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REDOX PROPERTIES OF THE DINITROGEN-CYANAMIDE COMPLEXES *trans*-[Mo(N_2)($NCNR_2$)($Ph_2PCH_2CH_2PPh_2$)$_2$]

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Abstract

The electrochemical behaviour, as studied by cyclic voltammetry and controlled potential electrolysis, of the dinitrogen-organocyanamide complexes *trans*-[Mo(N_2)($NCNR_2$)(dppe)$_2$] (**1**, R = Me; **2**, R = Et; dppe = $Ph_2PCH_2CH_2PPh_2$) is reported, and the electrochemical P_L ligand parameter for the cyanamides is estimated showing that they behave as effective net electron-donors with a remarkable stabilizing influence on the coordination of dinitrogen.

Key Words: Molybdenum complexes, dinitrogen, cyanamides, redox properties,
P_L electrochemical ligand parameter.

1. Introduction

Cyanamide (N≡C–NH_2) is an aminonitrile with interest in industry and in several areas of science, and in particular it has been recognized [1] as a substrate of nitrogenase, the reduction products being ammonia, methylamine and methane.

In spite of the versatile organic chemistry exhibited by this species [2], its coordination chemistry remains virtually unexplored, namely at N_2-binding metal sites. In this context, and in the pursuit of our interest in the study of alternative substrates of nitrogenase [3a-3c], we have previously demonstrated [3d] that $NCNH_2$ is reductively dehydrogenated to the cyanoimido form NCN(2-) by the electron-rich and readily oxidizable Mo(0) metal site at *trans*-[Mo(N_2)$_2$(dppe)$_2$], forming the bis(cyanoimido) complex *trans*-[Mo(NCN)$_2$(dppe)$_2$].

However, alkylcyanamides (N≡C–NR_2, R = Me or Et) display quite a diferent reactivity towards *trans*-[Mo(N_2)$_2$(dppe)$_2$], *i. e.* the replacement of an apical dinitrogen by an organocyanamide occurs, leading to the formation of the mixed dinitrogen-cyanamide complexes *trans*-[Mo(N_2)($NCNR_2$)(dppe)$_2$] (**1**, R = Me; **2**, R = Et). These species are related to the ones obtained [4] in the reaction between various organonitriles and the bis(dinitrogen) complex.

In this work, we report the redox properties of the dinitrogen-cyanamide complexes **1** and **2**, as studied by cyclic voltammetry and controlled potential electrolysis.

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2. Results and Discussion

The low temperature (-30 °C) cyclic voltammetry of complexes *trans*-$[Mo(N_2)(NCNR_2)(dppe)_2]$, in 0.2 M $[NBu_4][BF_4]$ / THF and at a platinum disc electrode, displays two successive reversible one-electron anodic processes (I and II), assigned to the formal Mo(0/I) and Mo(I/II) oxidations, respectively (Figure and Table). At a higher potential, an irreversible monoelectronic anodic wave is detected (III), involving the Mo(II/III) oxidation followed by a chemical reaction in which an electroactive species is generated, as revealed by the presence of two new cathodic waves (A and B) in the reverse sweep. It is believed that N_2 loss is the first occurring chemical step resulting from oxidation to Mo(III), which accounts for the irreversibility of wave III and is probably followed by nucleophilic attack at the resulting unsaturated Mo(III) species by the anion of the electrolyte, thus conceivably resulting in a fluorinated molybdenum complex which is subsequently reduced (waves A and B, Figure). Accordingly, this species is not observed when $Li[ClO_4]$ is the supporting electrolyte. This behaviour relates to that detected for *trans*-$[FeH(CNR)(dppe)_2]^+$ which, upon anodic oxidation, in the same electrolytic solution, forms a fluoro-complex [5].

The $E_{½}^{ox}$ values measured for the first reversible oxidation of complexes **1** and **2** allowed us to calculate the electrochemical P_L ligand parameter for the organocyanamides. It was proposed by Pickett *et al.* [6] as a measure of the net electron π-acceptor minus σ-donor ability of a ligand L, and we have estimated it in this study by using equation (1) in which $[M_sL]$ represents a closed-shell octahedral 18-electron complex, whereas E_s and β are the electron-richness and the polarisability, respectively, of the 16-electron binding site $\{M_s\}$.

$$P_L = (E_{½}^{ox}\,[M_sL] - E_s\{M_s\}) \,/\, \beta\{M_s\} \qquad (1)$$

Knowing E_s (-0.13 V) and β (0.84) for the *trans*-$\{Mo(N_2)(dppe)_2\}$ moiety [6] and the measured values of ${}^{I}E_{½}^{ox}$ of the complexes under study, we have estimated the P_L parameter for the organocyanamides as -0.72 and -0.70 V for $N{\equiv}C{-}NMe_2$ and $N{\equiv}C{-}NEt_2$, respectively. These values are rather low for neutral ligands, being remarkably lower than those known for organonitriles (NCR, -0.40 to -0.58 V) [6], although not so low as that of cyanide (CN^-, -1.00 V) [6]. Hence, organocyanamides are more effective net electron donors than organonitriles, although weaker than the anionic cyanide ligand.

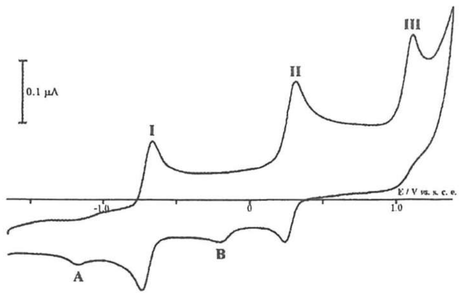

Figure. Cyclic voltammogram of *trans*-$[Mo(N_2)(NCNEt)(dppe)_2]$: 0.72 mM in 0.2 M $[NBu_4][BF_4]$ / THF, at -30 °C and at a platinum disc (∅ = 0.5 mm) working electrode (scan rate = 0.2 V s^{-1}).

Table. Cyclic voltammetric data [a] for complexes **1** and **2**.

Complex	${}^{I}E_{½}^{ox}$	${}^{II}E_{½}^{ox}$	${}^{III}E_{p}^{ox}$
1	-0.74	0.25	1.08
2	-0.72	0.27	1.11

[a] Potential values in Volts *vs.* SCE (scan rate = 0.2 V s^{-1}).

3. Final Comments

Organocyanamides $N{\equiv}C{-}NR_2$ (R = Me or Et) behave as efficient electron donor ligands which, by promoting the π-electron release from the metal to the dinitrogen co-ligand, have a remarkable stabilizing effect on the metal-N_2 bond which is retained, in the time scale of cyclic voltammetry, even upon oxidation of Mo(0) to the +2 oxidation state, in contrast with the usual known [7] behaviour of dinitrogen complexes which, upon a single electron oxidation, readily lose N_2.

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