

**Scheme 1** - Redox behaviour and interconversion of the vinylidene complexes  $\text{trans-}[\text{ReCl}(\text{=C=CHR})(\text{dppe})_2]$  and the derived carbyne compounds  $\text{trans-}[\text{ReCl}(\text{=C-CH}_2\text{R})(\text{dppe})_2]^+$ .

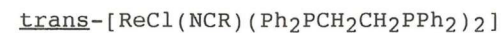
#### ACKNOWLEDGMENTS

This work has been partially supported by the Junta Nacional de Investigação Científica e Tecnológica and the Instituto Nacional de Investigação Científica.

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#### REDOX PROPERTIES OF THE NITRILE COMPLEXES



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#### Abstract

The nitrile complexes  $\text{trans-}[\text{ReCl}(\text{NCR})(\text{dppe})_2]$  ( $1; \text{R}=\text{alkyl}$  or aryl,  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) undergo, in tetrahydrofuran, by cyclic voltammetry and at a Pt electrode, two successive single-electron reversible (or quasi-reversible) oxidations and, from the values of the half-wave oxidation potential ( $E_{1/2}^{\text{OX}}$ ) of the first anodic wave, the electrochemical  $P_L$  ligand parameter was estimated for the nitrile ligands indicating that they behave as better net electron donors than isocyanides, dinitrogen or carbonyl ligands. For the aromatic nitrile complexes,  $E_{1/2}^{\text{OX}}$  is shown to vary linearly with the Hammett's  $\sigma_p$  constant of the phenyl substituent.

### Results and discussion

Within our interest on the investigation, by electrochemical methods, of ligand effects on the redox potential of transition metal complexes, we have been studying the redox behaviour of series of isocyanide and alkyne-derived vinylidene and allene compounds, namely of the types trans-[M(CNR)<sub>2</sub>(dppe)<sub>2</sub>] (M = Mo or W, dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) [1], trans-[ReClL(dppe)<sub>2</sub>] (L = CNR [2], C=CHR [3] or phenylallene [3]), trans-[Re(CNR)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup>[4] or trans-[Re(CNMe)L(dppe)<sub>2</sub>]<sup>+</sup> (L = CNR or NCMe) [5], as well as of complex products of their protonations [3].

Redox potential-structure-composition relationships have been recognized for these complexes and corresponding electrochemical ligand and metal-site parameters have been estimated [2-6]: P<sub>L</sub> ligand parameter (a measure of the net electron π-acceptor/σ-donor character of the ligand), E<sub>S</sub> and β (electron-richness and polarisability of the binding metal site, respectively), which are related or defined by eqs. 1-3 [7].

$$E_{1/2}^{\text{OX}} [M_S L] = E_S + \beta \cdot P_L \quad (1)$$

$$E_S = E_{1/2}^{\text{OX}} [M_S (\text{CO})] \quad (2)$$

$$P_L = E_{1/2}^{\text{OX}} [\text{Cr}(\text{CO})_5 L] - E_{1/2}^{\text{OX}} [\text{Cr}(\text{CO})_6] \quad (3)$$

However, nitrile ligands remain virtually unexplored and

therefore we have initiated the electrochemical study of the nitrile complexes trans-[ReCl(NCR)(dppe)<sub>2</sub>](1, R=alkyl or aryl) which are analogous to the above mentioned isocyanide compounds of Re(I) and present a metal site, {ReCl(dppe)<sub>2</sub>}, whose E<sub>S</sub> and β parameters have already been estimated [2].

Complexes (1) undergo, in thf/o.2M [Bu<sub>4</sub>N][BF<sub>4</sub>] and at a Pt electrode, by cyclic voltammetry, two successive single-electron reversible (or quasi-reversible) oxidations with half-wave oxidation potential in the ranges -0.20 to -0.03 V and +0.61 to 0.78 V vs s.c.e..

E<sub>1/2</sub><sup>OX</sup> for the first anodic wave lies below that quoted [2] for related isocyanide (+0.06 to 0.30 V), dinitrogen (+0.28 V) or carbonyl (+0.68 V) complexes, indicating that nitriles behave as better net electron donors than these ligands.

The P<sub>L</sub> ligand parameter was also estimated for the nitrile ligands, by using eqs. (1) and (2) applied to complexes (1) and from the knowledge [2] of E<sub>S</sub> (0.68 V) and β (3.4) for the binding centre {ReCl(dppe)<sub>2</sub>}.

Equations (4) and (5) were thus obtained and the derived P<sub>L</sub> values for the nitrile ligands lie in the range -0.26 to -0.21 V.

As expected, these values are lower than those known [2] for isocyanides at the same Re(I) site, in agreement with the weaker net electron  $\pi$ -acceptor/ $\sigma$ -donor ability of nitriles compared to isocyanides.

$$E_{1/2}^{\text{OX}} [\text{ReCl}(\text{NCR})(\text{dppe})_2] = E_S \{ \text{ReCl}(\text{dppe})_2 \} + \beta \{ \text{ReCl}(\text{dppe})_2 \} \cdot P_L(\text{NCR}) \quad (4)$$

$$P_L(\text{NCR}) = \frac{E_{1/2}^{\text{OX}}[\text{ReCl}(\text{NCR})(\text{dppe})_2] - 0.68}{3.4} \quad (5)$$

For the aryl nitrile complexes, a linear relationship appears to occur between  $E_{1/2}^{\text{OX}}$  and the Hammett's  $\sigma_p$  constant for the phenyl substituent (Fig. ): an increase of the electron withdrawing ability of the latter (by combined resonance and inductive effects) leads to a stabilization of the HOMO and therefore to an increase of the oxidation potential, as is known [1,2] for related isocyanide complexes.

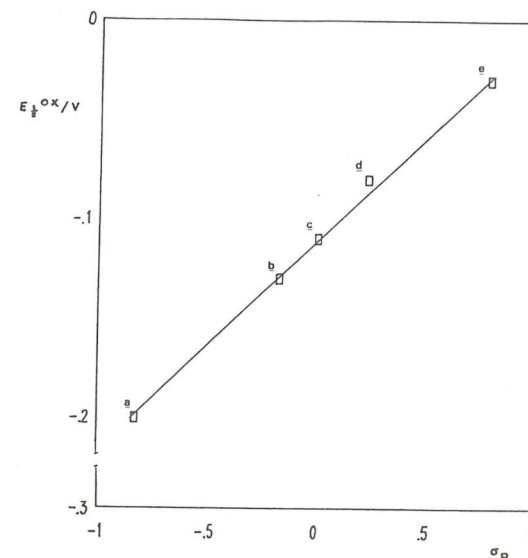


Fig. - Plot of  $E_{1/2}^{\text{OX}}$  vs. Hammett's  $\sigma_p$  constant for the aryl nitrile complexes trans-[ReCl(NCC<sub>6</sub>H<sub>4</sub>X-4)(dppe)<sub>2</sub>].

[X = NEt<sub>2</sub> (a), Me (b), H (c), Cl (d) and NO<sub>2</sub> (e)]

#### Acknowledgements

This work was partially supported by the J.N.I.C.T. and the I.N.I.C..

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REDOX PROPERTIES OF DINITROGEN AND MIXED DINITROGEN-ISOCYANIDE  
COMPLEXES OF RHENIUM WITH PHOSPHORUS LIGANDS

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Abstract

The electrochemical behaviour of mer-[ReCl(N<sub>2</sub>)L {P(OMe)<sub>3</sub>}<sub>3</sub>] (1, L = CNR or PPh<sub>3</sub>), trans-[ReCl(N<sub>2</sub>) {P(OMe)<sub>2</sub>Ph}<sub>4</sub>] (2), [ReCl(N<sub>2</sub>) (CNMe)(PPh<sub>3</sub>){P(OEt)<sub>3</sub>}<sub>2</sub>] (3) and [ReCl(N<sub>2</sub>)(CNMe)<sub>2</sub>(PBu<sub>2</sub>Ph)<sub>2</sub>] (4) was studied by cyclic voltammetry and controlled potential electrolysis, in tetrahydrofuran (or NCMe), at a Pt electrode. They undergo a one-electron quasi-reversible oxidation and, by comparing the values of E<sub>1/2</sub><sup>OX</sup> (also with others reported in the literature), the following order of the π - acceptor/σ-donor ability was established: CO > CNMe, CNet, CNBu<sup>t</sup> > P(OMe)<sub>3</sub> > P(OMe)<sub>2</sub>Ph > PPh<sub>3</sub>, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> > PMe<sub>2</sub>Ph.

A grossly linear correlation was recognized between E<sub>1/2</sub><sup>OX</sup> and  $\nu(\text{N} \equiv \text{N})$ , allowing the assignment of  $\nu(\text{N}=\text{N})$  and  $\nu(\text{C}=\text{N})$  for