Electrochemical Parametrization in Sandwich Complexes of the First Row Transition Metals

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Applying the ligand electrochemical parameter approach to sandwich complexes and standardizing to the Fe^{III}/Fe^{II} couple, we obtained $E_L(L)$ values for over 200 π-ligands. Linear correlations exist between formal potential ($E°$) and the $\sum E_L(L)$ for each metal couple. In this fashion, we report correlation data for many first row transition metal couples. The correlations between the $E_L(L)$ of the substituted π-ligand and the Hammett substituent constants (σ_p) are also explored.

Introduction

Models designed to predict chemical reactivity and physical properties of metal complexes are necessary for the advancement of organometallic chemistry. Such models and parametrization schemes have significantly aided organic chemists for years to fine-tune reaction processes, establish viable reaction mechanisms, and design novel synthons possessing specific physical properties.[1] However, the situation is less well defined for inorganic chemists, and the lack of comprehensive models to describe organometallic chemistry may have hindered the field's growth.[2]

Hammett and Taft substituent constants provide good correlations with ionization energetics data for (arene)chromium tricarbonyl complexes[3a] as well as alkylated nickelocene and ferrocene derivatives.[3] However, these models, originally developed for organic systems, have been noted to overinterpret the effects of ligands bearing electron-withdrawing substituents and are not readily convertible for rationalizing the enormous variety of inorganic systems.

Electrochemical potentials provide an extensive body of information which might be used to rationalize the complexity of chemical behavior in organometallic chemistry but so far, few attempts have been made to analyze these data systematically.

Linear relationships have previously been demonstrated,[4−6] in sandwich organometallic species, between the electrochemical potentials $E°_j$ ($j = 1-4$) of the several metal-centered redox processes and gas-phase ionization potentials of the corresponding free atomic metal (I_{Pj}), viz

$$E°_j = \sum a_i = 0.1 I_{Pj} \qquad (1)$$

where $\sum a_i$ ($i = 1, 2$) and values of a_i were reported for common sandwich ligands. In this fashion electrochemical potentials for numerous sandwich species were rationalized and used to estimate their reactivity and to design synthetic strategies for hitherto unknown species, etc.[4a,5] This earlier analysis laid the groundwork for the more extensive and flexible analysis presented here.

In this previous work, the predicted $E°$ values for $d^{5/6}$ and $d^{6/7}$ redox transitions, in many cases, deviated significantly from the linear $E°-I_P$ relationship. These deviations were explained in terms of crystal field theory.[4a,d,6] but their existence plus the absence of a clear strategy to compare and contrast different sandwich ligands limited the utility of this earlier procedure.

We have recently discussed the parametrization of metal-centered redox potentials,[7−10] ligand centered redox potentials,[11] and excited state potentials[12a] in terms of the so-called electrochemical parameter, $E_L(L)$ for nonsandwich complexes, a procedure which has been further developed elsewhere[13−19] and

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which is based upon scaling all data to the Ru^{III}/Ru^{II} couple. The $E_L(L)$ model enables one to predict the redox potentials of a wide variety of metal complexes by using eq 2 for metal-centered redox reactions or eq 3 for certain ligand-centered redox reactions.

$$E_{calc}(M^{n+1}/M^n) = S_M[\sum E_L(L)] + I_M \qquad (2)$$

$$E_{calc}((ML)^{n+1}/(ML)^n) = S_L[\sum E_L(L)] + I_L \qquad (3)$$

In eq 2, $\sum E_L(L)$ is the sum of $E_L(L)$ parameters for all ligands bonded to the metal complex. In eq 3 the quantity $\sum E_L(L)$ is for all ligands of the metal complex except for the ligand involved in the redox process. The parameters S_M and I_M are constants for a particular M^{n+1}/M^n couple undergoing a defined reduction process;[7] S_L and I_L are constants for a ligand-centered redox couple $(ML)^{n+1}/(ML)^n$.[11]

The approach depends upon ligand additivity; i.e., the various $E_L(L)$ contributions from each ligand are assumed to add to provide the observed redox potential for the Ru^{III}/Ru^{II} redox process, while for all other metal redox processes, this value is scaled by S_M and offset by I_M.

The accurate prediction of redox potentials is of benefit to (i) the design of new species with particular redox energies, (ii) the verification of the assignments of observed redox potentials, (iii) the prediction of charge transfer energies in optical spectroscopy, (iv) the design of species with particular excited-state potentials, (v) the elucidation of the mechanism of electrochemical reactions, and (vi) the variation of S_i and I_i (i = M, L) with the system under study, which also conveys fundamental information about the nature of metal-ligand bonding and ligand-ligand interactions. The correlations between $E_L(L)$ and other properties of complexes or ligands, e.g. IR frequencies, pK_a values of complexes or ligands, or Hammett substituent constants for the ligands, may provide further opportunity to gain insight into the fundamental nature of selected metal complexes.

Previous studies regarding $E_L(L)$ parametrization models dealt with classical octahedral complexes and simple organometallic carbonyls etc. but excluded sandwich complexes. Here, we explore the extension of the $E_L(L)$ models to sandwich complexes of bis(Cp), bis(arene) where arene = η^6-benzene and related systems.

Pseudooctahedral sandwich complexes, in which a metal atom is bonding between two planar and parallel ligands, provide an excellent model for electrochemical parametrization. For example:

(i) A very large number of such complexes have been investigated electrochemically.[6,20–25]

(ii) They exhibit an extended set of redox couples (eq 4).[6]

$$Cp_2M^{2+} \leftrightarrow Cp_2M^{+} \leftrightarrow Cp_2M \leftrightarrow Cp_2M^{-} \leftrightarrow Cp_2M^{2-} \qquad (4)$$

(iii) The redox processes are mostly metal-based and reversible or quasi-reversible.

(iv) The effects of solvent and supporting electrolyte are mainly electrostatic in nature and are very similar for isostructural complexes of equal charge.[5,26–29] The bulky ligands surrounding the metal center usually prevent inner-sphere solvent coordination or reactions with supporting electrolytes.

We do not expect the sandwich complexes to fall on the same Ru^{III}/Ru^{II} scaled correlation lines[7] as nonsandwich organometallic or coordination complexes of the same metal. Morris suggested the $E_L(L)$ approach can be used with half-sandwich complexes using correlation parameters of nonsandwich complexes to predict some properties of the half-sandwich complexes.[30] However, this approach has some limitations for universal application to all sandwich and half-sandwich complexes.

In order to establish a parameter scheme that is applicable over a large potential range for a wide variety of complexes, the following conditions were imposed. (i) Complexes which undergo significant structural changes, such as a variation in hapticity, inner-sphere solvent coordination, nucleophilic attack, or any other process indicative of an irreversible nonthermal oxidation and/or reduction process, are not included in this study. (ii) Arene or Cp ligand-based redox potentials are excluded. (iii) Only mononuclear complexes with two π-donor ligands are considered. Half-sandwich and polynuclear sandwich complexes will be discussed at a later date. (iv) Only hydrocarbon ligands are considered. Complexes with carborane and heteroaromatic ring ligands will be discussed elsewhere. (v) Redox processes must be relatively independent of solvent/electrolyte systems. Thus, all species chosen meet the criteria described in ref 7.

In this case, the Ru^{III}/Ru^{II} couple is not appropriate for scaling purposes because very few ruthenium sandwich species meet the above requirements.[31] On the other hand, there are a very large number of iron sandwich complexes whose Fe^{III}/Fe^{II} couple does meet these requirements.

We first analyze the data to determine $E_L(L)$ parameters for the sandwich ligands using as standard the low spin Fe^{III}/Fe^{II} couple. This generates a database of $E_L(L)$ values which is then further expanded using correlations with Hammett parameters. The range of $E_L(L)$ values is discussed as a function of the average ligand charge density. Next, linear relationships are derived between experimental potentials for a wide range of first row transition metal couples with the derived $E_L(L)$ values. The significance of the slopes and intercepts derived from the regression statistics follow, and finally, the potential application of the $E_L(L)$ model to the chemistry of sandwich complexes is presented.

In this first analysis we restrict discussion to sandwich complexes, with homoleptic and heteroleptic ligands with general formula $[(\eta^{n1}\text{-}L_1)M(\eta^{n2}\text{-}L_2)]^q$, where ligands L_1, L_2 are η^4-$C_4Ph_4^{2-}$, η^5-$C_5H_5^{-}$ (Cp) or substituted Cp, η^6-C_6H_6 (benzene) or substituted benzene, η^7-$C_7H_7^{+}$, etc. Condensed ligands such as indene and fluorene are omitted from this preliminary investigation but will be analyzed at a later date.

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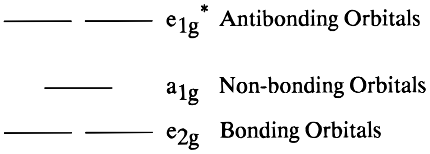
Scheme 1. Frontier Orbital Pattern of Iron Group Sandwich Complexes



Experimental Data

Data Analysis. The literature was explored to find a representatively large selection of sandwich complexes with metal based electrochemically reversible or quasi-reversible redox processes, according to the criteria noted above. For some unstable sandwich complexes, data at low temperature were selected where available.

Results and Discussion

1. Metal-Based Orbitals. Scheme 1 shows the d-orbital splitting pattern relevant for most types of first row transition metal sandwich complexes. Since the metal is low spin in the systems under study, occupation of the e_{1g} orbitals occurs only with d^7 and above. In some cases the order of the e_{2g} and a_{1g} orbitals is reversed.[32-36] According to Mossbauer,[33] ESR spectra,[37] and theoretical results,[38,39] the percentage of metal contribution to the HOMO orbitals of a_{1g} and e_{2g} in iron group sandwich complexes is more than 60%. Even in the e^*_{1g} orbitals, metal contributions are as high as 55%, 50%, and 37% for $FeCp_2$, $CoCp_2$, and $NiCp_2$ complexes.[38] In $NiCp_2$, the electrons in the e^*_{1g} orbitals delocalize extensively into the ligand π-framework.[34] However, in other nickel complexes, this percentage varies broadly, e.g. 77% for NiCp(COD) (COD = 1,5-cyclooctadiene).[40] These orbitals are still considered as metal-based orbitals.[34,38]

2. A Reference Standard for Evaluating the Redox Potentials of Sandwich Species. Using the extensive data base of low spin Fe^{III}/Fe^{II} potentials for sandwich species in organic solvents, we can define a value for $E_L(L)$ from homoleptic complexes

$$E_L(L) = (1/2)E°(Fe^{III}/Fe^{II}) \qquad (5)$$

while for mixed sandwich species, FeL_1L_2, the equation is

$$E°(Fe^{III}/Fe^{II}) = E_L(L_1) + E_L(L_2) \qquad (6)$$

In this way, $E_L(L)$ values for about 140 π-ligands have been derived (Table 1). When a ligand, such as $C_5H_4COOCHPh_2$-($E_L(L) = 0.58$ vs NHE), occurs in many complexes, an average best value was derived. Usually, the standard deviation is very small (less than 0.02 V).

The extent to which ligand additivity is valid in iron complexes (Fe^{III}/Fe^{II}) is shown in Figure 1, where the observed versus the calculated potentials are shown for 136 mixed-ligand–iron complexes. The intent of Figure 1 is to show that where there are several iron complexes with the same ligand, the scatter over the average $E_L(L)$ values is very small.

Solvent effects on the Fe^{III}/Fe^{II} couple are generally very small where different organic solvents are concerned, though with a few exceptions.[41] The observed and calculated values for these and all other data are collected in the Supporting Information, Appendix A. 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 2)

$$E_{obs}(Fe^{III}/Fe^{II}) = 0.99[\sum E_L(L)] + 0.00 \qquad R = 0.999 \qquad (7)$$

illustrating how well behaved is the Fe^{III}/Fe^{II} couple (in organic solvent).

3. Secondary Standards. Below are demonstrated linear correlations with a range of other metal ions and redox couples. In some cases an $E_L(L)$ value is not available from the Fe^{III}/Fe^{II} (organic solvent) database because of lack of a suitable complex. There may however be a Co^{III}/Co^{II} or Cr^I/Cr^0 or an Fe^{II}/Fe^I datum, or a Fe^{III}/Fe^{II} datum in aqueous phase, from which $E_L(L)$ can be extracted *if* one assumes that the complex concerned is well behaved with respect to that specific correlation. These secondary standards are likely to be a little less reliable and are listed in Table 3. Secondary standard $E_L(L)$ values may also be extracted from Hammett versus $E_L(L)$ correlations, to be described below.

3.1. Derivation of $E_L(L)$ for Benzene. There are virtually no data for the Fe^{III}/Fe^{II} couple for simple complexes containing benzene (Bz) or substituted derivatives thereof since the potentials would be rather too positive. This presents a problem to derive a standard E_L (Bz) value.

However there are a lot of data for the Fe^{II}/Fe^I couples in both organic and aqueous phase and for the Co^{III}/Co^{II}, Co^{II}/Co^I, Cr^{II}/Cr^I and Cr^I/Cr^0 couples. Therefore an iterative fit procedure was used to extract a value for benzene and its derivatives which would statistically best fit all these data.

A value for $E_L(Bz) = 1.86$ was iteratively derived by modifying both the $E_L(L)$ value for benzene and the regression parameters for the aforesaid processes until all errors converged to their minima. Once $E_L(L)(Bz)$ was established, similar procedures were performed to derive $E_L(L)$ values for other arene ligands where sufficient data allowed, i.e. where a substituted benzene ligand occurs in more than one complex. All regression fits were ultimately recalculated using optimized $E_L(L)$ values. Once the regression lines had been fixed, then the $E_L(L)$ for other substituted benzene derivatives could be extracted by assuming they lay on the particular regression line. Such points are not included in the plots of regression data (since they are extracted therefrom) except where there are complexes of the same substituted benzene occurring in several regression lines. A best fit value is derived and these points are shown on the regression lines in the figures to demonstrate accuracy of fit.

There is actually one benzene complex of iron for which the Fe^{III}/Fe^{II} datum is known, but it also contains a carborane ligand whose $E_L(L)$ can only be derived by referring to a condensed

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Table 1. $E_L(L)$ Parameters for π-Ligands Obtained from the Standard Fe(III)/Fe(II) Couple

ligand	$E_L(L)$/SD (V/NHE)	ref	ligand	$E_L(L)$/SD (V/NHE)	ref
1,2-$C_2Et_2B_4H_4$	−0.66	82	$C_5H_4C_6H_4CONHPh$-*p*	0.35	84
C_5H_2-1,2,4-Ph_3	0.37	aq,[a] 97	$C_5H_4C_6H_4COOCHPh_2$-*m*	0.40	91
$C_5H_3Et_2$-*o*	0.22	aq, 97	$C_5H_4C_6H_4COOCHPh_2$-*p*	0.42	91
$C_5H_3Et_2$-*m*	0.23	aq, 97	$C_5H_4C_6H_4COOEt$-*m*	0.41	91
$C_5H_3Ph_2$-*m*	0.34	aq, 97	$C_5H_4C_6H_4COOEt$-*p*	0.42	91
$C_5H_3(COMe)NHCOMe$-*o*	0.58	88	$C_5H_4C_6H_4COOH$-*m*	0.40	84, 91
$C_5H_3(COMe)Me$-*m*	0.53	88	$C_5H_4C_6H_4COOH$-*o*	0.38	91
$C_5H_3(Me)COOH$-*m*	0.52	aq, 97	$C_5H_4C_6H_4COOMe$-*m*	0.40	91
$C_5H_3(COOMe)COOH$-*o*	0.75	aq, 97	$C_5H_4C_6H_4COOMe$-*o*	0.39	91
$C_5H_3(Me)Et$-*o*	0.22	aq, 97	$C_5H_4C_6H_4F$-*o*	0.37	91
$C_5H_3(CH_2Ph)_2$-*o*	0.30	84	$C_5H_4C_6H_4I$-*o*	0.40	91
$C_5H_3(CH_2)_4$	0.21	85	$C_5H_4C_6H_4Me$-*m*	0.41	91
$C_5H_3(CH_2)_5$	0.20	85	$C_5H_4C_6H_4Me$-*o*	0.35	91
$C_5H_3(CH_2C_6H_4Br\text{-}m)_2$-*o*	0.34	84	$C_5H_4C_6H_4Me$-*p*	0.34	84, 91
$C_5H_3(CH_2C_6H_4Cl\text{-}p)_2$-*o*	0.33	84	$C_5H_4C_6H_4NPh_2$-*m*	0.40	91
$C_5H_3(CH_2C_6H_4F\text{-}p)_2$-*o*	0.31	84	$C_5H_4C_6H_4NPh_2$-*p*	0.40	91
$C_5H_3(CH_2C_6H_4Me\text{-}p)_2$-*o*	0.29	84	$C_5H_4C_6H_4NH_2$-*m*	0.34	84, 91
C_5H_4Br (3)[b]	0.50/0.01	80, 88	$C_5H_4C_6H_4NH_2$-*p*	0.26	84, 91
$C_5H_4C_6H_4COOH$-*p*	0.41	84, 91	$C_5H_4C_6H_4NHCOPh$-*m*	0.37	91
$C_5H_4CH_2CH_2Ph$	0.29	86	$C_5H_4C_6H_4NHCOPh$-*p*	0.35	91
$C_5H_4CH_2OH$	0.36	94, 95	$C_5H_4C_6H_4NO_2$-*m*	0.44	84, 91
$C_5H_4CH_2OMe$	0.33	86	$C_5H_4C_6H_4NO_2$-*o*	0.45	91
$C_5H_4CH_2OPh$	0.37	86	$C_5H_4C_6H_4NO_2$-*p*	0.46	84, 86[c]
$C_5H_4CH_2Ph$ (3)	0.31/0.01	86	$C_5H_4C_6H_4OEt$-*o*	0.31	91
C_5H_4CHO	0.61	80, 86	$C_5H_4C_6H_4OH$-*p*	0.31	84, 91
$C_5H_4CH(Me)CMe_3$	0.25	86	$C_5H_4C_6H_4OMe$-*o*	0.31	91
$C_5H_4CH(OH)Me$	0.32	74, 84	$C_5H_4C_6H_4OMe$-*p*	0.31	84, 86
$C_5H_4CH(OH)Ph$ (3)	0.34/0.01	74, 84	$C_5H_4C_6H_4Ph$-*o*	0.35	91
$C_5H_4CHPh_2$	0.34	84	$C_5H_4C_6H_4Ph$-*p*	0.36	84, 91
$C_5H_4CH(Ph)Et$	0.29	86	C_5H_4CHO	0.61	80, 86
$C_5H_4CH(Ph)Me$	0.54	84	$C_5H_4CH_2CH{=}CHPh$	0.58	86
$C_5H_4CONPh_2$ (3)	0.51/0.01	84	$C_5H_4C_{10}H_{21}$	0.27	86
$C_5H_4COOCHPh_2$ (6)	0.58/0.01	84	C_5H_4-*i*-C_3H_7 (2)	0.28/0.00	86
C_5H_4COOEt	0.57	84	$C_5H_4N_3P_3F_5$	0.72	92
C_5H_4COOH (3)	0.56/0.01	80, 84[c]	$C_5H_4N_3P_3(OCH_2CF_3)_5$ (2)	0.64/0.03	92
C_5H_4COOMe	0.58	84[c]	$C_5H_4N_4P_4F_7$	0.71	92
C_5H_4COPh (2)	0.58/0.01	74, 80[c]	$C_5H_4NHCOMe$ (2)	0.26/0.01	88
$C_5H_4CPh_3$	0.39	84	$C_5H_4NHCOOEt$	0.26	88
C_5H_4Et (3)	0.27/0.01	74, 86[c]	$C_5H_4NHCOOMe$ (3)	0.25/0.01	88
C_5H_4I	0.54	84	C_5H_4-*n*-C_3H_7	0.27	86
$C_5H_4CONPh_2$ (3)	0.51/0.01	84	$C_5H_4C_8H_{17}$	0.28	86
$C_5H_4COOCHPh_2$ (6)	0.58/0.01	84	$C_5H_4C_6H_2$-2,6-Me_2-4-NO_2	0.43	91
C_5H_4COOEt	0.57	84	$C_5H_4C_6H_3$-2-Me-4-NO_2	0.44	91
C_5H_4COOH (3)	0.56/0.01	80, 84[c]	$C_5H_4C_6H_3$-2-Me-5-NO_2	0.44	91
C_5H_4COOMe	0.58	84[c]	$C_5H_4C_6H_3$-2-Me-6-NO_2	0.45	91
C_5H_4COPh (2)	0.58/0.01	74, 80[c]	C_5HEt_4	0.11	aq, 97
$C_5H_4CPh_3$	0.39	84	C_5HPh_4	0.35	81
C_5H_4Et (3)	0.27/0.01	74, 86[c]	Cp (C_5H_5, cyclopentadienyl)) (97)	0.33/0.01	42, et al.
C_5H_4I	0.48	80, 84	Cp* (C_5Me_5, pentamethylcyclopentadienyl) (2)	0.06/0.01	42, 79[c]
C_5H_4Me (2)	0.28/0.00	86, 89	Ind (η^5-indenyl)	0.26	90
$C_5H_4NH_2$	−0.04	80	η^6-C_6H_6 (η^6-benzene)	1.86	83
$C_5H_4NMe_2$ (2)	−0.01/0.02	80, 87	η^6-IndH (η^6-indene)	1.82	82
$C_5H_4NPh_2$ (2)	0.11/0.02	80	(1/2)$C_5H_4CH_2OCH_2C_5H_4$	0.38	aq, 96
C_5H_4OEt	0.32	80	(1/2)($(C_5H_4CHMe)_2O$)	0.38	aq, 96
C_5H_4OMe	0.30	80, 88	(1/2)($(C_5H_4CHPh)_2O$)	0.38	aq, 96
C_5H_4OPh	0.32	80	(1/2)$C_5H_4CO(CH_2)_3C_5H_4$	0.46	aq, 96
C_5H_4Ph (2)	0.35/0.01	80, 86[c]	(1/2)$C_5H_4CO(CH_2)_4C_5H_4$	0.47	aq, 96
$C_5H_4SiMe_3$ (2)	0.34/0.01	86	(1/2)$C_5H_4CO(CH_2)_5C_5H_4$	0.49	aq, 96
C_5H_4-*s*-C_4H_9	0.28	86	(1/2)$(C_5H_4)_2$-1,3-$N_4P_4(OCH_2CF_3)_6$	0.59	92
$C_5H_4C_6H_4Br$-*m* (2)	0.40/0.01	84, 91	(1/2)$C_5H_4(CH_2)_2C_5H_4$	0.25	aq, 96
$C_5H_4C_6H_4Br$-*o*	0.40	91	(1/2)($(C_5H_4(CH_2)_2)_2CO$)	0.31	aq, 96
$C_5H_4C_6H_4Br$-*p* (2)	0.38/0.01	84, 86	(1/2)$C_5H_4(CH_2)_3C_5H_4$	0.30	aq, 96
$C_5H_4C_6H_4CF_3$-*m*	0.41	84	(1/2)$C_5H_4(CH_2)_4C_5H_4$	0.29	aq, 96
$C_5H_4C_6H_4CH_2OH$-*o*	0.36	91	(1/2)$C_5H_4(CH_2)_5C_5H_4$	0.27	aq, 96
$C_5H_4C_6H_4Cl$-*o*	0.39	91	(1/2)$(C_5H_4)_2$-1,3-$N_4P_4F_6$	0.64	92
$C_5H_4C_6H_4Cl$-*p*	0.38	84, 86	(1/2)$(C_5H_4)_2$-1,5-$N_4P_4F_6$	0.70	92
$C_5H_4C_6H_4CN$-*p*	0.45	84, 91	(1/2)$(C_5H_4)_2$-1,5-$N_4P_4(OCH_2CF_3)_6$	0.63	92
$C_5H_4C_6H_4COMe$-*p*	0.41	84, 86[c]	(1/2)$(C_5H_4)_2$-$N_3P_3(OC_6H_5)_4$	0.57	92
$C_5H_4C_6H_4CONHPh$-*m*	0.37	84	(1/2)$(C_5H_4)_2$-$N_3P_3(OCH_2CF_3)_4$	0.62	92

[a] $E_L(L)$ values were derived from aqueous solution. [b] Number in parentheses is the number of values used to obtain an average. [c] Data were obtained from more than two literature sources, but only two are cited.

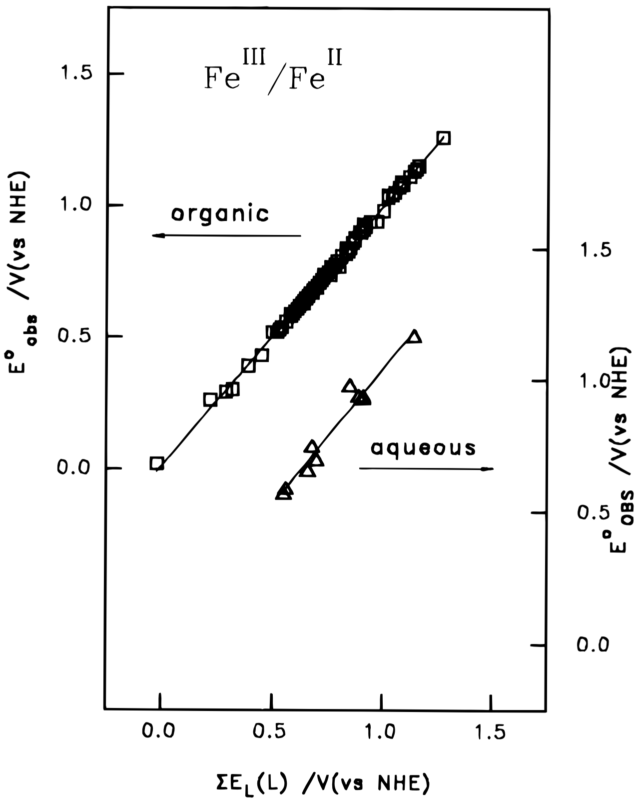

Figure 1. The $\Sigma E_L(L)$ plots for Fe^{III}/Fe^{II} sandwich complexes in organic phase (open squares, left-hand *y* axis) and in aqueous medium (open triangles, right-hand *y* axis). All data are referred to NHE. None of the complexes displayed in the aqueous medium plot were used to derive $E_L(L)$. For a listing of the data in these and subsequent plots, see Supporting Information, Appendix A.

Table 2. Regression Results for $E_L(L)$ Plots of the First Row Transition Metal Couples.

metal couple[a]	slope/SD	intercept / SD No. (V)	No.	*R*	medium
Ti^{II}/Ti^{I}	0.16/0.10	−2.45/0.04	5	0.678	organic
Cr^{III}/Cr^{II}	0.86/0.12	−0.85/0.05	3	0.991	organic
Cr^{II}/Cr^{I}	0.96/0.03	−2.50/0.09	5	0.999	organic
Cr^{I}/Cr^{0}	0.80/0.06	−3.46/0.06	15	0.970	organic
Fe^{III}/Fe^{II}	0.99/0.00	0.00/0.01	156	0.999	organic
Fe^{II}/Fe^{I}	1.02/0.01	−3.40/0.03	11	0.999	organic
Fe^{III}/Fe^{II}	1.03/0.07	0.01/0.04	11	0.981	aqueous
Fe^{II}/Fe^{I}	0.97/0.03	−3.45/0.06	11	0.995	aqueous
Co^{III}/Co^{II}	0.83/0.05	−1.16/0.13	11	0.985	organic
Co^{II}/Co^{I}	0.88/0.07	−2.21/0.16	10	0.976	organic
Ni^{IV}/Ni^{III}	0.78/0.02	0.46/0.05	5	0.999	organic
Ni^{III}/Ni^{II}	0.91/0.09	−0.40/0.14	4	0.991	organic

[a] All metal ions are low spin.

ligand complex of iron. This provides a "trail" whose accuracy is suspect if it were to be relied upon alone.

Thus a value for indene (Ind) can be extracted from the Fe^{III}/Fe^{II} couple of $E[(Ind)CpFe]^{+/0}$ which then leads to an $E_L(L)$ value for $C_2Et_2B_4H_4$ from $E[(Ind)(C_2Et_2B_4H_4)Fe]^{0/-}$ (see Supporting Information, Appendix A). Finally, we can derive $E_L(Bz) = 1.86$, the same value as acquired from the iterative procedure discussed above, from $E[(C_2Et_2B_4H_4)(Bz)Fe]^{+/0}$. This internal consistency corroborates the validity of the method described above. Note that all $E_L(L)$ values for Cp and its derivative originate from the Fe^{III}/Fe^{II} redox couple. Therefore, the iterative model, and thus $E_L(L)$ values for the arene ligands, is anchored to the Fe^{III}/Fe^{II} couple even though other redox couples were used in the analysis.

Table 3. Secondary $E_L(L)$ Database for π-Ligands

ligand	$E_L(L)$/SD (V/NHE)	source[a]	ref
$C_5H_3(i\text{-}C_3H_7)_2$	0.22	σ_p	
$C_5H_3(t\text{-}C_4H_9)_2$	0.18	σ_p	
C_5H_4−piperidyl	0.14	Fe(org)	60
$C_5H_4\text{-}t\text{-}C_4H_9$	0.26	σ_p	
C_5Ph_5 (2)[b]	0.54/0.09	Ni	109
$\eta^4\text{-}C_4Ph_4$ (tetraphenylcyclotetradiene) (2)	−1.59	see text	
$\eta^6\text{-}C_6H_2\text{-}1,2,4,5\text{-}Me_4$ (2)	1.71/0.01	Fe(both)	65, 100
$\eta^6\text{-}C_6H_3\text{-}1,3,5\text{-}Me_3$ (7)	1.73	see text	
$\eta^6\text{-}C_6H_3Ph_3$	1.97	Cr(org)	116[c]
$\eta^6\text{-}C_6H_3\text{-}1,4\text{-}Me_2\text{-}2\text{-}Cl$	1.95	Cr(org)	121
$\eta^6\text{-}C_6H_4Me_2\text{-}p$ (2)	1.75	see text	
$\eta^6\text{-}C_6H_4(Me)Cl\text{-}p$	1.96	Fe(org)	60
$\eta^6\text{-}C_6H_4(Me)CN\text{-}p$	2.17	Fe(org)	60
$\eta^6\text{-}C_6H_4(Me)F\text{-}p$	1.93	Fe(org)	60
$\eta^6\text{-}C_6H_4(Me)NHCOMe\text{-}p$	1.83	Fe(org)	60
$\eta^6\text{-}C_6H_4(Me)OMe\text{-}p$	1.81	Fe(org)	60
$\eta^6\text{-}C_6H_4(Me)SMe\text{-}p$	1.88	Fe(org)	60
$\eta^6\text{-}C_6H_5CF_3$ (2)	2.17	Cr(org)	121, 122
$\eta^6\text{-}C_6H_5CH_2COOEt$	1.85	Cr(org)	116
$\eta^6\text{-}C_6H_5CH_2OH$	1.82	Fe(aq)	102
$\eta^6\text{-}C_6H_5CHO$ (2)	2.10/0.02	Cr(org)	116
$\eta^6\text{-}C_6H_5CH{=}CHCOOEt$	1.94	Cr(org)	116
$\eta^6\text{-}C_6H_5CH{=}CHCOPh$	1.97	Cr(org)	116
$\eta^6\text{-}C_6H_5COMe$ (2)	2.06/0.01	Cr(org)	116, 122
$\eta^6\text{-}C_6H_5COOEt$	2.06	Cr(org)	115
$\eta^6\text{-}C_6H_5COOH$	1.95	Fe(aq)	102
$\eta^6\text{-}C_6H_5C{\equiv}CPh$	1.87	Cr(org)	122
$\eta^6\text{-}C_6H_5F$ (3)	2.05/0.02	Cr(org)	122
$\eta^6\text{-}C_6H_5I$	2.09	Cr(org)	122
$\eta^6\text{-}C_6H_5(CH_2)_2COOEt$	1.79	Cr(org)	116
$\eta^6\text{-}C_6H_5(CH_2)_4Ph$	1.77	Cr(org)	116
$\eta^6\text{-}C_6H_5C_6H_4CF_3\text{-}p$	2.14	Cr(org)	121, 122
$\eta^6\text{-}C_6H_5Ph$ (2)	1.96	see text	
$\eta^6\text{-}C_6H_5(CF_3)_2\text{-}m$	2.51	Cr(org)	121
$\eta^6\text{-}C_6H_5\text{-}(CF_3)_2\text{-}p$	2.48	Cr(org)	121
$\eta^6\text{-}C_6H_5CH_2Ph$	1.93	Fe(org)	124
$\eta^6\text{-}C_6H_5Cl$	2.03	Fe(org)	124
$\eta^6\text{-}C_6H_5(Cl)CF_3\text{-}o$	2.37	Cr(org)	121
$\eta^6\text{-}C_6H_5(Cl)CF_3\text{-}p$	2.35	Cr(org)	121
$\eta^6\text{-}C_6H_5CN$	2.18	Fe(org)	124
$\eta^6\text{-}C_6H_5COOMe$	2.11	Fe(org)	124
$\eta^6\text{-}C_6H_5COPh$	2.17	Fe(org)	124
$\eta^6\text{-}C_6H_5Et$ (2)	1.77	see text	
$\eta^6\text{-}C_6H_5Me$ (2)	1.79	see text	
$\eta^6\text{-}C_6H_5NMe_2$	1.69	Fe(org)	124
$\eta^6\text{-}C_6H_5NO_2$	2.58	Fe(org)	124
$\eta^6\text{-}C_6H_5OMe$	1.81	Fe(org)	124
$\eta^6\text{-}C_6H_5OPh$	1.90	Fe(org)	124
$\eta^6\text{-}C_6H_5SC_6H_4Me\text{-}p$	1.98	Fe(org)	124
$\eta^6\text{-}C_6H_5SO_2C_6H4Me\text{-}p$	2.18	Fe(org)	124
$\eta^6\text{-}C_6H_5\text{-}t\text{-}C_4H_9$	1.82	Fe(org)	124
$\eta^6\text{-}C_6H_6$	1.86	see text	
$\eta^6\text{-}C_6HMe_5$	1.60	see text	
$\eta^6\text{-}C_6Me_6$	1.66	see text	
$\eta^6\text{-}C_6Ph_6$	2.12	Cr(org)	122
η^6-FluH(η^6-fluorene) (2)	1.94/0.02	Fe(org)	60, 110
η^6-dihydroxanthracene	1.81	Fe(org)	101
η^6-thioxanthene	1.94	Fe(org)	101
η^6-xanthene	1.89	Fe(org)	101
$\eta^7\text{-}C_7H_7$(η^7-cycloheptatrienium)	3.62	Cr(org)	114
(1/2)(η^6-2,2′-paracyclophone)-benzene	1.86	Cr(org)	114
(1/2)($\eta^6\text{-}C_6H_5(CH_2)_4C_6H_5\text{-}\eta^6$)	1.79	Cr(org)	116

[a] Fe, extracted from $Fe^{II/I}$ regression; Fe(org), from organic medium data; Fe(aq), from aqueous medium data; Fe(both), from both organic and aqueuous media; Co, from Co^{III}/Co^{II} and Co^{II}/Co^{I} data; Ni, from Ni^{IV}/Ni^{III} and Ni^{III}/Ni^{II} data; Cr, from Cr^{I}/Cr^{0}; and σ_p, $E_L(L)$ is calculated from the correlation parameters between $E_L(L)$ and σ_p. [b] The number in parentheses is number of values used to obtain an average. [c] Data were obtained from more than two literature sources, but only two are cited.

4. Errors. All the electrochemical data were extracted from the literature. Erroneous data may have been reported if inadequate care had been taken concerning the purity of solvents, the electrochemical cell design, the quality of the reference electrode, and the fact that where organic solvents are concerned, excessive cell resistance can lead to an appreciable *IR* drop thereby leading to error, as indeed, can the presence of junction potentials. The pseudoreversibility of some chosen redox potentials may also be a source of error. Moreover, data in the literature are reported against a variety of reference electrodes including NHE, SCE, SSCE, ferrocenium/ferrocene, and several different silver-based couples. In this collection, data are corrected to a common electrode, NHE. In the frequent case where the ferrocenium/ferrocene couple was used as the internal standard, the potentials are converted based upon the assumption that the $E°$ value is 0.66 V vs NHE,[42] a value commonly accepted for CH_3CN. This value was used for all solvents. Other commonly encountered internal standards[28b] include $CoCp_2(Co^{III}/Co^{II})$ (-0.69 V), and $Cr(biphenyl)_2$ (-0.47 V), (potential vs NHE noted in parentheses, in MeCN).

In cases where ferrocene (or another internal standard) was not used, the data were corrected according to conversion factors in ref 43. Note that if the authors used a value different from that quoted here, e.g. 0.36 V vs SCE (0.60 vs NHE) for Fc^+/Fc, in MeCN, and then listed all their data vs SCE, then all the data in that article would be amended by 0.06 V for use in this analysis; similar corrections were made for other references and are listed in the footnotes to the Appendices A and B in the Supporting Information. These corrections may be a source of additional error inasmuch as we have assumed specific correction factors which may be subject themselves to error.

Supporting electrolyte effects on the electrochemistry of the sandwich complexes (mainly can be explained by ion pair formation) are typically small when tetraalkylammonium BF_4^- or PF_6^- salts are used but sometimes may cause irreversibility, for example with $FeCp*_2$.[41,44] It is evident that the experimental values are subject to some error and the scatter in the line may reflect such experimental limitations rather than breakdown in ligand additivity.

Overall, where a given Cp ligand may appear in several complexes, the variation of its $E_L(L)$ value, cited in the tables, rarely exceeds 0.02 V. For arene ligands, the variation rarely exceeds 0.03 V, though for a limited number of multisubstituted benzene ligands (more than three substituents), the error could be more than 0.10 V. All $E_L(L)$ values with large errors are found in the secondary $E_L(L)$ database (Table 3). However, the relative percentage errors are generally not high because the $E_L(L)$ values themselves are large.

Since the Cp ligand appears in so many complexes, any error in its $E_L(Cp)$ value would repeat through the entire database. Therefore the value of $E_L(Cp) = 0.33$ V vs NHE was derived by minimizing the error over 97 Fe^{III}/Fe^{II} couples.

5. Correlation between E_L(L) and Hammett Substituent Constants. We have previously shown excellent relationships between $E_L(L)$ and substituent constants for substituted pyridines, bipyridines, diketones, etc.[10] Recently, Sharpe and coworkers noted a good correlation for oxidation and reduction potentials for tris(acetylacetonate) ruthenium complexes with Taft σ_I parameters.[3d] Good correlations of the oxidation potentials for some ferrocene derivatives with Hammett σ_p and σ_m constants for the substituents attached to the Cp ring have been previously reported.[45] Therefore, similar correlations with the present data base are expected for substituted Cp and arene ligands.

Due to the geometry of these systems, there are no obviously defined ortho or para positions, and it is not clear which substituent constants are most suitable to use. After analysis of possible relationships between sandwich $E_L(L)$ and the various substituent constants which include σ_m, σ_p, σ^+, σ^*,[46] and σ^{ph},[47] etc., the σ_p constant is found to be the most well behaved; see data in Table 4 and Figure 2. With some exceptions, noted below, the overall correlation is excellent and provides an important means of generating $E_L(L)$ values for a wide range of substituted cyclopentadiene and arene ligands.

5.1. Substituted Cp Series. For mono- or multisubstituted Cp ligands, an excellent correlation is shown in Figure 2 ($R = 0.98$) with least squared regression results shown in Table 5. There are a few scattered points mostly those of multisubstituted ligands with $\sum\sigma_p$ (the sum of σ_p values of the substituents) below zero. This may be due to a breakdown of the supposition that one can generate a value for $\sum\sigma_p$ in a simple additive fashion. Deviations may occur for a variety of reasons relating to synergic interactions between the substituents and possible distortion of the Cp framework. In this plot, the ligands C_5H_4-NHCOMe and $C_5H_4NH_2$ are poorly correlated (please see Figure 2, points 3 and 4).

5.2. Substituted Benzene Ligands. For mono- and multisubstituted benzene ligands, the $E_L(L)$ versus σ_p plot is shown in Figure 2 with data and regression results listed in Tables 4 and 5. In this plot, hexaphenylbenzene (point 1 in Figure 2), and nitrobenzene (point 2 in Figure 2) correlate poorly. These species are excluded from the correlation.

6. Extension of Fe^{III}/Fe^{II} Data in Aqueous Solutions. Some Fe^{III}/Fe^{II} potentials were recorded in aqueous solution. A linear correlation is observed between $E_L(L)$ and $E°_{obs}$ (Figure 1) defined by

$$E°_{obs}((Fe^{III}/Fe^{II})_{aq}) = 1.03\,[\sum E_L(L)] + 0.01 \qquad R = 0.981 \tag{8}$$

Regression and standard deviation data for this and subsequent correlations are shown in Table 2. In our previous analysis,[7] it was noted that the overall charge on the molecule was important in aqueous phase correlations because of significant variation of hydration energies when the charge varies. Equation 8 applies to iron systems whose Fe(II) species are uncharged; systems for which this is not true may not lie on this line. In subsequent discussion, cited charge always refers to the lower oxidation component.

In general, data obtained in aqueous medium are a little more scattered than those collected in common organic solvents because of the variation in electrolyte and pH. For some ligands, iron redox data are available in aqueous solution but not in an organic solvent. In these cases, the $E_L(L)$ values are calculated from eq 8 and are included in Table 1 (annotated as aq). The data used to calculate the $E_L(L)$ values are listed in the Supporting Information, Appendix B.

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Table 4. E_L(L) Parameters and Hammett Substituent Constants (σ_p) for π-Ligands

ligand	E_L(L) (V)	E_L(calc)[a] (V)	σ_p[b]	ligand	E_L(L) (V)	E_L(calc)[a] (V)	σ_p[b]
Figure 2.Substituted Cp Series							
$C_5H_3(CH_2)_4$ (σ_p is taken one time)	0.21	0.14	−0.48	$C_5H_4C_6H_4Br$-*m*	0.40	0.40	0.08
Cp*[c]	0.06	−0.02	−0.85	C_5H_4OEt	0.32	0.25	−0.24
C_5HEt_4	0.11	0.09	−0.60	$C_5H_3Ph_2$-*m*	0.34	0.35	−0.02
$C_5H_4NMe_2$	−0.01	−0.01	−0.83	C_5H_4OMe	0.30	0.24	−0.27
$C_5H_3(CH_2Ph)_2$-*o*	0.30	0.28	−0.18	$C_5H_4C_6H_4Br$-*p*	0.38	0.41	0.12
$C_5H_3(Me)Et$-*o*	0.22	0.22	−0.32	$C_5H_4C_6H_4Cl$-*p*	0.38	0.41	0.12
$C_5H_3Et_2$-*m*	0.23	0.22	−0.30	C_5H_2-1,2,4-Ph_3	0.37	0.35	−0.03
$C_5H_3Et_2$-*o*	0.22	0.22	−0.30	$C_5H_4C_6H_4NO_2$-*m*	0.44	0.45	0.20
$C_5H_4CH_2Ph$	0.31	0.32	−0.09	$C_5H_4CONHPh$	0.54	0.54	0.41
C_5H_4-*s*-C_4H_9	0.28	0.31	−0.12	C_5HPh_4	0.35	0.34	−0.04
$C_5H_4CH_2CH_2Ph$	0.29	0.31	−0.12	$C_5H_4C_6H_4NO_2$-*p*	0.46	0.48	0.26
C_5H_4Et	0.27	0.29	−0.15	C_5H_4OPh	0.32	0.35	−0.03
C_5H_4Me	0.28	0.28	−0.17	$C_5H_4CONH_2$	0.54	0.52	0.36
C_5H_4-*n*-C_3H_7	0.27	0.30	−0.13	$C_5H_3(COMe)Me$-*m*	0.53	0.51	0.33
$C_5H_4SiMe_3$	0.34	0.33	−0.07	C_5H_4COPh	0.58	0.55	0.43
$C_5H_4CHPh_2$	0.34	0.34	−0.05	C_5H_4CHO	0.61	0.55	0.42
$C_5H_4NHCOOMe$	0.25	0.28	−0.17	C_5H_4I	0.48	0.44	0.18
$C_5H_4CPh_3$	0.39	0.37	0.02	$C_5H_4COOCHPh_2$	0.58	0.61	0.56
Cp	0.33	0.36	0.00	C_5H_4COOH	0.56	0.56	0.45
$C_5H_4CH(OH)Ph$	0.34	0.35	−0.03	C_5H_4COOMe	0.58	0.56	0.45
$C_5H_4CH{=}CHMe$ (σ_p from *trans*-$CH{=}CHMe$)	0.31	0.32	−0.09	C_5H_4COOEt	0.57	0.56	0.45
$C_5H_4CH{=}CHPh$	0.32	0.33	−0.07	C_5H_4Cl	0.51	0.46	0.23
$C_5H_4C_6H_4OMe$-*p*	0.31	0.32	−0.08	C_5H_4COMe	0.58	0.59	0.50
$C_5H_4C_6H_4Me$-*p*	0.34	0.35	−0.03	C_5H_4Br	0.50	0.46	0.23
C_5H_4Ph	0.35	0.36	−0.01	C_5H_4CN	0.69	0.66	0.66
$C_5H_4CH_2OPh$	0.37	0.39	0.07	$C_5H_3(COMe)NHCOMe$-*o*	0.58	0.59	0.50
$C_5H_4CH{=}CH_2$	0.35	0.34	−0.04	$C_5H_3(COOMe)COOH$-*o*	0.75	0.77	0.90
$C_5H_4CH_2OMe$	0.33	0.36	0.01	$C_5H_4NH_2$[c]	−0.04	0.06	−0.66
$C_5H_4CH(OH)Me$	0.32	0.33	−0.07	$C_5H_4NHCOMe$[d]	0.26	0.36	0.00
Figure 2.Substituted Benzene Series[e]							
$C_6H_4(CF_3)_2$-*m*	2.51	2.40	1.08	C_6H_5F	2.05	1.98	0.06
$C_6H_4(CF_3)_2$-*p*	2.48	2.40	1.08	C_6H_5I	2.09	2.03	0.18
$C_6H_4(Cl)CF_3$-*o*	2.37	2.27	0.77	C_6H_5Ph	1.96	1.95	−0.01
$C_6H_4(Cl)CF_3$-*p*	2.35	2.27	0.77	$C_6H_5CH_2Ph$	1.93	1.91	−0.09
C_6H_2-1,2,4,5-Me_4	1.71	1.66	−0.68	C_6H_5Cl	2.03	2.05	0.23
C_6H_3-1,3,5-Me_3	1.73	1.74	−0.51	C_6H_5CN	2.18	2.23	0.66
$C_6H_3Ph_3$	1.97	1.94	−0.03	C_6H_5COOMe	2.11	2.14	0.45
C_6H_3-1,4-Me_2-2-Cl	1.95	1.90	−0.11	C_6H_5COPh	2.17	2.13	0.43
$C_6H_4Me_2$-*p*	1.75	1.81	−0.34	C_6H_5Et	1.77	1.89	−0.15
$C_6H_4(Me)Cl$-*p*	1.96	1.98	0.06	C_6H_5Me	1.79	1.88	−0.17
$C_6H_4(Me)CN$-*p*	2.17	2.16	0.49	$C_6H_5NMe_2$	1.69	1.60	−0.83
$C_6H_4(Me)F$-*p*	1.93	1.90	−0.11	C_6H_5OMe	1.81	1.84	−0.27
$C_6H_4(Me)NHCOMe$-*p*	1.83	1.88	−0.17	C_6H_5OPh	1.90	1.94	−0.03
$C_6H_4(Me)OMe$-*p*	1.81	1.77	−0.44	C_6H_5-*t*-But	1.82	1.87	−0.20
$C_6H_4(Me)SMe$-*p*	1.88	1.88	−0.17	C_6H_6	1.86	1.95	0.00
$C_6H_5CF_3$	2.17	2.18	0.54	C_6HMe_5	1.60	1.59	−0.85
C_6H_5CHO	2.10	2.13	0.42	C_6Me_6[c]	1.66	1.52	−1.02
C_6H_5COMe	2.06	2.16	0.50	C_6Ph_6[d]	2.12	1.92	−0.06
C_6H_5COOEt	2.06	2.14	0.45	$C_6H_5NO_2$[d]	2.59	2.28	0.78

[a] E_L(calc) was calculated from the correlation results listed in Table 5. [b] The σ_p data are from ref 84. [c] Although the correlation is poor for these species, they are included in the regression. [d] These very poorly correlated complexes were excluded from the correlation. [e] For the sake of simplicity, the hapticity of η^6- is omitted for all substituted benzene.

7. Range of E_L(L) Values. As with the spectrochemical series of *Dq*, and the previous reported electrochemical series of ligands, the E_L(L) values of all the Cp, arene, and other ligands must lie in the same sequence toward all metal ions if this analysis is to be viable. The ligand sequence may be abbreviated into ranges which can be used as a guide to estimate the E_L values of ligands that do not appear in Tables 1 and 3.

The E_L(L) range sequence for π-ligands is as follows: (i) η^4-$C_4Ph_4^{2-}$, −1.59 V; (ii) substituted Cp ligands, −0.04 → 0.72 V; (iv) substituted benzene ligands, 1.6 → 3.0 V; (v) η^7-$C_7H_7^+$ ligand, +3.62 V.

The E_L(L) values so far derived vary from ca. −1.59 to +3.62 V. For comparison with the earlier analysis,[7] these numbers should be divided by three since the ligands generally occupy three sites on the metal complex. The overall range from most positive to most negative is comparable to that in the previous Ru^{III}/Ru^{II} standardized series.[7]

7.1. Effects of the Average Charge Density (ACD) of a Ligand on its E_L(L) Value. In the initial Ru^{III}/Ru^{II}-based ligand electrochemical series,[7] the ligands are ordered roughly as π-donor < non-π-ligand < π-acceptor with superimposed thereon, a trend toward increasing E_L(L) values with decreasing negative charge (increasing positive charge). The question then arises as to whether the sandwich-based series might be similarly factorized.

The average charge densities of ligands are calculated trivially by dividing the total charge of the ligand by the hapticity number, e.g. for Cp, ACD = (−1)/5 = −0.2. The average charge density is a formal value and does not reflect the actual charge distribution on the ligand. For analogous ligands with

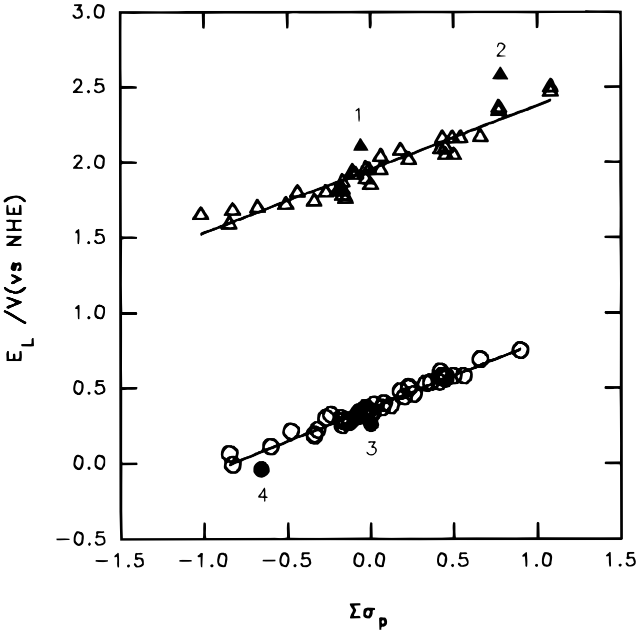

Figure 2. Plots of E_L(L) ligand values versus the Hammett substituent parameter $\sum\sigma_p$ for substituted cyclopentadienyl (open circles, lower plot) and arene ligands (open triangles, upper plot). The numbered ligands are the most poorly correlated: (1) C_6Ph_6; (2) $C_6H_5NO_2$; (3) $C_5H_4NHCOMe$; (4) $C_5H_4NH_2$.

Table 5. Regression Results between E_L(L) Values of π-Ligands and Their Substituent Constants (σ_p)

π-ligand group name	slope/SD[a]	intercept/SD	no.	*R*
substituted Cp series	0.45/0.01	0.36/0.03	57	0.98
substituted C_6H_6 series	0.42/0.02	1.95/0.06	36	0.96

[a] The slopes are the coefficients of σ_p.

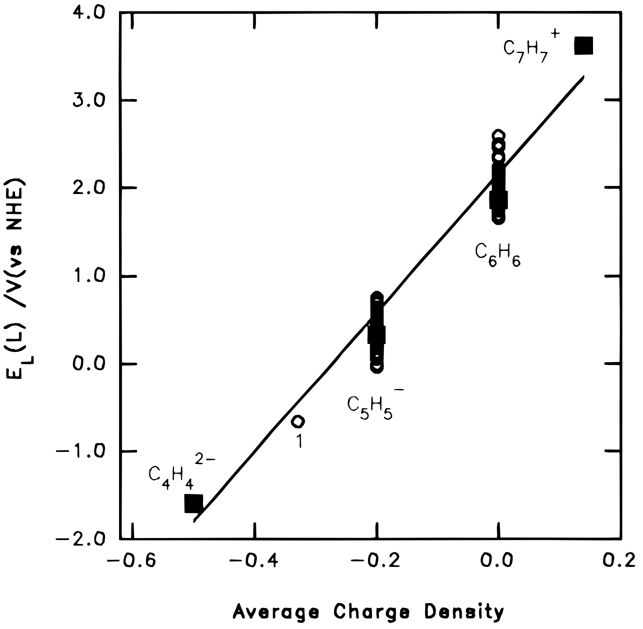

Figure 3. Plot of ligand E_L(L) values vs their average charge density. The parent unsubstituted species is identified as a solid square. Ligand 1 is a carborane, $[1,2\text{-}C_2(Et)_2B_4H_4]^{2-}$.

different hapticity, the more negative the average charge density is, the smaller is E_L(L) in keeping with the Ru^{III}/Ru^{II}-based parameters.[7]

Figure 3 shows a plot of all the data collected here. The unsubstituted ligands correlate roughly linearly. While obviously there is a spread in the substituted species, it is noteworthy that the vertical ranges of E_L(L) do not overlap. To test the validity further, a carborane($1,2\text{-}C_2(Et)_2B_4H_4^{2-}$) data point is added, and it correlates well with the Cp and arene data. Thus overall charge/carbon atom, at least in a formal sense, is a major factor in defining the E_L(L) value of the sandwich ligand.

8. Comparison with Other Electrochemical Data Sets. As with the non-sandwich complexes, 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 the Fe^{III}/Fe^{II} couple. Thus, the observed potentials for an M^{n+1}/M^n couple, for the general species ML_1L_2, are plotted against the sum $\sum E_L$(L), to obtain the so-called $\sum E_L$(L) plot. Least-squares analysis to fit the calculated to the observed data, yields the general equation

$$E_{obs}(M^{n+1}/M^n) = S_M[\sum E_L(L)] + I_M \qquad (9)$$

from which values of S_M and I_M for the specific couple M^{n+1}/M^n are extracted.

For any given M^{n+1}/M^n E_L(L) correlation, the spin states and stereochemistry must remain constant; i.e., systems of a given M^{n+1}/M^n couple involving different spin states will lie on different correlation lines. Sandwich complexes have almost the same parallel ring stereochemistry except for a few examples with distorted structures[48−51] and some examples where the dihedral angle between the rings may open up.[49,51] Such distortions may affect the E_L(L) values. Most metal ions found in sandwich complexes are low spin.[38,52−54] Only a few are high spin, or demonstrate an equilibrium between high and low spin states, e.g. $Mn(C_5H_4Me)_2$,[52,55] and would not fit their standard correlation line. In this paper, all the metal ions in their various oxidation states are low spin with respect to Scheme 1.

8.1. The Ni^{III}/Ni^{II} (d^7/d^8) Couple. The Ni(III)/Ni(II) $\sum E_L$ plot, in organic solvent, is shown in Figure 4. The four available complexes with 1− and 0 charge all correlate very well, though $NiCp_2$ is reported to have significant delocalization of the d-electrons into the π-framework of the Cp ligands.[34,56]

8.2. The Ni^{IV}/Ni^{III} (d^6/d^7) Couple. Figure 4 also shows the Ni(IV)/Ni(III) potential plot in organic solvent. The e^*_{1g} orbitals involved in the redox reactions are mainly metal-based. A good correlation is obtained regardless of the various total charges of the complexes (0 and +1) though with a limited data set.

8.3. The Co^{II}/Co^I (d^7/d^8) Couple. The Co^{II}/Co^I potentials are plotted against $\sum E_L$(L) values in organic solvent in Figure 5. In these complexes, the charge varies from 1+ to 1−. All species with a zero charge correlate very well but those with 1− charge correlate less well and, like the zero charge species discussed above, have less reliably known experimental values; i.e. there is some variation in the potential reported for the same species from different laboratories; the average was used.

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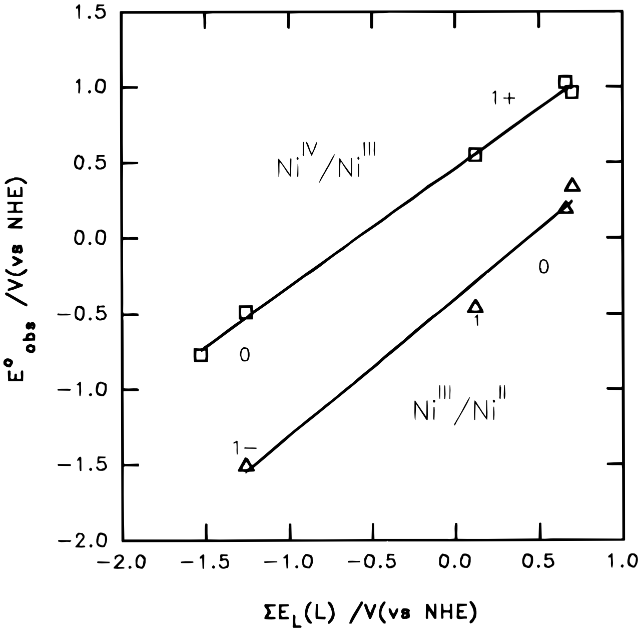

Figure 4. $\sum E_{\mathrm{L}}$(L) plots for nickel sandwich complexes in organic phase as identified. The appended numerals in this and subsequent plots, are the net charges of the lower oxidation state complex.

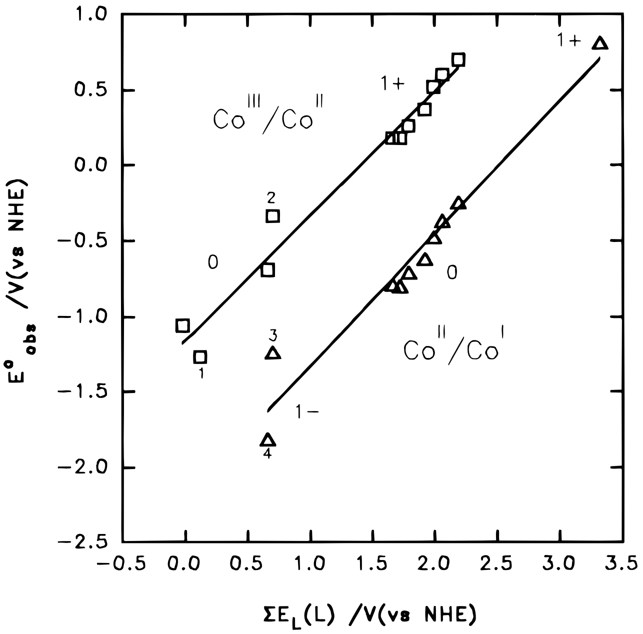

Figure 5. The $\sum E_{\mathrm{L}}$(L) plots for cobalt sandwich complexes in organic phase as identified. Poorly behaved compounds: 1, CoCp*$_2$; 2 and 3, Co(C$_5$HPh$_4$)$_2$; 4, CoCp$_2$.

8.4. The Co^{III}/Co^{II} (d^6/d^7) Couple. The Co^{III}/Co^{II} $\sum E_{\mathrm{L}}$(L) plot in organic phase is shown in Figure 5. There are two kinds of complexes with zero and 1+ charge. The complexes with 1+ charge correlate very well though squeezed into a relatively very narrow range. The complexes with zero charge do not correlate so well by themselves. They are scattered in a range of low $\sum E_{\mathrm{L}}$(L) value. The reasons for the scatter may be as follows: (i) in this group of complexes there is considerable uncertainty in the reference electrode corrections, which is reflected in the large variation of redox potential for the same species from different laboratories e.g. the variation is as high as 0.09 V for CoCp*$_2$ with the average being taken in the E_{L}(L) plot; (ii) there is a significant difference in steric effects between iron and cobalt complexes, especially for the octophenyl metallocene.[57] Such large steric differences (structure distortions) may affect the E_{L}(L) plot. If all species are considered together regardless of charge, the correlation is satisfactory with $R = 0.985$. Only two complexes (CoCp*$_2$ and Co(C$_5$HPh$_4$)$_2$) are more poorly behaved but are still satisfactory (with 95% confidence).

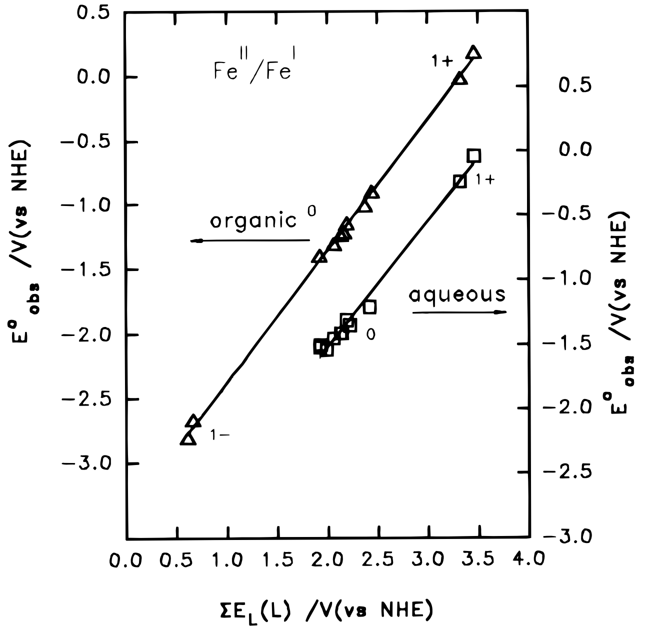

Figure 6. The $\sum E_{\mathrm{L}}$(L) plots for Fe^{II}/Fe^{I} sandwich complexes in organic phase (open triangles, left-hand *y* axis) and in aqueous medium (open squares, right-hand *y* axis).

8.5. The Fe^{II}/Fe^{I} (d^6/d^7) Couple. The ESR spectra of Fe^{I}C$_p$-(arene) or Fe^{I}(arene)$_2$ complexes reveal that the unpaired electron is mainly localized on the iron atom. Molecular orbital calculations and other spectroscopic results also confirm these conclusions.[33,37,38,58,59] The $\sum E_{\mathrm{L}}$(L) plots are shown in Figure 6 in aqueous and non-aqueous solvents. In non-aqueous solvent, all species correlate very well regardless of the charge they carry.

In non-aqueous solution, FeCp(arene)$^+$ complexes were reduced to neutral radical FeC$_p$(arene)[60−65] in a reversible step. In basic aqueous medium, the reduction of CpFe(arene)$^+$ cations to neutral radicals is followed by a slow decomposition or dimerization reaction,[66,67] but give rise to reversible or quasi-reversible electrochemistry. In the $\sum E_{\mathrm{L}}$(L) plot for the aqueous system (Figure 6) all complexes with zero charge gather in a narrow range of $\sum E_{\mathrm{L}}$(L) values. The correlation is quite good but the slope of 0.69 is rather low compared with the organic phase data (1.01). Two species with a 1+ charge are also plotted. If all species are considered together regardless of the charge they carry, the correlation is excellent (0.996) and the slope of the $\sum E_{\mathrm{L}}$(L) plot is increased to near unity (0.97) comparable with that in organic solution. The low value of the slope, 0.69 for the zero-charged species, may be an artifact

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due to the very narrow range of $\sum E_L(L)$ values. Further data are needed to confirm the regression line for aqueous Fe^{II}/Fe^{I} couple.

8.6. Chromium ($Cr^{III}/Cr^{II}/Cr^{I}/Cr^{0}$ $d^3/d^4/d^5/d^6$). The chromium dataset is especially valuable since it is relatively large and exists for three different redox couples. Magnetic susceptibility, EPR, and NMR studies indicate that the redox reactions are metal-based for all the Cr^{III}/Cr^{II}, Cr^{II}/Cr^{I}, and Cr^{I}/Cr^{0} couples.[68−71] For example the HOMOs of $Cr(Cp)_2^+$, $Cr(Cp^*)_2^+$ and $Cr(arene)_2^0$ are all mainly composed of the metal $3d_{z^2}$.[72,73]

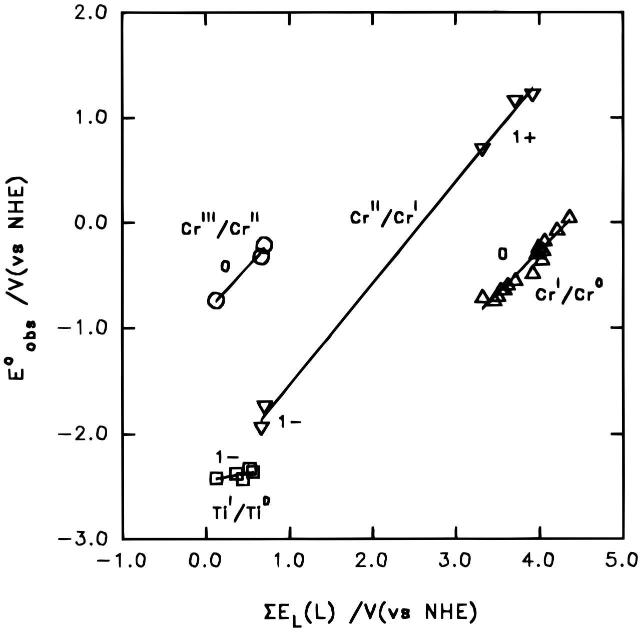

Figure 7. $\sum E_L(L)$ plots for chromium and titanium sandwich complexes in organic phase as identified.

Figure 7 shows the $\sum E_L(L)$ plot for these various chromium couples in organic medium. The $\sum E_L(L)$ plot for the $Cr^{III}/Cr^{II}(d^3/d^4)$ couple is included though clearly more data points are desirable. The $\sum E_L(L)$ plot for the $Cr^{II}/Cr^{I}(d^4/d^5)$ couple in organic phase has five complexes which belong to two types, (η^5, η^5) and (η^6, η^6), and have different charges, 1− and 1+. The correlation is excellent with $R = 0.999$. The complexes gather at the two ends of the correlation line in two narrow regions of $\sum E_L(L)$. Data in the middle region are needed to confirm this correlation. In the $\sum E_L(L)$ plot for the $Cr^{I}/Cr^{0}(d^5/d^6)$ couple in organic phase (Figure 7) all the complexes have the same charge of zero and the same ligand type (η^6, η^6).

8.7. The Ti^{II}/Ti^{I} (d^2/d^3) Couple. The Ti^{II}/Ti^{I} $\sum E_L(L)$ plot is shown in Figure 7. This couple has a poor correlation coefficient with limited data points within a narrow range of

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Table 6. Intercepts of the E_L(L) Plots and the Ionization Potentials (I_{pj}) of Metal in Gas Phase

metal ion	I_{pj}	I_p(eV)	intercept(V)
Fe^I	I_{P2}	16.2	−3.40
Fe^{II}	I_{P3}	30.7	0.00
Co^I	I_{P2}	17.1	−2.21
Co^{II}	I_{P3}	33.5	−1.12
Ni^{II}	I_{P3}	35.2	−0.40
Ni^{III}	I_{P4}[a]	54.9	0.46
Cr^0	I_{P1}	6.8	−3.46
Cr^I	I_{P2}	16.5	−2.50
Cr^{II}	I_{P3}	31	−0.85
Ti^I	I_{P2}	13.6	−2.45

[a] I_{Pj} values are less reliable.

E_L values. The slope of 0.16 (Table 2) is extremely small compared with those of chromium and the iron group members. Thus, the redox potentials of substituted titanocenes are comparatively insensitive to variation in the ligands, presumably due to the comparative lack of d electrons. More data are urgently needed to confirm, or disprove, this conclusion.

8.8. Additional General Comment. Thus, in the bis-sandwich series, ligand additivity is observed, and as in the earlier studies,[7] the potentials of a wide range of metal ions and oxidation states can be scaled against a standard, in this case, the Fe^{III}/Fe^{II} couple, via the general equation (2).

It is somewhat unfortunate that the dearth of ruthenium sandwich species compels us to standardise these sandwich data on a different couple, the Fe^{III}/Fe^{II} process, than used previously, Ru^{III}/Ru^{II} for the original analysis.[7] A direct comparison between E_L(L) values in the two series is complicated by this difference in standard, and also by the observation that the stereochemistry of a sandwich species is not octahedral as are all species in the earlier analysis.[7] Such a comparison must therefore await a more detailed theoretical understanding of the significance of these parameters.[12b] In the meantime, we are studying the behaviour of half-sandwich species where E_L(L) values from each series need be considered and from which data set relationships between the two sets of parameters might be derivable.

Data collected in organic solvents and in water appear very similar; i.e. the slopes within the experimental error are the same. This was not observed in the Ru^{III}/Ru^{II} series. Probably, in this case, the Cp and arene rings inhibit any specific interactions with the water solvent.

It is also important that redox couples involving more than 6 electrons, where the $e_{1g}\sigma^*$ orbitals are occupied, appear well behaved. In distinction to the $E°$ vs I_p plots,[6] no special corrections are necessary, a somewhat surprising result. It may arise because any σ-antibonding effects to the Cp or arene ligand are scaled with E_L(L). This is an extremely fortunate observation since any major nonlinear variations in the σ-antibonding character of the e_{1g} orbitals would render this simple analysis invalid for any couples involving more than 6 electrons.

9. Significance of the Parameters. 9.1. Slope S_M. The slope of an E_L(L) plot is a measurement of the redox sensitivity of a metal core toward change of ligand compared with the standard couple.[7] Too little data are yet available to draw any firm conclusion about variations in S_M; it may be relevant that with the exception of Ti^{II}/Ti^I all the S_M values are close to unity suggesting that at least for the various couples of Cr, Fe, Co and Ni, the variation from the behavior of the Fe^{III}/Fe^{II} couple is small. Concomitantly, for a given metal ion, the regression lines for the different pairs of redox processes are roughly parallel, as commented upon previously.[7−9]

9.2. Intercept I_M. The value of the intercept is a function of several terms including the gas phase binding energy to the ligands in each oxidation state, differential solvation energy and reference electrode.[7] Thus there is a possible correlation with the gas phase ionization potentials (Table 6) especially since an earlier compilation[6] showed that the observed redox potentials of some metallocene species correlate with the corresponding gas phase ionization potential following eq 1.

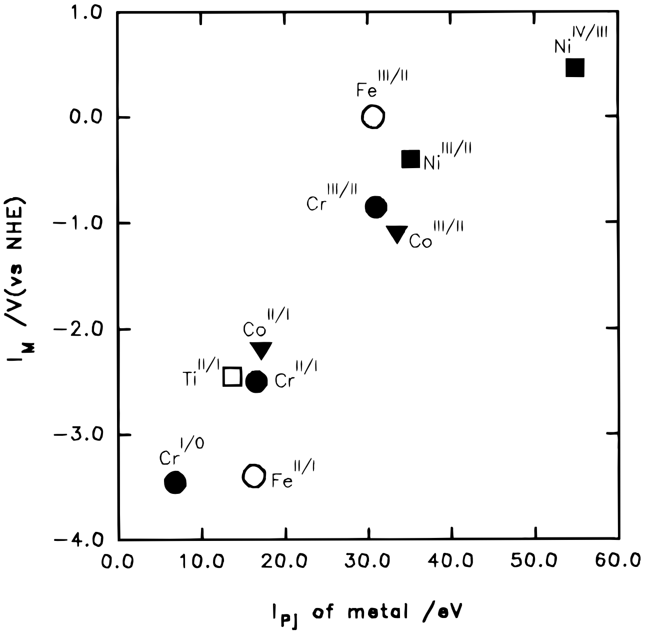

Figure 8. Plot of the intercept I_M values (V) of the first row transition metal sandwich complexes regression lines versus the corresponding gas-phase atomic ionization potential (eV).

At first glance, there appears there might be a similar linear relationship between I_M and I_p, but obviously with some scatter (Figure 8). However this may be illusory. The three chromium points lie on a perfect line ($R = 1.00$), but it is not the same as the least-squares line through all the points. Moreover the iron data, albeit only two points, lie on a very different line, yet one must surely suppose that iron of all elements would be well behaved in this correlation if it should exist. Thus more data are needed to test any relationship between I_M and I_p. For a given metal it may well be true that all redox couples lie on the same $I_M - I_p$ line, but that there are different lines for different elements.

This correlation should provide valuable information about the variation in bonding as a function of metal ion. There is surely a greater variety in interaction between the metal center and the sandwich ligand than would be inferred if there indeed was one common line for all (first row) transition elements.

10. Conclusions. We have demonstrated that a wide range of cyclopentadiene and arene couples of first row transition metal ions can be scaled directly against the corresponding Fe^{III}/Fe^{II} couples. The ligand electrochemical parameters based upon this latter couple, correlated with the Hammett σ_p parameter, can now be used to predict the electrochemical potentials of literally thousands of most first row transition metal sandwich species. The extension to later transition series will be published in due course. The eventual detailed analyses of the variations in the I_M and S_M parameters promises to provide a fundamental new view of metal−ligand binding in sandwich species across the Periodic Table.

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Supporting Information Available: Appendix A contains a listing of the datapoints, experimental versus calculated in Figures 1, 4−7, and Appendix B contains a listing of the compounds used to derive the E_L(L) values (15 pages). Ordering information is given on any current masthead page.

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