Transition-metal Binding Sites and Ligand Parameters

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A scale of ligand constants, P_L, is defined according to equation (1). This scale is used to analyse the $E_{\frac{1}{2}}^{ox}$ of

$$P_L = E_{\frac{1}{2}}^{ox}[Cr(CO)_5L] - E_{\frac{1}{2}}^{ox}[Cr(CO)_6] \qquad (1)$$

various closed-shell octahedral complexes $[M_sL]$, in terms of the linear approximation of equation (2), where E_s is a

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

measure of the electron-richness of the site M_s and β a measure of its polarisability. Other properties of $[M_sL]$ such as the type of ligand which binds to M_s, spectroscopic properties, and chemical reactivity are discussed in terms of the parameters P_L, E_s, and β. It is shown that equation (2) can be used in the identification of unknown $[M_sL]$ and conversely in the design of electron-rich or -poor $[M_sL]$.

THE concepts of electron-withdrawing or -donating groups and inductive or mesomeric influences upon the properties of organic molecules have been invaluable in rationalising relationships between structure and reactivity. Various linear free-energy scales have been introduced to measure relative inductive and mesomeric effects of substituent groups upon an organic framework. For example, in an organic molecule p-$C_6H_4(X)R$ the inductive influence of the ring substituent X upon centres within the organic *rest* R to which X is not conjugated can be correlated with Hammett's substituent constants, σ_P. Such correlations have proved particularly useful in analysing kinetic, thermodynamic, and spectroscopic data.[1] In a transition-metal complex, $[M_sL]$ where M_s is the transition metal and associated ligands other than L (and represents the site which binds L), the electron-withdrawing or -donating influence of L is reflected in the properties of $[M_sL]$. Conversely, the electron-donating or -withdrawing influence of M_s is reflected in the properties of the co-ordinated ligand, L.

In this paper we have defined a scale of *ligand constants*, P_L, and we have used it to characterise various transition-metal binding sites M_s in terms of site constants E_s and β. We have confined our study to square-pyramidal 16-electron moieties M_s which combine with L to give 18-electron octahedral complexes, $[M_sL]$.

RESULTS AND DISCUSSION

Ligand Constants, P_L.—As a standard 16-electron square-pyramidal binding site, M_s, we have chosen the moiety $[Cr(CO)_5]$ which gives 18-electron octahedral complexes, $[Cr(CO)_5L]$, with a wide variety of ligands, L, ranging from essentially σ,π donors L such as Cl^- through σ donors such as H^- to π-acceptor ligands such as CO. The reversible one-electron oxidation potential, $E_{\frac{1}{2}}^{ox}$, of $[Cr(CO)_5L]$ is very sensitive to the nature of L and we have therefore defined our scale of *ligand constants*, P_L, according to equation (1).[2,3] The energy of

$$P_L = E_{\frac{1}{2}}^{ox}[Cr(CO)_5L] - E_{\frac{1}{2}}^{ox}[Cr(CO)_6] \qquad (1)$$

the highest-occupied molecular orbital, h.o.m.o., in a transition-metal complex is related to the $E_{\frac{1}{2}}^{ox}$ of that complex. This has a theoretical basis, for example, Sarapu and Fenske[4] have shown that the h.o.m.o. energies of the complexes $[Mn(CO)_{6-x}(CNPh)_x]^+$, $x = 1$—6, which were calculated by an approximate m.o. method, correlate linearly with experimentally determined $E_{\frac{1}{2}}^{ox}$. If this is generally true, then P_L represents the change in the energy of the h.o.m.o. of $[Cr(CO)_6]$ when one CO ligand is replaced by L.

Listed in Table 1 are values of P_L which we have measured and values which we have deduced by interpolation from data from other series of complexes (see below). These ligand constants refer to L as a two-electron donor ligand which must be added to the 16-electron moiety to give the closed-shell 18-electron complexes $[M_sL]$, π bonding being ignored. Considered in this way the nitride ligand in $[M_sN]$ is formally N^+, the nitrosyl NO^+, and the hydride H^-. From Table 1 it can be seen that charged ligands occupy the extremes of the scale. The weakest σ donors with strong π-acceptor

TABLE 1

Table of ligand constants P_L calculated from data of (a) this work, (b) ref. 8, or (c) ref. 3

Ligand, L	Ligand constant, P_L/V (±0.05 V estimated error)	Ref.
N^+	+1.46	(a)
NO^+	1.40	(a)
CO	0.00	(b)
N_2	−0.07	(a)
$P(OPh)_3$	−0.18	(c)
PPh_3	−0.35	(c)
CNPh	−0.38	(c)
NCPh	−0.40	(a)
CNMe	−0.43	(c)
NCMe	−0.58	(a)
Pyridine	−0.59	(c)
NH_3	−0.77	(c)
CF_3COO^-	−0.78	(b)
NCS^-	−0.88	(a)
CN^-	−1.00	(a)
NCO^-	−1.16	(a)
I^-	−1.15	(c)
Br^-	−1.17	(a)
Cl^-	−1.19	(c)
H^-	−1.22	(a)
N_3^-	−1.26	(a)
OH^-	−1.55	(a)

properties such as N^+, NO^+, CO, and N_2 have the most positive P_L constants whereas strong σ-donor and π-donor ligands such as halide ions, N_3^-, and especially OH^- have the most negative. Thus this scale of ligand constants appears to reflect the net (σ-donor plus π-acceptor) or donor properties of the ligands L. We now consider why this may be so.

First, the energy of the electrons in the h.o.m.o. of the $[Cr(CO)_5L]$ complexes should be sensitive to the effective nuclear charge of the central metal: if L is a good net donor of charge the electrons in the h.o.m.o. will be more effectively screened than if L is a good net acceptor of charge and, as a consequence, the oxidation potential in the former case will be at a less positive potential than in the latter. The net electron-donating or -accepting ability of L will be determined by the flow of electron density from the metal d_π orbitals into the ligand π^* orbitals and the counter flow of electron density from the ligand σ, p_π, or d_π bonding orbitals onto the metal. Thus the h.o.m.o. in the $[Cr(CO)_5L]$ complexes will be sensitive to the net transfer of electronic charge to the metal by L. Secondly, the energy of the h.o.m.o. may be modified by a mesomeric influence: if L conjugates with the h.o.m.o., *i.e.* if there is significant mixing of ligand orbitals with the h.o.m.o., the energy of the h.o.m.o. may be lowered. This may also contribute to the observed values of P_L. Whichever effect predominates, the value of P_L must be determined by the σ and π interactions between L and the standard site $[Cr(CO)_5]$.

Theoretical calculations by Lloyd *et al.*[3] suggest that, for $[Cr(CO)_5L]$ in which L = NH_3, PH_3, or PMe_3, the h.o.m.o. possesses little L character although its energy is sensitive to the particular L.[5] This implies that these ligands L exert their influence upon the energy of the h.o.m.o. principally *via* the inductive mechanism and that L is not conjugated to the h.o.m.o. If this is true for all ligands L the values of P_L represent a measure of the inductive influence of L on the h.o.m.o. transmitted *via* the σ- and π-bonding framework of the site. In this discussion we have neglected differences in solvation-energy changes. This is usually justified for series of closely related complexes.

Earlier studies have shown that the ligand influence upon the energy of the h.o.m.o. in certain First-Row transition-metal complexes of the type $[M(CO)_{6-x}L_x]^{n+}$ is additive and for isostructural closed-shell complexes, differing only in the nature of M (and consequently, n), is independent of M.[6-8] For these complexes, equation (2) may be written. That the influence of L upon the

$$P_L = (\delta E_{\frac{1}{2}}^{\mathrm{ox}}/\delta x)_L \qquad (2)$$

h.o.m.o. in such complexes appears to be rather insensitive to M and the co-ordination environment is somewhat surprising. We have now explored the influence of L at various binding sites, M_s, upon certain properties of $[M_sL]$ complexes and have analysed these in terms of our ligand constant, P_L, and the constants E_s and β defined by equation (3), characteristic of the binding site on M_s; E_s is a measure of the electron-richness of the site and β of its polarisability. These relationships are discussed below.

The Electron-richness of Binding Sites, E_s.—The energies of the h.o.m.o. in a series of closed-shell octahedral complexes $[M_sL]$ should correlate with P_L provided either that the influence of L in such series is primarily inductive or that the perturbation of the h.o.m.o. by conjugation with orbitals of L varies in a regular manner with P_L.

We have examined the relationship between $E_{\frac{1}{2}}^{\mathrm{ox}}$ and P_L for a series of related sites M_s = $MoY(dppe)_2$ where Y, the axial ligand, is NO^+, CO, N_2, NCPh, or N_3^- and dppe = $Ph_2PCH_2CH_2PPh_2$. Figure 1 shows plots of

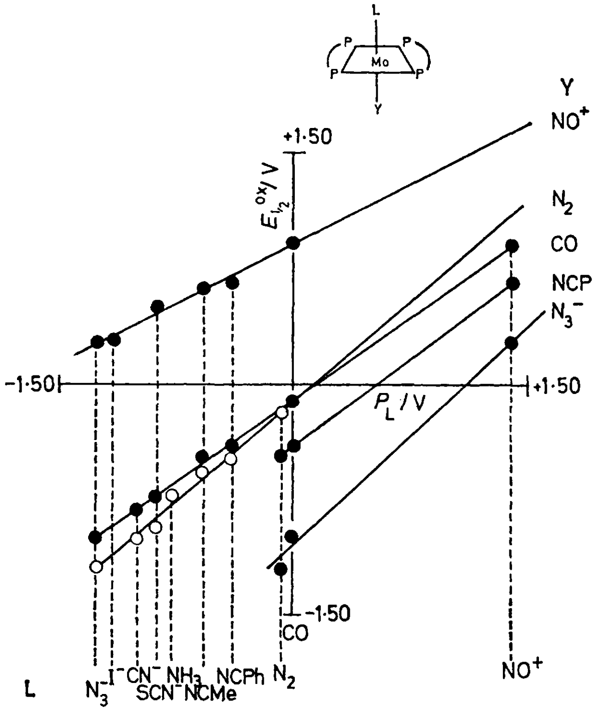


FIGURE 1 Plots of $E_{\frac{1}{2}}^{\mathrm{ox}}$ for various closed-shell molybdenum complexes *versus* the ligand constant, P_L. The circles represent estimated errors of ±15 mV in the measurements of P_L and $E_{\frac{1}{2}}^{\mathrm{ox}}$

$E_{\frac{1}{2}}^{\mathrm{ox}}$ *vs.* P_L for each of these $[M_sL]$ series: the correlations are essentially linear but their slopes are different. It is evident that the influence of L upon the h.o.m.o. in these molecules varies in a regular manner with P_L and therefore most probably is primarily inductive; moreover, it is not a constant property but varies with the nature of M_s. The oxidation potential of a complex in each $[M_sL]$ series can be represented by the linear approximation of equation (3).[2] E_s, the value of $E_{\frac{1}{2}}^{\mathrm{ox}}$

$$E_{\frac{1}{2}}^{\mathrm{ox}} = E_s + \beta \,.\, P_L \qquad (3)$$

when the site is occupied by the standard ligand, CO, is a measure of the site electron-richness. The coefficient β corresponds to the gradient of the plots of $E_{\frac{1}{2}}^{\mathrm{ox}}$ *vs.* P_L and is dimensionless; it is a measure of the efficiency of the transmission of the electronic influence from L to the h.o.m.o. and essentially the polarisability of the site. Provided at least two oxidation potentials for a given series of complexes can be measured and the corresponding P_L values are known, E_s and β may be estimated for a particular site. The corollary also applies, if the oxidation potential of a given complex $[Cr(CO)_5L]$ cannot be measured, *e.g.* if the complex cannot be prepared, that P_L may be deduced from $E_{\frac{1}{2}}^{ox}$ data from other series of complexes which contain the appropriate $[M_sL]$ member. Using such relationships, the values of P_L in Table 1 not obtainable directly from $E_{\frac{1}{2}}^{ox}$ for $[Cr(CO)_5L]$ were calculated.

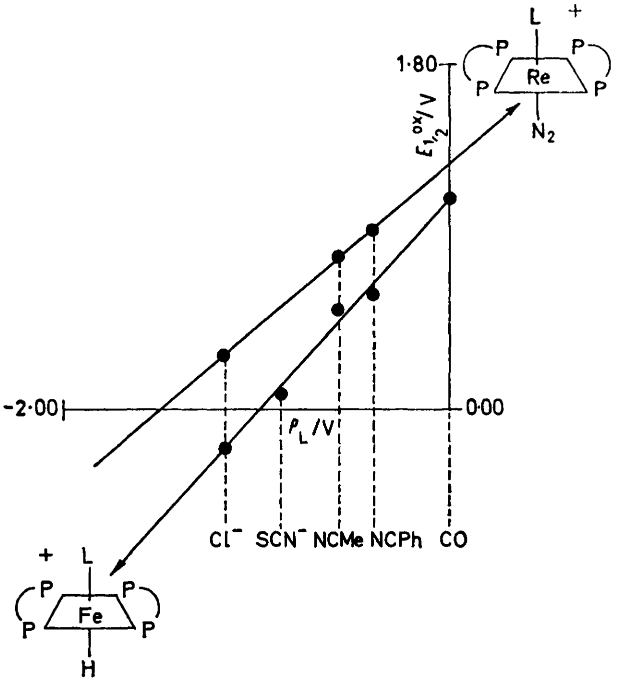


FIGURE 2 Plots of $E_{\frac{1}{2}}^{ox}$ for complexes of Fe and Re *versus* the ligand constant, P_L. Details as in Figure 1

Figure 2 shows a plot of $E_{\frac{1}{2}}^{ox}$ *vs.* P_L for the sites $Re(N_2)(dppe)_2^+$ and $FeH(dppe)_2^+$. Equation (3) also holds for these sites. Table 2 lists the various E_s parameters which we have measured for seven different M_s. The E_s values for the Mo sites, $MoY(dppe)_2$, are governed by the axial ligand Y, which is *trans* to L in the $[M_sL]$ complexes. The range of E_s for the various Mo sites emphasises the change of electron-richness of the site which can be induced by varying only Y. As one would expect E_s increases as the overall charge on M_s increases, *i.e.* the sites become less electron-rich, *cf.* $Mo(N_3)(dppe)_2^-$, $ReCl(dppe)_2$, and $FeH(dppe)_2^+$ for which P_L, for the ligand Y, is approximately constant, where $E_s = -1.00$, $+0.64$, and $+1.04$ V respectively.

TABLE 2

Site, M_s	E_s/V *	β	P_L of ligand Y/V
$Mo(NO)(dppe)_2^+$	+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
$Mo(NCPh)(dppe)_2$	−0.40	0.82	−0.40
$Mo(N_3)(dppe)_2^-$	−1.00	1.0	−1.26
$FeH(dppe)_2^+$	+1.04	1.0	−1.22
$Re(N_2)(dppe)_2^+$	+1.20	0.74	−0.07

* Quoted *versus* the saturated calomel electrode (s.c.e.) in tetrahydrofuran (thf) −0.2 mol dm^{-3} $[NBu_4][BF_4]$.

We have also examined the relationship between P_L and $E_{\frac{1}{2}}^{ox}$ for the quite different complexes $[Ru(NH_3)_5L]^{2+}$ shown in Figure 3. The redox-potential data, which we have obtained from the literature,[9,10] have been measured in aqueous electrolytes of variable compositions and presumably pH, and moreover the oxidation of $[Ru(NH_3)_5(N_2)]^{2+}$ is irreversible. Despite these limitations the correlation between P_L and $E_{\frac{1}{2}}^{ox}$ for this series shows essentially the same trend.

The Polarisability of the Binding Site, β.—The parameter β of equation (3), the gradient of the plots of $E_{\frac{1}{2}}^{ox}$ *vs.* P_L, varies in magnitude with M_s (Table 2). If β is unity then the influence of a ligand change upon the energy of the redox orbital in complexes $[M_sL]$ is the same as at the standard binding site $Cr(CO)_5$. We find that, for the Mo sites, β ranges from *ca.* 1.00 to *ca.* 0.50. This means that the influence of L upon the energy of the h.o.m.o. is a function of M_s. If we assume that the orthogonal dppe ligands on these Mo sites exert a constant influence upon the electronic properties of the site then the magnitude of β should be primarily a function of the *trans*-axial ligand, Y. Table 2 shows that as P_L of Y becomes more negative, β increases. The smallest β value, 0.51, is observed for the Y = NO⁺ series, the largest for the Y = N_3^- series. When the *trans*-site ligand Y is strongly donating, *e.g.* N_3^- ($P_L = -1.36$ V), more charge donated to the site of L will reside upon the metal than if Y is weakly donating or accepting, *e.g.* NO⁺ ($P_L = 1.3$ V). In the former case, the energy of the h.o.m.o. is less ' buffered ' with respect to a change in L than in the latter. Thus the polarisation of electron

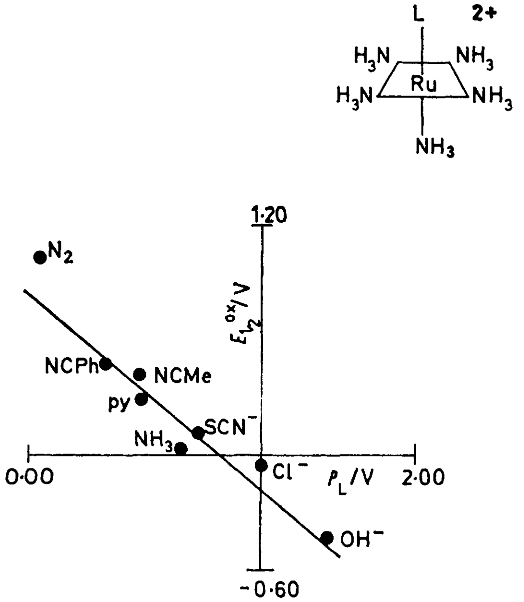


FIGURE 3 Data for $E_{\frac{1}{2}}^{ox}$ for various $[Ru(NH_3)_5]^{2+}$ complexes[9,10] *versus* P_L; py=pyidine

density along the delocalised axial system Y–M–L is reflected in the magnitude of β.

Spectroscopic Properties.—Infrared data for complexes containing NO^+, CO, or N_2 often show linear correlations of ν(Y), where Y = NO^+, CO, or N_2, with $E_{\frac{1}{2}}^{ox}$. We have shown that ν(Y) correlates reasonably well with $E_{\frac{1}{2}}^{ox}$ [M_sL] or P_L in the two series *trans*-[$Mo(N_2)(dppe)_2L$] and *trans*-[$Mo(CO)(dppe)_2L$].[2,11] We now find that for the analogous series *trans*-[$Mo(NO)(dppe)_2L$]$^+$ there is similar correlation between ν(NO^+) and $E_{\frac{1}{2}}^{ox}$ (or P_L) as illustrated by Figure 4(*a*) and 4(*b*).

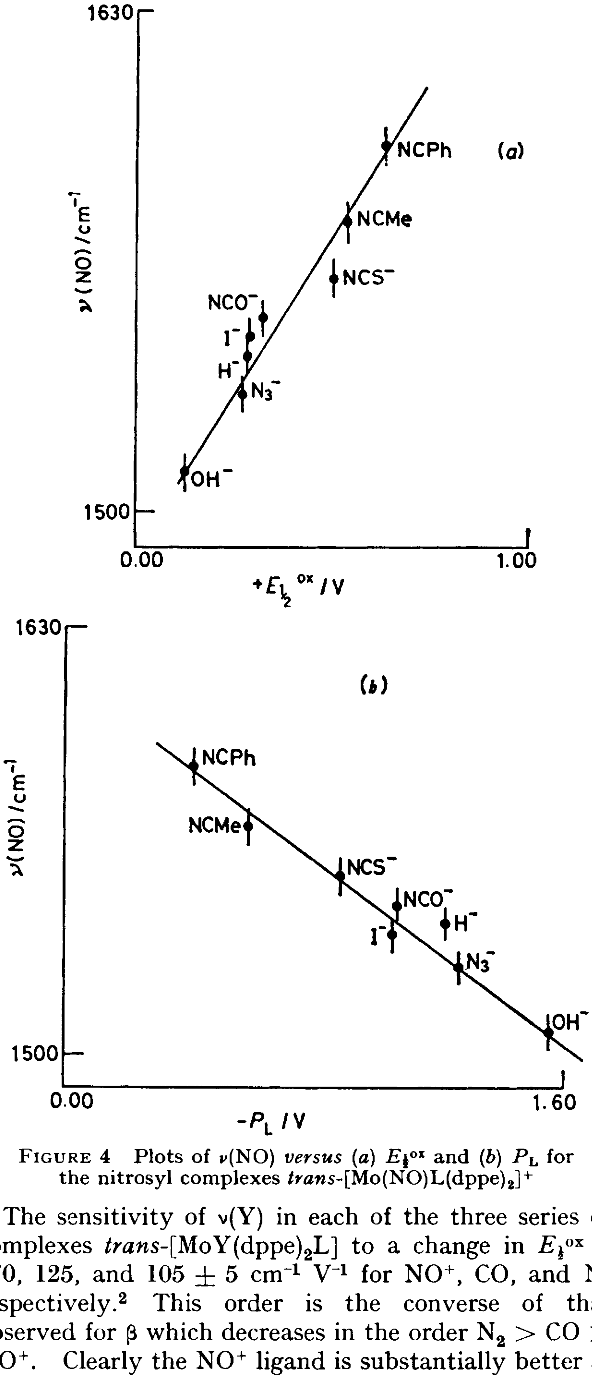


FIGURE 4 Plots of ν(NO) *versus* (*a*) $E_{\frac{1}{2}}^{ox}$ and (*b*) P_L for the nitrosyl complexes *trans*-[$Mo(NO)L(dppe)_2$]$^+$

The sensitivity of ν(Y) in each of the three series of complexes *trans*-[$MoY(dppe)_2L$] to a change in $E_{\frac{1}{2}}^{ox}$ is 170, 125, and 105 ± 5 cm^{-1} V^{-1} for NO^+, CO, and N_2 respectively.[2] This order is the converse of that observed for β which decreases in the order $N_2 > CO > NO^+$. Clearly the NO^+ ligand is substantially better at accommodating charge from L *via* the Mo centre than CO which, in turn, is better than N_2. Thus for a given ligand (L) change, the NO^+ complexes show a greater perturbation in ν(Y) but a smaller perturbation in $E_{\frac{1}{2}}^{ox}$ than do their CO or N_2 analogues.

Various studies of the electronic spectra of closed-shell transition-metal complexes have shown that metal-to-ligand charge-transfer band energies, ν_{CT}, often vary regularly with $E_{\frac{1}{2}}^{ox}$.[12,13] If the h.o.m.o. is a function of P_L as discussed above, and the lowest unoccupied molecular orbital, l.u.m.o., is independent of P_L, one would expect a linear correlation of ν_{CT} and P_L with a slope approaching β. On the other hand, the l.u.m.o. may vary regularly with P_L but in a fashion differently from the h.o.m.o.; one would still expect a linear correlation of ν_{CT} and P_L but the magnitude of the slope could be greater or less than β. This presupposes that the l.u.m.o. is not derived from L itself. The complexes so far studied do not lend themselves to such an analysis. We would expect similar correlations from Mössbauer ionisation-potential, and photoelectron-spectroscopic, data. These have yet to be investigated.

Ligand Binding.—To a first approximation, those sites which are more electron-poor, *i.e.* having more positive E_s values, should bind preferentially those ligands with the more negative P_L values. How far this is true is illustrated by the examples below.

The site on *trans*-$Mo(N_2)(dppe)_2$ which is electron-rich ($E_s = -0.13$ V) will bind N_2 ($P_L = -0.07$) but not Cl^- ($P_L = -1.19$) whilst NH_3 ($P_L = -0.74$) and N_3^- ($P_L = -1.26$) are labile on this site and may be displaced by N_2. In contrast, the site on *trans*-$Re(N_2)(dppe)_2^+$ which is electron-poor ($E_s = +1.20$ V), will bind Cl^-, PhCN, and MeCN but not N_2. Similarly the site on *trans*-$FeH(dppe)_2^+$ ($E_s = +1.04$ V) will bind Cl^- and NH_3 whilst N_2 is only weakly bound and may be displaced by NH_3. Again *trans*-$Mo(NO)(dppe)_2^+$ ($E_s = +0.91$ V) binds halides or organonitriles, but not N_2; the CO complex formed with this site is unstable with respect to rearrangement to the *cis* isomer.

Superimposed upon these associations of the crude trends in ligand binding with P_L and E_s are the more specific conjugative effects of the other ligands within M_s, particularly those of the ligand *trans* to the vacant co-ordination site. Thus *trans*-$Mo(CO)(dppe)_2$ and *trans*-$Mo(N_2)(dppe)_2$ have similar E_s values yet N_2 is particularly labile when bound to the former. Clearly the competition for d_π electron density through the N_2–Mo–CO system leaves the Mo–N_2 bond relatively weak. That CO is a better competitor for electron density is also reflected by the β values of the two sites which are 0.84 and 0.72 for the N_2- and CO-containing sites, respectively.

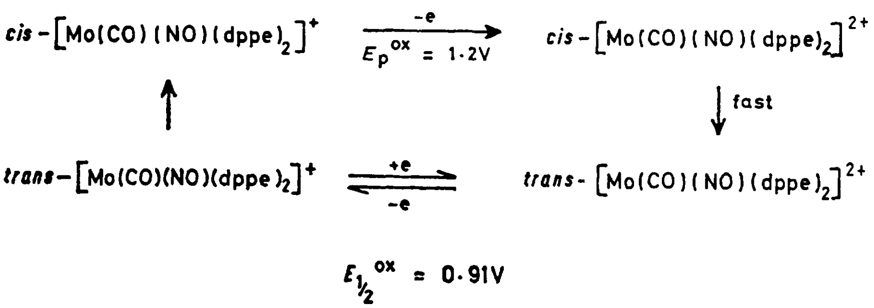
This brings us to consider the binding of N_2 at the various sites we have studied. Dinitrogen will give thermally stable complexes at sites with E_s values ranging from +1.3 to −1.3 V {*i.e.* a variation in [M_s(CO)] h.o.m.o. energies of *ca.* 250 kJ}. This is a remarkably wide range of electron-richness. Although we would expect that M_s–N_2 bonding interactions would be strongest where M_s is electron-rich, this cannot be an overriding condition for N_2 binding. Those complexes with high E_s values which form stable M_s–N_2 complexes invariably have a strong donor ligand (negative P_L) *trans* to the N_2 ligand, *e.g. trans*-[Re(CO)$_2$Cl(N$_2$)(PPh$_3$)$_2$] and *trans*-[FeH(N$_2$)(dppe)$_2$], and consequently their β values are at the higher end of the range. We may conclude that M_s–N_2 binding interactions are strongest at sites with low E_s and high β values.

Chemical Reactivity of Co-ordinated N_2.—In previous papers we have discussed the influence of L upon the chemical reactivity of the [M_sL] complexes *trans*-[Mo(N$_2$)L(dppe)$_2$] and have drawn certain conclusions. These may be summarised as follows:[2,14] (*i*) as the electron-donor influence of L increases (P_L becomes more negative) the stability of the one- and two-electron oxidation products [M_sL]$^+$ and [M_sL]$^{2+}$ increases; (*ii*) with P_L in the range *ca.* 0.0 to −0.6 V, attack by protic acids upon N_2 in these complexes is possible, whilst with $P_L > -0.8$ V oxidation of [M_sL] is the major pathway of attack by protic acids and certain alkyl halides.

Our data for the reactivity of N_2 co-ordinated in other [M_sL] is somewhat restricted. We can, however, make certain salient observations.

First, simple inductive arguments would suggest that only electron-rich sites which have relatively negative E_s values should favour electrophilic attack upon N_2 in their complexes. The sites M_s = Mo(N$_2$)(dppe)$_2$, ReCl(dppe)$_2$, and FeH(dppe)$_2^+$ have $E_s = -0.13$, $+0.64$, and $+1.04$ V *vs.* s.c.e., respectively: only the N_2 complex of the first site reacts with protic acids to form NH or Mo–H bonds. The compounds *trans*-[ReCl(N$_2$)(dppe)$_2$] and *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] have very similar ν(N$_2$) suggesting at first sight that the N_2 ligands in both compounds are in an electronically similar condition, but the former does not protonate either at N_2 or at the metal. At least for these three sites, the E_s value more accurately reflects N_2 reactivity towards H$^+$ than does simple comparison of ν(N$_2$).

Secondly, similar arguments suggest that the opposite should hold true, *i.e.* N_2 bound to electron-poor sites should be susceptible to nucleophilic attack. The only example of such attack is of methyl- or phenyl-lithium upon [Mn(η-C$_5$H$_5$)(CO)$_2$(N$_2$)] which has ν(N$_2$) at 2 160 cm^{-1} and $E_s \sim 1.20$ V and is clearly electron-poor.[15] However, *trans*-[Re(CO)$_2$Cl(N$_2$)(PPh$_3$)$_2$] which is also electron-poor, $E_s = +1.37$ V, ν(N$_2$) at 2 120 cm^{-1}, reacts with LiMe but exclusively at a CO rather than at N_2.[16] Further, *trans*-[Re(CO)$_3$Cl(PPh$_3$)$_2$] (E_s = 1.37 V) is attacked at the metal by LiMe to give the metathesis product *trans*-[ReMe(CO)$_3$(PPh$_3$)$_2$] and there is no attack upon CO.[16] Thus these electron-poor sites give [M_s(CO)] or [M_s(N$_2$)] which are susceptible to LiMe attack although the actual site of attack (N_2, CO, or the metal) cannot be deduced simply from E_s arguments alone. This is also true when considering H$^+$ attack upon [M_s(N$_2$)].



SCHEME 1

In summary, E_s may be used as a criterion of whether a particular [M_s(N$_2$)] will be susceptible to electrophilic or nucleophilic attack. We can define a broad range of *potential* reactivity of co-ordinated N_2 in closed-shell octahedral complexes based upon E_s parameters and $E_{\frac{1}{2}}^{ox}$ measurements and this is illustrated by Figure 5.

Application of E_s, β, *and* P_L *to the Identification of Complexes*.—We have previously used the relationship between $E_{\frac{1}{2}}^{ox}$, β, and P_L to characterise a species *trans*-[Mo(N$_2$)(NH$_3$)(dppe)$_2$] which is labile in solution.[2] Here we describe two new examples which illustrate our application of these relationships to the characterisation of species [M_s(L)].

First, we found that the relationship between P_L and $E_{\frac{1}{2}}^{ox}$ for the series [Mo(NO)L(dppe)$_2$]$^+$ is linear when L = Cl$^-$, SCN$^-$, NCPh, or NCMe but that the oxidation of [Mo(CO)(NO)(dppe)$_2$]$^+$ is irreversible with E_P some 300 mV more positive than that expected from the plot of $E_{\frac{1}{2}}^{ox}$ *versus* P_L. This prompted us to examine ^{31}P n.m.r. spectra in thf, which showed unambiguously that this carbonyl complex is the *cis* isomer whereas all the other complexes are *trans*. Moreover, the oxidation product of *cis*-[Mo(CO)(NO)(dppe)$_2$]$^+$ in thf is reduced reversibly at $E_{\frac{1}{2}}^{ox} = +0.91$ V. This oxidation potential corresponds to that predicted for *trans*-[Mo(CO)(NO)(dppe)$_2$]$^+$ from the $E_{\frac{1}{2}}^{ox}$ *versus* P_L relationship. The redox chemistry of *cis*-[Mo(CO)(NO)(dppe)$_2$] is sketched in Scheme 1 and closely parallels that of *cis*-[Mo(CO)$_2$(dppe)$_2$].[17]

Our second example is rather less explicit. Compounds formulated as octahedral complexes of the type [M(N$_2$H)L(dppe)$_2$] (L = F$^-$, Br$^-$, or Cl$^-$; M = Mo or W) have been prepared in this laboratory.[18] However, the i.r. spectra of the complexes where L = Br^- or Cl^- are somewhat anomalous because of the strong band observed at *ca.* 1 880—1 890 cm^{-1} and assigned to ν(NN), and also the absence of ν(NH). Complexes *trans*-$[M(N_2R)L(dppe)_2]^+$ (where R = alkyl; L = Br^- or Cl^-; M = Mo or W) have considerably lower ν(NN) at *ca.* 1 500—1 550 cm^{-1}. However, a band assigned to ν(NH) has been observed for the complex M = W and L = F^-. An alternative formulation for the L = Br^- or Cl^- complexes could be as the seven-co-ordinate dinitrogen complexes $[MH(N_2)L(dppe)_2]^+$. The corresponding cationic species with M = W and L = N_2 have been characterised by *X*-ray structural analysis.[19]

If we assume that the P_L and β data and the linear relationship between P_L and $\nu(N_2)$ which we have noted for the six-co-ordinate $[M(N_2)L(dppe)_2]$ complexes[2] apply to the seven-co-ordinate complexes $[MH(N_2)(dppe)_2]^+$, we can estimate the value of $\nu(N_2)$ for the L = Br^- or Cl^- species. From Table 1, ΔP_L for Br^- and N_2 may be calculated; thus, $\Delta P_L = P(N_2) - P(Br^-) = 1.2$ V. It is reasonable to assume from comparison with all the other series containing N_2 that β for $[MH(N_2)L(dppe)_2]^+$ lies in the range 0.8 ± 0.2. Hence $\beta\Delta P_L = 1.2 \times (0.8 \pm 0.2) = 0.96 \pm 0.24$ V. Because $\Delta\nu(N_2) = 115\ cm^{-1}$, $\beta\Delta P_L = 110 \pm 25\ cm^{-1}$ (ref. 2), and $\nu(N_2)$ for $[WH(N_2)_2(dppe)_2]^+$ occurs at 1 995 cm^{-1} (ref. 19), then $\nu(N_2)$ for $[WBr(H)(N_2)(dppe)_2]$ is expected at $(1\,995 - 110) \pm 25\ cm^{-1} = 1\,885 \pm 25\ cm^{-1}$. The calculated value for the hydrido-dinitrogen complex compares well with that (1 880 cm^{-1}) found for the 'diazenido'-complex $[WBr(N_2H)(dppe)_2]$. We therefore conclude that the formulation $[WX(H)(N_2)(dppe)_2]$, X = Cl or Br, is a possible alternative to the $[WX(N_2H)(dppe)_2]$ formulation previously proposed and this possibility is now being explored. It carries the important implication that ligating dinitrogen may insert into metal–hydrogen bonds because the next stage of protonation undoubtedly gives the highly conjugated planar M=N–NH_2 structure (Scheme 2).[20,21]

Conclusions.—The relationships we have described and their application have so far been restricted to a rather limited range of closed-shell octahedral complexes. We believe however that these results may be used more generally both for the identification of solution species and for the design of complexes with specific electron-richness. It may be possible to apply the relationship between redox potential and P_L to probe the properties of more complicated binding sites such as those in metalloenzymes.

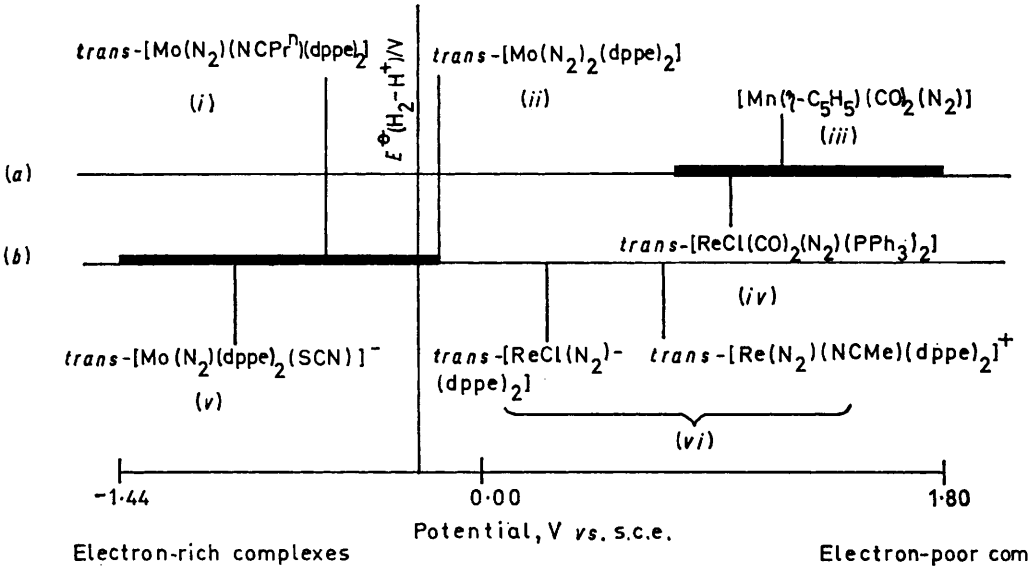
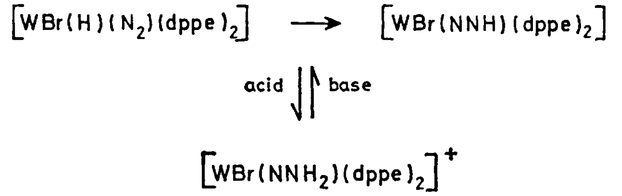


FIGURE 5 Schematic representation of the crude correlation of reactivity with the electron-richness of various dinitrogen complexes. Vertical lines represent $E_{\frac{1}{2}}^{ox}$ values for specific complexes. Key: (*a*) complexes reactive toward LiMe–thf at 25 °C; (*b*) complexes attacked by H_2SO_4–thf at 25 °C: (*i*) protonated at N_2; (*ii*) protonated at N_2 or Mo; (*iii*) attacked at N_2 by LiMe; (*iv*) attacked at CO by LiMe; (*v*) oxidised by H^+ in thf at 25 °C; (*vi*) unreactive towards H^+ or LiMe in thf at 25 °C



SCHEME 2

EXPERIMENTAL

The preparations of the *trans*-$[MoL(N_2)(dppe)_2]$ and $[Mo(CO)L(dppe)_2]$ complexes have been described in an earlier paper.[2] The preparation of the corresponding $[MoL(NO)(dppe)_2]^+$ will be described elsewhere.[22] The complexes $[Cr(CO)_5L]$ and $[FeH(L)(dppe)_2]^+$ were prepared according to the literature methods,[3,23] *trans*-$[ReL(N_2)(dppe)_2]^+$ complexes were prepared by Dr. R. H. Morris and will be described in detail elsewhere.[24]

The redox potentials for the various complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf or CH_2Cl_2 at a platinum electrode. Generally the complexes exhibited a diffusion-controlled reversible one-electron oxidation at scan rates 0.01—0.3 V s^{-1} as evidenced by the ratio of their peak currents and the separation of E_p^{ox} and E_p^{red}.[2] The potentials were internally referenced to the $[Mo(N_2)_2(dppe)_2]^{0/+}$ couple which has $E_{\frac{1}{2}}^{ox} = -0.16$ V *vs.* s.c.e. in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf.

The preparation of supporting electrolyte, the purification of solvents, and the measurement technique have been described previously.[13] Cyclic voltammograms were recorded on a Phillips type PM8041 X-Y recorder using a type DT2101 Hi-Tek potentiostat and a Chemical Electronics type 01 waveform generator. Infrared spectra were recorded as Nujol mulls on a Unicam type SP 2000 spectrometer.

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