REDOX POTENTIAL - (ELECTRONIC) STRUCTURE RELATIONSHIPS IN 18- AND 17-ELECTRON MONONITRILE (OR MONOCARBONYL) DIPHOSPHINE COMPLEXES OF Re AND Fe

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Dedicated to the memory of Professor Antonín A. Vlček.

The organonitrile or carbonyl complexes *cis*-[ReCl(RCN)(dppe)$_2$] (**1**) (R = 4-Et$_2$NC$_6$H$_4$ (**1a**), 4-MeOC$_6$H$_4$ (**1b**), 4-MeC$_6$H$_4$ (**1c**), C$_6$H$_5$ (**1d**), 4-FC$_6$H$_4$ (**1e**), 4-ClC$_6$H$_4$ (**1f**), 4-O$_2$NC$_6$H$_4$ (**1g**), 4-ClC$_6$H$_4$CH$_2$ (**1h**), *t*-Bu (**1i**); dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), or *cis*-[ReCl(CO)(dppe)$_2$] (**2**), as well as *trans*-[FeBr(RCN)(depe)$_2$]BF$_4$ (**3**) (R = 4-MeOC$_6$H$_4$ (**3a**), 4-MeC$_6$H$_4$ (**3b**), C$_6$H$_5$ (**3c**), 4-FC$_6$H$_4$ (**3d**), 4-O$_2$NC$_6$H$_4$ (**3e**), Me (**3f**), Et (**3g**), 4-MeOC$_6$H$_4$CH$_2$ (**3h**); depe = Et$_2$PCH$_2$CH$_2$PEt$_2$), novel *trans*-[FeBr(CO)(depe)$_2$]BF$_4$ (**4**) and *trans*-[FeBr$_2$(depe)$_2$] (**5**) undergo, as revealed by cyclic voltammetry at a Pt-electrode and in aprotic non-aqueous medium, two consecutive reversible or partly reversible one-electron oxidations assigned as Re^I → Re^{II} → Re^{III} or Fe^{II} → Fe^{III} → Fe^{IV}. The corresponding values of the oxidation potentials $^IE_{1/2}^{ox}$ and $^{II}E_{1/2}^{ox}$ (waves I and II, respectively) correlate with the Pickett's and Lever's electrochemical ligand and metal site parameters. This allows to estimate these parameters for the various nitrile ligands, depe and binding sites (for the first time for a Fe$^{III/IV}$ couple). The electrochemical ligand parameter show dependence on the "electron-richness" of the metal centre. The values of $^IE_{1/2}^{ox}$ for the Re^I complexes provide some supporting for a curved overall relationship with the sum of Lever's electrochemical ligand parameter. The Pickett parametrization for closed-shell complexes is extended now also to 17-electron complexes, *i.e.* with the 15-electron Re^{II} and Fe^{III} centres in *cis*-{[ReCl(dppe)$_2$]}$^+$ and *trans*-{FeBr(depe)$_2$}$^{2+}$, respectively.
Keywords: Electrochemistry; Redox potential; Nitrile complexes; Carbonyl complexes; Rhenium; Iron; Cyclic voltammetry.

The possibility to correlate redox potentials with other molecular properties of coordination compounds has long time been a matter of interest[1]; in particular, the investigation of their dependence on electronic properties of ligands and metal centres has been the object of increasing attention[2–35].

Hence, a systematic approach to express quantitatively the relation between the redox potential and the electronic properties was presented by Pickett *et al.*[3] who, based on the experimentally observed linear relationships between the oxidation potentials of members of a series of closed-shell octahedral-type complexes $[M_SL]$ (with a variable L ligand binding the 16-electron M_S metal site) and the oxidation potentials of the homologous $[Cr(CO)_5L]$ complexes, proposed the expressions (*1*) and (*2*).

$$E^{ox}[M_SL] = E_S\{M_S\} + \beta\{M_S\}\, P_L \qquad (1)$$

$$E_S = E^{ox}[M_S(CO)] \qquad (2)$$

Equation (*1*) relates the oxidation potential of a member of the $[M_SL]$ series with the electrochemical ligand parameter P_L which is a measure of the net π-electron acceptor minus σ-donor character of the ligand[3]. The parameters E_S and β are associated to the binding metal centre M_S; the former is a measure of its electron-rich nature and is given (Eq. (*2*)) by the oxidation potential of the carbonyl complex $[M_S(CO)]$ (the higher E_S the lower the "electron-richness" of the metal), whereas β is a measure of the polarizability of the metal site[3].

Another electrochemical parametrization approach was developed by Lever[7,8] who proposed a general redox potential–structure relationship expressed by Eq. (*3*) in which the redox potential of a complex (expressed in V *vs* NHE) is related to electrochemical parameters determined by ligand and metal centre properties. Hence, ΣE_L is the sum of the values of the electrochemical ligand parameter E_L for all the ligands (additive effects), whereas S_M and I_M depend upon the metal and redox couple, the spin state and stereochemistry

$$E = I_M + S_M\,(\Sigma E_L) \qquad \text{(V *vs* NHE)} \qquad (3)$$

The Pickett's approach has been applied to various series of 18-electron octahedral complexes, usually of the type $[M_SL]$ (refs[3,12,15,17–21,23–33]) mentioned above, but scant applications have been reported for types $[M'_sL_2]$ (ref.[13]), $[M'_sLL']$ (ref.[16]) and $[M''_sL_3]$ (ref.[14]). Recently, it has been extended[34] to square-pyramidal 18-electron and square-planar 16-electron d^8 metal

complexes. Further extensions to other types of complexes, in particular paramagnetic ones, have not yet been proposed. However, since for the sets of the d^6 Re(I) and Fe(II) complexes in this study we observed two consecutive oxidation processes ($d^6 \rightarrow d^5 \rightarrow d^4$), they are in particular promising for such a purpose. Moreover, the iron set also provides an opportunity to attempt the application, for the first time, of the Lever's correlation to an Fe(III)/Fe(IV) redox couple.

EXPERIMENTAL

All manipulations and reactions were carried out under anaerobic conditions using standard inert-gas flow and vacuum techniques. Solvents were purified by standard procedures, and the complexes *cis*-[ReCl(L)(dppe)$_2$] (L = RCN (**1**) (refs[23,24]), CO (**2**) (ref.[30])), *trans*-[ReCl(RCN)(dppe)$_2$] (R = 4-Et$_2$NC$_6$H$_4$, 4-MeC$_6$H$_4$ (refs[24,35])), *trans*-[FeBr(L)(depe)$_2$]BF$_4$ (L = RCN (**3**) (ref.[36])) and *trans*-[FeBr$_2$(depe)$_2$] (**5**) (ref.[37]) were prepared by published methods.

The novel complex *trans*-[FeBr(CO)(depe)$_2$]BF$_4$ (**4**) was obtained as follows: *trans*-[FeBr$_2$(depe)$_2$] (0.21 g, 0.33 mmol) was dissolved in MeOH (50 cm^3) and CO was bubbled for *ca* 10 min. The solution was stirred at room temperature for 1 h, followed by addition of Bu$_4$NBF$_4$ (0.11 g, 0.34 mmol) in methanol (2 cm^3). Cooling to *ca* –18 °C led to precipitation of **4** as a yellow solid which was filtered off, washed with MeOH–Et$_2$O (1 : 8) and dried *in vacuo* (*ca* 0.050 g, 33% yield). IR: ν (C≡O) 1 920 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.48 (sextet 1 : 3 : 4 : 4 : 3 : 1, resulting from the overlap of a doublet ^2J(HP$_A$) = 15.6 Hz, of doublets, ^3J(HP$_B$) = 7.8 Hz, of triplets, ^3J(HH) = 7.8 Hz, 4 H, 1/2 PCH$_2$); 2.02 (m, 4 H, 1/2 PCH$_2$); 1.88 (sextet 1 : 3 : 4 : 4 : 3 : 1 resulting from the overlap of a doublet ^2J(HP) = 15.2 Hz, of quartets, ^3J(HH) = 7.1 Hz, 8 H, 1/2(CH$_3$CH$_2$)$_2$P); 1.73 (sextet 1 : 3 : 4 : 4 : 3 : 1 resulting from the overlap of a doublet ^2J(HP) = 15.2 Hz, of quartets ^3J(HH) = 7.1 Hz, 8 H, 1/2 (CH$_3$CH$_2$)$_2$P); 1.20 (m, 24 H, (CH$_3$CH$_2$)$_2$P). ^{31}P{^{1}H} NMR (CDCl$_3$): δ –77.80 (s). For C$_{21}$H$_{48}$BBrF$_4$FeOP$_4$ (663.1) calculated: 38.0% C, 7.3% H; found: 37.8% C, 7.4% H.

The electrochemical experiments were performed either on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface, or on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PAR 175 universal programmer connected to a Nicolet-310 Digital Oscilloscope.

Cyclic voltammograms were obtained in 0.2 M Bu$_4$NBF$_4$ in CH$_2$Cl$_2$ or THF, at a platinum disc working electrode (0.5 or 1.0 mm diameter) whose potential was controlled *vs* a Luggin capillary connected to a silver wire pseudoreference electrode; a Pt auxiliary electrode was employed.

Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The two compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. A Luggin capillary connected to a silver wire pseudoreference electrode was used to control the working electrode potential. The CPE experiments were monitored regularly by cyclic voltammetry (CV), thus assuring that no significant potential drift occurred along the electrolyses.

The oxidation potentials of the complexes were measured by CV (see above) in the presence of *trans*-[ReCl(dppe)$_2$(N$_2$)] or of ferrocene as the internal standard, and the redox potential values are initially quoted relative to the SCE by using the *trans*-[ReCl(N$_2$)(dppe)$_2$]$^{0/+}$ ($E^{ox}_{1/2}$ = 0.28 V *vs* SCE) or [Fe(η^5–C$_5$H$_5$)$_2$]$^{0/+}$ ($E^{ox}_{1/2}$ = 0.55 V *vs* SCE) redox couples in 0.2 M Bu$_4$NBF$_4$ in THF and CH$_2$Cl$_2$, respectively. The conversion to the NHE was done by addition of 0.24(5) V (ref.[27]) to the values quoted relative to SCE. The use, as reference, of an electrode in aqueous medium was avoided due to the sensitivity of the complexes to water.

RESULTS AND DISCUSSION

The organonitrile Re(I) complexes *cis*-[ReCl(RCN)(dppe)$_2$] (**1**) (R = 4-Et$_2$NC$_6$H$_4$ (**1a**), 4-MeOC$_6$H$_4$ (**1b**), 4-MeC$_6$H$_4$ (**1c**), C$_6$H$_5$ (**1d**), 4-FC$_6$H$_4$ (**1e**), 4-ClC$_6$H$_4$ (**1f**), 4-O$_2$NC$_6$H$_4$ (**1g**), 4-ClC$_6$H$_4$CH$_2$ (**1h**), *t*-Bu (**1i**); dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and their carbonyl analogue *cis*-[ReCl(CO)(dppe)$_2$] (**2**) as well as the related Fe(II) complexes *trans*-[FeBr(RCN)(depe)$_2$]BF$_4$ (**3**) (R = 4-MeOC$_6$H$_4$ (**3a**), 4-MeC$_6$H$_4$ (**3b**), C$_6$H$_5$ (**3c**), 4-FC$_6$H$_4$ (**3d**), 4-O$_2$NC$_6$H$_4$ (**3e**), Me (**3f**), Et (**3g**), 4-MeOC$_6$H$_4$CH$_2$ (**3h**); depe = Et$_2$PCH$_2$CH$_2$PEt$_2$), *trans*-[FeBr(CO)(depe)$_2$]BF$_4$ (**4**) and *trans*-[FeBr$_2$(depe)$_2$] (**5**) in non-aqueous aprotic medium, 0.2 M Bu$_4$NBF$_4$ in THF (or CH$_2$Cl$_2$), at a Pt electrode, exhibit two consecutive one-electron reversible or partially reversible oxidation waves (I and II) assigned to sequential Re^I → Re^{II} → Re^{III} or Fe^{II} → Fe^{III} → Fe^{IV} oxidations. Full reversibility was hampered in the cases of complexes **1** (ref.[28]) and **2** (ref.[30]) by their anodically-induced *cis–trans* isomerization which, however, at low temperature (–20 °C or below), was

1, L = RCN
2, L = CO

3, L = RCN
4, L = CO

BF$_4^{\ominus}$

5
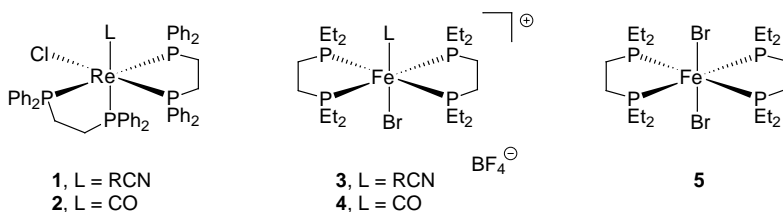
1	R	**3**	R
a	4-Et$_2$NC$_6$H$_4$	a	4-MeOC$_6$H$_4$
b	4-MeOC$_6$H$_4$	b	4-MeC$_6$H$_4$
c	4-MeC$_6$H$_4$	c	C$_6$H$_5$
d	C$_6$H$_5$	d	4-FC$_6$H$_4$
e	4-FC$_6$H$_4$	e	O$_2$NC$_6$H$_4$
f	4-ClC$_6$H$_4$	f	Me
g	4-O$_2$NC$_6$H$_4$	g	Et
h	4-ClC$_6$H$_4$CH$_2$	h	4-MeOC$_6$H$_4$CH$_2$
i	t-Bu		

slowed down sufficiently to avoid interference with the measurements of the redox potentials of the oxidation waves of the starting complexes. The low stability of the iron complexes in the electrolyte medium also required the use of low temperature (–10 °C or below). Under such experimental conditions, the redox processes follow, in an acceptable way, the common criteria for reversible single-electron processes. Hence, the ratio of the anodic and corresponding cathodic peak currents is close to unity the peak potential separation ($\Delta E_p \approx 0.06$–0.1 V) is comparable with those observed for ferrocene/ferrocenium and $trans$-[ReCl(N$_2$)(dppe)$_2$]$^{0/+}$, the current function $i_p C^{-1} v^{-1/2}$ (i_p, peak current; C, concentration; v, scan rate) for each wave is close to that of this related dinitrogen complex, and neither the current function nor the redox potential vary appreciably with the scan rate. Con-

TABLE I
Cyclic voltammetric data for cis-[ReCl(L)(dppe)$_2$] (L = RCN (**1**) or CO (**2**)) and $trans$-[FeBr(L)(depe)$_2$](BF$_4$)$_n$ (L = RCN (**3**) or CO (**4**), $n = 1$; L = Br$^-$, $n = 0$ (**5**))[a]

No.[b]	L	$^{\mathrm{I}}E_{1/2}^{\mathrm{ox}}$, V	$^{\mathrm{II}}E_{1/2}^{\mathrm{ox}}$, V	No.[c]	L	$^{\mathrm{I}}E_{1/2}^{\mathrm{ox}}$, V	$^{\mathrm{II}}E_{1/2}^{\mathrm{ox}}$, V
1a	4-Et$_2$NC$_6$H$_4$CN	–0.20	0.65	**3a**	4-MeOC$_6$H$_4$CN	0.67	1.29
1b	4-MeOC$_6$H$_4$CN	–0.16	0.74	**3b**	4-MeC$_6$H$_4$CN[e]	0.69	1.28
1c	4-MeC$_6$H$_4$CN	–0.14	0.76	**3c**	PhCN[f,g]	0.71	1.31
1d	PhCN	–0.13	0.78	**3d**	4-FC$_6$H$_4$CN	0.75	1.31
1e	4-FC$_6$H$_4$CN	–0.10	0.76	**3e**	4-O$_2$NC$_6$H$_4$CN	0.78	1.31
1f	4-ClC$_6$H$_4$CN	–0.09	0.77	**3f**	MeCN[g]	0.65	1.23
1g	4-O$_2$NC$_6$H$_4$CN	–0.02	0.80	**3g**	EtCN[g]	0.65	1.27
1h	4-ClC$_6$H$_4$CH$_2$CN	–0.14	0.72	**3h**	4-MeOC$_6$H$_4$CH$_2$CN	0.66	1.29
1i	t-BuCN	–0.14	0.75	**4**	CO[h]	1.32	1.98
2	CO[d]	0.41	1.42	**5**	Br$^-$ [h,i]	–0.01	1.30

[a] Values in V ± 0.01 relative to SCE, measured at a Pt disc (d = 0.5 or 1 mm) electrode; scan rate 100 or 200 mV s^{-1}. [b] In THF/0.2 M Bu$_4$NBF$_4$, at –20 °C (**1**) or –40 °C (**2**); values measured by using the $trans$-[ReCl(N$_2$)(dppe)$_2$]$^{0/+}$ couple as internal reference ($E_{1/2}^{\mathrm{ox}}$ = 0.28 V vs SCE or –0.26(5) V vs the ferrocene/ferrocenium redox couple), unless stated otherwise; data for **1** (ref.[23]) and **2** (wave I)[30] already reported. [c] In CH$_2$Cl$_2$/0.2 M Bu$_4$NBF$_4$, at –10 °C, values measured by using the ferrocene/ferrocenium redox couple as internal reference ($E_{1/2}^{\mathrm{ox}}$ = 0.55 V vs SCE), unless stated otherwise. [d] In CH$_2$Cl$_2$. [e] At –65 °C. [f] The counterion is [BPh$_4$]$^-$ instead of [BF$_4$]$^-$, and its irreversible anodic wave is observed at E_p^{ox} = 1.13 V. [g] At –30 °C. [h] At 25 °C. [i] Included for comparative purposes.

trolled-potential electrolyses were also performed in a number of cases confirming the involvement of a single-electron transfer.

The measured values of the half-wave oxidation potentials, $^IE_{1/2}^{ox}$ and $^{II}E_{1/2}^{ox}$ (for waves I and II, respectively), are given in Table I. The cationic nitrile and carbonyl iron(II) complexes are oxidized at potentials $^IE_{1/2}^{ox}$ in the range 0.65–1.32 V, that are much more anodic than those for the corresponding neutral rhenium(I) compounds ($^IE_{1/2}^{ox}$ in the range –0.20 to 0.41 V), in agreement with the lower electron density on the former metal centre. For both the Re and Fe complexes, the oxidation potential values roughly follow the expected order of the net π-electron acceptor minus σ-donor character of the ligand L, *i.e.* its stabilizing effect on the HOMO. Hence, the carbonyl compounds *cis*-[ReCl(CO)(dppe)$_2$] (**2**) and *trans*-[FeBr(CO)(depe)$_2$]BF$_4$ (**4**) are oxidized at much higher potentials than those of the corresponding nitrile complexes (**1** and **3**, respectively) and, within the latter, the arene nitrile complexes (except those with strong electron-releasing substituents) exhibit higher oxidation potentials than the alkanenitriles. Moreover, for the complexes with an arenenitrile ligand (4-XC$_6$H$_4$CN), those with an electron-acceptor substituent (X = Cl, F or NO$_2$) are oxidized at more anodic potentials than those with an electron-donor substituent (X = NEt$_2$, OMe or Me). In addition, the oxidation potential of the dibromo complex *trans*-[FeBr$_2$(depe)$_2$] is the lowest within the iron series, in accord with the much strong electron-donor character of the bromide ligands compared with the nitriles or carbonyl.

The values of the oxidation potentials have been analyzed in terms of the Pickett[3] and Lever[7,8] semi-empirical parametrization proposals expressed by the above Eqs (*1*)–(*3*).

Electrochemical Parameters of the Rhenium Systems

For the common *cis*-{ReCl(dppe)$_2$} metal site within the series of the rhenium(I) complexes **1**, the "electron-richness" parameter is $E_S = 0.41$ V (Table II) since this is (Eq. (*2*)) the oxidation potential of the carbonyl complex **2** with this centre. However, the estimate of the polarizability (β) is not so straightforward and, in principle, requires (Eq. (*1*)) the knowledge of oxidation potentials for complexes of the series with L ligands of known P_L values. Although these are not known, we can overcome the difficulty by applying the general Eq. (*1*) to our complexes **1** (Eq. (*4*)) and to an auxiliary set of compounds with the common L ligand and a metal centre with known E_S and β, *e.g.* the related *trans* isomers (Eq. (*5*)). From Eqs (*4*) and (*5*),

where {*cis*} and {*trans*} denote the *cis*- and *trans*-{ReCl(dppe)$_2$} sites, Eq. (*6*) can be derived that allows the estimate of β for the *cis*-{ReCl(dppe)$_2$} centre from the knowledge of the oxidation potentials of a pair of *cis*- and *trans*-[ReCl(L)(dppe)$_2$] isomers, since the other parameters are known: E_S{*cis*-ReCl(dppe)$_2$} = 0.41 V (see above), E_S{*trans*-ReCl(dppe)$_2$} = 0.68 V (ref.[12]), β{*trans*-ReCl(dppe)$_2$} = 3.4 (ref.[12]).

$$^{I}E_{1/2}^{ox}\,[\textit{cis}\text{-ReCl(L)(dppe)}_2] = E_S\{\textit{cis}\} + \beta\{\textit{cis}\}\,P_L(L) \tag{4}$$

$$^{I}E_{1/2}^{ox}\,[\textit{trans}\text{-ReCl(L)(dppe)}_2] = E_S\{\textit{trans}\} + \beta\{\textit{trans}\}\,P_L(L) \tag{5}$$

$$\frac{\beta\{\textit{cis}\}}{\beta\{\textit{trans}\}} = \frac{^{I}E_{1/2}^{ox}\,[\,\textit{cis}-\text{ReCl(L)(dppe)}_2\,] - E_S\{\textit{cis}\}}{^{I}E_{1/2}^{ox}\,[\,\textit{trans}-\text{ReCl(L)(dppe)}_2\,] - E_S\{\textit{trans}\}} \tag{6}$$

TABLE II
Estimated metal-centre and ligand electrochemical parameters for the rhenium systems

Metal centre	E_S, V	β
cis-{ReCl(dppe)$_2$}	0.41[a]	1.88[b]
cis-{ReCl(dppe)$_2$}$^+$	1.42[a]	1.30[c]
Ligand	P_L, V[d]	E_L,V *vs* NHE[e]
4-Et$_2$NC$_6$H$_4$CN	–0.33	0.45
4-MeOC$_6$H$_4$CN	–0.30	0.48
4-MeC$_6$H$_4$CN	–0.29	0.49
PhCN	–0.29	0.50
4-FC$_6$H$_4$CN	–0.27	0.50
4-ClC$_6$H$_4$CN	–0.27	0.50
4-O$_2$NC$_6$H$_4$CN	–0.23	0.54
4-ClC$_6$H$_4$CH$_2$CN	–0.29	0.49
t-BuCN	–0.29	0.49

[a] From Eq. (*2*). [b] From Eq. (*6*). [c] From the plot of Fig. 2. [d] Estimated for the 18-electron complexes *cis*-[ReCl(RCN)(dppe)$_2$] (**1**), from Eq. (*4*). [e] From Eq. (*7*).

The application of Eq. (*6*) for the two pairs of isomers *cis*- and *trans*-[ReCl(L)(dppe)$_2$] (L = 4-MeC$_6$H$_4$CN, $^I E_{1/2}^{ox}$ = –0.14 (**1c**) or –0.31 V (*trans* isomer)[24]; L = 4-Et$_2$NC$_6$H$_4$CN, $^I E_{1/2}^{ox}$ = –0.20 (**1a**) or –0.44 V (*trans* isomer, measured in this study)) led to a pair of identical values (1.89 or 1.87) of polarizability, *i.e.* the average β{*cis*-ReCl(dppe)$_2$} = 1.88 (Table II).

In comparison with the isomeric *trans* form, the metal centre *cis*-{ReCl(dppe)$_2$} displays lower E_S and β values, indicating that the HOMO of the carbonyl complex is less stabilized in the *cis* isomer and that the energy of the HOMO along the series of complexes is less sensitive (in the *cis* isomers) to a change of the ligand L.

The order of the E_S values can be accounted for by considering the metal d$_\pi$ orbital splitting for both isomers[30]. For the *cis* isomer, the HOMO corresponds to the metal d$_\pi$ orbital in the plane that contains the Re–Cl bond and is perpendicular to the Re–CO bond, thus being stabilized by interaction with a filled chlorine p orbital, without any possible stabilizing interaction with empty π*(CO) orbitals. In contrast, for the *trans* isomer, the metal d$_\pi$ orbitals with destabilizing interactions with filled chlorine p orbitals contain the Re–CO bond and therefore undergo a concomitant stabilizing interaction with vacant π*(CO) orbitals, thus lying at a lower energy level than in the *cis* isomer.

The order of the β values agrees with the earlier observations[3,12,13] that a strong electron-donor ligand (like chloride) in *trans* position to the variable L ligand presents a low "buffering" capacity (high β) in the HOMO energy upon a change of L, whereas an effective net electron acceptor (like N$_2$, isocyanide or CO) exhibits the opposite behaviour leading to a low β. In this work, the *cis*-[ReCl(L)(dppe)$_2$] series possesses a phosphine ligand (with an appreciable π-electron-acceptor character) in *trans* position to the variable L ligand, whereas in the *trans* series such a *trans* ligand is chloride, and therefore β in the *cis* metal centre would be expected to be lower than in the *trans* case, as observed.

Although the value (0.41 V) of E_S for *cis*-{ReCl(dppe)$_2$} is not so low as those for the more electron-rich Mo(0) centres {Mo(L)(dppe)$_2$} (*e.g.* L = CO (–0.11 V), N$_2$ (–0.13 V), NCPh (–0.40 V))[3], it is much lower than those reported for the cationic sites *trans*-{Re(N$_2$)(dppe)$_2$}$^+$ (1.20 V)[3], *trans*-{FeH(dppe)$_2$}$^+$ (1.04 V)[3] or for the polycarbonyl centres {M(CO)$_5$} (M = Cr (ref.[3]), Mo (ref.[20]) or W (ref.[5]) (1.50 V)). Hence, our Re(I) site is much more electron-rich than the latter centres, although less than the Mo(0) ones.

From Eq. (*4*), we have estimated the P_L ligand parameter for the various nitrile ligands (Table II), considering the estimated values of E_S and β for

the metal centre (Table II) and the measured values (Table I) of the first oxidation potential of the corresponding nitrile complexes **1**.

It is noteworthy that the estimated P_L values are significantly higher (by *ca* 0.20 V) than those observed for the less electron-rich *trans*-$\{FeBr(depe)_2\}^+$ site (see below), suggesting that nitriles, like isocyanides[12], when binding to an electron-rich Re(I) centre behave as much stronger net electron acceptors than in other less electron-rich sites, showing a P_L dependence on the binding metal centre. However, nitriles do not show such a strong π-electron-acceptor ability as isocyanides and, accordingly, the P_L values estimated above are significantly lower than those observed[11–13] (–0.07 to –0.18 V) for the latter ligands in *trans*-$[ReCl(RCN)(dppe)_2]$.

From the above P_L values of the nitrile ligands, one can estimate (Table II) the corresponding Lever E_L values by taking into account the observed[7] linear relationship (except for carbon monoxide) between the two parameters (Eq. (*7*), in which P_L is in V and E_L in V *vs* NHE).

$$P_L = 1.17E_L - 0.86 \qquad (7)$$

For nitriles RCN (R = $4\text{-}Et_2NC_6H_4$, $4\text{-}FC_6H_4$, $4\text{-}O_2NC_6H_4$, $4\text{-}ClC_6H_4CH_2$ or *t*-Bu) the estimated E_L values are reported herein for the first time, whereas for the other nitriles (R = $4\text{-}MeOC_6H_4$, $4\text{-}MeC_6H_4$, C_6H_5 or $4\text{-}ClC_6H_4$), they are higher (by *ca* 0.10 V) than those previously quoted[7]. This discrepancy is in accord with the above nitrile P_L anomaly and can be accounted for by the same interpretation, but can also result in part from the different type of media in which the studies were performed (organic in our case and usually aqueous in the other).

In order to test the validity of the general Eq. (*3*) for our Re(I) complexes, and in view of the peculiarities of behaviour previously detected[7,27] for the Re(I)/Re(II) redox systems, we plotted $^1E_{1/2}^{ox}$ (V *vs* NHE) *versus* ΣE_L (the E_L values for the ligands other than RCN were taken from the literature[7]), as shown in Fig. 1. The relationships postulated by Lever[8] on the basis of two available sets of data, are also included: either two distinct linear relationships (an "upper" and a "lower" one, but the latter with highly scattered points) or a curved one.

The points that represent our nitrile complexes **1** are situated below the upper line and provide supporting evidence for the latter hypothesis (a curved relationship), also corroborated by earlier studies[27] on the vinylidene complexes *trans*-$[ReCl(=C=CHR)(dppe)_2]$ (R = H, *t*-Bu, CO_2Me, CO_2Et,

Ph or 4-MeC$_6$H$_4$), although further confirmation by other Re(I)/Re(II) systems with lower oxidation potentials is still required. An alternative hypothesis involves consideration of the possible dependence of S_M and I_M on the particular type of Re(I) metal centre, but further studies on a variety of sites will be required to test it.

Interestingly, this study also allows, for the first time, to attempt at the extension of the Pickett parametrization method to 17-electron octahedral-type complexes. In fact, from the plot (Fig. 2) of $^{II}E^{ox}_{1/2}$ (V *vs* SCE) of *cis*-[ReCl(L)(dppe)$_2$] (L = RCN (**1**) or CO (**2**)) *versus* P_L, one obtains the polarizability of the 15-electron *cis*-{ReCl(dppe)$_2$}$^+$ centre (β = 1.30, the line slope), whereas the "electron-richness" parameter E_S (given by $^{II}E^{ox}_{1/2}$ of the carbonyl complex **2**) assumes the value of 1.42 V (Table II).

For the nitrile ligands, we have considered the P_L values (see Table III and the discussion below) obtained at the cationic *trans*-{FeBr(depe)$_2$}$^+$ centre
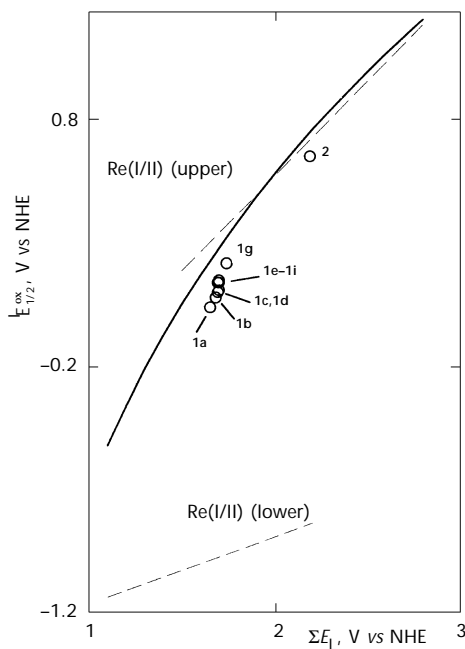

FIG. 1

Plot of $^I E^{ox}_{1/2}$ (V *vs* NHE) *versus* ΣE_L (V *vs* NHE) for *cis*-[ReCl(L)(dppe)$_2$] (L = 4-Et$_2$NC$_6$H$_4$CN (**1a**), 4-MeOC$_6$H$_4$CN (**1b**), 4-MeC$_6$H$_4$CN (**1c**), PhCN (**1d**), 4-FC$_6$H$_4$CN (**1e**), 4-ClC$_6$H$_4$CN (**1f**), 4-O$_2$NC$_6$H$_4$CN (**1g**), 4-ClC$_6$H$_4$CH$_2$CN (**1h**), *t*-BuCN (**1i**), CO (**2**)). The broken lines are taken from ref.[8] in the original, the two upper lines extend up to ΣE_L = 4.5 V and the curved one goes down to $\Sigma E_L \approx 0.8$ V)

which possesses an "electron-richness" (E_S = 1.32 V) similar to that of the cis-{ReCl(dppe)$_2$}$^+$ site (1.42 V), in preference to those estimated (Table II) for the much more electron-rich cis-{ReCl(dppe)$_2$} centre (E_S = 0.41 V) in which the nitriles behave as much stronger π-electron acceptors.

The linear plot of Fig. 2 is suggested to correspond to a particular case of a more general Eq. (*8*) which we now propose for 17-electron octahedral-type complexes [M$'_S$L] with a 15-electron metal site {M$'_S$}, identical to that (Eq. (*1*)) given by Pickett for 18-electron complexes. The "electron-richness" parameter E_S for {M$'_S$} would then be given by Eq. (*9*), analogous to Eq. (*2*).

$$E^{ox}[M'_S L] = E_S\{M'_S\} + \beta\{M'_S\}\,P_L \tag{8}$$

$$E_S\{M'_S\} = E^{ox}[M'_S(CO)] \tag{9}$$

However, further sets of 17-electron complexes have yet to be considered before the generality of this proposal can be ascertained.
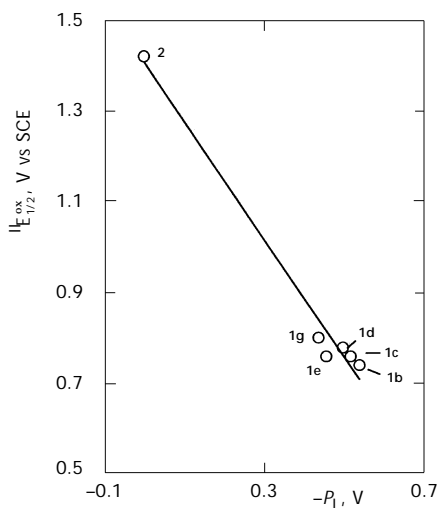

Fig. 2
Plot of $^{II}E^{ox}_{1/2}$ (V *vs* SCE) *versus* $-P_L$ (V) for cis-[ReCl(L)(dppe)$_2$] (L = 4-MeOC$_6$H$_4$CN (**1b**), 4-MeC$_6$H$_4$CN (**1c**), PhCN (**1d**), 4-FC$_6$H$_4$CN (**1e**), 4-O$_2$NC$_6$H$_4$CN (**1g**), CO (**2**)). $^{II}E^{ox}_{1/2}$ = $1.30P_L$ + 1.48 (r = 0.99)

Electrochemical Parameters for the Iron Systems

For the iron complexes *trans*-[FeBr(L)(depe)$_2$]BF$_4$ (L = RCN (**3**) or CO (**4**)), a linear relationship was also observed (Fig. 3, curve *1*) between $^I E_{1/2}^{ox}$ and P_L for the ligands with known[3] P_L values (L = CO, PhCN, MeCN, Br$^-$). From the linear plot, one obtains the polarizability (as the slope β = 1.10) of the metal site *trans*-{FeBr(depe)$_2$}$^+$, whereas its "electron-richness" parameter E_S is 1.32 V, *i.e.* the $^I E_{1/2}^{ox}$ potential for the carbonyl complex **4**. Compared with the isoelectronic Re(I) site *cis*-{ReCl(dppe)$_2$}, the iron(II) centre has a much lower electron density and polarizability.

From the linear relationship *1* in Fig. 3 and the measured $^I E_{1/2}^{ox}$ values for complexes **3** (Table I) we have estimated P_L for a number of nitrile ligands (Table III). The obtained values are *ca* 0.2 V lower than the corresponding ones (Table II) when the nitriles ligate to the much more electron-rich Re(I) sites, thus corroborating the above hypothesis of the nitrile P_L dependence on the "electron-richness" on the binding metal centre. The E_L values (Table III) were estimated from the corresponding P_L by using Eq. (*7*). For the previously reported[7] cases of RCN (R = 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, C$_6$H$_5$,
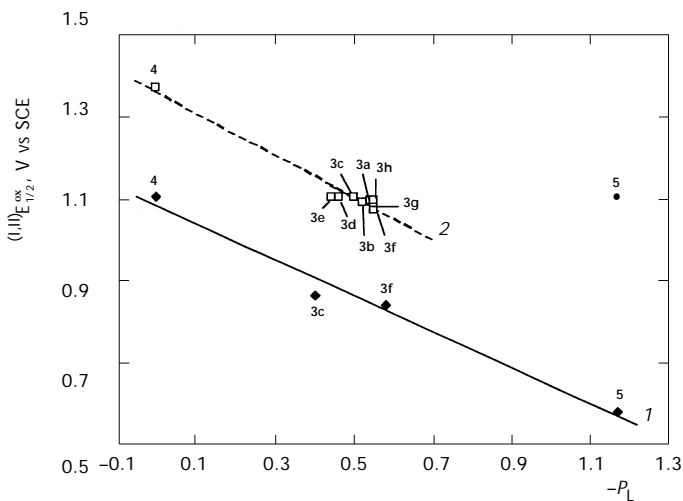

FIG. 3

Plots of $^{II} E_{1/2}^{ox}$ (*1*) or $^{II} E_{1/2}^{ox}$ (*2*) (V *vs* SCE) *versus* $-P_L$ (V) for *trans*-[FeBr(L)(depe)$_2$]BF$_4$ (L = 4-MeOC$_6$H$_4$CN (**3a**), 4-MeC$_6$H$_4$CN (**3b**), PhCN (**3c**), 4-FC$_6$H$_4$CN (**3d**), 4-O$_2$NC$_6$H$_4$CN (**3e**), MeCN (**3f**), EtCN (**3g**), 4-MeOC$_6$H$_4$CH$_2$CN (**3h**), CO (**4**)) and *trans*-[FeBr$_2$(depe)$_2$] (**5**). For *1* the P_L values are taken from literature[3], whereas for *2* they are estimated in this work (Table III). *1* $^I E_{1/2}^{ox}$ = 1.10P_L + 1.26 (*r* = 0.98), *2* $^{II} E_{1/2}^{ox}$ = 1.30P_L + 1.96 (*r* = 0.97) (neglecting point **5**, see text)

Me or Et), our values are slightly lower (usually by no more than 0.08 V). However, those already estimated[7] values (except for PhCN) refer to aqueous systems.

The plots of $^I E_{1/2}^{ox}$ and $^{II} E_{1/2}^{ox}$ (V *vs* NHE) for the iron(II) complexes *versus* ΣE_L are depicted in Fig. 4, allowing the estimate of S_M and I_M for our systems (see Eq. (*3*)). The former plot *1* ($S_M = 1.32$, $I_M = -0.57$ V *vs* NHE) approaches the general linear relationship recognized by Lever[7] (see dotted line, Fig. 4) for the low-spin Fe(II/III) series ($S_M = 1.10$, $I_M = -0.43$ V *vs* NHE), whereas the latter one *2* for the second oxidation potential, provides the first estimate of the electrochemical parameters ($S_M = 1.49$, $I_M = -0.18$ V *vs* NHE) for an Fe(III/IV) redox couple. However, these values should be taken with caution since they are based on a limited number of data points which are spread along a considerably narrow range of ΣE_L values. Moreover, the point representative of the second oxidation potential of the dibromo complex **5** lies markedly off the correlation. In fact, $^{II} E_{1/2}^{ox}$ for this complex is unexpectedly very close to those of the nitrile compounds **3**. This can be

TABLE III
Estimated metal-centre and ligand electrochemical parameters for iron systems

Metal centre	E_S, V	β	S_M	I_M, V *vs* NHE
trans-{FeBr(depe)$_2$}$^+$	1.32[a]	1.10[b]	1.32[c]	−0.57[c]
trans-{FeBr(depe)$_2$}$^{2+}$	1.98[a]	1.30[d]	1.49[e]	−0.18[e]
Ligand	P_L, V[f]	E_L, V *vs* NHE[g]		
4-MeOC$_6$H$_4$CN	−0.54	0.27		
4-MeC$_6$H$_4$CN	−0.52	0.29		
PhCN	−0.50	0.31		
4-FC$_6$H$_4$CN	−0.46	0.34		
4-O$_2$NC$_6$H$_4$CN	−0.44	0.36		
4-MeOC$_6$H$_4$CH$_2$CN	−0.55	0.26		
MeCN	−0.55	0.26		
EtCN	−0.55	0.26		
depe	−0.53[h]	0.28[i]		

[a] From Eq. (*2*). [b] From the plot *1* of Fig. 3. [c] From the plot *1* of Fig. 4. [d] From the plot *2* of Fig. 3. [e] From the plot *2* of Fig. 4. [f] Estimated for the 18-electron complexes *trans*-[FeBr(RCN)(depe)$_2$]BF$_4$, from the plot *1* of Fig. 3 and the values of Table I. [g] From Eq. (*7*). [h] Estimated from Eq. (*7*) (the value corresponds to each P-coordination). [i] Estimated from Eq. (*10*) (the value corresponds to each P-coordination).

tentatively explained by invoking (i) a hypothetical change, upon oxidation, of the spin state from low to high spin (if the oxidized complexes are high-spin d^5 species, with $d_{x^2-y^2}$ as the HOMO, a levelling of this orbital energy along the series, and therefore also of the $^{II}E_{1/2}^{ox}$ values, would be expected) or (ii) a Jahn–Teller distortion (expected, although being not strong, for low-spin d^5 complexes) with a resulting stabilization of the HOMO (d_{xz} or d_{yz}) for the oxidized dibromo complex with two weak-field bromide ligands (increase in $^{II}E_{1/2}^{ox}$ relatively to the expected value, as observed) and destabilization of the HOMO (d_{xy}) of the oxidized nitrile complexes **3** (with a strong-field nitrile ligand), thus leading to HOMOs of similar energies (hence to close $^{II}E_{1/2}^{ox}$ values).

For the above plots, we had first to estimate the unknown E_L value for the depe ligand. The value ($E_L = 0.28$ V *vs* NHE) was obtained from Eq. (*10*) derived by applying Eq. (*3*) to both complexes *trans*-[ReCl(N$_2$)(dppe)$_2$] ($^IE_{1/2}^{ox} = 0.53$ V *vs* NHE) and *trans*-[ReCl(N$_2$)(depe)$_2$] ($^IE_{1/2}^{ox} = 0.03$ V *vs* SCE (ref.[38]), *i.e.* 0.28 V *vs* NHE) and considering the known values for the other parameters: $S_M = 0.76$ V *vs* NHE (ref.[8]), E_L(dppe) $= 0.36$ V *vs* NHE (ref.[7]).

$$E_{1/2}^{ox} [ReCl(N_2)(depe)_2] - E_{1/2}^{ox} [ReCl(N_2)(dppe)_2] = \qquad (10)$$

$$4S_M[E_L(depe) - E_L(dppe)]$$
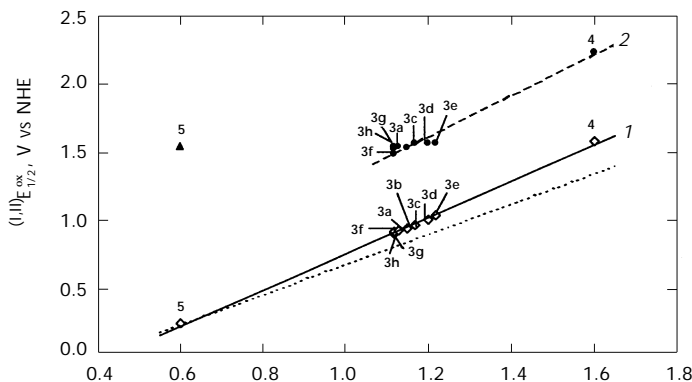
FIG. 4

Plots of $^{II}E_{1/2}^{ox}$ (*1*) or $^{II}E_{1/2}^{ox}$ (*2*) (V *vs* NHE) *versus* ΣE_L (V *vs* NHE) for *trans*-[FeBr(L)(depe)$_2$]BF$_4$ (L = 4-MeOC$_6$H$_4$CN (**3a**), 4-MeC$_6$H$_4$CN (**3b**), PhCN (**3c**), 4-FC$_6$H$_4$CN (**3d**), 4-O$_2$NC$_6$H$_4$CN (**3e**), MeCN (**3f**), EtCN (**3g**), 4-MeOC$_6$H$_4$CH$_2$CN (**3h**), CO (**4**)) and *trans*-[FeBr$_2$(depe)$_2$] (**5**). The lower dotted line is taken from ref.[7]. *1* $^IE_{1/2}^{ox} = 1.32 \Sigma E_L - 0.57$ (*r* = 0.99), *2* $^{II}E_{1/2}^{ox} = 1.49 \Sigma E_L - 0.18$ (*r* = 0.97)

The available data also allow to estimate E_S and β for the 15-electron *trans*-{FeBr(depe)$_2$}$^{2+}$ site (Table III). The value of E_S, as $^{II}E^{ox}_{1/2}$ of the carbonyl complex, is 1.98 V *vs* SCE (Table I), whereas β (1.30) is given by the slope of the conceivable linear plot (Fig. 3, curve *2*) of $^{II}E^{ox}_{1/2}$ (V *vs* SCE) for the series *trans*-[FeBr(L)(depe)$_2$]BF$_4$ (L = RCN (**3**) or CO (**4**)) *versus* P_L. The point representing dibromo complex **5** does not follow the correlation, as could be expected (see above). However, as indicated for the isoelectronic Re centre *cis*-{ReCl(dppe)$_2$}$^+$, those values have to be considered as rather preliminary due to the small number of available points for their estimate. Nevertheless, the results appear to open up the possibility of further extension of the Pickett parametrization method to the paramagnetic 17-electron complexes.

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