

Preparation and Redox Properties of the Complexes *trans*-[ReL₂(dppe)₂]BF₄ (L = CO or Isocyanide). Estimate of the Oxidation Potential of Octahedral 18-Electron Complexes with 14-Electron Square Planar Metal Centres and of Related Electrochemical Parameters for Derived 16-Electron Sites

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Abstract

The complexes *trans*-[ReL₂(dppe)₂]BF₄ (**I**, L = CO, CNR with R = Me, Bu^t, C₆H₄OMe-4, C₆H₄Me-4, C₆H₄Cl-4 and C₆H₃Cl₂-2,6) were prepared from the reaction of the parent dinitrogen complex *trans*-[ReCl(N₂)(dppe)₂] with the appropriate ligand, in thf and in the presence of TlBF₄.

Their redox properties were studied by cyclic voltammetry at a Pt electrode in [Bu₄N][BF₄]/thf or acetonitrile; they undergo a one-electron reversible oxidation and the observed $E_{1/2}^{\text{ox}}$ values were applied to test the validity of a proposed general expression—derived from the electrochemical ligand (P_L) and 16-electron metal site (E_s, β) parameters [6]—to estimate $E_{1/2}^{\text{ox}}$ for 18-electron octahedral complexes of the type [M_sL₂] with a square planar 14-electron metal centre {M_s}. E_s and β parameters were also estimated for the auxiliary {ReL(dppe)₂}⁺ (L = CO or CNR) centres.

Introduction

Isocyanides are organic species with a versatile electronic and binding ability which have been recognized [1] as probes in the study of the properties of dinitrogen and its ligating transition metal sites.

Series of 18-electron octahedral isocyanide complexes which are analogous to dinitrogen compounds have been prepared by replacement of N₂ ligand in the latter by isocyanide, and their redox behaviour and chemical properties have been studied.

Hence, the neutral complexes *trans*-[ML₂(dppe)₂] (M = Mo or W) [2] and *trans*-[ReCl(dppe)₂] [3] (L = CNR or CO) were prepared in this way. We now report the synthesis of the related cationic *trans*-[ReL₂(dppe)₂]⁺ (**I**) series with the 14-electron metal site {Re(dppe)₂}⁺ derived from the 16-electron {ReCl(dppe)₂} neutral centre.

All these complexes undergo a one-electron reversible oxidation and, within the aryl isocyanide complexes [M(CNR)₂(dppe)₂] and [ReCl(CNR)(dppe)₂], linear correlations were observed between $E_{1/2}^{\text{ox}}$ and the Hammett's σ parameter for the phenyl substituent of the isocyanide [2, 3], and between $E_{1/2}^{\text{ox}}$ and the energy of the metal to isocyanide charge transfer band [4, 5].

A comparison between the values of $E_{1/2}^{\text{ox}}$ of the homologous members of these group VII and VI series, $E_{1/2}^{\text{ox}}[\text{ReCl}(\text{dppe})_2]$ vs. $E_{1/2}^{\text{ox}}[\text{MoL}_2(\text{dppe})_2]$ (L = CNR, N₂ or CO), also provided information on the relative electron-richness of the metal centres, on the relative electron acceptor character of the isocyanide and the dinitrogen ligands and on their chemical reactivity [5].

However, a more elaborate and systematic approach to quantify the redox potential–electronic relationship was initiated by other authors [6] for octahedral 18-electron complexes as follows.

A scale of 2-electron ligand constants (P_L) was proposed [6]* according to the eqn. 1, this parameter being a measure of the net electron donor/acceptor character of the ligand (the stronger this character, the more negative is P_L).

$$P_L = E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5\text{L}] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6] \quad (1)$$

The $E_{1/2}^{\text{ox}}$ of an 18-electron octahedral complex with the ligand L, [M_sL], is given by eqn. 2 where the E_s and β parameters are a measure of the electron-richness and the polarisability, respectively, of the metal site {M_s} [6].

$$E_{1/2}^{\text{ox}}[\text{M}_s\text{L}] = E_s + \beta P_L \quad (2)$$

The electron-richness site parameter, E_s , is $E_{1/2}^{\text{ox}}$ exhibited by the carbonyl complex (eqn. 3) [6].

$$E_s = E_{1/2}^{\text{ox}}[\text{M}_s(\text{CO})] \quad (3)$$

* P_L is identical to the ligand parameter $(dE^{\text{ox}}/dx)_L$, defined [7] for first-row transition metal complexes of the type [M(CO)_{6-x}L_x]^{y+}, when M = Cr, y = 0 and x = 0 → 1.

The equations express the linear relationship experimentally observed between $E_{1/2}^{\text{ox}}$ of two series of complexes, $[\text{M}_s\text{L}]$ and the isoelectronic and isostructural $[\text{Cr}(\text{CO})_5\text{L}]$ reference species. It may also be expressed by eqn. 4 which is a combination of the previous expressions.

$$E_{1/2}^{\text{ox}}[\text{M}_s\text{L}] - E_{1/2}^{\text{ox}}[\text{M}_s(\text{CO})] = \beta \{E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5\text{L}] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6]\} \quad (4)$$

Based on these electrochemical parameters, criteria were also proposed [6] for ligand coordination, chemical reactivity and characterization of complexes.

In the above mentioned expressions, the metal site $\{\text{M}_s\}$ is a 16-electron square pyramid, and parameters have already been quoted for a variety of sites of this type: $\{\text{MoY}(\text{dppe})_2\}^n$ ($\text{Y} = \text{NO}$; $n = +1$. $\text{Y} = \text{N}_2$, CO , NCPH ; $n = 0$. $\text{Y} = \text{N}_3$; $n = -1$) [6], $\{\text{FeH}(\text{dppe})_2\}^+$, $\{\text{Re}(\text{N}_2)(\text{dppe})_2\}^+$ [6], and $\{\text{ReCl}(\text{dppe})_2\}$ [3].

In the present work, the possibility to extend this type of treatment to 14-electron metal sites $\{\text{M}'_s\}$ in 18-electron complexes $[\text{M}'_s\text{L}_2]$ is discussed by studying the redox behaviour of the newly synthesized bis-isocyanide and dicarbonyl complexes $\text{trans}-[\text{ReL}_2(\text{dppe})_2]\text{BF}_4$ (**I**) and relating their half-wave oxidation potential to that known [3] for the related compounds $\text{trans}-[\text{ReCl}(\text{dppe})_2]$.

Experimental

Preparation of the Complexes $\text{trans}-[\text{ReL}_2(\text{dppe})_2]\text{BF}_4$, (**I**, $L = \text{CNR}$ or CO)

All the reactions and manipulations were carried out in the absence of air using standard inert gas flow and vacuum techniques.

Solvents were purified by standard techniques, $\text{trans}-[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ [8], CNMe and the other isocyanides [9] were prepared by published methods.

Infrared measurements were carried out on a Perkin-Elmer 683 spectrometer, ^1H and ^{31}P NMR spectra were recorded on a Jeol JNM-PS-100 or a Jeol PFT 100 Fourier-transform spectrometer.

$\text{trans}-[\text{Re}(\text{CNMe})_2(\text{dppe})_2]\text{BF}_4$, (**I**, $L = \text{CNMe}$)

CNMe (0.060 cm³, 1.3 mmol) was added to a suspension of $\text{trans}-[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ (0.21 g, 0.20 mmol) and TIBF_4 (0.20 g, 0.69 mmol) in thf (75 cm³) and the mixture was stirred at room temperature and under N_2 for three days. The resulting white solid (**I**, $L = \text{CNMe}$) was filtered off, thoroughly washed with H_2O and dried under vacuum. A further crop was obtained upon concentration of the filtered solution followed by addition of pentane (0.13 g, 56% yield). The bis-isocyanide complex could then be recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$.

$\text{trans}-[\text{Re}(\text{CNBu}^t)_2(\text{dppe})_2]\text{BF}_4$, (**I**, $L = \text{CNBu}^t$)

The same procedure as described above was used, although with a smaller excess of the CNBu^t (4.9:1 molar ratio relative to the dinitrogen rhenium complex) (ca. 50% yield).

$\text{trans}-[\text{Re}(\text{CNC}_6\text{H}_4\text{OMe-4})_2(\text{dppe})_2]\text{BF}_4$, (**I**, $L = \text{CNC}_6\text{H}_4\text{OMe-4}$)

thf (35 cm³) was added to a mixture of $\text{trans}-[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ (0.174 g, 0.166 mmol) with TIBF_4 (0.17 g) and $\text{CNC}_6\text{H}_4\text{OMe-4}$ (0.110 g, 0.826 mmol) and the system was left refluxing under argon for 10 days. A yellow solid remained in suspension and because its infrared spectrum still showed the presence of unreacted parent complex (shoulder at ca. 1960 cm⁻¹ of the main band at 2000 cm⁻¹ due to the bis-isocyanide species), tungsten filament irradiation was started and left for four days. The solution was then filtered, concentrated and cooled, leading to the precipitation of complex (**I**, $L = \text{CNC}_6\text{H}_4\text{OMe-4}$) as a crystalline yellow solid. A further crop of this species could be obtained from the mother liquor upon addition of pentane and cooling (ca. total 70 mg, 32% yield).

$\text{trans}-[\text{Re}(\text{CNC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2]\text{BF}_4$, (**I**, $L = \text{CNC}_6\text{H}_4\text{Me-4}$)

An analogous procedure was used as for (**I**, $L = \text{CNMe}$), using a 4.3:1 molar excess of $\text{CNC}_6\text{H}_4\text{-CH}_3\text{-4}$ relative to the dinitrogen rhenium complex. The pale yellow solid (**I**, $L = \text{CNC}_6\text{H}_4\text{Me-4}$), after washing with H_2O and dried, was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, (ca. 40% yield).

$\text{trans}-[\text{Re}(\text{CNC}_6\text{H}_3\text{Cl}_2\text{-2,6})_2(\text{dppe})_2]\text{BF}_4$, (**I**, $L = \text{CNC}_6\text{H}_3\text{Cl}_2\text{-2,6}$)

This complex may be prepared by a procedure similar to that of (**I**, $L = \text{CNMe}$), but a greater excess of isocyanide has to be used. The yellow solid which was present in the mixture, after three days reaction, was mainly the dinitrogen rhenium complex. Concentration of the filtered solution afforded a yellow solid from which pure (**I**, $L = \text{CNC}_6\text{H}_3\text{Cl}_2\text{-2,6}$) could be obtained upon recrystallisation from $\text{CH}_2\text{-Cl}_2/\text{Et}_2\text{O}$, (ca. 10% yield).

$\text{trans}-[\text{Re}(\text{CO})_2(\text{dppe})_2]\text{BF}_4$, (**I**, $L = \text{CO}$)

thf (75 cm³) was added to a mixture of $\text{trans}-[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ (0.220 g, 0.210 mmol) with TIBF_4 (0.25 g, 0.86 mmol) and the system was left refluxing for ca. 12 days (during the first day under one 100 W bulb tungsten filament irradiation) with continuous bubbling of CO through the refluxing mixture. The final pale yellow solution was filtered, concentrated under vacuum and complex (**I**, $L = \text{CO}$) precipitated as a white solid upon slow addition, with heating, of 40–60° pet. ether followed by cooling to ambient temperature. The precipitate

was filtered-off, washed first with thf/pentane, then thoroughly with water and dried under vacuum (ca. 0.13 g, 55% yield).

Electrochemical Measurements

The redox potentials of the complexes were measured by cyclic voltammetry in 0.2 M [NBu₄]-[BF₄]/thf or acetonitrile at a platinum electrode.

The $E_{1/2}^{ox}$ values are quoted relative to SCE by using as internal reference the [Mo(N₂)₂(dppe)₂]^{0/+} or the [ReCl(N₂)(dppe)₂]^{0/+} couple, which present $E_{1/2}^{ox} = -0.16$ V or $+0.28$ V vs. SCE, respectively, in 0.2 M [NBu₄][BF₄]/thf.

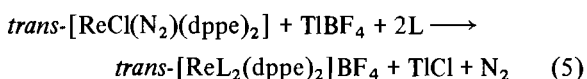
The electrochemical experiments were carried out on an EG&G PAR 173 Potentiostat/Galvanostat and an EG&G PARC 175 Universal Programmer.

Results and Discussion

Preparation and Characterization of Complexes *trans*-[ReL₂(dppe)₂]BF₄, (I, L = CO or CNR)

The dinitrogen complex *trans*-[ReCl(N₂)(dppe)₂] is a convenient precursor for a series of complexes with the 16-electron {ReCl(dppe)₂} centre, *trans*-[ReClL(dppe)₂] (L = CO or CNR) [3], obtained by replacement reactions of the ligating dinitrogen by a strong net electron acceptor ligand. However, by reacting the N₂ complex with an halide abstractor, TIBF₄, in the presence of a nitrile (NCMe or NCPH), the mixed dinitrogen–nitrile complexes [R(N₂)(NCR)(dppe)₂]⁺ with the {Re(Ne₂)(dppe)₂}⁺ centre, were obtained [10].

We have now found that by reacting the parent dinitrogen complex of Re(I) with TIBF₄ in the presence of isocyanide or carbon monoxide, a range of complexes with the 14-electron centre {Re(dppe)₂}, *trans*-[ReL₂(dppe)₂][BF₄] (I, L = CNR or CO), is synthesised according to eqn. 5:



In this reaction, the chloride replacement is assisted by the thallium salt, and the presence at the metal centre of the isocyanide or carbonyl ligand promotes the evolution of N₂ due to the strong competition for the metal d electron release, thus affording the bis-isocyanide or the dicarbonyl complexes (I) as the final products.

Complexes (I) are white or pale yellow in colour and they were characterized by their IR, ¹H and ³¹P NMR spectroscopic properties, elemental analysis and molar conductivity measurements (Tables I and II).

In their IR spectra, complexes (I, L = CNR) show a strong band in the 2075–1935 cm⁻¹ range assigned to N–C stretching of the isocyanide ligand, whereas for the analogous dicarbonyl complex, $\nu(\text{CO})$ occurs at 1905 cm⁻¹. This value is intermediate between those (1940 and 1880 cm⁻¹) reported [11] for the isomeric *cis*-[Re(CO)₂(dppe)₂]I complex. The observation of a single IR band associated to the stretching mode of the two unsaturated C≡N or C=O groups indicates the *trans* geometry of complexes (I), which is also confirmed by ³¹P NMR data (see below).

As expected, the arylisocyanide ligands present $\nu(\text{CN})$ at lower values than those observed for the weaker π acceptor ligating alkylisocyanides, and, within the former, the lowering of $\nu(\text{CN})$ upon coordination follows the electron withdrawing ability of the phenyl substituent. Hence, e.g., the lowest $\nu(\text{CN})$ value (1935 cm⁻¹) is observed for the dichlorophenyl isocyanide complex, whereas the *p*-methoxyphenyl species exhibits $\nu(\text{CN})$ at 2000 cm⁻¹.

For all these complexes, a singlet is observed in their ³¹P{¹H} NMR spectra in agreement with a *trans* geometry.

In their ¹H NMR spectra, the dppe methylene proton resonance appears as a broad triplet due to coupling to the phosphorus nuclei ($J_{\text{PH}} = 8 \pm 1$ Hz).

The aromatic isocyanide proton resonances of the CNC₆H₄OMe-4 complex are clearly observed as

TABLE I. Physical Data for Complexes *trans*-[ReL₂(dppe)₂]BF₄ (I, L = CNR or CO).

L	Colour	$\nu(\text{CN})$ or $\nu(\text{CO})^a$	Elemental analysis ^b		
			% C	% H	% N
CNMe ^c	White	2075 s	58.5(58.9)	5.5(5.1)	2.3(2.3)
CNBu ^t	White	2035 s	59.8(60.2)	5.5(5.4)	2.2(2.3)
CNC ₆ H ₄ OMe-4	Pale yellow	2000 s	61.0(61.1)	4.6(4.7)	2.1(2.1)
CNC ₆ H ₄ Me-4	Pale yellow	1995 s	62.0(62.6)	5.3(4.8)	2.1(2.1)
CNC ₆ H ₄ Cl-4	Pale yellow	1985 s	58.3(58.9)	4.5(4.2)	2.1(2.1)
CNC ₆ H ₃ Cl ₂ -2,6 ^d	Yellow	1935 s, br	56.0(55.4)	4.7(4.3)	1.9(1.8)
CO	White	1905 s	57.7(57.6)	4.4(4.3)	

^aIn Nujol mull (cm⁻¹). ^bRequired values in parenthesis.

^dWith Et₂O of crystallisation.

^cWith thf of crystallisation as shown by the ¹H NMR spectrum.

TABLE II. ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR Data for Complexes $\text{trans-}[\text{ReL}_2(\text{dppe})_2]\text{BF}_4$ (I, L = CNR or CO).

L	^1H NMR			$^{31}\text{P}\{^1\text{H}\}$ NMR δ^b
	δ^a	Intensity	Assignment	
CNMe	7.4–6.7 m	40(40)	$-\text{C}_6\text{H}_5(\text{dppe})$	108.3
	3.60 mbr	4(4)	$-\text{CH}_2(\text{thf})^c$	
	2.87 s	6(6)	$-\text{CNCH}_3$	
	2.34 tbr ^d	8(8)	$-\text{CH}_2(\text{dppe})$	
	1.75 mbr	4(4)	$-\text{CH}_2(\text{thf})^c$	
CNBu ^t	7.5–6.9 m	40(40)	$-\text{C}_6\text{H}_5(\text{dppe})$	105.9
	2.48 tbr ^d	8(8)	$-\text{CH}_2(\text{dppe})$	
	0.67 s	9(9)	$-\text{CNC}(\text{CH}_3)_3$	
CNC ₆ H ₄ OMe-4	7.4–6.8 m	40(40)	$-\text{C}_6\text{H}_5(\text{dppe})$	108.2
	6.75 d ^e	4(4)	Isocyanide aromatic <i>ortho</i> to OMe	
	6.20 d ^e	4(4)	Isocyanide aromatic <i>ortho</i> to N	
	3.81 s	6(6)	$\text{CNC}_6\text{H}_4\text{OCH}_3\text{-4}$	
	2.45 tbr ^d	8(8)	$-\text{CH}_2(\text{dppe})$	
CNC ₆ H ₄ Me-4	7.5–6.9 m	44(44)	$-\text{C}_6\text{H}_5(\text{dppe})$ + isocyanide aromatic <i>ortho</i> to Me	110.3
	6.15 d ^e	4(4)	Isocyanide aromatic <i>ortho</i> to N	
	3.64 mbr	3	$-\text{CH}_2(\text{thf})^c$	
	2.50 tbr ^d	7(8)	$-\text{CH}_2(\text{dppe})$	
	2.31 s	6(6)	$-\text{CNC}_6\text{H}_4\text{CH}_3\text{-4}$	
	1.87 mbr	3	$-\text{CH}_2(\text{thf})^c$	
CNC ₆ H ₄ Cl-4	7.5–6.9 m } 7.22 d ^e	44(44)	$-\text{C}_6\text{H}_5(\text{dppe})$ + isocyanide aromatic <i>ortho</i> to Cl	112.5
	6.12 d ^e			
	2.55 tbr ^d	8(8)	$-\text{CH}_2(\text{dppe})$	
CNC ₆ H ₃ Cl ₂ -2,6	7.3–6.8 m	46(46)	$-\text{C}_6\text{H}_5(\text{dppe})$ + isocyanide aromatic	117.2
	3.65 m	2	$-\text{CH}_2(\text{thf})^c$	
	2.97 tbr ^d	8(8)	$-\text{CH}_2(\text{dppe})$	
	1.75 m	2	$-\text{CH}_2(\text{thf})^c$	
CO ^f	7.6–6.8 m	40(40)	$-\text{C}_6\text{H}_5(\text{dppe})$	113.5
	3.73 m	4(4)	$-\text{CH}_2(\text{thf})^c$	
	2.58 tbr ^d	8(8)	$-\text{CH}_2(\text{dppe})$	
	1.84 m	4(4)	$-\text{CH}_2(\text{thf})^c$	

^aValues (ppm) relative to internal TMS; in CD₂Cl₂ (unless otherwise stated) at ca. 30 °C. ^bppm upfield from external TMP.
^cSolvent of crystallisation. ^dTriplet due to coupling to phosphorus nuclei ($J = 8 \pm 1$ Hz). ^e $^3J_{\text{HH}} = 9 \pm 1$ Hz. ^fIn CDCl₃.

two doublets ($^3J_{\text{HH}} = 9$ Hz, centered at δ 6.75 and 6.20 ppm and each of them integrating for four protons) which correspond to the expected AB type pattern. The higher field half may be assigned to the phenyl ring protons in *ortho* positions relative to the N atoms by analogy with that observed [12] in other *p*-substituted arylisocyanide complexes. The coupling between the *ortho* and the *meta* protons was confirmed by spin decoupling experiments.

A similar AB type pattern is followed by the isocyanide phenyl protons of the other *p*-substituted phenylisocyanide complexes, although the lower field half may be buried under the phenyl dppe complex multiplet, as observed for CNC₆H₄Me-4.

In agreement with the ionic formulation for complexes (I), their nitromethane solutions present a molar conductivity in the usual range expected for a 1:1 electrolyte (e.g., $\Lambda_{\text{M}} = 81 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for the CNBu^t complex).

Redox Properties of Complexes $\text{trans-}[\text{ReL}_2(\text{dppe})_2]\text{BF}_4$ (L = CO or CNR)

Each of these complexes (I) displays, by cyclic voltammetry in 0.2 M [NBu₄][BF₄]/thf or acetonitrile at a Pt electrode, diffusion controlled one-electron reversible oxidations at scan rates 0.02–0.2 V s⁻¹ as shown by the peak current separation, $[E_{\text{p}}^{\text{ox}} - E_{\text{p}}^{\text{red}}]$, and by the ratio of the peak currents. For the isocyanide complexes, a second, irreversible,

oxidation wave is also observed at a higher potential in acetonitrile (Table III). The oxidation potentials are quoted relative to SCE by using as internal reference the [Mo(N₂)₂(dppe)₂]^{0/+} or the [ReCl(N₂)(dppe)₂]^{0/+} couple which present $E_{1/2}^{\text{ox}}$ at -0.16 V or $+0.28$ V vs. SCE, respectively, in 0.2 M [NBu₄]-[BF₄]/thf.

TABLE III. Cyclic Voltammetric Data^a for Complexes *trans*-[ReL₂(dppe)₂]BF₄ (I, L = CNR or CO).

L	$E_{1/2}^{\text{ox}}$	$\Pi E_{\text{P}}^{\text{ox}}$
CNMe	0.79	1.24
CNBut	0.80	1.70
CNC ₆ H ₄ OMe-4	0.88	1.64
CNC ₆ H ₄ Me-4	0.93	1.71
CNC ₆ H ₄ Cl-4	0.98	1.70
CNC ₆ H ₃ Cl ₂ -2,6	1.05	1.9
CO	1.42	

^aValues in Volt (± 0.02) relative to SCE, measured by using as internal reference the [ReCl(N₂)(dppe)₂]^{0/+} or the [Mo(N₂)₂(dppe)₂]^{0/+} couple (with $E_{1/2}^{\text{ox}} = +0.28$ or -0.16 V vs. SCE in 0.2 M [NBu₄][BF₄]/thf, respectively). Experiments carried out in 0.2 M [NBu₄][BF₄]/acetonitrile at a Pt electrode.

The half-wave oxidation potential of the first wave, $E_{1/2}^{\text{ox}}$, is about 0.7 V higher than that observed [3] for the homologous complex of the related series *trans*-[ReClL(dppe)₂] (II, L = CO or CNR), in agreement with the lower electron-richness of the cationic {ReL(dppe)₂}⁺ centre relative to the neutral {ReCl(dppe)₂} moiety.

The oxidation potentials of the complexes (I) increase in the order of R = Me \approx Bu^t < C₆H₄OMe-4 < C₆H₄Me-4 < C₆H₄Cl-4 < C₆H₃Cl₂-2,6 which reflects the increasing electron-withdrawing ability of the corresponding isocyanide.

In the isocyanide complexes (I), an increase of $E_{1/2}^{\text{ox}}$ follows a decrease of $\nu(\text{C}\equiv\text{N})$ and this trend (which, however, is not linear) agrees with the dominant influence of the electron acceptor character of the isocyanide on both $E_{1/2}^{\text{ox}}$ and $\nu(\text{C}\equiv\text{N})$.

Estimate of the Half-wave Oxidation Potential of 18-Electron Octahedral Complexes of the Type [M'_sL₂] with a 14 Electron Square Planar Metal site {M'_s}

(a) General Treatment

Expression 2 [or 4] allows the prediction of $E_{1/2}^{\text{ox}}$ for a closed-shell octahedral complex, [M_sL], provided the 16-electron metal site {M_s} constants (E_s , β) and the P_L ligand parameter are known. However, for the prediction of $E_{1/2}^{\text{ox}}$ of complexes *trans*-[M'_sL₂] which exhibit two equal L ligands binding a 14-electron metal site {M'_s'}, the use of

such an expression would require the knowledge of E_s and β for the various {M'_sL} 16-electron metal sites involved. Moreover, a linear relationship does not appear to be followed by $E_{1/2}^{\text{ox}}$ of the standard series [Cr(CO)₅L] [13] and of the corresponding *trans*-[M'_sL₂], such as *trans*-[ReL₂(dppe)₂]BF₄.

The absence of a linear correlation in this comparison is not surprising because it relates different types of metal sites and different number of L ligands.

Nevertheless, it is possible to estimate $E_{1/2}^{\text{ox}}$ {*trans*-[M'_sL₂]} with the aid of those expressions, provided $E_{1/2}^{\text{ox}}$ of one member of the series, $E_{1/2}^{\text{ox}}$ {*trans*-[M'_s(CO)₂]}, and E_s and β of an auxiliary and related 16-electron metal site, {M'_sL'} (L' \neq CO), are known, as well as the P_L values for the ligands L and L'.

This may be demonstrated as shown below by following a preliminary treatment presented previously [14].

By applying eqn. 2 to the complexes *trans*-[M'_sL₂] – onwards simply denoted as [M'_sL₂] – one gets the expression:

$$E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}_2] = E_s\{\text{M}'_s\text{L}\} + \beta\{\text{M}'_s\text{L}'\} P_L(\text{L}) \quad (6)$$

where $E_s\{\text{M}'_s\text{L}\}$ and $\beta\{\text{M}'_s\text{L}'\}$ are the electron-richness and the polarisability parameters, respectively, of the {M'_sL} metal sites; $P_L(\text{L})$ is the ligand parameter of the ligand L.

By definition of E_s (eqn. 3):

$$E_s\{\text{M}'_s\text{L}\} = E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}(\text{CO})] \quad (7)$$

and, by applying eqn. 2:

$$E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}(\text{CO})] = E_s\{\text{M}'_s(\text{CO})\} + \beta\{\text{M}'_s(\text{CO})\} P_L(\text{L}) \quad (8)$$

By definition of E_s :

$$E_s\{\text{M}'_s(\text{CO})\} = E_{1/2}^{\text{ox}}[\text{M}'_s(\text{CO})_2] \quad (9)$$

whereas, by applying eqn. 2:

$$\beta\{\text{M}'_s(\text{CO})\} = \frac{E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}'(\text{CO})] - E_{1/2}^{\text{ox}}[\text{M}'_s(\text{CO})_2]}{P_L(\text{L}')} \quad (10)$$

However, by definition of E_s :

$$E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}'(\text{CO})] = E_s\{\text{M}'_s\text{L}'\} \quad (11)$$

Substitution for $E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}'(\text{CO})]$ in eqn. 10 from eqn. 11 gives:

$$\beta\{\text{M}'_s(\text{CO})\} = \frac{E_s\{\text{M}'_s\text{L}'\} - E_{1/2}^{\text{ox}}[\text{M}'_s(\text{CO})_2]}{P_L(\text{L}')} \quad (12)$$

Substitution for $\beta\{\text{M}'_s(\text{CO})\}$ in eqn. 8 from eqn. 12, for $E_s\{\text{M}'_s(\text{CO})\}$ in eqn. 8 from eqn. 9 and for $E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}(\text{CO})]$ in eqn. 7 from eqn. 8, gives:

$$E_s\{\text{M}'_s\text{L}\} = E_{1/2}^{\text{ox}}[\text{M}'_s(\text{CO})_2] + \frac{E_s\{\text{M}'_s\text{L}'\} - E_{1/2}^{\text{ox}}[\text{M}'_s(\text{CO})_2]}{P_L(\text{L}')} P_L(\text{L}) \quad (13)$$

which, upon rearrangement, leads to:

$$E_s\{M'_sL\} = \left[1 - \frac{P_L(L)}{P_L(L')} \right] E_{1/2}^{\text{ox}}[M'_s(\text{CO})_2] + \frac{P_L(L)}{P_L(L')} E_s\{M'_sL'\} \quad (14)$$

Moreover, by applying eqn. 2 to the $\{M'_sL\}$ and the $\{M'_sL'\}$ sites, one gets:

$$\beta\{M'_sL\} = \frac{E_{1/2}^{\text{ox}}[M'_sLL'] - E_s\{M'_sL\}}{P_L(L')} \quad (15)$$

and:

$$E_{1/2}^{\text{ox}}[M'_sLL'] = E_s\{M'_sL'\} + \beta\{M'_sL'\} P_L(L) \quad (16)$$

Substitution for $E_{1/2}^{\text{ox}}[M'_sLL']$ and for $E_s\{M'_sL\}$ in eqn. 15 from eqns. 16 and 14, respectively, gives:

$$\beta\{M'_sL\} = \frac{\left[1 - \frac{P_L(L)}{P_L(L')} \right] E_s\{M'_sL'\} - \left[1 - \frac{P_L(L)}{P_L(L')} \right] E_{1/2}^{\text{ox}}[M'_s(\text{CO})_2] + \beta\{M'_sL'\} P_L(L)}{P_L(L')} \quad (17)$$

Substitution for $E_s\{M'_sL\}$ and for $\beta\{M'_sL\}$ in eqn. 6 from eqns. 14 and 17, respectively, and rearrangement gives:

$$E_{1/2}^{\text{ox}}[M'_sL_2] = \left[1 - \frac{P_L(L)}{P_L(L')} \right]^2 E_{1/2}^{\text{ox}}[M'_s(\text{CO})_2] + \left[\frac{2P_L(L)}{P_L(L')} - \frac{P_L^2(L)}{P_L^2(L')} \right] E_s\{M'_sL'\} + \frac{P_L^2(L)}{P_L(L')} \beta\{M'_sL'\} \quad (18)$$

This is an equation which allows one to estimate $E_{1/2}^{\text{ox}}$ of any member of the *trans*- $[M'_sL_2]$ series (M'_s is a square planar 14-electron binding site), provided $E_{1/2}^{\text{ox}}$ of the dicarbonyl complex, *trans*- $[M'_s(\text{CO})_2]$, of this series is known, as well as the E_s , β parameters of a related 16-electron quadrangular pyramid (with the common square planar moiety, M'_s), $\{M'_sL'\}$. The ligand parameters $P_L(L)$ and $P_L(L')$ have also to be known. It was also assumed, as in the original proposal [6], that the $P_L(L)$ and $P_L(L')$ values were constant.

In the derivation of this expression, a sequential relationship was established among the following 16-electron metal sites: $\{M'_sL\}$, $\{M'_s(\text{CO})\}$ and the auxiliary and known $\{M'_sL'\}$ site. Hence, incidentally, it is also possible to estimate the E_s and β parameters for the new $\{M'_sL\}$ and $\{M'_s(\text{CO})\}$ metal sites (by applying eqns. 14, 17, and 9, 12), see section (c).

As noted above, the $P_L(L)$ value was assumed to be independent of the metal binding site. However, isocyanides (whose geometry is dependent on the electron-richness of this site) exhibit P_L values when binding $\{\text{ReCl}(\text{dppf})_2\}$ which differ by *ca.* 0.3 V from the corresponding values when they ligate the less electron-rich $\{\text{Cr}(\text{CO})_5\}$ site [3]. The dependence of the ligand P_L parameter on the electron-richness of the metal site may reflect a general behaviour presented by isocyanides and other ligands (*e.g.*, NO, N_2R) whose geometry is also dependent on the electron-richness of the binding site.

If this dependence is taken into account, the expression 18 has to be replaced by a more complicated one, with different $P_L(L)$ values corresponding to the various metal sites involved in its derivation.

Hence, $P_L(L)$ in eqns. 6, 8 and 16 should be replaced by $P_L(L)\{M'_sL\}$, $P_L(L)\{M'_s(\text{CO})\}$ and $P_L(L)\{M'_sL'\}$, respectively, thus expressing its value is associated to the concerned metal site.

In eqns. 13 and 14, $P_L(L)$ should be $P_L(L)\{M'_s(\text{CO})\}$.

Hence, from the new eqns. 15, 16 and 14, and upon rearrangement, one obtains:

$$\beta\{M'_sL\} = \frac{\left[1 - \frac{P_L(L)\{M'_s(\text{CO})\}}{P_L(L')} \right] E_s\{M'_sL'\} - \left[1 - \frac{P_L(L)\{M'_s(\text{CO})\}}{P_L(L')} \right] E_{1/2}^{\text{ox}}[M'_s(\text{CO})_2]}{P_L(L')} + \frac{\beta\{M'_sL'\} \times P_L(L)\{M'_sL'\}}{P_L(L')} \quad (19)$$

This expression 19 should replace eqn. 17.

Substitution for $E_s\{M'_sL\}$ and for $\beta\{M'_sL\}$ in the new eqn. 6 – with $P_L(L)\{M'_sL\}$ – from the new eqn. 14 – with $P_L(L)\{M'_s(\text{CO})\}$ – and the eqn. 19, and rearrangement gives:

$$\begin{aligned}
E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}_2] = & \left[1 - \frac{P_L(\text{L})\{\text{M}'_s(\text{CO})\} + P_L(\text{L})\{\text{M}'_s\text{L}\}}{P_L(\text{L}')} + \frac{P_L(\text{L})\{\text{M}'_s\text{L}\} P_L(\text{L})\{\text{M}'_s(\text{CO})\}}{P_L^2(\text{L}')} \right] \\
& \times E_{1/2}^{\text{ox}}[\text{M}'_s(\text{CO})_2] + \left[\frac{P_L(\text{L})\{\text{M}'_s(\text{CO})\} + P_L(\text{L})\{\text{M}'_s\text{L}\}}{P_L(\text{L}')} - \frac{P_L(\text{L})\{\text{M}'_s\text{L}\} P_L(\text{L})\{\text{M}'_s(\text{CO})\}}{P_L^2(\text{L}')} \right] \\
& \times E_s\{\text{M}'_s\text{L}'\} + \frac{P_L(\text{L})\{\text{M}'_s\text{L}\} P_L(\text{L})\{\text{M}'_s\text{L}'\}}{P_L(\text{L}')} \beta\{\text{M}'_s\text{L}'\} \quad (20)
\end{aligned}$$

which is a more general equation than 18 but presents a greater complexity. It is valid for the cases when the ligand $P_L(\text{L})$ parameter depends on the nature of the metal binding site and its application to estimate $E_{1/2}^{\text{ox}}[\text{M}'_s\text{L}_2]$ requires the knowledge of $P_L(\text{L})$ when L binds $\{\text{M}'_s(\text{CO})\}$, $\{\text{M}'_s\text{L}\}$ and $\{\text{M}'_s\text{L}'\}$. It was, however, assumed that $P_L(\text{L}')$ was constant by considering the same value for both $\{\text{M}'_s(\text{CO})\}$ (eqn. 10) and $\{\text{M}'_s\text{L}\}$ (eqn. 15) metal sites; if $P_L(\text{L}')$ differs at these centres, a somewhat more complex expression than 20 may be derived in an analogous way.

(b) Prediction of $E_{1/2}^{\text{ox}}[\text{Re}(\text{CNR})_2(\text{dppe})_2]^+$ from the Knowledge of E_s and β of the $\{\text{ReCl}(\text{dppe})_2\}$ Metal Site

The validity of the expression 20 was tested by estimating $E_{1/2}^{\text{ox}}[\text{Re}(\text{CNR})_2(\text{dppe})_2]^+$, with the new 14-electron metal site $\{\text{Re}(\text{dppe})_2\}^+$, from the knowledge [3] of the 16-electron $\{\text{ReCl}(\text{dppe})_2\}$ metal centre which was taken as the auxiliary $\{\text{M}'_s\text{L}'\}$ site ($E_s = +0.68$ V, $\beta = 3.4$). The comparison of the estimated $E_{1/2}^{\text{ox}}$ values with those obtained experimentally would allow to get some information on the validity of eqn. 20.

The redox properties of the series *trans*-[ReClL(dppe)₂] (L = CNR, CO, N₂) were previously quoted [3], and from the plot of $E_{1/2}^{\text{ox}}$ versus P_L it was proposed [3] that, when binding the $\{\text{ReCl}(\text{dppe})_2\}$ site, the isocyanides have P_L values *ca.* +0.3 V higher than when bound to the less electron-rich $\{\text{Cr}(\text{CO})_5\}$ site where they display a linear geometry. From the same plot a more precise correlation (eqn. 21) is now proposed and the P_L values are given in Table IV.

$$P_L(\text{CNR})\{\text{ReCl}(\text{dppe})_2\} = P_L(\text{CNR})\{\text{Cr}(\text{CO})_5\} + 0.26 \quad (21)$$

The $P_L(\text{L})\{\text{M}'_s\text{L}'\}$ values correspond to the quoted $P_L(\text{CNR})\{\text{ReCl}(\text{dppe})_2\}$.

The sites $\{\text{M}'_s(\text{CO})\}$ and $\{\text{M}'_s\text{L}\}$ are now the cationic $\{\text{Re}(\text{CO})(\text{dppe})_2\}^+$ and $\{\text{ReL}(\text{dppe})_2\}^+$ centres, with a considerable weaker electron-richness than the neutral $\{\text{ReCl}(\text{dppe})_2\}$ site. Moreover, the ligands CO and L (isocyanide) present a much weaker net electron-donor character than Cl, as evidenced by their P_L values, *e.g.* [6]: $P_L(\text{CO}) = 0.00$, $P_L(\text{linear CNMe}) = -0.43$, $P_L(\text{Cl}^-) = -1.19$ V. Hence, the

TABLE IV. Ligand Parameters P_L for Isocyanides at the $\{\text{ReCl}(\text{dppe})_2\}$ and $\{\text{Cr}(\text{CO})_5\}$ Sites (Values in Volt ± 0.02).

CNR	$P_L(\text{CNR})\text{-}\{\text{ReCl}(\text{dppe})_2\}$	$P_L(\text{CNR})\text{-}\{\text{Cr}(\text{CO})_5\} = P_L^i(\text{CNR})$
CNMe	-0.17	-0.43
CNBU ^t	-0.18	-0.44
CNC ₆ H ₄ CH ₃ -4	-0.13	-0.39
CNC ₆ H ₄ CH ₃ -2	-0.12	-0.38
CNC ₆ H ₄ OCH ₃ -4	-0.14	-0.40
CNC ₆ H ₄ Cl-4	-0.11	-0.37
CNC ₆ H ₃ Cl ₂ -2,6	-0.07	-0.33

isocyanides are considered to be linear, at least as a first approximation, when binding the cationic $\{\text{Re}(\text{CO})(\text{dppe})_2\}^+$, and $\{\text{ReL}(\text{dppe})_2\}^+$ sites. The corresponding P_L values for the linear isocyanides, $P_L(\text{CNR})\{\text{Cr}(\text{CO})_5\}$ are then denoted by $P_L^i(\text{CNR})$.

Hence, eqn. 20 becomes, upon rearrangement:

$$\begin{aligned}
E_{1/2}^{\text{ox}}[\text{Re}(\text{CNR})_2(\text{dppe})_2]^+ & = \left[1 - \frac{P_L^i(\text{CNR})}{P_L(\text{Cl}^-)} \right]^2 E_{1/2}^{\text{ox}}[\text{Re}(\text{CO})_2(\text{dppe})_2]^+ \\
& + \left\{ \frac{P_L^i(\text{CNR})}{P_L(\text{Cl}^-)} \left[2 - \frac{P_L(\text{CNR})}{P_L(\text{Cl}^-)} \right] \right\} \\
& \times E_s\{\text{ReCl}(\text{dppe})_2\} \\
& + \frac{P_L^i(\text{CNR}) P_L(\text{CNR})\{\text{ReCl}(\text{dppe})_2\}}{P_L(\text{Cl}^-)} \\
& \times \beta\{\text{ReCl}(\text{dppe})_2\} \quad (22)
\end{aligned}$$

For this expression, the known values of the parameters are as follows: $P_L^i(\text{CNR})$ and $P_L(\text{CNR})\text{-}\{\text{ReCl}(\text{dppe})_2\}$ are given in Table I [3], $P_L(\text{Cl}^-) = -1.19$ [6], $E_s\{\text{ReCl}(\text{dppe})_2\} = +0.68$ V [3], $\beta\{\text{ReCl}(\text{dppe})_2\} = 3.4$ [3] and $E_{1/2}^{\text{ox}}[\text{Re}(\text{CO})_2(\text{dppe})_2]^+ = +1.42$ V (experimentally measured in this work).

The values of $E_{1/2}^{\text{ox}}$ of the *trans*-[Re(CNR)₂(dppe)₂]⁺ complexes (for various isocyanides) were then estimated by application of the expression 22,

and they compare well (within less than 7% difference) with those obtained experimentally (Table V). This close agreement constitutes evidence in favour of the approach used in the derivation of the general eqn. 20 and in favour of the assumption that isocyanides are linear when bound to the cationic $\{\text{Re}(\text{CO})(\text{dppe})_2\}^+$ and $\{\text{Re}(\text{CNR})(\text{dppe})_2\}^+$ sites (their P_L values being equal to those known when they ligate $\{\text{Cr}(\text{CO})_5\}$).

TABLE V. Estimated Values of $E_{1/2}^{\text{ox}}[\text{Re}(\text{CNR})_2(\text{dppe})_2]\text{-BF}_4$ (by application of eqn. 22) and Comparison with those Obtained Experimentally.

R	$E_{1/2}^{\text{ox}}[\text{Re}(\text{CNR})_2(\text{dppe})_2]\text{BF}_4$		Difference (%)
	Estimated (eqn. 22)	Experimental	
Me	0.77	0.79	2.6
Bu [†]	0.75	0.80	6.7
C ₆ H ₄ OMe-4	0.85	0.88	3.4
C ₆ H ₄ Me-4	0.87	0.93	6.9
C ₆ H ₄ Cl-4	0.92	0.98	6.5
C ₆ H ₃ Cl ₂ -2,6	1.05	1.05	5.0

(c) Estimate of E_s and β Parameters for the 16-Electron Square Pyramid $\{\text{ReL}(\text{dppe})_2\}^+$ Centres (L = CO or CNR)

As mentioned above, the involvement of the auxiliary $\{\text{Re}(\text{CO})(\text{dppe})_2\}^+$ and $\{\text{Re}(\text{CNR})(\text{dppe})_2\}^+$ metal centres in the derivation of the expression 18 to estimate $E_{1/2}^{\text{ox}}[\text{Re}(\text{CNR})_2(\text{dppe})_2]^+$ allows us to evaluate the E_s and β parameters for those centres through the application of eqns. 9, 12 (for the CO site) and 14, 17 (for the isocyanide centres).

The values estimated in this way of E_s and β for these centres, and those known for the related $\{\text{Re}(\text{N}_2)(\text{dppe})_2\}^+$ and $\{\text{ReCl}(\text{dppe})_2\}$ centres are shown in Table VI. One may observe that:

(i) All the cationic centres display an electron-rich character (E_s) and a polarisability (β) which are lower than those exhibited by the related neutral $\{\text{ReCl}(\text{dppe})_2\}$ centre.

(ii) The electron-richness and the polarisability of the $\{\text{ReL}(\text{dppe})_2\}^+$ centres follow the order $\text{L} = \text{Cl}^- > \text{alkylisocyanide} > \text{CNC}_6\text{H}_4\text{OMe-4} > \text{CNC}_6\text{H}_4\text{Me-4} > \text{CNC}_6\text{H}_4\text{Cl-4} > \text{CNC}_6\text{H}_3\text{Cl}_2\text{-2,6} > \text{CO}$ which parallels the net electron-donor character of the L ligand as measured by P_L : an increase of the net electron-donor ability of this ligand (*i.e.*, a decrease of P_L) results in an enhancement of both the electron-rich character of the metal centre and its polarisability; similar trends have been observed [6] for the molybdenum series $\{\text{MoL}(\text{dppe})_2\}$ (L = N_3^- , NCPH, N_2 , CO, NO^+). Hence, the sensitivity (measured by β) of the energy of the redox orbital to

a change of a ligand increases with the net electron-donor character of the ligand (L) in *trans* position.

(iii) The dinitrogen $\{\text{Re}(\text{N}_2)(\text{dppe})_2\}^+$ centre does not follow the general trend and exhibits an electron-richness ($E_s = 1.20$ V) which is somewhat higher than that expected (E_s ca. 1.3 ~ 1.4 V) on the basis of the behaviour presented by the analogous CO and CNR centres. This may suggest that N_2 , when binding the cationic $\{\text{Re}(\text{dppe})_2\}^+$ centre, behaves as a weaker net electron acceptor than expected from the behaviour of the related CO and CNR ligands, in agreement with a similar observation quoted [5] for N_2 when binding the related $\{\text{ReCl}(\text{dppe})_2\}$ centre.

TABLE VI. Estimated E_s and β Parameters for the 16-Electron Square Pyramid $\{\text{ReL}(\text{dppe})_2\}^+$ Centres.

L	E_s	β	P_L^a
CO	+1.42 ^b	+0.62	0
CNC ₆ H ₃ Cl ₂ -2,6	1.29	0.72	-0.33
CNC ₆ H ₄ Cl-4	1.29	0.83	-0.37
CNC ₆ H ₄ Me-4	1.27	0.86	-0.39
CNC ₆ H ₄ OMe-4	1.23	0.87	-0.40
CNBu [†]	1.23	0.99	-0.44
CNMe	1.19	0.93	-0.43
$\text{N}_2^{\text{a,c}}$	1.20	0.74	-0.07
$\text{Cl}^{\text{a,d}}$	0.68	3.4	-1.19

^aIncluded for comparative purposes. ^bMeasured experimentally. ^cRef. [6]. ^dRef. [3].

The estimated values of $E_s\{\text{Re}(\text{CNR})(\text{dppe})_2\}^+$ given in Table VI correspond, by definition, to $E_{1/2}^{\text{ox}}$ of the corresponding mixed carbonyl-isocyanide complexes *trans*- $\{\text{Re}(\text{CO})(\text{CNR})(\text{dppe})_2\}^+$, and, by applying eqn. 2, it is possible to evaluate $E_{1/2}^{\text{ox}}$ of any isocyanide complex of the type *trans*- $\{\text{Re}(\text{L})(\text{CNR})(\text{dppe})_2\}^+$ provided P_L is known for the L co-ligand.

Conclusions

The application of the general expression 20 to the prediction of $E_{1/2}^{\text{ox}}$ for 18-electron octahedral *trans*- $[\text{M}'_s\text{L}_2]$ complexes requires, as mentioned above, the knowledge of the electrochemical parameters (E_s , β) of a suitable auxiliary 16-electron square pyramid metal site, $\{\text{M}'_s\text{L}'\}$, which should include the basic square planar 14-electron metal site $\{\text{M}'_s\}$. This expression is not a simple function of the ligand parameter: it is also necessary to know the values of P_L for the ligand L when it binds to three distinct metal sites, $\{\text{M}'_s\text{L}'\}$, $\{\text{M}'_s(\text{CO})\}$ and $\{\text{M}'_s\text{L}'\}$. Moreover, $P_L(\text{L}')$ should be the same at both $\{\text{M}'_s(\text{CO})\}$ and $\{\text{M}'_s\text{L}'\}$ sites although this equation may

be adapted for the cases when this requirement is not obeyed.

For the ligands (L) this parameter is constant (independent of the metal site), eqn. 20 assumes the simplified form 18.

However, in the case of P_L dependence on the electron-richness of the metal-site (e.g., for isocyanide ligands), the more general expression 20 has to be used. The estimated value $E_{1/2}^{ox}$ is appreciably sensitive to the particular values of $P_L(L)$ and these have to be known with high accuracy. This is also a main limitation on the use of this equation.

In spite of these limitations, the approach of this study appears to succeed in the prediction of $E_{1/2}^{ox}$ for complexes of the type $[M'_sL_2]$, and also allows the estimation of E_s and β for the related $\{M'_sL\}$ and $\{M'_s(CO)\}$ centres.

Although the expressions appear complex, they involve very simple calculations. The necessity for auxiliary series of complexes could be avoided if the square planar 14-electron metal centre, *trans*-[Cr(CO)₄], formed a series of complexes of the type *trans*-[Cr(CO)₄L₂].

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References

- 1 A. J. L. Pombeiro, *Rev. Port. Quím.*, **26**, 30 (1984); A. J. L. Pombeiro, *V Int. Symp. Nitrogen Fixation*, Noordwijkerhout, The Netherlands, 2-2, 1983.
- 2 J. Chatt, C. M. Elson, A. J. L. Pombeiro, R. L. Richards and G. H. D. Royston, *J. Chem. Soc., Dalton Trans.*, 165 (1978).
- 3 A. J. L. Pombeiro, C. J. Pickett and R. L. Richards, *J. Organomet. Chem.*, **224**, 285 (1982).
- 4 A. J. L. Pombeiro and R. L. Richards, *J. Organomet. Chem.*, **179**, 459 (1979).
- 5 A. J. L. Pombeiro, *Rev. Port. Quím.*, **23**, 179 (1981).
- 6 J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 2032 (1980); J. Chatt, *Coord. Chem. Rev.*, **43**, 337 (1982).
- 7 C. J. Pickett and D. Pletcher, *J. Organomet. Chem.*, **102**, 327 (1975).
- 8 J. Chatt, J. R. Dilworth and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 612 (1973).
- 9 R. E. Schuster, J. E. Scott and J. Casanova Jr., *Org. Synth.*, **46**, 75 (1966); I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer and K. Offermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 472 (1965).
- 10 G. J. Leigh, R. H. Morris, C. J. Pickett, D. R. Stanley and J. Chatt, *J. Chem. Soc., Dalton Trans.*, 800 (1981).
- 11 M. Freni, V. Valenti and D. Giusto, *J. Inorg. Nucl. Chem.*, **27**, 2635 (1965).
- 12 E. Bordignon, U. Croatto, U. Mazzi and A. A. Orio, *Inorg. Chem.*, 935 (1974).
- 13 J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1246 (1972); M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 1743 (1973).
- 14 A. J. L. Pombeiro, *Port. Electrochim. Acta* (Proc. III Nat. Electrochem. Meeting, Lisbon), 165 (1983).