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LIGAND EFFECTS

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CONTENTS

A. INTRODUCTION

The author was delighted to have the opportunity to contribute to this symposium, dedicated to the pioneering and seminally important works of Luigi Sacconi on the occasion of his 70th birthday and retirement. The influence of ligands on the magnetic properties of complexes has been one of his greatest interests and here the author describes an attempt to quantify other ligand effects on the central metal atom to which they are attached in terms of a ligand constant, P_L [1], closely analogous to the Hammett substituent constant, σ, of aromatic substitution [2]. It is early yet to assess its predictive value, but it shows promise of having reasonably quantitative predictive qualities relating to redox potentials, kinetic and equilibrium data in at least the closed shell octahedral complexes of transition metals. The approach to be described arose from observations on the effect of mono-substitution in the phenyl group of the formally molybdenum(III) phenyldiazenido-complex $[Mo(N{=}NPh)(dtc)_2]$ ($dtc = Me_2NCS_2^-$) on its oxidation potential ($E^{ox}_{1/2}$) measured by cyclic voltammetry [3]. It was found that a plot of $E^{ox}_{1/2}$ against the Hammett σ-constant of the *meta* or *para* substituent gave an excellent straight line except in the case of *m*-nitrosubstitution (Fig. 1). This anomaly was explained on a steric basis; the somewhat negatively charged oxygen is suitably placed to interact with the positively charged

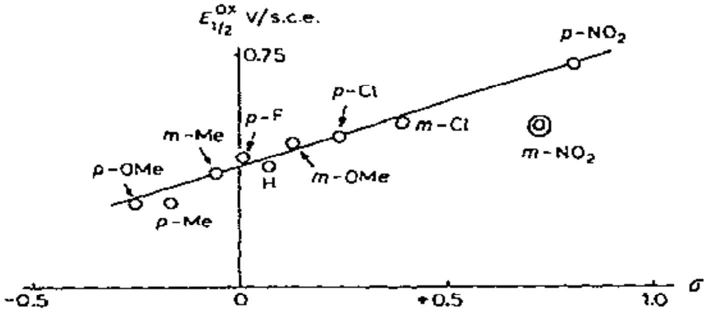


Fig. 1. Plot of Hammett σ-constants against $E^{ox}_{1/2}$ for the series of complexes [Mo(N=N–C_6H_4X)(dtc)$_3$] (X=substituents as shown on the plot, dtc=dimethylthiocarbamate).

nitrogen of the thiocarbamate ligand so introducing an anomalous electron drift across the *m*-nitro-substituted complex.

The observed linear relationship between $E^{ox}_{1/2}$ and the Hammett σ-constant suggested that ligands could each be given a ligand constant or parameter (P_L) closely analogous to the σ-constant and to serve as a measure of the overall electron attracting or releasing quality of a ligand.

B. THE DERIVATION OF LIGAND CONSTANTS AND THEIR RELATION TO HAMMETT CONSTANTS

Hammett used benzoic acid as a standard aromatic and measured the change in its acid strength induced by mono-substitution in the *meta-* or *para*-positions by a substituent X; *ortho*-substitution gave no meaningful constant. He defined his constant as in eqn. (1)

$$\sigma = \log K_i^X - \log K_i^0 \tag{1}$$

where K_i^X is the ionization constant of the X-substituted benzoic acid and K_i^0 is that of benzoic acid under standard conditions. The authors of ref. 1 chose [Cr(CO)$_6$] as their parent substance because it gives a great number of mono-substitution products [Cr(CO)$_5$L] (L = substituting ligand), CO as the standard ligand, and $E^{ox}_{1/2}$ as standard equilibrium because it provides a measure of the electron richness at the metal centre. The ligand constant is defined by eqn. (2) analogous to eqn. (1).

$$P_L = E^{ox}_{1/2}[Cr(CO)_5L] - E^{ox}_{1/2}[Cr(CO)_6] \tag{2}$$

The ligand constant is the change in oxidation potential measured in volts induced by the replacement of one carbonyl ligand by the ligand L. It follows that the carbonyl ligand has a ligand constant of zero. The ligand constant, P_L, has the same sign as Hammett's σ-constant, the more electron releasing the ligand or substituent the lower or more negative the value of the constant.

If each ligand produced the same change in $E_{1/2}^{ox}$ on substitution for carbonyl in $[M_sCO]$ (M_s = metal and associated non-substituted ligands) then a plot of $E_{1/2}^{ox}$ for $[M_sL]$ against $E_{1/2}^{ox}[Cr(CO)_5L]$ would produce a series of parallel straight lines corresponding to each M_s entity. Actually non-parallel straight lines were obtained (e.g. Fig. 2). Each of these straight lines can be represented by the linear eqn. (3)

$$E_{1/2}^{ox}[M_sL] = E_s + \beta P_L \qquad (3)$$

which introduces two new constants E_s and β_L. These characterize the metal site binding the ligand L, thus $E_{1/2}^{ox}$ is defined by two site constants and the ligand constant.

The site constant E_s gives a measure of the inherent electron richness of the site M_s and is ideally the $E_{1/2}^{ox}$ for the complex $[M_sCO]$. The more negative E_s the more electron rich is the site. The site constant β, the slope of the line, is a measure of the ease of transmission of electronic effects from the site of substitution to the highest occupied molecular orbital (h.o.m.o.) in the complex, essentially a measure of the polarizability of the site. The greater is β the more strongly the effect of L is transmitted to the h.o.m.o.

Equation (3) resembles Hammett's eqn. (4)

$$\log k = \log k^0 + \rho\sigma \qquad (4)$$

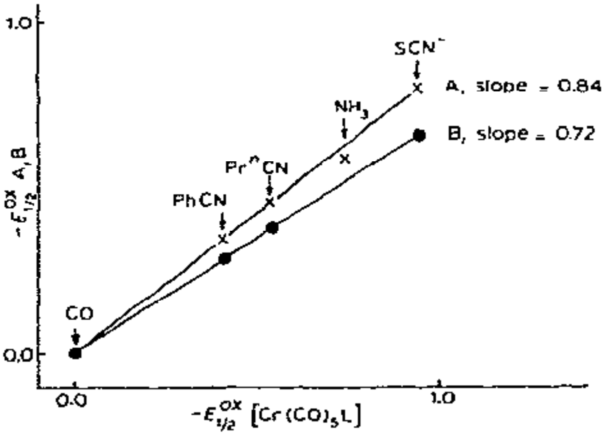


Fig. 2. Plots of $E_{1/2}^{ox}$ for the two series of complexes *trans*-$[MoL(N_2)(dppe)_2]$ (A) and *trans*-$[MoL(CO)(dppe)_2]$ (B) (dppe = $Ph_2PCH_2CH_2PPh_2$, L = ligands indicated on the plot) against $E_{1/2}^{ox}$ of $[Cr(CO)_5L]$. Potentials are measured against the couples $[Mo(N_2)(CO)(dppe)_2]$–$[Mo(N_2)(CO)(dppe)_2]^+$ and $[Mo(CO)_2(dppe)_2]$–$[Mo(CO)_2(dppe)_2]^+$ for the series of complexes A and B, respectively, and against the $[Mo(CO)_6]$–$[Mo(CO)_6]^+$ couple for the pentacarbonyl series.

where k is the rate or equilibrium constant for the substituted aromatic, k^0 is the rate or equilibrium constant for the parent aromatic, ρ is the reaction constant which is characteristic of the reaction or equilibrium in question, and σ is the Hammett substituent constant.

The resemblence is only superficial because ρ is a reaction constant not a site constant. Obviously if the ligand constants are to have the usefulness in coordination chemistry that Hammett's constants have in benzene chemistry a reaction constant may have to be introduced, thus the minimum requirements would be a ligand constant P_L, two site constants, E_s and β, and possibly an, as yet undefined, reaction constant. The need for at least two site constants arises because of the complexity of coordination chemistry. There is no real "parent" each homoligated metal and oxidation state is a separate "parent", whereas there is only one supremely important aromatic "parent", benzene, for which Hammett determined his constants.

From measurements of $E_{1/2}^{ox}$ for the substances $[Cr(CO)_5L]$ where they are available and interpolation from other series of complexes where necessary a series of P_L values has been obtained for the ligands listed in Table 1. In this table each ligand is treated as a formal two electron donor. Thus it is not surprising that the two formally positively charged entities N^+ and NO^+, which as ligands π-back-bond so strongly that they usually carry negative charge, have the highest P_L values. These are followed by neutral strong π-back-bonders such as CO and N_2 then stronger donors and weak back bonders such as tertiary phosphines and finally anionic ligands, pure σ-donors such as H^- and at the bottom of the list such strong σ–π-donors as OH^-. The poorest over-all electron donors are at the top of the list and the best at

TABLE 1

Ligand constants (P_L) (volts ± 0.05, relative to CO = 0)

Ligand	(P_L)	Ligand	(P_L)
N^+	+1.46	NH_3	−0.77
NO^+	+1.40	CF_3COO^-	−0.78
CO	0.00	NCS^-	−0.88
N_2	−0.07	CN^-	−1.00
$P(OPh)_3$	−0.18	NCO^-	−1.16
PPh_3	−0.35	H^-	−1.22
PhNC	−0.38	I^-	−1.15
PhCN	−0.40	Br^-	−1.17
MeNC	−0.43	Cl^-	−1.19
MeCN	−0.58	N_3^-	−1.26
Pyridine	−0.59	OH^-	−1.55

the bottom. It is those at the top, when counted as formal two electron donors, which will stabilize low formal oxidation states, those at the bottom stabilize high formal oxidation states, steric and such non-electronic factors being equal.

C. PREDICTIVE USE OF LIGAND CONSTANTS

The ligand constants will be useful if they allow reasonably quantitative prediction of the influence of ligand substitution on complex properties which depend mainly on electron drift between ligand and metal such as oxidation and reduction potentials, some spectroscopic properties, equilibria, and reaction rates.

Plots of oxidation potential $E_{1/2}^{ox}$ against ligand constants P_L give good straight lines similar to plots of aromatic reaction rates against the Hammett σ-constants. Figure 3 shows examples for series of closely similar d^6-molybdenum complexes of type *trans*-[Mo(Y)L(dppe)$_2$], where dppe = $Ph_2PCH_2CH_2PPh_2$ and together with the metal and ligand Y constitute the M_s framework, and L in *trans*-position to Y is the variable ligand. E_s, the intercept on the $E_{1/2}^{ox}$ axis, varies over the wide range −1.00 for $Y = N^{3-}$ ($P_{N^{3-}} = -1.26$) to almost +1.00 for $Y = NO^+$ ($P_{NO^+} = +1.40$). It is evi-

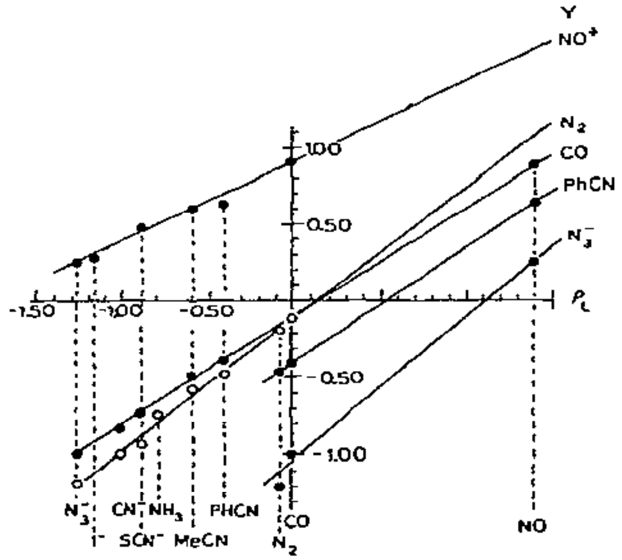
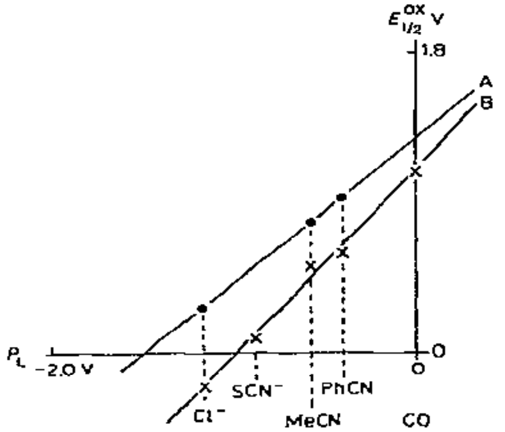


Fig. 3. Plots of $E_{1/2}^{ox}$ for the series of complexes *trans*-[MoLY(dppe)$_2$] (Y = ligands indicated on R.H.S. of plot, dppe = $Ph_2PCH_2CH_2PPh_2$) against the ligand constants P_L of the variable ligands L as indicated on the plots.



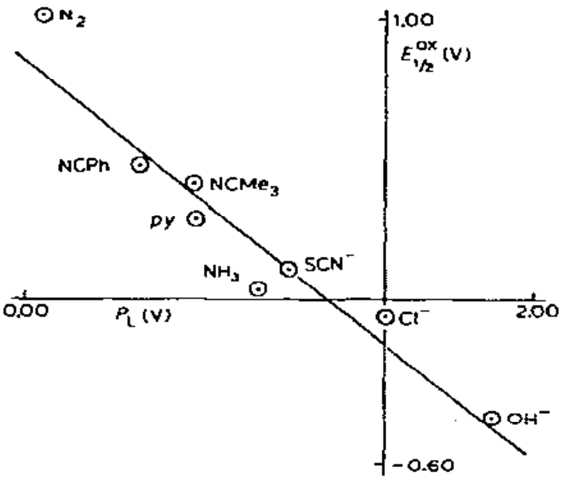


Fig. 4. Plots of $E^{ox}_{1/2}$ for the complexes *trans*-$[ReL(N_2)(dppe)_2]^+$ (A) and *trans*-$[FeLH(dppe)_2]^+$ (B) against the ligand constants P_L of the variable ligands L as indicated on the plots.

Fig. 5. Plot of $E^{ox}_{1/2}$ for $[Ru(NH_3)_5L]^{2-}$ (lit. values) against ligand constants P_L (L = variable ligands indicated on the plot).

dent that the ligands Y have a great influence on the electron richness of metal site and also on its polarizability β, the more electron donating Y the greater the electron richness of the metal site and also the greater its ability to transmit the effect of changing ligand L to the h.o.m.o.

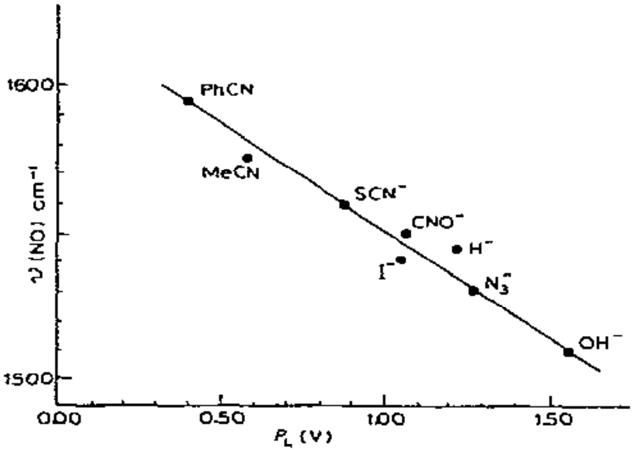


Fig. 6. Plot of ν(NO) against ligand constants (P_L) for the complexes *trans*-$[Mo(NO)L(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$, L = variable ligands indicated on plot).

The same relationships have been found for similar entities with different metal centres (Fig. 4) $FeH(dppe)_2^+$ and $Re(N_2)(dppe)_2^+$ and again the more electron rich centre has the greater polarizability, β. If oxidation potentials relating to the $[Ru(NH_3)_5L]^{2+}$ series of cationic complexes in aqueous solution are taken from the literature a reasonably linear plot of oxidation potentials against P_L is still obtained despite the measurements having been made independently by different people and at different pH and ionic strengths (Fig. 5).

The ligand constants have potential for the approximate prediction of other physical and chemical properties of complex compounds much as Hammett substituent constants in aromatic chemistry. For example a plot of NO stretching frequency, $\nu(NO)$, against P_L in the series of complexes *trans*-$[Mo(NO)L(dppe)_2]$ gives a good straight line (Fig. 6). Also the plot of $E_{1/2}^{ox}$ against the rates of the dissociation shown in eqn. 5 gives a good linear relationship (Fig. 7).

$$trans\text{-}[Mo(N_2)_2(R_2PCH_2CH_2PR_2)_2] \xrightarrow{k_1} [Mo(N_2)(R_2PCH_2CH_2PR_2)_2] + N_2 \qquad (5)$$

$(R = p\text{-}CF_3C_6H_4, p\text{-}ClC_6H_4, C_6H_5, p\text{-}MeC_6H_4, p\text{-}MeOC_6H_4$ and Et)

Since the ligand constants together with the site constants E_s and β define $E_{1/2}^{ox}$, this relationship gives an indication of the potential use of the constants in predicting reaction rates when a suitable framework of relationships and constants has been established.

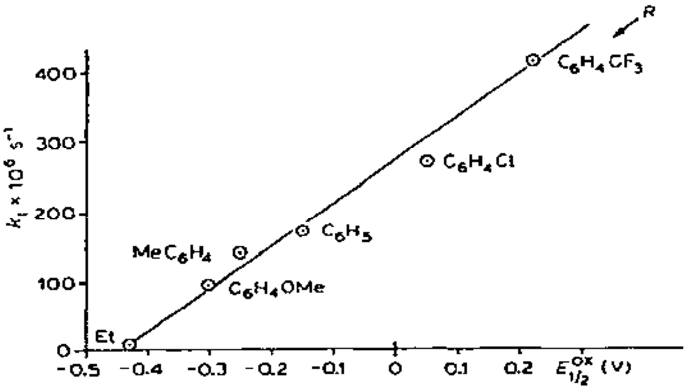


Fig. 7. Plot of dissociation rates (k_1, eqn. 5) against $E_{1/2}^{ox}$ for the complexes *trans*-$[Mo(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ (R = Et, etc. as indicated on the plot).

D. THE CHARACTER OF THE SITE CONSTANTS E_s AND β

The two site constants are important because they appear to be all that are needed to define reasonably accurately the nature of the site in octahedral closed shell complexes. It may be that change of oxidation state, coordination number, and geometry may also be sufficiently well quantified in terms of these two site constants to make them generally useful in predicting with reasonable accuracy the oxidation (or reduction) potentials and other properties of the whole range of transition metal complex compounds.

The site constants have now been determined for seven sites of type *trans*-MY(dppe)$_2$ (M = metal) where the site of attachment of ligand L is *trans* to the ligand Y so completing the octahedral arrangement of ligands (Table 2). The equatorial arrangement of the phosphorus donors of the dppe ligands is the only constant factor. As would be expected the complex becomes less electron rich, and E_s increases, the greater the total positive charge on the complex, compare the anionic, neutral and cationic complexes. The *trans* ligand Y also has an important influence, the electron richness ($-E_s$) being generally greater the more negative the P_L of Y. The polarizability, β, of the site also increases as the P_L of Y becomes more negative. It is readily seen why this should be. The less strongly electron donating ligands Y of high P_L are good π-acceptors and are able to remove from the metal some of the excess electronic charge resulting from the addition of a ligand of very low P_L, whereas good electron donor ligands Y, i.e. those of very low P_L, are unable to remove so much excess and may even add to it, resulting in a lowering of the E_s of the metal site and a raising of its β.

E. LIGAND BINDING IN RELATION TO SITE CONSTANTS, P_L

Electron poor sites, i.e. those of high E_s would be expected to bind ligands of low P_L, i.e. the good electron donors. This appears to be true, it is the transition metals in high oxidation states, i.e. electron poor, which bind hydroxide most strongly. On the other hand electron rich sites, i.e. those of low E_s would be expected to bind ligands of high P_L, especially as they owe their high P_L to a propensity for back-bonding, but β is also important. A high β means a high polarizability and enhanced ability of the site to transfer negative charge by back-bonding to the ligand of high P_L. This may be illustrated by reference to dinitrogen binding sites, which are of special interest. The three cationic complex entities in Table 2 have E_s ranging from 0.91 to 1.20 and β from 0.51 to 1.00; of these only FeH(dppe)$_2^+$ binds dinitrogen albeit weakly. It is not the one of lowest E_s, i.e. the most electron rich, but that of highest β. It appears that sites of low E_s and high β bind

TABLE 2

Electron richness ($-E_s$) and polarizability (β) of some complex sites (M_s) of the type *trans*-MoY(dppe)$_2$ (Y is as indicated in the M_s column, dppe$=Ph_2PCH_2CH_2PPh_2$)

M_s	E_s (V) [a]	β	Ligand const. P_Y
Mo(NO)(dppe)$_2^+$	$+0.91$	0.51	1.30
Mo(CO)(dppe)$_2$	-0.11	0.72	0.00
Mo(N$_2$)(dppe)$_2$	-0.13	0.84	-0.07
Mo(PhCN)(dppe)$_2$	-0.40	0.82	-0.40
Mo(N$_3$)(dppe)$_2^-$	-1.00	1.0	-1.26
Fe(H)(dppe)$_2^+$	$+1.04$	1.0	-1.22
Re(N$_2$)(dppe)$_2^+$	$+1.20$	0.74	-0.07

[a] Against saturated calomel electrode in THF, 0.2 M $Bu_4N(BF_4)$ at 20°.

dinitrogen best and in FeH(dppe)$_2^+$ the relatively high E_s is offset by the high β. Of all the entities in Table 2, Mo(PhCN)(dppe)$_2$ of $E_s = -0.40$ and $\beta = 0.82$ binds dinitrogen most strongly. The entity Mo(N$_3$)(dppe)$_2^-$ might be expected to bind dinitrogen even more strongly, but [Mo(N$_3$)(N$_2$)(dppe)$_2$]$^-$ is unstable and divests itself of excess electronic charge by loss of N_3^-.

The binding characteristics of the electron rich molybdenum(0) site in Mo(N$_2$)(dppe)$_2$ have been investigated by a study of the dissociation (eqn. 6)

$$trans\text{-}\left[Mo(N_2)L(dppe)_2\right] \xrightarrow{k} \left[Mo(N_2)(dppe)_2\right] + L \qquad (6)$$

The ligands L most strongly bonded to that site of relatively low E_s (-0.13) and relatively high β ($+0.84$) are not those of highest P_L, but those most capable of removing negative charge by back-bonding. When L = PhCN which can delocalize charge over the phenyl ring, the rate of dissociation (20° in THF in the dark) was too slow to measure. The dissociation rates ($10^4 k$ s^{-1}) for other ligands L were as follows: SCN$^-$ 0.8, Pr^{n}CN 0.6, N$_2$ 1.2, and others, CN$^-$, N_3^-, NH$_3$, were too fast to measure. Common ligands such as chloride and the very "soft" hydride, despite the very "soft" site, did not bind at all, doubtless because their vacant *d* or *p* orbitals are on too high an energy level to remove electronic charge from the metal by back-bonding. On the other hand so-called "hard" NH$_3$ binds weakly perhaps because it simulates a π-type acceptor through the interaction of its protons with the electrons in the high energy filled *d*-orbitals of the metal [4].

ECTLI 'RON RICHNESS AND THE ACTIVATION OF LIGATING DINITROGEN ROTPR ONATION

To activate dinitrogen the metal site must not only bind dinitrogen it must by back-donation render the terminal nitrogen sufficiently basic to be protonated. Thus low E_s and high β would again appear to be the criterion. Dinitrogen bonds to all three M_s represented by the moieties. $FeH(dppe)_2^+$ ($E_s = 1.04$, $\beta = 1.0$), $ReCl(dppe)_2$ ($E_s \approx 0.64$, $\beta \approx 5$), and $Mo(N_2)(dppe)_2$ ($E_s = -0.13$, $\beta = 0.84$) which bind dinitrogen, but is protonated to form N–H bonds only on the molybdenum complex. The three derived dinitrogen complexes $[M_s(N_2)]$ have closely similar $\nu(N_2)$ (2020 w, 1970 s; 1980; 2130 cm^{-1}, respectively), thus E_s appears to be a better indication of the suitability of a site to activate dinitrogen than the $\nu(N_2)$ of dinitrogen on the site.

G. CONCLUSIONS

The ligand constants, P_L, are sufficiently fundamental to allow the prediction of oxidation (and reduction) potentials in octahedral d^6-complexes. It is remarkable considering the complexity of ligand–metal interactions that so much information can be contained in only one constant. One constant associated with each ligand, or ligand atom in multidentate ligands, can never be sufficient for accurate prediction of the influence of ligands on reactions at the metal centre. Nevertheless if the ligand constants can serve as reasonably quantitative guides to the overall electron donor or withdrawing capacities of ligand atoms in a way comparable to the Hammett σ-constants in aromatic substitution, they will serve a useful purpose. It does appear that in d^6-closed shell complexes the ligand constants derived from one metal centre are directly applicable to another. It is possible that the same constants may be used in other electronic situations, e.g. in open shell and planar complexes, but this still has to be tested. Such situations can probably be allowed for by changes in the site constants E_s and β.

A fourth constant, a reaction constant corresponding to Hammett's ρ-constant, may be needed for predictions outside the area of oxidation and reduction potentials, and an analysis of suitable data is needed to see whether it is needed and if so how it can be fitted into the framework of P_L, E_S, and β. In their studies the authors of ref. 1 have examined different metal centres and different degrees of electron richness, but only in similar closed shell d^6-complexes. It is surprising that a single empirical constant like P_L shows such promise in predicting the effect of changing ligands on the properties and reactivities of complexes; only time will show whether the concept of ligand constants as defined in ref. 1 has general and lasting usefulness. Finally, the author wishes to thank his co-authors of refs. 1 and 3 for their vital contributions to the ideas and work outlined above.

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