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Characterization of Coordination Compounds by Electrochemical Parameters

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Attention is drawn to the interest in the use of the redox potential for the characterization and identification of coordination compounds on the basis of redox potential-structure relationships that define electrochemical parameters, which are shown for a wide variety of ligands and metal sites.

1. Introduction

Coordination compounds are usually characterized by common IR and multi-nuclear NMR spectroscopic methods, elemental analysis and, whenever possible, by single-crystal X-ray diffraction. In contrast, electrochemical methods, although being increasingly applied in the last few years (mainly cyclic voltammetry) to measure the redox potential, induce chemical reactions by electron transfer and study the mechanisms of redox processes,[1–4] have not yet found a common application as a characterization or identification tool for such compounds. This is somewhat surprising in view of the useful information associated with the redox potential of a compound.

The main aim of this Microreview is to draw the attention of the coordination and organometallic chemists to the fact that the redox potential of a complex can provide a relevant structural and electronic meaning, allowing for the quantification of the metal and ligand electron acceptor/donor properties, which can then be applied as an important characterization parameter, the use of which has still been neglected. For such a purpose, the review focuses on the seminal works of Pickett and Lever who have proposed useful models for the redox potential/structure relationships in metal complexes, and on the developments thereof, which have been introduced namely by the current author and his research group.

Since the redox potentials of metal complexes have been correlated over the years to a variety of other properties[5–7] that are also dependent on the electronic/structural features of the complexes, one could expect the possibility of using the redox potential to quantify the electron donor/acceptor properties of the ligands and their coordination metal

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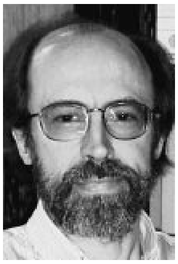

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centres. This would provide an important characterization method for the complexes based on their redox potentials, but would require the establishment of defined relationships between the redox potential and such electronic properties of all the particular ligands and metal sites that constitute the coordination entity under study. To keep matters simple additive effects on the redox potential have been sought.

Following preliminary additivity recognitions,[8,9] within a series of closely related 18-electron first-row transition-metal complexes of the general type $[M(CO)_{6-x}L_x]^{y+}$, which undergo a single-electron reversible oxidation centred at the metal atom, the main systematic approaches have been proposed by Pickett et al.,[10–12] Lever[13–16] and Bursten.[17–19]

The Bursten model is based on a direct linear correlation (with a negative slope) between the HOMO energy and the oxidation potential ($E_{1/2}$) of octahedral d^6 metal complexes of the type $[ML_nL'_{6-n}]$ (L = stronger π-acceptor than L′). This potential (viz. HOMO energy) is determined in an additive way by the effects (B) of all the nL and $(6-n)$L′ ligands and by the effects (C) of the ligands, xL and $(4-x)$L′, that π-interact with the metal dπ orbital comprised in the HOMO of the complex {[Equation (1)] in which A^0 depends on the metal atom, in particular its oxidation state, and trivially on the solvent and reference electrode}.

$$E_{1/2} = A^{o} + nB^{L} + (6-n)B^{L'} + xC^{L} + (4-x)C^{L'} \tag{1}$$

In spite of the immediate significance of this model, in terms of the redox potential/redox orbital energy relationship, its basic expression (1) (although it can adopt a simpler form) is considerably complex, requires the differentiation of the ligands in terms of their π-acceptance ability and still remains relatively unexplored. Moreover, it can be correlated to the other models (namely the Pickett one[20]), which are easier to apply and will not be considered further.

It is worth mentioning that, for comparative purposes, the redox potentials have to have a common reference, which often requires a conversion.[21,22] In Pickett's model the potentials have typically been quoted relative to the saturated calomel electrode (SCE), whereas in the Lever one they have been referenced to the normal hydrogen electrode (NHE).

2. Partial Additivity Models – Pickett's and Derived Models

In these models, some of the ligands (and therefore their effects) are included in the overall metal centre $\{M_s\}$ to which the other ligand(s) L_n is (are) bonded in the $[M_sL_n]$ complex and therefore the additive effects on the redox potential are assumed only for the $\{M_s\}$ and the nL ligand(s). In the extreme case, as in Pickett's model, $n = 1$, i.e. only one ligand is distinct from the binding metal site in the $[M_sL]$ complex, corresponding to a minimum additivity requirement. Extensions of this model to other cases, with a separation of more than one ligand ($n > 1$) from $\{M_s\}$ (a higher additivity assumption), have been proposed by the current author.

2.1. General

The linear relationships observed by Pickett et al. between the oxidation potentials ($E^{ox}_{1/2}$) of the members of a series of 18-electron octahedral-type complexes $[M_sL]$ (bearing a variable L ligand at a 16-electron M_s metal centre) and the oxidation potentials of the homologous complexes $[Cr(CO)_5L]$ [with the $\{Cr(CO)_5\}$ site and the common L ligand] can be expressed by the basic Equation (2). Herein, E_s is the oxidation potential of the carbonyl complex $[M_s(CO)]$ [Equation (3)], a measure of the *electron richness* of the metal centre (the higher this property, the lower E_s), the slope β is the *polarizability* of the metal site (a measure of the sensitivity of the HOMO energy to a variation of the ligand L) and the *ligand P_L parameter* [given by Equation (4)] is the shift in the oxidation potential resulting from the replacement of one CO group in $[Cr(CO)_6]$ by one L ligand.[10]

$$E^{ox}_{1/2}[M_sL] = E_s + \beta P_L \tag{2}$$

$$E_s\{M_s\} = E^{ox}_{1/2}[M_s(CO)] \tag{3}$$

$$P_L(L) = E^{ox}_{1/2}[Cr(CO)_5L] - E^{ox}_{1/2}[Cr(CO)_6] \tag{4}$$

Expression (2) allows (i) the estimate of E_s and β of the metal centre from the plot of the oxidation potential of a series of complexes $[M_sL]$ vs. P_L, or (ii) the estimate of P_L for the ligand L if E_s and β are known for a certain $\{M_s\}$ centre, as well as the oxidation potential of the particular complex $[M_sL]$ with this metal site and the ligand L, or (iii) the estimate of either E_s or β, when the other parameters and the oxidation potential of an $[M_sL]$ complex is known, or (iv) the prediction of the oxidation potential of any $[M_sL]$ complex provided the corresponding E_s, β and P_L parameters are known.

The above Pickett's approach has been adapted or extended to complexes of types other than $[M_sL]$ as follows.

Extension of the additivity to 18-electron complexes $[M_sL_n]$ ($n = 2, 3$; $n = 1$ was the original case) leads to Equations (5), (6) and (7),[5,23] with the P_{nL} ligand parameter rep-

$$E^{ox}_{1/2}[M_sL_n] = E_s + \beta P_{nL} \tag{5}$$

$$E_s = E^{ox}_{1/2}[M_s(CO)_n] \tag{6}$$

$$P_{nL} = E^{ox}_{1/2}[Cr(CO)_{6-n}L_n] - E^{ox}_{1/2}[Cr(CO)_6] \tag{7}$$

resenting the shift of the oxidation potential upon replacement of *n*CO ligands in $[Cr(CO)_6]$ by *n*L ligands. It is the sum of the *n* individual P_L values [Equation (8)] when the L ligands have independent effects on the oxidation potential.[5,23] The metal centre $\{M_s\}$ is then a 14-electron ($n = 2$) or a 12-electron ($n = 3$) site.

$$P_{nL} = n\,P_L \tag{8}$$

For the mixed-ligand complexes $[M_sLL']$, the oxidation potential was shown[24] to be the average of those of the corresponding $[M_sL_2]$ and $[M_sL'_2]$ [Equation (9)] when the metal sites $\{M_sL\}$ and $\{M_sL'\}$ exhibit analogous values of polarizability (β).

$$E^{ox}_{1/2}[M_sLL'] = 1/2\,\{E^{ox}_{1/2}[M_sL_2] + E^{ox}_{1/2}[M_sL'_2]\} \tag{9}$$

Moreover, the oxidation potential of the complexes $[M_sL_2]$ was demonstrated[25] to be given by Equation (10), showing that the potential of any member of the series can be predicted provided one knows the oxidation potential of the dicarbonyl complex $[M_s(CO)_2]$, the E_s and β values of an auxiliary $\{M_sL'\}$ site with the auxiliary L′ ligand and the P_L values of both L and L′. The knowledge of these auxiliary parameters also allows for the estimate of the electron richness and polarizability of the $\{M_sL\}$ centre [Equations (11) and (12)].[25]

These expressions, (9)–(12), with an evident predictive value, have been successfully applied to the series of isocyanido and carbonyl complexes of rhenium(I), *trans*-$[ReLL'(dppe)_2]^+$ (L, L′ = CNR, CO; dppe = $Ph_2PCH_2CH_2PPh_2$) and *trans*-$[ReL_2(dppe)_2]^+$ (L = CNR, CO),[24–25] and of nitrile and carbonyl complexes of iron(II), *trans*-$[FeL_2(depe)_2]^{2+}$ (L = NCR, CO; depe = $Et_2PCH_2CH_2PEt_2$).[26] The E_s and β values of the corresponding *trans*-$\{ReL(dppe)_2\}^+$ and *trans*-$\{FeL(depe)_2\}^{2+}$ metal sites have also been estimated (see below).[24–26]

An extension of the model to open-shell 17- and 16-electron complexes has also been carried out.[27,28] The general expressions (2)–(4) can be kept but now the metal site $\{M_s\}$ is a 15- or a 14-electron centre, respectively. The approach has been applied to the 17-electron complexes *cis*-$[ReCl(L)(dppe)_2]^+$ (L = NCR, CO) and *trans*-$[FeBr(L)(depe)_2]^{2+}$, with a 15-electron Re^{II} or Fe^{III} centre,[27] and to the square-planar 16-electron Rh^I complexes $[Rh(O^\frown O)(CO)L]$ [$O^\frown O$ = $MeC(O)CHC(O)Me^-$ (acac), $PhC(O)CHC(O)Me^-$ (bac)].[28]

$$E_s\{M_sL\} = \left[1 - \frac{P_L(L)}{P_L(L')}\right] E^{ox}_{1/2}[M_s(CO)_2] + \frac{P_L(L)}{P_L(L')} E_s\{M_sL'\} \tag{11}$$

$$\beta\{M_sL\} = \frac{\left[1 - \frac{P_L(L)}{P_L(L')}\right] E_s\{M_sL'\} - \left[1 - \frac{P_L(L)}{P_L(L')}\right] E^{ox}_{1/2}[M_s(CO)_2] + \beta\{M_sL'\} P_L(L)}{P_L(L')} \tag{12}$$

2.2. P_L Ligand Parameter

The P_L ligand parameter can be obtained from expression (4) if the oxidation potential of the corresponding $[Cr(CO)_5L]$ complex is known, or otherwise by using the general Equation (2) if one knows the oxidation potential of a particular $[M_sL]$ complex with that ligand binding a metal centre $\{M_s\}$ with known E_s and β values. It can also be derived from the Lever E_L parameter (see below). P_L values are already known for a wide variety of ligands[5,10,24–56] and lists have been collected[36,56] with particular emphasis on the estimate of the values for carbynes, carbenes, vinylidenes, allenylidenes and alkynyls.[36] Representative examples are given in Table 1, which also includes those reported recently.

The P_L ligand parameter reflects both σ- and π-effects in an overall manner and is considered as a *measure* of the net electron-donor minus the electron-acceptor ability of the ligand L, since the higher this property the less stabilized will be the HOMO for $[Cr(CO)_5L]$ and hence the lower oxidation potential of this complex and the lower the P_L parameter [Equation (4)]. Although the oxidation potential of a compound depends on the energetics of both the compound and its oxidized form, a linear correlation of the oxidation potential with the HOMO energy (see above) is expected for a series of closely related complexes such as $[Cr(CO)_5L]$ with a variable L.

The strongest net π-electron acceptors exhibit the highest P_L values (≥0), namely NO^+ (+1.40 V)[10] > carbynes (+0.24 to +0.21 V)[29] > η^2-vinyl (+0.22 V)[31] > benzoyl isocyanide (+0.20 V)[30] > PF_3 (+0.14 V)[32] > aminocarbyne ($=CNH_2^+$) (+0.09 V)[31] > CO (0 V).

Dinitrogen and the phosphaalkyne P≡C*t*Bu, coordinated in the η^1-mode, have P_L values (–0.07[10] and –0.04[33] V, respectively) close to that of CO (0 V), but this is accounted for by the limited σ-donor and π-acceptor abilities of the former ligands. Similar P_L values can be displayed by both a weak π-acceptor/weak σ-donor ligand and a strong π-acceptor/strong σ-donor one, since P_L is determined by the net π-electron acceptor minus σ-donor character of the ligand.

$$E^{ox}_{1/2}[M_sL_2] = \left[1 - \frac{P_L(L)}{P_L(L')}\right]^2 E^{ox}_{1/2}[M_s(CO)_2] + \left[\frac{2P_L(L)}{P_L(L')} - \frac{P_L{}^2(L)}{P_L{}^2(L')}\right] E_s\{M_sL'\} + \frac{P_L{}^2(L)}{P_L(L')}\beta\{M_sL'\} \tag{10}$$

Table 1. P_L and E_L values for selected ligands.[a]

	P_L [V]	Ref.	E_L [V vs. NHE]	Ref.
NO^+	1.40	[10]	>1.5	[13,16]
Carbynes (≡CR)	0.24 to 0.21	[29]	ca. 1.2	[29]
η^2-Vinyl (η^2-CH_2CCH_2Ph)	0.22	[31]	ca. 1.2	[36]
Benzoyl isocyanide (C≡NCOPh)	0.20	[30]	0.16	[30]
PF_3	0.14	[32]	–	–
Aminocarbyne (=CNH_2^+)	0.09	[31]	ca. 1.1	[36]
CO	0	[10]	0.99	[13]
η^1-Phosphaalkyne (η^1-P≡C*t*Bu)	–0.04	[33]	–	–
N_2	–0.07	[10]	–	–
Isocyanides (bent) (C≡NR)[b]	–0.07 to –0.18	[24,25,34,35]	–	–
Hydrazinium ($NH_2NH_3^+$)	–	–	0.80	[57]
Ethylene (CH_2=CH_2)	–	–	0.76	[13]
N-Pyrrolylphosphanes $PPh_n(NC_4H_4)_{3-n}$ (n = 0–3)	–	–	0.69 to 0.53	[28]
Vinylidenes (=C=CHR)	0 to –0.6	[29,36]	0.7 to 0.2	[36]
$P(OPh)_3$	–0.18	[10]	0.58	[13]
η^2-Allene (η^2-CH_2=C=CHPh)	–0.21	[31]	0.56	[36]
Metallo-dinitriles (N≡C–X–C≡N–ML_{n-1})	–0.18 to –0.40	[37]	0.58 to 0.39	[36]
Ferricinium isocyanides	–0.22 to –0.28	[38,39]	0.55 to 0.50	[36]
Nitriles (N≡CR)	–0.23 to –0.58	[10,27]	0.49 to 0.33	[13]
C≡N–BF_3^-	–0.24	[30]	0.20	[30]
Metallo-cyanides (C≡N–ML_{n-1}^-)	–0.25 to –0.61	[30,40]	0.50 to 0.21	[36]
Phosphonium isocyanides	–0.28 to –0.36	[41]	0.50 to 0.43	[41]
Allenylidenes (=C=C=CR_2)	0 to –0.8	[36,42]	0.8 to 0	[36]
Me_2SO (S-coordinated)	–0.19	[36]	0.57	[57]
Isocyanides (linear) (C≡NR)[c]	–0.33 to –0.44	[24,25,34,43]	–	–
Organophosphanes	–0.3 to –0.5	[10,32,45]	0.5 to 0.3	[13,36]
Bithiophene-carbenes	–0.38 to –0.62	[44]	0.41 to 0.21	[36]
Phosphirene	–0.43	[45]	–	–
Protonated indole derivatives	–0.44 to –0.62	[41]	–	–
Indazole	–0.56	[36]	0.26	[71]
C≡N–BPh_3^-	–0.51	[46]	–0.05	[30]
Pyridine	–0.59	[10]	0.25	[13]
Oxocarbenes [=C(OR)Y]	–0.51 to –0.64	[36]	0.30 to 0.19	[36]
Cyanamides (N≡C–NR_2)	–0.57 to –0.85	[26, 47–49]	0.25 to 0.0	[36]
Pyrazole	–	–	0.20	[13]
4-Methylpyrazole	–	–	0.18	[75]
Triazole	–	–	0.18	[13]
1-Methyltriazole	–	–	0.17	[75]
Thiocarbenes [=C(SR)Y]	–0.66 to –0.68	[36]	0.17 to 0.15	[36]
Aminocarbenes [=C(NRR′)Y]	–0.69 to –0.80	[5,36]	0.15 to 0.05	[36]
Hydrotris(pyrazolyl)methane ($HCpz_3$)	–	–	0.14	[72]
Imidazole	–	–	0.12	[13]
Benzoyldiazenide ($NNCOPh^-$)	–	–	0.11	[72]
Benzimidazole	–	–	0.10	[75]
1-Alkylimidazole	–	–	0.08 to 0.06	[13,75]
Ferrocenyl-oxocarbenes	–0.70 to –0.9	[36]	0.14 to 0.0	[36]
NH_3	–0.77	[10]	0.07	[13]
CF_3COO^-	–0.78	[10]	–0.15	[13]
Phosphoylide-aminocarbenes	–079 to –0.87	[41]	0.06 to 0.0	[41]
Cyanoguanidine [N≡C–NC$(NH_2)_2$]	–0.86	[50]	–	–
Hydrogendicyanamide (N≡CNHCN)	–0.88	[50]	–	–
NCS^-	–0.88	[10]	–	
Tris(pyrazolyl)methanesulfonate ($SO_3Cpz_3^-$)	–	–	–0.09	[73]
Ferrocenyl-aminocarbenes	–0.99 to –1.1	[36]	–0.11 to –0.21	[36]
Indole derivatives	–0.92 to –1.0	[41]	–	–
C≡N^-[d]	–1.00	[10]	0.02	[13]
	–0.74	[30]	–0.26	[30]
Hydrotris(3,5-dimethylpyrazolyl)borate [$HB(Me_2pz)_3^-$]	–	–	–0.23	[64]
Bis(pyrazolyl)borate ($H_2Bpz_2^-$)	–	–	–0.24	[64]
Pyrazolate	–1.14	[36]	–0.24	[13]
2-Pyridinecarboxylate (2-pyCOO^-)[e]	–	–	–0.24	[74]
Dicyanamide ($NCNCN^-$)	–1.14	[50]	–	–
I^-	–1.15	[10]	–	–
NCO^-	–1.16	[10]	–0.25	[13]
Br^-	–1.17	[10]	–	–

Table 1. *(continued)*

	P_L [V]	Ref.	E_L [V vs. NHE]	Ref.
Cl^-	–1.19	[10]	–0.24	[13]
Acyl- or aroyl-cyanamide $[NCNC(O)R^-]$	–1.19	[51]	–	–
Monodeprotonated cyanoguanidine $[NCNC(NH)NH_2^-]$	–1.22	[50]	–	–
Alkynyls ($–C{\equiv}CR^-$)	–0.9 to –1.7	[5,36,42,52,53]	–0.1 to –0.7	[36]
H^-	–1.22	[10]	–0.30	[13]
N_3^-	–1.26	[10]	–0.30	[13]
Me_2SO (O-coordinated)	–	–	–0.37	[57]
F^-	–1.3	[54]	–0.42	[13]
Hydrogen cyanamide ($NCNH^-$)	–1.34	[49]	–0.41	[36]
$S_2P(OEt)_2^-$	–1.34	[55]	–	–
Oxycarbenes (anionic) $[=C(O^-)Y]$	–1.1 to –1.7	[36]	–0.16 to –0.73	[36]
OH^-	–1.55	[10]	–0.59	[13]
Aryls, alkyls, NO^-	–1.7 to –1.9	[36]	–0.7 to –0.9	[16]
O^{2-}	–	–	–1.8	[73]

[a] Ordered generally from higher to lower P_L and/or E_L values; for multidentate ligands the values refer to each ligating arm. [b] At an electron-rich metal centre such as *trans*-$\{MX(dppe)_2\}$ (M = Re, Tc; X = Cl, H). [c] At an electron-poor metal centre such as $\{Cr(CO)_5\}$. [d] The P_L values of –1.0 and –0.74 V have been estimated at the $\{Cr(CO)_5\}$ and *trans*-$\{FeH(dppe)_2\}^+$ centres, respectively. [e] Carboxylate arm.

Isocyanides show P_L values that are spread over a wide range, from +0.2 to –0.4 V (Table 1): benzoyl isocyanide[30] > bent isocyanides[24,25,34,35] > ferricinium isocyanides[38,39] > phosphonium isocyanides[41] ≥ linear isocyanides.[24,25,34,43]

Metallo-cyanide adducts and other cyano adducts are quite sensitive to the Lewis acid but are always stronger net electron acceptors than cyanide: $CNBF_3^-$[30] ≥ $CN–NiCl_2(Pcy_3)^-$[40] > $CN–VCl_3(thf)_2^-$[30] > $CN–BPh_3^-$[46] > $CN–PdCl_2(PPh_3)^-$[40] > CN^-.[10,30]

Carbenes and related ligands are spread over an even wider window of P_L values (from 0 to –1.7 V): vinylidenes $C{=}CHR$[29,36] ≥ allenylidenes $C{=}C{=}CR_2$[36,42] > bithiophene-carbenes[44] ≥ oxocarbenes $C(OR)Y$[36] > thiocarbenes $C(SR)Y$[36] > aminocarbenes $C(NRR')$ Y,[5,36] ferrocenyl-oxocarbenes[36] ≥ phosphoylide-aminocarbenes[41] > ferrocenyl-aminocarbenes[36] > anionic oxycarbenes $C(O^-)Y$.[36]

Organonitriles (P_L from –0.23 to –0.58 V)[10,27] behave as weaker π-acceptors than analogous isocyanides, whereas cyanamides $N{\equiv}C–NR_2$ (with the electron-donor amino group)[26,47–49] and related species, such as cyanoguanidine $N{\equiv}C–NC(NH_2)_2$[50] and hydrogen dicyanamide $N{\equiv}CNHCN$,[50] are quite strong net electron-donor neutral ligands, being comparable to NCS^-[10] or CF_3COO^-.[10]

The strongest net electron-donors are the following, with P_L values below –1.0 V: aryls, alkyls and NO^-,[36] OH^-,[10] anionic oxycarbenes $[=C(O^-)Y]$,[36] hydrogen cyanamide ($NCNH^-$),[49] F^-,[54] N_3^-,[10] H^-,[10] alkynyls ($C{\equiv}CR^-$),[5,36,42,52,53] monodeprotonated cyanoguanidine $[NCNC(NH)NH_2^-]$,[50] acyl- or aroylcyanamide $[NCNC(O)R^-]$,[51] Cl^-,[10] Br^-,[10] NCO^-,[10] I^-,[10] dicyanamide ($NCNCN^-$).[50]

A *modification of a ligand* naturally leads to a change of P_L. Hence, protonation is expected to result in an increase of P_L due the promotion of the net electron acceptance (or hampering of the net electron donation), as shown in the following cases (see Table 1): protonation of vinylidenes $C{=}CHR$ to carbynes CCH_2R^+ (ΔP_L = 0.5 V),[29,36] of a bent isocyanide $C{\equiv}NR$ to an aminocarbyne $C{=}NR_2^+$ (R = H) (ΔP_L = 0.2 V),[31,36] of phosphoylide-aminocarbenes (protonation at the ylide carbon atom) (ΔP_L = 0.3 V)[41] and of indole derivatives (protonation at N) (ΔP_L = 0.5 V).[41]

Oxidation of a metallo-ligand has the same type of effect if there is electronic communication between the two metal atoms, as observed for the ferrocene–isocyanide $C{\equiv}N–Fc$[38,39] and fumaronitrile–iron $N{\equiv}CCH{=}CHC{\equiv}N-\{FeH(dppe)_2\}^+$[37] systems ($\Delta P_L \approx$ 0. 2 V).

Linkage isomerization with an ambidentate ligand can result in a high P_L variation, as in the case of dimethyl sulfoxide (DMSO) ($\Delta P_L \approx$ 1.1 V upon changing from O- to S-binding).[57]

A further important matter concerns the possibility, in some cases, of P_L *dependence on the metal centre*, which was not accounted for by the initial Pickett's model. Although such a behaviour poses difficulties to the application of this model, the recognition of the failure of Equation (2) in particular cases enables us to propose corrections to the P_L values for such cases. This has been recognized for isocyanides,[24,25,34,35] nitriles,[27] cyanamides[26,47–49] and cyanide.[30] A high electron richness of the metal centre and a strong electron release from the *trans* ligand promote the net π-electron acceptance (or hamper the net electron donation) of the ligand under study, resulting in a positive correction (up to 0.34 V) for its usual P_L value.

Hence, in such cases, P_L also conveys information on the electronic properties of the metal centre and, for isocyanides, is also diagnostic of their bent or linear geometry. For *trans*-$\{ReCl(dppe)_2\}$ (E_s = 0.68 V) or for $\{Cr(CO)_5\}$ (E_s = 1.50 V), the former with a much higher electron richness, isocyanides are bent (stronger π-acceptors, higher P_L values by ca. 0.26 V) or linear (weaker π-acceptors), respectively. For *trans*-$\{TcH(dppe)_2\}$, with a higher electron richness (E_s = 0.34 V), an even greater correction (+0.34 V)[35] is required.

2.3. E_s and β Metal-Site Parameters

The electron richness (E_s) of a metal centre $\{M_s\}$ is given, by definition [Equation (3)], as the oxidation potential of its carbonyl complex $[M_s(CO)]$. It can also be obtained, as well as the polarizability (β), from the plot of $E_{1/2}^{ox}[M_sL]$ vs. $P_L(L)$ [Equation (2)], comprising as many points as possible. Less direct methods can be applied, namely by considering an auxiliary site $\{M'_s\}$ with known E_s and β values, and comparing the oxidation potentials of $[M_sL]$ with those of homologues of the related series $[M'_sL]$ [from the intercept and the slope of Equation (13), E_s and β can be estimated for $\{M_s\}$]. Other cases have been indicated above [Equations (11) and (12)].

$$E^{ox}[M_sL] - E^{ox}[M'_sL] = (E_s\{M_s\} - E_s\{M'_s\}) + (\beta\{M_s\} - \beta\{M'_s\})\,P_L(L) \tag{13}$$

E_s and β values are known[10,24–28,34,35,41,43,56,58–61] for the following $\{M_s\}$ centres, ordered, within each group, according to decreasing E_s values: (a) 16-electron square-pyramidal ones: $\{FeL(depe)_2\}^{2+}$ (L = CO, NCR),[26] $\{W(\equiv CR)(CO)_2(dppe)\}^+$,[43] $\{M(CO)_5\}$ (M = Cr, Mo, W),[41] $\{ReL(dppe)_2\}^+$ (L = CO, N_2, CNR),[5,24,25] $\{FeX(LL)_2\}^+$ (X = Br, H; LL = depe, dppe),[27,10] $\{Mo(NO)(dppe)_2\}^+$,[10] $\{Mn(CO)(dppm)_2\}^+$,[58] $\{ReX(dppe)_2\}$ (X = CN, NCS, Cl, NCO, N_3),[34,59,60] *cis*-$\{ReCl(dppe)_2\}$,[27] $\{TcH(dppe)_2\}$,[35] $\{MoL(dppe)_2\}$ (L = CO, N_2, NCPh),[10] $\{Mo(N_3)(dppe)_2\}^-$;[10] (b) 16-electron half-sandwich ones: $\{Mo(\eta^7\text{-}C_7H_7)(LL)\}^+$ (LL = dppe, *t*Bu$_2$-diazabutadiene, bipyridine);[56,61] (c) 15-electron ones: $\{FeBr(depe)_2\}^{2+}$,[27] *cis*-$\{ReCl(dppe)_2\}^+$;[27] (d) 14-electron T-shaped one: $\{Rh(acac)(CO)\}$.[28]

The electron richness is unfavoured (increase of E_s) by the presence, within $\{M_s\}$, of ligands (e.g. carbyne or CO) with a strong π-acceptance (high P_L), by the increase of charge and by the metal oxidation state. Thus, the least electron-rich sites are the dicationic Fe^{II} centres $\{FeL(depe)_2\}^{2+}$ (L = CO, NCR) (E_s = 2.3–1.7 V vs. SCE),[26] the dicationic Fe^{III} site $\{FeBr(depe)_2\}^{2+}$ (E_s = 1.98 V vs. SCE)[27] and the cationic carbyne-carbonyl centres $\{W(\equiv CR)(CO)_2(dppe)\}^+$ (E_s = 1.7–1.6 V vs. SCE),[43] followed by the pentacarbonyls $\{M(CO)_5\}$ (M = Cr, Mo, W) (E_s = 1.50 V vs. SCE).[41]

At the other extreme, as the most electron-rich centre, lies the anionic Mo^0 site $\{Mo(N_3)(dppe)_2\}^-$ (E_s = –1.00 V vs. SCE)[10] with the strong electron-donor azide ligand, followed by the neutral $\{MoL(dppe)_2\}$ (L = NCPh, N_2, CO) sites, all with negative E_s values.

Interestingly, the polarizability (β) of the metal centre also tends to decrease (as does the electron richness) with the increase of the net π-electron acceptor ability of a ligand (increase of P_L) comprised in $\{M_s\}$, as observed for a series of related centres such as *trans*-$\{M(L)(dppe)_2\}^+$ (M = Tc,[35] L = H; M = Re;[5,24,25,34,59,60] L = Cl^-, CN^-, CNR, CO). In accord, $\{Mo(NO)(dppe)_2\}^+$ and $\{W(\equiv CR)(CO)_2(dppe)_2\}$, with the very strong π-acceptors NO^+ and carbyne/CO ligands, are the centres with the lowest β values (0.51[10] and 0.61–0.73,[43] respectively). The delocalization of the HOMO towards the strong π-acceptor ligands in $\{M_s\}$, as shown by MO calculations in the W–carbyne case,[43] leads to an attenuation effect (energy "buffering", low β) on the changes of the HOMO energy upon change of another ligand (L) bound to the centre in the complex $[M_sL]$.

3. Full Additivity Lever's Model

3.1. General

In this model, the additivity is extended to all the ligands, and the redox potential of a complex with the $M^{n+1/n}$ redox couple is given by Equation (14) in V vs. NHE, where S_M (slope) and I_M (intercept) depend on the metal and redox couple, the spin state and the stereochemistry, and E_L is an additive ligand parameter that was obtained through a statistical analysis on the known redox potentials of the high number of complexes with the $Ru^{III/II}$ redox couple.[13–16]

$$E_{1/2}[M^{n+1/n}] = S_M(\Sigma E_L) + I_M \quad / \text{ V } vs. \text{ NHE} \tag{14}$$

On account of its wide scope of application, simple use and availability of data, Lever's model became the most popular one and has been reviewed.[13–16] However, its high generality is concomitant with the risk of failure for particular cases, and for strong π-acceptor ligands, e.g. CO, carbynes and isocyanides. Equation (14) requires the use of empirical terms that reflect additional HOMO stabilization effects. Corrections have also been introduced[13] to account for isomeric effects.

The attenuation of the CO ligand additivity effect, also in agreement with electronic spectroscopic and X-ray data, has been recognized[62] for the $Os^{IV/III}$ and $Os^{III/II}$ redox potentials in a series of hexacoordinate mixed halide/carbonyl and halide/carbonyl/nitrile complexes, i.e. the shift of the redox potential upon the first replacement of a halide or a nitrile by a CO ligand is much more pronounced (ca. two to three times) than the shift resulting from the second replacement. Similar nonlinear trends are exhibited by related (isocyanido)Os complexes,[62] although a roughly constant potential shift is observed per each halide replacement by nitrile either in the Os series[62] or in the Ru analogues.[63]

Hence, the mutual influence of the strong π-accepting CO or isocyanido ligands, in such series, leads to an attenuation of the corresponding ligand additivity effects.

The deviation from linearity [Equation (14)] for a wide range of ΣE_L, as observed for the $Re^{I/II}$ redox system,[14] can be overcome by the consideration of either different expressions along the ΣE_L scale or of a curved relationship, the latter is supported by some studies on a series of Re^I–vinylidene or –nitrile[27] complexes.

Although typically applied only to hexacoordinate complexes, the model has been recently extended by the current author to square-planar tetracoordinate[28,64] and pentacoordinate[28] $Rh^{I/II}$ complexes; the former has also been studied by others[65] although with a smaller number of compounds. Extensions to particular Ru clusters,[66–68] sandwich and half-sandwich complexes,[15,16,69] and to reduction processes centred at ligands[15,16] have also been proposed.

3.2. E_L Ligand Parameter and Associated Ones

The ligand E_L parameter depends on the reference electrode (it has been referenced to the NHE), in contrast with the P_L parameter, but both are related by the experimentally observed Equation (15), which, however, fails for strong π-acceptor ligands (see above) when the Lever Equation (14) also requires corrections. Hence, for such ligands, Equation (15) has to be used cautiously for the estimate of the value of one of the parameters from that of the other one. Recognized examples of failure of Equation (15) include, apart from CO, carbynes and bent isocyanides, as well as a number of metallo-cyanide and other cyano adducts e.g. $C{\equiv}N{-}A^-$ [A = BF_3,[30] BPh_3,[30] ML_{n-1} (M = V^{III}, Re^V, Ni^{II}, Pd^{II})[30,40]]. Nevertheless, Equation (15) is valid for allenylidenes and alkynyls.[28,36,42]

$$P_L = 1.17\,E_L - 0.86 \tag{15}$$

E_L values are already known for a wide variety of ligands,[13–16,28–30,36,41,57,64,70–75] including an extensive list of recently estimated values by the current author[36] for many carbyne, carbene, vinylidene, allenylidene and alkynyl ligands. Examples are given in Table 1.

S_M and I_M values (listed in refs.[13–16,36,56]) have already been proposed for the following $M^{n+1/n}$ redox couples: M = Nb (n = 3, 4),[13] Ta (n = 4),[13] Cr (n = 0, 2),[13] Mo (n = 0, 1),[13] Tc (n = 1–3),[14] Re (n = 1–3),[14] Fe (n = 2, 3),[13,26,27] Ru (n = 2, 3),[13,71] Os (n = 2)[13] and Rh (n = 1).[28,64] Normally, the redox centres are six-coordinate, with the exception of the four- and five-coordinate $Rh^{II/I}$,[28,64] and in particular the five-coordinate $Fe^{III/II}$[13] and $Mn^{II/III}$[13] cases. The parameters usually have been obtained in organic media, but different values are observed in water where solvation effects and the complex charge can play a relevant role, as observed for $Cr^{III/II}$,[13] $Fe^{III/II}$,[13] $Ru^{III/II}$ (2+/1+),[13] $Ru^{III/II}$ (1–/2–)[71,75] and $Os^{III/II}$[13] systems. The charge effect has been studied[75] particularly for the $Ru^{III/II}$ system.

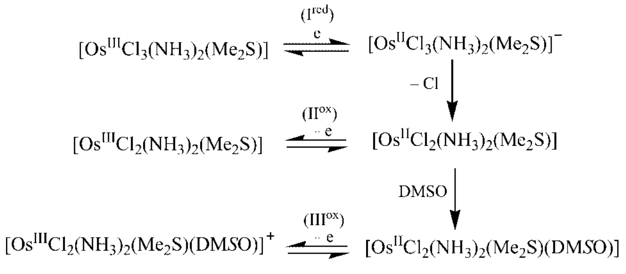
Moreover, particular sets of S_M and I_M values, different from the general ones but that better fit an expression of the type (14), have been proposed[26,27] for certain series of complexes.

4. Identification of Coordination Compounds

The relationships discussed above [in particular (2) and (14)] between the redox potential of a complex and the electrochemical ligand and metal centre parameters can be used not only to estimate (from the measured redox potential) these parameters that characterize the components of the complex, as discussed above, but also conversely to predict the redox potential of any complex, provided the values of those parameters are known. This latter approach has been much less explored but its significance towards the identification of coordination compounds is rather valuable. It can assist in the identification not only of isolated complexes but also of those generated in situ in a reaction process. This can be conveniently done by cyclic voltammetry, an expedient and rapid method to search for redox waves and measure their potentials, provided these lie within the available solvent/electrolyte potential range and the species have a sufficient lifetime for the wave detection. The redox waves should also be reversible, at least partially, since irreversible processes can lead to considerable shifts in the redox potential.

The identification of the new species generated upon an electron-transfer induced chemical reaction greatly contributes to the understanding of the redox process whose mechanism, in some cases, has been established by digital simulation of the cyclic voltammograms. This is illustrated by the following cases investigated in the author's laboratory.

The trichloro-Os^{III} complex *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ undergoes, by cyclic voltamemtry in DMSO, a single-electron partially reversible reduction wave (I^{red}, Figure 1), which involves heterolytic Os–Cl bond rupture with loss of Cl^- followed by its replacement by DMSO to afford the *S*-coordinated complex $[Os^{II}Cl_2(NH_3)(Me_2S)(DMSO)]$ (Scheme 1).[57] This product as well as an intermediate species that was postulated as the pentacoordinate complex $[OsCl_2(NH_3)_2(Me_2S)]$ were detected by their oxidation waves (II^{ox} and III^{ox}, respectively, Figure 1) upon scan reversal following the reduction wave (I^{red}) of the starting complex.[57] The identification of the product was based on the very close agreement between the measured value of its oxidation potential (III^{ox}) and the predicted one by applying Lever's Equation (14).[57]



Scheme 1.

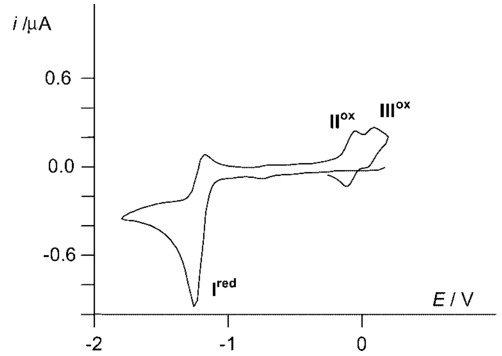
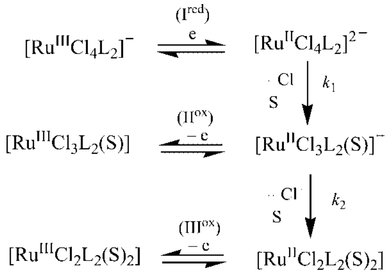


Figure 1. Cyclic voltammogram of *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ in DMSO with 0.2 M $[Bu_4N][BF_4]$ at a Pt electrode (scan rate: 0.2 V s^{-1}).[57]

Other recent examples concern various series of chlorido/azole–ruthenium(III) complexes with antitumor activity, such as $[RuCl_4L_2]^-$[71,75] (L = imidazole, benzimidazole, triazole, pyrazole, indazole or a substituted derivative), $[RuCl_3L_3]$[75] or $[RuCl_2L_4]^+$.[75] They exhibit a single electron reduction (wave I^{red}) to the corresponding Ru^{II} complexes, which then readily undergo sequential dechlorination steps upon solvolysis [S = dimethylformamide (DMF) or DMSO] (Scheme 2 for $[RuCl_4L_2]^-$).



Scheme 2.

The partially dechlorinated/solvated Ru^{II} products, such as $[RuCl_3L_2(S)]^-$ and $[RuCl_2L_2(S)_2]$ derived from $[RuCl_4L_2]^-$, were detected in situ by the appearance of their Ru^{II}/Ru^{III} oxidation waves (II^{ox} and III^{ox}, respectively) and identified by the similarity of the corresponding measured oxidation potential values with those predicted by using Lever's Equation (14). A similar behaviour was observed for the other series of azole complexes.

The mechanisms of the processes were investigated in detail by digital simulation of cyclic voltammetry,[71,75] allowing us to estimate the kinetic rate constant of solvolysis upon reduction (k_1 and k_2), which interestingly were shown to correlate with the redox potential[71,75] (thus, with the azole E_L parameter) and with the anti-tumor activity.[76,77]

5. Final Comments

The redox potential of a coordination compound bears rich structural/electronic information, which has started to be explored, in a systematic way, by ligand and metal parameterizations that constitute the bases of simple additive models. The electron donor/acceptor properties of the ligands and binding metal centres can thus be quantified through the values of associated electrochemical parameters, which, conversely, once known, can be used to predict the redox potentials of their complexes.

The latter approach (the estimate of the redox potential) can provide an important contribution towards the identification of unknown complexes by comparing the predicted and the experimentally measured values of the redox potential. The complexes, products or intermediates in reactions, can thus be identified in situ, without the need for their isolation from the solution, lowering the risks of their loss upon further reaction or decomposition.

Another important perspective concerns the possibility of correlating not only the redox potential but also, in a more perceivable way, the above electrochemical ligand (and/or metal site) parameters, with a variety of other properties of the complexes that are also determined by electronic and structural features,[5,6,15,16,69,78] such as ligand IR stretching frequencies,[74] energy of MLCT bands,[16] Hammett's σ-substituent constants and related ones,[69,79,80] Tolman's electronic parameter[81] or metal–metal interaction in ligand-bridged dinuclear complexes. Some of those correlations can allow the estimate of E_L or P_L for further ligands.

Ligand coordination[10,11,34,57] and chemical reactivity[10,37,82–85] criteria have also been proposed in a few cases. A different type of relationship, between the azole E_L ligand parameter and the anticancer activity, has recently been recognized[76,77] for some ruthenium complexes.

However, one should be aware of the model's limitation, associated with the additivity assumption that does not take into account interactions and synergisms. Pickett's model, in its initial form, bears the minimum additivity (only the effect of a single ligand is separated from all the others, taken as a whole) and is expected to be more accurate for particular sets of complexes but has the lowest generality, while Lever's model assumes a full additivity and is more general but has a higher risk of failure in particular cases. These include isomeric effects that require the consideration of corrective terms in Lever's equation,[14] whereas they can be handled by Pickett's model by considering distinct (E_s, β) sets of values for the different isomers.[27,34] The isomeric dependence of the redox potential is particularly relevant in accounting for the type of mechanism of electron-transfer-induced isomerizations in coordination compounds.[86–89]

Another frequent limitation results from the small number of available data (in some cases limited to a single complex) used to estimate the ligand or metal parameters. Many more complexes have to be studied and the values of these parameters averaged.

Although extensions of the initial models have already been proposed, they have still to be further applied to other types of complexes with different metals and ligands, electron counts, geometries, etc. The results so far achieved, as illustrated above, are promising and the field hopefully will attract wider attention.

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[1] A. J. L. Pombeiro, C. Amatore (Eds.), *Trends in Molecular Electrochemistry*, Marcel Dekker/FontisMedia, New York/Lausanne, **2004**.
[2] A. J. L. Pombeiro, J. McCleverty (Eds.), *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*, NATO ASI Series, Kluwer, Dordrecht, **1993**.
[3] P. Zanello, *Inorganic Electrochemistry: Theory, Practice and Application*, Royal Society of Chemistry, Cambridge, **2003**.
[4] D. Astruc, *Electron Transfer and Radical Processes in Transition-metal Chemistry*, VCH, New York, **1995**.
[5] A. J. L. Pombeiro, *New J. Chem.* **1997**, *21*, 649.
[6] A. J. L. Pombeiro, *Port. Electrochim. Acta* **1983**, *1*, 19.
[7] A. Vlcëk, *Chemtracts – Inorg. Chem.* **1993**, *5*, 1.
[8] A. C. Sarapu, R. F. Fenske, *Inorg. Chem.* **1975**, *14*, 247.
[9] C. J. Pickett, D. Pletcher, *J. Organomet. Chem.* **1975**, *102*, 327.
[10] J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett, D. R. Stanley, *J. Chem. Soc., Dalton Trans.* **1980**, 2032.
[11] J. Chatt, *Coord. Chem. Rev.* **1982**, *43*, 337.
[12] C. J. Pickett, in: G. Wilkinson, R. D. Gillard, J. A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, **1987**, vol. 1, chapter 8.3, p. 493.
[13] A. B. P. Lever, *Inorg. Chem.* **1990**, *29*, 1271.
[14] A. B. P. Lever, *Inorg. Chem.* **1991**, *30*, 1980.
[15] A. B. P. Lever, E. S. Dodsworth, *Inorganic Electronic Structure and Spectroscopy*, Wiley, New York, **1999**, vol. 2, p. 227.
[16] A. B. P. Lever, in: *Comprehensive Coordination Chemistry II*, vol. 2 (Ed.: A. B. P. Lever), Elsevier, Oxford, **2004**, chapter 2.19, p. 251.
[17] B. E. Bursten, *J. Am. Chem. Soc.* **1982**, *104*, 1299.
[18] B. E. Bursten, M. R. Green, *Prog. Inorg. Chem.* **1988**, *36*, 393.
[19] B. E. Bursten, M. R. Green, V. Katovic, D. Lightner Jr, *Inorg. Chem.* **1986**, *25*, 831.
[20] D. Datta, *J. Chem. Soc., Dalton Trans.* **1986**, 1907.
[21] A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, 2nd ed., Wiley, New York, **2001**.
[22] A. J. L. Pombeiro, M. F. C. Guedes da Silva, M. A. N. D. A. Lemos, *Coord. Chem. Rev.* **2001**, *53*, 219.
[23] A. J. L. Pombeiro, *Port. Electrochim. Acta* **1985**, *3*, 41.
[24] M. F. N. N. Carvalho, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **1989**, 1209.
[25] A. J. L. Pombeiro, *Inorg. Chim. Acta* **1985**, *103*, 95.
[26] L. M. D. R. S. Martins, A. J. L. Pombeiro, *Port. Electrochim. Acta* **1996**, *14*, 151.
[27] M. F. C. Guedes da Silva, L. M. D. R. S. Martins, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Collect. Czech. Chem. Commun.* **2001**, *66*, 139.
[28] M. F. C. Guedes da Silva, A. M. Trzeciak, J. J. Ziólkowski, A. J. L. Pombeiro, *J. Organomet. Chem.* **2001**, *620*, 174.
[29] S. S. P. R. Almeida, A. J. L. Pombeiro, *Organometallics* **1997**, *16*, 4469.
[30] S. S. P. R. Almeida, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Port. Electrochim. Acta* **2001**, *19*, 371.
[31] M. A. N. D. A. Lemos, A. J. L. Pombeiro, *J. Organomet. Chem.* **1988**, *356*, C79.
[32] C. J. Pickett, in *Electrochemistry* (Ed.: D. Pletcher), Royal Society of Chemistry, Cambridge, **1983**, vol. 8, p. 81.
[33] M. F. Meidine, M. A. N. D. A. Lemos, A. J. L. Pombeiro, J. F. Nixon, P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.* **1998**, 3319.
[34] A. J. L. Pombeiro, C. J. Pickett, R. L. Richards, *J. Organomet. Chem.* **1982**, *224*, 285.
[35] Y. Wang, A. J. L. Pombeiro, L. Kaden, M. Wahren in ref.[2], p. 63.
[36] A. J. L. Pombeiro, *J. Organomet. Chem.* **2005**, *690*, 6021.
[37] A. I. F. Venâncio, M. L. Kuznetsov, M. F. C. Guedes da Silva, L. M. D. R. S. Martins, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Inorg. Chem.* **2002**, *41*, 6456.
[38] T. El-Shihi, F. Siglmüller, R. Herrman, M. F. N. N. Carvalho, A. J. L. Pombeiro, *J. Organomet. Chem.* **1987**, *335*, 239.
[39] T. El-Shihi, F. Siglmüller, R. Herrman, M. F. N. N. Carvalho, A. J. L. Pombeiro, *Port. Electrochim. Acta* **1987**, *5*, 179.
[40] S. S. P. R. Almeida, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Collect. Czech. Chem. Commun.* **2003**, *68*, 1663.
[41] G. Facchin, M. Mozzon, R. A. Michelin, M. T. A. Ribeiro, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **1992**, 2827.
[42] A. I. F. Venâncio, M. F. C. Guedes da Silva, L. M. D. R. S. Martins, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Organometallics* **2005**, *24*, 4654.
[43] L. Zhang, M. F. C. Guedes da Silva, M. L. Kuznetsov, M. P. Gamasa, J. Gimeno, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Organometallics* **2001**, *20*, 2782.
[44] A. Limberg, M. A. N. D. A. Lemos, A. J. L. Pombeiro, S. Maiorana, A. Papagni, E. Licandro, *Port. Electrochim. Acta* **1995**, *13*, 319.
[45] A. J. L. Pombeiro, M. T. A. R. S. Costa, Y. Wang, J. F. Nixon, *J. Chem. Soc., Dalton Trans.* **1999**, 3755.
[46] S. S. P. R. Almeida, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **1999**, 467.
[47] S. M. P. R. M. Cunha, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Port. Electrochim. Acta* **1999**, *17*, 221.
[48] L. M. D. Ribeiro, A. J. L. Pombeiro, *Port. Electrochim. Acta* **1995**, *13*, 329.
[49] M. F. N. N. Carvalho, A. J. L. Pombeiro, *J. Organomet. Chem.* **1991**, *410*, 347.
[50] M. F. N. N. Carvalho, A. J. L. Pombeiro, A. Hills, D. L. Hughes, R. L. Richards, *J. Organomet. Chem* **1993**, *469*, 179.
[51] E. C. B. A. Alegria, S. M. P. R. M. Cunha, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Port. Electrochim. Acta* **2004**, *22*, 19.
[52] A. I. F. Venâncio, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Port. Electrochim. Acta* **2003**, *21*, 85.
[53] A. Hills, D. L. Hughes, N. Kashef, M. A. N. D. A. Lemos, A. J. L. Pombeiro, R. L. Richards, *J. Chem. Soc., Dalton Trans.* **1992**, 1775.
[54] M. F. N. N. Carvalho, M. T. Duarte, A. M. Galvão, A. J. L. Pombeiro, *J. Organomet. Chem.* **1994**, *469*, 79.
[55] L. Zhang, M. P. Gamasa, J. Gimeno, M. F. C. Guedes da Silva, A. J. L. Pombeiro, C. Graiff, M. Lanfranchi, A. Tiripicchio, *Eur. J. Inorg. Chem.* **2000**, 1707.
[56] A. J. L. Pombeiro, in: *Inorganic Electrochemistry* (Eds.: F. Scholz, C. J. Pickett), *Encyclopedia of Electrochemistry*, Wiley-VCH, Weinheim, **2006**, vol. 7A, p.77.
[57] M. F. C. Guedes da Silva, A. J. L. Pombeiro, S. Geremia, E. Zangrando, M. Calligaris, A. V. Zinchenko, V. Yu. Kukushin, *J. Chem. Soc., Dalton Trans.* **2000**, 1363.
[58] G. A. Carriedo, V. Riera, N. G. Connelly, S. J. Raven, *J. Chem. Soc., Dalton Trans.* **1987**, 1769.
[59] M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, M. A. Pellinghelli, A. Tiripicchio, *J. Chem. Soc., Dalton Trans.* **1996**, 2763.
[60] Y. Wang, A. J. L. Pombeiro, *Port. Electrochim. Acta* **1993**, *11*, 111.
[61] S. P. M. Disley, R. W. Grime, E. J. L. McInnes, D. M. Spencer, N. Swainston, M. W. Whiteley, *J. Organomet. Chem.* **1998**, *566*, 151.
[62] G. A. Heath, D. G. Humphrey, *J. Chem. Soc., Chem. Commun.* **1991**, 1668.
[63] C. M. Duff, G. A. Health, *J. Chem. Soc., Dalton Trans.* **1991**, 2401.

[64] A. M. Trzeciak, B. Borak, Z. Ciunik, J. J. Ziólkowski, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* **2004**, 1411.
[65] I. Kovacik, O. Gevert, H. Werner, M. Schmittel, R. Söllner, *Inorg. Chim. Acta* **1998**, *275–276*, 435.
[66] H. E. Toma, K. Araki, A. D. P. Alexiou, S. Nikolaou, S. Dovidauskas, *Coord. Chem. Rev.* **2001**, *219*, 187.
[67] D. J. Bierdeman, J. B. Keister, D. A. Jelski, *J. Organomet. Chem.* **2001**, *633*, 51.
[68] W. G. Feighery, H. Yao, A. F. Hollenkamp, R. D. Allendoerfer, J. B. Keister, *Organometallics* **1998**, *17*, 872.
[69] S. Lu, V. V. Strelets, M. F. Ryan, W. J. Pietro, A. B. P. Lever, *Inorg. Chem.* **1996**, *35*, 1013.
[70] For a list of values of Lever's electrochemical parameters see his website: http://www.chem.yorku.ca/profs/lever
[71] E. Reisner, V. B. Arion, M. F. C. Guedes da Silva, R. Lichtenecker, A. Eichinger, B. K. Keppler, V. Yu. Kukushkin, A. J. L. Pombeiro, *Inorg. Chem.* **2004**, *43*, 7083.
[72] E. C. B. Alegria, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *J. Organomet. Chem.* **2005**, *690*, 1947.
[73] E. C. B. Alegria, L. M. D. R. S. Martins, M. Haukka, A. J. L. Pombeiro, *Dalton Trans.* **2006**, 4954.
[74] A. M. Kirillov, M. Haukka, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *J. Organomet. Chem.* **2006**, *691*, 4153.
[75] E. Reisner, V. B. Arion, A. Eichinger, N. Kandler, G. Geister, A. J. L. Pombeiro, B. K. Keppler, *Inorg. Chem.* **2005**, *44*, 6704.
[76] E. Reisner, V. B. Arion, C. G. Hartinger, M. A. Jakupec, A. J. L. Pombeiro, B. K. Keppler in *Education in Advanced Chemistry Vol. 9: Perspectives of Coordination Chemistry* (Ed.: A. Trzeciak), Poznan-Wroclaw, **2005**, p. 215.
[77] E. Reisner, V. B. Arion, B. K. Keppler, A. J. L. Pombeiro, V. Yu. Kukushkin, *J. Russ. Chem. Soc.* **2004**, *48*, 137.
[78] M. Masui, A. B. P. Lever, *Inorg. Chem.* **1993**, *32*, 2199.
[79] M. E. N. P. R. A. Silva, A. J. L. Pombeiro, J. J. R. Fraústo da Silva, R. Herrmann, M. Deus, R. E. Bozak, *J. Organomet. Chem.* **1994**, *480*, 81.
[80] M. E. N. P. R. A. Silva, A. J. L. Pombeiro, J. J. R. Fraústo da Silva, R. Herrmann, N. Deus, T. J. Castilho, M. F. C. Guedes da Silva, *J. Organomet. Chem.* **1991**, *421*, 75.
[81] L. Perrin, E. Clot, O. Eisenstein, J. Loch, R. H. Crabtree, *Inorg. Chem.* **2001**, *40*, 5806.
[82] J. Chatt, G. J. Leigh, H. Neukomm, C. J. Pickett, *J. Chem. Soc., Dalton Trans.* **1980**, 121.
[83] G. J. Leigh, R. H. Morris, C. J. Pickett, D. R. Stanley, *J. Chem. Soc., Dalton Trans.* **1981**, 300.
[84] A. J. L. Pombeiro, *Rev. Port. Quím.* **1981**, *23*, 179.
[85] M. A. N. D. A. Lemos, A. J. L. Pombeiro, *J. Organomet. Chem.* **1992**, *438*, 159.
[86] A. J. L. Pombeiro, M. F. C. Guedes da Silva, M. A. N. D. A. Lemos, *Coord. Chem. Rev.* **2001**, *219–221*, 53.
[87] M. F. C. Guedes da Silva, C. M. P. Ferreira, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **1998**, 4139.
[88] M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, C. Amatore, J.-N. Verpeaux, *Inorg. Chem.* **1998**, *37*, 2344.
[89] M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, C. Amatore, J.-N. Verpeaux, *Organometallics* **1994**, *13*, 3943.

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