

Contribution from the Department of Chemistry,
York University, North York (Toronto), Ontario, Canada M3J 1P3

Electrochemical Parametrization of Metal Complex Redox Potentials, Using the Ruthenium(III)/Ruthenium(II) Couple To Generate a Ligand Electrochemical Series

A. B. P. Lever

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A ligand electrochemical parameter, $E_L(L)$, is described to generate a series which may be used to predict $M(n)/M(n-1)$ redox potentials by assuming that all ligand contributions are additive. In this fashion it performs a purpose similar to that of the Dq parameter in electronic spectroscopy. The parameter is defined as one-sixth that of the Ru(III)/Ru(II) potential for species RuL_6 in acetonitrile. The $E_L(L)$ values for over 200 ligands are presented, and the model is tested over a wide range of coordination complexes and organometallic species. The redox potential of a $M(n)/M(n-1)$ couple is defined to be equal to $E_{calc} = S_M[\sum E_L(L)] + I_M$. The values of S_M and I_M , which are tabulated, depend upon the metal and redox couple, and upon spin state and stereochemistry, but, in organic solvents, are generally insensitive to the net charge of the species. Consideration is given to synergism, the potentials of isomeric species, and the situations where the ligand additivity model is expected to fail. In this initial study, the redox couples are restricted almost exclusively to those involving the loss or addition of an electron to the t_{2g} (in O_h) sublevel.

Introduction

In the mid 1970s there appeared a series of papers dealing with the possibility of correlating electrochemical (oxidation) potentials with HOMO energies and ligand substitution effects.

Treichel and co-workers^{1,2} demonstrated that in a series of manganese carbonyl isocyanide derivatives successive replacement of CO by MeCN raised the oxidation half-potentials by 0.5 V per ligand substituted. Sarapu and Fenske³ further showed that these changes in half-potentials upon ligand substitution were linearly correlated with the HOMO energy (from which orbital oxidation occurred) as calculated by the nonempirical Fenske-Hall MO analysis. Parallel studies by Pickett and Pletcher^{4,5} also with general complexes of the type $[M(CO)_{6-n}L_n]^{p+}$ led them to introduce the equation

$$E(ox) = A + n[dE^\circ/dn]_L + Cy \quad (1)$$

where dE°/dn is the change in potential upon replacement of n CO by n ligands, $E(ox)$ is the metal oxidation potential, and A and C are constants.

This relationship does not permit a distinction to be made between isomeric pairs of complexes such as *cis*- and *trans*- $ML_4L'_2$, and this led to the development of rather more complex relationships, which, in the case of the carbonyl complexes, were related to how many of the metal $d\pi$ orbitals overlapped carbonyl π^* orbitals.^{6,7} This area has recently been reviewed.⁸

Subsequently, there have been a relatively small number of papers⁹⁻¹⁵ that have developed these equations and utilized ligand parameters, P_L , where $P_L = dE^\circ/dn$ initially being defined⁴ as

$$P_L = E_{1/2}[Cr(CO)_6] - E_{1/2}[Cr(CO)_5L] \quad (2)$$

There has not been widespread use of this approach, since P_L values are known for relatively few ligands. Its lack of use may also be because it was seen to be of value to organometallic

chemistry, rather than to coordination chemistry in general.

However, the common basis of this approach is the concept that electrochemical potentials are additive with respect to ligand substitution, at least with respect to substituted metal carbonyls. In this paper we explore the premise that this is in fact a very general observation, common to both organometallic and coordination chemistry. Indeed we demonstrate that, for a wide range of different complexes, electrochemical potentials are additive with respect to ligand variation, and we discuss well defined and predictable situations where this is not the case.

Assuming ligand additivity to be widely justifiable, the intent is to define a ligand electrochemical parameter which, in the fashion that Dq defines the crystal field electronic spectrum of a metal complex, would permit the definition of the redox energies of a metal complex.

An important implication of such a parameter is the conclusion that all ligands would behave in the same relative way to many metal redox couples, be the ligands hard or soft, and this observation would require some rethinking of our chemical bonding models and concepts.

We introduce an electrochemical standard based upon the change in the ruthenium(III)/ruthenium(II) couple in organic solvent (usually acetonitrile), as a function of bound ligand. A new set of ligand parameters, E_L , are proposed that have broad utilization across both organometallic and coordination chemistry, with values for over 200 ligands being currently defined here.

Previously, there have been many studies relating electrochemical potentials to a wide range of other properties such as charge-transfer transition energies, photoelectron binding energies, kinetic parameters, and many different infrared vibrational frequencies, such as CO, N_2 , and M-H stretching frequencies, etc.⁸ Thus, the E_L parameter has the promise of wide applicability. A preliminary report of this method has been made.¹⁶ Haga and co-workers¹⁷ have recently noted the additivity of ligand contributions to ruthenium(III)/ruthenium(II) potentials in some mixed bidentate (amine)ruthenium complexes, while, earlier, Tfouni and co-workers¹⁸ noted similar behavior for some ruthenium complexes in aqueous medium.

Data are restricted to electrochemically reversible or, at least, quasi-reversible redox couples involving the metal ion, $M(n)/M(n-1)$. Data in this paper refer almost exclusively to redox processes occurring within the nonbonding or weakly π -bonding (or antibonding) t_{2g} (in octahedral) subset. This procedure should be used with caution in situations where (a) there are extraordinary synergistic interactions between metal and ligand, (b) the potentials are significantly solvent dependent because of a special solvent

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interaction, (c) strong covalent interaction leads to "noninnocent" behavior, or noninnocent ligands are present, e.g. NO, (d) equilibria are present such that the potential of a complex, in either oxidation state $M(n)$ or $M(n-1)$, such as ML_xY_y , depends upon the bulk concentration of L or Y, e.g. where L and/or Y are solvolyzed rapidly, or where, for example, a supporting electrolyte ion, X^- , might displace L or Y, or in general any preceding or following coupled chemical reaction that significantly changes the inner-shell environment of the metal ion in either oxidation state, (e) the additivity contribution of a bulky ligand depends upon possible steric interactions with other coligands, and (f) for example, the hole size in a macrocycle is fixed and therefore will be an important factor in determining the metal ligand binding energy (e.g. the metal may be in or out of the plane). While caution should be exercised in these cases, the deviation of the observed from calculated potential may provide useful energy information concerning, for example, synergism or noninnocence, etc.

Redox couples involving ligand processes are not included, but there is evidence that these are related to metal couples¹⁹ so that these may ultimately be included.

Experimental Section

All the electrochemical data discussed here, drawn from the previous literature as appropriately referenced in the Appendix, are cited against the NHE. Where other standard electrodes (SCE, SSCE, AgCl/Ag, etc.) were used, the data were corrected according to Bard and Faulkner.²⁰ Many authors added ferrocene as an internal reference to their electrochemical cell. To correct to the NHE, the ferrocenium/ferrocene couple is assumed to lie at 0.665 V vs NHE in acetonitrile.²¹

Results and Discussion

A Standard Electrochemical Data Set. A standard parameter set should (i) be based upon a single standard redox process of a metal center, (ii) be available for a very wide range of compounds by variation of ligand, (iii) be electrochemically reversible or quasi-reversible, (iv) be relatively solvent and supporting electrolyte independent, (v) have potentials that are largely independent of the net charge on the molecule in organic solvents, and (vi) be largely independent of isomerism (cis/trans, *mer/fac*, etc.).

The set of compounds $[Ru(bpy)_xX_{6-2n}]^{n+}$ ($n = 0-3$) (bpy = 2,2'-bipyridine), where X may represent monodentate or polydentate ligands, meet criteria i-vi par excellence, and an extraordinarily large number are known.^{19,22,23} These formed the initial basis set from which the ligand parameters could be derived. The relevant redox process is the Ru(III)/Ru(II) couple, and electrochemical information exists for over 200 different ligands, for these complexes, mostly collected in acetonitrile.

The $[Ru(bpy)_3]^{2+}$ cation was first considered; its Ru(III)/Ru(II) potential occurs at 1.53 V vs NHE (average reported potential) in acetonitrile solution.²³ Since this complex contains six identical Ru-N bonds, the E_L contribution for 2,2'-bipyridine was first defined to be $1.53/6 = 0.255$ V.

In the complex $[Ru(bpy)_xL_{6-2n}]^{m+}$ ($n = 0-3$), with potential E_{obs} , the E_L value for ligand L, $E_L(L)$, was derived such that

$$E_{obs}(Ru^{III}/Ru^{II}) = 2n \times 0.255 + (6 - 2n)E_L(L) \quad (3)$$

In general one may have data for complexes of the type $Ru(bpy)_2L_2$ and $Ru(bpy)L_4$, providing two independent evaluations of $E_L(L)$, once a value for $E_L(bpy)$ is assumed. Values for RuL_6 , where available, (where L may also be $(LL)_3$ bidentate, etc.) are also included in the data set, providing three independent evaluations for $E_L(L)$. In this fashion E_L values for over 100 ligands were initially defined. Subsequently, these values for L other than 2,2'-bipyridine were used to define the best (least squares) average

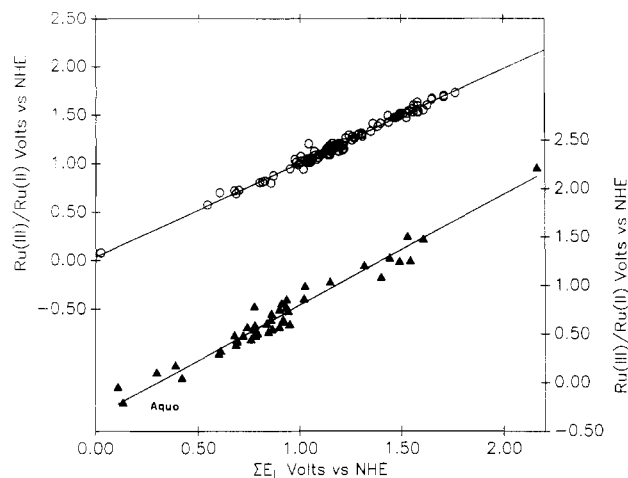


Figure 1. Plot of observed Ru(III)/Ru(II) potentials for $RuX_xY_yZ_z$ complexes against ΣE_L : (top, open circles) measured in organic phase solvent and referred to left-hand y axis; (bottom, closed triangles) measured in water and referred to right-hand y axis. All data are vs NHE. None of the complexes here plotted were used to derive $E_L(L)$ values. For a listing of the data plotted here and in subsequent figures, and for the relevant references, please see the Appendix.

value for $E_L(2,2'$ -bipyridine) by using a data base of 94 ruthenium bipyridine complexes—this final average value of $E_L(2,2'$ -bipyridine) = 0.259 V then became the primary electrochemical standard value against which all other ligand values were subsequently reevaluated. The ruthenium data base was then expanded to include Ru(III)/Ru(II) couples in a range of well-defined species, not restricted to those containing 2,2'-bipyridine.

Generally, several values for $E_L(L)$ for a given ligand were determined from the Ru(III)/Ru(II) couples of the general complexes $RuX_xY_yZ_z$, assuming ligand additivity for X, Y, and Z. The averages of these values (which usually do not differ by more than 20 mV) are listed, for a large range of ligands, in Table I. Ligands showing larger variations from one complex to another,

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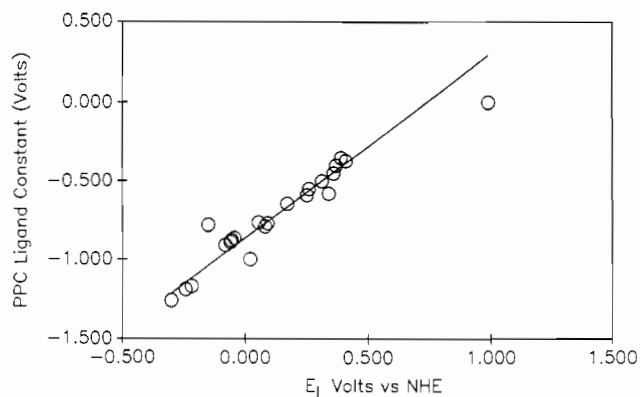


Figure 2. Plot of Pickett/Pletcher ligand parameters against corresponding $E_L(L)$ values.

are indicated (by an asterisk) in Table I and are discussed in more detail below.

Thus for $RuX_xY_yZ_z$, the calculated potential, E_{calc} (in acetonitrile), using the $E_L(L)$ data presented in Table I, is given by

$$E_{calc} = xE_L(X) + yE_L(Y) + zE_L(Z) \quad (4a)$$

$$E_{calc} = \sum_0^i a_i E_L(L_i) = [\sum E_L] \text{ (in abbreviation)} \quad (4b)$$

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The extent to which ligand additivity is valid in ruthenium complexes is shown in Figure 1, where the observed versus calculated potentials for 103 mixed-ligand ruthenium complexes (which were not included in the basis set to define $E_L(L)$) are displayed. Supporting electrolyte effects are generally small.^{24,25} Solvent effects on Ru(III)/Ru(II) couples are also generally very small where different organic solvents are concerned, though with some exceptions.^{26–28} Nevertheless, where possible data recorded in acetonitrile, a very common electrochemical solvent, are utilized. The actual calculated and observed values for these and all other displayed data are collected in the Appendix. Ideally the best line through this data set should have a slope of unity and pass through the origin. In fact, the equation of the best line is (Table II)

$$E_{obs} (V) = 0.97[\sum E_L] + 0.04 \quad R = 0.99 \quad (5)$$

Within the ruthenium series, with few exceptions, there is little difference in potential between pairs of isomers. Moreover, the good correlation shows that the overall net charge on the complex plays little role, at least in acetonitrile, in determining the observed redox potential.

These data were collected from the literature. Erroneous data may have been reported if inadequate care had been taken concerning the purity (especially dryness) of solvents, the electrochemical cell design, the quality of the reference electrodes, and the fact that where organic solvents are concerned excessive cell resistance can lead to appreciable IR drop thereby leading to error, as indeed, can the presence of junction potentials. Moreover, data are reported against a variety of reference electrodes including NHE, SCE, SSCE, ferrocenium/ferrocene, and several different silver-based couples. While, in this collection, data are corrected to a common electrode, NHE, it is evident that the experimental values are subject to some error and the scatter in this line (and those presented later) (Figure 1) may reflect such experimental limitations as much, or more, than it reflects breakdown in ligand additivity.

Correlation with Previous Ligand Parameters. The Ru(III)/Ru(II) data set should correlate with parameters previously introduced by Pickett and co-workers and developed particularly by Pombeiro.^{12–15} Figure 2 shows a plot of the previous ligand parameters, P_L , versus E_L —the correlation is clearly linear except for carbon monoxide, to which we return below. The relationship between these parameters is given by (Table II)

$$P_L (V) = 1.17E_L - 0.86 \quad R = 0.98 \quad (6)$$

for 18 ligands.

This correlation is used to derive values of E_L where the P_L value is known but where there are no appropriate ruthenium complexes from which to derive E_L . Such values are annotated as PPLC in Table I.

Extension to Ruthenium Data in Water. The Ru(III)/Ru(II) potentials of many ruthenium complexes have also been recorded in water. When they are compared with the values calculated by using eq 4, being those that would be observed in acetonitrile, there is a small but significant shift in potential. In Figure 1 is shown a plot of the potential calculated with expression 4 (or in some cases observed directly in acetonitrile) and the observed potentials in water.

A straight-line correlation is observed for the large set of net 2+ charged species, given by

$$E_{obs}(Ru_{eq}) (V) = 1.14[\sum E_L] - 0.35 \quad R = 0.97 \quad (7)$$

The correlation line characteristics for this and subsequent plots are listed in Table II; both regression and standard error data are included. The significance of the values of slopes and intercepts is discussed below. Data for a limited number of 1+ species are also plotted in Figure 1 and appear, perhaps fortuitously, to lie on the same line. A small group of complexes of net charge zero do not appear to fall on this line (vide infra). In general, data in water may be rather more scattered than those collected in a common organic solvent because of the variation in electrolyte and pH. For some ligands, ruthenium redox data are available

Table I. E_L Parameter Values, vs NHE

ligands ^a	E_L , V	ref ^b	ligands ^a	E_L , V	ref ^b
1,10-phenanthroline (phen) {16}	0.26	23	bis(4-pyridyl)acetylene	0.27	23
1,10-phenanthroline, 2,9-dimethyl (2,9-Me ₂ phen)	0.20	23	bis(alkyl)-1,3-diazabutadiene	0.13	CrCO, 57
1,10-phenanthroline, 4,7-dimethyl (4,7-Me ₂ phen)	0.23	23	bibenzimidazolato(1-)	-0.03	58
1,10-phenanthroline-5,6-dione (phendione)	0.28	45	bibenzimidazolato(2-)	-0.18	58
1,1,1,5,5,5-hexafluoro-2,4-pentanedionato(1-) (hfac)	0.17	46	bibenzimidazole (BiBizim)	0.17	58
1,1,1-trifluoro-2,4-pentanedionato(1-) (tfac)	0.03	46	biimidazole (BiimH ₂)	0.13	58
1,1-bis(diphenylarsino)methane (PDA)	0.35	23	bromide(1-) {5}	-0.22	23
1,1-bis(diphenylphosphino)methane (dppm)	0.43	47	1-butanethiolate(1-)	-0.55	59
1,2-bis(dimethylphosphino)ethane	0.28	PPLC, 12	butylamine (BA)	0.13	23
1,2-bis(dimethylphosphino)benzene (diphos)	0.31	48	butyronitrile (PRC)	0.35	23
1,2-bis(dimethylarsino)benzene	0.30	48	carbon monoxide (CO)	0.99	23
1,2-bis(diphenylarsino)benzene (diars)	0.34	23	chloride(1-) {45}	-0.24	23
1,2-bis(diphenylphosphino)benzene (ophenPPh ₂)	0.45	Os, 44	cyanate(1-)	-0.25	PPLC
1,2-bis(diphenylarsino)ethane (Ph ₂ AsCCAsPh ₂)	0.44	Os, 44	cyclam ([14]aneN ₄)	0.10	aq, 60
1,2-bis(diphenylphosphino)acetylene (ADP)	0.46	23	cyanide(1-) {6}	0.02	23, 61
1,2-bis(diphenylphosphino)ethane (Ph ₂ PCCPPh ₂) (dppe)	0.36	23	cyclohexyl isocyanide	0.32	PPLC
cis-1,2-bis(diphenylphosphino)ethene (Ph ₂ PC=CPPH ₂)	0.49	47	diethylthiocarbamate(1-)	-0.08	23, 62
1,2-bis(diphenylphosphino)propane (PDP)	0.42	47	diethyl sulfide {6}	0.35	47
1,2-bis(ethylthio)ethane	0.32	47	dimethylthiocarbamate(1-)	-0.12	23
1,2-bis(methylthio)ethane	0.33	47	dimethylglyoximate(1-)	0.01	53
1,2-bis(phenylthio)ethane	0.36	47	dimethyl dimercaptomaleato(2-)	-0.47	59
1,2-diamino-2-methylpropane	0.11	23	dimethylphenylphosphine (MMP)	0.34	23
1-(2-pyridyl)-3,5-dimethylpyrazole (pydipy)	0.23	23	dimethylphosphine	0.34	PPLC
1,2,4-triazole, 2,3,5-tri-2'-pyridyl	0.29	23	dimethyl sulfide	0.31	47
1,3-diphenyl-1,3-propanedionato(1-) (dbmo)	-0.04	46	dimethyl sulfoxide* (DMSO) {8}	0.47	47, 50, 63
1,4,5,8-tetrazaphenanthrene	0.36	23	dinitrogen	0.68	PPLC
1-phenyl-1,3-butanedionato(1-) (bzac)	-0.06	46	di-2-pyridyl ketone* (dpk)	0.28	64
1-phenyl-4,4,4-trifluoro-2,4-pentanedionato(1-) (bztfo)	0.05	46	di-2-pyridylaminato(1-)*	-0.16	65
1,2-bis(4-pyridyl)ethane (BPA)	0.26	23	di-2-pyridylamine	0.18	65
2,2'-bipyridine {94}	0.259	23	ethanethiolate(1-)	-0.56	59
2,2,6,6-tetramethyl-3,5-heptanedionato(1-) (dpmo)	-0.13	46	ethyl nitrite	0.70	23
2,2'-bipyrazine (bpz) {6}	0.36	23	ethylene	0.76	aq, 66
2,2'-bipyrazinium(1+)	0.75	23	ethylenediamine	0.06	23, 27
2,2'-bipyridine, 4,4'-dibromo (4,4-Br ₂ bpy)	0.28	23	ethylnitrile {4}	0.33	23
2,2'-bipyridine, 4,4'-dimethyl (4,4-Me ₂ bpy)	0.23	23	ethyl xanthato(1-)	-0.02	23
2,2'-bipyridine, 4,4'-diphenyl	0.23	23	fluoride(1-)	-0.42	CrCO, 67
2,2'-bipyridine, 4-methyl-4'-vinyl	0.23	23	formate(1-) (For)	-0.30	23
2,2'-bipyridine, 4-nitro	0.30	23	glycine(1-) (glyc)	-0.05	23
2,2'-bipyridine, 5,5'-dimethyl (5,5-Me ₂ bpy)	0.23	23	hydride(1-)	-0.30	PPLC
2-(2-pyridyl)quinoline (pq)	0.25	23	hydroxide(1-)	-0.59	PPLC
2,4-pentanedionato(1-) (acac)	-0.08	23, 46, 49	imidazole	0.12	23
2-methylthioquinoline	0.30	47	imidazole, 4-vinyl	0.14	23
3,3'-biisoquinoline (i-biq)	0.24	23	imidazole, N-methyl (MeIm)	0.08	23
3,4-bis(methylthio)toluene	0.38	47	iodide(1-)	-0.24	23
3,6,9-trithiaundecane	0.34	50	isonicotinamide (isna)	0.26	aq, 68
3-amino-1-propene	0.13	23	isonitrosopropiophenoato(1-)	0.01	23
3-bromo-2,4-pentanedionato(1-) (3-Br-acac)	-0.03	51	isopropyl nitrite	0.68	23
3-chloro-2,4-pentanedionato(1-) (3-Cl-acac)	-0.03	51	isopropylamine	0.05	23
3-iodo-2,4-pentanedionato(1-) (3-I-acac)	-0.03	51	isopropyl isocyanide	0.36	PPLC
3-methyl-2,4-pentanedionato(1-) (3-Meacac)	-0.11	51	maleonitriledithiolate(2-) (mnt)	-0.33	59
3-phenyl-2,4-pentanedionato(1-) (3-Phacac)	-0.09	51	methyl nitrite	0.72	23
4-cyanopyridine-Ru(NH ₃) ₅ ²⁺	0.33	52	methylidiphenylphosphine (MPP)	0.37	23
4-methoxyphenyl cyanide	0.60	23	methyl isocyanide	0.37	PPLC
4,4'-bipyridine (4,4-bpy)	0.27	23	methyl phenyl sulfide	0.33	47
4,4'-bithiazole (btz)	0.20	23	naphthyridine	0.24	23
8-hydroxyquinolinato(1-)	-0.09	53	nitrate(1-) {8}	-0.11	23
8-methylthioquinoline	0.30	23	nitrite(1-)	0.02	23
acetonitrile {18}	0.34	23	norbornadiene	0.46	23
acrylonitrile (ECN)	0.38	23	n-butyl isocyanide	0.45	69
ammonia	0.07	23, 27	N-methylbenzohydroximato, p-methyl (1-)	-0.22	54
azide(1-)	-0.30	23	N-methylbenzohydroximato, p-nitro (1-)	-0.18	54
benzohydroximato, p-methoxy (2-)	-0.54	54	N-methylpyrazinium (1+) (NMePyz)	0.79	Os, 26, 68
benzohydroximato, p-nitro (2-)	-0.50	54	N-methylpyridinium, 4-cyano (1+)*	0.45	52
benzohydroximato(2-)	-0.52	54	N-(2-pyridylmethylidene)methylamine (pymi)	0.27	23
phenyl isocyanide	0.41	23	octaethylporphyrin(2-) (OEP) (metal in plane)	-0.07	71
phenyl isocyanide, 2,6-dichloro	0.46	PPLC	oxalate(2-)	-0.17	23
phenyl isocyanide, p-chloro	0.38	PPLC	o-acetylphenolate(1-)	-0.07	70
phenyl isocyanide, p-methoxy	0.36	PPLC, 37	o-propionylphenolate(1-)	-0.10	70
phenyl isocyanide, p-methyl	0.37	PPLC	pentafluorobenzenethiolato(1-)	-0.33	23
benzylamine (PMA)	0.14	23	perchlorate(1-)	0.06	23
benzyl isocyanide	0.56	37	phenol, 2-benzimidazolato (1-)	-0.20	58
binaphthyridine* (binapy)	0.27	55	phenol, 2-benzimidazolato (2-)	-0.35	58
bipyridazine	0.30	23	phenyl cyanide	0.37	23
bipyrimidine	0.31	23	phenyl cyanide, 3-cyano	0.43	aq, 72
bipyrimidine, 4,4-dimethyl	0.24	23	phenyl cyanide, 4-chloro	0.40	aq, 72
biquinoline (biq) {17}	0.29	55, 56	phenyl cyanide, 4-cyano	0.49	aq, 72

Table I (Continued)

ligands ^a	E_L , V	ref ^b	ligands ^a	E_L , V	ref ^b
phenyl cyanide, 4-methoxy	0.38	aq, 72	pyrrolidinecarbodithionato(1-)	-0.12	23
phenyl cyanide, 4-methyl	0.37	aq, 72	<i>p</i> -chlorothiophenolate(1-)	-0.43	59
polyvinylimidazole	0.11	23	<i>p</i> -methylthiophenolate(1-)	-0.48	59
pyridazine (pyd)	0.32	23, 68	<i>p</i> -toluenethiolate(1-)	-0.48	59
pyrazine (pyz) {5}	0.33	23	<i>p</i> -toluenesulfonate(1-)	-0.13	23
pyrazine, 2,3-bis(2-pyridyl)* (dppyz)	0.32	23, 73, 74	salicylaldehyde(1-)	-0.04	70
pyrazole	0.20	23	selenocyanate(1-)	-0.23	75
pyrazole(1-)	-0.24	23	dipyrido[3,2- <i>c</i> :2',3'- <i>e</i>]pyridazine (Taphen)	0.37	23
pyridine {24}	0.25	23	terpyridine {16}	0.25	23
pyridine, 2-(aminoethyl)	0.17	23	tetrahydrothiophene	0.30	50
pyridine, 2-(aminomethyl)	0.13	23	tetraphenylporphyrin(2-) (TPP) (metal in plane)	0.00	71
pyridine, 2-benzimidazolato (1-)	-0.03	58	tetraaza macrocycle (TZ) ^c	0.14	63
pyridine, 2-benzimidazolyl	0.20	58	thiocyanato(1-)	-0.06	23
pyridine, 2-imidazolyl	0.18	58	thiophenolato(1-)	-0.53	23
pyridine, 2-isoquinolyl	0.26	23	thiourea	-0.13	23
pyridine, 2-phenylazo (Azpy)	0.40	23	1,2,4-triazole	0.18	23
pyridine, 2-quinolyl	0.25	23	1,2,4-triazole, 3,5-bis(pyridin-2-yl) (1-)	0.05	76
pyridine, 2-tolylazo (MeAzpy)	0.41	23	1,2,4-triazole, 3,5-bis(pyridin-2-yl)	0.11	76
pyridine, 2-(2'-naphthylridinyl)	0.22	23	1,2,4-triazole, 4-allyl	0.12	23
pyridine, 3,5-dichloro	0.33	aq, 72	1,2,4-triazole, 4-methyl	0.11	23
pyridine, 3,5-dimethyl	0.21	aq, 72	1,2,4-triazole, 4-phenyl	0.14	23
pyridine, 3-(aminoethyl)	0.12	23	1,2,4-triazole(1-)	-0.17	23
pyridine, 3-carboxamido	0.26	aq, 72	triethylphosphine	0.34	42, 56
pyridine, 3-iodo	0.29	23	trifluoroacetate(1-) (TFA)	-0.15	23
pyridine, 4-acetyl	0.30	23	trifluorosulfonate(1-)	0.13	Os, 77
pyridine, 4-carbaldehyde	0.31	aq, 72	trimethylphosphine	0.33	Os, 56, 77
pyridine, 4-carboxamido	0.28	aq, 72	trimethyl phosphite	0.42	69
pyridine, 4-carboxy	0.29	aq, 72	triphenylarsine	0.38	23
pyridine, 4-chloro	0.26	aq, 72	triphenylphosphine {10}	0.39	23
pyridine, 4-cyano	0.32	52	triphenyl phosphite	0.58	PPLC
pyridine, 4-cyano (nitrile bonded)	0.38	52	triphenylstibine	0.38	23
pyridine, 4-methyl (4-pic)	0.23	23	tritolyphosphine (MeP)	0.37	23
pyridine, 4-phenyl	0.23	Os, 68	tri- <i>n</i> -butylphosphine	0.29	56
pyridine, 4-styryl	0.23	23	tri- <i>n</i> -propylphosphine	0.34	56
pyridine, 4-(trifluoromethyl)	0.32	aq, 72	<i>t</i> -1,2-diaminocyclohexane	0.09	23
pyridine, 4- <i>tert</i> -butyl	0.23	23	<i>t</i> -1,2-bis(4-pyridyl)ethene (BPE)	0.26	23
pyridine, 4-vinyl {6}	0.20	23	<i>tert</i> -butyl isocyanide	0.36	PPLC
pyridine, poly(4-vinyl) (PVP)	0.23	23	<i>tert</i> -butyl mercaptan(1-)	-0.55	59
pyrimidine (pyrim)	0.29	23	vinylimidazole	0.13	23
pyrimidinium(1+)	0.43	23	water* {6}	0.04	42, 78

^aThe number in parentheses is the net charge on the ligand; the letter code in parentheses is the abbreviation used in the Appendix and in ref 23. Most data were derived from potentials observed with one to three compounds—numbers in braces show where more than three compounds were used and the data averaged. An asterisk means that the E_L datum is somewhat variable from one complex to another. ^bOs, CrCO, and aq mean that the data were derived from osmium, chromium carbonyl, or aqueous ruthenium ammine data as referenced, respectively, assuming a perfect fit to the appropriate correlation expression. PPLC signifies derived by fitting to the Pickett/Pletcher ligand parameter. ^cTZ = 2,7,12,17-tetramethyl-1,6,11,16-tetrazaporphyrinogen.⁶³

in water but not in an organic solvent. In these cases E_L values are calculated from eq 7 and are included in Table I (annotated as aq).

Comparison with Other Electrochemical Data Sets. It is necessary to demonstrate that these $E_L(L)$ parameters may be used for many other metal ions in a range of oxidation states and are not restricted to ruthenium and closely related metal ions such as osmium.

Thus, we plot the observed potentials for any $M(n)/M(n-1)$ couple, for the general species $MX_xY_yZ_z$, against those calculated with eq 4, to obtain what we refer to here as an E_L plot. Least-squares analysis to fit calculated to the observed data yields the equation

$$E_{\text{obs}} = S_M \left[\sum_0^i a_i E_L(L_i) \right] + I_M$$

$$E_{\text{obs}} = S_M [\sum E_L] + I_M \quad (8)$$

to derive S_M and I_M for the specific couple $M(n)/M(n-1)$ in the species $MX_xY_yZ_z$.

For any given $M(n)/M(n-1)$ couple, all complexes of given stereochemistry and spin state should fall on the same correlation line, i.e. have the same slope S_M and intercept I_M . Using the Fe(III)/Fe(II) couple, by way of example, one expects that all species where the Fe(III) complex is six-coordinate and low spin, and the Fe(II) complex is six-coordinate and low spin, will fall

on the same correlation line. However, species where, for example, both the iron oxidation states form high-spin six-coordinate complexes will generally have values for S_M and I_M different from those for the aforesaid line. Similarly if the Fe(III) species is low spin, but the Fe(II) species is high spin, yet another correlation line may be generated.

Thus, for each oxidation state couple $M(n)/M(n-1)$, a series of correlations may exist if there is variability in stereochemistry and/or spin state. This follows because the observed redox potential is a measure of the relative binding constants for the ligands with $M(n)$ and with $M(n-1)$, and such binding constants will generally depend upon both stereochemistry and spin state.

Consider first a series of osmium complexes (Os(III)/Os(II) couple), where it is not surprising that an E_L plot shows an excellent correlation (Figure 3); indeed it has been previously demonstrated that the corresponding potentials for analogous ruthenium(II) and osmium(II) species are linearly related.²⁴ There is also a good correlation for aqueous-phase osmium(III)/osmium(II) data (Figure 3). Table I includes a few ligands derived from osmium data and the appropriate correlation line (Table II), where such data were not available from ruthenium species. They are annotated as Os.

The E_L plot for the Cr(III)/Cr(II) data set (low-spin Cr(II)) shown in Figure 4 illustrates a comparison of the observed Cr(III)/Cr(II) couples for a variety of chromium complexes, in organic solvents, with a notation indicating their net charge (of

Table II. Slope and Intercept Data^a (V vs NHE)

	slope, S_M/SD^d	intercept, I_M/SD^d	regress ^b	no. ^c	solvent
Chromium					
Cr(III)/Cr(II)(LS)	1.18/0.06	-1.72/0.15	0.98	18	organic
Cr(III)/Cr(II)(LS)	0.575/0.04	-1.12/0.05	0.98	8	water
Cr(III)/Cr(II)(HS)	0.84/0.05	-1.18/0.09	0.98	14	organic
Cr(I)/Cr(0) ^e	0.52/0.02	-1.75/0.12	0.97	39	organic
Iron					
Fe(III)/Fe(II)(LS)	0.68/0.02	0.24/0.04	0.99	24	water
Fe(III)/Fe(II)(LS) ^e	1.10/0.05	-0.43/0.12	0.99	14	organic
Fe(III)/Fe(II)(HS)	0.89/0.04	-0.25/0.04	0.99	8	organic
Fe(III)/Fe(II)[5CN] ^f	1.60/0.14	g	0.99	5	organic
Fe(III)/Fe(II)[5CN] ^h	1.61/0.12	g	0.99	5	organic
Manganese					
Mn(III)/Mn(II)[5CN]	0.38/0.12 ^f	g	0.85	6	organic
Mn(II)/Mn(I) ^e	0.81/0.02	-1.76/0.08	0.99	23	organic
Molybdenum					
Mo(I)/Mo(0)	0.74/0.03	-2.25/0.10	0.99	24	organic
Niobium					
Nb(V)/Nb(IV)	0.76/0.02	1.24/0.02	0.999	3	organic
Nb(IV)/Nb(III)	0.75/0.01	-0.12/0.01	0.999	3	organic
Osmium					
Os(III)/Os(II)	1.01/0.02	-0.40/0.11	0.98	80	organic
Os(III)/Os(II)	1.61/0.05	-1.30/0.11	0.99	18	water
Rhenium					
Re(IV)/Re(III)	0.85/0.05	0.50/0.13	0.98	18	organic
Ruthenium					
Ru(III)/Ru(II)	1.14/0.04	-0.35/0.09	0.97	44	water
Tantalum					
Ta(V)/Ta(IV)	0.79/0.08	0.66/0.07	0.985	5	organic
Pickett/Pletcher					
	1.17/0.05	-0.86/0.04	0.98	18	
Ruthenium					
Ru(III)/Ru(II) XYZ	0.97/0.01	0.04/0.03	0.99	103	organic

^aAll six-coordinate except where noted. ^bCorrelation coefficient. ^cNumber of data points. ^dStandard error in volts. ^eSee Table III for isomer. ^fTetraphenylporphyrin—metal out of plane. ^gIndeterminate intercept due to use of a macrocycle core of uncertain E_L value. ^hFrom octaethylporphyrin—metal out of plane. 5CN = five coordinate; LS = low spin; HS = high spin.

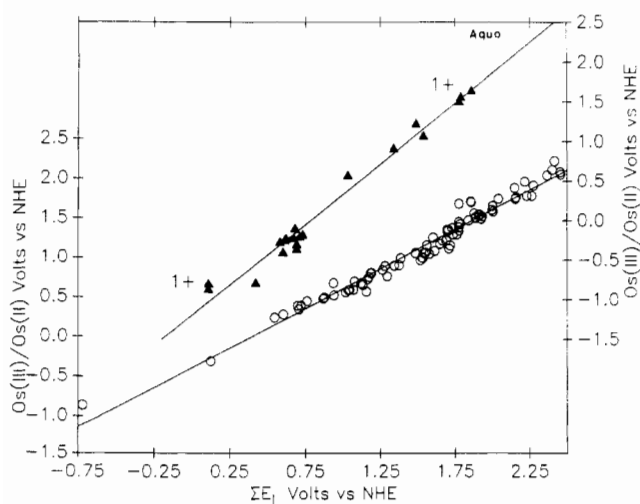


Figure 3. Plot of observed Os(III)/Os(II) potentials for OsX_yZ_z complexes against ΣE_L : (bottom, open circles) measured in organic phase solvent and referred to left-hand y axis; (top, closed triangles) measured in water and referred to right-hand y axis.

the lower oxidation state species here and henceforth). The reasonable linearity of this plot shows that these chromium data are fairly well behaved vis-à-vis ligand additivity. Note that the 2+, 0, and 2- species all lie on the same line and thus the relative unimportance of net charge is demonstrated. Figure 4 also shows corresponding organic solvent data for high-spin chromium(II) species (charges 1-, 1+, 2+) with the slope and intercept differing

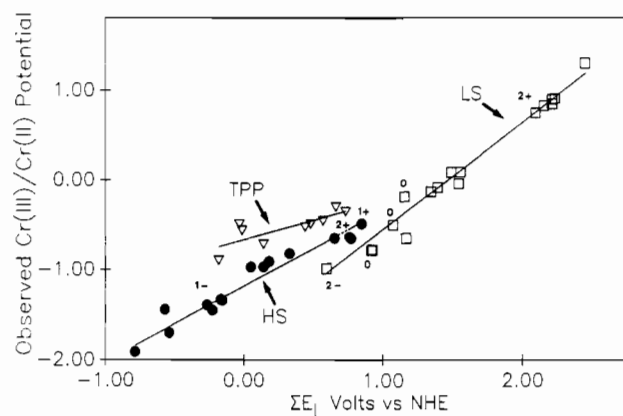


Figure 4. Plot of observed Cr(III)/Cr(II) potentials in organic phase solvent against ΣE_L . The open squares (upper right) represent six-coordinate, low-spin (LS) chromium(II) species, all of which carry a net 2+ charge except for those indicated to carry a 0 or 2- charge. The closed circles (lower left) represent six-coordinate, high-spin (HS) chromium(II) species, all of which carry a 1- charge except for those indicated with a 1+ or 2+ charge. The open triangles (center left) represent six-coordinate XYCr(TPP) species (TPP = tetraphenylporphyrin). In this figure and those which follow, the charge refers to the lower oxidation state complex.

from those of the low-spin species.

In water solvent (Figure 5), an excellent line is observed for all the low-spin chromium(II) net charge 2+ species; the $[Cr(CN)_6]^{4-}$ species also lies on this line though this is rather unexpected and may be fortuitous (see further comment below).

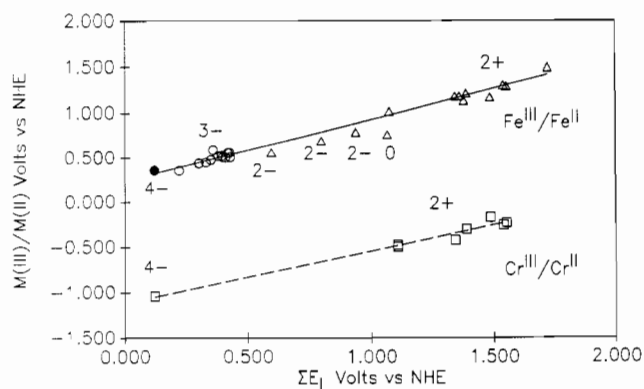


Figure 5. Top: Plot of observed Fe(III)/Fe(II) potentials in water, for six-coordinate, low-spin iron(II) complexes against ΣE_L . The open triangles represent net 2+ species except for those marked with 0 or 2- charges. The species represented by open circles all carry a 3- net charge. The closed circle is a 4- charged species. Bottom: Plot of observed Cr(III)/Cr(II) potentials in water, for six-coordinate, low-spin chromium(II) complexes against ΣE_L . All species carry a 2+ charge except for the 4- species, as indicated.

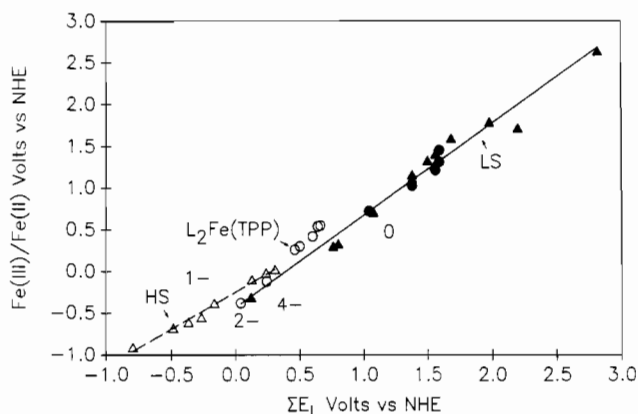


Figure 6. Plots of observed Fe(III)/Fe(II) potentials in organic phase solvent against ΣE_L : (upper right, closed triangles) low-spin (LS, both Fe(III) and Fe(II)) complexes with 2+ charges except where otherwise indicated (line also includes the species Fe(DMG-BF₂)₂XY (closed circles) and L₂FeTPP (open circles) (see text)); (lower left, open triangles) high-spin (HS, both Fe(III) and Fe(II)) six-coordinate complexes of 1-charge.

Similar data are observed with iron. Figure 6 shows how the Fe(III)/Fe(II) potential, as measured in an organic solvent, of a series of six-coordinate iron(II) complexes (low-spin Fe(II) and Fe(III)) depends upon their E_L sum. There is clearly a linear correlation independent of charge. Thus, for the (LS)Fe(III)/(LS)Fe(II) couple illustrated in Figure 6, the least-squares equation is

$$E_{\text{obs}} (\text{V}) = 1.11[\Sigma E_L] - 0.43 \quad R = 0.99 \quad (9)$$

This equation should be appropriate for *all* iron complexes in an organic solvent, provided that both the iron(II) and iron(III) complexes are low-spin octahedral and generally excluding situations as defined in the Introduction. Six-coordinate high-spin complexes (Fe(III)/Fe(II) couple, both high spin) in organic solvents exhibit potentials that fall on a different line (Figure 6).^{29,30} Thus, these two lines (Table II) should provide the means of predicting the Fe(III)/Fe(II) potentials for most six-coordinate iron complexes, in organic solvents.

In water (Figure 5) some (low-spin Fe(II), Fe(III)) charged species have potentials that fall on a line which is apparently defined by a group of 2+ net charge species and the range of [Fe(CN)₅(R-py)]³⁻ species (vide infra). Species of 0 and 2- charge fall somewhat off this line, but as in the chromium plot (Figure 5), the [Fe(CN)₆]⁴⁻ species appears to fall on the main line.

We can expect to generate a species of such relationships for, in general, all metal redox couples (at least those involving the

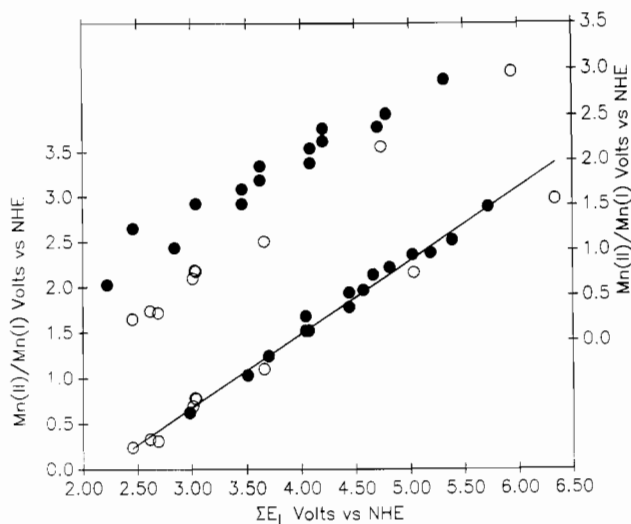


Figure 7. Plot of the Mn(II)/Mn(I) potentials in organic phase solvent for a variety of organometallic, six-coordinate manganese species versus ΣE_L : (upper data set, right-hand y axis) raw ΣE_L data uncorrected for the specific isomer involved; (lower data set, left-hand y axis) isomer correction for carbon monoxide and isonitrile ligands included. The open circles are carbonyl complexes that do not contain an isonitrile ligand. The closed circles are complexes that do contain at least one isonitrile ligand.

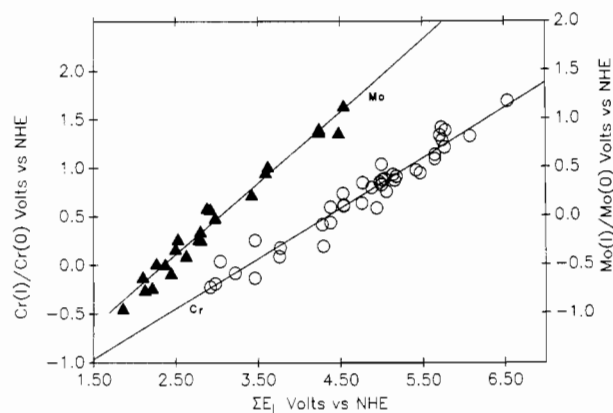


Figure 8. Lower data set (left-hand y axis, open circles): Plot of the Cr(I)/Cr(0) potentials in organic phase solvent for a variety of organometallic, six-coordinate chromium species versus ΣE_L , including an isomer correction for carbon monoxide or isonitrile ligands. Upper data set (right-hand y axis, closed triangles): Plot of the Mo(I)/Mo(0) potentials in organic phase solvent for a variety of organometallic, six-coordinate molybdenum species versus ΣE_L (not isomer corrected; see text).

t_{2g} set in O_h) allowing for changes in spin state, stereochemistry, and coordination number and also for water or organic solvent measurements.

In Figures 7–10 are shown data sets for a variety of other couples ranging from classical six-coordinate coordination complexes of iron, chromium, ruthenium, rhenium, osmium, niobium, and tantalum to organometallic derivatives containing carbonyls, dinitrogen, phosphines, etc. Some five-coordinate species are also included. There is no doubt that these plots are generally linear and that ligand additivity is amply demonstrated over a very wide range of complexes.

Correction for Isomers. Within the ruthenium data set, *cis/trans*, *mer/fac* isomers, etc. usually have essentially the same potential, and indeed, for many such pairs of coordination complex isomers for other redox couples, there is little difference in potential, though there are certainly a few exceptions.

This is not generally true for organometallic species, where such differences may be 0.1–0.2 V. We follow here the method of Treichel and Bursten,²⁸ who developed a correction for the HOMO energy of a carbonyl complex in terms of the number of carbonyl

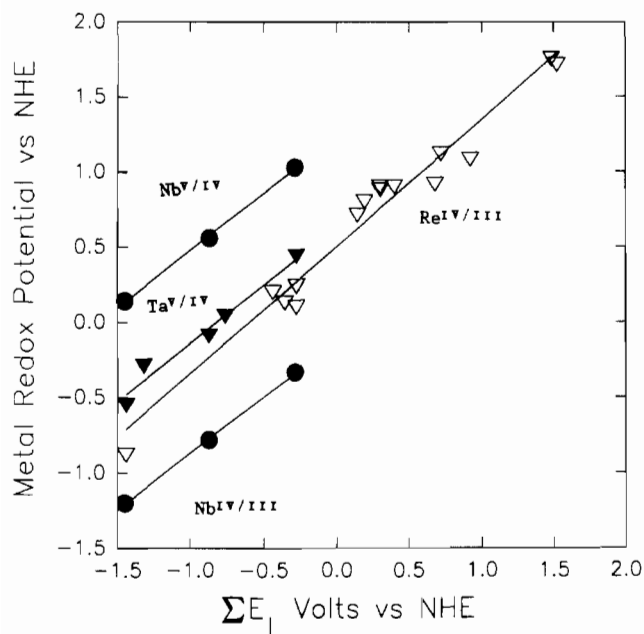


Figure 9. Plots of redox data for six-coordinate Nb(V)/Nb(IV) (top, solid circles), Nb(IV)/Nb(III) (bottom, solid circles), Ta(V)/Ta(IV) (solid triangles), and Re(IV)/Re(III) (open triangles) versus ΣE_L , as annotated.

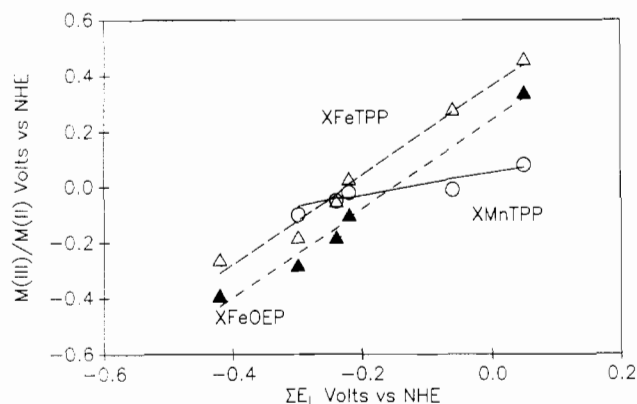


Figure 10. Plots of some redox data for five-coordinate macrocyclic species versus ΣE_L , as annotated: XFeTPP (open triangles); XMnTPP (open circles); XFeOEP (closed triangles) (OEP = octaethylporphyrin).

π^* orbitals that interact with the HOMO. Thus, for a d^6 $M(\text{CO})_6$ species, all three t_{2g} orbitals (degenerate HOMO) interact with four CO π^* orbitals. For a *trans*- $\text{ML}_4(\text{CO})_2$ species, the t_{2g} splits to place xy (HOMO) above xz, yz , assuming that xy is now stabilized by zero CO π^* and xz, yz is stabilized by two CO π^* interactions. In the case of *cis*- $\text{ML}_4(\text{CO})_2$ xz, yz (one π^* interaction) lies above xy (two π^* interactions). For the moment, we ignore the possible stabilization of the d orbitals by non-carbonyl ligands. Since such stabilization of the HOMO is proportional to the number of CO groups bonded thereto and the relevant potential is proportional to the HOMO energy,^{3,8} one may introduce a variable x such that, for the carbonyl species under discussion, eq 8 is replaced by

$$E_{\text{obs}} = S_M[\Sigma E_L] + I_M + mx \quad (10)$$

where $m = 4, 0$, and 1 , respectively, for the hexacarbonyl and *trans*- and *cis*-dicarbonyl, with similar corrections for other isomeric species (shown in Table III).

Isonitrile complexes frequently have higher potentials than those directly derived from eq 8. This suggests that isonitrile ligands also strongly influence the π -bonding d orbitals. They may also be included in eq 10 by adding thereto the energy variable y modified by the number of isonitrile ligands, m' , that interact directly with the HOMO orbital (eq 11).

$$E_{\text{obs}} = S_M[\Sigma E_L] + I_M + mx + m'y \quad (11)$$

Table III. Contributions to the HOMO Orbital Energies in Isonitrile and Carbonyl Derivatives^a

	$M(\text{CNR})_x(\text{CO})_y$		$\text{ML}_x(\text{CO})_y$ $n(\text{CO})$
	$n(\text{CO})$	$n(\text{CNR})$	
$M(\text{CNR})_6$	0	4	
$M(\text{CNR})_5\text{CO}$	1	3	0
<i>c</i> - $M(\text{CNR})_4(\text{CO})_2$	2	2	1
<i>t</i> - $M(\text{CNR})_4(\text{CO})_2$	2	2	0
<i>m</i> - $M(\text{CNR})_3(\text{CO})_3$	3	1	1
<i>f</i> - $M(\text{CNR})_3(\text{CO})_3$	2	2	2
<i>c</i> - $M(\text{CNR})_2(\text{CO})_4$	3	1	2
<i>t</i> - $M(\text{CNR})_2(\text{CO})_4$	4	0	2
$M(\text{CNR})(\text{CO})_5$	3	1	3
$M(\text{CO})_6$	4	0	4

^a Corrections for $M(\text{CNR})_x(\text{CO})_y$ in columns 1 and 2 assuming that the isonitrile ligand stabilizes the d orbitals to a greater degree than carbon monoxide. Corrections for $\text{ML}_x(\text{CO})_y$ in column 3 assuming no interaction by ligand L. N.B. HOMO corrections for data (V) in Table II (see text for significance) are as follows. Cr(I)/Cr(0): PhNC, 0.19; MeNC, 0.00; CO, 0.15. Mn(II)/Mn(I): PhNC, 0.31; MeNC, 0.19; CO, 0.10. Mo(I)/Mo(0): no corrections applied. Fe(III)/Fe(II): MeNC, 0.10.

Values for m and m' , for mixed carbonyl-isonitrile species, are shown in Table III.

First, Figure 7 (top) shows data for the Mn(II)/Mn(I) couple in a series of carbonyl derivatives following eq 8 and hence *uncorrected* for the specific isomer or for enhanced isonitrile bonding. Two linear correlations are evident, the isonitriles being badly scattered but the carbonyl being reasonably linear. A value for y , in eq 11, was derived from $[\text{Mn}(\text{CNR})_6]^+$ (for each R, $y(\text{R})$):

$$y(\text{R}) = \frac{1}{4}[\text{observed potential} - \text{calculated potential using eq 11 } (m = 0, m' = 4)] \quad (12)$$

Similarly, with use of the value of $y(\text{Me})$, an initial value of x (eq 11) was derived by fitting the observed potential for $[\text{Mn}(\text{CO})_5(\text{CNR})]^+$ ($m = 3, m' = 1$). These two values were then used in eq 11 to recalculate all the manganese data according to Table III. The fit was improved by allowing y to vary to a best fit (least squares) over all manganese complexes with given CNR, resulting in a final value of $y(\text{R})$ slightly different from that calculated via eq 12. Energy variable x was also varied to a best fit over all the carbonyl complexes. The result is also shown in Figure 7 (bottom), where the improvement is dramatic. Importantly, the final line upon which all the complexes lie is essentially that of the carbonyl complexes in the uncorrected version shown in Figure 7, within experimental error. Such corrections (eq 11) add some complexity to the analysis. They can be ignored with the higher oxidation state species. Ignoring them with carbonyl, non-isonitrile data leads to some scatter, but relatively accurate data can be obtained nevertheless. It would be prudent to include these corrections where isonitriles are concerned (vide infra). Values of x and y are shown in Table III. Corrections have not been made for other ligands.

It is noteworthy that there is a reasonable linear correlation for these carbonyl derivatives and for the chromium and molybdenum species shown in Figure 8. The scatter is somewhat larger than observed in the non-carbonyl chromium, iron, and osmium data sets in part because of the lack of correction for specific (non-carbonyl) ligand interactions with the π -d electrons but probably mostly as a result of the synergistic interactions that take place within these species.

Incomplete Data Sets. When E_L values for all ligands in a complex are known, its calculated potential may be derived from the regression line where available (eqs 4 and 8). However, the method may also be used for generic series of complexes when the E_L value for a specific ligand is not available. Consider, for example, a set of complexes ML_4XY , for which $E_L(\text{L})$ is unavailable but $E_L(\text{X})$ and $E_L(\text{Y})$ are known. We require

$$E_{\text{obs}} = S_M[4E_L(\text{L}) + E_L(\text{X}) + E_L(\text{Y})] + I_M \quad (13)$$

An experimental slope and intercept may be derived from

$$E_{\text{obs}} = S'_M[E_L(X) + E_L(Y)] + I'_M \quad (14)$$

However, (13) may be rewritten

$$E_{\text{obs}} = S_M[E_L(X) + E_L(Y)] + 4S_M E_L(L) + I_M \quad (15)$$

Hence

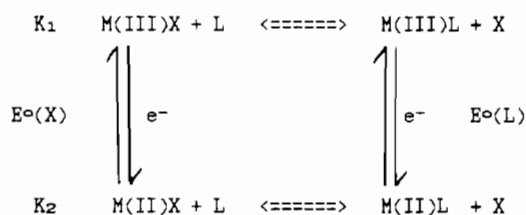
$$S_M = S'_M \quad I'_M = I_M + 4S_M E_L(L) \quad (16)$$

The key observation is that for a generic series of complexes with a constant core, in this case ML_4 , the slope of the correlation will be the same as that calculated had the $E_L(L)$ been known. Thus, the slope is defined but the intercept is indeterminate. For a specific group of complexes of M , of given structure, a correlation line may already have been derived. If the generic set of complexes belong to the same structural type and if the slope is the same as that previously deduced, then one might conclude that these complexes must lie on the same line—hence, C is known and $E_L(L)$ may be derived.

Consider, for example, the series of complexes $Fe(DMG-BF_2)_2XY$ ($Fe(DMG-BF_2)_2 = \text{bis}[(\text{difluoroboryl})\text{dimethylglyoximate}]_{\text{iron}}$), where a direct value for $E_L(DMG-BF_2)_2$ is unavailable. A plot of eq 14 yields a straight line of slope 1.06. These complexes (probably) belong to the same stereochemistry and spin-state group as $[Fe(\text{bpy})_3]^{2+}$ and indeed display essentially the same slope. They are shown plotted in Figure 6 using a value of I_M that gives the best fit to this line. From this value of I_M , one may derive $E_L(DMG-BF_2) = 0.22$ V.

While it is obvious that the $E_L(L)$ value for an unknown ligand could be derived by fitting its electrochemical datum to a correlation line, one may, in general, not know which correlation line to use, leading to ambiguity in the $E_L(L)$ value. The key proposition here is that one may study a group of related complexes all containing the same unknown core ligand and use the resulting slope to infer the correct correlation line and hence spin state and stereochemistry.

Significance of Slope and Intercept. Slope. The potential of a given redox couple reflects the relative binding strength of the two oxidation states to the ligand concerned, the more positive the potential, the more strongly binding being the lower oxidation state. This is clearly seen in the free energy correlation shown in the following simplified scheme:



where

$$E^\circ(L) - E^\circ(X) = (RT/nF) \ln (K_2/K_1)$$

A slope of unity for correlation of a specific $M(n)/M(n-1)$ couple with $[\sum E_L]$ indicates that the binding of $M(n)$ to a set of ligands relative to $M(n-1)$ is the same as for the $Ru(\text{III})/Ru(\text{II})$ couple. A slope exceeding unity shows a greater sensitivity of the metal core toward the ligand; i.e. there is a greater degree of polarization by the ligand or, in other words, stabilization of the lower oxidation state is increasingly favored with increasing E_L , relative to $Ru(\text{II})$.

It is surprising how many slopes are close to unity though this may possibly be fortuitous given the relatively small number of data sets which have been processed to date and the fact that all but one involve the t_{2g} (in O_h) orbitals. It is also surprising that both π acids and π donors tend to fall on the same line, for a given structural type, even though one expects them to bind in differing relative degrees to the lower and higher oxidation states.

There are few data sets yet available for different oxidation states of the same metal ion. Nevertheless one can expect that the slope will vary with the couple involved if only because of the changing degree of σ and π bonding that will occur. For example, a low-spin d^5/d^6 couple where the lower oxidation state species

is stabilized by π acids through back-donation should yield a slope different (greater) from that of the corresponding d^4/d^5 couple where the extent of π back-donation in the d^5 ion would be greatly reduced relative to that in the d^6 ion. In the case of niobium, where π bonding is not likely significant, both the $Nb(\text{V})/Nb(\text{IV})$ and $Nb(\text{IV})/Nb(\text{III})$ couples have the same slope. However many more data are clearly necessary before this can usefully be discussed.

Intercept. The value of the intercept I_M is determined by a number of contributions. Thus, the potential might be written

$$E_{\text{obs}} = a + nb + c + S_M[\sum E_L] \quad (17)$$

where a (always positive) is defined as the $M(n)/M(n-1)$ ionization energy in the gas phase. The variable b (always negative) may then be defined in a fashion identical with that of the spherical electrostatic term in ligand field theory, raising all the energy levels by the same degree determined by n , the number of ligands, and arising from the electrostatic repulsion between ligand lone pair and metal d electrons. Variable c (either sign) then depends upon the reference electrode and upon the difference in solvation energies of $M(n)$ and $M(n-1)$; thus, $I_M = a + nb + c$.

The sum $a + nb + c$ is defined as zero for a basis set of ruthenium complexes in acetonitrile, versus NHE. Given that essentially all six-coordinate $Ru(\text{III})/Ru(\text{II})$ couples, in acetonitrile, fall on the same line and given that charge appears not to be an important factor (c is constant), we might conclude that b is a constant for that set of complexes and therefore, for a given oxidation state, does not significantly depend upon the nature of the ligand. The discrimination of the ligand is then all contained within $[\sum E_L]$ and provides the linearity that would not otherwise be observed; i.e., if b did vary significantly with ligand, a linear plot would not be observed (unless the variation itself is a linear function of some property of the ligand). The value of b will vary with different metals and vary with different oxidation states of the same metal. The variation in a , with oxidation couple, makes a major contribution to the magnitude of the intercept, especially to the larger negative values derived for low oxidation state couples.

Further Comments on Charge Effects and Solvation. Charge effects will reveal themselves in comparisons of aqueous with organic solvent data. While the $Ru(\text{III})/Ru(\text{II})$ couple for net charge $2+$ species in water has roughly the same slope (1.14) as that (defined as unity) in organic solvent, that of the $Os(\text{III})/Os(\text{II})$ couple in water is 1.61 for the net charge $2+$ species. Unfortunately, there are insufficient data to define the slopes for other net charge species. However the marked variation in the osmium slope for organic to aqueous solvent does reveal that the redox dependence on solvent is not confined to the intercept; the slope is also influenced by the solvent. It is true that both the ruthenium and osmium water data sets presented here are dominated by polyamine species (see Appendix) that may interact with water in a fashion different from that of species such as $[M(\text{terpy})_3]^{2+}$. Nevertheless the amine and non-amine complexes do appear to lie on essentially the same line; if the amine complexes of ruthenium or osmium are considered alone, the slope increases only slightly (1.28 for ruthenium, 1.76 for osmium). This may not be significant given the scatter in the water data.

That the slope in water is higher is an intriguing new observation likely due to several factors including a modification of the $M-L$ bond by outer-sphere solute-solvent interactions and by entropy changes due to modifications in solvent (water) structure by the charged species.^{27,28}

It is surely significant that, in Figure 5, the $[Fe^{II}L_6]^{2+}$ type species lie on the same line as the $[Fe^{III}L_6]^{3+}$ species. Both the solvation enthalpy (Born equation) and solvation entropy are functions of charge squared.²⁷ Species having the same difference in solvation free energy for the $M(n)$ and $M(n-1)$ redox levels would make the same contribution to c and lie on the same line; this is seen to be the case here, since $(3+)^2 - (2+)^2 = (3-)^2 - (2-)^2$.

Other Coordination Numbers. One can anticipate that a set of six-coordinate species, which, for example, lose a ligand upon reduction to form five-coordinate species, will generate a separate correlation line from those where ligand loss does not occur.

Table IV. Data (Volts) Presented in the Figures

ref	complex	potential			ref	complex	potential		
		obs	calc	ΣE_L			obs	calc	ΣE_L
Figure 1 Data in Organic Solvent; Ruthenium(III)/Ruthenium(II) (open circles)									
23	Ru(bpy) ₂ (CH ₃ CN)NO ³⁺	0.8	0.87	0.86	23	Ru(phen) ₂ (naphthyridine) ²⁺	1.51	1.50	1.51
23	Ru(bpy) ₂ (CH ₃ CN)NO ₂ ⁺	1.41	1.39	1.40	82	Ru(phen) ₂ (py) ₂ ²⁺	1.515	1.52	1.53
23	Ru(bpy) ₂ (CH ₃ CN)NO ₃ ⁺	1.26	1.26	1.27	82	Ru(phen) ₂ (en) ²⁺	1.125	1.19	1.19
23	Ru(bpy) ₂ (py)N ₃ ⁺	0.82	0.84	0.83	82	Ru(phen) ₂ (py)Cl ⁺	1.045	1.04	1.04
23	Ru(bpy) ₂ (py)NO ₂ ⁺	1.3	1.30	1.31	82	Ru(phen) ₂ (acac) ⁺	0.875	0.88	0.87
23	Ru(bpy) ₂ (py)NO ₃ ⁺	1.167	1.18	1.18	82	Ru(phen) ₂ (ox)	0.725	0.71	0.70
23	Ru(bpy) ₂ (4- <i>t</i> -Bupy)NO ₃ ⁺	1.12	1.15	1.15	82	Ru(phen) ₂ Cl ₂	0.573	0.56	0.54
23	Ru(bpy) ₂ (4-vinyl-py)NO ₂ ⁺	1.275	1.26	1.26	23	Ru(4,7-Me ₂ phen) ₂ (pyz)Cl ⁺	1.01	1.04	1.03
23	Ru(bpy) ₂ (4-vinyl-py)NO ₃ ⁺	1.15	1.13	1.13	23	Ru(terpy)(BPE) ₃ ²⁺	1.47	1.51	1.52
23	Ru(bpy) ₂ (Cl)NO ₂	0.81	0.83	0.81	83	Ru(terpy)(py) ₃ ²⁺	1.5	1.485	1.49
23	Ru(bpy) ₂ (Cl)NO ₃	0.69	0.70	0.68	83	Ru(terpy)(CH ₃ CN) ₃ ²⁺	1.73	1.75	1.76
23	Ru(bpy) ₂ (py)CH ₃ CN ²⁺	1.6	1.61	1.63	83	<i>c</i> -Ru(terpy)(CH ₃ CN) ₂ Cl ⁺	1.17	1.18	1.18
23	Ru(bpy) ₂ (py)CN ⁺	1.28	1.30	1.31	83	<i>t</i> -Ru(terpy)(py) ₂ Cl ⁺	1.07	1.01	1.00
23	Ru(bpy) ₂ (py)Cl ⁺	1.019	1.05	1.04	83	Ru(terpy)(py) ₂ (CH ₃ CN) ²⁺	1.53	1.57	1.58
23	Ru(bpy) ₂ (py)TFA ⁺	1.13	1.14	1.14	83	Ru(terpy)(py)(CH ₃ CN)Cl ⁺	1.09	1.095	1.09
23	Ru(bpy) ₂ (4-Acapy)Cl ⁺	1.06	1.09	1.09	83	Ru(terpy)(py)(PPh ₃)Cl ⁺	1.1	1.14	1.14
23	Ru(bpy) ₂ (4-vinyl-py)CH ₃ CN ²⁺	1.53	1.57	1.58	23	Ru(pydipy) ₂ (CH ₃ CN) ₂ ²⁺	1.6	1.55	1.56
23	Ru(bpy) ₂ (4-vinyl-py)Cl ⁺	1	1.00	1.00	23	Ru(Azpy) ₂ Br ₂	1.19	1.21	1.21
23	Ru(bpy) ₂ (pyrimH)Cl ²⁺	1.21	1.21	1.21	23	Ru(Azpy) ₂ Cl ₂	1.205	1.16	1.16
23	Ru(bpy) ₂ (pyr)Cl ⁺	1.12	1.12	1.12	23	Ru(MeAzpy) ₂ Br ₂	1.137	1.21	1.21
23	Ru(bpy) ₂ (pyr)NO ₂ ³⁺	1.38	1.38	1.38	23	Ru(MeAzpy) ₂ Cl ₂	1.147	1.16	1.16
23	Ru(bpy) ₂ (BPA)Cl ⁺	1.01	1.05	1.05	63	Ru(TZ)(CH ₃ CN) ₂	1.29	1.24	1.24
23	Ru(bpy) ₂ (BPE)Cl ⁺	1.02	1.06	1.05	63	Ru(TZ)(py) ₂	1.05	1.06	1.06
23	Ru(bpy) ₂ (MPP)Cl ⁺	1.15	1.165	1.16	63	Ru(TZ)(py)(CH ₃ CN)	1.16	1.15	1.15
23	Ru(bpy) ₂ (MeP)Cl ⁺	1.18	1.16	1.16	63	Ru(TZ)(4,4-bpy) ₂	1.08	1.07	1.07
23	Ru(bpy) ₂ (PDP)Cl ⁺	1.15	1.21	1.21	56	Ru(biq) ₂ Cl ₂	0.72	0.69	0.68
23	Ru(bpy) ₂ (PPh ₃)NO ₂ ⁺	1.49	1.43	1.43	56	Ru(biq) ₂ (PEt ₃)H ₂ O ²⁺	1.48	1.47	1.48
23	Ru(bpy) ₂ (PPh ₃)NO ₃ ⁺	1.31	1.30	1.30	61	Ru(biq) ₂ (CN) ₂	1.17	1.20	1.20
45	Ru(bpy)(phendione) ₂ ²⁺	1.67	1.64	1.65	84	<i>m</i> -Ru(py) ₃ Cl ₃	0.08	0.06	0.02
47	<i>c</i> -Ru(bpy) ₂ (Ph ₂ MeP)Cl ⁺	1.15	1.165	1.16	50	RuBr ₂ (SMe ₂) ₃ (DMSO)	1.055	1.06	1.055
47	<i>c</i> -Ru(bpy) ₂ (Ph ₃ P)Cl ⁺	1.18	1.17	1.17	50	RuBr ₂ (SEt ₂) ₃ (DMSO)	1.035	1.045	1.04
23	Ru(bpy)(terpy)(CH ₃ CN) ²⁺	1.55	1.60	1.61	50	RuBr ₂ (SEt ₂) ₂ (DMSO) ₂	0.985	1.00	0.99
23	Ru(bpy)(terpy)(NH ₃) ²⁺	1.41	1.35	1.36	50	RuCl ₂ (SMe ₂) ₄	0.805	0.81	0.8
61	Ru(bpy)(terpy)(CN) ⁺	1.3	1.285	1.29	50	RuCl ₂ (SEt ₂) ₃ (DMSO)	1.045	1.055	1.05
79	Ru(bpy)(biq)(4,4-Me ₂ bpy) ²⁺	1.54	1.536	1.54	50	RuCl ₂ (SMe ₂) ₂ (DMSO) ₂	0.945	0.96	0.95
79	Ru(bpy)(biq)(phen) ²⁺	1.59	1.57	1.58	61	Ru(DMCH) ₂ (CN) ₂	1.04	1.08	1.08
79	Ru(bpy)(biq)(pq) ²⁺	1.63	1.57	1.58	61	Ru(<i>i</i> -biq) ₂ (CN) ₂	1.01	0.99	0.98
79	Ru(bpy)(biq)(<i>i</i> -biq) ²⁺	1.53	1.55	1.56	85	Ru(terpy)(dppyz)Cl ⁺	1.18	1.14	1.14
79	Ru(bpy)(biq)(biimH ₂) ²⁺	1.33	1.34	1.35	23	Ru(Azpy) ₂ (N ₃) ₂	1.2	1.045	1.04
79	Ru(bpy)(biq)(bipyrim) ²⁺	1.7	1.69	1.71	23	Ru(bpy) ₂ (CH ₃ CN)Cl ⁺	1.09	1.14	1.13
79	Ru(bpy)(biq)(binapy) ²⁺	1.51	1.48	1.49	23	Ru(bpy) ₂ (NH ₃)(NO ₂) ⁺	1.09	1.15	1.15
52	Ru(bpy)(biq)Cl ₂	0.7	0.62	0.60	23	Ru(bpy) ₂ (NH ₃)(NO ₃) ⁺	0.94	1.02	1.02
80	Ru(bpz) ₂ (CH ₃ CN)Cl ⁺	1.56	1.54	1.55	83	<i>t</i> -Ru(terpy)(4-pic) ₂ Cl ⁺	1.02	1.01	1.00
80	Ru(bpz) ₂ Cl ₂	1.04	0.98	0.97	83	Ru(terpy)(4-pic) ₃ ²⁺	1.47	1.46	1.46
81	Ru(bpz) ₂ Br ₂	1.03	1.03	1.02	83	Ru(terpy)(Py) ₂ (4-pic) ²⁺	1.47	1.47	1.47
81	Ru(bpz) ₂ (NO ₂) ₂	1.42	1.43	1.44	56	Ru(bpy)(biq)(PMe ₃)Cl ⁺	1.2	1.19	1.19
23	Ru(phen) ₂ (CH ₃ CN) ₂ ²⁺	1.685	1.69	1.71	56	Ru(bpy)(biq)(PEt ₃)Cl ⁺	1.19	1.18	1.18
23	Ru(phen) ₂ (CN) ₂	1.122	1.07	1.07	56	Ru(bpy)(biq)(P(<i>n</i> -Pr) ₃)Cl ⁺	1.2	1.19	1.19
23	Ru(phen) ₂ (py) ₂ ²⁺	1.515	1.52	1.53	56	Ru(bpy)(biq)(P(<i>n</i> -Bu) ₃)Cl ⁺	1.2	1.19	1.19
23	Ru(phen) ₂ (4-vinyl-py) ₂ ²⁺	1.49	1.48	1.49	56	Ru(bpy)(biq)(PPh ₃)Cl ⁺	1.26	1.22	1.22
23	Ru(phen) ₂ (pyz)Cl ⁺	1.1	1.12	1.11					
Figure 1 Data in Water; Ruthenium(III)/Ruthenium(II) (Closed Triangles)									
28	Ru(en) ₃ ²⁺	0.18	0.10	0.39	60	Ru(en) ₂ (bpy) ²⁺	0.59	0.54	0.78
72	Ru(NH ₃) ₆ ²⁺	0.05	0.135	0.42	60	Ru(en) ₂ (phen) ²⁺	0.55	0.54	0.77
72	Ru(NH ₃) ₅ pyz ²⁺	0.49	0.43	0.68	60	Ru(cyclam)(py) ₂ ²⁺	0.57	0.68	0.90
72	Ru(NH ₃) ₅ py ²⁺	0.3	0.34	0.6	60	Ru(cyclam)(bpy) ²⁺	0.65	0.70	0.92
72	Ru(NH ₃) ₅ (4-Acapy) ²⁺	0.39	0.44	0.685	60	Ru(cyclam)(phen) ²⁺	0.63	0.70	0.91
72	Ru(NH ₃) ₅ (CH ₃ CN) ²⁺	0.43	0.44	0.69	88	<i>c</i> -Ru(NH ₃) ₄ (py) ₂ ²⁺	0.505	0.55	0.78
72	Ru(NH ₃) ₅ (PhCN) ²⁺	0.485	0.48	0.72	73, 88	<i>t</i> -Ru(NH ₃) ₄ (py) ₂ ²⁺	0.49	0.55	0.78
72	<i>c</i> -Ru(NH ₃) ₄ (PhCN) ₂ ²⁺	0.87	0.82	1.02	73	Ru(NH ₃) ₄ (dppyz) ²⁺	0.82	0.695	0.91
68	Ru(NH ₃) ₅ (pyrim) ²⁺	0.44	0.44	0.69	23	Ru(bpy) ₃ ²⁺	1.51	1.40	1.53
68	Ru(NH ₃) ₅ (4,4-bpy) ²⁺	0.33	0.35	0.61	23	Ru(bpy) ₂ (PMA) ²⁺	1.21	1.16	1.32
86	<i>t</i> -Ru(NH ₃) ₄ (4-pic)(py) ²⁺	0.45	0.52	0.76	23	Ru(bpy) ₂ (4-vinyl-py) ₂ ²⁺	1.285	1.30	1.44
86	<i>t</i> -Ru(NH ₃) ₄ (4-pic)(pyz) ²⁺	0.61	0.61	0.84	23	Ru(bpy) ₂ (PVP)(CH ₃ CN) ²⁺	1.48	1.49	1.61
86	<i>t</i> -Ru(NH ₃) ₄ (4-pic)(4-Acapy) ²⁺	0.52	0.62	0.845	23	Ru(bpy) ₂ (PVP)Cl ⁺	1	0.83	1.02
86	<i>t</i> -Ru(NH ₃) ₄ (py) ₂ ²⁺	0.48	0.55	0.78	23	Ru(4,4-Me ₂ bpy) ₃ ²⁺	1.09	1.25	1.40
86	<i>t</i> -Ru(NH ₃) ₄ (py)(4-Acapy) ²⁺	0.55	0.64	0.865	23	Ru(bpz) ₃ ²⁺	2.22	2.125	2.16
86	<i>t</i> -Ru(NH ₃) ₄ (py)(pyz) ²⁺	0.65	0.64	0.86	23	Ru(bpy) ₂ (NH ₃) ₄ ²⁺	0.756	0.68	0.9
86	<i>t</i> -Ru(NH ₃) ₄ (4-Acapy) ₂ ²⁺	0.60	0.74	0.95	23	Ru(phen) ₃ ²⁺	1.26	1.42	1.54
86	<i>t</i> -Ru(NH ₃) ₄ (pyz)(4-Acapy) ²⁺	0.74	0.73	0.94	89	Ru(phen) ₂ (en) ²⁺	1.04	0.97	1.15
86	<i>t</i> -Ru(NH ₃) ₄ (pyz) ₂ ²⁺	0.78	0.72	0.93	89	Ru(phen)(en) ₂ ²⁺	0.79	0.54	0.77
86	<i>c</i> -Ru(NH ₃) ₄ (pyz) ₂ ²⁺	0.86	0.72	0.93	89	Ru(terpy) ₂ ²⁺	1.25	1.36	1.49
60	<i>c</i> -Ru(NH ₃) ₄ (bpy) ₂ ²⁺	0.51	0.56	0.79	28	Ru(NH ₃) ₅ Cl ⁺	-0.04	-0.22	0.11
87	Ru(NH ₃) ₅ (4-CNpy) ²⁺	0.57	0.50	0.74	28	Ru(NH ₃) ₅ (NCS) ⁺	0.105	-0.01	0.295
78	Ru(NH ₃) ₄ (P- <i>n</i> -Bu) ₃ ²⁺	0.71	0.64	0.86	28	Ru(NH ₃) ₅ Br ⁺	-0.21	-0.19	0.13

Table IV (Continued)

ligand	P_L potential		E_L vs NHE	ligand	P_L potential		E_L vs NHE
	obs	calc			obs	calc	
CO	0	0.295	0.99	bibizim	-0.645	-0.665	0.17
PPh ₃	-0.35	-0.41	0.39	CF ₃ PhAcAc ⁻	-0.765	-0.80	0.05
CF ₃ CO ₂ ⁻	-0.78	-1.04	-0.15	NH ₃	-0.77	-0.78	0.07
CN ⁻	-1.0	-0.84	0.02	en	-0.79	-0.79	0.06
PhCN	-0.4	-0.43	0.37	Ph ₂ AcAc ⁻	-0.865	-0.92	-0.04
Azpy	-0.37	-0.40	0.40	NCS ⁻	-0.88	-0.93	-0.06
bpz	-0.45	-0.44	0.36	bzac ⁻	-0.89	-0.935	-0.06
bipyrimid	-0.5	-0.50	0.31	AcAc ⁻	-0.91	-0.96	-0.08
bpy	-0.55	-0.56	0.26	Br ⁻	-1.17	-1.12	-0.22
MeCN	-0.58	-0.47	0.34	Cl ⁻	-1.19	-1.15	-0.24
Py	-0.59	-0.57	0.25	azide(1-)	-1.26	-1.22	-0.30

ref	complex	potential			ref	complex	potential		
		obs	calc	ΣE_L			obs	calc	ΣE_L
Figure 2									
Figure 3 Data in Organic Solvent; Osmium(III)/Osmium(II) (Open Circles)									
44, 82	Os(phen) ₂ Cl ₂	0.24	0.14	0.54	45	Os(bpy) ₂ (phendione) ²⁺	1.25	1.21	1.60
90	Os(bpy) ₂ Br ₂	0.28	0.20	0.60	44	<i>m</i> -Os(bpy)(PPhMe ₂) ₃ (NO ₂) ⁺	1.29	1.37	1.76
24	Os(bpy) ₂ (ox)	0.345	0.31	0.71	44	Os(bpy) ₂ (Ph ₂ MeP)(CH ₃ CN) ²⁺	1.29	1.34	1.74
82	Os(phen) ₂ (ox)	0.39	0.30	0.70	44	Os(phen) ₂ (Me ₂ PhP) ₂	1.33	1.305	1.70
48	Os(diphos) ₂ Cl ₂	0.45	0.36	0.76	44	<i>t</i> -Os(bpy) ₂ (Ph ₂ MeP) ₂ ²⁺	1.34	1.38	1.78
48	Os(diphos) ₂ Br ₂	0.39	0.32	0.72	44	Os(phen) ₂ (diars) ²⁺	1.35	1.305	1.70
82	Os(phen) ₂ (acac) ⁺	0.48	0.47	0.87	44	Os(bpy) ₂ (diars) ²⁺	1.35	1.31	1.71
24, 44, 82	Os(bpy) ₂ (acac) ⁺	0.495	0.48	0.88	77	Os(bpy) ₂ (CO)(O ₂ CH) ⁺	1.37	1.34	1.73
44	Os(bpy) ₂ (4,4-bpy)Cl ⁺	0.56	0.62	1.02	77	Os(phen) ₂ (CO)Cl ⁺	1.38	1.38	1.78
82	Os(phen) ₂ (en) ²⁺	0.57	0.76	1.16	77	Os(bpy) ₂ (CO)Cl ⁺	1.42	1.39	1.78
82	Os(bpy) ₂ (py)Cl ⁺	0.58	0.64	1.04	44	<i>c</i> -Os(bpy) ₂ (Ph ₂ MeP) ₂ ²⁺	1.45	1.38	1.78
44	Os(bpy) ₂ (py)Cl ⁺	0.59	0.65	1.04	94	Os(bpy) ₂ (MeAzpy) ²⁺	1.47	1.45	1.84
44	Os(bpy) ₂ (py)Br ⁺	0.59	0.67	1.07	77	<i>t</i> -Os(phen)(Me ₃ P) ₂ (CO)Cl ⁺	1.49	1.53	1.93
44	Os(bpy) ₂ (CH ₃ CN)Cl ⁺	0.65	0.74	1.13	77	Os(bpy) ₂ (CO)(O ₂ CCF ₃) ⁺	1.5	1.49	1.89
90	Os(bpy) ₂ (py ₂)Cl ⁺	0.67	0.72	1.12	44	Os(bpy) ₂ (dppm) ²⁺	1.51	1.49	1.89
82	Os(bpy) ₂ (glyc) ⁺	0.675	0.54	0.94	77	<i>t</i> -Os(phen)(PhMe ₂ P) ₂ (CO)Cl ⁺	1.52	1.54	1.93
82, 90	Os(bpy) ₂ (CN) ₂	0.695	0.68	1.08	44	Os(bpy) ₂ (dppe) ²⁺	1.54	1.52	1.92
82, 90	Os(bpy) ₂ (en) ²⁺	0.725	0.77	1.16	44	Os(phen) ₂ (dppe) ²⁺	1.54	1.52	1.91
44	Os(bpy) ₂ (Ph ₃ As)Cl ⁺	0.75	0.78	1.17	44	Os(phen) ₂ (dppm)	1.56	1.49	1.88
44	<i>m</i> -Os(bpy)(PEt ₃) ₃ Cl ⁺	0.76	0.90	1.30	47	Os(bpy) ₂ (dppy) ²⁺	1.64	1.615	2.01
44	Os(bpy) ₂ (Ph ₃ P)Cl ⁺	0.8	0.79	1.18	44	Os(phen) ₂ (dppy) ²⁺	1.6	1.61	2.00
26	Os(NH ₃) ₅ (<i>N</i> -Mepz) ³⁺	0.80	0.79	1.19	77	<i>t</i> -Os(phen)(Ph ₂ MeP) ₂ (CO)Cl ⁺	1.65	1.61	2.00
44	<i>m</i> -Os(bpy)(PMe ₃) ₃ Cl ⁺	0.84	0.87	1.27	44	Os(bpy) ₂ (CNMe) ₂ ²⁺	1.68	1.38	1.78
44	<i>m</i> -Os(bpy)(PPhMe ₂) ₃ Cl ⁺	0.89	0.885	1.28	44	Os(bpy)(diars) ₂ ²⁺	1.7	1.47	1.86
82	Os(4,4-Me ₂ bpy) ₂ ²⁺	0.895	0.95	1.34	44	Os(phen)(diars) ₂ ²⁺	1.71	1.46	1.85
91	Os(bpy) ₂ (bibizimH ₂) ²⁺	0.9	0.98	1.38	77	<i>t</i> -Os(phen)(Ph ₃ P) ₂ (CO)Cl ⁺	1.74	1.65	2.04
44	Os(phen)(py) ₄ ²⁺	0.96	1.12	1.52	95	Os(bpz) ₃ ²⁺	1.76	1.77	2.16
44	<i>m</i> -Os(bpy)(PPh ₂ Me) ₃ Cl ⁺	0.99	0.99	1.39	44	Os(bpy) ₂ (CO)(NO ₂) ⁺	1.78	1.88	2.265
44	Os(bpy) ₂ (py) ₂ ²⁺	0.99	1.14	1.54	77	Os(phen)(dppy)(CO)Cl ⁺	1.78	1.84	2.23
44, 82	Os(phen) ₂ (py) ₂ ²⁺	0.995	1.13	1.53	94	Os(bpy)(MeAzpy) ₂ ²⁺	1.88	1.76	2.15
77	Os(phen)(dppy)(PhMe ₂ P)Cl ²⁺	1.04	1.18	1.58	77	Os(bpy) ₂ (CO)(py) ²⁺	1.91	1.89	2.28
82	Os(phen) ₃ ²⁺	1.05	1.15	1.54	44	Os(bpy)(dppm) ₂ ²⁺	1.96	1.83	2.22
44	Os(bpy) ₂ (4,4-Me ₂ bpy) ₂ ²⁺	1.05	1.09	1.48	77	Os(bpy) ₂ (CO)(CH ₃ CN) ²⁺	2.04	1.98	2.37
82	Os(bpy) ₃ ²⁺	1.06	1.16	1.55	44	Os(bpy)(dppy) ₂ ²⁺	2.05	2.07	2.46
44	Os(bpy) ₂ (pyz)(py) ²⁺	1.08	1.22	1.61	44	Os(phen)(dppy) ₂ ²⁺	2.08	2.07	2.45
44	Os(phen) ₂ (CH ₃ CN) ₂ ²⁺	1.11	1.315	1.71	77	Os(bpy) ₂ (CO)PPh ₃ ²⁺	2.22	2.03	2.42
92	Os(bpy) ₂ (CH ₃ CN) ₂ ²⁺	1.15	1.32	1.72	96	Os(dtc) ₃ ⁻	-0.86	-1.13	-0.72
93	Os(5-Cl-phen) ₃ ²⁺	1.15	1.17	1.56	94	Os(MeAzpy) ₃ ²⁺	2.11	2.01	2.40
45	Os(phen) ₂ (phendione) ²⁺	1.17	1.26	1.65	97	<i>f</i> -Os(bpy)(PMe ₂ Ph)Cl ₃	-0.31	-0.28	0.13
44	Os(bpy) ₂ (pyz) ₂ ²⁺	1.21	1.30	1.69	98	Os(bpy) ₂ Cl(<i>t</i> -BuNH ₂) ₂	0.52	0.54	0.94
44	Os(bpy) ₂ (Ph ₃ P)(NO ₂) ⁺	1.21	1.27	1.665	44	Os(bpy) ₂ (CNCH ₂ Ph) ₂ ²⁺	1.74	1.77	2.16
Figure 3 Data in Water; Osmium(III)/Osmium(II) (Closed Triangles)									
99	Os(NH ₃) ₅ Cl ⁺	-0.86	-1.12	0.11	66	Os(NH ₃) ₅ (EtCN) ²⁺	-0.35	-0.19	0.69
99	Os(NH ₃) ₅ Br ⁺	-0.79	-1.12	0.11	66	Os(NH ₃) ₅ (ECN) ²⁺	-0.17	-0.13	0.72
68	Os(NH ₃) ₅ py ²⁺	-0.395	-0.33	0.6	66	Os(NH ₃) ₅ (PhCN) ²⁺	-0.19	-0.16	0.71
68	Os(NH ₃) ₅ pyz ²⁺	-0.09	-0.21	0.68	100	Os(NH ₃) ₅ CO ²⁺	0.92	0.865	1.34
68	Os(NH ₃) ₅ pyd ²⁺	-0.21	-0.22	0.67	68	Os(NH ₃) ₅ pyrim ²⁺	-0.26	-0.36	0.58
68	Os(NH ₃) ₅ (4,4-bpy) ²⁺	-0.22	-0.30	0.62	101	Os(phen) ₂ (dppm) ²⁺	1.57	1.59	1.79
68	Os(NH ₃) ₆ ²⁺	-0.78	-0.62	0.42	101	Os(phen) ₂ (dppy) ²⁺	1.65	1.70	1.86
68	Os(NH ₃) ₅ (isna) ²⁺	-0.24	-0.32	0.61	101	Os(phen) ₃ ²⁺	1.08	1.19	1.54
100	Os(NH ₃) ₅ N ₂ ²⁺	0.58	0.36	1.03	101	Os(terpy) ₃ ²⁺	1.23	1.10	1.49
66	Os(NH ₃) ₅ (CH ₃ CN) ²⁺	-0.29	-0.19	0.69	101	Os(phen) ₂ CO(Cl) ⁺	1.51	1.57	1.78
Figure 4 Data in Organic Solvent; Chromium(III)/(LS)Chromium(II)									
102	Cr(CNPh) ₆ ²⁺	0.85	0.87	2.22	103	Cr(Azpy) ₃ ²⁺	1.30	1.16	2.46
102	Cr(CNPh-4-OMe) ₆ ²⁺	0.75	0.73	2.10	104	Cr(Azpy) ₂ Cl ₂	-0.19	-0.38	1.16
102	Cr(CNPh-4-Me) ₆ ³⁺	0.83	0.86	2.16	104	Cr(bpy) ₂ (CN) ₂	-0.50	-0.47	1.08
103	Cr(CNPh-4-Cl) ₆ ³⁺	0.90	0.87	2.22	27	Cr(phen)(CN) ₄ ²⁻	-0.99	-1.04	0.59

Table IV (Continued)

ref	complex	potential			ref	complex	potential				
		obs	calc	ΣE_L			obs	calc	ΣE_L		
Figure 4 Data in Organic Solvent; Chromium(III)/(LS)Chromium(II) (Continued)											
105	Cr(bpy) ₃ ²⁺	0.09	0.09	1.55	104	Cr(phen) ₂ (NH ₃) ₂ ²⁺	-0.65	-0.37	1.17		
105	Cr(phen) ₃ ²⁺	-0.04	0.08	1.54	104	Cr(phen) ₂ (NCS) ₂	-0.78	-0.67	0.92		
43	Cr(terpy) ₂ ²⁺	0.09	0.01	1.49	57	Cr(bpy) ₂ (NCS) ₂	-0.78	-0.65	0.93		
43	Cr(5,5-Me ₂ bpy) ₃ ²⁺	-0.08	-0.10	1.39	106	Cr(CNCMe ₃) ₄ (<i>t</i> -Bu-DAB) ²⁺	0.91	0.90	2.24		
104	Cr(4,4-Me ₂ bpy) ₃ ²⁺	-0.13	-0.16	1.34	48	Cr(diphos) ₂ Cl ₂	-0.45	-0.85	0.76		
Macrocyclic Species											
106, 107	Cr(TPP)(py) ₂	-0.49	-0.46	0.48	106	Cr(TPP)(4-OAcpy) ₂	-0.45	-0.42	0.57		
107	Cr(TPP)(py)Cl ⁻	-0.56	-0.67	-0.01	108	Cr(TPP)(3,5-Cl ₂ py) ₂	-0.30	-0.38	0.66		
106	Cr(TPP)(4-pic)Cl ⁻	-0.49	-0.68	-0.03	108	Cr(TPP)(Meim) ₂	-0.72	-0.60	0.14		
106	Cr(TPP)(4-CNpy) ₂	-0.35	-0.35	0.73	108	Cr(TPP)(Meim)Cl ⁻	-0.90	-0.74	-0.18		
106	Cr(TPP)(4-pic) ₂	-0.52	-0.47	0.44							
Figure 4 Data in Organic Solvent; Chromium(III)/(HS)Chromium(II)											
109	Cr(bda) ₃ ⁻	-1.44	-1.66	-0.57	109	Cr(tfac) ₃ ⁻	-0.82	-0.91	0.33		
109	Cr(3-SCNacac) ₃ ⁻	-0.97	-1.14	0.05	109	Cr(3-Br-acac) ₃ ⁻	-1.34	-1.31	-0.16		
109	Cr(3-CNacac) ₃ ⁻	-0.97	-1.06	0.14	109	Cr(3-Cl-acac) ₃ ⁻	-1.33	-1.32	-0.17		
109	Cr(3-NO ₂ acac) ₃ ⁻	-0.91	-1.03	0.18	109	Cr(acac) ₃ ⁻	-1.70	-1.64	-0.54		
109	Cr(bztfac) ₃ ⁻	-0.65	-0.64	0.65	104	Cr(phen) ₂ (acac) ⁺	-0.49	-0.47	0.85		
109	Cr(dbmo) ₃ ⁻	-1.39	-1.40	-0.27	104	Cr(bpy)(en) ₂ ²⁺	-0.64	-0.55	0.76		
109	Cr(dpmo) ₃ ⁻	-1.91	-1.84	-0.79	104	Cr(phen)(en) ₂ ²⁺	-0.65	-0.54	0.77		
109	Cr(bzac) ₃ ⁻	-1.45	-1.37	-0.23							
Figure 5 Data in Water; Chromium(III)/(LS)Chromium(II) (Open Squares)											
89	Cr(CN) ₆ ⁴⁻	-1.04	-1.05	0.12	104	Cr(bpy) ₂ (H ₂ O) ₂ ²⁺	-0.48	-0.48	1.11		
43	Cr(bpy) ₃ ²⁺	-0.23	-0.22	1.55	43	Cr(terpy) ₂ ²⁺	-0.17	-0.26	1.49		
104	Cr(phen) ₃ ²⁺	-0.26	-0.23	1.54	43	Cr(4,4-Me ₂ bpy) ₃ ²⁺	-0.42	-0.34	1.34		
104	Cr(phen) ₂ (H ₂ O) ₂ ²⁺	-0.50	-0.48	1.11	102	Cr(5,5-Me ₂ bpy) ₃ ²⁺	-0.30	-0.32	1.39		
Figure 5 Data in Water; (LS)Iron(III)/(LS)Iron(II)											
73	Fe(CN) ₄ (dpyz) ₂ ²⁻	0.69	0.79	0.80	112	Fe(CN) ₅ (4-vinpy) ³⁻	0.44	0.45	0.30		
89	Fe(Me ₂ bpy) ₃ ²⁺	1.18	1.16	1.34	112	Fe(CN) ₅ (4-CNpy) ³⁻	0.555	0.53	0.42		
89	Fe(5-NO ₂ phen) ₃ ²⁺	1.49	1.415	1.72	113	Fe(CN) ₅ (imid) ³⁻	0.36	0.39	0.22		
89	Fe(phen) ₃ ²⁺	1.3	1.29	1.54	113	Fe(CN) ₅ (pyr) ³⁻	0.56	0.54	0.43		
89	Fe(terpy) ₂ ²⁺	1.17	1.26	1.49	113	Fe(CN) ₅ (pyrazole) ³⁻	0.44	0.45	0.30		
89	Fe(CN) ₆ ⁴⁻	0.36	0.33	0.12	112	Fe(CN) ₅ (4-Mepy) ³⁻	0.45	0.47	0.33		
110	Fe(bpy)(CN) ₄ ²⁻	0.56	0.65	0.60	112	Fe(CN) ₅ (4-Clpy) ³⁻	0.59	0.49	0.36		
89	Fe(bpy) ₂ (CN) ₂	1.02	0.98	1.08	112	Fe(CN) ₅ (3-CONH ₂ py) ³⁻	0.52	0.50	0.38		
111	Fe(4,7-Me ₂ phen) ₃ ²⁺	1.18	1.17	1.36	112	Fe(CN) ₅ (4-CONH ₂ py) ³⁻	0.51	0.52	0.40		
43	Fe(bpy) ₃ ²⁺	1.29	1.30	1.55	112	Fe(CN) ₅ (4-COOHpy) ³⁻	0.505	0.52	0.41		
43	Fe(5,5-Me ₂ bpy) ₃ ²⁺	1.21	1.19	1.39	112	Fe(CN) ₅ (4-CHOpy) ³⁻	0.51	0.54	0.43		
43	Fe(4,4-Me ₂ bpy) ₃ ²⁺	1.13	1.18	1.38	89	Fe(phen) ₂ (CN) ₂	0.76	0.97	1.07		
112	Fe(CN) ₅ (4-OAcpy) ³⁻	0.525	0.51	0.395	87	Fe(CN) ₅ (<i>N</i> -Mepyr) ²⁻	0.79	0.88	0.94		
112	Fe(CN) ₅ (py) ³⁻	0.48	0.48	0.35							
Figure 6 Data in Organic Solvent; (LS)Iron(III)/(LS)Iron(II)											
33	Fe(CNMe) ₆ ²⁺	2.64	2.46	2.74	89	Fe(bpy) ₂ (CN) ₂	0.71	0.76	1.08		
89	Fe(phen) ₃ ²⁺	1.41	1.29	1.56	114	Fe(terpy) ₂ ²⁺	1.33	1.23	1.49		
43	Fe(5,5-Me ₂ bpy) ₃ ²⁺	1.16	1.09	1.38	115	Fe(dppe) ₂ (NCMe) ₂ ²⁺	1.72	1.95	2.16		
43	Fe(4,4-Me ₂ bpy) ₃ ²⁺	1.11	1.09	1.38	33	Fe(phen) ₂ (CNMe) ₂ ²⁺	1.79	1.76	1.98		
89	Fe(CN) ₆ ⁴⁻	-0.31	-0.29	0.12	93	Fe(5-Cl-phen) ₃ ²⁺	1.41	1.29	1.56		
43	Fe(bpy) ₃ ²⁺	1.27	1.28	1.55	48	Fe(diphos) ₂ Cl ₂	0.3	0.41	0.76		
45	Fe(phendione) ₃ ²⁺	1.6	1.42	1.68	48	Fe(diphos) ₂ Br ₂	0.33	0.45	0.80		
Macrocyclic Species											
116	Fe(DMG-BF ₂) ₂ (CH ₃ CN)(TMIC)	1.455	1.32	1.59	117	Fe(TPP)(4-OAcpy) ₂	0.42	0.21	0.57		
116	Fe(DMG-BF ₂) ₂ (CH ₃ CN)(BuNC)	1.315	1.32	1.59	117	Fe(TPP)(py) ₂	0.3	0.11	0.48		
116	Fe(DMG-BF ₂) ₂ (CH ₃ CN) ₂	1.215	1.29	1.56	117	Fe(TPP)(4-pic) ₂	0.26	0.06	0.44		
116	Fe(DMG-BF ₂) ₂ (py) ₂	1.025	1.09	1.38	117	Fe(TPP)(im) ₂	0.16	-0.18	0.22		
116	Fe(DMG-BF ₂) ₂ (Meim) ₂	0.725	0.72	1.04	117	Fe(TPP)(3,5-Cl ₂ py) ₂	0.55	0.29	0.64		
117	Fe(TPP)(4-CNpy) ₂	0.54	0.26	0.62	118	Fe(TPP)(CN) ₂ ²⁻	-0.38	-0.39	0.04		
Figure 6; (HS)Iron(II)/(HS)Iron(III)											
119	Fe(3-Cl-acac) ₃ ⁻	-0.38	-0.39	-0.17	119	Fe(dpmo) ₃ ⁻	-0.91	-0.96	-0.80		
119	Fe(acac) ₃ ⁻	-0.68	-0.68	-0.49	119	Fe(dbmo) ₃ ⁻	-0.55	-0.48	-0.27		
119	Fe(bzac) ₃ ⁻	-0.61	-0.57	-0.37	119	Fe(bzfa) ₃ ⁻	0.02	0.03	0.31		
119	Fe(tfac) ₃ ⁻	-0.02	-0.04	0.24	119	Fe(pfm) ₃ ⁻	-0.10	-0.14	0.13		
ref	complex	potential		ΣE_L^a	ΣE_L^b	ref	complex	potential		ΣE_L^a	ΣE_L^b
		obs	calc ^a					obs	calc ^a		
Figure 7; Manganese(II)/Manganese(I)											
120	Mn(CNPh) ₆ ⁺	1.24	1.24	3.7	2.46	120	<i>f</i> -Mn(PhNC) ₃ (CO) ₃ ⁺	2.36	2.31	5.02	4.2
120	Mn(PhNC) ₅ (CO) ⁺	1.52	1.54	4.07	3.04	120	<i>c</i> -Mn(PhNC) ₂ (CO) ₄ ⁺	2.52	2.61	5.39	4.78
120	<i>t</i> -Mn(PhNC) ₄ (CO) ₂ ⁺	1.78	1.84	4.44	3.62	3	Mn(CNMe) ₆ ⁺	0.62	0.66	2.98	2.22
120	<i>c</i> -Mn(PhNC) ₄ (CO) ₂ ⁺	1.94	1.84	4.44	3.62	3	Mn(CNMe) ₅ CO ⁺	1.03	1.09	3.51	2.84
120	<i>m</i> -Mn(PhNC) ₃ (CO) ₃ ⁺	2.22	2.14	4.81	4.2	3	<i>c</i> -Mn(CNMe) ₂ (CO) ₄ ⁺	2.38	2.45	5.19	4.7

Table IV (Continued)

ref	complex	potential				ref	complex	potential							
		obs	calc ^a	ΣE_L^a	ΣE_L^b			obs	calc ^a	ΣE_L^a	ΣE_L^b				
Figure 7; Manganese(II)/Manganese(I) (Continued)															
3	Mn(CNMe)(CO) ₅ ⁺	2.89	2.88	5.72	5.32	121	Mn(CO)(dpm) ₂ Br	0.24	0.23	2.45	2.45				
7	<i>f</i> -Mn(CO) ₃ (CNMe) ₃ ⁺	2.14	2.02	4.66	4.08	121	Mn(CO) ₂ (dpm) ₂ ⁺	1.1	1.21	3.66	3.66				
7	<i>m</i> -Mn(CO) ₃ (CNMe) ₃ ⁺	1.97	1.94	4.57	4.08	121	Mn(CO)(dpm) ₂ CN	0.31	0.42	2.69	2.69				
7	<i>t</i> -Mn(CO) ₂ (CNMe) ₄ ⁺	1.52	1.52	4.04	3.46	121	Mn(CO)(dpm) ₂ NCS	0.33	0.36	2.615	2.615				
7	<i>c</i> -Mn(CO) ₂ (CNMe) ₄ ⁺	1.68	1.52	4.04	3.46	121	Mn(CO)(dpm) ₂ (CNBu) ⁺	0.78	0.70	3.03	3.03				
121	Mn(CO)(dpm) ₂ (NCMe) ⁺	0.69	0.68	3.01	3.01	100	Mn(CO) ₅ Br	2.16	2.32	5.03	4.73				
121	Mn(CO)(dpm) ₂ (CNMe) ⁺	0.77	0.70	3.04	3.04	4	Mn(CO) ₆ ⁺	2.975	3.38	6.34	5.94				
ref	complex	potential			ref	complex	potential								
		obs	calc	ΣE_L			obs	calc	ΣE_L						
Figure 8; Chromium(I)/Chromium(0) (Open Circles)															
122	<i>f</i> -Cr(CH ₃ CN) ₃ (CO) ₃	0.20	0.48	4.29	100	<i>c</i> -Cr(CO) ₂ (dppe) ₂	0.26	0.05	3.46						
122	<i>t</i> -Cr(CO) ₄ (PPh ₃) ₂	0.89	0.87	5.04	100	Cr(CO) ₄ bpy	0.85	0.73	4.77						
122	<i>c</i> -Cr(CO) ₄ (MeCN) ₂	0.59	0.81	4.94	100	Cr(CO) ₄ (dppe)	1.04	0.84	5.00						
122	<i>c</i> -Cr(CO) ₄ (py) ₂	0.64	0.72	4.76	4	Cr(CO) ₅ CNMe	1.215	1.24	5.77						
100	Cr(CO) ₆	1.69	1.64	6.54	6	Cr(CNPh) ₆	-0.08	-0.08	3.22						
100	Cr(CO) ₅ PPh ₃	1.39	1.25	5.78	6	Cr(CNPh-4-Cl) ₆	0.04	-0.17	3.04						
100	Cr(CO) ₅ PEt ₃	1.34	1.21	5.71	6	Cr(CNPh-4-OMe) ₆	-0.225	-0.23	2.92						
100	Cr(CO) ₅ PMe ₃	1.42	1.22	5.73	6	Cr(CNPh-4-Me) ₆	-0.19	-0.20	2.98						
100	Cr(CO) ₅ NH ₃	0.95	1.09	5.47	120	Cr(CO) ₅ (CNPh)	1.33	1.40	6.08						
100	Cr(CO) ₅ NCMe	1.29	1.23	5.74	120	Cr(CO)(CNPh) ₅	0.09	0.20	3.76						
100	Cr(CO) ₅ py	1.14	1.18	5.65	120	<i>f</i> -Cr(CO) ₃ (CNPh) ₃	0.80	0.78	4.88						
100	<i>t</i> -Cr(CO) ₄ (PPh ₃) ₂	0.88	0.85	5.01	120	<i>c</i> -Cr(CO) ₄ (CNPh) ₂	0.98	1.06	5.42						
100	<i>f</i> -Cr(CO) ₃ (PMe ₂ Ph) ₃	0.42	0.47	4.28	57	Cr(CO) ₃ (CNMe)(<i>t</i> -Bu-DAB)	0.18	0.21	3.77						
100	<i>m</i> -Cr(CO) ₃ (P(OMe) ₃) ₃	0.60	0.52	4.38	67	Cr(CO) ₃ Cl ⁻	0.875	0.93	5.16						
100	<i>f</i> -Cr(CO) ₃ (P(OMe) ₃) ₃	0.74	0.60	4.53	67	Cr(CO) ₃ Br ⁻	0.915	0.94	5.18						
100	<i>t</i> -Cr(CO) ₂ (dppe) ₂	-0.13	0.05	3.46	67	Cr(CO) ₃ I ⁻	0.935	0.92	5.14						
Figure 8; Molybdenum(I)/Molybdenum(0) (Closed Triangles)															
100	Mo(CO) ₄ bpy	0.86	1.06	4.48	100	<i>t</i> -Mo(N ₂)(PhCN)(dppe) ₂	-0.24	-0.38	2.53						
100	<i>c</i> -Mo(CO) ₄ (PBu ₃) ₂	1.14	1.10	4.54	100	<i>t</i> -Mo(N ₂)(MeCN)(dppe) ₂	-0.34	-0.40	2.5						
100	<i>c</i> -Mo(CO) ₂ (dppe) ₂	0.22	0.28	3.42	100	<i>t</i> -Mo(N ₂)(SCN)(dppe) ₂ ⁻	-0.63	-0.69	2.105						
100	<i>t</i> -Mo(CO)(NCPh)(dppe) ₂	-0.16	-0.18	2.8	100	<i>t</i> -Mo(N ₂)(N ₃)(dppe) ₂ ⁻	-0.95	-0.87	1.86						
100	<i>t</i> -Mo(CO)(CN)(dppe) ₂ ⁻	-0.59	-0.44	2.45	9	<i>t</i> -Mo(N ₂)(CN)(dppe) ₂ ⁻	-0.74	-0.61	2.22						
100	<i>t</i> -Mo(CO)(SCN)(dppe) ₂ ⁻	-0.5	-0.49	2.375	9	<i>t</i> -Mo(N ₂)(NH ₃)(dppe) ₂	-0.49	-0.57	2.27						
100	<i>t</i> -Mo(CO)(N ₃)(dppe) ₂ ⁻	-0.76	-0.67	2.13	124	Mo(CO) ₄ (<i>i</i> -PrDAB)	0.89	0.88	4.24						
9	<i>t</i> -Mo(CO)(NCMe)(dppe) ₂	-0.25	-0.17	2.81	124	Mo(CO) ₄ (<i>i</i> -BuDAB)	0.9	0.88	4.24						
123	<i>t</i> -Mo(N ₂) ₂ (PMePh ₂) ₄	-0.17	-0.09	2.92	124	Mo(CO) ₄ (<i>i</i> -CyDAB)	0.87	0.88	4.24						
100	Mo(N ₂) ₂ (4-pic)(PMePh ₂) ₃	-0.24	-0.19	2.78	124	Mo(CO) ₃ (CNMe)(<i>t</i> -BuDAB)	0.51	0.42	3.62						
100	Mo(N ₂) ₂ (NMeIm)(PMePh ₂) ₃	-0.41	-0.31	2.63	124	Mo(CO) ₃ (CH ₃ CN)(<i>t</i> -BuDAB)	0.45	0.40	3.59						
11	<i>t</i> -Mo(N ₂) ₂ (dppe) ₂	0.08	-0.12	2.88	124	Mo(CO) ₂ (CNCMe) ₂ (<i>t</i> -BuDAB)	-0.02	-0.05	2.98						
Figure 9; Niobium(V)/Niobium(IV) (Open Squares)															
125	NbCl ₆ ²⁻	0.14	0.13	-1.45	125	Nb(CH ₃ CN) ₂ Cl ₄	1.03	1.02	-0.29						
125	Nb(CH ₃ CN)Cl ₅ ⁻	0.56	0.58	-0.87											
Figure 9; Niobium(IV)/Niobium(III) (Open Squares)															
125	NbCl ₆ ²⁻	-1.2	-1.205	-1.45	125	<i>c</i> -Nb(CH ₃ CN) ₂ Cl ₄	-0.33	-0.335	-0.29						
125	Nb(CH ₃ CN)Cl ₅ ⁻	-0.78	-0.77	-0.87											
Figure 9; Tantalum(V)/Tantalum(IV) (Open Circles)															
125	TaCl ₆ ²⁻	-0.55	-0.49	-1.45	132	TaBr ₆ ²⁻	-0.29	-0.39	-1.32						
125	Ta(CH ₃ CN)Cl ₅ ⁻	-0.09	-0.03	-0.87	132	Ta(CH ₃ CN)Br ₅ ⁻	0.07	0.06	-0.76						
125	<i>c</i> -Ta(CH ₃ CN) ₂ Cl ₄	0.44	0.43	-0.29											
Figure 9; Rhenium(IV)/Rhenium(III) (Open Triangles)															
126	ReCl ₆ ³⁻	-0.88	-0.71	-1.44	97	<i>m</i> -Re(PPh ₃) ₂ (CH ₃ CN)Cl ₃	0.9	0.84	0.4						
127	ReCl ₄ (PMe ₂ Ph) ₂ ⁻	0.1	0.27	-0.28	97	<i>m</i> -Re(PMe ₂ Ph) ₃ Cl ₃	0.9	0.755	0.3						
128	Re(NCS) ₆ ³⁻	0.13	0.20	-0.36	130	Re(NCS) ₃ (PEt ₂ Ph)(bpy)	0.92	1.07	0.68						
97	Re(bpy)Cl ₄ ⁻	0.2	0.13	-0.44	130	Re(NCS) ₃ (PEt ₂ Ph)(phen)	0.92	1.08	0.68						
129	<i>c</i> -Re(CH ₃ CN) ₂ Cl ₄ ⁻	0.24	0.27	-0.28	130	Re(NCS) ₃ (PEt ₂ Ph)(dppe)	1.08	1.28	0.92						
97	<i>f</i> -Re(bpy)(PMe ₂ Ph)Cl ₃	0.71	0.62	0.14	97	<i>t</i> , <i>c</i> -Re(bpy)(PMe ₂ Ph) ₂ Cl ₂ ⁺	1.12	1.11	0.72						
97	<i>f</i> -Re(bpy)(PPh ₃)Cl ₃	0.8	0.66	0.19	131	Re(dppy) ₂ Br ₂ ⁺	1.71	1.79	1.52						
127	ReCl ₃ (PMe ₂ Ph) ₃	0.875	0.76	0.3	131	Re(dppy) ₂ Cl ₂ ⁺	1.75	1.75	1.48						
M(por)X	TPP Mn(III)/ Mn(II)		TPP Fe(III)/ Fe(II)		OEP Fe(III)/ Fe(II)		ΣE_L	M(por)X	TPP Mn(III)/ Mn(II)		TPP Fe(III)/ Fe(II)		OEP Fe(III)/ Fe(II)		ΣE_L
	obs	calc	obs	calc	obs	calc			obs	calc	obs	calc	obs	calc	
Figure 10															
fluoride			-0.26	-0.31	-0.39	-0.43	-0.42	chloride	-0.05	-0.04	-0.05	-0.03	-0.18	-0.15	-0.24
perchlorate	0.08	0.07	0.46	0.44	0.34	0.32	0.05	iodide	0.00	-0.04					-0.24
bromide	-0.02	-0.04	0.03	0.01	-0.1	-0.11	-0.22	thiocyanate	-0.01	0.03	0.28	0.27			-0.06
azide	-0.10	-0.07	-0.18	-0.12	-0.28	-0.24	-0.30								

^aIncluding isomer corrections. ^bExcluding isomer corrections—see Table III.

Following eqs 8 and 17, the Ru(III)/Ru(II) potential for a q -coordinate RuL_q species, in acetonitrile, might be written

$$E_{\text{obs}}(\text{RuL}_q) = \mathbf{a} + q\mathbf{b} + \mathbf{c} + qE_L \quad (18)$$

If we suppose that the numerical magnitudes of \mathbf{a} , \mathbf{c} are approximately the same as for the six-coordinate species (\mathbf{a} will be identical) and recall that for a six-coordinate ruthenium species (Ru(III)/Ru(II)) $\mathbf{a} + 6\mathbf{b} + \mathbf{c} = 0$, then it follows that

$$E_{\text{obs}}(\text{RuL}_q) = qE_L - (6 - q)\mathbf{b} \quad (19)$$

Thus, the E_L values derived from six-coordinate species cannot be directly used, with eq 8, for other coordination numbers, since they have effectively been modified by a contribution from the spherical term. However, since \mathbf{b} is assumed roughly constant for all ligands for a given redox process, we can expect other coordination numbers still to yield straight-line correlations with $\sum E_L$ following eq 8. The intercept will contain the term $-(6 - q)\mathbf{b}$ (which is positive), and the potential will be more positive than that for the corresponding ML_6 species. In principle this provides a useful method to evaluate \mathbf{b} ; straight-line correlations are indeed observed with the M(III)/M(II) couple in Fe(TPP)X, Fe(OEP)X, and Mn(TPP)X (Table II; Figure 10).

The Electrochemical Series of Ligands. The existence of this additivity provides a ligand sequence that is directly analogous to the spectrochemical series of Dq in that all ligands behave relatively the same way toward all metal ions. This sequence may be abbreviated into ranges that however certainly overlap and should be regarded only as a guide to estimate the E_L values of ligands that do not appear in Table I.

$$E_L: -0.63 \rightarrow 0 \text{ (V)}$$

OH^- , most $\text{X}^{\pi-}$ ions, including S anions, strong π bases

$$E_L: 0 \rightarrow 0.1 \text{ (V)}$$

saturated amines falling into a fairly narrow range,
weakly π -acid unsaturated amines

$$E_L: 0.1 \rightarrow 0.40 \text{ (V)}$$

unsaturated amines of stronger π -acid character,
pyridines, bipyridines, etc.

$$E_L: 0.30 \rightarrow 0.40 \text{ (V)}$$

hard thioethers, nitriles, softer phosphines

$$E_L: 0.35 \rightarrow 0.50 \text{ (V)}$$

isonitriles, harder phosphines, arsine, stibines,
softer phosphites

$$E_L: 0.50 \rightarrow 0.65 \text{ (V)}$$

harder phosphites

$$E_L: 0.65 \rightarrow 0.75 \text{ (V)}$$

dinitrogen, nitrites

$$E_L: 0.70 \rightarrow 0.95 \text{ (V)}$$

positively charged ligands, π -acid olefins

$$E_L: >0.9 \text{ (V)}$$

CO (0.99 most positive member)

The relative E_L values reflect availability of charge for donation to the metal ion and have little connection with the spectroscopic Dq values where, for example, cyanide and carbon monoxide are close together in Dq value. Indeed, being derived from the Ru(III)/Ru(II) t_{2g}^5/t_{2g}^6 couple, it is not surprising that they fall in a sequence largely determined by their π -bonding or π -antibonding behavior.

Less Well-Behaved Systems—CNR, NO, Water, DMSO, Hydride, and Macrocyclic Complexes. The considerable extent to which ligand additivity provides a viable means to estimate redox potentials would seem to "throw away" a lot of chemistry and

reduce redox behavior to the summation of a series of noninteracting M-L fragments. Indeed, for a wide range of ligands and metal redox couples this appears to be roughly true despite variation of π -acid or π -basic character in both metal and ligand. This is an unexpected result that does not appear to have been previously recognized. Solvation phenomena also appear only to play a small role in determining redox energies provided that specific solvent-solute interactions are absent. Those complexes that do not fit their apparent correlation line should be considered in some depth. If one can exclude trivial explanations such as important coupled preceding or following chemical reactions, then the failure may arise for cogent chemical bonding reasons.

Carbonyl species generally fit rather well even where the specific isomer corrections are ignored. Inclusions of these isomer corrections show stabilizations of the order of 0.1–0.15 eV per CO-d orbital interaction. However, it is likely that the $E_L(\text{CO})$ value itself actually contains within it some stabilization effect and should, in fact, be a little smaller if used with a metal ion in which there is no π back-bonding if such is possible. Thus, the value may be a little inflated, explaining why it falls off the PPLC correlation (Figure 2).

Isonitriles are a very special case that deserve more comment. Considering CNMe, an $E_L(\text{CNMe})$ value of 0.55 V is derived from $[\text{Ru}(\text{bpy})_2(\text{CNMe})_2]^{2+}$.³² However, isonitrile E_L values derived from correlation with the Pickett/Pletcher ligand parameters yield values around 0.4 (Appendix). A similar, but smaller, distinction is seen with the carbonyl ligand. The best fit for the manganese isonitrile data shown in Figure 7 was obtained by assuming a value of ca. 0.37 V for each CNMe plus a correction of 0.19 V for each CNMe bound to the HOMO orbital (isomer correction). The ligand CNPh required a larger correction, 0.31 V (Table III). Other metal isonitrile species were fitted in a similar manner. It is particularly relevant that the trivalent and non-back-donating d^3 $[\text{Cr}(\text{CNR})_6]^{3+}$ species could be fitted with the lower $E_L(\text{CNR})$ values (ca. 0.37 V) without a correction for the number of π -bonding isonitrile groups, while the low-spin d^6 $[\text{Fe}(\text{CNMe})_6]^{2+}$ ³³ and related species did require such correction (ca. 0.10 V/ π -bonding CNMe (Table III)), as did $[\text{Ru}(\text{CNMe})_6]^{2+}$, which shows no Ru(III)/Ru(II) redox process below 3.2 V (vs NHE)³³ (and therefore requires a large correction). The validity of this approach is inferred from the excellent regression fits obtained from a large body of data.

The variation in $E_L(\text{CNR})$ may be related to the fact that the isonitrile group may be linear or bent.^{34–36} The linear isonitrile parallels carbonyl in its binding. The bent isonitrile will occur in situations where there is extensive back-donation. The latter case may be exemplified by mixing of both $\text{M}^0(\text{CNR})$ and $\text{M}^1(\text{CNR}(1-))$, as might be inferred from the PES data for $[\text{Ru}(\text{bpy})_2(\text{CNR})_2]^{2+}$ species in the Ru(III) region.³⁷ Note that valence bond contributions of the $\text{CNR}(1-)$ canonical form will shift positively all metal d orbitals, not just the HOMO. Indeed Pombeiro, Pickett, and Richards¹⁴ had previously noted the variation in the PPLC parameter for isonitriles in various complexes and suggested that bent isonitriles should have a P_L value (eq 2) approximately 0.3 V larger than that of a linear isonitrile. X-ray structural data show significant variations in bond angles for coordinated isonitrile groups; thus, the actual correction may vary from one set of complexes to another.

It does not seem necessary to use this rather more complex fitting procedure for any other ligand yet studied.

A value for the macrocycle TPP can be derived from ruthenium data (Table I). This corresponds to a six-coordinate metal-in-the-plane species. If this number is used, the six-coordinate $\text{L}_2\text{Fe}^{\text{II}}(\text{TPP})$ species lie close to their correlation line for (LS)-Fe(III)/(LS)Fe(II) (Figure 6) (they apparently have the same slope) and a slight adjustment for $E_L(\text{TPP})$ due to the relative sizes of Ru(II) and Fe(II) and the fixed macrocycle hole size would place them on the line. However, the corresponding $\text{L}_2\text{Cr}^{\text{II}}(\text{TPP})$ species (spin state of $\text{L}_2\text{Cr}^{\text{II}}\text{TPP}$ is unknown) lie off both the low-spin and high-spin octahedral Cr(II) correlation lines (Figure 4) perhaps for reasons of hole size or possibly because the correct correlation line has not been identified. The slope for the L_2 -

Cr(TPP) data is relatively low (Table II), indicating that the Cr(III)-L bond does not significantly favor Cr(III) over Cr(II) in the TPP environment.

The nitrosyl ligand offers especial interest, since the contribution depends upon the amount of charge transferred thereto and hence upon the metal core; it will be discussed elsewhere.³⁸ Water, as a ligand, yields a somewhat variable E_L value near 0 in the range -0.05 to +0.1 V. The contribution of water likely depends upon how dry an organic solvent is and whether there are any hydrogen-bonding species around. In water the $E_L(\text{H}_2\text{O})$ value will depend critically upon pH. In coordinating organic solvents the water molecule may be partially or wholly solvolyzed, adding a complicating factor. DMSO is poorly behaved, yielding a variety of E_L values spanning ca. 0.4-0.55 V. This may be a consequence of variable S or O coordinate binding. The hydride ion usually gives rise to irreversible redox processes, but its E_L value may be estimated to lie near -0.5 V; the PPLC value of -0.3 V is likely somewhat low.

Summary. The availability of E_L parameters allows one to do the following: (a) predict the redox potential of a given metal couple when its structural and spin-state information are available (For example, in a complex voltammogram this will aid in redox couple assignment.); (b) predict the structure and spin state for a metal complex on the basis of fitting its observed redox potential to a previous correlation; (c) allow one to calculate the thermodynamic value for a redox couple when kinetic effects or coupled chemical reactions, etc. prevent it from being experimentally derived; (d) design a metal complex to have a specific redox potential (With further development, correlations with other properties such as infrared stretching frequencies, photoelectron binding energies, certain rate constants,^{8,38,40-42} charge-transfer transition energies,^{19,24,43,44} etc. can be included. Thus, molecules having a range of characteristics can be designed by using a procedure based upon E_L values.); (e) provide bonding (synergism, noninnocence, etc.) or structural information where a predicted value disagrees significantly with the experimental value; (f) provide a means of designing metal complexes with specific excited-state redox potentials, through analysis involving ground-state electrochemical predicted energies and excited-state transition energies; (g) provide a means of evaluating solvation energies, especially aquation energies; (h) through detailed understanding of the slopes and intercepts, provide additional insight into the nature of the metal-ligand bond.

To learn exactly how general is this approach requires considerable further data evaluation especially with data sets involving σ^* redox orbitals. Readers with extensive electrochemical data sets are invited to advise the author for inclusion in future E_L studies.

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Appendix

Data presented in the figures are listed in Table IV. All data

referenced to NHE. Charges refer to that of the reduced species in the couple, though, in many cases, the electrochemical observation may have been carried out on the bulk oxidized species. The regression lines listed in Table II do not necessarily include all the points on a given figure; outlying points have been omitted in some cases.

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