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Factorization of Ligand-Based Reduction Potentials

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The reduction potentials of a series of polypyridine complexes of Mo^0, Os^{II}, Re^I, and Ru^{II}, some nitrosyl Os^{II} and Ru^{II} complexes, and a series of dinitrosylmolybdenum species are parametrized with the $\sum E_L(L)$ parameter. The slope, S_L, and intercept, I_L, of the linear correlations are shown to relate to metal–ligand coupling and interligand coupling through the metal center.

Introduction

We recently discussed[1–4] the parametrization of metal-centered redox potentials in terms of the so-called electrochemical parameters, $E_L(L)$. These enable one to predict the redox potentials of a wide variety of metal complex species using the equation

$$E_{calc}(M^{n+1}/M^n) = S_M\sum E_L(L) + I_M \qquad (1)$$

where S_M and I_M are constants for a particular M^{n+1}/M^n couple and $\sum E_L(L)$ is the sum of the $E_L(L)$ parameters for the various ligands in the complex, which are assumed to be additive.

The ability to predict redox potentials accurately has obvious applications in (i) designing new species with particular redox energies, (ii) checking assignments of observed redox potentials, (iii) predicting charge-transfer energies in optical spectroscopy, (iv) enabling the design of species with particular excited-state potentials, etc. Analysis of the variations in the S_M and I_M parameters also provides fundamental information about metal–ligand binding as a function of metal ion and oxidation state. It is possible, using this method, to decide whether the metal or the ligand is reduced first in a metal complex; this is often useful where ambiguities exist.

Clearly we are interested in the possibility of extending these arguments to ligand-based redox potentials, and we explore here how this might be achieved.

Ligand Reduction Processes

Ligand reductions of classical coordination complexes are in most cases almost fully localized on the ligand.[5–8] In general, the interaction of the positively charged central metal ion with the ligand LUMO causes a stabilization of the lowest unoccupied molecular orbital (LUMO) such that ligand reduction in the metal complex occurs at a less negative potential than reduction of the free ligand, the so-called "central field effect".[7,9] Thus the central metal, through its charge and direct orbital overlap, "tunes" the ligand reduction potential. This is also understood from previous demonstrations of linear correlations between free ligand reduction potentials and complexed ligand reduction potentials[6] and between the former and LUMO energies.[6–9]

Further, the change in charge (between upper and lower oxidation state) on the central metal, which may be monitored by its oxidation potential, is tuned by interaction of the metal with other ligands, W, X, Y, Z, which, initially, we may assume to be electroinactive in the region under consideration. The contribution of the WXYZ ligands in modifying the oxidation potential of the central metal may be derived from $E_L(WXYZ)$ using eq 1. Further, the ligand-localized reduction potential correlates linearly with the metal oxidation potential in a series of ruthenium polypyridine derivatives.[10]

Give the above relationships, we can expect that the ligand reduction potential, E_{red}, in a species such as M(LL)WXYZ with reducible LL (not necessarily bidentate) will correlate with $\sum E_L$(WXYZ), with a slope factor S_L and an intercept I_L:

$$E_{red} = S_L\sum E_L(L) + I_L \qquad (2)$$

The slope factor should be different for each combination of metal ion and reducible ligand (reducible ML "fragment") and should convey information about the extent to which ligands WXYZ couple through the metal ion to influence the ligand-, LL-, localized orbital. The intercept, I_L, will be a monitor of the degree of interaction of the metal ion itself with the ligand LUMO.

In addition to the mundane value of allowing one to predict ligand localized redox potentials, these new parameters convey valuable new insight into the degree of electronic coupling between several ligands in a metal complex, specifically between WXYZ and (LL).

Comparison with Experimental Results

In analyzing the metal-localized potentials, no parameter is introduced for the metal itself. It is therefore logical that, in defining $\sum E_L(L)$, we do *not* include the ligand to be reduced.[12] Thus for considering the reduction potential of $[Ru(bpy)_3]^{2+}$, $\sum E_L(L)$ is defined as $4{*}E_L$(bpy) and not $6{*}E_L$(bpy), and for a species such as $M(LL)_2X_xY_y$, $\sum E_L(L) = 2{*}E_L(LL) + x{*}E_L(X) + y{*}E_L(Y)$ (assuming (LL) is bidentate).

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(11) For consistency with the development used for the ligand parameter $E_L(L)$, data are shown here vs NHE. Most experimental data were collected versus SCE, which is converted to NHE by the factor +0.24 V.

(12) Note that if $\sum E_L(L)$ is summed, as usually, over all six ligands, it would have no effect upon the analysis except to shift the intercept by the amount $S_L{*}E_L(LL)$.

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To obtain a reliable analysis of the data for any given M(LL) reducible fragment requires a sufficiently large database with a wide range of $\Sigma E_L(L)$ values and reduction potentials (e.g., at very least, four compounds with widely ranging potentials). Preferably the same solvent, ideally acetonitrile (dry and of high quality), should be used, with a well-defined reference electrode.[13] Further, there should be no following or preceding coupled chemical reactions which could influence the observed potentials.[14-16] Despite the prolific publication of (polypyridine)metal complexes, relatively few systems exist where all these criteria are met.

We begin with the very well-known[10,17] correlation of Ru^{III}/Ru^{II} potentials in $Ru(bpy)_nX_xY_y$ complexes, with the reduction potential of bound bpy, E_{red}. Figure 1 shows a correlation of the first bipyridine-localized reduction potential with $\Sigma E_L(L)$ as defined above. The correlation is, as expected from prior literature analysis, excellent. Values for S_L and I_L for the "unit" Ru^{II}(bpy), in $Ru(bpy)_2$ and $Ru(bpy)_3$ complexes, are extracted from this graph with regression data shown in Table 1.

We present here, together with that for Ru^{II}(bpy), analysis of data for Mo^0(bpy), $Mo(NO)_2$, Os(NO), Os^{II}(bpy), Re^I(bpy), $Re^I(4,4Me_2bpy)$, Ru(NO), Ru^{II}(bpym), and Ru^{II}(bpz), as shown in Figures 2–5 (see Appendix for observed and calculated data). With the exception of the Ru(bpy) system, where complexes have been selected from an enormous database, all the available data we were able to locate, fitting the criteria above, are included in the correlations.

Mo^0(bpy) System.[18-20] Few reliable data exist (Figure 2). The S_L factor (Table 1) is very low, 0.06. While more data are highly desirable to confirm this value, these data suggest a significantly lower transfer of "information"/charge from the X, Y ligands through molybdenum(0) to the bipyridine ligand. Coupling across the Mo^0 atom is small relative to Ru^{II} (and to the other systems discussed below).

M(NO) Systems, M = Ru, Os.[21-23] This nitrosyl $(NO)\pi^*$-localized redox process (Figure 3) shows a significantly higher slope, S_L, than those for the (polypyridine)ruthenium and -osmium species, revealing that the X, Y ligands couple more effectively to $\pi^*(NO)$, through ruthenium and osmium, than they do to the polypyridine ligands. The intercept is significantly more negative for the osmium species than for the ruthenium species, showing that the latter stabilizes the $\pi^*(NO)$ orbital to a much greater degree than does osmium, through the central field effect. Evidently the coupling between metal and NO orbitals is very strong. One species,[23] the $[Ru(NH_3)_5(NO)]^{3+}$ ion, is fairly poorly predicted and is excluded from the correlation.

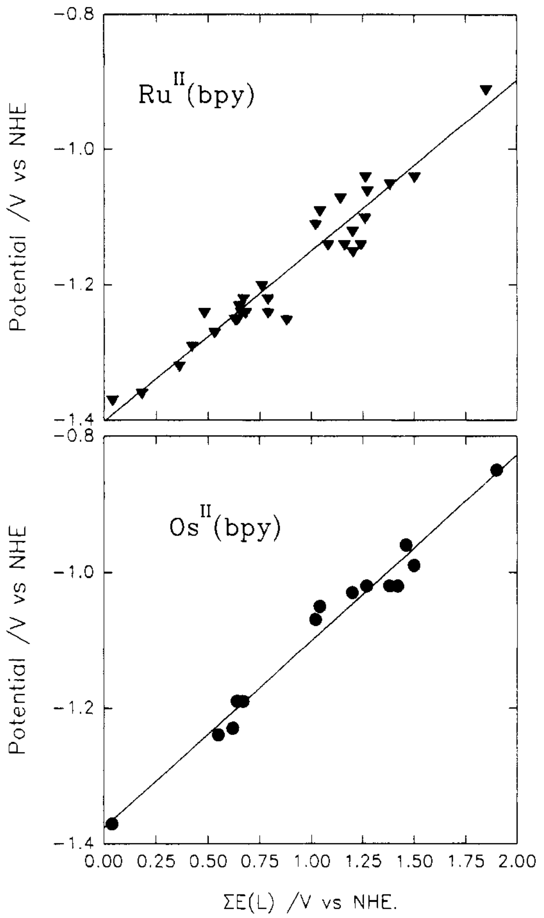

Figure 1. Reduction potentials, E_{red} (V vs NHE), for the fragments Ru^{II}(bpy) (upper, solid triangles) and Os^{II}(bpy) (lower, solid circles) plotted versus $E_L(L)$. See Appendix for listing of complexes and text for relevant references for this and subsequent figures.

Table 1. Regression Data for Reducible M(LL) Fragments (Data vs NHE)[a]

fragment	S_L[b]	I_L[b]	no.[c]	R[d]	bad[e]
Mo^0(bpy)	0.06(±0.02)	−1.56(±0.04)	4	0.900	0
$Mo(NO)_2$	0.43(±0.01)	−0.35(±0.02)	9	0.996	1
$Os^{II}NO$	0.5(±0.06)	−0.58(±0.03)	3	0.996	0
Os^{II}(bpy)	0.27(±0.01)	−1.38(±0.02)	14	0.985	0
Re^I(bpy)	0.27(±0.04)	−1.76(±0.03)	7	0.943	2
$Re^I(4,4Me_2bpy)$	0.49(±0.11)	−2.55(±0.04)	4	0.960	1
$Ru^{II}NO$	0.62(±0.04)	−0.06(±0.03)	7	0.987	1
Ru^{II}(bpy)	0.25(±0.01)	−1.40(±0.03)	30	0.964	0
Ru^{II}(bpym)	0.31(±0.04)	−1.08(±0.03)	6	0.975	0
Ru^{II}(bpz)	0.33(±0.03)	−0.95(±0.03)	10	0.971	0

[a] Fit to eq 7. See Appendix for abbreviations. [b] Standard deviation in parentheses. [c] Number of data points used for regression. [d] Regression coefficient. [e] Poorly behaved data points not used in regression—see text.

$Mo(NO)_2$ System.[24] Since the two NO groups are very closely coupled through the metal center, we treat this metal–double ligand as the unit being reduced and define $E_L(L)$ as the sum of the remaining four ligands. The correlation is excellent again (Figure 2), with a fairly large S_L, showing that the X, Y ligands transmit information to the $Mo(NO)_2$ unit very efficiently. Only one species is poorly predicted (see Appendix). Other metal nitrosyl species will be analyzed elsewhere.[25]

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(13) The evaluation of the exact potential of a reference electrode, unless it is a standard electrode, such as SCE, known to have a very small variation of its potential (usually no more than ±0.02 V) represents a serious problem in determining comparable values for compounds reported from various laboratories. The best procedure is to provide the potential against a standard reference couple (such as ferrocene) or to standardize the electrode against some couple of known redox potential, here frequently the Ru^{III}/Ru^{II} couple of $[Ru(bpy)_3]^{2+}$. Values of potentials given in this way were preferred in collecting the data used for our calculations. These ligand-centered reduction potentials do show some solvent dependence. Data here were primarily recorded in acetonitrile.

(14) While the solvent acetonitrile is regarded as a good electrochemical solvent, it is also quite a good ligand. Thus, for example, upon reduction of bipyridine in $Ru(bpy)_2(PR_3)Cl$, the chloride ion is solvolyzed, resulting in rather complex waves which have been incorrectly identified in the past.[15,16] While this example is known and hence can be taken care of, there may be other examples in the literature where similar chemistry occurs but has not been recognized.

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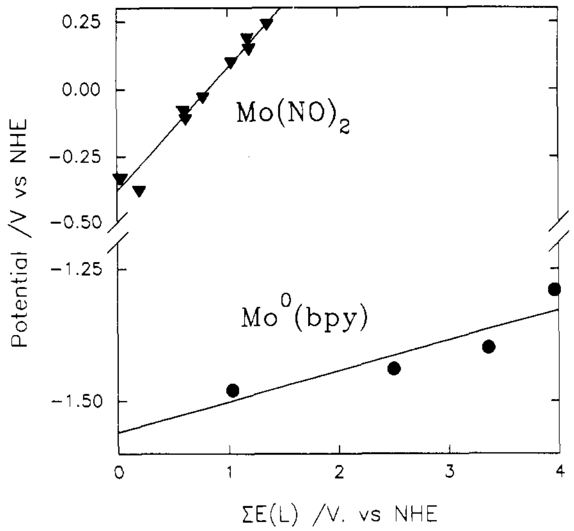

Figure 2. Reduction potentials, E_{red} (V vs NHE), for the fragments $Mo(NO)_2$ (solid triangles) and Mo^0(bpy) (solid circles) plotted versus E_L(L).

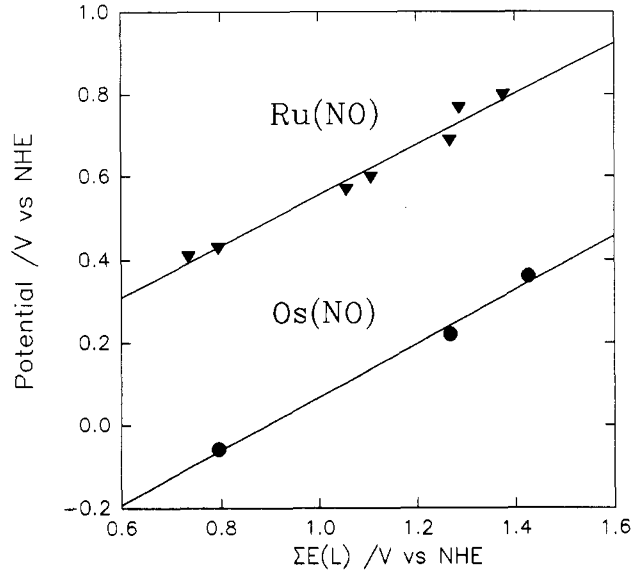

Figure 3. Reduction potentials, E_{red} (V vs NHE), for the fragments Ru(NO) (solid triangles) and Os^{II}(NO) (solid circles) plotted versus E_L(L).

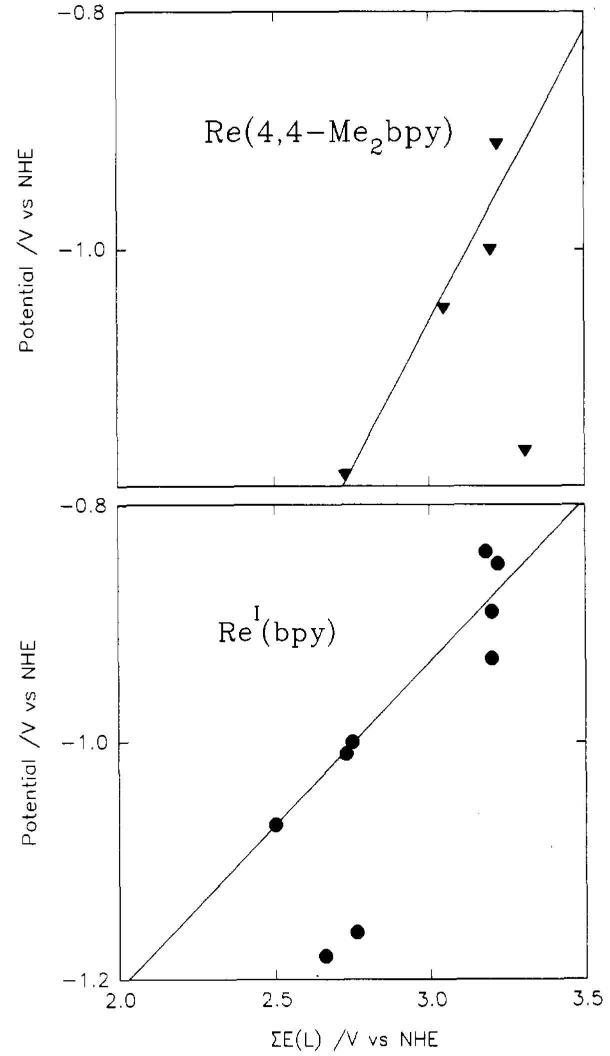

Figure 4. Reduction potentials, E_{red} (V vs NHE), for the fragments Re^I(4,4Me$_2$bpy) (upper, solid triangles) and Re^I(bpy) (lower, solid circles) plotted versus E_L(L).

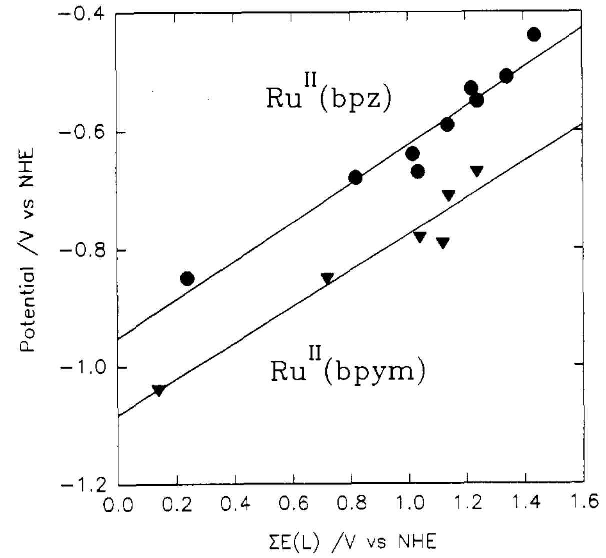

Figure 5. Reduction potentials, E_{red} (V vs NHE), for the fragments Ru^{II}(bpz) (solid circles) and Ru^{II}(bpym) (solid triangles) plotted versus E_L(L).

Os^{II}(bpy) System.[16,26] Since the system is similar to the ruthenium series, the correlation is excellent, with very similar S_L and I_L values. All complexes fitting the above criteria fit the correlation (Figure 1).

Re^I(bpy) System.[27-30] The correlation is excellent (Figure 4) for seven complexes with an S_L value essentially the same as that for Ru^{II}(bpy). There are, however, two complexes, both bis(carbonyl)bis(phosphine)(bipyridine)rhenium(I) species,[27] which are very poorly behaved; their electrochemistry perhaps should be reexamined.

Re^I(4,4Me$_2$bpy) System.[28,31] The correlation is of borderline acceptability (Figure 4) with four good complexes and one poorly behaved species. The S_L value is curiously large and would require that coupling of the X, Y ligands through Re^I to 4,4Me$_2$bpy be much more effective than to that bpy. However, until more data become available, this conclusion is suspect.

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Table 2. Example Showing Effect on Calculated Potential (V vs NHE) of Choice of Reducible Ligand

complex[a]	obs[b]	reducible ligand assumed		
		bpz	bpym	bpy
$[Ru(bpz)_2(bpym)]^{2+}$	–0.51	–0.51	–0.64	
$[Ru(bpz)(bpym)_2]^{2+}$	–0.55	–0.55	–0.67	
$[Ru(bpz)(bpym)(bpy)]^{2+}$	–0.59	–0.58	–0.70	–1.06
$[Ru(bpym)(bpy)_2]^{2+}$	–0.78		–0.76	–1.11

[a] First reduced ligand identified experimentally, cited first in formula. [b] Data in V vs NHE from ref 32.

$Ru^{II}(bpym)$[8c,32] and $Ru^{II}(bpz)$[32] Systems. Both provide excellent correlations (Figure 5) for all relevant data, with no badly behaved species. The S_L values are slightly higher than that for Ru^{II}(bpy), but the difference is small.

Complexes with several potentially reducible ligands, such as $[Ru(bpz)(bpym)(bpy)]^{2+}$ are included in the above correlations. They are treated in an analogous fashion once the ligand being reduced is identified. Generally speaking the reduction is localized in the ligand with the most stable LUMO,[5c,17] which is that whose homoleptic $Ru(LL)_3$ species has the least negative reduction potential, 2,2′-bipyrazine in this example. This particular complex is then grouped with the Ru(bpz) reducible unit with appropriate S_L and I_L values.

Note that if one places these compounds containing several ligands into the wrong group, i.e. misidentifies the first reduced ligand, then the predicted potential will generally not match the experimental value. Table 2 shows some examples where the reduction potential of a species containing two or more different reducible ligands (bpy, bpym, or bpz) is calculated on the basis of either Ru^{II}(bpy), Ru^{II}(bpym), or Ru^{II}(bpz). Thus this procedure provides a simple mechanism for identifying the first reduced ligand.

Significance of the I_L Values. If one were to compare a series of LL ligands for a given metal ion and if the S_L values remain roughly constant, then the I_L values should linearly correlate not only with the LUMO energy but also with both the free ligand (LL) reduction potential, $E_{f(LL)}$, and the potential for reduction of the tris-homoleptic species, $E_{Ru(LL)_3}$. Figure 6 shows this to be the case for the Ru^{II}(LL), LL = bpy, bpym, and bpz, systems. The equations of these lines are

$$I_L = (0.91(\pm0.08))E_{f(LL)} + 0.58(\pm0.03); \quad \text{three species, } R = 0.995 \quad (3)$$

$$I_L = (0.67(\pm0.04))E_{Ru(LL)_3} - 0.49(\pm0.02); \quad \text{three species, } R = 1.00 \quad (4)$$

More directly, in the limit of no interaction between the metal center[33] and the ligand LUMO, I_L would equal $E_{f(LL)}$. Thus the deviation of I_L from $E_{f(LL)}$ is a measure of the influence of the central metal, especially the central field effect.[7–9]

Significance of the S_L Values. This new parameter will provide important information about the metal–ligand interaction and interligand coupling processes. Clearly a broader database of ligands and metal ions is required before a full discussion can ensue; however from the comparison of Mo^0(bpy), Ru^{II}(bpy), and $Mo(NO)_2$, it is apparent that conclusions regarding interligand coupling through the metal can be drawn.

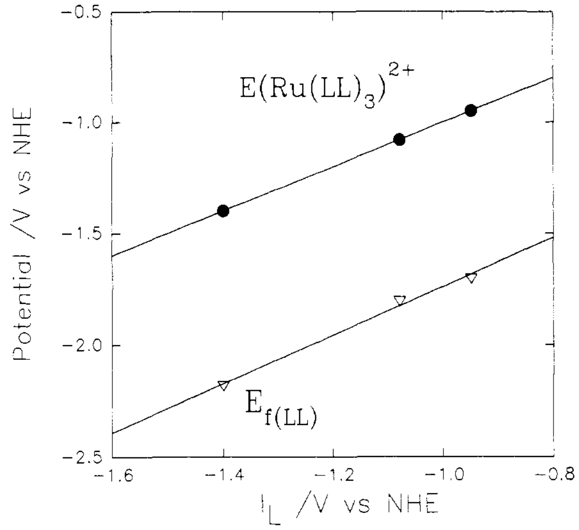

Figure 6. Plots of the intercept, I_L, vs E_{red} for $[Ru(LL)_3]^{2+}$ potentials (in acetonitrile)[7c] (solid circles) and vs the free ligand potential,[7c] $E_{f(LL)}$ (in acetonitrile) (open triangles).

This analysis will also provide relevant data for a theoretical *ab initio* approach to predicting both metal- and ligand-centered redox processes and the establishment of a global database for deriving these potentials from molecular information.

Nonadditive Behavior

The analysis described here assumes additive behavior. It therefore "throws away" possible interactions among the W, X, Y, Z ligands attached to the central ion or assumes their effect is buried in the experimental error. Where the reduced ligand orbital is energetically well separated from those of the X, Y ligands, as is the case with the commonly regarded electroinactive ligands in the potential region usually under study, such as the halides, pyridine, ammonia, etc., this assumption is valid.

However if W, X, Y, Z contain other readily reducible ligands, identical to LL or otherwise, their LUMO energies will be similar and some coupling (ligand–ligand interaction) may be anticipated. If this is important, then the S_L and I_L values for, e.g., M(LL) would differ slightly from those for $M(LL)_2$ or $M(LL)_3$ or M(LL)(LL′) (LL reduced before LL′).

Analysis of the data reported here provides little or no definite evidence for such a supposition being important for this application. For example, $[Re(bpy)_2(CO)_2]^+$ fits well on the line mainly defined by mono-bpy Re species, and mixed Ru(bpz)(bpym) and Ru(bpym)(bpy) fit well on their respective lines. The Ru(bpy) line is defined mainly by $Ru(bpy)_2$ species. In this case, neither $[Ru(bpy)(CN)_4]^{2-}$ nor $[Ru(bpy)(NH_3)_4]^{2+}$ fits well to this line (e.g. in CH_3CN, $[Ru(NH_3)_4bpy]^{2+}$: obs, –1.44 V;[35] calc, –1.33 V), but both these species are highly solvatochromic[34,35] and thus interact strongly with solvent molecules. It is not possible to decide whether their poor behavior is a real deviation from the best $Ru(bpy)_2$ line or is due to a solvent effect. The problem of possible interligand interactions will be addressed elsewhere.[36]

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council for financial support. A.A.V. also thanks the NSERC for an International Fellowship.

Appendix. Data Used to Generate Figures 1–5 and the Regression Data in Table 1

Data are expressed in volts vs NHE, in the following format: complex, observed reduction potential vs NHE, E_{red} (ΣE(L)), calculated reduction potential vs NHE using eq 7, and S_L and I_L from Table 1.

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Molybdenum, Mo^0(bpy): $Mo(bpy)_3$, –1.48 (1.04), –1.50; $Mo(CO)_2(bpy)_2$, –1.44 (2.50), –1.41, $Mo(CO)_3(PPh_3)(bpy)$, –1.40 (3.36), –1.37; $Mo(CO)_4(bpy)$, –1.29 (3.96), –1.33.

Molybdenum, $Mo(NO)_2$: $[Mo(NO)_2(CH_3CN)_4]^{2+}$, 0.24 (1.36), 0.24; $[Mo(NO)_2(CH_3CN)_2(Py)_2]^{2+}$, 0.19 (1.18), 0.16; $[Mo(NO)_2(bpy)(CH_3CN)_2]^{2+}$, 0.15 (1.20), 0.17; $[Mo(NO)_2(bpy)_2]^{2+}$, 0.10 (1.04), 0.10; $[Mo(NO)_2(CH_3CN)_3Cl]^+$, –0.03 (0.78), –0.01; $[Mo(NO)_2(Py)_2(CH_3CN)Cl]^+$, –0.08 (0.6), –0.09; $[Mo(NO)_2(bpy)(CH_3CN)Cl]^+$, –0.11 (0.62), –0.08; $Mo(NO)_2(Py)_2Cl_2$, –0.33 (0.02), –0.34; $Mo(NO)_2(bpy)Cl_2$, –0.33 (0.04), –0.33; $Mo(NO)_2(CH_3CN)_2Cl_2$, –0.38 (0.2), –0.26.

Osmium, Os^{II}(NO): $[Os(NO)(trpy)(bpy)]^{3+}$, 0.22 (1.27), 0.24; $[Os(NO)(bpy)_2(Cl)]^{2+}$, –0.06 (0.80), –0.07; $[Os(NO)(bpy)_2PPh_3]^{3+}$, 0.36 (1.43), 0.34.

Osmium, Os^{II}(bpy): $Os(bpy)_2Cl_2$, –1.37 (0.04), –1.37; $[Os(bpy)_2(diars)]^{2+}$, –1.03 (1.20), –1.06; $[Os(bpy)_2dppene]^{2+}$, –0.99 (1.50), –0.98; $[Os(bpy)_2en]^{2+}$, –1.19 (0.64), –1.21; $[Os(bpy)_2(CH_3CN)Cl]^+$, –1.23 (0.62), –1.21; $[Os(bpy)_2(CO)Cl]^+$, –1.02 (1.27), –1.04; $[Os(bpy)_2(DMSO)_2]^{2+}$, –0.96 (1.46), –0.99; $[Os(bpy)_2(dppb)]^{2+}$, –1.02 (1.42), –1.00; $[Os(bpy)_2(dppm)]^{2+}$, –1.02 (1.38), –1.01; $[Os(bpy)_2(PPh_3)Cl]^+$, –1.19 (0.67), –1.20; $[Os(bpy)_2(PPh_3)CO]^{2+}$, –0.85 (1.90), –0.87; $[Os(bpy)_2(Py)_2]^{2+}$, –1.07 (1.02), –1.11; $[Os(bpy)_2(Py)Br]^+$, –1.24 (0.55), –1.23; $[Os(bpy)_3]^{2+}$, –1.05 (1.04), –1.10.

Ruthenium, Ru^{II}(NO): $[Ru(NO)(bpy)_2(CH_3CN)]^{3+}$, 0.80 (1.38), 0.79; $[Ru(NO)(bpy)_2(Py)]^{3+}$, 0.77 (1.29), 0.73; $[Ru(NO)(trpy)(bpy)]^{3+}$, 0.69 (1.27), 0.72; $[Ru(NO)(bpy)_2(NH_3)]^{3+}$, 0.60 (1.11), 0.62; $[Ru(NO)(bpy)_2(NO_2)]^{2+}$, 0.57 (1.06), 0.59; $[Ru(NO)(bpy)_2(Cl)]^{2+}$, 0.43 (0.80), 0.43; $[Ru(NO)(bpy)_2(N_3)]^{2+}$, 0.41 (0.74), 0.39; $[Ru(NO)(NH_3)_5]^{2+}$, –0.12 (0.35), 0.15.

Ruthenium, Ru^{II}(bpy): $[Ru(bpy)_2(3\text{-}AEP)]^{2+}$, –1.20 (0.76), –1.21; $[Ru(bpy)_2(acac)]^+$, –1.32 (0.36), –1.31; $[Ru(bpy)_2(CH_3CN)_2]^{2+}$, –1.15 (1.20), –1.10; $Ru(bpy)_2Cl_2$, –1.37 (0.04), –1.39; $[Ru(bpy)_2(CO)Cl]^+$, –1.06 (1.27), –1.08; $[Ru(bpy)_2(CO)(CH_3CN)]^{2+}$, –0.91 (1.85), –0.94; $[Ru(bpy)_2(diars)]^{2+}$, –1.12 (1.20), –1.10; $[Ru(bpy)_2(dmpe)]^{2+}$, –1.14 (1.08), –1.13; $[Ru(bpy)_2(dppene)]^{2+}$, –1.04 (1.50), –1.03; $[Ru(bpy)_2(dppe)]^{2+}$, –1.14 (1.24), –1.09; $[Ru(bpy)_2(dppm)]^{2+}$, –1.05 (1.38), –1.06; $[Ru(bpy)_2(en)]^{2+}$, –1.25 (0.64), –1.24; $Ru(bpy)_2(EtXan)_2$, –1.24 (0.48), –1.28; $[Ru(bpy)_2(Glyc)]^+$, –1.29 (0.42), –1.30; $[Ru(bpy)_2(MeSMe)_2]^{2+}$, –1.07 (1.14), –1.12; $[Ru(bpy)_2(MePPh_2)_2]^{2+}$, –1.04 (1.26), –1.09; $[Ru(bpy)_2(NH_3)_2]^{2+}$, –1.24 (0.66), –1.24; $[Ru(bpy)_2(NMI)_2]^{2+}$, –1.24 (0.68), –1.23; $Ru(bpy)_2(Ox)$, –1.36 (0.18), –1.36; $[Ru(bpy)_2(PPh_3)Cl]^+$, –1.22 (0.67), –1.23; $[Ru(bpy)_2(pyd)]^{2+}$, –1.14 (1.16), –1.11; $[Ru(bpy)_2(Py)_2]^{2+}$, –1.11 (1.02), –1.15; $[Ru(bpy)_2(Py)Cl]^+$, –1.27 (0.53), –1.27; $[Ru(bpy)_2(Py)CN]^+$, –1.24 (0.79), –1.20; $[Ru(bpy)_2(Py)NO_2]^+$, –1.22 (0.79), –1.20; $[Ru(bpy)_2(EtSEt)Br]^+$, –1.23 (0.65), –1.24; $[Ru(bpy)_2(EtSEt)Cl]^+$, –1.25 (0.63), –1.24; $[Ru(bpy)_2(EtSEt)(PPh_3)]^{2+}$, –1.04 (1.26), –1.09; $[Ru(bpy)_2(Tol_3P)_2]^{2+}$, –1.10 (1.26), –1.09; $[Ru(bpy)_2(trz)_2]^{2+}$, –1.25 (0.88), –1.18; $[Ru(bpy)_3]^{2+}$, –1.09 (1.04), –1.14.

Ruthenium, Ru^{II}(bpym): $[Ru(bpym)_2(CH_3CN)Cl]^+$, –0.85 (0.72), –0.86; $Ru(bpym)_2Cl_2$, –1.04 (0.14), –1.04; $[Ru(bpym)_3]^{2+}$, –0.67 (1.24), –0.70; $[Ru(bpym)(bpy)_2]^{2+}$, –0.78 (1.04), –0.76; $[Ru(bpym)_2(bpy)]^{2+}$, –0.71 (1.14), –0.73; $[Ru(bpym)_2(Py)_2]^{2+}$, –0.79 (1.12), –0.74.

Ruthenium, Ru^{II}(bpz): $[Ru(bpz)_2bpym]^{2+}$, –0.51 (1.34), –0.51; $[Ru(bpz)(bpym)_2]^{2+}$, –0.55 (1.24), –0.55; $[Ru(bpz)(bpym)(bpy)]^{2+}$, –0.59 (1.14), –0.58; $[Ru(bpz)(bpy)(Py)_2]^{2+}$, –0.64 (1.02), –0.62; $[Ru(bpz)_2(Py)_2]^{2+}$, –0.53 (1.22), –0.55; $[Ru(bpz)_2(CH_3CN)Cl]^+$, –0.68 (0.82), –0.68; $Ru(bpz)_2Cl_2$, –0.85 (0.24), –0.87; $[Ru(bpz)_3]^{2+}$, –0.44 (1.44), –0.48; $[Ru(bpz)(bpy)_2]^{2+}$, –0.67 (1.04), –0.61; $[Ru(bpz)_2(bpy)]^{2+}$, –0.55 (1.24), –0.55.

Rhenium, Re^{I}(bpy): $[Re(bpy)_2(CO)_2]^+$, –1.07 (2.50), –1.07; $Re(bpy)(CO)_3Br$, –1.00 (2.75), –1.00; $Re(bpy)(CO)_3Cl$, –1.01 (2.73), –1.01; $[Re(bpy)(CO)_3Py]^+$, –0.85 (3.22), –0.87; $[Re(bpy)(CO)_3(3,5Me_2Py)]^+$, –0.84 (3.18), –0.88; $[Re(bpy)(CO)_3(4EtPy)]^+$, –0.93 (3.20), –0.88; $[Re(bpy)(CO)_3(4MePy)]^+$, –0.89 (3.20), –0.88; $[Re(bpy)(Me_2PPh)_2(CO)_2]^+$, –1.18 (2.66), –1.03; $[Re(bpy)(CO)_2(PPh_3)_2]^+$, –1.16 (2.76), –1.00.

Rhenium, $Re^{I}(4,4Me_2bpy)$: $[Re(4,4Me_2bpy)(CO)_3(NMI)]^+$, –1.05 (3.05), –1.04; $[Re(4,4Me_2bpy)(CO)_3Cl]^+$, –1.19 (2.73), –1.20; $[Re(4,4Me_2bpy)(CO)_3Py]^+$, –0.91 (3.22), –0.95; $[Re(4,4Me_2bpy)(CO)_3(4MePy)]^+$, –1.00 (3.20), –0.96; $[Re(4,4Me_2bpy)(CO)_3(CH_3CN)]^+$, –1.17 (3.31), –0.91.

Abbreviations: 3-AEP = 3-(aminoethyl)pyridine; 4MePy = 4-methylpyridine; 4EtPy = 4-ethylpyridine; $3,5Me_2py$ = 3,5-dimethylpyridine; $4,4Me_2bpy$ = 4,4′-dimethyl-2,2′-bipyridine; acac = acetylacetonate anion; bpy = 2,2′-bipyridine; bpym = 2,2′-bipyrimidine; bpz = 2,2′-bipyrazine; diars = *o*-phenylenebis(dimethylarsine); dmpe = 1,2-bis(diphenylphosphino)ethane; DMSO = dimethyl sulfoxide; dppe = 1,2-bis(diphenylphosphino)ethane; dppb = *cis*-1,2-bis(diphenylphosphino)benzene; dppm = bis(diphenylphosphino)methane; dppene = *cis*-1,2-bis(diphenylphosphino)ethylene; en = ethylenediamine; EtXan = ethyl xanthate anion; Glyc = glycinate; NMI = *N*-methylimidazole; Ox = oxalate; Py = pyridine; pyd = pyridazine; trpy = terpyridine; trz = 1,2,4-triazole.