

Comparative Electrochemical Behaviour of the Complexes
***trans*-[Mo(NCN){NCNC(O)R}(dppe)₂]Cl (R = Et or Ph)**
and *trans*-[Mo(NCN)Cl(dppe)₂][BF₄]

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Abstract

The bis(cyanoimide) complex *trans*-[Mo(NCN)₂(dppe)₂] (**1**, dppe = Ph₂PCH₂CH₂PPh₂) is susceptible of electrophilic attack to form the acylated and aroylated derivatives *trans*-[Mo(NCN){NCNC(O)R}(dppe)₂]Cl (R = Et **2a** or Ph **2b**). Herein, we report a preliminary study on the electrochemical behaviour of complexes **2** and the derivative *trans*-[Mo(NCN)Cl(dppe)₂][BF₄] **3**, as investigated by cyclic voltammetry (CV) and controlled-potential electrolysis (CPE), what has allowed a comparison of the electron-donor ability of the ligands.

Keywords: Molybdenum complexes, cyanoimide complexes, acylation, aroylation, derivative, electrophilic attack, electron richness.

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Introduction

Cyanamide (NCNH₂) is a small organonitrogen molecule with industrial, biological and scientific interest, *e.g.*, it is an alternative substrate [1] of both Mo- and V-nitrogenases, the nitrogen fixation enzymes.

In spite of the recognized significance of cyanamide, its coordination chemistry is still an underdeveloped field of research.

Within our interest in the activation of alternative substrates of nitrogenase by transition metal centres, we have attempted the reaction of the phosphinic bis(dinitrogen) complex of molybdenum *trans*-[Mo(N₂)₂(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂) with cyanamide, which gives the unexpected bis(cyanoimide) complex of Mo(IV) *trans*-[Mo(NCN)₂(dppe)₂] (**1**) [2,3]. In this reaction, cyanamide suffers reductive dehydrogenation by the electron-rich Mo(0) centre to the cyanoimide (NCN²⁻) form.

Complex **1** is susceptible of electrophilic attack by acid chlorides RC(O)Cl (R = alkyl or aryl) to form the acylated and aroylated derivatives *trans*-[Mo(NCN){NCNC(O)R}(dppe)₂]Cl (R = Et **2a** or Ph **2b**) [3]. On reaction with several electrophiles, both products **2a** and **2b** yield the new mono(cyanoimide) species *trans*-[Mo(NCN)Cl(dppe)₂][BF₄] (**3**), a reaction that will be reported elsewhere.

Complexes **2a** and **2b** were prepared by treatment of a CH₂Cl₂ solution of **1** with RC(O)Cl (R = Et **2a**, Ph **2b**) (added in a 1:1 molar ratio) [3]. Cyclic voltammetry (CV) and controlled-potential electrolysis (CPE) were performed by using an EG&G PAR 273A potentiostat/galvanostat. CV was undertaken in a two-compartment three-electrode cell, at a Pt disc working electrode ($\phi = 500 \mu\text{m}$). CPE was performed in a three-compartment three-electrode cell, at a Pt gauze working electrode. Both techniques were carried out in a non-aqueous aprotic medium, 0.2 M [Bu₄N][BF₄]/CH₂Cl₂. The redox potentials are quoted relative to the SCE by using as internal reference the ferrocene/ferricinium couple ($E_{1/2}^{\text{ox}} = 0.525 \text{ V vs. SCE in CH}_2\text{Cl}_2$).

Results and Discussion

Solutions of the compounds **2a** and **2b** show similar cyclic voltammograms. They exhibit a first single-electron (CPE) irreversible oxidation wave (**A**), at E_p^{ox} *ca.* 1.1-1.2 V *vs.* S.C.E., corresponding to the oxidation of the Cl⁻ counter-ion, which is followed at higher potentials by a monoelectronic (CPE) partially reversible anodic process (**B**) (Fig. 1 and Table 1). The latter is assigned to the oxidation of Mo(IV) to Mo(V).

The measured potentials for the Mo(IV)/Mo(V) oxidation **B** are identical in both cationic complexes: 1.65 (**2a**) or 1.63 (**2b**) V, being significantly higher than the corresponding value (0.79 V *vs.* S.C.E.) [2] of the neutral bis(cyanoimide) complex **1**, and much higher than the first oxidation process of *trans*-[MoL₂(dppe)₂] [-0.16 (L = N₂) [4], -0.11 (L = CO) [4] or -0.55 (L = CNMe) [5,6]], in agreement with the higher electron-richness of the Mo centre in all these neutral complexes with the metal in the zero oxidation state.

Complexes **2a** and **2b** show two reduction waves, the first at a potential (*ca.* -0.5 V) much less cathodic than that of the starting compound **1** (-1.89 V), also in accord with the higher electron-richness of the metal centre in the latter complex. However, these reduction processes were not further investigated.

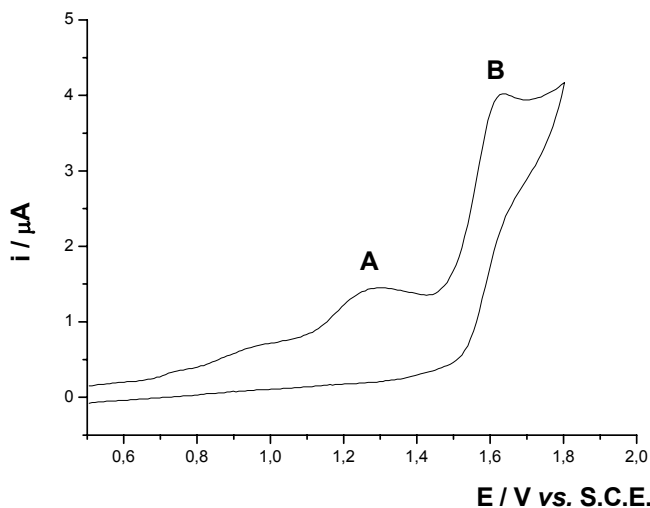


Figure 1. Cyclic voltammogram at 0.2 Vs⁻¹ for [Mo(NCN){NCNC(O)Et}(dppe)₂]Cl **2a** (1.5 mM) in a 0.2 M [Bu₄N][BF₄]/CH₂Cl₂ solution at a Pt disc working electrode.

As expected the Mo mono(cyanoimide) derivative **3** does not display the anodic wave **A** due to the oxidation of a chloride counter-ion. However, similarly to complexes **2a** and **2b**, it exhibits a monoelectronic anodic wave (**B**) assigned to the Mo(IV/V) oxidation at a potential that is very close to those of such complexes. In the case of complex **3**, this wave has a reversible character.

Final Comments

In view of the results presented for *trans*-[Mo(NCN){NCNC(O)R}(dppe)₂]Cl (R = Et **2a**, Ph **2b**) and *trans*-[Mo(NCN)Cl(dppe)₂][BF₄] **3**, with a common *trans*-{Mo(NCN)(dppe)₂}⁺ moiety, we can consider that the acyl- or aroyl-cyanoimide ligands NCNC(O)Et⁻ and NCNC(O)Ph⁻ (in **2a** and **2b**, respectively) have a net electron-donor ability identical to that of the ligated chloride (in **3**), thus behaving as quite strong electron donors.

Table 1. Anodic cyclic voltammetric data^a for solutions of *trans*-[Mo(NCN){NCNC(O)R}(dppe)₂] Cl (R = Et **2a** or Ph **2b**) and *trans*-[Mo(NCN)Cl(dppe)₂][BF₄] **3** in 0.2 M [NBu₄][BF₄] / CH₂Cl₂

Complex	ANODIC WAVES	
	^I E _p ^{ox} (A)	^{II} E _p ^{ox} (B)
2a	1.1 ^b	1.65
2b	1.2 ^b	1.63
3	-	1.63

^a Potential values in Volts vs S.C.E. at a Pt disc working electrode determined by using the [Fe(η⁵-C₅H₅)₂]^{0/+} redox couple (E_{1/2}^{ox} = 0.525 V vs S.C.E.) as internal standard at a scan rate of 200 mVs⁻¹. ^b Oxidation wave of the counter-ion Cl⁻.

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