With Maxwell-Garnett theory, the obtained ε_{2A} spectra have the same order of magnitude as experimental spectra. Nevertheless the general shapes of experimental and calculated spectra are rather different, indicating that Ni-P structure would be different in pure sample than in Ni-P-Teflon..
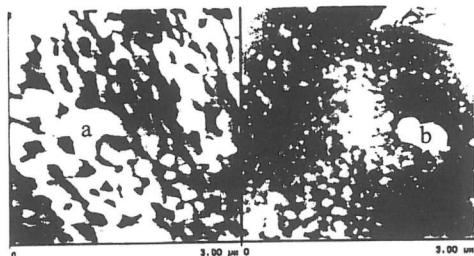

Figure 6 - AFM images of Ni-P-Teflon (a) and Ni-P (b) with the same film thickness, 10 μm.

4. AFM images of Ni-P and Ni-P-Teflon

Images in fig. 6, among several others, illustrate that the configuration of Ni-P is appreciably different in Ni-P-Teflon than in pure Ni-P.

CONCLUSIONS

The composition of Ni-P electroless deposits varies during the first stages of the film growth.

Ellipsometry reveals an efficient technique to characterize composite materials (e.g. Ni-P and Ni-P-Teflon) and the main conclusions that can be taken are:

- The effective volume of Teflon in Ni-P-Teflon is about 50 %.

- The microstructure of Ni-P is different in both pure Ni-P and Ni-P-Teflon, being this confirmed by AFM images.

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CHEMICAL AND ELECTROCHEMICAL REACTIONS OF LIGANDS ON MOLYBDENUM AND TUNGSTEN COMPLEXES

M A Queirós
Centro de Química, Escola de Ciências, Universidade do Minho, 4710 Braga, Portugal

1. Introduction

Molybdenum dinitrogen complexes have been proposed as structural models for the nitrogenase active site. Chat [1,2] reported the production of ammonia by protolysis of cis - $[Mo\ (N_2)_2\ (PMe_2Ph)_4]$.and postulated the nitride complexes trans - $[Mo(N)X(dppe)_2]$ as intermediates in the reduction of molecular nitrogen to ammonia catalyzed by the enzyme nitrogenase. Subsequent work by Picket et al [3-5] showed that ammonia can be produced from dinitrogen complexes in a cyclic process, including protonation and electronation steps, that parallels the Lowe and Thorneley [6] mechanism for the biological fixation of nitrogen.

Research undertaken on the chemical models of nitrogenase, besides allowing the establishment of chemical precedents for the transformation of enzymic substrates, resulted in the development of new chemistry and electrochemistry.
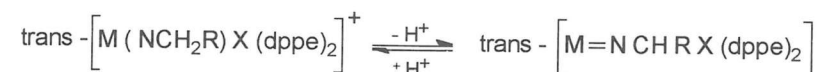
The aim of this lecture is to outline electrochemical processes leading to the electrosynthesis of dinitrogen complexes and organo-nitrogen compounds. The electron transfer chemistry of molybdenum and tungsten carboxylate-hydrides presented shows that carboxylate can be a leaving group at a reduced metal center exposing a site where dinitrogen or other substrates of nitrogenase can coordinate.

2. Chemical and electrochemical reactions of trans - $[M(N)X(dppe)_2]$ complexes

The nitride ligand in the complexes trans - $[M(N)X(dppe)_2]$ (M = Mo or W; X= halide; dppe= diphenylphosphinoethane) is a strong nucleophile and reacts with organic iodides, ICH_2R (R= alkyl, benzyl, carboxylate) to form imide complexes, according to the reaction [7-10]:

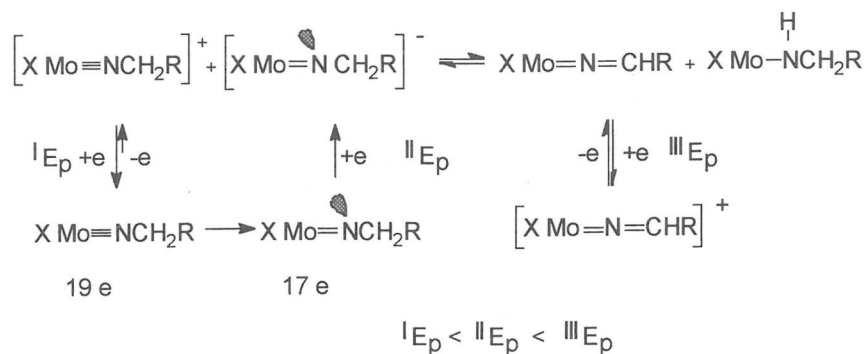$$\text{trans -}\left[M\,(N)\,X\,(dppe)_2\right] \xrightarrow{\text{thf}} \text{trans -}\left[M\,(N\,CH_2\,R)\,X\,(dppe)_2\right]I$$
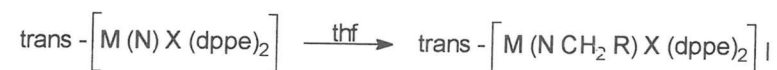
The α - carbon protons are acidic and, in the presence of a base, an amide complex is formed that can be reprotonated [11]:.

$$\text{trans -}\left[M\,(\,NCH_2R)\,X\,(dppe)_2\right]^+ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \text{trans -}\left[M=N\,CH\,R\,X\,(dppe)_2\right]$$

The amide complexes have an incipient carbanionic character and can be methylated at the α - carbon atom. As expected a racemic mixture of trans - $[Mo\ X\ \{NCH(CH_3)R\}\ (dppe)_2]^+$ is obtained.

Cyclic voltammetry of trans - $[M\ X\ (NCH_2R)\ (dppe)_2]$ (R = alkyl, benzyl) in thf / TBAB

shows a one electron and reversible oxidation at potentials in the range + 0.5 to + 0.7 V vs. fc^+/fc. Products of the oxidation have not been identified. They also undergo an irreversible reduction with a coupled chemical reaction. Two electroactive products are formed which undergo oxidation processes at negative potentials characteristic of Mo (II) complexes [11]. The reversible oxidation process at less negative potentials is associated with the deprotonated complex formed by reaction with a base generated within the process. This can be the anion formed after reduction of the 17 electron complex resulting from the rearrangement of the 19 electron complex formed after reduction of trans - $[M(NCH_2R)X(dppe)_2]^+$, according to scheme 1:

$$\left[X\,Mo\equiv NCH_2R\right]^+ + \left[X\,Mo=N\,CH_2R\right]^- \rightleftharpoons X\,Mo=N=CHR + X\,Mo\overset{H}{-}NCH_2R$$

$$^IE_p\; +e\updownarrow -e \qquad\qquad \uparrow +e \quad ^{II}E_p \qquad -e\updownarrow +e \; ^{III}E_p$$

$$X\,Mo\equiv NCH_2R \longrightarrow X\,Mo=NCH_2R \qquad \left[X\,Mo=N=CHR\right]^+$$

$$\qquad 19\,e \qquad\qquad\qquad 17\,e$$

$$^IE_p < \,^{II}E_p < \,^{III}E_p$$

Scheme 1: Chemical reactions coupled with the reduction of alkylimide complexes.

Controlled potential electrolysis of trans - $[Mo\,X\{NCH(CH_3)R\}\,(dppe)_2]^+$ (R = Me, Et, benzyl) in a thf solution containing an excess of phenol, affords the corresponding amine together with trans - $[Mo\,(N_2)_2\,(dppe)_2]$. Accordingly, when R = COOEt, the ethyl esters of glycine and DL-alanine are obtained, but in moderate yields (ca. 40%). Current vs. charge plots showing the consumption of 1.3 faradays mole^{-1}, together with the formation of trans - $[Mo\,X\,(NC(CH_3)R)\,(dppe)_2]$ (yield ca. 60%) supports the idea of the imide ester complex acting as both the electroactive species and a proton donor [9].

In order to increase the yield, controlled potential electrolysis were carried out in the presence of acetic acid. A new behaviour was observed according to following mechanism:

The monohydride trans - $[Mo\,H\,(\eta^2 - OOCCH_3)\,(dppe)_2]$ formed is protonated in solution to the dihydride and this is reduced at the potentials used liberating hydrogen [9,10].

3. Synthesis of ethyl cyanoformate from trans- [MoX(NCH₂COOEt)(dppe)₂]

Previous mechanistic studies [12] showed that trans - $[MoX(NCH_2COOEt)(dppe)_2]$ can loose the two protons from the α - carbon by reaction with a strong base. It is also known that either, CO or N_2, replace halides coordinated to $\{Mo^0(dppe)_2\}$complexes. A thf solution of trans - $[MoX(NCCOOEt)(dppe)_2]^-$, generated in situ by addition of K [Bu^t O], was stirred, for 40 hours, with CO. Work - up afforded cis and trans - isomers of $[Mo\,(CO)_2\,(dppe)_2]$ together with ethyl cyanoformate (yield ca. 80 % when X=I). The same reaction carried out under N_2 gave trans - $[Mo\,(N_2)_2\,(dppe)_2]$ and ethyl cyanoformate (yield ca. 60 % when X=Cl) [9, 10].

The mechanism presented in scheme 3 is based on infrared and cyclovoltammetric studies giving evidence for the formation of the intermediate trans - $[Mo\,(N_2)\,(NCCOOEt)(dppe)_2]$
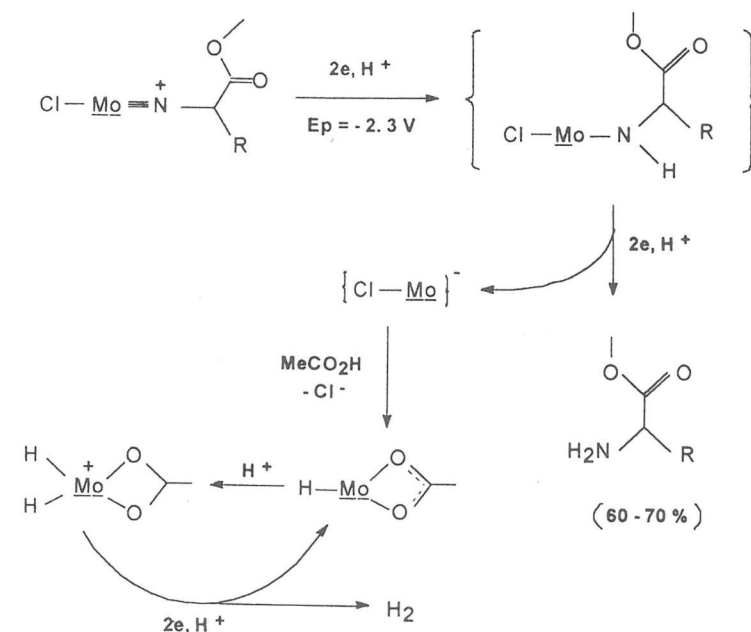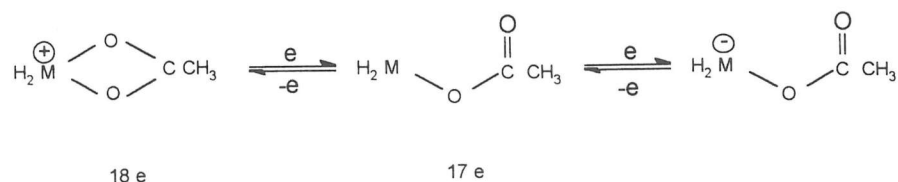

Scheme 2: Formation of aminoacids from imide esters by electrolysis in the presence of acetic acid.
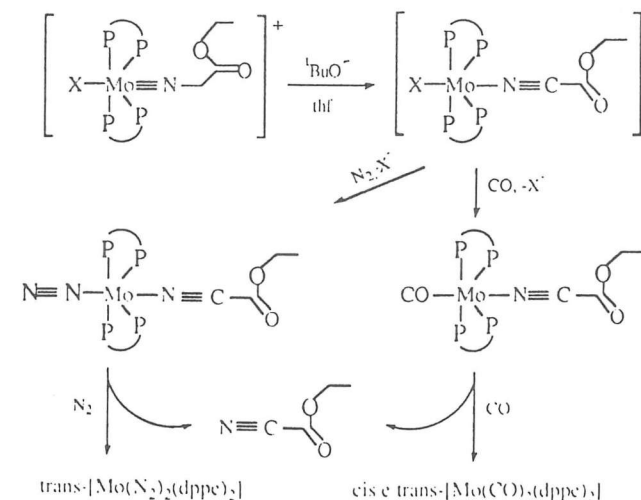
Scheme 3: Formation of ethyl cyanoformate from imide ester

4. Electrochemical reactions of [Mo H$_2$ (η^2- OOCCH$_3$) (dppe) $_2$]$^+$

These complexes undergo a quasi-reversible monoelectronic reduction at a vitreous carbon electrode in 0.2 M [NBu$_4$] [BF$_4$] - dimethylformamide [13].

18 e   17 e

The 17 electron species obtained after cleavage of the metal-oxygen bond undergo a fast reduction at low temperatures (0 °C for M=Mo and -20 °C for M=W). The anions are unstable but can be trapped by protonation. Evidence for [Mo H$_3$ (η^2 - OOCCH$_3$) (dppe)$_2$] was found on a cyclic voltammogram run in acetonitrile at -20 °C in the presence of acetic acid. The trihydride decomposes to the monohydride by loosing H$_2$:
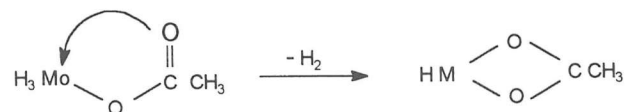
Controlled potential electrolysis of [W H$_2$ (η^2- OOCCH$_3$) (dppe) $_2$]$^+$ in the presence of one equivalent of acetic acid gives the stable trihydride[W H$_3$ (η^2- OOCCH$_3$) (dppe) $_2$] as yellow crystals.

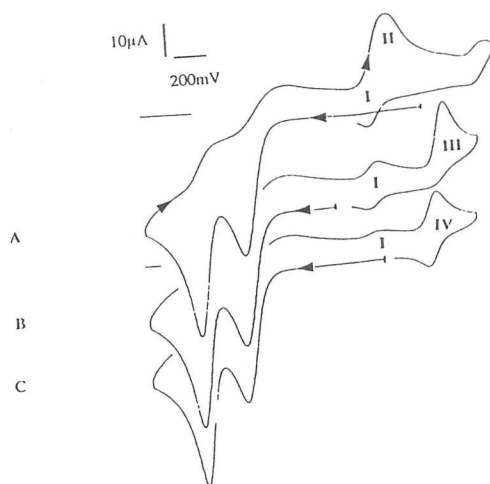So, protonation of the reduced form can lead to the formation of hydrogen preventing carboxylate loss.

Figure 1: Cyclic voltammogram of [Mo H$_2$ (η^2- OOCCH$_3$) (dppe) $_2$]$^+$ at a vitreous carbon electrode in dmf - 0.2M [NBu$_4$] [BF$_4$], at 295.5 K, in the presence of: A - dinitrogen; B - dihydrogen; C - carbon monoxide; scan rate 100mV s^{-1}.

.In the absence of an acid [Mo H$_2$ (OCOCH$_3$) (dppe) $_2$]$^-$ looses the carboxylate group and a site is left available for coordination with other substrates. In fact, as can be seen from figure 1, cyclic voltammetry of [Mo H$_2$ (η^2- OOCCH$_3$) (dppe) $_2$]$^+$ under H$_2$ gives [MoH$_4$ (dppe) $_2$] and, under N$_2$, gives [MoH$_2$ (N$_2$) (dppe) $_2$] that decomposes to [Mo (N$_2$) $_2$ (dppe) $_2$]. This observation shows that the release of H$_2$ can occur after N$_2$ binds to the metal.

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