

**Redox Properties and Ligand Effects for the
Dinitrogen or Carbon Monoxide Complexes *trans*-
[ReXLL'₄] (X = N₃, NCO or NCS; L = N₂ or CO;
L' = 1/2 Ph₂PCH₂CH₂PPh₂ or PMe₂Ph)**

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ABSTRACT

By cyclic voltammetry, at a Pt electrode, complexes *trans*-[ReXLL'₄] (X = N₃, NCO or NCS; L = N₂ or CO; L' = 1/2 Ph₂PCH₂CH₂PPh₂ or PMe₂Ph), in aprotic medium, undergo a first *quasi*-reversible single electron anodic process at E^{ox}_{1/2} in the range 0.12-0.36 (L = N₂) or 0.55-0.73 V vs. SCE (L = CO). Within each of these series, the variation of the oxidation potential is determined by the effect of the pseudo-halide ligand (X) (E^{ox}_{1/2} increases in the order N₃ < NCO < NCS), following their net electron donor/acceptor ability, as measured by the P_L ligand parameter (N₃⁻ > NCO⁻ > NCS⁻ >> N₂ > CO), and the observed values of E^{ox}_{1/2} for the dinitrogen complexes are shown to agree with those predicted on the basis of the additive E_L parameter. The values of the electron-richness parameter, E_S, for the metal sites *trans*-{ReX(dppe)₂} (X = N₃, NCO or NCS) have also been obtained, and linear correlations between E^{ox}_{1/2} and IR ν(N₂) or ν(CO) frequencies have been recognised.

Results and discussion

The electrochemical behaviour of the series of novel 18-electron octahedral complexes *trans*-[ReXLL'₄] [1] has been studied by cyclic voltammetry, in 0.2M [Bu₄N][BF₄]/CH₂Cl₂, at a Pt disc electrode.

Each of these complexes displays a first *quasi*-reversible or reversible anodic wave(I) followed, at a higher potential, by another, irreversible or reversible, oxidation wave(II).

A summary of the cyclic voltammetric data for these complexes is given in Table 1, where the E^{ox}_{1/2} (or E^{ox}_{p/2}) values are quoted relative to the saturated calomel electrode (SCE) by using , as internal standard, the ferrocene/ferricinium redox pair which presents E^{ox}_{1/2} = 0.545 V vs. SCE in that medium.

Table 1 - Summary of CV data for complexes *trans*-[ReXLL'₄] (X = N₃, NCO, C[†] or NCS) and estimated first oxidation potential (E_{calc.}) on the basis of the E_L ligand parameter

complex	I _E ^{ox} * 1/2	II _E ^{ox} *† 1/2	E _{calc.} * (eq. 1)	ΣE _L **
[ReX(N ₂)(dppe) ₂]	0.16	(0.82)	0.15	1.82
	0.36	1.24	0.35	2.06
[ReX(N ₂)(PMe ₂ Ph) ₄]	0.12	(0.75)	0.11	1.74
	0.28	1.14	0.27	1.98
[ReX(CO)(dppe) ₂]	0.55	(1.13)	0.40	2.13
	0.73	1.40	0.59	2.37

‡ Known complexes (considered for comparison)

* V vs. SCE

† The values in brackets correspond to the half peak oxidation potential

** V vs. NHE

The first half-wave oxidation potential (I_E^{ox}_{1/2}) of the complexes clearly depends on their composition, the dinitrogen compounds with dppe co-ligands oxidizing at a much less anodic potential (0.12-0.36 V) than their corresponding carbonyls (0.55-0.73 V). Moreover, the dimethylphenylphosphine complexes also present lower I_E^{ox}_{1/2} values than those for the analogous dppe species, whereas, for each of the series, this oxidation potential increases in the order N₃ < NCO ≈ Cl < NCS, i.e., from 0.16 to 0.36 V for *trans*-[ReX(N₂)(dppe)₂], from 0.12 to 0.28 V for *trans*-[ReX(N₂)(PMe₂Ph)₄], and from 0.55 to 0.73 V for *trans*-[ReX(CO)(dppe)₂].

Table 2 - Ligand parameters (P_L [2] and E_L [3])

Ligand	P _L /V	E _L /V vs. NHE
N ₃	-1.26	-0.30
Cl	-1.19	-0.24
NCO	-1.16	-0.25
NCS	-0.88	-0.06
PMe ₂ Ph	-0.46*	0.34
dppe	-0.43*	0.36
N ₂	-0.07	0.68
CO	0	0.99

* Estimated from P_L = 1.17E_L - 0.86 [3a]

These trends follow the expected net electron donor/acceptor ability of those ligands, as measured by the P_L ligand parameter [2] (N₃⁻ > NCO⁻ ≈ Cl⁻ > NCS⁻ > PMe₂Ph > dppe > N₂ > CO) (Table 2).

The "electron-richness" electrochemical parameter (E_S) of the {ReX(dppe)₂} metal centers (X = N₃, NCO or NCS), defined [2] as the oxidation potential of their carbonyl complexes were also obtained for the first time in this study and are quoted in Table 3. {Re(N₃)(dppe)₂} and {Re(NCO)(dppe)₂} are more electron-rich than {ReCl(dppe)₂}, whereas {Re(NCS)(dppe)₂} is less electron-rich than the latter. However, those rhenium metal centers are much less electron rich than the isoelectronic Mo(0) anionic sites as indicated on Table 3.

Table 3 - Metal site "electron-richness" parameter (E_S)

Metal center	E _S	Metal center*	E _S
{Re(N ₃)(dppe) ₂ }	0.55	{Mo(N ₃)(dppe) ₂ } ⁻	-1.22
{Re(NCO)(dppe) ₂ }	0.63		
{ReCl(dppe) ₂ }	0.66		
{Re(NCS)(dppe) ₂ }	0.73	{Mo(NCS)(dppe) ₂ } ⁻	-0.78

* Included for comparison (data from ref. [4])

Another electrochemical ligand parameter, E_L, has been recently proposed [3a] to generate a series which may be used to estimate the redox potential of complexes by assuming an additive contribution of all their ligands. The general empirical relationship is given by equation(1) (in volts vs. NHE), where S_M and I_M depend on the metal, the redox couple, the spin state and the stereochemistry. In the case of Re^{III/I}, the values of S_M and I_M are 0.76 and -0.95 [3b], respectively.

$$E_{\text{calc.}} = S_M \Sigma E_L + I_M \quad (1)$$

The estimated half-wave potentials of the complexes of the present study, corrected for the SCE reference, are given in Table 1. For the dinitrogen complexes they are in close agreement with the experimentally observed values, but for the carbonyl compounds they lie ca. 0.15 V below the latter, thus suggesting that E_L for the CO ligand should be corrected to a slightly higher value, as indicated [3a] in other systems, possibly as a result of the high π-electron donor ability of our metal centers to this ligand.

Grossly linear relationships, expressed by eqs. (2) and (3) (R = 0.76 and R = 0.98, respectively) appear to occur between E^{ox}_{1/2} and ν(N₂) or ν(CO)

for complexes $[\text{ReX}(\text{N}_2)(\text{dppe})_2]$ and $[\text{ReX}(\text{CO})(\text{dppe})_2]$, respectively, as shown in Fig. 1. A decrease in $E^{\text{ox}}_{1/2}$ (corresponding to an increase of the net electron donor character of the X ligand) is usually followed by a decrease of $\nu(\text{N}_2)$ as a result of the enhancement of the π -electron release from the metal to the dinitrogen ligand.

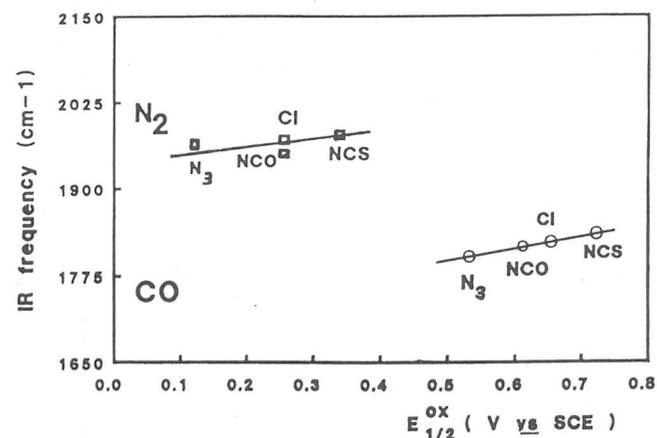


Fig. 1 Plots of the $\nu(\text{N}_2)$ and $\nu(\text{CO})$ frequencies against the half-wave oxidation potential for the N_2 and CO series of complexes with dppe co-ligands.

$$\nu(\text{N}_2) = 100 E_{1/2}^{\text{ox}} + 1949 \quad (2)$$

$$\nu(\text{CO}) = 87 E_{1/2}^{\text{ox}} + 1953 \quad (3)$$

Moreover, these two equations can be applied, in suitable cases, to predict $\nu(\text{N}_2)$, $\nu(\text{CO})$ or the redox potential of adequate complexes.

Final comments

We have successfully tested the application of the P_L and E_L concepts to Re centers which are electron-rich and able to bind N_2 . Moreover, they provide examples of very rare dinitrogen complexes in which the N_2 bond is stabilized by a pseudo-halide ligand which can interact with the active site of nitrogenase. The electronic effects of such ligands on the redox properties of

the complexes have also been investigated, aiming to get an insight into a better knowledge of their interaction with the binding sites, a subject of significance to the understanding of the enzyme function.

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