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ELECTROCHEMICAL INVESTIGATION OF THE COMPLEXES *trans*-[MCl(NCOCH₂I)(Ph₂PCH₂CH₂PPh₂)₂][BF₄]

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Summary

The electrochemical behaviour of the complexes *trans*-[MCl(NCOCH₂I)(dppe)₂][BF₄] (M = Mo or W, dppe = Ph₂PCH₂CH₂PPh₂) was investigated by cyclic voltammetry and controlled potential electrolysis. The complexes undergo two successive mono-electronic reductions. The first reduction process follows a well-defined EC mechanism, leading to iodide loss. The second reduction is reversible and is associated with the novel complex *trans*-[MCl(NCOCH₂I)(dppe)₂]⁺ produced after the first reduction process.

Key words: Dinitrogen complex, molybdenum, tungsten, nitride ligand, alkylimide complex, electrosynthesis.

Introduction

Development of a chemical dinitrogen-fixing system converting a quite inert dinitrogen molecule into nitrogenous compounds under mild conditions is a challenging topic in chemistry. In certain systems, molecular nitrogen is incorporated into organometallic compounds with concurrent nitrogen-nitrogen bond scission, although in most cases the resultant nitride species are poorly defined [1, 2].

Nitrides complexes of the type *trans*-[MX(N)(dppe)₂] (X = halide) can be synthesised from the dinitrogen complexes *trans*-[M(N₂)₂(dppe)₂] by reaction with trimethylsilyl azide or cleavage of the N-N bond after conversion of coordinated dinitrogen to a M^{II} dialkylhydrazide [3, 4, 5].

The nitride ligand is a strong nucleophile and reacts with protons or other electrophiles to form the cationic imide complexes *trans*-[MX(NR)(dppe)₂] (R = H or alkyl) [6]. The M-N bond can be electrochemically cleaved in the presence of a weak acid to give the free amine. The cleavage reaction occurs with conservation of the *trans*-[M(dppe)₂] assembly and, under molecular nitrogen, the parent dinitrogen complex is regenerated in reasonable yields [7, 8].

In this work the results obtained on the reductive electrochemistry of *trans*-[MCl(NCOCH₂I)(dppe)₂]⁺ are reported and compared with other imide complexes. On the basis of the evidence found, a mechanism is proposed.

Results and Discussion

Cyclic voltammetry in thf - 0.2 mol dm⁻³ [NBu₄][BF₄] at a vitreous carbon-disc electrode shows that the molybdenum and tungsten organoimide cations, *trans*-[MCl(NR)(dppe)₂]⁺, undergo an irreversible, diffusion-controlled reduction which is nominally an one-electron process on the basis of current function measurements. The irreversibility remains even at low temperatures.

Table 1 summarises reduction potential data together with the yields for the products of the electrochemical cleavage in acid media for some imide complexes.

It can be seen that both the metal and the axial ligands influence the reduction potentials.

Table 1 - Reduction potentials of *trans*-[MX(NR)(dppe)₂]⁺ and yields for the electrochemical reduction

Complexes	$E_p^{red} / \text{V a}$	Yields /%
<i>trans</i> -[MoCl(NCH ₂ CH ₃)(dppe) ₂] ⁺	-2.31	66 b
<i>trans</i> -[MoCl(NCH ₂ Ph)(dppe) ₂] ⁺	-2.26	52 b
<i>trans</i> -[MoBr(NCH ₂ Ph)(dppe) ₂] ⁺	-2.09	59 b
<i>trans</i> -[MoI(NCH ₂ Ph)(dppe) ₂] ⁺	-2.01	55 b
<i>trans</i> -[WCl(NCH ₂ Ph)(dppe) ₂] ⁺	-2.36	—
<i>trans</i> -[WBr(NCH ₂ Ph)(dppe) ₂] ⁺	-2.17	—
<i>trans</i> -[MoCl(NCH ₂ COOEt)(dppe) ₂] ⁺	-2.16	73 c

a - Potentials are relative to the fc^+/fc in $\text{thf} - 0.2 \text{ mol dm}^{-3} [\text{NBu}_4][\text{BF}_4]$.

b - The yield is determined from *trans*-[Mo(N₂)₂(dppe)₂].

c - The yield is determined from [MoH₂(η^2 -OOCH₃)(dppe)₂]⁺.

To develop the chemistry of organoimide complexes of molybdenum and tungsten and to extend the range of organonitrogen compounds we examined the possible ways of electrosynthesising oligopeptides by modification of the starting materials. The initial approach was to synthesise an imido complex with a functionalised end group that could be subsequently coupled to other groups. Accordingly, pentafluorophenyl iodoacetate was synthesised and reacted with the nitride complexes with the aim of producing the imide *trans*-[MoCl(NCH₂COOC₆F₅)(dppe)₂]⁺ (A). Two products were invariably produced independently of the stoichiometric ratios. An orange-brown compound deposited from the reaction mixture was characterised as [MoCl(NCOCH₂I)(dppe)₂]⁺ (B) and the expected compounds A was obtained after work up of the filtrate.

The tungsten complex *trans*-[WCl(NCOCH₂I)(dppe)₂]⁺ (C) was obtained from the reaction of *trans*-[WCl(N)(dppe)₂] with ethyliodoacetate.

Figure 1 shows cyclic voltammograms for complex B in $\text{thf} - 0.2 \text{ mol dm}^{-3} [\text{NBu}_4][\text{PF}_6]$ at a carbon disc electrode. It can be seen that complex B undergoes two successive reductions. The first reduction at $E_p^{red} = -0.98 \text{ V vs. } fc^+/fc$ has all the characteristics of an EC process and the second, at $E_{1/2}^{red} = -1.44 \text{ V vs. } fc^+/fc$ is reversible. A similar behaviour was observed for complex C, whose potentials for the first and second processes are $E_p^{red} = -1.18 \text{ V}$ and $E_{1/2}^{red} = -1.62 \text{ V vs. } fc^+/fc$, respectively. The tungsten complexes always harder to reduce than their molybdenum analogues. The addition of one electron to the closed-shell 18-electron complexes presumably involves a LUMO which has substantial ligand character and lies at a lower energy on molybdenum than on tungsten [2].

It also can be observed that the intensity of the second peak is less dependent on the potential scan rate than the first peak, this indicating that it can be associated with a product of the chemical reaction coupled with the first process.

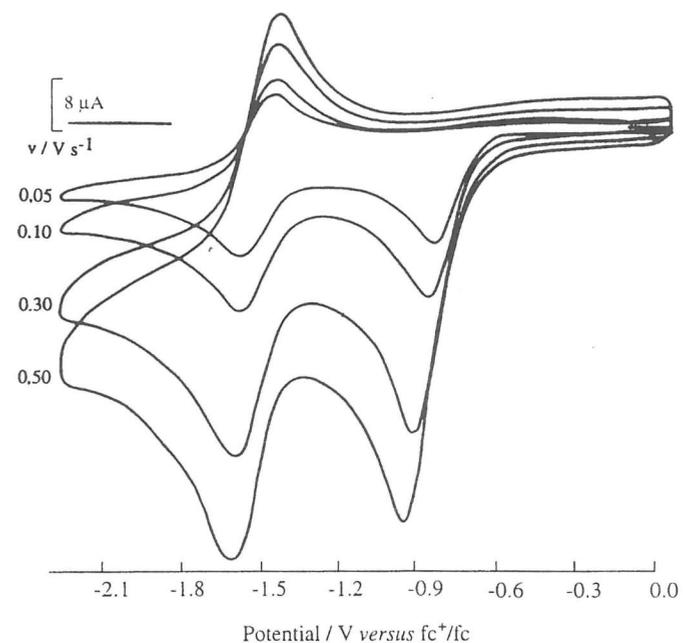


Figure 1 - Cyclic voltammograms of the complex *trans*-[MoCl(NCOCH₂I)(dppe)₂][BPh₄] ($1.2 \times 10^{-3} \text{ mol dm}^{-3}$) in $\text{thf} - 0.2 \text{ mol dm}^{-3} [\text{NBu}_4][\text{PF}_6]$ at a carbon disc electrode.

Figure 2 shows that, when the potential scan is reversed before the second peak, a new oxidation is observed at $E_p^{ox} = +0.1 \text{ V vs. } fc^+/fc$. This could be assigned to the oxidation of iodide as after addition of [NBu₄][I] to the solution an increase in the oxidation peak intensity was observed.

Controlled-potential electrolyses of B and C, in $\text{thf} - 0.2 \text{ mol dm}^{-3} [\text{NBu}_4][\text{PF}_6]$, carried out under molecular nitrogen, at a Pt gauze cathode and at a potential *ca.* 50 mV after the second peak, showed the consumption 1,9 Faradays mol⁻¹. The cyclic voltammogram in figure 3, run at the end of the electrolysis only shows the second reduction process. From the peak intensity a yield of 80 % was estimated. All attempts to isolate this product were unsuccessful.

In order to get more evidence on the mechanism, the complex *trans*-[MoCl(NCOCH₃)(dppe)₂][BPh₄] was synthesised, by reaction of *trans*-[MoCl(N)(dppe)₂] with CH₃COCl. The cyclic voltammogram of *trans*-[MoCl(NCOCH₃)(dppe)₂][BPh₄] run in $\text{thf} - 0.2 \text{ mol dm}^{-3} [\text{NBu}_4][\text{PF}_6]$ at a carbon disc electrode, presented in figure 4, shows a reversible reduction process at $E_{1/2}^{red} = -1.45 \text{ V vs. } fc^+/fc$. The complex *trans*-[MoCl(NCOCH₃)(dppe)₂][BPh₄] is more easily reduced than the imides included in table 1 due to the more electron-withdrawing character of the carbonyl group directly bonded to the nitrogen [9, 10].

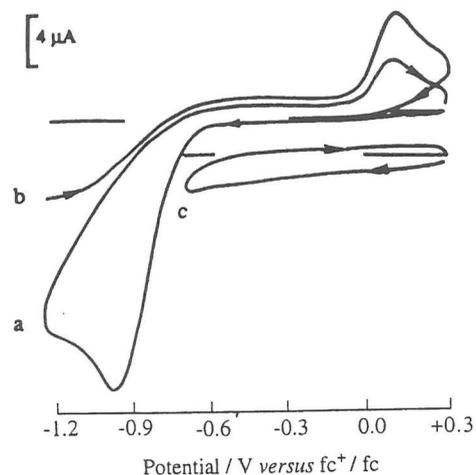


Figure 2 - Cyclic voltammograms of the complex *trans*-[MoCl(NCOCH₂I)(dppe)₂][BPh₄] ($1.1 \times 10^{-3} \text{ mol dm}^{-3}$) in thf - 0.2 mol dm^{-3} [NBu₄][PF₆] at a carbon disc electrode. Potential scan rate 0.1 V s^{-1} :
 a) Between +0.3 V and -1.2 V vs. fc^+/fc ;
 b) After holding the potential at -1.2 V for 30 s;
 c) Between +0.3 V and -0.7 V vs. fc^+/fc .

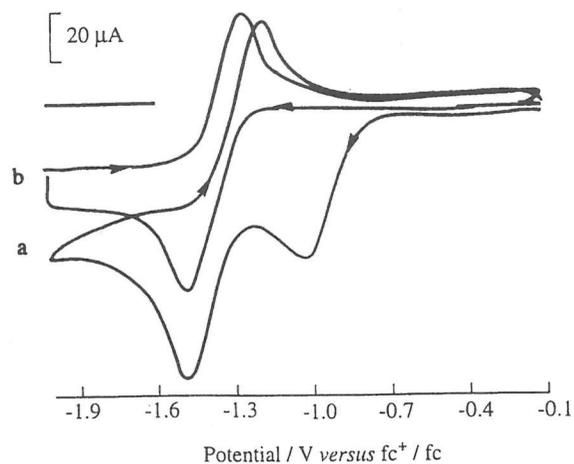


Figure 3 - Cyclic voltammetry of catholyte of *trans*-[MoCl(NCOCH₂I)(dppe)₂][BPh₄] in thf - 0.2 mol dm^{-3} [NBu₄][PF₆] at a Pt gauze cathode. $E_{\text{applied}} = -1.5 \text{ V vs. fc}^+/\text{fc}$.
 a - Before electrolyses;
 b - After electrolyses.

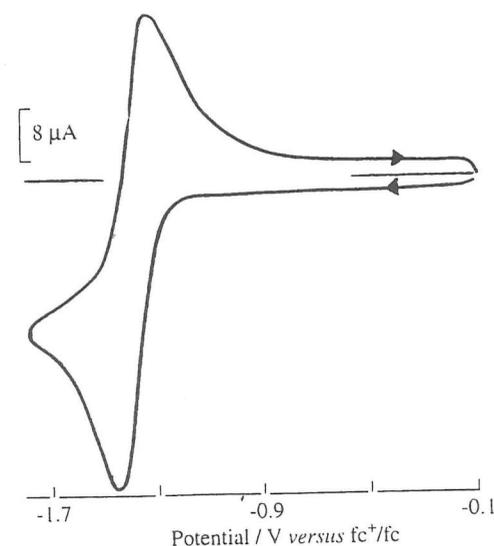
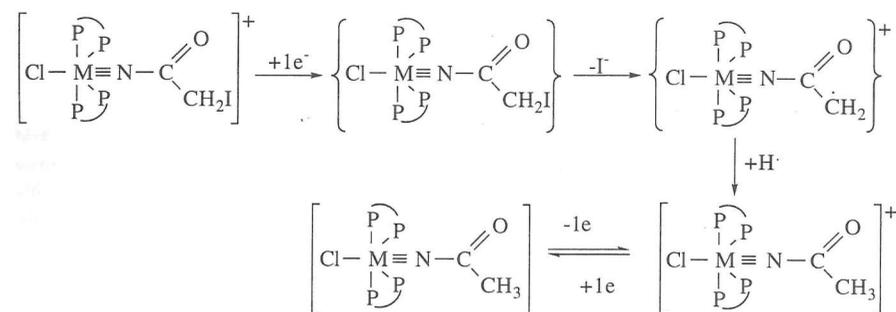


Figure 4 - Cyclic voltammogram of the complex *trans*-[MoCl(NCOCH₃)(dppe)₂][BPh₄] ($1.2 \times 10^{-3} \text{ mol dm}^{-3}$) in thf - 0.2 mol dm^{-3} [NBu₄][BF₄] at a carbon disc electrode. Potential scan rate 0.1 V s^{-1} .

The above mentioned behaviour is identical to that described before for the second reduction of complex **B** and gives evidence for the formation of *trans*-[MoCl(NCOCH₃)(dppe)₂]⁺ after the first reduction of **B**. The chemical process leading to *trans*-[MoCl(NCOCH₃)(dppe)₂]⁺ is not yet well known, but a radical process seems likely to occur involving the transfer of H[·] from the tetrahydrofuran.

On the basis of all the evidence found the following mechanism is proposed:



Final Comments

Important advances in the chemistry of dinitrogen complexes are found in the discovery of numerous transformations of coordinated N₂ into organonitrogen compounds through the carbon-nitrogen bond formation by reactions with organic compounds.

The reduction potentials of the alkylimide complexes reflect the electronic properties of the metal centres involved. Cathodic processes are observed when M^{IV} metal centres are present, and the strong electron-withdrawing capacity of the ligand facilitates the reduction on the metal.

Acknowledgments

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STUDY OF THE REDOX PROPERTIES OF SOME PALLADIUM AND NICKEL COMPLEXES WITH AZINE DIPHOSPHINE TYPE LIGANDS

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Abstract

The redox properties of [$\{L_2M\}_2(\mu-P^{\ominus}P^{\ominus})_2$] (M=Pd, L₂= C(CO₂Me)≡C(CO₂Me) (1); M=Ni, L=CO (2) or Bu¹NC (3); P[⊖]P[⊖]= PPh₂CH₂C(Bu¹)=NN=C(Bu¹)CH₂PPh₂, [Pd{η³-CH₂C(CH₃)=CH₂}(P[⊖]P[⊖])Cl] (4), [PdCl{PPh₂CH=C(Bu¹)NN=C(Bu¹)CH₂PPh₂}] (5), or [{PdCl(η¹,η²-CH₂C(CH₃)=CH₂)}₂(μ-P[⊖]P[⊖])] (6), as well as [Ni{C(CO₂Me)≡C(CO₂Me)}(P[⊖]P[⊖])] (7), were studied by cyclic voltammetry and controlled potential electrolysis, in 0.2 M [NBu₄][BF₄]/THF. By reductive electron transfer chemical reactivity was induced at complex (1) and the new species [Pd(PPh₂CH₂C(Bu¹)=N-NC(Bu¹)=C(H)PPh₂)(MeCO₂C=C(H)CO₂Me)] was formed.

Key words

Redox properties, azine diphosphine, nickel, palladium, electrosynthesis.

Introduction

Since the first synthesis, in 1992 [1], of the azine diphosphine Z,Z-PPh₂CH₂C(Bu¹)=N-N=C(Bu¹)CH₂PPh₂, (Z,Z-P[⊖]P[⊖]), a considerable number of transition metal complexes with this ligand were prepared. Commonly, this versatile ligand isomerizes, upon coordination, to the E,Z form [2], affording mononuclear complexes. However, zero valent polynuclear palladium or platinum compounds were synthesized in which the ligand bridges two metal atoms keeping the Z,Z form [2].

In order to have an insight into the redox properties of the azine diphosphine and some of the derived palladium and nickel complexes we started their study by cyclic voltammetry and controlled potential electrolysis.