

REDOX BEHAVIOUR OF A BISCYANAMIDE-DIHYDRIDE Mo COMPLEX. A  
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<sup>b</sup>Secção de Química Inorgânica, DEQ, Instituto Superior de Engenharia de Lisboa, R. Conselheiro Emídio Navarro,  
1949-014 Lisboa, Portugal.**Abstract**

The cyclic voltametric behaviour of the biscyanamide-dihydride Mo complex  $[\text{MoH}_2(\text{NCNH}_2)_2(\text{dppe})_2][\text{BF}_4]_2$  ( $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) is reported and interpreted by considering the occurrence of a cathodically-induced monodehydrogenation process of the cyanamide ligand.

*Key words:* Mo complexes; cyanamide; dehydrogenation; deprotonation

**Introduction**

The recognition of cyanamide ( $\text{N}=\text{CNH}_2$ ) as a substrate of both Mo- and V- nitrogenases has prompted our interest on the study of its coordination chemistry, which is still an unexplored field of research, in spite of the rich organic chemistry which has been developed for this species.

We have previously shown [1] that cyanamide is susceptible to dehydrogenation induced by the  $\text{N}_2$ -binding electron-rich Mo(0) or W(0) centres  $\{\text{M}(\text{dppe})_2\}$  ( $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) and we have extended the study to the polyhydride complex  $[\text{MoH}_4(\text{dppe})_2]$  which, upon reaction with cyanamide in the presence of  $\text{HBF}_4$ , leads to the biscyanamide-dihydride complex  $[\text{MoH}_2(\text{NCNH}_2)_2(\text{dppe})_2][\text{BF}_4]_2$  whose electrochemical behaviour, as studied by cyclic voltammetry, is now reported.

**Results and discussion**

The redox properties of  $[\text{MoH}_2(\text{NCNH}_2)_2(\text{dppe})_2][\text{BF}_4]_2$  ( $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) were studied by cyclic voltammetry at a Pt-disc electrode ( $\phi=1\text{mm}$ ) in 0.2M  $[\text{NBu}_4][\text{BF}_4]/\text{THF}$  at room temperature, using the VoltaMaster 2 program of Volta Lab. 31 potentiostat.

This complex displays one oxidation wave ( $O_1$ ) assigned to the oxidation of Mo(IV) to Mo(V) and three irreversible cathodic waves ( $R_1, R_2$  and  $R_3$ ) (Fig. 1) (Table 1).

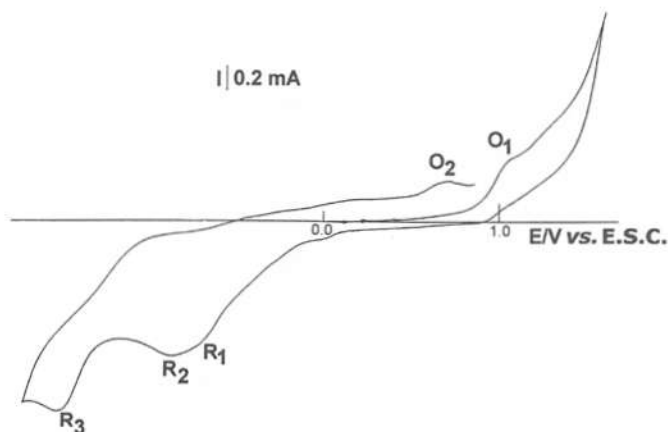


Fig. 1. Cyclic voltammogram of the complex  $[\text{MoH}_2(\text{NCNH}_2)_2(\text{dppe})_2][\text{BF}_4]_2$ , initiated by the anodic sweep, at a Pt electrode, in THF/0.2M  $[\text{NBu}_4][\text{BF}_4]$  solution ( $v=200\text{mV/s}$ ).  $O_1$  - anodic wave;  $R_1, R_2$  and  $R_3$  - irreversible cathodic waves;  $O_2$  - new oxidation wave detected only after the cathodic scan.

Table 1 - Electrochemical data<sup>a</sup> for the  $[\text{MoH}_2(\text{NCNH}_2)_2(\text{dppe})_2][\text{BF}_4]_2$  complex

Anodic process	Cathodic process		
	<sup>I</sup> $E_p^{\text{red}}/\text{V}$	<sup>II</sup> $E_p^{\text{red}}/\text{V}$	<sup>III</sup> $E_p^{\text{red}}/\text{V}$
<sup>I</sup> $E_p^{\text{ox}}/\text{V}$	-0.68	-0.85	-1.53
1.10			

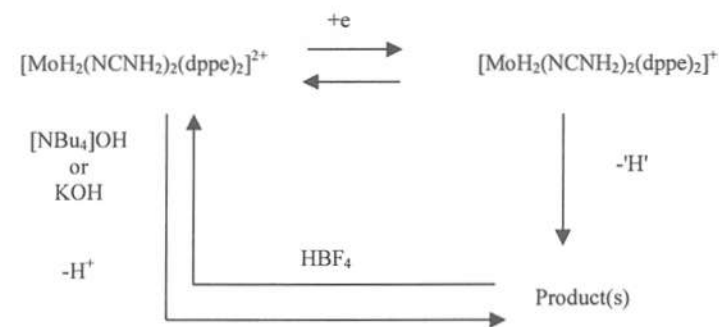
<sup>a</sup>Potential values vs. S.C.E. (scan rate =  $0.2 \text{ Vs}^{-1}$ ), measured by using the ferrocene/ferricinium redox pair as an internal standard.

In addition, a new irreversible anodic wave at  $E_p^{\text{ox}} = 0.67 \text{ V}$  (wave  $O_2$  - Fig. 1) is observed upon scan reversal following the cathodic scan. This new wave appears after the first reduction wave (wave  $R_1$ ), indicating that it corresponds to the oxidation of a specie formed at the first reduction process.

Further, upon addition of base (1M  $[\text{NBu}_4]\text{OH}/\text{MeOH}$  solution in the base:complex molar ratio of 2:1) directly to the solution of the complex in the voltammetric cell, this new oxidation wave (wave  $O_2$ ) already appears when the scan is initiated by the anodic sweep, while the original

oxidation wave  $O_1$  decreases in intensity. Conversely, subsequent neutralization by acid ( $\text{HBF}_4$  in the 2:1 molar ratio) leads to the disappearance of the new oxidation wave  $O_2$  with full regeneration of the initial oxidation wave  $O_1$ .

These results suggest the occurrence, at the first reduction wave, of a cathodically-induced dehydrogenation process, to give a deprotonated specie which is also formed when our initial complex  $[\text{MoH}_2(\text{NCNH}_2)_2(\text{dppe})_2][\text{BF}_4]_2$  reacts with base (see Scheme).



Scheme

In order to identify the dehydrogenation product(s), chemical studies are being performed, namely the reaction of the starting complex with base (in several proportions). The electrochemical behaviour of the isolated solid from this reaction was studied under the same conditions as those used above, and the oxidation wave  $O_2$  was also exhibited by its anodic cyclic voltammogram, showing the formation, by base reaction, of the same species as that obtained in the electrochemical cell.

The IR spectrum of the solid product of the reaction with base, exhibits a strong or medium intensity band at *ca.*  $2056 \text{ cm}^{-1}$ , a value that is much lower than that observed,  $2260 \text{ cm}^{-1}$ , for the cyanamide ligand  $\text{N}\equiv\text{CNH}_2$  in the bis-cyanamide dihydride complex. This is in accordance with the previously observed behaviour of the complexes *trans*- $[\text{FeH}(\text{NCNH})(\text{dppe})_2]$  [2] and *trans*- $[\text{Re}(\text{NCNH})(\text{NCR})(\text{dppe})_2]$  [3] ( $\text{R}=\text{Me}$  or  $\text{Bu}^t$ ), whose  $\nu(\text{N}\equiv\text{C})$  frequencies for the  $\text{NCNH}$  ligand, obtained from deprotonation of cyanamide, are also well below those of the corresponding cyanamide complex.

The cleavage of a N—H bond of the cyanamide ligand at our Mo complex, by base attack, is also corroborated by IR and NMR spectroscopies and therefore the above product from the cathodic reduction of our complex is tentatively formulated as *trans*-[MoH<sub>2</sub>(NCNH)(NCNH<sub>2</sub>)(dppe)<sub>2</sub>][BF<sub>4</sub>].

#### References

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## REDOX BEHAVIOUR OF ALKYNOL-DERIVED ALLENYLIDENE COMPLEXES OF IRON(II)

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#### Abstract

The cyclic voltammetric behaviour of the allenylidene complexes *trans*-[FeBr(L)(depe)<sub>2</sub>][BF<sub>4</sub>] (L = CCC(Me)Ph **1a**, CCCPh<sub>2</sub> **1b**, CCCEt<sub>2</sub> **1c**) is reported and the electrochemical *P<sub>L</sub>* and *E<sub>L</sub>* ligand parameters for the allenylidene ligands are estimated showing that they behave as slightly weaker *net* electron-donors than organonitriles.

*Key Words:* Allenylidene, redox properties, iron complexes, electrochemical ligand parameters.

#### Introduction

Correlating the redox-potential with molecular properties of coordination compounds has been a matter of interest since long and in particular the investigation of its dependence on the electronic properties of the ligands and the metal centres has been the object of growing attention [1]. The latter aspect suggests that it should be possible to define electrochemical parameters, as determined by the oxidation potential, that could constitute a measure of such properties.

An approach was presented by C. J. Pickett *et al.* [2] who proposed a scale of ligand constants, *P<sub>L</sub>*, which is defined according to equation (1) and is a measure of the *net* electron π-electron acceptor minus σ-donor ability of the ligand:

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

This scale is used to analyse the *E<sub>1/2</sub><sup>ox</sup>* of various closed-shell octahedral complexes [M<sub>s</sub>L], in terms of the linear approximation given by equation (2) in which *E<sub>s</sub>* and β are the electron-richness and polarisability, respectively, of the metal site {M<sub>s</sub>}.