LIGAND AND STRUCTURAL EFFECTS ON THE REDOX POTENTIAL OF OCTAHEDRAL 18-ELECTRON COMPLEXES WITH 14-ELECTRON OR 12-ELECTRON METAL CENTRES

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Summary

Electrochemical P_L ligand and E_s (electron-richness) and β (polarisability) metal site parameters, defined by other authors⁽⁸⁾ for octahedral 18-electron complexes with 16-electron square pyramid metal centres, are extended to octahedral 18-electron compounds of the types $[M_sL_n]$ with 14-electron (n = 2) or facial 12-electron (n = 3) metal sites, by defining new overall P_{nL} ligand parameters as, e.g.,

 $P_{nL} = E_{1/2}^{ox} [Cr(CO)_{6-n}L_n] - E_{1/2}^{ox} [Cr(CO)_6]$

and considering the following general linear expression

 $E_{1/2}^{ox} \left[M_{s} L_{n} \right] = E_{s} + \beta \cdot P_{nL}$

which appears to be valid for all these types of complexes.

The $\rm P_L$ ligand parameter appears to be additive for cis ligands, the new P_{nL} parameter being then equal to n.P_L.

The new expressions are applied to complexes with the $\{\text{Re}(\text{dppe})_2\}^+$, $\{\text{Mo}(\text{dppe})_2\}$, $\{\underline{\text{cis}}-\text{M}(\text{CO})_4\}$ (M = Cr, Mo, W) and $\{\underline{\text{fac}}-\text{M}(\text{CO})_3\}$ (M = Cr, Mo) binding metal centres, and the corresponding ligand P_{nL} and metal site (E_s, β) parameters are estimated. For the <u>cis</u>-14-electron metal sites (n = 2), bidentate chelating ligands (LL) are also considered.

Resumo Através da definição de novos parâmetros globais de ligandos, P_{n1}, designadamente pela equação

 $P_{nL} = E_{1/2}^{ox} [Cr(CO)_{6-n}L_n] - E_{1/2}^{ox} [Cr(CO)_6]$,

e da apresentação da expressão linear geral

 $E_{1/2}^{OX} [M_s L_n] = E_s + \beta P_{nL}$,

foi possível estender a aplicação dos parâmetros electroquímicos propostos por outros autores — P_L de ligando, riqueza electrónica E_s e polarizabilidade β de centro metálico, válidos para complexos octaé-

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dricos de 18 electrões de centros metálicos de 16 electrões piramidais quadrangulares — a complexos octaédricos de 18 electrões dos tipos $\left[M_{s}L_{n}\right]$ com centros metálicos de 14 electrões (n = 2) ou de 12 electrões (isómero facial) (n = 3).

Os ligandos em posição <u>cis</u> apresentam um efeito aditivo sobre o parâmetro de ligando, sendo $P_{nL} = n.P_L$.

As novas expressões foram aplicadas a complexos com os centros {Re(dppe)₂}⁺, {Mo(dppe)₂}, {<u>cis-M(CO)</u>₄} (M = Cr, Mo ou W) e {<u>fac-M(CO)</u>₃} (M = Cr ou Mo), tendo sido estimados os valores dos parâmetros correspondentes P_{nL}, E_s e β . Para os centros de 14 electrões de geometria <u>cis</u> (n = 2), foram também considerados ligandos bidentados quelantes (LL).

I - Introduction

The chemical reactivity of a transition metal complex is deter mined by the electronic properties of both the metal binding site and the ligated species.

The electron richness of the site and the net electron with drawing/donating ability of a ligand and their co-ligands, as well as the structure of the complex, play an important role.

The redox behaviour of a complex also depends on these factors and hence it may parallel its chemical reactivity.

Moreover, in a series of closely related complexes, $E_{1/2}^{ox}$ may reflect the energy of the highest occupied molecular orbital (HOMO), ⁽¹⁾ and correlations have been reported between this parameter and, <u>e.g.</u>, the energy of a metal \rightarrow ligand charge transfer band, ⁽²⁻⁴⁾ the Hammett's σ constant (for the substituent, <u>e.g.</u>, of an aromatic isocyanide ^(5,6) or of a cyclopentadienyl ligand ⁽⁷⁾), the infrared stretching frequencies of ligands [<u>e.g.</u>, $\nu(N_2)^{(8)}$, $\nu(NO)^{(8)}$, $\nu(CO)^{(9)}$], and the reactivity ^(8,10,11) of the complex.

Hence, the importance of the knowledge of the redox potential of a complex is apparent and a systematic approach was developed by C.J. Pickett⁽⁸⁾ to quantify the redox potential-electronic and structural relationships in closed-shell 18-electron octahedral complexes of the type $[M_{c}L]$ with a 16-electron square pyramid metal centre $\{M_{c}\}$.

 $E_{1/2}^{ox}[M_sL]$ is determined by the electronic properties of both the metal centre and the ligand L, and is given by equation (1) where E_s and β denote the electron-richness ant the polarisability of the metal centre {M_s}, respectively (the former being defined by $E_{1/2}^{ox}$ of the carbonyl complex with {M_s} as the binding metal site - equation 2), and P_L is the so-called ligand parameter, defined by equation 3, which constitutes a measure of the net electron donor/acceptor character of the ligand L.

$$E_{1/2}^{\text{ox}}[M_{s}L] = E_{s} + \beta P_{L}$$
(1)

$$E_{s} = E_{1/2}^{ox} [M_{s}(CO)]$$
⁽²⁾

$$P_{L} = E_{1/2}^{ox} [Cr(CO)_{5}L] - E_{1/2}^{ox} [Cr(CO)_{6}]$$
(3)

These equations have been applied to a variety of 2-electron donor L ligands and of complexes with square pyramid 16-electron metal centres and the corresponding P_L , E_s and β values have been quoted.^(8,6) Equations (1-3) were also applied⁽¹²⁾ in the derivation of

mathematical expressions (<u>e.g.</u> - equation 4) to estimate $E_{1/2}^{ox}$ of octahedral 18-electron complexes of the type <u>trans</u>-[$M_s^{'}L_2$] with a square planar { $M_s^{'}$ } metal centre such as <u>trans</u>-[ReL₂(dppe)₂] BF₄ (L = CNR).

$$E_{1/2}^{ox} |M_{s}^{*}L_{2}| = \left[1 - \frac{P_{L}(L)}{P_{L}(L^{*})}\right]^{2} \cdot E_{1/2}^{ox} [M_{s}^{*}(CO)_{2}] + \left[\frac{2P_{L}(L)}{P_{L}(L^{*})} - \frac{P_{L}^{2}(L)}{P_{L}^{2}(L^{*})}\right] \cdot E_{s} \{M_{s}^{*}L^{*}\} + \frac{P_{L}^{2}(L)}{P_{L}(L^{*})} \cdot \beta \{M_{s}^{*}L^{*}\}$$

$$(4)$$

In order to apply this equation the E_s and β parameters of an auxiliary related 16-electron $\{M_s^tL^t\}$ site (with the common square planar moiety M_s^t) and $E_{1/2}^{ox}$ of the dicarbonyl complex $[M_s^t(CO)_2]$ have to be known. Moreover, the ligand parameters $P_L(L)$ and $P_L(L^t)$ have also to be known and equation (4) is valid only if they are independent of the metal centre. In cases the P_L ligand parameter is dependent on the metal site (e.g., for isocyanide ligands), a more elaborate expression should be used and its application requires the previous synthesis and redox study of series of complexes with the L ligands and with related metal sites, such as $\underline{\mathrm{trans}}-[M_s^tL^tL]$ or $\underline{\mathrm{trans}}-[M_s^t(CO)L]$, which would allow the accurate evaluation of the values of the $P_L(L)$ ligand parameter at various metal centres. Such a study was applied ⁽¹²⁾ to estimate $E_{1/2}^{ox}[\mathrm{ReL}_2(\mathrm{dppe})_2]\mathrm{BF}_4$ (L = CNR) on the basis of the knowledge ⁽⁶⁾ of the

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redox properties of the auxiliary [ReCl(L)(dppe),] series.

 $E_{1/2}^{ox}[M'_{s}L_{2}]$, as given by equation (4), or related expressions, shows a considerable sensitivity to the $P_{L}(L)$ values (e.g., a negligible variation of \pm 0.01 V in P_{L} may result in a change of ca. \pm 0.05 V in the value of $E_{1/2}^{ox}$) and the use of these expressions appears some - what cumbersome.

In the present study an alternative mode to estimate $E_{1/2}^{ox}[M_{s}^{*}L_{2}]$ is proposed and the possibility to extend it to complexes of the type $[M_{s}^{*}L_{3}]$, with a 12-electron metal site $\{M_{s}^{*}\}$, is discussed; new ligand parameters, P_{2L} and P_{3L} , for two and three ligands, respectively, are then proposed.

II - Square planar 14-electron {M'} metal centres.

(a) The hypothetical <u>trans</u>-{Cr(CO)₄}centre as the ideal square planar 14-electron reference binding metal centre

If it is possible to define a convenient square planar 14-electron metal centre as a reference binding metal site, and a new ligand parameter ($P_{2L,trans}$) concerned with two equal L ligands in trans position, the prediction of $E_{1/2}^{0x}[M^{t}L_{2}]$ will not require the knowledge of an auxiliary series of complexes. The value of $E_{1/2}^{0x}$ may then be given by a linear expression such as equation (5) proposed by analogy with equation (2).

 $E_{1/2}^{ox}[M_{s}^{t}L_{2}] = E_{s}\{M_{s}^{t}\} + \beta\{M_{s}^{t}\}.P_{2L,trans}$

(5)

 $E_s\{M_s^{\prime}\}$ and $\beta\{M_s^{\prime}\}$ represent the electron-richness and polarizability, respectively, of the 14-electron square planar metal site $\{M_s^{\prime}\}$, and $P_{2L, trans}$ is a new ligand parameter for the two trans L ligands in a 18-electron octahedral complex.

For the definition of P_{2L} it would be advantageous to consider the trans-{Cr(CO)₄} metal site as the 14-electron square planar binding metal centre, by analogy with the reference site {Cr(CO)₅} for the definition of the P_L parameter (equation 1). $P_{2L,trans}$ would then be given by equation (6) which, with equation (5), expresses the expected

linear relationship between $E_{1/2}^{ox}[M_s'L_2]$ and $E_{1/2}^{ox}$ of the auxiliary trans-[Cr(CO)₄L₂] series.

$$P_{2L,\underline{trans}} = E_{1/2}^{ox} \{ \underline{trans} - [Cr(CO)_4 L_2] \} - E_{1/2}^{ox} [Cr(CO)_6]$$
(6)

However, complexes $[Cr(CO)_4L_2]$ with a trans geometry are not known. In the preparation of tetracarbonylcromium(0) complexes only the <u>cis</u> geometrical isomers have been isolated, ${}^{(3,13,14)}$ <u>cis</u>- $[Cr(CO)_4L_2]$ and attempts ${}^{(14a)}$ to convert them into the trans species, by heating in solution, only resulted in disproportionation to give mono- and tri-carbonyl complexes.

 $\begin{array}{l} \text{The } \{\underline{\text{cis-Cr}(\text{CO})}_4\} \text{ metal site does not appear to be a suitable} \\ \text{reference } 14\text{-electron binding centre for square planar sites, accurate} \\ \text{linear correlations not holding for } & \text{E}_{1/2}^{\text{ox}} \left[\text{ReL}_2(\text{dppe})_2\right]^+ \stackrel{(12)}{} \text{or} \\ \text{E}_{1/2}^{\text{ox}} \left[\text{MoL}_2(\text{dppe})_2\right] \stackrel{(10)}{} \underbrace{\text{versus}} & \text{E}_{1/2}^{\text{ox}} \left\{\underline{\text{cis-[Cr(CO)}_4\text{L}_2]}\right\} \stackrel{(3,13)}{} (\text{figure 1}). \end{array}$

This is not surprising in view of the different geometries of the metal sites (trans and cis). Moreover, although for the carbonyl complexes $[Mo(CO)_4(PR_3)_2]$ (R = n-Bu, Et or Ph), which can exist in trans and cis isomeric forms (15) the redox potentials of the trans and cis complexes appear not to differ by more than ca. 50 mV, it has been reported that



Figure 1 - (a) Plot of
$$E_{1/2}^{[ReL_2(dppe)_2]BF_4}$$
 versus
 $E_{1/2}^{ox} {cis} - [Cr(CO)_4L_2] {(3,13)}.$
(b) Plot of $E_{1/2}^{ox} [MoL_2(dppe)_2]^{(10)}$ versus
 $E_{1/2}^{ox} {cis} - [Cr(CO)_4L_2] {(3,13)} (L = CNR \text{ or } CO).$

for the group VI transition metal complexes $[M(CO)_2(LL)_2]$ (LL = diphosphine (16,17) or dicarbene (18)) the trans isomers exhibit $E_{1/2}^{ox}$ at considerable lower values than the corresponding cis isomers: the difference lies usually in the 0.2 - 0.6 V range, being (17), e.g., 0.58 V between the two isomeric forms of $[Cr(CO)_2(Ph_2PCH_2PPh_2)_2]$.

The prediction of $E_{1/2}^{0x} \{ \frac{trans}{trans} - [Cr(CO)_4 L_2] \}$ by applying equation (4), or a related one, is unfortunatly also not possible since a series of complexes $\frac{trans}{cr(CO)_4 LL'}$ with an auxiliary site $\{M'_{s}L'\} = \{Cr(CO)_4 L'\}$ (L' \neq CO) is unknown.

(b) The square planar 14-electron metal centre {Re(dppe)₂} + as a reference binding metal site. P_{2L} values for linear isocyanide ligands

Due to the unavailability of the <u>trans</u>- $\{Cr(CO)_4\}$ as a reference centre for metal sites with a <u>trans</u> geometry, one may propose, as a provisional reference 14-electron square planar binding site, either $\{Re(dpe)_2\}^+$ or $\{Mo(dpe)_2\}$ which correspond to well studied $\frac{trans}{s}-[M_s^*L_2]$ systems. The former is more suitable at this stage once it is believed the isocyanides display a linear geometry when they bind such a site (the same geometry would occur for the isocyanide ligands at the $\{Cr(CO)_4\}$ site), whereas at the $\{Mo(dpe)_2\}$ centre they are bent (as proved by X-ray analysis⁽¹⁹⁾ and chemical reactivity⁽²⁰⁻²²⁾ and the parameter $P_{2L, trans}$ may be sensitive to this bending as it is expected by analogy with the observed dependence of P_r .

The overall P_{2L} , <u>trans</u> ligand parameter (for two <u>trans</u> L ligands) may then be defined by expression (7). For L = isocyanide, the

 $P_{2L, trans} = E_{1/2}^{ox} [ReL_2(dppe)_2]^+ - E_{1/2}^{ox} [Re(CO)_2(dppe)_2]^+$ (7)

 $P_{2L, trans}$ parameter refers to the linear geometry. By definition, $P_{2L, trans} = 0$ for L = CO, and, from equation (5),

 $E_{s} \{M_{s}^{\dagger}\} = E_{1/2}^{ox} [M_{s}^{\dagger}(CO)_{2}]$

(8)

For the reference $\{\text{Re}(\text{dppe})_2\}^+$ site, $\beta = 1$ and $E_s = E_{1/2}^{\text{OX}} [\text{Re}(\text{CO})_2(\text{dppe})_2]^+ = + 1.42 \text{ V}^{(12)}$.

In table 1 are quoted the values of P_{2L,trans} for various linear isocyanide ligands, estimated from equation (7) and the available experimental data⁽¹²⁾.

TABLE 1

Ligand P_{2L}, trans constants (for two <u>linear</u> isocyanide ligands in trans position) defined by equation (7)

2L	$P_{2L, trans}/v a)$
2CNMe	- 0.63
2CNBu ^t	- 0.62
CNC, H, OMe-4	- 0.54
CNC, H, Me-4	- 0.49
CNC_H, C1-4	- 0.44
CNC6H3C12-2,6	- 0.37

Equations (5, 7,8) express the expected linear relationship between $E_{1/2}^{ox} [M_s^t L_2]$ and $E_{1/2}^{ox}$ of the Re(I) series, $[ReL_2(dppe)_2]^{\dagger}$, with the 14-electron square planar $\{Re(dppe)_2\}^{\dagger}$ reference metal site, as shown by the expression (9) which results from those equations.

$$E_{1/2}^{ox}[M_{s}^{'}L_{2}] - E_{1/2}^{ox}[M_{s}^{'}(CO)_{2}] =$$

= $\beta\{M_{s}^{'}\} \cdot \{E_{1/2}^{ox}[ReL_{2}(dppe)_{2}]^{+} - E_{1/2}^{ox}[Re(CO)_{2}(dppe)_{2}]^{+}\}$ (9)

Once the ligand P_{2L,trans} parameter is know, the prediction of $E_{1/2}^{ox}$ for the series $[M'L_2]$ may be carried out in a simple way by using equation (5) provided it is known $E_{1/2}^{ox}$ of two elements of the series which would allow the evaluation of $E_{s}\{M'_{s}\}$ and $\beta\{M'_{s}\}$: a system of two equations with these two unknown parameters results from the application of the expression (5) to those two complexes.

This approach to predict $E_{1/2}^{ox} [M_s^t L_2]$ is simpler than the abovementioned based on P_L parameters (equation 4), and does not require the knowledge of an auxiliary metal site or of P_L values for three distinct binding sites. However, the $P_{2L, trans}$ parameter defined in this way (equation 7) is not directly comparable with the other ligand parameters considered in this study because the former is based on different reference metal site and standard series.

(c) {Mo(dppe)₂} as an electron-rich 14-electron metal site.

 $\frac{(i) P_{2L}}{site} \frac{values for bent isocyanide ligands at the{Mo(dppe)_2}}{z}$

The $P_{2L, \underline{trans}}$ values for isocyanide ligands obtained from equation (7) and quoted in table 1 refer to two <u>linear</u> isocyanides binding the {Re(dppe)₂}⁺ site in <u>trans</u> positions.

However, when the isocyanides ligate an electron-rich metal site, they display a bent geometry, and they behave as weaker net electron donors; the $P_{2L,trans}$ values may then become less negative, as it was previously observed (6) for the P_L parameter. The {Mo(dppe)} centre exhibits a high electron rich character, and it would be interesting to test the possibility of dependence of $P_{2L,trans}$ for isocyanide ligands on the electron-richness of the metal site.



Figure 2 - Plot of E^{ox}_{1/2}[MoL₂(dppe)₂]⁽¹⁰⁾versus P_{2L,trans}

From the plot of $E_{1/2}^{0x} [MoL_2(dppe)_2]$ (L = CO and CNR) ⁽¹⁰⁾<u>versus</u> $P_{2L, \underline{trans}}$ (figure 2), it is observed that although the isocyanide comple xes appear to follow a gross linear correlation, the CO species lies substantially off this line. However, all the points would follow the same straight line, if the previous $P_{2L, \underline{trans}}$ (2CNR) values are corrected by <u>ca.</u> + 0.27 V, suggesting that the bent isocyanides exhibit at the {Mo(dppe)_2} site $P_{2L, \underline{trans}}$ values more positive (by + 0.27 V) than those observed for the linear isocyanides at the {Re(dppe)_2}⁺ site (equation 10, table 2).

 $P_{2L,trans} [2CNR, bent at {Mo(dppe)_2}] \simeq P_{2L,trans} [2CNR, linear] + 0.27 \forall (10)$

This expression is similar to another one, $proposed^{(6)}$ on the basis of an analogous procedure, for the P_L values of isocyanides ligating 16-electron metal sites. These results evidence the expected dependence of the isocyani de P_{2L,trans} parameter on the electron-richness of the 14-electron binding metal centre.

Incidentally, from the plot of figure 2, a $P_{2L, trans}$ value of <u>ca</u>. -0.04 V is estimated for two N₂ ligands in <u>trans</u> position.

(ii) E_s and β parameters for the {Mo(dppe)₂} site

It was already mentioned that the {Mo(dppe)₂} bindig site is more electron-rich than the cationic isoelectronic {Re(dppe)₂}⁺ centre. This may be expressed by the values of the E parameter: for the latter site, E_s = + 1.42 V, {E^{ox}_{1/2}[Re(CO)₂(dppe)₂]⁺}, whereas, for the former, E_s = E^{ox}_{1/2}[Mo(CO)₂(dppe)₂] = - 0.11 V.

The molybdenum(0) site also exhibits a higher polarisability than the Re(I) centre. The latter has the unity value for β and the former has $\beta = 1.3$ as estimated from equations (5) [with P_{2L,trans} values given by the expression (10)] or from the slope of the straight line of the plot of figure 2.

The values of the abovementioned electrochemical parameters of the 14-electron metal site $\{Mo(dppe)_2\}$ the studied ligands are quoted in table 2.

TABLE 2

Electrochemical metal site and ligand constants for the square planar 14-electron metal site {Mo(dppe)₂} and for 2L ligands in trans position.

E _s /Va)	β	2L	P _{2L,trans} /V ^b)
- 0.11	1.3	2CNMe	- 0.36
		2CNBu ^t	- 0.35
		2CNC6H40Me-4	- 0.27
		2CNC6H4Me-4	- 0.22
		2CNC6H4C1-4	- 0.17
		2CNC6H3C12-2,6	- 0.10
	2N2	- 0.04	

 4 +0.05V.Quoted versus s.c.e.in thf-0.2M[NBu₄][BF₄] 0 + 0.05 V

III - cis-14 electron {M'_}and fac-12-electron {M''} metal sites

(a) Ligand parameters

The P_{2L,trans} parameter defined above (equation 7) refers to two L ligands in trans position bound to a square planar 14-electron metal site {M'}.

However, octahedral complexes of the type $[M'_{c}L_{2}]$ with a cis geometry are also known, and it would be advantageous the use of a simple parameter to allow the comparison of the net electron acceptor properties of the ligands at the 14-electron metal site with such a geometry.

As mentioned above, the tetracarbonyl complexes of Cr(0), [CrL₂(CO)₄] exhibit a <u>cis</u> geometry and, by analogy with the definitions of P_L (equation 1) and $P_{2L,trans}$ (equation 7), a new P_{2L} ligand parameter valid for two cis-L ligands may be proposed (equation 11).

$$P_{2L,\underline{cis}}(\text{or } P_{LL}) = E_{1/2}^{\text{ox}}[Cr(CO)_{4}L_{2}] - E_{1/2}^{\text{ox}}[Cr(CO)_{6}]$$
(11)

This definition may also be applied to 4 electron-donor dihapto (bidentate) chelating ligands (LL), such as diamines and diphosphines; the ligand parameter may then be denoted by P₁₁.

The values of this new P_{2L,cis} or P_{LL} parameter, estimated from published data^(3, 13), are shown in table 3.

For the isocyanide ligands, P2L, cis refers to the linear geometry and, interestingly, their values are roughly the double of the

Ligand P_{2L,cis} or P_{LL} constants defined by equation (11), and 2 P_t constants for linear isocyanides

2L or LL	$P_{2L,\underline{cis}}/V \text{ or } P_{LL}/V a)$	2P _L /V ^{b)} (linear isocyanide)
2CNMe	- 0.94	- 0.86 c,d)
2CNEt	- 0.96	- 0.88 ^{c)}
2CNPr ⁱ	- 0.95	- 0.88 ^{c)}
2CNBu ^t	- 0.96	- 0.88 ^{c,e)}
2CNC _{cH} , f)	- 0.98	
2CNC, H, Me-4	- 0.86	- 0.78 ^{c,e)}
2CNC_H,C1-4	- 0.77	- 0.74 ^{c,e)}
2PMe ₂ H	- 0.92	
o-phenanthroline	- 0.64	
bipyridyl	- 0.92	
Me2PCH2CH2PMe2	- 1.07	
o-Me_NC_H_NMe_	- 1.09	
Me_NCH_CH_NMe_	- 1.17	
Me_NCH(Me)CH(Me)NMe_	- 1.17	
H_NCH(Ph)CH(Ph)NH_	- 1.31	
H2NCH(Me)CH(Me)NH2	- 1.39	
H2NCH2CH2NH2	- 1.39	

a)

a) ± 0.05 V. Estimated from refs. (3,13).^{b)} ± 0.10 V.^{c)} P_L estimated from data of ref.(3).^{d)} P_L taken from ref.(8).^{e)} P_L taken from ref.(6).^{f)} Estimated by extrapolation of the plot of $E_{1/2}^{\text{ox}}$ <u>cis</u>-[Mo(CO)₄(CNR)₂] <u>versus</u> P_{2L,cis}.

corresponding linear P_L values⁽⁶⁾ (within 9% differences); since a common reference, $[Cr(CO)_6]$, was chosen in their definitions, this suggests that it is additive the influence of the replacement of a carbonyl (which is <u>trans</u> to another carbonyl) by an isocyanide on the $E_{1/2}^{OX}$ of the derived complexes. This additive effect is also substantiated by considering the complexes $[Cr(CO)_3L_3]$ which show a <u>facial</u> geometry and the definition of the new $P_{3L,fac}$ parameter concerned with three L ligands in <u>facial</u> position (equation 12).

$$P_{3L,\underline{fac}} = E_{1/2}^{ox} [Cr(CO)_{3}L_{3}] - E_{1/2}^{ox} [Cr(CO)_{6}]$$
(12)

The values of $P_{3L, \underline{fac}}$, estimated from published data⁽³⁾, for three <u>fac</u>-isocyanide ligands, which exhibit a linear geometry, are displayed in table 4, and they agree, within 10%, with $3P_{T}$.

TABLE 4

Ligand P_{3L} constants (for three <u>linear</u> isocyanide ligands in facial position) defined by equation (12)

L	P _{3L,fac} (Linear)/V ^{a)}	3 P _L (linear)/V ^{b)}
CNPr ⁱ	- 1.33 V	- 1.32
CNBut	- 1.34	- 1.32
CNC6H11	- 1.33	-1.47^{c}
CNC ₆ H ₄ Me-4	- 1.13	- 1.17
CNC6H4C1-4	- 1.02	- 1.11

a) <u>+</u> 0.05 V. ^{b)} <u>+</u> 0.15 V. ^{c)} Estimated from P_{2L,cis}(-0.98 V) given in table 3.

Considering that the additive character of the P_L parameter is valid not only for isocyanides but also for the other two electron donor ligands, the corresponding values of P_{2L,cis} and P_{3L,fac} are easily estimated as 2P_L and 3P_L, respectively, and are shown in table 5.

The additive effect on the oxidation potential of the successive replacement of carbonyl ligands by other molecules is not surprising since it was previously recognized by other authors $^{(13,23,24)}$ for ligands such as CNMe or NCMe in some octahedral 18-electron first-row transition metal complexes of the type $[M(CO)_{6-x} L_x]^{y+}$ and a linear relationship between the formal electrode (oxidation) potential and the degree of carbonyl substitution (x) was proposed: $^{(23)}$

 $E^{0} = A + x (dE^{0}/dx)_{T} + 1.48 y$

where <u>y</u> is the charge of the complex, <u>A</u> is a constant which depends upon the solvent and reference potential. $(dE^{\circ}/dx)_{L}$ is a ligand parameter which, for M = Cr, is identical to P_L; hence, $x(dE^{\circ}/dx)_{L}$ corresponds to n. P_L (or P_{nL}) of the present study where <u>n</u> represents the number of L ligands in complexes [Cr(CO)_{6-n} L_n] (n=1-3).

TABLE 5

Ligand $P_{2L, \underline{cis}}$ and $P_{3L, \underline{fac}}$ constants estimated from the corresponding P_L constants.

L	P _{2L,cis} /V ^{a)}	P _{3L,<u>fac</u>/V b)}	P _L / V ^{c)}
NO ⁺	2.80	4.20	1.40
CO	0	0	0
N ₂	- 0.14	- 0.21	- 0.07
P(OPh)	- 0.36	- 0.54	- 0.18
CNC6H3C12-2,6	- 0.66	- 0.99	- 0.33 ^d)
PPh ₃	- 0.70	- 1.05	- 0.35
CNC6H4C1-4	- 0.74	- 1.11	- 0.37 ^d)
CNPh	- 0.76	- 1.14	- 0.38
CNC ₆ H ₄ Me-2	- 0.76	- 1.14	- 0.38 ^d)
CNC_6H_4Me-4	- 0.78	- 1.17	- 0.39 ^d)
CNC ₆ H ₄ OMe-4	- 0.80	- 1.20	- 0.40 ^d)
NCPh	- 0.80	- 1.20	- 0.40
CNMe	- 0.86	- 1.29	- 0.43
CNEt	- 0.88	- 1.32	- 0.44 e)
CNPr ⁱ	- 0.88	- 1.32	- 0.44 ^{e)}
CNBu ^t	- 0.88	- 1.32	- 0.44 ^d)
PMe_H	- 0.92	- 1.38	- 0.46 f)
CNC ₆ H ₁₁	- 0.98	- 1.47	- 0.49 f)
NCMe	- 1.16	- 1.74	- 0.58
Ру	- 1.18	- 1.74	- 0.59
NH2	- 1.54	- 2.31	- 0.77
CF COO	- 1.56	- 2.34	- 0.78
NCS	- 1.76	- 2.64	- 0.88
CN ⁻	- 2.00	- 3.00	- 1.00
1_	- 2.30	- 3.45	- 1.15
NCO	- 2.32	- 3.48	- 1.16
Br	- 2.34	- 3.51	- 1.17

c1 ⁻	- 2.38	- 3.57	- 1.19
н	- 2.44	- 3.66	- 1.22
N 3	- 2.52	- 3.78	- 1.26
OH-	- 3.10	- 4.65	- 1.55

a) <u>+</u> 0.10V. ^{b)} <u>+</u> 0.15V. ^{c)} <u>+</u> 0.05 V. Values taken from ref (8), unless otherwise stated. ^{d)} Value taken from ref. (6). ^{e)} Estimated from data of ref. (3). ^{f)} Estimated from P_{2L,cis}.

From the values of the P_{LL} (or P_{2L}) ligand parameter quoted in Table 3, a few comments may be mentioned, in accordance with observations reported by other authors:

- The net electron-donor character of the quoted ligands follows the order chelating diamine > chelating diphosphine > two <u>cis</u> alkyl isocyanides > bipyridyl > two <u>cis</u> arylisocyanides > <u>o</u>-phenantroline.

- Within the chelating LL ligands, an increase in the π -conjugation in the backbone structure between the ligating atoms parallels an increase in the net electron-acceptor character of the ligand as deduced by comparing the P_{LL} values of Me₂NCH₂CH₂NMe₂ and of bipyridyl with those of <u>o</u>-Me₂NC₆H₄NMe₂ and <u>o</u>-phenantroline, respectively.

- Within the chelating diamine ligands, a surprising enhance - ment of the net electron acceptor ability occurs from primary to tertiary amines.

(b) Metal centre parameters

For the 14-electron metal sites with a <u>cis</u> geometrical confi guration, {<u>cis-M'</u>} and for the <u>fac-12-electron sites</u> {<u>fac-M''</u>}, it is also possible to consider the E_s and β parameters according to equations (13-16) where P_{2L,cis} and P_{3L,fac} are given by the expressions (11) and (12).

$$E_{1/2}^{ox} \{ \underline{cis} - [M_{s}^{'}L_{2}] \} = E_{s} \{ \underline{cis} - M_{s}^{'} \} + \beta \{ \underline{cis} - M_{s}^{'} \} \cdot P_{2L, \underline{cis}}$$
(13)
$$E_{s} \{ \underline{cis} - M_{s}^{'} \} = E_{1/2}^{ox} \{ \underline{cis} - [M_{s}^{'}(CO)_{2}] \}$$
(14)

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$$E_{\rm ex}^{\rm ox} \{ fac - [M''L_{\rm c}] \} = E \{ fac - M'' \} + \beta \{ fac - M'' \} . P_{\rm ox}$$
(15)

$$\frac{1/2}{E_{s}} = \frac{1}{s} \frac{1}$$

For the standard { \underline{cis} -Cr(CO)₄} and { \underline{fac} -Cr(CO)₃} metal sites, $E_s = E_{1/2}^{ox} [Cr(CO)_6] = 1.53 V$ and $\beta = 1$ (table 6).

Complexes with the <u>cis-</u>{ $M(CO)_4$ }(M = Mo or W) and the <u>fac-</u>{ $Mo(CO)_3$ } centres with measured $E_{1/2}^{ox}$ have been reported in the literature^(3,13). Moreover, E_s of these centres is also known since, by definition, it equals $E_{1/2}^{ox}$ [$M(CO)_6$] (M = Mo or W) which has also been measured ⁽²⁵⁾: all the group VI carbonyl complexes [$M(CO)_6$] (M = Cr, Mo or W) exhibit analogous values of $E_{1/2}^{ox}$ at 1.53 V.

Hence, the polarisability (β) of those centres may be evaluated from the slopes of the plots of $E_{1/2}^{OX}$ of the complexes versus P_{2L} (or P_{LL}) or versus $P_{3L,cis}$. Such a procedure was applied to the known complexes cis-[Mo(CO)₄ L_2] (L = CNR or CO) or cis-[Mo(CO)₄(LL)] (LL = = Me_2PCH_2CH_2PMe_2, bipyridy1) (figure 3), cis-[W(CO)_4L_2] (L = CNR or CO) or cis-[W(CO)_4(LL)] (LL = Me_2PCH_2CH_2PMe_2) (figure 4), and fac-[Mo(CO)_{3}L_3] (L = CNR or CO) (figure 5).

The plots of $E_{1/2}^{ox}$ of these families of complexes <u>versus</u>[•] the corresponding P_{2L} or P_{LL} parameters follow the expected linear correlations - only the point corresponding to $[Mo(CO)_4(dipy)]$ lies appreciably







off the linear relationship - and it is observed (figures 3-5) that their slopes are very similar (Table 6):

$$\beta\{\underline{\operatorname{cis-Mo}(CO)}_{4}\} = \beta\{\underline{\operatorname{cis-W}(CO)}_{4}\} = 0.83$$

 $\beta \{ fac-Mo(CO)_{3} \} = 0.85$

Hence, a change of ligand L (or LL) at the Mo complexes $[Mo(CO)_4L_2]$ (or $[Mo(CO)_4(LL)]$) leads to a variation in $E_{1/2}^{ox}$ which is analogous to that observed for the homologous W complexes upon the same ligand change.

Moreover, since $P_{3L} = \frac{3}{2} P_{2L}$, a change in ligand L results in a variation of $E_{1/2}^{0x} \{ \underline{fac} - [Mo(CO)_{3}L_{3}] \}$ which is <u>ca</u>. $\frac{3}{2}$ of the corresponding variation of $E_{1/2}^{0x} [Mo(CO)_{4}L_{2}]$ for the analogous ligand exchange.

TABLE 6

 ${\tt E}_{\rm g}$ and β constants for cis-14-electron and fac-12-electron metal sites

Metal site	E _s / V ^{a)}	β
{cis-Cr(CO) ₄ }	1.53	1
{ <u>cis</u> -Mo(CO) ₄ }	1.53	0.83
{ <u>cis</u> -W(CO) ₄ }	1.53	0.83
{fac-Cr(CO)_3}	1.53	1
{ <u>fac</u> -Mo(CO) ₃ }	1.53	0.85

a) See note a) of table 2.

Equations (12, 15, 16) only refer to facial isomers, not applying to the corresponding meridional isomeric forms which are expected to present different $E_{1/2}^{ox}$ values. Hence, e.g., within the series $[Mn(CO)_3(LL)X]$ (LL = bidentate phosphine or arsine, X = hali de)⁽²⁶⁾, the meridional complexes are easier to oxidize than the corres ponding facial isomers by <u>ca</u>. 0.5 V. The approach used in the present study was not extended to this type of complexes due to unavailability of experimental data. IV - Final remarks

Half-wave oxidation potential values for 18-electron octahedral complexes, $E_{1/2}^{ox}$ $[M_{sL_n}]$, and the overall net electron donor properties of the p Lligands (as measured by a P_{nL} ligand parameter) appear to obey the following general linear relationship(equation 17)

$$E_{1/2}^{ox}[M_{s}L_{n}] = E_{s} + \beta P_{nL}$$
(17)

where:

 $n = 1 \rightarrow M_s$ = square pyramid 16-electron metal site $n = 2 \rightarrow M_s = \underline{cis}$ or <u>trans</u>-14-electron metal site (M's) $n = 3 \rightarrow M_s = \underline{fac}$ -12-electron metal site (M's)

 $E_{\rm g}$ and β characterize the electron-richness and the polarisability of the metal site, the former being given by the general equation (18).

$$E_{s} = E_{1/2}^{OX} [M_{s}(CO)_{n}]$$
(18)

The P_{nL} ligand parameter is defined by the expression (19) (except for the <u>trans</u>-14-electron metal sites) based on polycarbonylchromium(0) metal sites, and it appears to be additive for cis ligands (equation 20 is valid in the examples tested).

$$P_{nL} = E_{1/2}^{0x} [Cr(C0)_{6-n} L_n] - E_{1/2}^{0x} [Cr(C0)_6]$$
(19)

$$P_{nL} = n. P_{L}$$
(20)

For the <u>trans</u>-14-electron (square planar) metal site, the lack of available experimental data — <u>trans</u>- $[Cr(CO)_4L_2]$ complexes are unknown — prevents the application of the expression (19) and the $\{Re(dppe)_2\}^+$ site is proposed as the reference binding centre, the P_{2L} parameter being defined by equation (7).

These expressions constitute an attempt to quantify the electronic properties of different types of binding metal sites and their ligands, and their effects on the oxidation potential. They allow the comparison among various sites of the same type and also among a wide variety of ligands. By combined application of these equations it is possible to predict metal site and ligand parameters for new binding centres and different ligands, as well as the redox properties of complexes with these sites and ligands.

However, the prospects of the application of this approach to types of metal sites other than those already mentioned depend on both the previous chemical preparation and electrochemical redox study of series of adequate complexes.

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