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# Electrocarboxylation of chloroacetonitrile by a Cobalt(I) complex of terpyridine

Dancheng Chen<sup>a,b</sup>, Paul-Louis Fabre<sup>a,b,1</sup>, Olivier Reynes<sup>a,b,\*</sup>

<sup>a</sup> Université de Toulouse; Université Paul Sabatier; Laboratoire de Génie Chimique; Bat. 2R1, 118 route de Narbonne; F-31062 Toulouse cedex009, France

<sup>b</sup> CNRS; Laboratoire de Génie Chimique UMR 5503; F-31062 Toulouse cedex 09, France

## A B S T R A C T

The electrocarboxylation of chloroacetonitrile (NC-CH<sub>2</sub>-Cl=RCI) mediated by [Co<sup>II</sup>L<sub>2</sub>]<sup>2+</sup> (L = terpyridine) was investigated by cyclic voltammetry. Electrochemical studies under argon atmosphere showed that the monoelectronic reduction of [Co<sup>II</sup>L<sub>2</sub>]<sup>2+</sup> yielded a Cobalt(I) complex which after the loss of a terpyridine ligand reacted with chloroacetonitrile. The oxidative addition of chloroacetonitrile on [Co<sup>I</sup>L]<sup>+</sup> gave an alkylCobalt(III) complex [R-Co<sup>III</sup>L]<sup>2+</sup> which was reduced into an alkylCobalt(II) complex, highly unstable and decomposed into an alkyl anion and a Cobalt(II) complex. Under carbon dioxide atmosphere, Cobalt(I) complex was shown to be unreactive towards CO<sub>2</sub> but CO<sub>2</sub> insertion was observed in the alkyl-Cobalt(III) complex [R-Co<sup>III</sup>L]<sup>2+</sup> giving probably a CO<sub>2</sub> adduct [R-Co<sup>III</sup>L(CO<sub>2</sub>)]<sup>2+</sup>. This adduct presented a strong adsorption at the carbon electrode and was reduced at potential less cathodic than the one of alkyl-Cobalt(III) complex. After reduction, the carboxylate RCO<sub>2</sub><sup>-</sup> (NC-CH<sub>2</sub>-CO<sub>2</sub><sup>-</sup>) was released and a catalytic bielectronic carboxylation of chloroacetonitrile took place. Controlled potential electrolyses confirmed the catalytic process and gave for cyanoacetic acid faradic yields up to 60% under low overpotential conditions.

## 1. Introduction

The formation of carbon-carbon bonds between CO<sub>2</sub> and organic halides is an easy way to prepare carboxylated products [1]. Moreover, carbon dioxide which is an abundant waste and relatively inexpensive can be valorized. Among the wide range of available organic halides RX, carboxylation of chloroacetonitrile has received much attention [2,3]. This is due to the relevant interest of the resulting carboxylic acid, cyanoacetic acid, in many industrial processes [4,5] and the particularly toxic and unfriendly environmental method of its chemical preparation [6]. That is why greener processes of synthesis are of interest. Among them, electrocarboxylation seems to be a promising way. Three main electrochemical methods have been described:

The first one is based on the direct electrolysis of acetonitrile saturated by CO<sub>2</sub> [7,8]. The faradic yield was low (less than 30–40%) and the process required a very high overpotential on the working potential (<−2.3 V versus SCE).

The second way consists in the direct electroreduction at various electrodes (carbon [2,3] or Hg [2]) of chloroacetonitrile in CO<sub>2</sub>-saturated aprotic solvents. The performances depended on the cathode material. On carbon or mercury electrodes, high yields

of conversion were obtained in undivided cells equipped with a sacrificial anode (Mg or Al). However, highly negative working potentials were required and passivation phenomena were observed. Recently, Gennaro and coll. have demonstrated the benefit of a silver cathode [9]. Indeed, an excellent faradic yield was obtained under low overpotential condition. This effect is attributed to the specific reactivity of silver towards halides.

The third method consists in the electrocatalytic reduction of chloroacetonitrile in CO<sub>2</sub>-saturated aprotic solvents through the use of a catalytic system based on transition metal complexes. Ni(salen) has been shown to be the best catalytic system with a faradic yield up to 70% under a working potential near −1.7 V [2]. With different benzyl chlorides, higher yields were obtained [10]. However, few catalysts for electrochemical synthesis of cyanoacetic acid have been studied. To our knowledge, only one example of cobalt complex has been used for the electrocarboxylation of chloroacetonitrile [11] while the electrocarboxylation properties of cobalt complexes have been demonstrated [12–14]. In all cases, the electrochemical reduction of a Co(II) complex gives a Co(I) which reacts with alkyl halides through a S<sub>N</sub>2 mechanism (oxidative addition) and yields an alkylcobalt(III). The reduction of this Co(III) complex leads to its decomposition into the starting complex and a carbanion or an organic radical. Under CO<sub>2</sub>, carbon coupling yields the carboxylate. In these works [12–14], the cobalt complexes presented a square planar structure which was in favour of the oxidative addition of alkyl halides. This chemical step was probably the key of the catalytic mechanism. Moreover, taking in

\* Corresponding author. Tel.: +33 0 5 61 55 61 21; fax: +33 0 5 61 55 61 39.

E-mail address: reynes@chimie.ups-tlse.fr (O. Reynes).

<sup>1</sup> ISE Member.

mind the previous works [12–14], it appears that the reductions of the RX and CO<sub>2</sub> are competitive, giving different chemical routes and then different products. That is why the aim of our work is to activate selectively the alkyl halide RX under the lowest overpotential conditions [11]. Once activated, the alkylcobalt must react with carbon dioxide. Before our work [11], hexacoordinated complexes have been never studied as potential catalysts because of their full coordination sphere which prevents the addition of the alkyl halide. However, fast ligand exchange reactions have been described [15,16] in these complexes that explain their relative reactivities.

In this paper, we describe the catalytic properties of hexacoordinated [Co(II)(terpy)<sub>2</sub>]<sup>2+</sup> complex (Scheme 1) which go through the electrogenerated [Co(I)(terpy)]<sup>+</sup>. Cyclic voltammetry gave the evidence of a catalytic cycle and bulk electrolyses in an undivided cell confirmed the capacity of this catalyst in the mediated electrocarboxylation of chloroacetonitrile into cyanoacetic acid.

## 2. Experimental

### 2.1. Reagents

2,2':6',2''-Terpyridine, cobalt (II) chloride hexahydrated, chloroacetonitrile, potassium hexafluorophosphate (KPF<sub>6</sub>) were used as received. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was recrystallised from ethylacetate and dried at 70 °C under vacuum. Acetonitrile (HPLC grade) was stored on molecular sieves (3 Å). The Co(terpyridine)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> was synthesized as described in the literature [17]. Brown crystals of complex were obtained by slow diffusion of diethyl ether in a concentrated solution of acetonitrile. Elemental analysis: Calculated: C: 44.19%, N: 10.31%, H: 2.72%. Found: C: 43.68%, N: 10.00%, H: 2.36%.

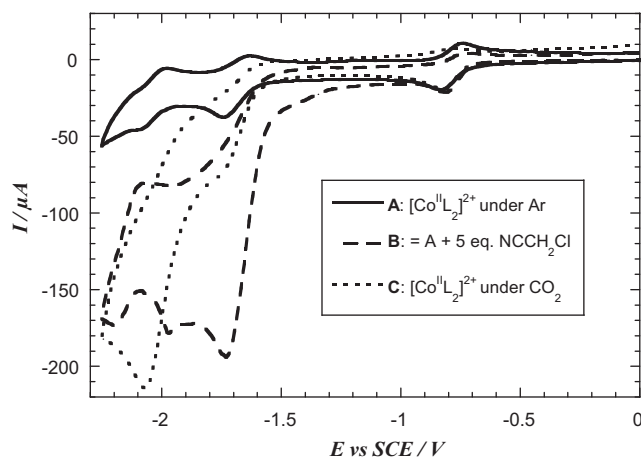
### 2.2. Instrumentations

Electrochemical measurements were carried out at room temperature with an Autolab 20 potentiostat (EcoChemie). Voltammetric experiments were conducted at room temperature in a classical three electrodes cell: a glassy carbon (GC) disk (diameter 3 mm, EDI Tacussel, and 1 mm, BioLogic) as the working electrode; a saturated calomel electrode (S.C.E.) with a double junction as the reference electrode and a platinum wire as the counter electrode. All experiments were carried out in dry acetonitrile + TBAPF<sub>6</sub> 0.1 mol.L<sup>-1</sup> under argon or carbon dioxide atmospheres. The potentials are referred to the saturated calomel electrode (S.C.E.).

Spectroelectrochemical experiments were performed in a quartz cuve (l=1 cm) with a Cary 1E spectrophotometer for the UV-vis spectra recordings. The spectrum of Co<sup>I</sup> complex were recorded after electrolysis ( $E_{\text{applied}} = -1\text{ V}$  versus SCE) of Co(II)(terpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> in acetonitrile + TBAPF<sub>6</sub> 0.1 mol.L<sup>-1</sup> solution under argon atmosphere.

A Bruker EMX 8/2.7 Band X was used for the e.p.r. determinations. The electrolysis was carried out under galvanostatic conditions ( $I = -300\ \mu\text{A}$ ) in a thin electrochemical cell, placed in the cavity of the spectrometer. The working electrode potential was followed with a millivoltmeter. The conditions were: NC-CH<sub>2</sub>-Cl 10<sup>-1</sup> mol.L<sup>-1</sup>, complex 2 × 10<sup>-3</sup> mol.L<sup>-1</sup>, PBN 10<sup>-2</sup> mol.L<sup>-1</sup> where PBN is a spin trap, the *N*-tert-butyl- $\alpha$ -phenylnitron. This spin trap has been already used for the detection of radicals during photolysis experiments of alkylcobaloximes [18].

Preparative scale electrolyses were performed in an undivided cell equipped with a magnesium bar as the sacrificial anode, a saturated calomel electrode (S.C.E) as the reference electrode and carbon fibres as the working electrode. Acetonitrile + TBAPF<sub>6</sub> 0.1 mol.L<sup>-1</sup> solution (volume 25 mL) containing



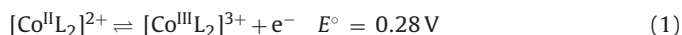
**Fig. 1.** Cyclic voltammetry in CH<sub>3</sub>CN + 0.1 mol.L<sup>-1</sup> TBAPF<sub>6</sub> at a glassy carbon disk electrode (diameter 3 mm), potential scan rate  $\nu = 0.1\text{ V s}^{-1}$ : (A) Co(terpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (10<sup>-3</sup> mol.L<sup>-1</sup>) under an argon atmosphere; (B) same as (A) after addition of 5 × 10<sup>-3</sup> mol.L<sup>-1</sup> of chloroacetonitrile NCCH<sub>2</sub>Cl; (C) Co(terpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (10<sup>-3</sup> mol.L<sup>-1</sup>) under CO<sub>2</sub> atmosphere.

chloroacetonitrile (10<sup>-2</sup> mol.L<sup>-1</sup> or more) and Co(II)(terpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (10<sup>-3</sup> mol.L<sup>-1</sup>) were saturated with carbon dioxide by bubbling ([CO<sub>2</sub>] = 0.28 mol.L<sup>-1</sup> [19]). The electrolysis potential was applied until that the desired coulometric charge was obtained or that the current dropped to 10% of its initial value. The cyanoacetic acid, the electrolysis product, was extracted using the procedure previously reported by Gennaro and Isse [2]. Cyanoacetic acid was analyzed by HPLC using a HP 1100 HPLC with a UV-vis detector operating at 200 nm, equipped with a Sugar SH1011 column eluted with 5 × 10<sup>-3</sup> mol.L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

## 3. Results

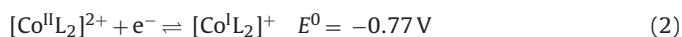
### 3.1. Cyclic voltammetry

Under argon atmosphere in acetonitrile and at a glassy carbon electrode, [Co<sup>II</sup>(terpy)<sub>2</sub>]<sup>2+</sup> complex (represented by [Co<sup>II</sup>L<sub>2</sub>]<sup>2+</sup>) exhibits several electronic transfers in the electroactivity domain of the solvent [20–22]. In the oxidative domain, a monoelectronic reversible oxidation process is observed, far displaced from the Co<sup>3+</sup>/Co<sup>2+</sup> system ( $E^0 = 1.85\text{ V}$ ):

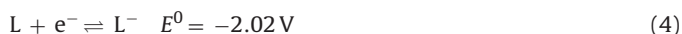
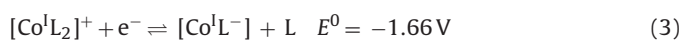


This potential displacement underlines the strong complexation of Co<sup>3+</sup> and the relative inertness of [Co<sup>III</sup>L<sub>2</sub>]<sup>3+</sup>.

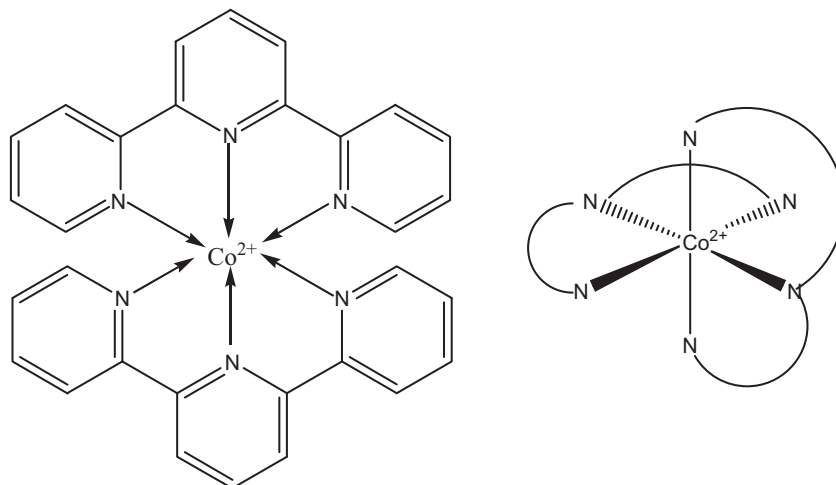
In the reductive domain, Fig. 1 – curve A, three mono-electronic reversible reductions are observed. The first electrochemical electron transfer is centered on the metallic center yielding a Co(I) complex; the standard potential which is related to the complexation constants is near the couple Co<sup>2+</sup>/Co<sup>+</sup> ( $E^0 = -0.86\text{ V}$  [23]):



The second electron transfer is described as the reduction of a coordinated terpyridine ligand while the third one would be the reduction of terpyridine [20]:



After addition of chloroacetonitrile, Fig. 1 – curve B, the voltammogram is modified. The electron transfer (2) is affected during the backward scan, the backward peak current is decreased. The peak current of the electron transfer (3) has increased while the



Scheme 1. The cobalt complex of terpyridine,  $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$ .

one of the electron transfer (4) is unchanged. The high increase of the peak current at  $-1.73\text{ V}$  (3) traduces a strong catalytic reductive behaviour of  $[\text{Co}^{\text{I}}\text{L}^-]$  towards chloroacetonitrile. The peak potential at  $-1.95\text{ V}$  corresponds to the direct electroreduction of chloroacetonitrile whose standard potential is  $E^0 = -0.85\text{ V}$  [9]; the electron transfer rate is quite slow in order to give such an overpotential at this potential scan rate.

Under  $\text{CO}_2$  atmosphere, Fig. 1 – curve C, the voltammogram is in agreement with the work of Abruna and coll.; they have shown that the electrogenerated  $[\text{Co}^{\text{I}}\text{L}^-]$  complex catalyzed the reduction of carbon dioxide [21] while the  $\text{Co}(\text{II})/\text{Co}(\text{I})$  system was unreactive. Indeed, the peak current of the electron transfer (3) has increased while the one of the electron transfer (2) is only affected during the backward scan, as above. The peak potential at  $-2.08\text{ V}$  corresponds to the direct electroreduction of  $\text{CO}_2$ .

Thus, the electron transfer (3) yielding  $[\text{Co}^{\text{I}}\text{L}^-]$  is involved in the activation of both carbon dioxide and chloroacetonitrile and will not be selective. Moreover, in order to consider a future development, the potential of the couple  $[\text{Co}^{\text{I}}\text{L}^-]^+ / [\text{Co}^{\text{I}}\text{L}^-]$  is too much cathodic versus the direct reduction of chloroacetonitrile or  $\text{CO}_2$ . However, it appears on Fig. 1 – curve B a specific signal around  $-1.4\text{ V}$  associated to the electron transfer (2) and the addition of chloroacetonitrile. So, the  $\text{Co}(\text{II})/\text{Co}(\text{I})$  system was only considered.

When the potential scan rate was restricted to the first reduction process (2), the voltammograms showed the behaviour of a reversible monoelectronic system (Fig. 2 – curve A). The peak ratio  $R_{\text{Ip}} = |I_{\text{p,backward}}/I_{\text{p,forward}}|$  was close to 1 and the peak current  $I_{\text{p,forward}}$  was linearly related to the  $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$  concentration and to the square root of the potential scan rate  $\nu$  as for a simple diffusion controlled process. The peak separation  $\Delta E_{\text{p}} = |E_{\text{p,backward}}/E_{\text{p,forward}}|$  was constant and began to increase when the potential scan rate  $\nu$  reached  $4\text{ V s}^{-1}$  according to the electron transfer rate  $k^0$  value [24].

### 3.2. Activation of chloroacetonitrile

In presence of chloroacetonitrile ( $\text{NC}-\text{CH}_2-\text{Cl}=\text{RCI}$ ) under argon atmosphere, the voltammogram of  $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$  was modified (Fig. 1 – curve B or Fig. 2 – curves B, C, D): a new cathodic peak appeared at  $E_{\text{p}} = -1.4\text{ V}$ . This cathodic peak increased when the chloroacetonitrile concentration was increased but reached a limit around four equivalent of chloroacetonitrile (at the potential scan rate of Fig. 2). When the potential scan rate was raised (Fig. 3), the cathodic peak around  $-1.4\text{ V}$  disappeared in the foot of the direct electroreduction of chloroacetonitrile. Moreover, for potential scan rate higher

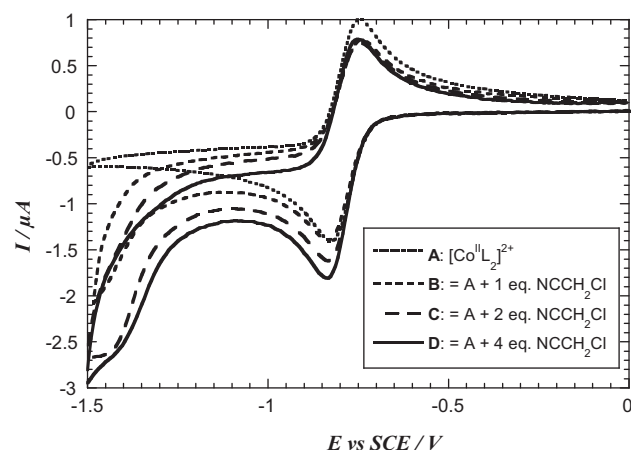


Fig. 2. Cyclic voltammetry under argon atmosphere in  $\text{CH}_3\text{CN} + 0.1\text{ mol L}^{-1}$  TBAPF<sub>6</sub> at a glassy carbon disk electrode (diameter 1 mm), potential scan rate  $\nu = 0.05\text{ V s}^{-1}$ : (A)  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $10^{-3}\text{ mol L}^{-1}$ ); (B) same as (A) after addition of  $1 \times 10^{-3}\text{ mol L}^{-1}$  of chloroacetonitrile  $\text{NCCH}_2\text{Cl}$ ; (C) same as (A) after addition of  $2 \times 10^{-3}\text{ mol L}^{-1}$  of chloroacetonitrile  $\text{NCCH}_2\text{Cl}$ ; (D) same as (A) after addition of  $4 \times 10^{-3}\text{ mol L}^{-1}$  of chloroacetonitrile  $\text{NCCH}_2\text{Cl}$ .

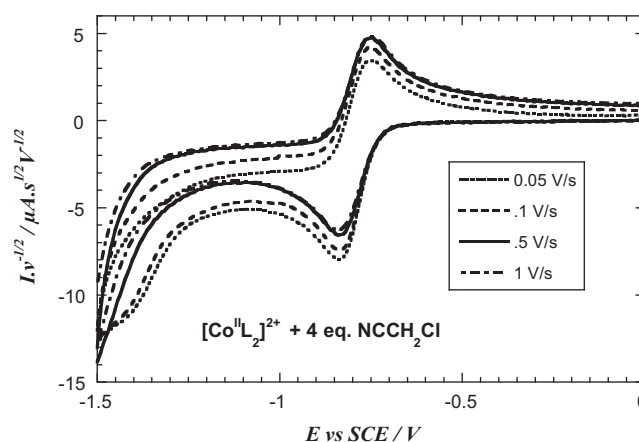


Fig. 3. Cyclic voltammetry under argon atmosphere in  $\text{CH}_3\text{CN} + 0.1\text{ mol L}^{-1}$  TBAPF<sub>6</sub> at a glassy carbon disk electrode (diameter 1 mm) for different potential scan rate  $\nu$ , normalized current  $I/\nu^{1/2}$  versus potential:  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $10^{-3}\text{ mol L}^{-1}$ ) + chloroacetonitrile  $\text{NCCH}_2\text{Cl}$  ( $4 \times 10^{-3}\text{ mol L}^{-1}$ ).

than  $0.5 \text{ V s}^{-1}$  (in Fig. 3), the signals of the electron transfer (2) Co(II)/Co(I) are in the same order of magnitude with or without chloroacetonitrile.

This behaviour is typical of the reactivity of square planar cobalt complexes [12–14,25–27] wherein the electrogenerated Co(I) reacts with alkyl chloride to give an alkylcobalt(III),  $[\text{R-Co}^{\text{III}}\text{L}]^{2+}$ , which is then reduced. In our case, the oxidative addition of chloroacetonitrile requires the loss of a terpyridine ligand in order to liberate coordination sites on the cobalt; this release may be in a concerted or a step wise manner. In this way, the cathodic peak around  $-1.4 \text{ V}$  is attributed to the reduction of the alkylcobalt(III), (Figs. 2 and 3):



The electrochemical system appeared irreversible, no backward peak was observed. This is due to the reduced alkyl cobalt complexes  $[\text{R-Co}^{\text{II}}\text{L}]^+$  which are highly unstable species and undergo homolytic (6) or heterolytic (7) Co–C bond cleavages [12], EC scheme:



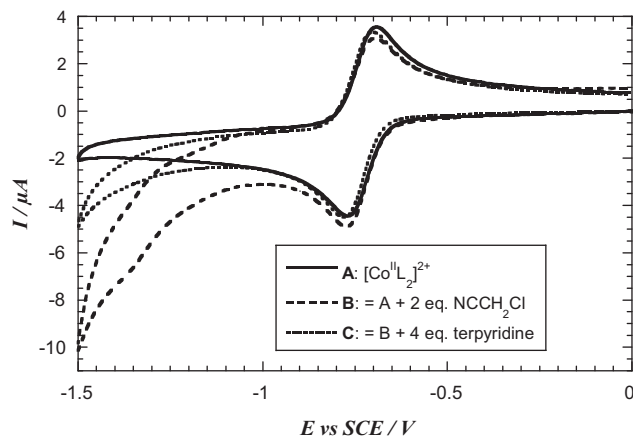
The bond cleavage is an important step because different products will be obtained according to the pathway. So, e.p.r. spectroscopies were carried out in order to give the evidence of radicals. The electrolyses in  $\text{CH}_3\text{CN} + 0.1 \text{ mol L}^{-1}$  TBAPF<sub>6</sub> were conducted in the cavity in presence of a spin trap PBN, already used during photolysis experiments of alkylcobaloximes [18]. Electrolysis of chloroacetonitrile  $\text{NC-CH}_2\text{-Cl}$  ( $10^{-1} \text{ mol L}^{-1}$ ) alone did not give any signal. The direct reduction of chloroacetonitrile occurs under high overpotentials: at a potential scan rate of  $0.1 \text{ V s}^{-1}$ , the reduction potential peak is  $-1.95 \text{ V}$  (Fig. 1). According to the standard redox potential of  $\text{NC-CH}_2^{\bullet}/\text{NC-CH}_2^-$   $E^0 = -0.69 \text{ V}$  [28], the radical  $\text{NC-CH}_2^{\bullet}$  is immediately reduced into  $\text{NC-CH}_2^-$  under this high cathodic potential. Therefore, the overall process is a bielectronic reduction [9] which explains the untrapping of radicals.

Electrolysis of  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $2 \times 10^{-3} \text{ mol L}^{-1}$ ) + chloroacetonitrile ( $10^{-1} \text{ mol L}^{-1}$ ) did not give any e.p.r. signal although the reactant concentrations were sufficiently high for e.p.r. experiments, PBN concentration was  $10^{-2} \text{ mol L}^{-1}$ . By contrast, when the degassing was insufficient, a classic e.p.r. signal was recorded due to the trapping of the superoxide radical anion under lower concentrations. It may be noted that the spin trapping gave the evidence of the methyl radical in the photolysis of methylcobaloximes [18]. Taking into account these results, the heterolytic cleavage would be the chemical pathway, reaction (7).

Furthermore, Figs. 2 and 3 show, under low potential scan rate, that the cathodic forward peak of  $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$  is enhanced when chloroacetonitrile is added. Above a scan rate of  $0.5 \text{ V s}^{-1}$ , the cathodic peak currents were of the same order of magnitude with or without chloroacetonitrile. If we consider the ratio peak current versus the pure diffusion current, it is observed that this ratio tended towards 1 when the scan rate was increased and was not linearly related to chloroacetonitrile concentration but reached a plateau. These observations do not match with the oxidative addition scheme. The current increase implies an EC<sub>cat</sub> scheme in which the chemical reaction gives back the Co(II) complex: an electron transfer between the electrogenerated Co(I) complex and chloroacetonitrile RCl would account for the phenomenon.

Therefore, the reactivity of the electrogenerated Co(I) complex and chloroacetonitrile (RCl) appeared competitive between the oxidative addition of alkyl chloride yielding an alkylcobalt(III) and an electron transfer process giving rise to a catalytic current.

When free terpyridine was added in solution (Fig. 4 – curve C), the cathodic peak corresponding to the reduction of the



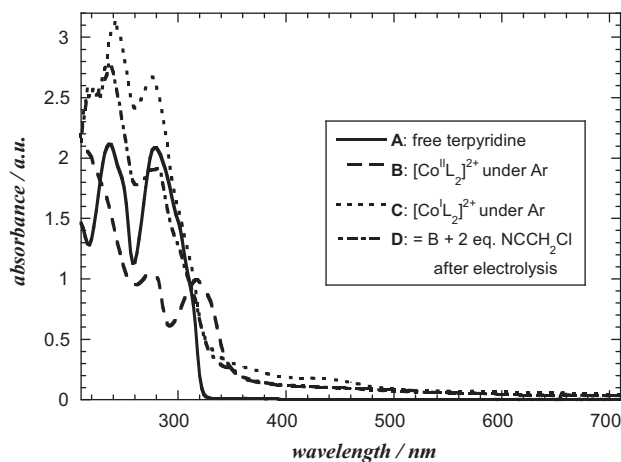
**Fig. 4.** Cyclic voltammetry under argon atmosphere in  $\text{CH}_3\text{CN} + 0.1 \text{ mol L}^{-1}$  TBAPF<sub>6</sub> at a glassy carbon disk electrode (diameter 1 mm), potential scan rate  $\nu = 0.5 \text{ V s}^{-1}$ : (A)  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $10^{-3} \text{ mol L}^{-1}$ ); (B) same as (A) after addition of  $2 \times 10^{-3} \text{ mol L}^{-1}$  of chloroacetonitrile  $\text{NCCH}_2\text{Cl}$ ; (C) same as (B) after addition of  $4 \times 10^{-3} \text{ mol L}^{-1}$  of terpyridine.

organocobalt(III) complex (5) was strongly decreased. Excess terpyridine prevents the oxidative addition of chloroacetonitrile RCl on the electrogenerated Co(I) complex which requires the release of a terpyridine. Moreover, the signal of the Co(II)/Co(I) system appeared similar to that of the free complex (Fig. 4 – curve A). The electron transfer between the electrogenerated Co(I) and chloroacetonitrile RCl is reduced.

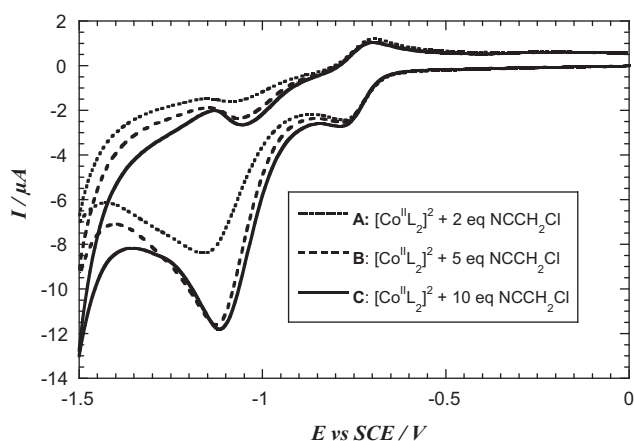
### 3.3. Spectroelectrochemical studies

Spectroelectrochemical experiments were carried out in order to give the evidence of intermediates. UV–vis spectra recorded under argon atmosphere between 210 nm and 700 nm are shown Fig. 5.

Free terpyridine was used as a reference. The spectrum of  $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$  is consistent with a hexacoordinated Co(II) complex [29,30] with a low molar absorbance in the visible domain. After electrolysis under argon atmosphere at a potential of  $-1 \text{ V}$ , the observed modifications in the UV domain were similar in



**Fig. 5.** Spectroelectrochemical experiments under argon atmosphere, UV–vis spectra in  $\text{CH}_3\text{CN} + 0.1 \text{ mol L}^{-1}$  TBAPF<sub>6</sub>: (A) free terpyridine ( $10^{-4} \text{ mol L}^{-1}$ ); (B)  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $2.5 \times 10^{-5} \text{ mol L}^{-1}$ ) before electrolysis; (C)  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $2.5 \times 10^{-5} \text{ mol L}^{-1}$ ) after electrolysis at a potential of  $-1 \text{ V}$ ; (D)  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $2.5 \times 10^{-5} \text{ mol L}^{-1}$ ) + chloroacetonitrile  $\text{NCCH}_2\text{Cl}$  ( $5 \times 10^{-5} \text{ mol L}^{-1}$ ) after electrolysis at a potential of  $-1 \text{ V}$ .



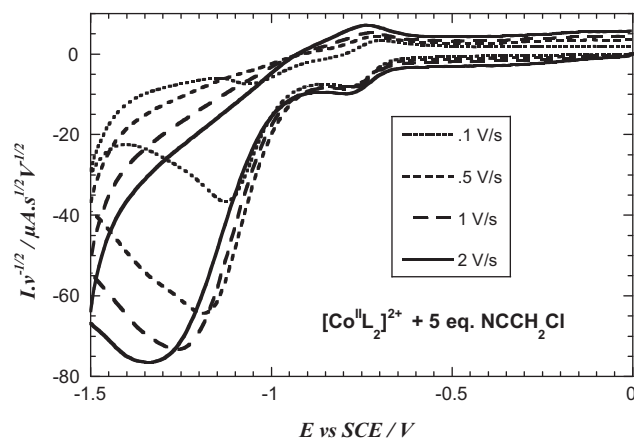
**Fig. 6.** Cyclic voltammetry under  $\text{CO}_2$  atmosphere in  $\text{CH}_3\text{CN} + 0.1 \text{ mol L}^{-1}$  TBAPF<sub>6</sub> at a glassy carbon disk electrode (diameter 1 mm), potential scan rate  $\nu = 0.1 \text{ V s}^{-1}$ : (A)  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $10^{-3} \text{ mol L}^{-1}$ ) + chloroacetonitrile  $\text{NCCH}_2\text{Cl}$  ( $2 \times 10^{-3} \text{ mol L}^{-1}$ ); (B)  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $10^{-3} \text{ mol L}^{-1}$ ) + chloroacetonitrile  $\text{NCCH}_2\text{Cl}$  ( $5 \times 10^{-3} \text{ mol L}^{-1}$ ); (C)  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $10^{-3} \text{ mol L}^{-1}$ ) + chloroacetonitrile  $\text{NCCH}_2\text{Cl}$  ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ).

free chloroacetonitrile solution or in presence of alkyl halide. Indeed, the pattern of free terpyridine was observed and the band at 316 nm which is characteristic to the bound terpyridine [29,30] disappeared. These observations showed (with or without chloroacetonitrile) the loss of a terpyridine ligand. Moreover, in free chloroacetonitrile solution the loss of terpyridine would occur also during the reduction of  $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$  complex. The large time scale of spectroelectrochemical experiments allowed the observation of the coordination change.  $[\text{Co}^{\text{I}}\text{L}]^+$  is the final structure but its formation is too slow to be observed by cyclic voltammetry. So, the release of a ligand allows the further oxidative addition of chloroacetonitrile on the  $\text{Co}(\text{I})$  complex.

#### 3.4. Electrocarboxylation of chloroacetonitrile

Under carbon dioxide atmosphere in free chloroacetonitrile solution, the electrochemical behaviour of  $\text{Co}(\text{II})/\text{Co}(\text{I})$  couple was unchanged (Fig. 1 – curve C) showing the unreactivity of electrogenerated  $\text{Co}(\text{I})$  towards  $\text{CO}_2$  [21]. In  $\text{CO}_2$ -saturated solution of chloroacetonitrile in acetonitrile + TBAPF<sub>6</sub>  $0.1 \text{ mol L}^{-1}$ , the electrochemical behaviour of the  $\text{Co}(\text{II})$  complex was strongly modified (Fig. 6).

The backward peak current of the  $\text{Co}(\text{II})/\text{Co}(\text{I})$  system has decreased but the reduction peak of  $\text{Co}(\text{II})$  complex was unchanged as under an argon atmosphere. The peak current was related to the complex concentration and to the square root of the potential scan rate but independent of chloroacetonitrile concentration; the electron transfer, above mentioned, is reduced. This peak was followed by a new reduction peak at  $E_p \sim -1.2 \text{ V}$ , potential less cathodic than the one observed under an argon atmosphere. The peak current increased with chloroacetonitrile concentration up to a limit (around 5 equivalent of chloroacetonitrile) and was not related to the square root of the potential scan rate  $\nu$  as for a diffusion process (Fig. 7). Under slow potential scan rate, the current followed almost a linear as for an adsorption process, but deviated rapidly when the sweep rate increased (Fig. 7); the transfer may be represented by an  $\text{CE}_{\text{ads}}$  scheme. Moreover, on the reverse scan, a singularity appeared around  $-1.1 \text{ V}$  which corresponds to a reduction. Such a signal was often observed in organic electrochemistry, for example the electrooxidation of alcohols [31]. As the forward peak presented a strong adsorption character, adsorption sites were occupied. After the electron transfer, desorption took place and these free sites were engaged in a new cycle of



**Fig. 7.** Cyclic voltammetry under  $\text{CO}_2$  atmosphere in  $\text{CH}_3\text{CN} + 0.1 \text{ mol L}^{-1}$  TBAPF<sub>6</sub> at a glassy carbon disk electrode (diameter 1 mm) for different potential scan rate  $\nu$ , normalized current  $I/\nu^{1/2}$  versus potential:  $\text{Co}(\text{terpy})_2(\text{PF}_6)_2$  ( $10^{-3} \text{ mol L}^{-1}$ ) + chloroacetonitrile  $\text{NCCH}_2\text{Cl}$  ( $5 \times 10^{-3} \text{ mol L}^{-1}$ ).

reduction giving rise to a reduction peak on the anodic reverse scan.

This adsorption peak was due to the presence of the complex, chloroacetonitrile and  $\text{CO}_2$ . As  $\text{Co}(\text{I})$  complex was unreactive towards  $\text{CO}_2$ ,  $\text{Co}(\text{I})$  complex must react at first with chloroacetonitrile; then, the  $\text{CO}_2$  insertion would occur on the alkyl $\text{Co}(\text{III})$  complex yielding a  $\text{CO}_2$  adduct which would adsorb at the electrode before the electron transfer. The overall reaction is the carboxylation of chloroacetonitrile into cyanoacetate ( $\text{RCOO}^- = \text{NC}-\text{CH}_2-\text{COO}^-$ ).

#### 3.5. Bulk electrolyses

In order to confirm the electrocatalytic behaviour of cobalt(II) terpyridine complex for the synthesis of cyanoacetic acid, preparative electrolyses were carried out in  $\text{CO}_2$ -saturated solution in presence of chloroacetonitrile and cobalt(II) complex. The influence of the applied potential on faradic and carboxylate product yields is summarized in Table 1. Note that acetonitrile which can be obtained by protonation of the carbanion  $\text{R}^-(\text{NC}-\text{CH}_2^-)$  could not be determined.

In presence of ten-fold excess of chloroacetonitrile, when the working potential was in the  $[-1, -1.3 \text{ V}]$  domain (entry 3–6), the good faradic (50–60%) and carboxylate product (46–60%) yields confirmed the interesting electrocatalytic properties of  $[\text{Co}(\text{terpy})_2]^{2+}$  complex for the electrocatalytic synthesis of cyanoacetic acid. Best conditions were found when the applied potential was in the domain  $[-1.2 \text{ V}, -1.3 \text{ V}]$ . Indeed, as observed by cyclic voltammetry, the efficient electrocarboxylation of chloroacetonitrile took place when the electrolysis potential was on the reduction potential ( $E_p = -1.2 \text{ V}$ ) of the adsorbed adduct. The theoretical faradic charge was reached and the faradic yield was good and constant (around 60%).

On the other hand, by applying a potential under  $-1 \text{ V}$  (entry 1 and 2), the faradic and carboxylate product yields decreased and the theoretical faradic charge was never reached. In order to estimate the number of turnover of catalyst, bulk experiments have been performed with higher amounts of chloroacetonitrile (entry 7 and 8). The faradic yields were good (around 55%). However, the theoretical charge was not reached and the charge passed whatever the amounts of chloroacetonitrile was constant (around 80–90 C). The catalyst is probably deactivated during the electrocatalytic cycle as already reported [2].

**Table 1**  
Electrocarboxylation of chloroacetonitrile<sup>a</sup>.

Entry	Electrolysis potential vs S.C.E/V	Charge passed/C	Carboxylate yield (%) <sup>e</sup>	Faradic efficiency (%) <sup>f</sup>	Duration of electrolysis/min
1	-0.8	30 <sup>b</sup>	28	45	90
2	-0.9	40.5 <sup>b</sup>	41	49	60
3	-1	45 <sup>b</sup>	46	49	40
4	-1.1	47.6 <sup>b</sup>	50	51	30
5	-1.2	50 <sup>b</sup>	55	53	20
6	-1.3	55 <sup>b</sup>	60	53	13
7	-1.3	80 <sup>c</sup>	31	37	20
8	-1.3	88 <sup>d</sup>	30	49	25

<sup>a</sup> Electrolyses were performed in an undivided cell at room temperature in presence of  $10^{-3}$  mol L<sup>-1</sup> of [Co(II)(terpy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. The electrolytic solution (acetonitrile + 0.1 mol L<sup>-1</sup> TBAPF<sub>6</sub>) were saturated with carbon dioxide. Sacrificial magnesium anode.

<sup>b</sup> In presence of  $10^{-2}$  mol L<sup>-1</sup> of ClCH<sub>2</sub>CN (ten-fold excess). The Theoretical charge is 48 C for the total conversion of the substrate in a 2e<sup>-</sup> process.

<sup>c</sup> In presence of  $2 \times 10^{-2}$  mol L<sup>-1</sup> of ClCH<sub>2</sub>CN (twenty-fold excess). The Theoretical charge is 96 C for the total conversion of the substrate in a 2e<sup>-</sup> process.

<sup>d</sup> In presence of  $3 \times 10^{-2}$  mol L<sup>-1</sup> of ClCH<sub>2</sub>CN (thirty-fold excess). The Theoretical charge is 144 C for the total conversion of the substrate in a 2e<sup>-</sup> process.

<sup>e</sup> Calculated as  $N_{\text{RCOOH}}/N_{\text{RCl}}$ .

<sup>f</sup> Calculated as  $f = Q_{\text{RCOOH}}/Q_{\text{passed}}$ . Where  $Q_{\text{RCOOH}} = 2FN_{\text{RCOOH}}$  ( $N_{\text{RCOOH}}$  is the number of moles of cyanoacetic acid produced by electrolysis) and  $Q_{\text{passed}}$  is the measured electric charge.

## 4. Discussion

### 4.1. Activation of chloroacetonitrile

By cyclic voltammetry, two competitive pathways have been evidenced for the electrogenerated Co(I) complex: a catalytic electron transfer (ET) towards chloroacetonitrile and the oxidative addition (OA) of chloroacetonitrile. The oxidative addition requires the release of a terpyridine ligand. When terpyridine was added, both processes were slowed down (Fig. 4). Moreover, for both processes, their importances increased with the chloroacetonitrile concentration according first order rate reactions, but quickly reached a limit as an enzymatic reaction (Figs. 2 and 3). Although a structure determination of [Co<sup>I</sup>(bipy)<sub>3</sub>]<sup>+</sup> has been resolved [32], the electrogenerated Co(I) complex can lose a terpyridine yielding the active species [Co<sup>I</sup>L]<sup>+</sup>, an undercoordinated complex (Fig. 5):



Such a dissociation implies a square scheme, associated with the electron transfer (2):



Taking into account the redox potential in acetonitrile of Co<sup>2+</sup>/Co<sup>+</sup> ( $E^0 = -0.86$  V/SCE [23]) and the complexation coefficients of Co(II) and Co(I), the potential E(9) must be between -0.85 V and -0.77 V. By contrast to the high potential displacement of the Co(III)/Co(II) around 1.5 V by complexation, this weak potential displacement indicates that the complex formation constants are of the same order of magnitude for Co<sup>+</sup> and Co<sup>2+</sup>. Concerning the dissociation constants  $K_{\text{I}}$  and  $K_{\text{II}}$ , the values range from  $10^{-4}$  to  $10^{-10}$  in water [33]; in acetonitrile, the same order is waited: according a constant  $K = 10^{-5}$ , the complex is dissociated in the spectroelectrochemical conditions while the CoL<sub>2</sub> core is predominant in the electrochemical experiments. When terpyridine is added, the formation of [Co<sup>I</sup>L]<sup>+</sup> is restricted and the reactivity is weakened. So, the reactivity is controlled by the loss of the terpyridine ligand on [Co<sup>I</sup>L<sub>2</sub>]<sup>+</sup> which gives the active species [Co<sup>I</sup>L]<sup>+</sup>; it is the rate determining step. Pulse radiolysis experiments [34] have been reported on the rate of dissociation from Co(II) complexes such as [Co<sup>II</sup>(phen)<sub>3</sub>]<sup>2+</sup> and [Co<sup>II</sup>(bipy)<sub>3</sub>]<sup>2+</sup>:  $0.8$  s<sup>-1</sup> and  $2.6$  s<sup>-1</sup> respectively. Considering the terpyridine ligand, the complexation coefficient of Co<sup>+</sup> is around 20 times larger than Co<sup>2+</sup> one; we might expect a lower rate of dissociation for [Co<sup>I</sup>L<sub>2</sub>]<sup>+</sup>, reaction (8).

The reactivity of the active species [Co<sup>I</sup>L]<sup>+</sup> goes through two ways:

1 – a direct concerted electron transfer [35] with chloroacetonitrile (Scheme 2) which gives R<sup>•</sup>, Cl<sup>-</sup> and [Co<sup>II</sup>L]<sup>2+</sup> which is reduced back into [Co<sup>I</sup>L]<sup>+</sup> through reaction (9), EC<sub>cat</sub> mechanism:



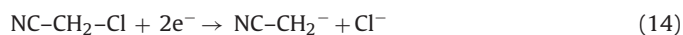
At this potential of [Co<sup>I</sup>L]<sup>+</sup> formation, the R<sup>•</sup> is directly reduced into the carbanion R<sup>-</sup> which can react with itself, acetonitrile or electrophilic species [36]. The overall pathway is controlled by the dissociation of [Co<sup>I</sup>L<sub>2</sub>]<sup>+</sup>. Under low chloroacetonitrile concentrations, the electron transfer is related to the chloroacetonitrile concentration. On the contrary, for higher concentration the electron transfer depends on the [Co<sup>I</sup>L<sub>2</sub>]<sup>+</sup> dissociation.

2 – the oxidative addition of chloroacetonitrile on [Co<sup>I</sup>L]<sup>+</sup> (Scheme 2) which gives an organo-cobalt(III) [R-Co<sup>III</sup>L]<sup>2+</sup> complex [12–14,25–27]. This complex is reduced at a lower potential (Figs. 2 and 3) into [R-Co<sup>II</sup>L]<sup>+</sup> which decomposes rapidly into R<sup>-</sup> and [Co<sup>II</sup>L]<sup>2+</sup>, as suggested by e.p.r. experiments. Dissociation of [R-Co<sup>II</sup>L]<sup>+</sup> is fast, the kinetic constants of methyl-cobaloximes dissociations have been evaluated around  $5 \times 10^3$  s<sup>-1</sup> [37]:



At the potential of electron transfer (5), the cobalt(II) complex [Co<sup>II</sup>L]<sup>2+</sup> is reduced back into [Co<sup>I</sup>L]<sup>+</sup> giving rise to a catalytic current; the carbanion R<sup>-</sup> reacts as above mentioned. In this case also, the overall pathway depends on the dissociation of [Co<sup>I</sup>L<sub>2</sub>]<sup>+</sup>.

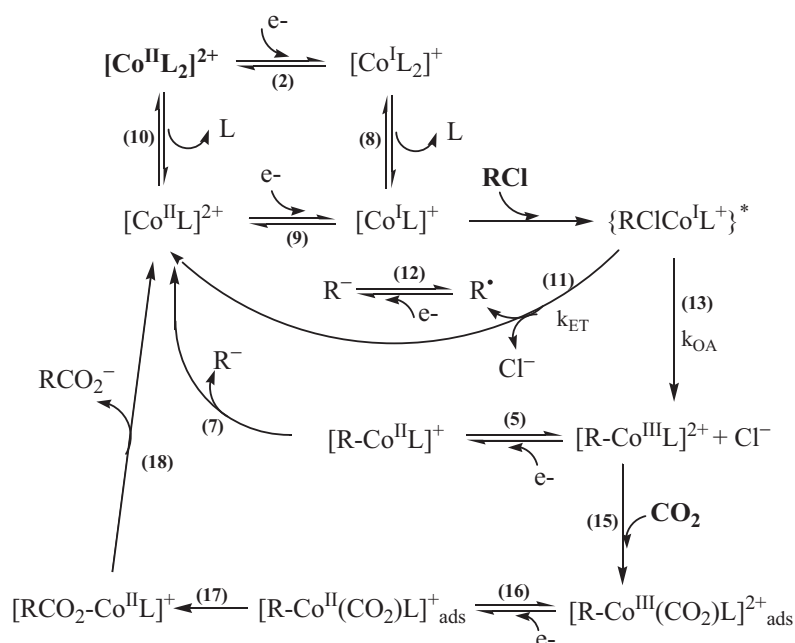
Whatever is the pathway (1 or 2), the final product is the carbanion R<sup>-</sup>, the overall reaction is the bielectronic reduction of chloroacetonitrile RCl:



The observation of the two competitive reactions appeared surprising for the same reactives: electron transfer is a mono-electronic exchange while oxidative addition is a bielectronic one; these reactions may result from the same activated complex {RCICoL<sup>+</sup>}<sup>\*</sup>. These reactions are slow but may present good selectivities under the electrochemical process.

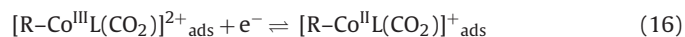
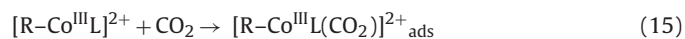
### 4.2. Electrocarboxylation of chloroacetonitrile

In CO<sub>2</sub>-saturated solution, the electrocatalytic properties of [Co<sup>II</sup>L<sub>2</sub>]<sup>2+</sup> complex were enhanced showing the CO<sub>2</sub> activation by the [R-Co<sup>III</sup>L]<sup>2+</sup> complex (Figs. 6 and 7). By reference to the



**Scheme 2.** Synthetic routes of chloroacetonitrile RCl activation by  $[\text{Co}^{\text{I}}\text{L}]^+$ , L = terpyridine.

behaviour under argon, the appearance of the reduction peak at  $-1.2\text{V}$  implies that carbon dioxide enters in the catalytic cycle and interferes in the reduction cycle of chloroacetonitrile. This peak presented the characteristics of a strong adsorption process on the forward and backward scans. Taking into account, the behaviour of Ni or Pd complexes used as catalysts for electrocarboxylation [38,39], the activation of  $\text{CO}_2$  may go through the reactions of addition, coupling and dissociation:



The desorption gave the carboxylate and a free adsorption site, ready for a new cycle. In this catalytic cycle, the rate determining step would be the oxidative addition of chloroacetonitrile onto the cobalt(I) complex, reaction (13) or the addition of  $\text{CO}_2$ , reaction (15). Considering the high  $\text{CO}_2$  concentration ( $0.28\text{ mol L}^{-1}$ ), reaction (13) may control the catalytic cycle. This explains that the peak current of the electron transfer (16) was related to the potential scan rate for low  $\nu$  values (below  $0.5\text{ V s}^{-1}$ ); when the potential scan rate increased, the  $[\text{R-Co}^{\text{III}}\text{L}]^{2+}$  and  $[\text{R-Co}^{\text{III}}\text{L}(\text{CO}_2)]^{2+}$  formations were limited and then the current of reaction (16) as an  $\text{CE}_{\text{ads}}$  scheme (Fig. 7). The release of the carboxylate is unclear and represented by the reactions (17) and (18).

As in the chloroacetonitrile activation under an argon atmosphere, a catalytic bi-electronic carboxylation of chloroacetonitrile was observed under  $\text{CO}_2$  atmosphere. The overall process is:



### 4.3. Bulk electrolyses

In ideal conditions, applied potential  $[-1.2\text{V}, -1.3\text{V}]$ , the theoretical faradic charge was reached and the faradic yield was good and constant (around 60%). The electrochemical process works on the potential where it was observed the strong adsorption of the  $\text{CO}_2$  adduct. However, the carboxylate product yields were lower

than the one obtained with Ni(salen) but the overpotential is much lower, about  $0.4\text{V}$  [2].

By applying a potential under  $-1\text{V}$  (entry 1 and 2), the faradic and carboxylate product yields decreased and the theoretical faradic charge was never reached. Moreover, the electrolysis time was strongly increased. In this domain of applied potential  $[-0.8\text{V}, -0.9\text{V}]$ , the formation of cyanoacetic acid is explained by the electron transfer (11) between the electrogenerated  $[\text{Co}^{\text{I}}\text{L}]^+$  and chloroacetonitrile which yields the reactive carbanion  $\text{R}^-$ . According to the law of mass action, the high concentration of  $\text{CO}_2$  ( $0.28\text{ mol L}^{-1}$ ) is in favour of the direct carboxylation of the carbanion. The process speed is controlled by the electron transfer (11).

Concerning the number of turnover of catalyst, bulk experiments with higher amounts of chloroacetonitrile have shown that the faradic yields were good but the theoretical charge was never reached. The catalyst is probably deactivated during the electrocatalytic cycle as already reported [2] for other catalysts. Electrode fouling might also explain the current drop along the process because the strong adsorption of the  $\text{CO}_2$  adduct.

## 5. Conclusions

The electrocarboxylation of chloroacetonitrile mediated by  $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$  (L = terpy) has been investigated by cyclic voltammetry. Electrochemical studies under argon atmosphere showed that the oxidative addition of chloroacetonitrile RCl on  $[\text{Co}^{\text{I}}\text{L}_2]^+$  implied at first the loss of a ligand terpyridine and gave an alkylcobalt(III) complex  $[\text{R-Co}^{\text{III}}\text{L}]^{2+}$ . This complex was then reduced into alkylcobalt(II) complex which decomposed through a heterolytic Co-C bond cleavage to form the carbanion and a Cobalt(II) complex. A side reaction, direct electron transfer, was also evidenced yielding the same products. Under carbon dioxide atmosphere,  $\text{CO}_2$  insertion was observed in the alkylcobalt(III) complex  $[\text{R-Co}^{\text{III}}\text{L}]^{2+}$  giving a  $\text{CO}_2$  adduct  $[\text{R-Co}^{\text{III}}\text{L}(\text{CO}_2)]^{2+}$ . This adduct presented a strong adsorption and was reduced at a potential less cathodic than the one of  $[\text{R-Co}^{\text{III}}\text{L}]^{2+}$  under an argon atmosphere. After reduction, the carboxylate  $\text{NC-CH}_2\text{-CO}_2^-$  was released and a catalytic bi-electronic carboxylation of chloroacetonitrile took place.



Cyanoacetic acid could be obtained with a good faradic yield (60%) under less cathodic working potentials compared to nickel(salen). These potential conditions prevented the competitive reduction of CO<sub>2</sub>. The formation of alkylcobalt(III) complex prevents side reactions in the activation of chloroacetonitrile. The [Co<sup>II</sup>L<sub>2</sub>]<sup>2+</sup> complex is the match of the catalytic system which is based on the undercoordinated [Co<sup>I</sup>L]<sup>+</sup>, engaged in the activation of chloroacetonitrile. At the present time, it appears that the oxidative addition should be accelerated and the concentration of the active complex should be increased. Work is in progress for the design of new cobalt complexes.

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