

for the tantalum tubing employed in the gadolinium reduction reactions.

Registry No. YCl<sub>3</sub>, 14530-75-7; Y, 7440-65-5; YCl<sub>3</sub>, 10361-92-9; LiCl, 7447-41-8; YBr<sub>3</sub>, 13469-98-2; KGd<sub>2</sub>Cl<sub>7</sub>, 71619-19-7; Li,

7439-93-2; Gd, 7440-54-2; GdCl<sub>3</sub>, 10138-52-0; YBr, 17655-40-2.

**Supplementary Material Available:** Observed and calculated structure factor amplitudes for the three structures (3 pages). Ordering information is given on any current masthead page.

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## Solvent Dependence of Metal-to-Ligand Charge-Transfer Transitions. Evidence for Initial Electron Localization in MLCT Excited States of 2,2'-Bipyridine Complexes of Ruthenium(II) and Osmium(II)

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Metal-to-ligand charge-transfer (MLCT) absorption bands for the complexes Ru(bpy)<sub>3</sub><sup>2+</sup>, Os(bpy)<sub>3</sub><sup>2+</sup>, Os(bpy)<sub>2</sub>(py)<sub>2</sub><sup>2+</sup>, Os(bpy)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub><sup>2+</sup>, and Os(bpy)<sub>2</sub>(1,2-(Ph<sub>2</sub>P)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sup>2+</sup> (bpy is 2,2'-bipyridine; py is pyridine) are solvent dependent. The dependence can be interpreted with use of dielectric continuum theory but for the D<sub>3</sub> ions Ru(bpy)<sub>3</sub><sup>2+</sup> and Os(bpy)<sub>3</sub><sup>2+</sup> only if in the excited state the excited electron is localized on a single ligand rather than delocalized over all three.

### Introduction

Although metal-to-ligand charge-transfer (MLCT) excited states of molecules such as Ru(bpy)<sub>3</sub><sup>2+</sup> and Os(bpy)<sub>3</sub><sup>2+</sup> (bpy is 2,2'-bipyridine) have found extensive use as redox photosensitizers,<sup>1</sup> a number of questions remain concerning the electronic structures of the excited states. A particularly troublesome one has been that of whether the MLCT excited states are better described as being localized or delocalized (having the promoted electron confined to the π\* orbital over all three bpy ligands). An electronic structural model has been presented that assumes that both the absorbing and emitting MLCT states are delocalized,<sup>2</sup> but the available experimental evidence is in disagreement with the predictions of this model.<sup>3-7</sup> In fact, in dealing with the problem of localized vs. delocalized descriptions, there are two different types of excited states to consider that are probed by two different spectroscopic techniques. Optical absorption, which interconverts the thermally equilibrated ground and nonequilibrium excited states, is dominated by transitions to states largely singlet in character. Emission from vibrationally equilibrated excited

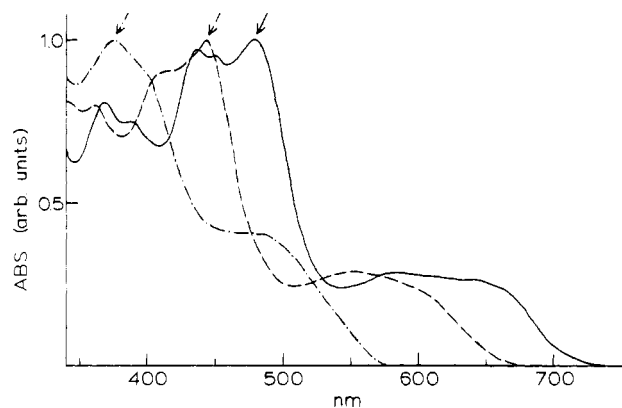
states to nonequilibrium ground states occurs from states largely triplet in character.<sup>6,7</sup>

For the equilibrated excited states, evidence has accumulated in favor of a localized description. It has been noted that polarization ratio data are inconsistent with excited states having rigorous D<sub>3</sub> symmetry as do the tris chelates M(bpy)<sub>3</sub><sup>2+</sup> (M = Fe<sup>II</sup>, Ru<sup>II</sup>, Os<sup>II</sup>) in their ground states, and it was suggested that this may be due to a static environmental inhomogeneity.<sup>3,6</sup> A more exhaustive study argues that only localized emitting states could account for the observed polarization data.<sup>4</sup> The temperature dependence of the EPR signals and the observation of a broad low-energy absorption band assignable as a bpy → bpy intervalence charge-transfer transition of the related ligand-reduced species Ru(bpy)<sub>3</sub><sup>+0/-</sup> have been interpreted as implying that each of the added electrons is localized in the π\* orbital of one of the bpy ligands.<sup>8</sup> Finally, time-resolved resonance Raman spectra of the emitting excited state(s) of Ru(bpy)<sub>3</sub><sup>2+</sup> have been interpreted as being consistent with the formulation of a localized excited state, i.e., Ru<sup>III</sup>(bpy)<sub>2</sub>(bpy<sup>-</sup>)<sup>2+</sup>, on a time scale ranging from a few hundred picoseconds to 10 ns after excitation.<sup>9</sup>

It has previously been argued that in the absence of specific polarization effects, the dipole moment of an excited state can be determined from the solvent dependence of the energy of the electronic absorption band.<sup>10-13</sup> The prediction concerning dipole moment has been verified quantitatively for several systems.<sup>13-15</sup> Considering the expense of specialized equipment

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**Figure 1.** Visible absorption spectra of  $[\text{Os}(\text{bpy})_3][\text{PF}_6]_2$  (—),  $[\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$  (---), and  $[\text{Os}(\text{bpy})_2(1,2\text{-}(\text{PPH}_2)_2\text{C}_6\text{H}_4)][\text{PF}_6]_2$  (-·-·), in acetonitrile. Bands used for the solvent dependence study are indicated by arrows.

necessary for some of the above experiments, examination of the solvent dependence provides a "poor man's" probe of the character of the "initially" populated MLCT excited states with regard to their localized or delocalized character. In this context, the experiment is of special interest since, given the time scale of electronic transitions, the excited states are formed in non-equilibrium vibrational geometries. If the initial MLCT excited state or states (depending on excitation wavelength) are delocalized, a dipole moment cannot exist because of the resulting  $D_3$  symmetry. If the electron is excited to a single ligand, a dipole moment should exist and be manifested by a solvent dependence of the excitation energy. In principle, the solvent dependence can provide a quantitative measure of the excited-state dipole moment and therefore provide a basis for determining whether the excited state is truly localized or simply delocalized with non- $D_3$  symmetry.

### Experimental Section

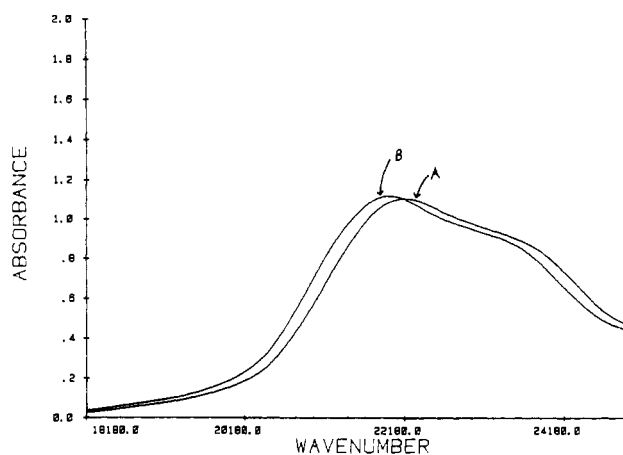
**Measurements.** Absorption spectra were measured on Cary 17 or Bausch & Lomb Spectronic 2000 recording spectrophotometers. The measurements made were vs. a solvent blank using matched 1-cm quartz cells. Slow scan rates (0.25 nm/s) were used to maximize resolution. For all solvents, the slit width was less than 0.1 mm in the region of interest.

**Materials.**  $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ ,  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ ,  $[\text{Os}(\text{bpy})_2(\text{py})_2](\text{PF}_6)_2$ ,  $[\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ , and  $[\text{Os}(\text{bpy})_2(\text{dppb})][\text{PF}_6]_2$  (dppb = 1,2-bis(diphenylphosphino)benzene) were prepared as described elsewhere.<sup>16</sup> Solvents were obtained from commercial sources (Fisher, Aldrich, and Burdick-Jackson) and were spectrograde where available. In the cases of nitrobenzene, benzonitrile, cyclopentanone, hexamethylphosphoramide, and *N*-methylformamide, reagent grade solvents were used (Aldrich). Water was doubly distilled from  $\text{KMnO}_4$ . Single- and dual-parameter fitting programs were written in this laboratory for a Commodore PET 4032 microcomputer and are available on request from the authors.

### Results

Typical visible absorption spectra for three of the complexes,  $\text{Os}(\text{bpy})_3^{2+}$ ,  $\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})_2^{2+}$ , and  $\text{Os}(\text{bpy})_2(\text{dppb})^{2+}$  as  $\text{PF}_6^-$  salts in acetonitrile solution (dppb is 1,2-bis(diphenylphosphino)benzene) are shown in Figure 1. All complexes show at least one well-resolved absorption band whose maximum could be determined to an accuracy of  $\pm 0.5$  nm ( $\pm 20$   $\text{cm}^{-1}$ ). All of the bands in this region are readily assigned as  $\text{Os}(5d) \rightarrow \text{bpy}(\pi^*)$  MLCT transitions.<sup>2d,6c,7,16,17</sup>

The energies of the MLCT bands in these complexes and in  $\text{Os}(\text{bpy})_2(\text{py})_2^{2+}$  and  $\text{Ru}(\text{bpy})_3^{2+}$  were found to be slightly



**Figure 2.** Absorption spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  in (A)  $\text{CH}_3\text{CN}$  solution and (B)  $\text{PhCN}$  solution.

solvent dependent. In Figure 2 is shown a typical effect of changing the solvent on the CT band maximum of  $\text{Ru}(\text{bpy})_3^{2+}$  for the solvents benzonitrile and acetonitrile. The data for the  $\text{Os}(\text{II})$  complexes were taken for the most well-resolved band for each complex (shown by the arrows in Figure 1) and are given in Table I. For  $\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})_2^{2+}$ , both "singlet" and a "triplet" absorptions were examined. For all complexes, the band position is seen to shift by 200–300  $\text{cm}^{-1}$  on going from solvents such as benzonitrile to solvents such as acetonitrile, and the remaining bands for each complex show very similar shifts as can be seen in Figure 2. It should be noted that for solvents available in varying grades of purity (such as acetonitrile, acetone, and dimethyl sulfoxide), the band positions had little or no dependence on the solvent purity. The solvent origins ranged from reagent grade from Fisher to spectrograde from Burdick and Jackson.

Also included in Table I are values of the dielectric functions  $(1 - D_s)/(2D_s + 1)$ ,  $(1 - D_{\text{op}})/(2D_{\text{op}} + 1)$ , and  $\theta(D_s) = (3D_s \ln D_s)/D_s \ln D_s - D_s + 1 - 6/(\ln D_s) - 2$ .<sup>19a</sup>  $D_s$  is the static dielectric constant, and  $D_{\text{op}}$  is the optical dielectric constant, equal to  $n^2$ , where  $n$  is the refractive index. Values for  $D_s$  and  $n$  are taken from standard sources.<sup>18</sup>

As discussed below, if solvent effects are observed, it is expected that the transition energies will vary linearly with combinations of the dielectric functions  $(1 - D_{\text{op}})/(2D_{\text{op}} + 1)$  and either  $(1 - D_s)/(2D_s + 1)$  or  $\theta(D_s)$ . In particular, transition energies for  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Os}(\text{bpy})_3^{2+}$ , which have  $D_3$  symmetry in the ground state, are observed to increase linearly with the function  $(1 - D_{\text{op}})/(2D_{\text{op}} + 1)$ , which is predicted theoretically by assuming localization in the initially formed excited state. Inclusion of the static dielectric functions containing  $D_s$ ,  $(1 - D_s)/(2D_s + 1)$ , or  $\theta(D_s)$ , in dual-parameter fits of the type shown in eq 1 for  $\text{Os}(\text{bpy})_3^{2+}$ ,  $\text{Ru}(\text{bpy})_3^{2+}$ , or  $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$ , does not noticeably improve the quality of the correlations.

$$E_{\text{op}} = X \left( \frac{1 - D_{\text{op}}}{2D_{\text{op}} + 1} \right) + Y(f(D_s)) + z \quad (1)$$

$$f(D_s) = f(D_s), f((1 - D_s)/(2D_s + 1)), \text{ or } f(\theta(D_s))$$

On the other hand, for the complexes  $\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})_2^{2+}$  and  $\text{Os}(\text{bpy})_2(1,2\text{-}(\text{PPH}_2)_2\text{C}_6\text{H}_4)^{2+}$  where a dipole moment is predicted for the ground state, dual-parameter fits of the form

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Table I. Solvent Parameters and Transition Energies<sup>a</sup>

no.	solvent	transition energies, $\text{cm}^{-1} \times 10^{-3}$					
		$\text{Os}(\text{bpy})_3^{2+}$	$\text{Os}(\text{bpy})_2^-(\text{py})_2^{2+}$	$\text{Os}(\text{bpy})_2^-(\text{CH}_3\text{CN})_2^{2+}$	$\text{Os}(\text{bpy})_2^-(\text{dppb})_2^{2+}$	$\text{Ru}(\text{bpy})_3^{2+}$	$\text{Os}(\text{bpy})_2^-(\text{CH}_3\text{CN})_2^{2+}$
1	nitrobenzene	20.70	22.45	22.20	22.20	21.91	18.05
2	benzonitrile	20.73	22.56	22.25	22.25	21.99	18.10
3	pyridine	20.73	22.53	22.22	22.22	21.98	18.07
4	dimethyl sulfoxide	20.75	22.47	22.25	22.25	22.03	18.05
5	hexamethylphosphoramide	20.81	22.52	22.27	22.27	22.08	
6	dimeylacetamide	20.77	22.60	22.25	22.25	22.08	18.07
7	cyclopentanone	20.73	22.58	22.35	22.35	22.12	18.09
8	N-methylformamide	20.75	22.55	22.27	22.27	22.03	18.12
9	dimethylformamide	20.79	22.66	22.32	22.32	22.03	18.07
10	methylene chloride	20.80	22.68	22.35	22.35	22.09	18.12
11	propylene carbonate	20.84	22.66	22.35	22.35	22.08	18.08
12	n-butyronitrile	20.83	22.73	22.33	22.33	22.12	18.15
13	nitromethane	20.84	22.68	22.38	22.38	22.12	18.08
14	methyl ethyl ketone	20.92	22.71	22.40	22.40	22.14	18.13
15	ethanol	20.87	22.70	22.40	22.40	22.18	
16	acetone	20.92	22.75	22.42	22.42	22.22	18.10
17	acetonitrile	20.96	22.75	22.50	22.50	22.17	18.17
18	methanol	20.96	22.75	22.50	22.50	22.17	18.21
19	water		22.50	22.50	22.50	22.22	18.21

<sup>a</sup> Energy of band indicated by arrow in Figure 1. Singlet refers to the intense MLCT transitions of states largely singlet and triplet to lower energy, less intense transitions of states largely triplet in character. <sup>b</sup>  $D_{\text{op}} = n^2$ ;  $n$  = refractive index;  $D_s$  = static dielectric constant. Data from ref 18. <sup>c</sup>  $\theta(D_s) = (3D_s \ln D_s)/(D_s - D_s + 1) - 6/(\ln D_s) - 2$ ; see text. <sup>d</sup> Excluded from least-squares fit by statistical rejection.

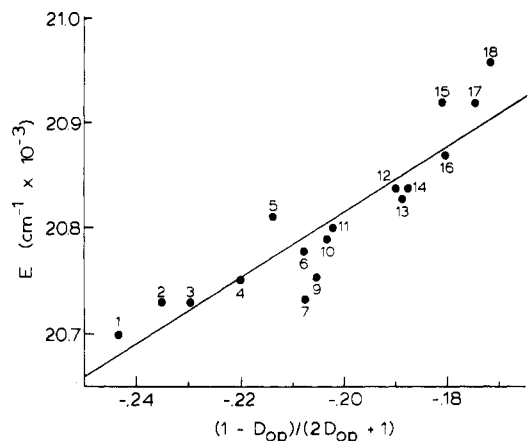


Figure 3. Plot of the absorption band energy of  $[\text{Os}(\text{bpy})_3][\text{PF}_6]_2$  vs.  $(1 - D_{\text{op}})/(2D_{\text{op}} + 1)$ . The straight line represents the linear least-squares best fit with a slope of  $3249 \text{ cm}^{-1}$  (see Table II). The solvents are labeled according to Table I. The estimated error in the individual data points is  $\pm 20 \text{ cm}^{-1}$ .

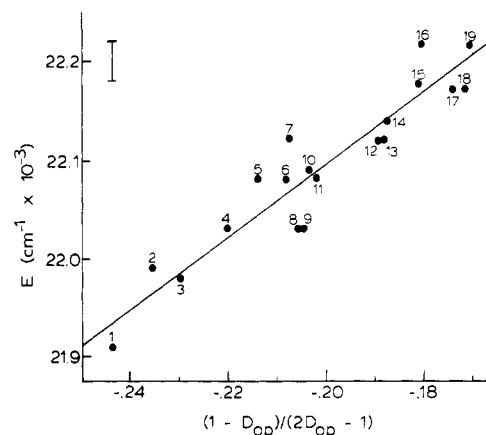


Figure 4. Plot of the absorption band energy of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  vs.  $(1 - D_{\text{op}})/(2D_{\text{op}} - 1)$ . The linear least-squares line is drawn through the points. The solvents are labeled according to Table I.

shown in eq 1 were necessary to obtain reasonable correlations with experimental data. The  $E_{\text{op}}$ -dielectric function correlations were fit by using a linear least-squares analysis, and the results of the analyses are shown in Table II. In the table, correlation coefficients for single or dual fits and the coefficients  $X$ ,  $Y$ , and  $Z$  with their associated errors are shown (in the 95% confidence level). Figures 3 and 4 illustrate the quality of the fits for  $\text{Os}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{bpy})_3^{2+}$ , respectively.

## Discussion

**Background Theory and General Approach.** The theory of solvent dielectric effects on electronic transition energies has been developed by several authors.<sup>10-13</sup> The treatment of Marcus<sup>12</sup> is the most general, and his notation is adopted here. The expression for the *total polar* contribution to the spectral transition energy ( $\Delta E_T$ ) of a polar solute in a polar solvent is given in eq 2. Here,  $F_1$  and  $F_0$  are the polar contributions

$$\Delta E_T = F_1 - F_0 + F_{1-0}^{\text{op}} - F_{1-0} \quad (2)$$

to the Helmholtz free energy of the thermally equilibrated system with the solute in its initial and final states, respectively (i.e., the solvation energy, neglecting changes in volume).  $F_{1-0}$  is the corresponding contribution for the hypothetical solute whose permanent charge distribution is that for the final state minus that of the initial state.  $F_{1-0}^{\text{op}}$  is the polar contribution to the free energy of the system in which the medium responds to the final minus initial charge distribution only via optical polarization.

Table II. Results of Fitting the Transition Energies for the Complexes to Eq 1

complex	X, cm <sup>-1</sup>	Y, cm <sup>-1</sup>	Z, cm <sup>-1</sup>	correln coeff	μ <sub>T</sub> , <sup>c</sup> D	dipole length, <sup>d</sup> Å
Ru(bpy) <sub>3</sub> <sup>2+</sup>	3670 ± 690		22 830 ± 140	0.939	14.1 ± 6.1	3.0, 3.6 (±1.3)
Os(bpy) <sub>3</sub> <sup>2+</sup>	3249 ± 810		21 470 ± 165	0.911	13.3 ± 6.6	2.8, 3.4 (±1.4)
Os(bpy)(py) <sub>2</sub> <sup>2+</sup>	3890 ± 1050		23 410 ± 210	0.900	14.6 ± 7.6	3.0, 3.7 (±1.6)
Os(bpy) <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub> <sup>2+a</sup>	3593 ± 895	-709 ± 900	22 720 ± 200	0.916	13.6 ± 7.0	2.9, 3.6 (±1.4)
Os(bpy) <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub> <sup>2+b</sup>	3667 ± 860	-226 ± 300	22 970 ± 180	0.929	14.1 ± 6.9	2.9, 3.6 (±1.4)
Os(bpy) <sub>2</sub> (dppb) <sub>2</sub> <sup>2+a</sup>	1975 ± 1290	-2107 ± 1020	26 140 ± 255	0.870	11.6 ± 8.1	2.4, 3.0 (±1.7)
Os(bpy) <sub>2</sub> (dppb) <sub>2</sub> <sup>2+b</sup>	1943 ± 1260	-640 ± 320	26 935 ± 250	0.871	11.5 ± 8.0	2.4, 3.0 (±1.7)

<sup>a</sup>  $f(D_s) = (1 - D_s)/(2D_s + 1)$ . <sup>b</sup>  $f(D_s) = \theta(D_s) = (3D_s \ln D_s)/(D_s \ln D_s - D_s + 1) - 6/(\ln D_s) - 2$ . <sup>c</sup> Transition dipole in debyes. <sup>d</sup> First figure is assuming complete electron transfer; second refers to 10% mixing of metal orbitals into ligand orbitals. See text.

An expression for the solvation energy of an ion of radius  $b$  with a general interior charge distribution in a continuous medium of dielectric constant  $D$  has been derived by Kirkwood.<sup>20</sup> When the dielectric constant of the interior of the ion and of the reference medium is taken to be equal to unity, the Kirkwood expression reduces to the form shown in eq 3.

$$W = \frac{1}{2} \sum_{n=0}^{\infty} \left( \frac{(n+1)Q_n}{b^{2n+1}} \right) \left( \frac{1-D}{(n+1)D+n} \right) \quad (3)$$

Here,  $W$  is the free energy of solvation of the charge distribution in a medium of dielectric constant  $D$ , which can be associated with Marcus'  $F_{1-0}^{op}$ ,  $F_{1-0}$ ,  $F_1$ , and  $F_0$  terms, on the assumption that the volume change on optical excitation is negligible.  $Q_n$  depends on the electric field distribution of the solute  $Q_0 = z^2 e^2$ , where  $z$  is the ionic charge and  $e$  the unit electron charge.  $Q_1 = \mu^2$ , where  $\mu$  is the dipole moment of the solute. The succeeding terms  $Q_n$  ( $n = 2$  and larger) are higher order multipole moments and will be neglected in our analysis. Implicit in the derivation of eq 3 is a "primitive" model of the dielectric continuum surrounding the solute. In this model, the charge distribution is situated at the center of a nonpolarizable sphere of radius  $b$ , and the bulk dielectric constant of the medium ( $D$ ) is assumed to be appropriate from the solute-solvent boundary throughout the medium. Although the continuum approximation is probably realistic for electronic polarization ( $D_{op}$ ), it has been shown to be incorrect for the static polarization ( $D_s$ ). The breakdown in the approximation occurs because the solute imposes a short-range order in the medium at the solute-solvent interface. The origin of short-range order can be in specific bonding effects between solute and solvent, in an electric field dependence of the permittivity of the medium, and possibility from ion-pairing effects. Collectively, these effects will be alluded to as an "apparent" dielectric saturation near the solute-solvent interface, and the effect of dielectric saturation will be discussed in a later section.

From the definitions above, eq 3 can be written as in eq 4, which is an expression for the solvation energy of a solute in a medium of dielectric constant  $D$  neglecting the multipole terms higher than  $Q = 1$ . The first term in eq 4 is the familiar

$$F \approx W = \frac{z^2 e^2}{2b} \left( \frac{1}{D} - 1 \right) + \frac{\mu^2}{b^3} \left( \frac{1-D}{2D+1} \right) \quad (4)$$

Born expression for solvation energies of ions<sup>21</sup> while the second term is the Onsager dipole solvation energy term.<sup>22</sup> More general expressions that include effects of apparent dielectric saturation on the solvation energies of ions and dipoles have been derived.<sup>19c,23</sup> One approach to the problem has been to

introduce theoretical expressions that describe the variation of the permittivity of the medium as a function of the distance from the cavity occupied by the solute. We will utilize a result of this kind in a later section.

With the results of eq 4, the solvation terms that appear in eq 2 lead to eq 5. The relative simplicity of eq 5 arises from  $\Delta E_T =$

$$\frac{(\bar{\mu}_1 - \bar{\mu}_0)^2}{b^3} \left( \frac{1 - D_{op}}{2D_{op} + 1} \right) + \frac{2\bar{\mu}_0(\bar{\mu}_1 - \bar{\mu}_0)}{b^3} \left( \frac{1 - D_s}{2D_s + 1} \right) \quad (5)$$

the fact that the ionic charge of the complexes does not change as a consequence of the optical excitation and this leads to a cancellation of the Born charging terms. If the ground state does not have a permanent dipole moment, eq 5 assumes the more simplified form given in eq 6, where  $\mu$  is the dipole moment in the excited state. In eq 5 the term  $\bar{\mu}_1 - \bar{\mu}_0$  is the

$$\Delta E_T = \frac{\mu^2}{b^3} \left( \frac{1 - D_{op}}{2D_{op} + 1} \right) \quad (6)$$

transition dipole, which is a measure of the change in the electron dipole distribution before and after excitation. The term containing  $\bar{\mu}_0(\bar{\mu}_1 - \bar{\mu}_0)$  has its origin in the interaction energy between the ground state dipole and the transition dipole and is equivalent to  $(\mu_0(\mu_1 - \mu_0) \cos \phi)$  where  $\phi$  is the angle between the two dipoles.

Equations 5 and 6 provide a basis for determining ground- and excited-state dipole moments based on changes in transition energies induced by systematic variations in the solvent. The equations have been derived previously by other authors,<sup>10,11,13</sup> and their validity in determining values of excited- and ground-state dipole moments has been tested experimentally with reasonably good results.<sup>13-15</sup> The overall validity of the use of a dielectric continuum model for the solvent has also been successfully tested for other systems. A notable example is in the use of a continuum model for predicting the solvent dependence of intervalence charge-transfer transitions.<sup>24</sup>

It is interesting to note that all of the terms in eq 3 are essentially linear functions of  $1/D$ . For example, for the 19 solvents listed in Table I, the relationship between the function  $(1 - D_{op})/(2D_{op} + 1)$  and  $1/D_{op}$  by linear least-squares fitting is  $(1 - 1/D_{op})/(2D_{op} + 1) = 0.483(1/D_{op}) - 0.442$  ( $r = 0.99982$ ) and the same type of correlation for the static dielectric constant gives  $(1 - D_s)/(2D_s + 1) = 0.711(1/D_s) - 0.499$  ( $r = 0.99986$ ). Cannon<sup>25</sup> has, in fact, proposed the use of  $1/D_s$  and  $1/D_{op}$  as solvent parameters for use in determining the dipole moment change upon excitation of spherical solutes, but there are difficulties with this approach. Even though  $1/D_s$  and  $1/D_{op}$  correlate with  $(1 - D_s)/(2D_s + 1)$  and  $(1 - D_{op})/(2D_{op} + 1)$ , respectively, the background theory has been developed in terms of the more complex dielectric functions.

(20) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351-361.

(21) Born, M. *Z. Phys.* **1920**, *1*, 45.

(22) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486-1493.

(23) See, for example: (a) Beveridge, D. L.; Schnuelle, G. W. *J. Phys. Chem.* **1975**, *79*, 2562-2566. (b) Abraham, M. H.; Liszi, J.; Meszaros, L. *J. Chem. Phys.* **1979**, *70*, 2491-2496. (c) Abraham, M. H.; Liszi, J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1604-1614. (d) Abraham, M. H.; Liszi, J. *Ibid* **1980**, *76*, 1219-1231.

(24) (a) Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. *Now. J. Chim.* **1980**, *4*, 643-650. (b) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289-1297 and references therein.

(25) Cannon, R. D. "Electron Transfer Reactions"; Butterworths: London, 1980.

As a consequence, there is no direct theoretical basis for microscopic interpretation of the slopes and intercepts of correlations involving  $1/D_{op}$  and  $1/D_s$  using a point dipole in a sphere model.

**Solvent Dependences as Evidence for Localized Excited States in Ru(bpy)<sub>3</sub><sup>2+</sup> and Os(bpy)<sub>3</sub><sup>2+</sup>.** Application of the fitting procedure to the variation in the transition energies with solvent predicted by eq 6 gave the values of  $X$ , the coefficient for the dielectric function  $(1 - D_{op})/(2D_{op} + 1)$  shown in Table II. As noted above, inclusion of the static dielectric functions did not improve the quality of the correlations for Ru(bpy)<sub>3</sub><sup>2+</sup> and Os(bpy)<sub>3</sub><sup>2+</sup>. That eq 6 should apply to the tris complexes is expected since these species possess no permanent ground-state dipole moment. Interestingly, data for the complex Os(bpy)<sub>2</sub>(py)<sub>2</sub><sup>2+</sup> also correlate well, assuming a simple  $(1 - D_{op})/(2D_{op} + 1)$  dependence, and the value of the coefficient  $X$  is very similar to that for Os(bpy)<sub>3</sub><sup>2+</sup>.

In fact, there is a potential source of solvent dependence even if the excited states were delocalized arising from dispersion forces. From the work of McRae<sup>11</sup> this contribution can be calculated from eq 7, where  $f$  is the oscillator strength of the

$$\Delta E_{disp} = \frac{3.30Lf}{b^3} \left( \frac{1 - D_{op}}{2D_{op} + 1} \right) \quad (7)$$

molecular transition,  $b$  is the molecular radius in Å, and  $L$  is the weighted mean energy of absorption for the solvent. The latter term is a measure of the dispersion of electron density in the solvent. Using  $L = 80\,000 \text{ cm}^{-1}$  from McRae, a value that is typical of many solvents,  $b = 6.5 \text{ Å}$ , and  $f = 0.1$  gives eq 8. Values calculated by using eq 8 show that variations in  $\Delta E_T$  from dispersion effects are numerically insignificant compared to the actual variations observed.

$$\Delta E_{disp} = 91 \left( \frac{1 - D_{op}}{2D_{op} + 1} \right) \quad (\text{in cm}^{-1}) \quad (8)$$

The most notable aspect of the values obtained from the correlations for the  $X$  coefficients shown in Table II is that they are *nonzero* and similar in magnitude for all the complexes studied. These data clearly suggest that a substantial excited-state dipole moment must exist for all cases, which is clearly inconsistent with a delocalized description for the initially populated, largely singlet MLCT states.

Returning to the values for the  $X$  coefficient, a more detailed interpretation further emphasizes the suggestion of localization in the excited states. As shown by eq 1 and 6,  $X$  can be used to calculate the excited-state dipole moment if the radius of the solute,  $b$ , is known. The structures of Ru and Os polypyridyl complexes are expected to be essentially identical so that the results of an X-ray crystallographic structure for Ru(bpy)<sub>3</sub><sup>2+</sup> can be used for estimating  $b$ .<sup>26</sup> From the structure, the metal to outermost hydrogen distance was found to be  $\sim 7.0 \text{ Å}$ . Including van der Waals contact distances and appreciating that there are small pockets between the bpy ligands, the radius of Os(bpy)<sub>3</sub><sup>2+</sup> should probably be taken as being in the range 6.0–7.0 Å. The value  $b = 6.5 \text{ Å}$  will be used here for Os(bpy)<sub>3</sub><sup>2+</sup>. Molecular models suggest that a radius of  $b = 6.5 \text{ Å}$  should also be appropriate for Os(bpy)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub><sup>2+</sup>. Because of the phenyl rings present in the complex Os(bpy)<sub>2</sub>(dppb)<sub>2</sub><sup>2+</sup>, a slightly larger radius is involved and a value of  $b = 7.0 \text{ Å}$  seems a reasonable estimate.

From the values of  $b$  above, the transition dipoles for Ru(bpy)<sub>3</sub><sup>2+</sup> and for the Os–bpy complexes are calculated to be in the range 11–15 ( $\pm 6$ –8) D, which give dipole lengths of 2.4–3.0 Å if it is assumed that a unit electronic charge is

transferred from metal to ligand upon excitation (see Table II). More realistically, the mixing of metal and ligand orbitals should be taken into account, so that less than a full unit of electronic charge is transferred. An estimate of the extent of metal ligand mixing is  $\sim 10\%$ , that is to say that in the  $d\pi-\pi^*$  transition the composition of  $d\pi$  is  $\sim 90\%$  Os (5d) and  $\sim 10\%$  bpy ( $\pi^*$ ), and the composition of the "ligand" orbital is  $\sim 90\%$  bpy ( $\pi^*$ ) and  $\sim 10\%$  Os (5d).<sup>7,16,27</sup> If this estimate is correct, 80% of a unit electronic charge is transferred upon excitation and the charge-transfer distances vary between 3.0 and 3.7 Å.

The distances involved are physically reasonable since they coincide roughly with the distance from the metal ion to the center of the bpy ( $\pi^*$ ) ligand. Given also the similarities in the magnitudes of the values, the results are clearly consistent with a completely localized description of the excited states.

**Estimation of Ground-State Dipole Moments for the Complexes Os(bpy)<sub>2</sub>L<sub>2</sub><sup>2+</sup>.** From the analysis presented above, the magnitudes found for  $X$  from the fitting procedure are reasonable in terms of molecular size and expected dipole length of the optical transition. It is also of value to consider the values for the  $Y$  coefficients obtained from the two-parameter fits based on eq 5, since they should relate to the dipole moment of the ground state.

As noted earlier, two-parameter fit correlations were made by using both the dielectric functions  $(1 - D_s)/(2D_s + 1)$  and  $\theta(D_s) = (3 \ln D_s)/(D_s \ln D_s - D_s + 1) - 6/(\ln D_s) - 2$ . The first function excludes dielectric saturation, but it is included explicitly in the second. As this juncture, it is appropriate to briefly discuss the origin and use of functions like  $\theta(D_s)$ . The original formulation of the Onsager model<sup>22</sup> assumes a discontinuous change in permittivity between that of the interior of the solute and the bulk solvent at the solute–solvent interface. This is unrealistic mostly due to the dielectric saturation effects alluded to earlier. Attempts to modify the Onsager model to include saturation (within the continuum approximation) have focused on constructing a model in which the value of the dielectric constant in the vicinity of the solute varies as a function of increasing distance from the solute between the interior value of the solute and the bulk value of the solvent. Ehrenson<sup>19c</sup> has given a discussion and comparison of various methods of modifying the Onsager model in this manner. In our evaluation of ground-state dipole moments we chose to adopt the Block–Walker function because of previously favorable results obtained by other workers.<sup>19</sup>

The parameters obtained from our fitting procedure are shown in Table II. It is significant that values of the coefficient  $X$  for the optical dielectric function are independent, within the error of the fits, whether  $(1 - D_{op})/(2D_{op} + 1)$  or  $1/D_{op}$  is used. The values of the coefficient for the static dielectric constant term, which for simplicity will be referred to as  $Y$  for  $(1 - D_s)/(2D_s + 1)$  and  $Y'$  for  $D_s$ , vary for the series Os(bpy)<sub>2</sub>L<sub>2</sub><sup>2+</sup> as  $\text{py} > \text{CH}_3\text{CN} > 1/2 \text{ dppb}$ . The negative values obtained for either  $Y$  or  $Y'$  imply that the net dipole moment of the ground state is opposite in direction to that of the excited state.

The ordering of the magnitude of both the  $Y$  and  $Y'$  coefficients is in accord with the expected electronic density distribution within the ground state on the basis of the electronic properties of the ligands. In the ground state the ordering of Ru( $d\pi$ ) to L back-bonding is expected to be  $\text{bpy} \sim \text{py} \lesssim \text{CH}_3\text{CN} < \text{PR}_3$ . One basis for such a conclusion is that Os<sup>III/II</sup> potentials increase in the order 0.81 V (L =  $1/2$  bpy), 0.80 V (L = py), 0.91 V (L = CH<sub>3</sub>CN), and 1.36 V (L =  $1/2$  dppb).<sup>16</sup> The electrochemical potentials cited above are  $E_{1/2}$  values vs. the saturated calomel electrode at room temperature and  $\mu$

(26) Rillema, D. P.; Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* 1979, 849–851.

(27) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J., manuscript in preparation.

= 0.1 M. Although the observed order could arise from more than one effect, an important component is no doubt the increased stabilization of Os(II) by the increased  $\pi$  acidity of the ligands on going from  $L = \text{py}$  to  $L = 1/2 \text{ dpbb}$ .

As a consequence, the negative end of the ground-state dipole for the  $L = \text{CH}_3\text{CN}$  and  $L = 1/2 \text{ dpbb}$  complexes must be situated on the non bpy ligands, in part because of their greater  $\pi$  acidity, and the positive end must be on the metal. Because of the  $M(d\pi) \rightarrow \text{bpy}(\pi^*)$  nature of the optical process, the transition dipole would have the negative end on one of the bpy ligands and the positive end on the metal. The angle between the ground- and excited-state dipoles would then be  $120^\circ$ , and since  $\cos 120^\circ = -0.5$  (see eq 5), the values of  $Y$  and  $Y'$  are expected to be negative as is observed.

Ground-state dipole moments can be calculated (note eq 5) by using the transition dipoles, the  $Y$  and  $Y'$  coefficients and the values of the molecular radii,  $b$ , mentioned above. For the complexes  $\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})_2^{2+}$  and  $\text{Os}(\text{bpy})_2(\text{dpbb})$ , the calculated values are  $6.2 \pm 7.0$  and  $13 \pm 7.4 \text{ D}$  from the  $(1 - D_s)/(2D_s + 1)$  fits and  $3.5 \pm 4.0$  and  $5.9 \pm 4.2 \text{ D}$  from the  $\theta(D_s)$  fits. Only the dpbb complex appears to have a ground-state dipole beyond experimental uncertainty, and the values calculated including dielectric saturation seem to be more reasonable when compared to the available information on bond dipole moments. For example, from the work of Chatt<sup>28</sup> it can be inferred that osmium–nitrogen and osmium–phosphine bond dipoles should be very similar in magnitude. The value of 13 D for  $\text{Os}(\text{bpy})_2(\text{dpbb})^{2+}$  obtained by assuming no dielectric saturation appears unreasonable since it requires that nearly an entire electron reside on the dpbb ligand and that the metal core closely resemble that of  $\text{Os}^{\text{III}}$ . Independent evidence based upon ESCA measurements<sup>29</sup> of  $\text{Os}^{\text{II}}$ ,  $\text{Os}^{\text{III}}$ , and  $\text{Os}^{\text{IV}}$  complexes shows that charge distribution in complexes like  $\text{Os}(\text{bpy})_2(\text{diphos})^{2+}$  is much closer to that of  $\text{Os}^{\text{II}}$  than of  $\text{Os}^{\text{III}}$ . However, it is important to realize that there are relatively large errors associated with the absorption band measurements. Consequently, the use of functions like  $\theta(D_s)$  or  $(1 - D_s)/(2D_s + 1)$  to determine ground-state dipole moments or to distinguish between the appropriateness of the two functions is limited.

**Concluding Remarks.** The data presented here suggest that a dielectric continuum theory of solvation provides a reasonable basis for interpreting variations in MLCT transition energies induced by solvents. With respect to the excited-state dipole moment it appears that the use of the parameter  $(1 - D_{\text{op}})/(2D_{\text{op}} + 1)$ , which is a measure of the electronic polarization induced in the solvent by the transition dipole, can be interpreted to give physically reasonable estimates of the excited-state dipole.<sup>30</sup> The situation for estimation of the ground-state dipole moments is less clear, although it appears that, of the two dielectric functions,  $(1 - D_s)/(2D_s + 1)$  and  $\theta(D_s)$ , the latter gives a physically more realistic estimate. This, however, is a point that deserves further experimental efforts on systems with known ground-state dipole moments. It should be noted that the complexes used in this study were carefully selected so as to minimize specific interactions with individual solvent molecules. Work in progress clearly shows that in related complexes specific solvent effects can play a significant role in determining variations in charge-transfer energies with solvent.<sup>31</sup>

An important conclusion to be reached from the data was that in the MLCT excited states observed spectroscopically for  $\text{Os}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{bpy})_3^{2+}$ , the excited electron is localized on a single ligand. Since the conclusion was based on variations in the transition energy as determined by the optical polarization properties of the solvent, the time scale involved is that of electronic polarization changes within individual solvent molecules. Since this time scale is competitive with and shorter than the time scale for the electronic transition, it must be concluded that in the initially populated excited state, the excited electron must be localized on a single ligand. This conclusion would appear to present a paradox in that it has been concluded that the absorption spectra must be explained by using a delocalized model.<sup>6,7</sup> The two conclusions are not irreconcilable. Because all of the bpy ligands are equivalent in the ground state, from exciton theory<sup>32</sup> the absorption spectra *must* be treated on the basis of on a delocalized model. There is no force from coulombic interactions to counteract the coupling of the transition moments involving the individual bpy ligands. The conclusion reached from exciton theory does not mean that an initially populated MLCT excited state is delocalized over all three ligands, but rather that the absorption spectra must be treated as if they were.

The solvent-dependence data clearly suggest that, on the electronic time scale, the excited electron in the initially populated state is localized on a single ligand. Combined with the evidence cited earlier for the emitting states, it appears that both absorption, which is dominated by transitions to MLCT states largely singlet in character, and emission, from MLCT states largely triplet in character, involve localized excited states for polypyridyl complexes of Os(II) and Ru(II). Although only a single band for each complex was analyzed here because of resolution problems, the general absorption manifold was observed to shift in a parallel manner as illustrated in Figure 2. Analyses of the less well-resolved bands gave equivalent values of  $X$  and  $Y$  within experimental error. This is an important observation because the suggestion has been made that some of the MLCT states may be localized while others are delocalized.<sup>4c,6d,e</sup> We find no evidence for the suggestion and are led to conclude that all of the excited states are localized, at least following their initial population by optical excitation.

The question remains as to why the excited states should be localized. By their nature multiple-chelate MLCT excited states like  $(\text{bpy})_2\text{Ru}^{\text{III}}(\text{bpy})^{2+*}$  are mixed-valence systems. In mixed-valence systems the question of localization vs. delocalization has been discussed in detail.<sup>33-35</sup> The key factors are the relative magnitudes of the delocalization energy ( $V$ ), arising from electronic coupling between the electron donor and acceptor ligands, and the vibrational trapping energy. Contributions to vibrational trapping arise from intramolecular normal modes where there are differences in equilibrium coordinates or frequencies between the ground and excited states and from the solvent. The contribution by the solvent arises from charge–dipole interactions, and the magnitude varies as  $(1/D_{\text{op}} - 1/D_s)$  in the dielectric continuum limit.

For the thermally equilibrated excited states, solvent and intramolecular vibrational trapping do appear to exist. This conclusion is based on Franck–Condon analyses of low-temperature emission spectra<sup>36</sup> assuming that emission,

(28) Chatt, J. *Adv. Chem. Ser.* 1976, No. 150, 95–103.

(29) Sullivan, B. P., unpublished data.

(30) The analysis we have used to obtain the excited-state dipole moments ignores polarizability corrections of the solute and the error induced by not addressing the realistic situation of an *off-center* excited-state dipole. For the former, it was found that our results did not change significantly by including the polarizability term, in eq 8. The latter correction has been shown by model calculations to yield results that are significantly different from a centered dipole. See: Böttcher, C. F. "The Theory of Electric Polarization"; Elsevier: New York, 1952.

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(35) Cribb, P. H.; Nordholm, S.; Hush, N. S. *Chem. Phys.* 1979, 44, 315.

$(\text{bpy})_2\text{Ru}^{\text{III}}(\text{bpy}^-)^{2+*} \rightarrow (\text{bpy})_2\text{Ru}^{\text{II}}(\text{bpy})^{2+}$ , and ligand to ligand electron transfer,  $(\text{bpy})_2\text{Ru}^{\text{III}}(\text{bpy}^-)^{2+*} \rightarrow (\text{bpy}^-)\text{Ru}^{\text{III}}(\text{bpy})^{2+*}$ , are related processes. With nonnegligible vibrational trapping, localization is expected to occur if electronic coupling between ligands is small.

Optical excitation is rapid ( $10^{-15}$  s) on the time scale for vibrational equilibration so that the excited states are formed in the solvent and vibrational environments of the symmetrical ground states. In the absorption experiment there is no significant basis for vibrational or solvent trapping of the excited electron, and yet our data show that electron transfer in the initial excitation is confined to a single ligand. This apparent paradox can be resolved if electronic coupling is weak. In the absence of any trapping, the frequency of electron hopping

between ligands is given by  $\nu \approx 4V/h$ ,<sup>37</sup> which neglects statistical effects. Even with  $V = 800 \text{ cm}^{-1}$  ( $0.1V$ ),  $\nu \approx 10^{14} \text{ s}^{-1}$  and electron hopping between ligands would be too slow to couple with electronic excitation. The same conclusions should apply to the excited states in polymeric films, glasses, or crystals. Even in the absence of medium or vibrational trapping, relatively strong electronic coupling between bpy ligands is required for electron hopping to become competitive with the time scale for an individual emission event.

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**Registry No.**  $\text{Ru}(\text{bpy})_3^{2+}$ , 15158-62-0;  $\text{Os}(\text{bpy})_3^{2+}$ , 23648-06-8;  $\text{Os}(\text{bpy})_3(\text{py})_2^{2+}$ , 47779-78-2;  $\text{Os}(\text{bpy})_2(\text{CH}_3\text{CN})_2^{2+}$ , 75441-70-2;  $\text{Os}(\text{bpy})_2(\text{dppb})^{2+}$ , 80502-63-2.

(36) (a) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583-5590. (b) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *Ibid.*, in press.

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## Synthetic Routes to Luminescent 2,2'-Bipyridyl Complexes of Rhenium: Preparation and Spectral and Redox Properties of Mono(bipyridyl) Complexes of Rhenium(III) and Rhenium(I)

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New methods of preparing 2,2'-bipyridyl (bpy) complexes of rhenium are described. The procedures involve starting complexes of Re(IV), Re(III), and Re(I) and result in new bpy complexes of the type *fac*- $\text{Re}^{\text{III}}(\text{bpy})(\text{P})\text{Cl}_3$ , *trans,cis*- $[\text{Re}^{\text{III}}(\text{bpy})(\text{P})_2\text{Cl}_2]^+$ , and *trans,cis*- $[\text{Re}(\text{bpy})(\text{P})_2(\text{CO})_2]^+$ , where P is a tertiary phosphine. In addition, the complex *cis*- $[\text{Re}(\text{bpy})_2(\text{CO})_2]^+$  has been prepared, which is a rare example of a bis(bipyridyl)rhenium species. Aspects of the NMR spectra, electronic spectra, and electrochemistry of the complexes are discussed, and special attention is given to the fact that the  $\text{Re}^{\text{I}}(\text{bpy})$  complexes luminescence in fluid solution at room temperature. They represent a growing class of potentially exploitable metal-to-ligand charge-transfer (MLCT) excited-state species of Re(I) that have potential interest for use in photochemical energy conversion schemes.

There is now an extensive photochemistry of charge-transfer (CT) excited states based on polypyridyl acceptor ligands such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) and spin-paired  $d^6$  donor metals like Ir(III),<sup>1</sup> Ru(II),<sup>1</sup> Os(II),<sup>1,2-5</sup> Re(I),<sup>5,6,8</sup> W(0), and Mo(0).<sup>5,7</sup> One of our goals is the development of synthetic procedures for the preparation of emitting excited states. Earlier we described the excited-state

properties of a series of Os(II)-bpy and -phen complexes<sup>2</sup> of the type  $\text{Os}(\text{bpy})_2\text{L}_2^{2+}$  and  $\text{Os}(\text{bpy})\text{L}_4^{2+}$  (L = py,  $1/2$ bpy,  $1/2$ phen,  $\text{PR}_3$ ,  $\text{AsR}_3$ ,  $\text{CH}_3\text{CN}$ , ...), which have long-lived CT excited states in fluid solution at room temperature.<sup>2b</sup>

In this paper we describe an extension of our synthetic efforts to a new series of luminescent CT excited states based on Re(I) of the type  $\text{Re}^{\text{I}}(\text{bpy})\text{L}_2(\text{CO})_2^+$ . An initial example of this type of excited state, *trans,cis*- $[\text{Re}^{\text{I}}(\text{phen})(\text{PPh}_3)_2(\text{CO})_2]^+$ , has been previously reported.<sup>8</sup> Since some of our synthetic routes proceed via the intermediacy of high-valent rhenium precursors, we also report the preparation and spectral and redox properties of mono(bipyridyl) complexes of Re(III) of the type  $\text{Re}^{\text{III}}(\text{bpy})(\text{PR}_3)\text{Cl}_3$  and  $\text{Re}^{\text{I}}(\text{bpy})(\text{PR}_3)_2\text{Cl}_2^+$ . The latter complex is particularly valuable as a synthetic entrée to low-valent Re-bpy chemistry.

### Experimental Section

**Measurements.** <sup>1</sup>H NMR spectra were all acquired at 250 MHz on a Bruker Cryospec WM250 NMR, and shifts are reported vs.  $\text{Me}_4\text{Si}$  as an internal standard. <sup>31</sup>P NMR spectra at 101 MHz were

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