

K'accounts for the potential of the reference electrode, and  $c_I$  is the concentration of I.

From the above equation it can be easily shown that the results obtained at the foot of the wave agree with the theoretical predictions. In the same way are explained the logarithmic analyses and the variation of the half-wave potential with both the pH and the concentration of proton-donor.

Above pH 8 the polarographic and kinetic parameters show that the reduction process is irreversible, being the rds the second one-electron transfer. The reaction orders with respect to I and to the  $H^+$  ion were 1 and zero, respectively. In the pH range 6-8, both the logarithmic analyses and the shape of the variation of the half-width of DP polarograms with the pH indicate the occurrence of the reduction of two species at very close potentials, and related by a protonation equilibrium. Since the reduction potential of the monohydrated species is much more negative, we can conclude that above pH 8 the electroactive species is the unprotonated form of I.

In this case, the i-E relationship at potentials corresponding to the foot of the wave reads:

$$i = 2FKK' c_I \exp[-(1+\beta)FE/RT] \quad (3)$$

and the proton-donors are not involved in the process, as is experimentally found.

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## REDOX PROPERTIES AND LIGAND EFFECTS OF SOME PHOSPHONIUM-FUNCTIONALIZED ISOCYANIDE COMPLEXES OF GROUP VI TRANSITION METAL CARBONYLS

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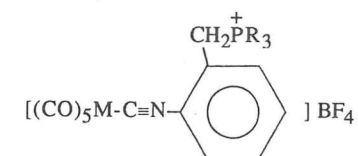
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### INTRODUCTION

Within our interest on the electrochemical investigation of the electron-donor/acceptor properties of isocyanide ligands  $C\equiv NR$  ( $R=H$ , alkyl, aryl or ferrocenyl-functionalized species) [1], we now report the anodic behaviour of the following complexes presenting phosphonium-functionalized isocyanides, which, to our knowledge, provides the first example of an electrochemical study of coordination compounds with such a type of ligands:



[M=Cr;  $R_3=Me_3$  (1) or  $Ph_2Bz$  (2). M=Mo;  $R_3=Ph_2Bz$  (3) or  $Ph_3$  (4). M=W;  $R_3=Ph_2Bz$  (5) or  $Ph_3$  (6)].

ANODIC BEHAVIOUR

Upon cyclic voltammetry, at a Pt electrode in NCMe / 0.2M [Bu<sub>4</sub>N] [BF<sub>4</sub>] they undergo an oxidation (which, in some cases, is fully reversible or presents at least some degree of reversibility) in the range 1.1-1.3 V vs. s.c.e. which commonly is followed, at a higher potential, by a second (irreversible) anodic process.

The first anodic wave corresponds to the metal (0/1+) oxidation and, at least for Cr, it appears to occur at values of half-wave oxidation potentials which are analogous to those found in related non-functionalized aromatic isocyanide complexes, e.g., [Cr(CO)<sub>5</sub>(CNPh)] (1.15 V) [2], thus suggesting that the phosphonium group has not a significant effect on the metal-centred anodic process, possibly as a result of its considerable distance to the metal.

P<sub>L</sub> and E<sub>L</sub> parameters for the phosphonium-functionalized isocyanide ligands

P<sub>L</sub> parameter

From the definition of the P<sub>L</sub> ligand parameter (eq. 1) [2], a measure of the net electron σ-donor/π-acceptor ability of a ligand, and taking into consideration the measured values of E<sub>1/2</sub><sup>ox</sup> for the Cr complexes (1) and (2) and the known [3] oxidation potential (E<sub>1/2</sub><sup>ox</sup> = 1.50 V) for [Cr(CO)<sub>6</sub>], that ligand parameter has been estimated for the following isocyanides: CNC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub><sup>+</sup>PR<sub>3</sub>-2 (R<sub>3</sub> = Me<sub>3</sub>, P<sub>L</sub> = -0.36; R<sub>3</sub> = Ph<sub>2</sub>Bz, P<sub>L</sub> = -0.30 V).

$$P_L = E_{1/2}^{ox} [Cr(CO)_5L] - E_{1/2}^{ox} [Cr(CO)_6] \quad (1)$$

Moreover, from the expected linear dependence of the oxidation potential on P<sub>L</sub> (eq.2), and by taking into account the measured E<sub>p</sub><sup>ox</sup> values for complexes (3) and (5) and those obtained from the literature for the related species [M(CO)<sub>5</sub>L] -- M = Mo or W; L = CO [3], I<sup>-</sup>, Br<sup>-</sup> or Cl<sup>-</sup> [4] -- as well as the P<sub>L</sub> values for the corresponding isocyanide and L ligands, one obtains the expressions (3) and (4) (with a correlation coefficient of 0.99).

$$E_{1/2}^{ox} = E_s + \beta \cdot P_L \quad (2)$$

$$E_p^{ox} [Mo(CO)_5L] = 1.51 + 0.85 P_L \quad (3)$$

$$E_p^{ox} [W(CO)_5L] = 1.55 + 0.88 P_L \quad (4)$$

From these expressions, and the measured oxidation potentials for complexes (4) and (6), we have obtained a P<sub>L</sub> value of -0.26V for CNC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub><sup>+</sup>PPh<sub>3</sub>-2. Therefore, according to their net electron-donor ability, the phosphonium functionalized isocyanides can be ordered, as expected, as follows:



E<sub>L</sub> parameter

Another ligand electrochemical parameter, E<sub>L</sub>, has been described recently [5] to generate a series which may be used to predict the redox potential of complexes by assuming an additive contribution of all their

ligands. The proposed empirically derived relationship can assume the general form indicated by the expression (5), where  $S_M$  and  $I_M$  depend upon the metal and redox couple, the spin state and stereochemistry, whereas  $(mx+m'y)$  is a correction for ligands with an extensive  $\pi$ -influence on the HOMO energy ( $m, m'$  -- number of CO and isocyanide ligands, in our case, which interact directly with the HOMO).

$$E^{OX} = S_M[\Sigma E_L + mx + m'y] + I_M \quad (5)$$

From the linear relationship (6), which has been experimentally observed [5], between this and the abovementioned  $P_L$  parameter, it was possible to estimate  $E_L$  for the isocyanides  $CNC_6H_4CH_2^+PR_3-2$ : 0.51 ( $R_3=Ph_3$ ), 0.48 ( $R_3=Ph_2Bz$ ) and 0.43 ( $R_3=Me_3$ ).

$$P_L = 1.17 E_L - 0.86 \quad (6)$$

Moreover the corresponding  $\gamma$  correction has then been estimated from eq. (5), and its magnitude (0.2-0.3) appears to increase with the  $\pi$ -acceptance of the phosphonium group, in accord with the expected dominant role of  $\pi$ -effects on such a correction (see above).

#### FINAL COMMENTS

This cyclic voltammetric study allowed, for the first time, the evaluation of the  $P_L$  and  $E_L$  electrochemical ligand parameters for phosphonium-functionalized isocyanides, as well as of the polarisability  $\beta$  parameter for the  $\{M(CO)_5\}$  ( $M = Mo$  or  $W$ ) metal centers.

Moreover, although not detailed in this report, cyclic voltammetry also appears to be a convenient tool to monitor the reactions of those isocyanide complexes with a base, such as  $Bu^nLi$  or  $[Bu_4N] OH$ , e.g., to form carbene compounds of the type  $[(CO)_5M = \overline{C}(NH)C_6H_4CPR_3-2]$  which are oxidized at a considerably lower oxidation potential (in the 0.63-0.87 V range).

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