

### Acknowledgements

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### References

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## COMPARATIVE ELECTROCHEMICAL BEHAVIOUR OF PROTONATED

### DERIVATIVES OF $trans$ -[Mo(NCN)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] AND

### $trans$ -[Mo(NCNEt)(NCN)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup>

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### Abstract

The bis(cyanoimido) complex  $trans$ -[Mo(NCN)<sub>2</sub>(dppe)<sub>2</sub>] (**1**, dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) is susceptible to electrophilic attack to form protonated compounds  $trans$ -[Mo(NCNH)(NCN)(dppe)<sub>2</sub>]<sup>+</sup> (**2**) and  $trans$ -[Mo(NCNH)<sub>2</sub>(dppe)<sub>2</sub>]<sup>2+</sup> (**3**), as well as the alkylated derivative  $trans$ -[Mo(NCNEt)(NCN)(dppe)<sub>2</sub>]<sup>+</sup> (**4**) which in turn can be protonated to give  $trans$ -[Mo(NCNEt)(NCNH)(dppe)<sub>2</sub>]<sup>2+</sup> (**5**). A preliminary description of the electrochemical behaviour of these complexes is presented and the observed redox induced interconversion of some of them is discussed in terms of their activation upon electron transfer.

*Key Words:* Molybdenum complexes; bis(cyanoimido) complex; alkylcyanoimido complex; protonation; alkylation; electrochemistry; electron transfer activation.

### 1. Introduction

Cyanamide, N≡C-NH<sub>2</sub>, is a small, unsaturated molecule with biological and industrial relevance. In particular, it has recently been recognized as an alternative substrate of both Mo- and V-nitrogenases [1], the N<sub>2</sub>-reducing enzymes.

The versatility of cyanamide [2] is being explored in the field of coordination chemistry at transition metal centres, in particular with Mo. Its activation at an electron-rich and readily oxidisable Mo(0) centre such as  $trans$ -[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] results in the metal induced reductive dehydrogenation of the substrate and the concomitant formation of the bis(cyanoimido) complex **1** [3], which can be of potential significance towards the development of a chemical mimetic system for the activity of Mo-nitrogenase.

Compound **1** undergoes electrophilic attack (by H<sup>+</sup> or Et<sup>+</sup>) at the terminal nitrogen of the NCN ligand to form the addition products **2**, **3**, **4** and **5**. We now describe the electrochemical behaviour of these complexes as studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in 0.2 M [NBu<sub>4</sub>][BF<sub>4</sub>] / CH<sub>2</sub>Cl<sub>2</sub>, and at glassy carbon or platinum disc working electrodes.

## 2. Results and discussion

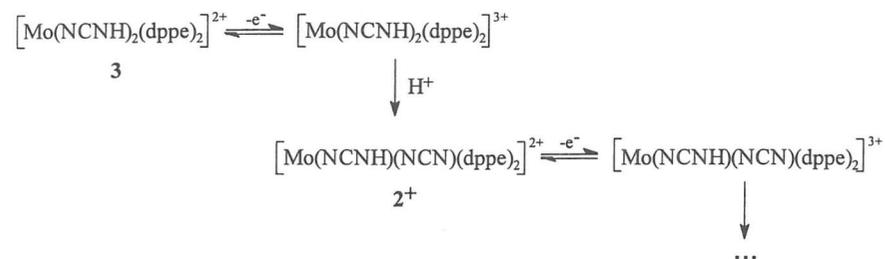
Complexes 1-5 undergo two oxidation steps (Figure 1 and Table 1) which may be followed by a chemical reaction.

As expected, and in accord with the decrease of electron-richness of the metal centre, the oxidation potentials of complexes 1-3 increase in this order. Moreover, the presence of an alkylcyanoimido group instead of a protonated cyanoimido ligand appears to have a small influence in the oxidation potential of the corresponding complexes.

Although the single-electron oxidation at wave I of complex 2 did not lead to any identified product, the anodic process of compound 3 involves H<sup>+</sup> liberation and the concomitant formation of the oxidized form of compound 2 (Scheme 1) as confirmed by running the cyclic voltammogram of the electrolyzed solution.

While the bis(cyanoimido) complex 1 exhibits a two-electron partially reversible cathodic process at -1.60 V, compounds 2 and 3 are easier to reduce, exhibiting irreversible or partially reversible waves at -0.40 and -0.91 V, respectively.

For compound 2, the parent compound 1 is regenerated upon cathodic scan, as indicated by the detection of its corresponding cathodic and anodic waves (Figure 1 (b)). The cathodically induced dehydrogenation of the NCNH ligand was also confirmed by CPE which consumes one Faraday / mole and leads to the quantitative formation of 1 as indicated by the cyclic voltammogram of the electrolyzed solution.



Scheme 1.

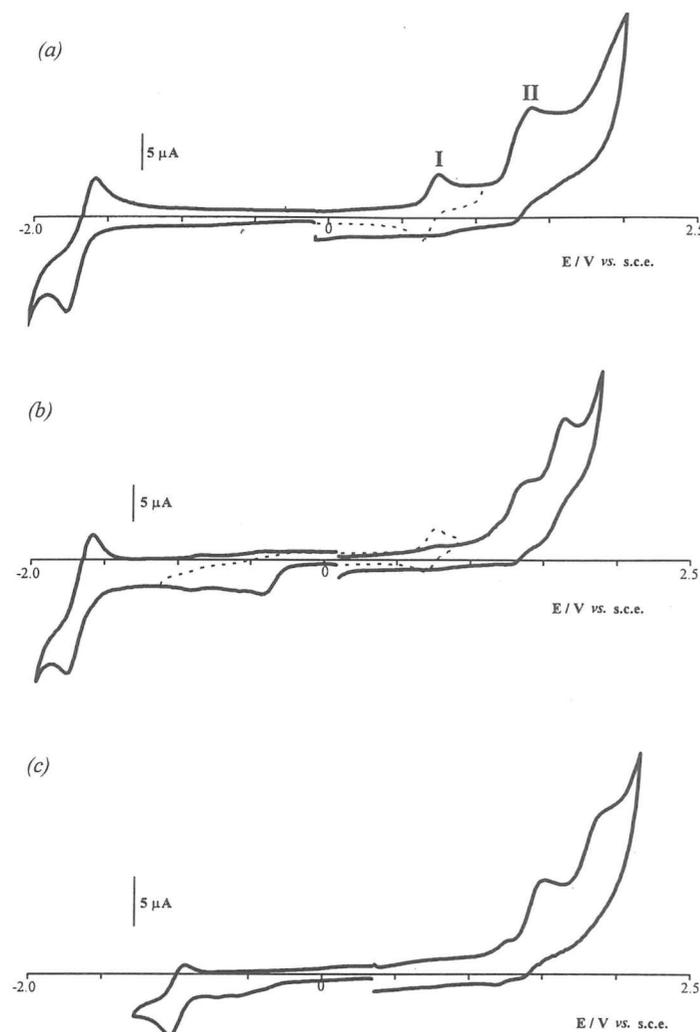


Figure 1. Cyclic voltammograms of complexes 1 (1.30 mM) (a), 2 (1.90 mM) (b) and 3 (1.28 mM) (c) in 0.2 M [NBu<sub>4</sub>][BF<sub>4</sub>] / CH<sub>2</sub>Cl<sub>2</sub> at a glassy carbon disc working electrode ( $\phi = 1$  mm). Anodic (right) and cathodic (left) scan (scan rate = 200 mV s<sup>-1</sup>).

**Table 1.** Cyclic voltammetric data of complexes 1-5 <sup>a</sup>.

Complex	<sup>I</sup> E <sup>ox</sup> (V)	<sup>II</sup> E <sup>ox</sup> (V)	<sup>I</sup> E <sup>red</sup> (V)	<sup>II</sup> E <sup>red</sup> (V)
1	0.73	(1.37)	-1.60	-
2	(1.41)	(1.65)	(-0.40) <sup>b</sup>	-1.62
3	(1.53)	(1.88)	-0.91	-
4	1.30	(1.70)	-0.66	(-1.73)
5	(1.67)	(1.89)	-0.64 <sup>c</sup>	(-1.63)

<sup>a</sup> In 0.2 M [NBu<sub>4</sub>][BF<sub>4</sub>] / CH<sub>2</sub>Cl<sub>2</sub> and at a glassy carbon disc electrode, unless otherwise stated. Potential values in volts vs. SCE determined by using the [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>0/+</sup> redox couple ( $E_{1/2}^{ox} = 0.525$  V vs. SCE) as internal standard at a scan rate of 200 mV s<sup>-1</sup>. Potential values refer to  $E_{1/2}$  or ( $E_p$ ).

<sup>b</sup> A set of ill-defined and broad cathodic processes were observed at lower cathodic potentials up to -0.86 V.

<sup>c</sup> At set of ill-defined and broad cathodic processes were observed at higher potentials in the range -0.37 to -0.58 V.

### 3. Final Comments

This work demonstrates the possibility of ready interconversion of the NCNH<sub>x</sub> (x = 2, 1 or 0) species when activated by a suitable transition metal centre. However, in order to develop a model for the nitrogenase action, further reactions of these species have to be achieved, in particular leading to ammonia and/or amines.

The value of the oxidation potential of the second anodic wave of *trans*-[Mo(NCN)<sub>2</sub>(dppe)<sub>2</sub>] **1** is comparable to those of the first anodic waves of the protonated **2** and alkylated **3** derivatives, and therefore the effect (on the oxidation potential) of the removal of one electron is similar to that of the addition of H<sup>+</sup> or Et<sup>+</sup>. Similarly, the second anodic wave of **2** or **4** occurs at a potential identical to that of the first oxidation wave of the protonated derivatives **3** or **5**, respectively. Such a type of behaviour is also observed for the isocyanide and derived aminocarbonyl complexes of rhenium *trans*-[ReCl(CNR)(dppe)<sub>2</sub>] and *trans*-[ReCl(CNHR)(dppe)<sub>2</sub>]<sup>+</sup> (R = alkyl or aryl group), respectively.

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