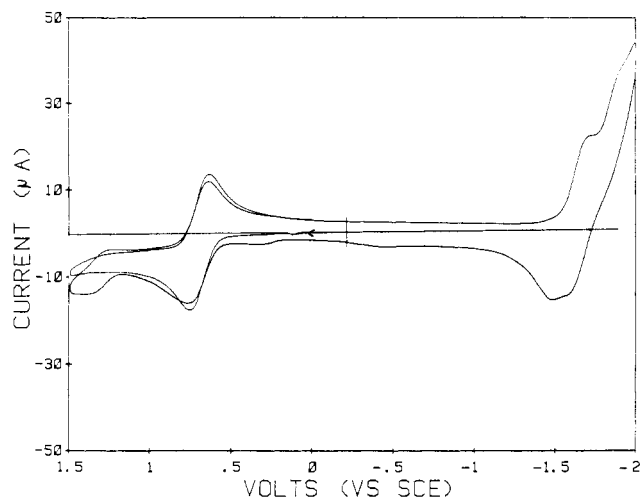
**Figure 1.** Plots illustrating the linear relationships between  $E_{1/2}(M^{III}/M^{II})$  (horizontal axis) and  $E_{1/2}$  for bpy-based reductions (vertical axis) for the complexes  $cis-[M(bpy)_2L_2]^{2+}$  (starred data points),  $cis-[M(bpy)_2(L)Cl]^+$ , and  $cis-M(bpy)_2Cl_2$  (crossed data points). All potential values are vs. the SCE reference electrode and were obtained at a Pt-bead working electrode in  $CH_3CN$  solution with 0.1 M TEAP as supporting electrolyte.

a neutral donor like  $NH_3$ , pyridine, or a tertiary phosphine. Indirect evidence for the bpy-ligand-localized nature of the first two reduction processes for the complexes  $cis-$  and  $trans-[Ru(bpy)_2(py)_2](PF_6)$ , which like  $[Ru(bpy)_3]^{2+}$  show a ligand to ligand charge-transfer transition between reduced and oxidized bpy ligands (eq 2), has been presented by Heath, Yellowlees, and



Brateman.<sup>15</sup> Furthermore, the energy, extinction coefficient, and bandwidth of the optical transition ( $E_{op}$ ) are all consistent with electronically weakly interacting bpy sites, at least in the ligand-reduced state.<sup>15,16</sup> A more direct demonstration of the ligand-localized nature of the first bpy reduction is provided by the solution electronic spectrum of  $[Os(bpy)_2(dppb)]^+$  ( $dppb = 1,2$ -bis(diphenylphosphino)benzene), where the visible and near-UV absorptions can be interpreted in terms of the presence of a relatively unperturbed bpy radical anion<sup>17a</sup> and in the spectra of mixed polypyridine complexes of Ru where clean evidence for localized reductions has been found.<sup>18</sup>

Another indication of the ligand-localized nature of the first two reductions is provided by the electrochemical data in Tables I and II. The tables give  $E_{1/2}$  values for the  $M^{III}/M^{II}$  couples ( $M = Ru, Os$ ) and for the first two ligand-based reductions for the series  $cis-[M(bpy)_2L_2]^{2+}$  ( $E_{1/2}(r,1)$ ) and  $cis-[M(bpy)_2(L)X]^+$



**Figure 2.** First- and second-scan cyclic voltammograms for  $[Ru(bpy)_2(py)Cl](PF_6)$  in the region +1.5 to -2.0 (vs. SCE). Voltammograms were run in  $CH_3CN$  solution with 0.1 M TEAP as supporting electrolyte, a Pt-bead electrode, and a scan rate of 200 mV/s.

( $E_{1/2}(r,2)$ ). The reduction potentials were obtained in  $CH_3CN$  solution with 0.1 M  $[NEt_4][ClO_4]$  (TEAP) as supporting electrolyte. For a given metal, Ru or Os, changes in the ancillary ligand (L) from an electron donor like  $NH_3$  to an electron acceptor like a phosphine lead to shifts in potential for the  $M^{III}/M^{II}$  couple by up to 1 V. On the other hand, the shifts in the two reductive couples are less than 0.2 V. In Figure 1 are shown plots of the bpy-localized reduction potentials  $E_{1/2}(r,1)$  and  $E_{1/2}(r,2)$  vs.  $E_{1/2}(M^{III}/M^{II})$ . The  $E_{1/2}(M^{III}/M^{II})$  couples are metal based, and they respond in a dramatic way to variations in the non-bpy ligands. By contrast, the reduction waves vary only slightly as the non-bpy ligand is varied, suggesting that the reduction waves are bpy based. Note from the data in Tables I and II for the complexes  $[M(bpy)_2(L)Cl]^+$  that potentials for the second reduction vary with L as in the series  $[M(bpy)_2L_2]^{2+}$  where the reductions are ligand localized.

In Tables I and II the quantity  $\Delta E_r$  measures the difference between potentials for the ligand-based reductions  $E_{1/2}(r,1)$  and  $E_{1/2}(r,2)$ . While  $\Delta E_r$  varies from 0.19 to 0.27 V through the series, the average values of  $\Delta E_r$  for both metals are experimentally the same, i.e.,  $0.24 \pm 0.05$  V for Ru(II) and  $0.23 \pm 0.05$  V for Os(II). There is a slight shift to more oxidizing potentials for the bpy-localized reductions as the combined back-bonding ability of the ligands L increases. A way of viewing the origin of this effect is that as back-bonding with L is increased, back-bonding with bpy is decreased, which lowers the energy of the largely  $\pi^*$  (bpy) acceptor levels.

That there may be an electrostatic contribution to the separation between the two sequential bpy-based reductions (eq 3 and 4) can be inferred from data for  $cis$ - $trans$  isomeric pairs such as  $[M(bpy)_2(PMe_2Ph)_2]^{2+}$ : (1) for  $M = Os$ ,  $\Delta E_r(cis) = 0.27$  V and  $\Delta E_r(trans) = 0.21$  V; (2) for  $M = Ru$ ,  $\Delta E_r(cis) = 0.26$  V and  $\Delta E_r(trans) = 0.19$  V.<sup>17b</sup> Note that  $\Delta E_r$  is substantially greater for the  $cis$  isomer than for the  $trans$  isomer<sup>17b</sup> and is metal independent. In the  $trans$  isomers where the two electrons are placed further apart there are decreased electrostatic repulsions apparently independent of  $M = Os$  or Ru.

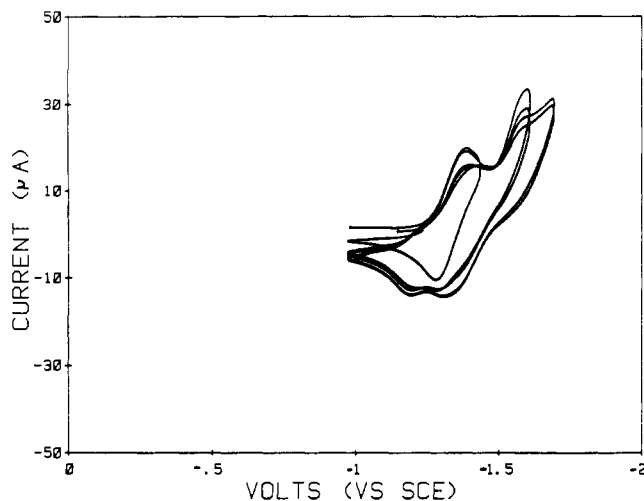
**Chloride Ion Substitution Induced by 2,2'-Bipyridine-Localized Reduction in  $cis-[M(bpy)_2(L)Cl]^+$ .** Figure 2 shows the complete first-scan cyclic voltammogram of  $[Ru(bpy)_2(py)Cl](PF_6)$  in  $CH_3CN$  with 0.1 M TEAP as supporting electrolyte taken with a Pt-bead working electrode and a scan rate of 200 mV/s in the region +1.5 to -2.0 V (vs. SCE). The irreversibility of the second reductive wave is immediately apparent, as is the appearance on the anodic sweep of two new product waves, an irreversible wave at  $E_p = 1.02$  V and a reversible product wave at  $E_{1/2} = 1.35$  V (vs. SCE). The wave at  $E_p = 1.02$  V is due to the presence of free  $Cl^-$ , and the wave at  $E_{1/2} = 1.35$  V is due to  $[Ru^{II}(bpy)_2(py)(AN)]^{2+}$  (AN = acetonitrile), as shown by comparisons with

(15) Heath, G.; Yellowlees, L.; Brateman, P. *Chem. Phys. Lett.* **1982**, *92*, 646.

(16) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. *Electrochim. Acta* **1968**, *13*, 1005. (b) See also: Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. *Nouv. J. Chim.* **1980**, *4*, 643.

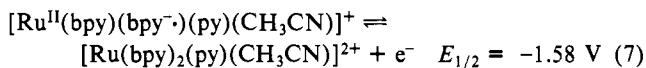
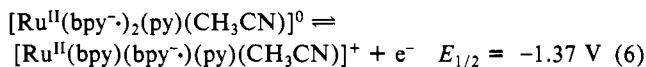
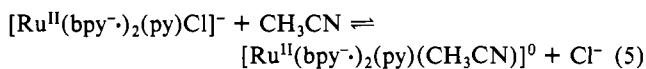
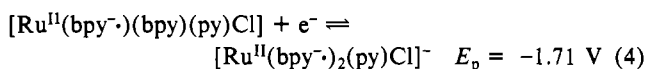
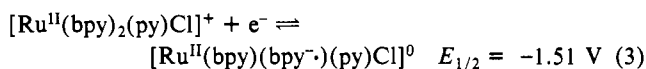
(17) (a) Kober, E. M., unpublished results. (b) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J., submitted for publication.

(18) Bugnon, P.; Hester, R. E. *Chem. Phys. Lett.* **1983**, *102*, 537.



**Figure 3.** Reductive cyclic voltammety (first four scans) for the complex  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}](\text{PF}_6)$  showing the isoelectric behavior associated with the appearance of bpy-localized reduction of the chloride ion loss product  $[\text{Ru}(\text{bpy})_2(\text{py})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ . Scans were recorded in  $\text{CH}_3\text{CN}$  solution with 0.1 M TEAP as supporting electrolyte, a Pt-bead working electrode, and a scan rate of 200 mV/s. A scan through only the first reduction wave is shown for comparison.

known samples.<sup>19</sup> Another confirmation of the nature of the reduction process is seen by careful inspection of the region for the two reduction waves for  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+$ . Figure 3 shows that, after the first four cyclic scans between -1.0 and -1.8 V, two new waves appear as products of the *second* reduction of  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+$ . Most clearly resolved in Figure 3 is the most oxidative of the product waves, having  $E_{1/2} = -1.37$  V; the second wave is ill-resolved, but  $E_{1/2}$  can be estimated as being between -1.5 and -1.7 V. This first wave is identical with and the second wave is consistent with the first two reductions in the chloride ion loss product,  $[\text{Ru}(\text{bpy})_2(\text{py})\text{AN}]^{2+}$ . The electron-transfer scheme suggested by the above data is shown in eq 3-7. Additional



reductive processes also occur for the complexes  $[\text{M}(\text{bpy})_2(\text{L})\text{Cl}]^+$ , but they will not be considered further here.<sup>20</sup>

(19) The cyclic voltammety investigations were carried out in the region +1.9 to -2.0 V. For some of the complexes studied additional faradaic processes occur at potentials more negative than -1.9 V, but they were not investigated in detail.

(20) The reductive substitution reactions are not completely specific for loss of the halide ion. For example, pyridine can also be lost. CV under slow scan rate conditions (100 mV/s) for  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+$  shows some  $\text{Ru}^{\text{II}}(\text{bpy})\text{Cl}_2$  produced ( $E_{1/2}^{\text{obsd}} = 0.34$  V). Loss of pyridine could arise from events like  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+ + \text{AN} \rightleftharpoons [\text{Ru}(\text{bpy}^-)_2(\text{py})(\text{AN})]^0 + \text{Cl}^-$  and  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+ + \text{Cl}^- \rightleftharpoons [\text{Ru}(\text{bpy}^-)_2\text{Cl}_2]^{2-}$ . The reduced *cis*-dichloro complex would then be reoxidized during the anodic sweep. Reoxidation of the solution after bulk electrolysis shows little  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (<3%), predominantly  $[\text{Ru}(\text{bpy})_2(\text{py})(\text{AN})]^{2+}$ , and possibly some  $[\text{Ru}(\text{bpy})_2(\text{AN})_2]^{2+}$  on the basis of the broadening of the oxidative wave at  $E_{1/2} = +1.35$  V (note that the bis(acetonitrile) complex has a potential of +1.44 V) and an unsymmetrical disposition of the two new bpy reduction waves. The appearance of the bis(acetonitrile) complex suggests that an exchange of acetonitrile for pyridine also occurs upon reduction, i.e.  $[\text{Ru}(\text{bpy})_2(\text{py})(\text{AN})]^0 + \text{AN} \rightleftharpoons [\text{Ru}(\text{bpy})_2(\text{AN})_2]^+ + \text{py}$ .

**Table III.** Results of Controlled-Potential Electrolyses in Acetonitrile<sup>a</sup>

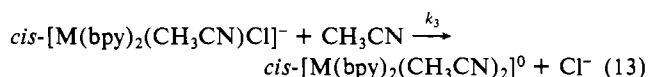
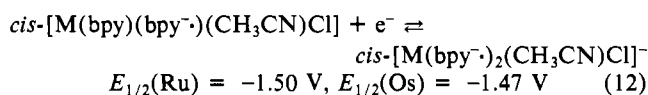
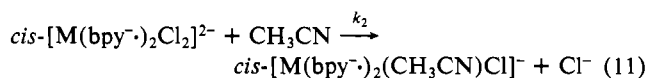
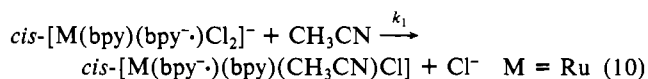
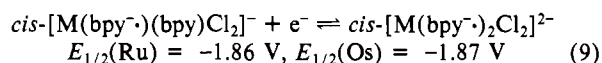
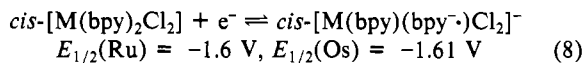
complex <sup>b</sup>	$n_r$ <sup>c</sup>	potential, V	$n_o$ <sup>c</sup>	potential, V
$[\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$	3.17	-1.90	1.46	-0.80
$[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$	1.90	-1.80	1.80	-0.80
$[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+$	1.89	-1.90	1.80	-0.80
$[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$	1.91	-1.60	1.20	-0.50

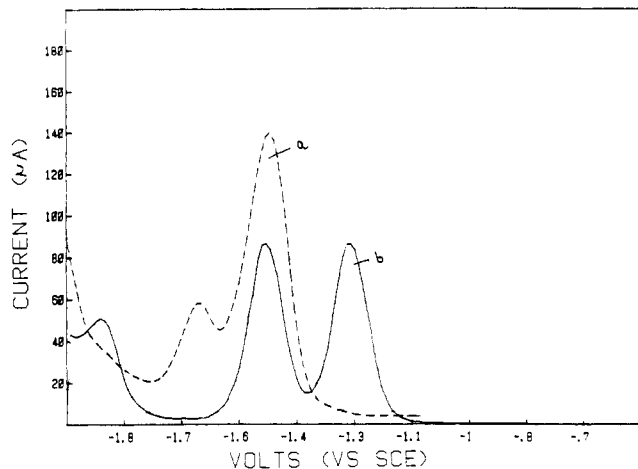
<sup>a</sup> Electrolyses were performed in a  $\text{N}_2$ -filled inert-atmosphere box with a Pt-gauze working electrode (see Experimental Section). <sup>b</sup> All as  $\text{PF}_6^-$  salts. <sup>c</sup>  $n_r$  is the number of electrons consumed upon reduction past the second bpy wave;  $n_o$  is the number of electrons removed upon reoxidation of the reduced solution.

Controlled-potential electrolysis of  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}](\text{PF}_6)$  in  $\text{CH}_3\text{CN}/0.1$  M TEAP solution confirmed the general scheme shown in eq 3-7, although the comment in footnote 19 should be noted. The results of this and other coulometry experiments are shown in Table III for four complexes of the type  $[\text{M}(\text{bpy})_2(\text{L})\text{Cl}]^+$ . In the table the number of electrons consumed by reducing at a potential ca. 120 mV more negative than the second reduction is shown. Also shown is the number of electrons removed after reduction with the electrode held at a potential 400 mV more oxidizing than the oxidative component of the bpy-based reduction waves for the products. In the cases of  $[\text{Ru}(\text{bpy})_2(\text{L})\text{Cl}]^+$  (L =  $\text{PPh}_3$ , py), ca. two electrons are consumed reductively and they are removed upon reoxidation. The net effect is simply a cyclic, redox-induced loss of  $\text{Cl}^-$ . For  $[\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$ , over three electrons are consumed upon reduction and less than two are removed upon oxidation. The product distribution following the redox cycle shows the presence of both  $\text{Cl}^-$  and  $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$  in the solution. On the basis of these observations, it is reasonable to assume that the catalytic behavior exhibited here involves solvent reduction or, more likely, reduction of trace water. Work in progress has shown that related polypyridine complexes of Ru are efficient catalysts for the reduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$  in acetonitrile solution.

For  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$ , the reduction is a two-electron process and a cyclic voltammogram immediately following electrolysis shows the presence of some of the starting complex. Thus in the electroreduction scheme in eq 3-7, the  $\text{Cl}^-$  loss step in eq 5 must be slower for the carbonyl complex than for the pyridine complex, based on the results of differential-pulse polarography studies, which will be discussed below.

**Chloride Ion Substitution Induced by Ligand Reduction in *cis*- $[\text{M}(\text{bpy})_2\text{Cl}_2]$  (M =  $\text{Ru}^{\text{II}}$ ,  $\text{Os}^{\text{II}}$ ).** For the complexes *cis*- $[\text{M}(\text{bpy})_2\text{Cl}_2]$ , a notable observation is that the first reduction wave is reversible for M =  $\text{Os}^{\text{II}}$  and irreversible for M =  $\text{Ru}^{\text{II}}$ .<sup>19</sup> Inspection of the following oxidative scan shows the presence of free  $\text{Cl}^-$  and  $[\text{M}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$  in both cases but no evidence for significant amounts of  $[\text{M}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$ . In general, for the complex *cis*- $[\text{M}(\text{bpy})_2\text{Cl}_2]$ , the electron-transfer-ligand-loss scheme shown in eq 8-13 appears to apply. According to this





**Figure 4.** Differential-pulse polarograms of (a)  $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$  and (b)  $[\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}](\text{PF}_6)$  taken in  $\text{CH}_3\text{CN}$  solution with 0.1 M TEAP as supporting electrolyte, a Pt-bead working electrode, and a scan rate of 200 mV/s.

scheme, the absence of  $[\text{M}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$  as a product (at least on the cyclic voltammetry time scale) is due to the fact that the potential required to reduce  $[\text{M}(\text{bpy})_2\text{Cl}_2]$  at either the first or second bpy ligand is more negative than the second ligand reduction for  $[\text{M}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$ . Reduction of  $[\text{M}(\text{bpy})_2\text{Cl}_2]$  necessarily leads to reduction of  $[\text{M}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$  if it appears as an intermediate, and the only product that is expected is  $[\text{M}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$ . For the case of  $\text{M} = \text{Ru}$  the reduction scheme could be described as an ECECE process, and for  $\text{M} = \text{Os}$  it is an ECECE process.

**Dependence of Reductive Anion Loss on Ligand Type. Relative Rates of Anion Loss.** A number of related complexes, including  $[\text{Os}(\text{bpy})_2(\text{py})\text{Br}]^+$ , the series  $[\text{Ru}(\text{bpy})_2(\text{py})\text{X}]^+$  ( $\text{X} = \text{NO}_2^-$ ,  $\text{CN}^-$ ), and  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{O}_2\text{CH}]^+$ , were examined for anion loss in order to define the generality of the phenomenon. As judged by cyclic voltammetry,  $[\text{Os}(\text{bpy})_2(\text{py})\text{Br}]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{O}_2\text{CH}]^+$  underwent anion loss, all after the second reduction, while  $[\text{Ru}(\text{bpy})_2(\text{py})\text{X}]^+$  ( $\text{X} = \text{NO}_2^-$ ,  $\text{CN}^-$ ) exhibited only reversible, ligand-based electrochemistry without ligand loss.

In order to provide a reasonable measure of the dependence of the rate of ligand loss upon the type of anion and ancillary ligands, the relative peak areas of the reductive waves were examined by differential-pulse polarography. Figure 4 shows typical polarographic traces for cases of reversible and irreversible reductions, the examples being  $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  and  $[\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$ . The relative areas under the polarographic curves are a measure of the rates of the substitutional processes that follow the reversible electron transfer at the electrode surface. It is possible to establish a relative scale of anion loss rates by taking the ratio of the areas of the irreversible polarographic peak to the reversible, one-electron peaks due to the  $\text{M}^{\text{III}}/\text{M}^{\text{II}}$  or  $\text{bpy}/\text{bpy}^{\cdot-}$  redox couples. The peak area ratios are referred to as  $R_r$  in Table IV.

By inspection of the  $R_r$  values, trends affecting ligand substitution rates that can be related to the electronic properties of the ligands are apparent. For the complexes  $[\text{M}(\text{bpy})_2(\text{L})\text{Cl}]^+$ , where isostructural comparisons (see, for example,  $\text{L} = \text{CO}$  or  $\text{PPh}_3$ ) can be made, Os is less prone toward anion loss than is Ru. This, of course, parallels the usual lability variations found in comparing related polypyridyl or polyphosphine complexes of Os(II) and Ru(II). As the  $\pi$ -back-bonding character of L increases,  $R_{r,2}$  tends to increase as shown by the order  $\text{CO} > \text{PPh}_3 > \text{py} > \text{Cl}$  for the Os(II) complexes. The electron-donating ligands  $-\text{OC}_2\text{H}$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$  are all prone to be lost readily while the electron-accepting groups  $-\text{NO}_2$  and  $-\text{CN}$  are inert.

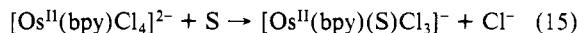
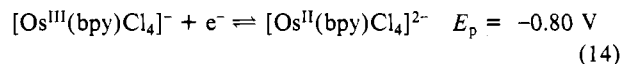
Observations of this kind suggest that the ease of anion substitution can be influenced by placing more electron density at the metal through changes in the ancillary ligands and point to a striking analogy between reductively induced chloride ion

**Table IV.** Relative Rates of Anion Loss from the Os(II) and Ru(II) Complexes As Determined by Differential-Pulse Polarography<sup>a</sup>

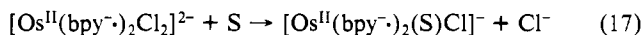
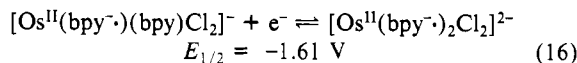
complex <sup>b</sup>	$R_{r,1}$ <sup>c</sup>	$R_{r,2}$ <sup>d</sup>
$[\text{Os}(\text{bpy})_2\text{Cl}_2]$	0.97	0.41
$[\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$	0.98	0.50
$[\text{Os}(\text{bpy})_2(\text{py})\text{Br}]^+$	0.97	
$[\text{Os}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$	1.03	0.68
$[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}]^+$	0.95	0.96
$[\text{Ru}(\text{bpy})_2\text{Cl}_2]$	$>0.2$ <sup>e</sup>	
$[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+$	1.01	0.30
$[\text{Ru}(\text{bpy})_2(\text{py})\text{NO}_2]^+$	$[1.0]$ <sup>f</sup>	1.03
$[\text{Ru}(\text{bpy})_2(\text{py})\text{CN}]^+$	$[1.0]$ <sup>f</sup>	1.01
$[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$	0.99	0.23
$[\text{Ru}(\text{bpy})_2(\text{CO})(\text{O}_2\text{CH})]^+$	$[1.0]$ <sup>f</sup>	0.78
$[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$	0.97	0.49

<sup>a</sup> All measurements made in  $\text{CH}_3\text{CN}$  solution with 0.1 M TEAP as supporting electrolyte with a Pt-bead working electrode. <sup>b</sup> All  $\text{PF}_6^-$  salts. <sup>c</sup> Relative area of the polarographic wave for the first bpy-based reduction compared to that for metal oxidation. <sup>d</sup> Relative area of the polarographic wave for the second bpy reduction compared to that for metal oxidation. <sup>e</sup> Obscured by product wave. <sup>f</sup> Relative area of the polarographic wave for the first bpy-based reduction compared to that for metal oxidation assumed to be 1.0. In these examples metal oxidation results in a chemical reaction.

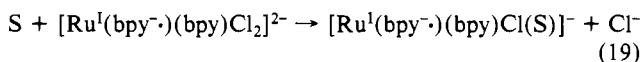
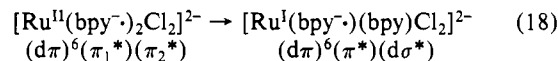
substitution in the  $[\text{Os}^{\text{III}}(\text{bpy})\text{Cl}_4]^-$  system and in  $[\text{Os}^{\text{II}}(\text{bpy})_2\text{Cl}_2]$ . As shown in eq 14 and 15, cyclic voltammetric studies have



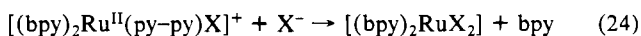
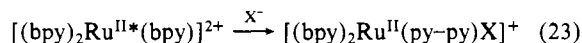
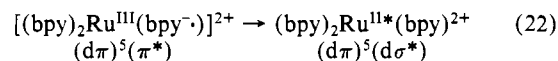
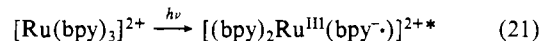
previously shown that electrochemical reduction of  $[\text{Os}^{\text{III}}(\text{bpy})\text{Cl}_4]^-$  leads to a kinetically labile  $\text{Os}^{\text{II}}$  product.<sup>21</sup> The striking resemblance to chloride substitution in  $[\text{Os}^{\text{II}}(\text{bpy})_2\text{Cl}_2]^{2-}$  suggests that the coordinated, reduced form of bpy may have an electronic effect at the metal not unlike a halide ion (eq 16 and 17).



At this point, it seems clear that the anion loss chemistry is induced by reductions initially at the bpy ligands. Given the electronic structures of the complexes, there is the interesting possibility that, mechanistically, the substitution reactions occur not from the initially formed complexes of  $\text{M}(\text{II})$  but rather indirectly following thermal excitation of an electron from a  $\pi^*$  (bpy) level to  $d\sigma^*$ , e.g.



In this context it is interesting to note that photochemical evidence is available to suggest that in complexes of this type based on Ru(II),  $\text{Ru}^{\text{II}} \rightarrow \text{bpy}$  excitation can lead to ligand loss via intramolecular sensitization of  $dd$  states.<sup>22</sup>



At present, we have no evidence for the intervention of low-lying excited states, and qualitatively, the labilization can be accounted for by the inductive effect of converting bpy into  $\text{bpy}^-$ , as noted above. It should also be noted that reduction of bpy to  $\text{bpy}^-$  is expected to increase the  $\sigma$ -donor ability of bpy markedly, which would have the effect of destabilizing the  $d\sigma^*$  levels relative to the unreduced complexes, which would tend to increase the energy

gap between the  $(d\pi)^6(\pi_1^*)(\pi_2^*)$  and  $(d\pi)^6(\pi_1^*)(d\sigma^*)$  states; note eq 18.

In future papers we will demonstrate the use of the ligand-based reductive chemistry in the electrocatalysis of  $\text{H}_2$  production from  $\text{H}_2\text{O}$  and of  $\text{CO}_2$  reduction. An important feature in such applications appears to be the role of the ligand-based reductions in inducing substitution and in providing an "electron reservoir" for the necessary reductive redox equivalents on demand.

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**Registry No.** [Os(bpy)<sub>2</sub>Cl<sub>2</sub>], 79982-56-2; [Os(bpy)<sub>2</sub>(CH<sub>3</sub>CN)Cl](PF<sub>6</sub>), 81831-14-3; [Os(bpy)<sub>2</sub>(py)Br](PF<sub>6</sub>), 97335-07-4; [Os(bpy)<sub>2</sub>(PPh<sub>3</sub>)Cl](PF<sub>6</sub>), 81831-16-5; [Os(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>), 80502-54-1; [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>], 19542-80-4; [Ru(bpy)<sub>2</sub>(py)Cl](PF<sub>6</sub>), 36413-31-7; [Ru(bpy)<sub>2</sub>(py)NO<sub>2</sub>](PF<sub>6</sub>), 36309-80-5; [Ru(bpy)<sub>2</sub>(py)CN](PF<sub>6</sub>), 97335-09-6; [Ru(bpy)<sub>2</sub>(PPh<sub>3</sub>)Cl](PF<sub>6</sub>), 67710-99-0; [Ru(bpy)<sub>2</sub>(CO)(O<sub>2</sub>CH)](PF<sub>6</sub>), 84117-41-9; [Ru(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>), 79850-20-7; [Ru(bpy)<sub>2</sub>(CO)(CH<sub>3</sub>CN)](PF<sub>6</sub>), 97335-10-9; [Os(bpy)<sub>2</sub>(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)](PF<sub>6</sub>), 97277-66-2; [Ru(bpy)<sub>2</sub>(py)(CH<sub>3</sub>CN)](PF<sub>6</sub>), 72525-79-2; TEAP, 2567-83-1; bpy, 366-18-7; CH<sub>3</sub>CN, 75-05-8; Cl<sub>2</sub>, 7782-50-5.

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- (23) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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## Electrochemistry and Spectroelectrochemistry of Indium(III) Porphyrins. Reactions of Five-Coordinate Ionic Complexes

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The electrochemistry and spectroelectrochemistry of In(III) tetraphenyl- and octaethylporphyrins were investigated in nonaqueous media. Counterions on the In(III) complexes were either Cl<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>. Each oxidized and reduced species was characterized by UV-visible spectroscopy, and ESR spectra were obtained for each of the generated cation and anion radicals. Singly oxidized species gave rise to ESR spectra with values of  $g \approx 2.00$  but with values of  $\Delta H$  that varied between 16.8 and 221 G depending upon the nature of the porphyrin ring and the composition of the solvent-supporting electrolyte system. Analysis of the ESR data indicated  $\pi$ -ring-centered reactions with a small amount of spin density residing upon the metal.

### Introduction

Recently, indium(III) porphyrins have been demonstrated to be an essential starting product in the synthesis of novel groups of metalloporphyrins with metal-metal bonds.<sup>2,3</sup> The second metal  $\sigma$ -bonded to the In center in these bimetallic complexes may be Mo, W, Cr, Mn, Fe, or Co. In(III) porphyrins are also the starting product for the formation of In(III) complexes containing  $\sigma$ -bonded alkyl or aryl groups.<sup>4</sup> These latter species have been shown to insert carbon dioxide into the In-carbon  $\sigma$  bond<sup>5</sup> or alternatively to insert sulfur dioxide between the metal atom and the alkyl or aryl group of In(III).<sup>6</sup>

For the case of the metal-metal-bonded species, indium can exist as a formal In(III) or an In(I) species and the overall complex can be reduced by two single-electron-transfer reactions without cleavage of the metal-metal bond.<sup>3</sup> Likewise, the  $\sigma$ -bonded alkyl or aryl complexes can be reduced by two single-electron transfers without cleavage of the metal-carbon bond. This stability does

not occur for the case of oxidations where both series of compounds are highly reactive and undergo either metal-metal or metal-alkyl (aryl) bond cleavage after the addition of either one or two electrons.

In order to better understand the stability and reactivity of In porphyrins with  $\sigma$ -bonded metal complexes or with alkyl (aryl) axial ligands, we have undertaken a series of parallel studies on the electrochemistry of different  $\sigma$ -bonded and ionic In(III) porphyrins. The first of these studies involved an investigation of 16 different  $\sigma$ -bonded alkyl tetraphenylporphyrin and octaethylporphyrin derivatives in nonaqueous media and is presented in another paper.<sup>7</sup> This present study describes detailed investigations on the tetraphenyl and octaethylporphyrin complexes where the complex is ionic and the associated counterion is Cl<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>. Partial electrochemical characterization for reduction of one of these compounds, (TPP)InClO<sub>4</sub>,<sup>3</sup> has been published, but no UV-visible spectral data of the reduction products were reported. This is now given in the present manuscript. In addition, we present the first UV-visible and ESR spectra of electrooxidized In(III) porphyrins.

### Experimental Section

**Instrumentation.** UV-visible spectra were taken with a Tracor Northern 1710 holographic optical spectrometer multichannel analyzer or an IBM 9430 spectrophotometer. ESR spectra were recorded on an IBM Model ER 100D spectrometer equipped with an ER 040-X microwave bridge and an ER 080 power supply. IR spectra were performed

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