Electrochemical synthesis and reactivity of carbonato–niobocene complexes

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Abstract

The addition of the CO_3^{2-} dianion to the electrogenerated species $Nb(\eta^5\text{-}C_5H_3RR')_2Cl$ (2: R = H, R' = SiMe$_3$; 2': R = R' = SiMe$_3$) gives in ca. 50% yields the anionic carbonato niobium(III) complex $[Nb(\eta^5\text{-}C_5H_3RR')_2(OC(O)O\text{-}O,O')]^-$ (3: R = H, R' = SiMe$_3$; 3': R = R' = SiMe$_3$) which are oxidized electrochemically to the corresponding paramagnetic niobium(IV) complex $[Nb(\eta^5\text{-}C_5H_3RR')_2(OC(O)O\text{-}O,O')]$ (5: R = H, R' = SiMe$_3$; 5': R = R' = SiMe$_3$). These paramagnetic derivatives have been characterized by ESR and IR spectroscopy. Mechanistic aspects concerning the formation of 3 and 3' are discussed.

3 can also be obtained from two-electron reduction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O)Cl$, 4, in the presence of carbon dioxide. The addition of the formate anion HCO_2 to 3 gives the formato complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(OC(O)H\text{-}O,O')$ 6.

Keywords: Niobium; Electrochemistry; Carbonato complexes; Carbon dioxide; Cyclopentadienyl; Reduction

1. Introduction

The transformation of carbon dioxide into useful chemical derivatives constitutes an attractive goal in the field of chemistry. While a number of discrete CO_2-containing metal complexes have been described [1], few reactivity studies of coordinated CO_2 are known. Insertion of unsaturated molecules into metal hydride or carbon or oxygen bonds are considered as fundamental chemical steps in several catalytic cycles and frequently lead to reactive intermediates. Recently, in connection with our studies of carbon dioxide activation [2], the formation of formato niobocene complexes was achieved from carbon dioxide insertion into a niobium–hydrogen bond of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$ [3].

Similarly, the insertion of carbon dioxide into M–C or M–O bonds produces O-bound carboxylato [4] or carbonato [5] complexes respectively. The formation of carbonato complexes can also involve nucleophilic attack of the metal oxygen bond atom on the carbon dioxide [6].

Transition metal carbonates and bicarbonates in which the ligand acts as bidentate, monodentate or bridges two metals have attracted considerable interest [5]. In part, this attention stems from studies pertaining to carbonic anhydrase and to transition-metal-catalysed organic reactions with carbon dioxide [7].

bidentate   monodentate   bridging
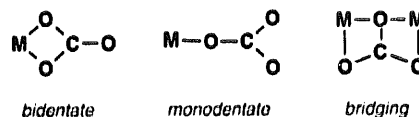
We report here the electrochemical synthesis of the carbonato complexes $[Nb(\eta^5\text{-}C_5H_3RR')_2(OC(O)O\text{-}O,O')]^-$ (3: R = H, R' = SiMe$_3$; 3': R = R' = SiMe$_3$) by the addition of the CO_3^{2-} dianion to the electrogener-

ated species $Nb(\eta^5\text{-}C_5H_3RR')_2Cl$. **3'** can also be obtained from the CO_2 insertion reaction into the metal–oxygen bond of the species generated by two-electron reduction of the oxo complex $Nb(\eta^5\text{-}C_5H_4RR')(O)Cl$ (**4**: R = H, R' = $SiMe_3$). Furthermore, we report an interesting ligand exchange reaction between formiate and carbonate ions of the corresponding complexes.

2. Results and discussion

2.1. Electrosynthesis of carbonato complexes $Nb(\eta^5\text{-}C_5H_3RR')_2(OC(O)O\text{-}O,O')$ from electroreduction of niobocene dichlorides $Nb(\eta^5\text{-}C_5H_3RR')_2Cl_2$

In a $THF\text{-}NaBPh_4$ (0.2 M) solution (THF = tetrahydrofuran), the one-electron reduction of $Nb(\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2)_2Cl_2$ **1'**, ($Cp_2''NbCl_2$), at the potential of wave A (Fig. 1) yields an orange solution containing the diamagnetic neutral complex $Cp_2''NbCl$ **2'** which exhibits a polarographic oxidation wave A_1^- ($E_{1/2} = -0.61$ V) and by cyclic voltammetry [8] a system A'_1/A_1 (Fig. 2(a)). The addition of one equivalent of CO_3^{2-} (Na_2CO_3 or Li_2CO_3 in water) (Fig. 1(c)) causes another oxidation wave C'_1 ($E_{1/2} = -1.06$ V) to appear. The colour changes from orange to green: the height of wave C'_1 is nearly half as large as that of wave A'_1. ESR spectroscopy of this solution containing **3'** is silent. In cyclic voltammetry on a vitreous carbon electrode, a well-defined system C'_1/C_1 is observed (Fig. 2(b)). C_1/C'_1 presents the characteristics of a reversible system.

By polarography and cyclic voltammetry no modification occurs on addition of LiCl. In IR spectroscopy a band at $1580\,cm^{-1}$ appears. The oxidation of the green solution containing **3'** at the potential of wave C'_1 con-
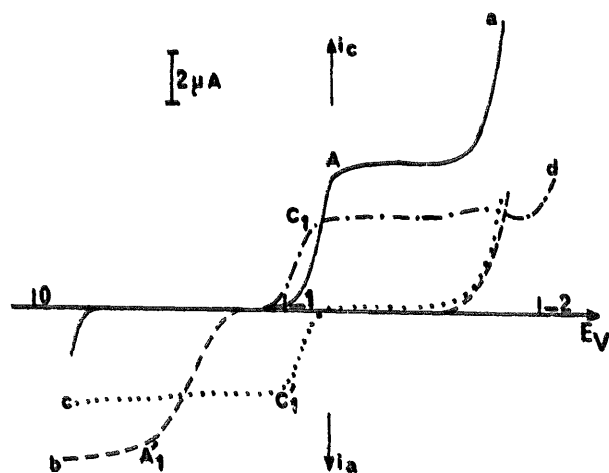

Fig. 1. Polarogram (average current) of $Cp_2''NbCl_2$ **1'** in $THF\text{-}NaBPh_4$ (0.2 M) solution: (a) initial polarogram; (b) after one-electron reduction; (c) after addition of one equivalent of Na_2CO_3 in water; (d) after oxidation at -0.2 V.
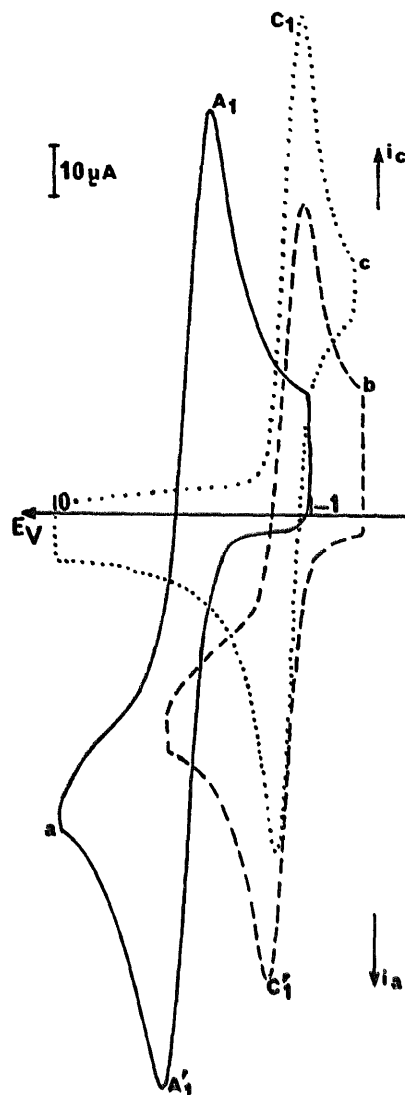

Fig. 2. Cyclic voltammogram of $Cp_2''NbCl$ **2'** in $THF\text{-}NaBPh_4$ (0.2 M) solution. Sweep rate $0.2\,V\,s^{-1}$. Starting potential: (a) $= 1$ V; (b) $= 1.2$ V; (c) 0 V. (a) Initial cyclic voltammogram; (b) after addition of one equivalent of Na_2CO_3 in water; (c) after oxidation at -0.2 V.

sumes 0.5 equivalent of electrons per molecule of initial niobocene dichloride and an orange solution is obtained. The cyclic voltammogram of this electrolyzed solution containing **5'** exhibits the same reversible system C_1/C'_1 (Fig. 2(c)). By ESR spectroscopy a well-defined spectrum is recorded (Fig. 3). It shows a characteristic ten line signal for a niobium(IV) ($I = 9/2$) paramagnetic complex **5'** ($\langle g \rangle = 1.977$, $\langle a_{Nb} \rangle = 54.01$ G).

The reduction of this niobium(IV) complex at the potential of peak C_1 gives again the cyclic voltammogram of Fig. 2(b) after consumption of 0.5 equivalent of electrons.

The addition of CO_3^{2-} to the electrogenerated neutral complex $Cp_2''NbCl$ **2'** causes the formation of the anionic carbonato niobium(III) complex $Cp_2''Nb(OC(O)\text{-}$
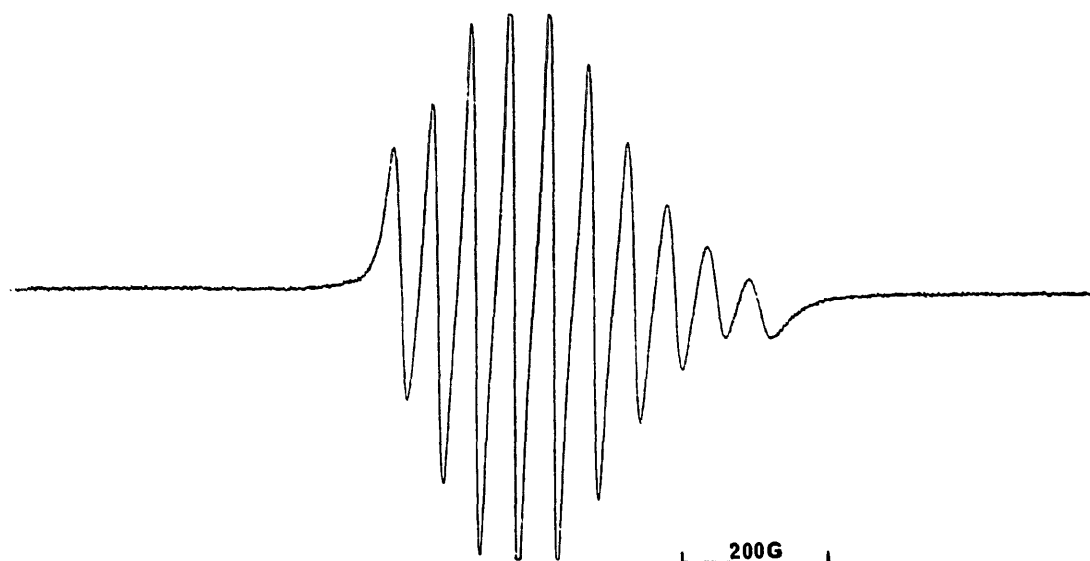
Fig. 3. ESR spectrum of the carbonato neutral complex $Cp''_2Nb(OC(O)O\text{-}O,O'')$ **5'**.

O,O') **3'**. Two limit forms **A** and **B** can be formulated for **3'**:


In form **A** the negative charge is localized on the oxygen atom and in form **B** the metallic atom retains this charge; the oxidation potential of the complex is in accord with the formulation **B**.

As the analysis of the oxidation wave C'_1 corresponds to a one-electron process, we can postulate that **3'** is obtained in ca. 50% yield in accord with the wave height $(C')_1$ and the coulometric data (0.5 equivalent of electrons is consumed).

We suggest that the initial step (Eq. (1)) corresponds to the formation of a binuclear dianionic complex **3'a**, in accordance with the fact that carbonato complexes often possess dimeric dianionic structures (for some complexes of dimeric structures see Ref. [9]), since the carbonato anion contains two nucleophilic centres and is able to bridge two metals.

(1)
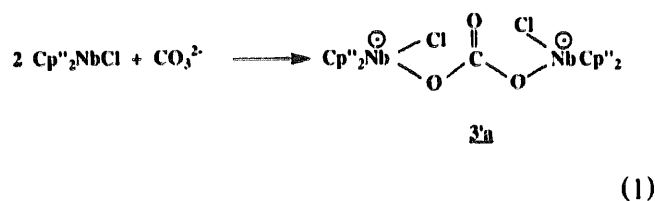
We can also postulate that **3'a** is in equilibrium with **3'b**, which is formed by elimination of a chloride ion (Eq. (2)):

(2)
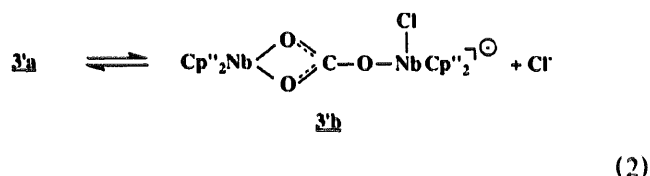
Under the influence of water, **3'b** (or **3'a**) would give the carbonato complex **3'** and the oxo complex **4'** with evolution of H_2, according to the reaction in Eq. (3).

(3)
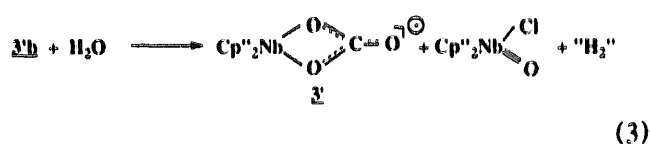
Under our experimental conditions we were unable to detect the formation of the proposed H_2, although the formation of the oxo complex has been verified in the case of derivative **1** (vide infra).

3' is oxidized at the potential of wave C'_1 to the neutral carbonato paramagnetic niobium(IV) complex $Cp''_2Nb(OC(O)O\text{-}O,O')$ **5'**, according to the following redox reaction (Eq. (4)).

(4)
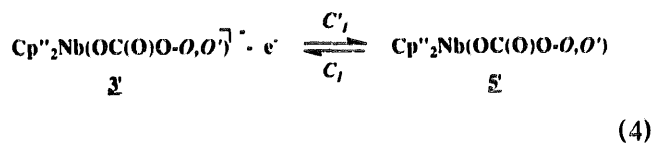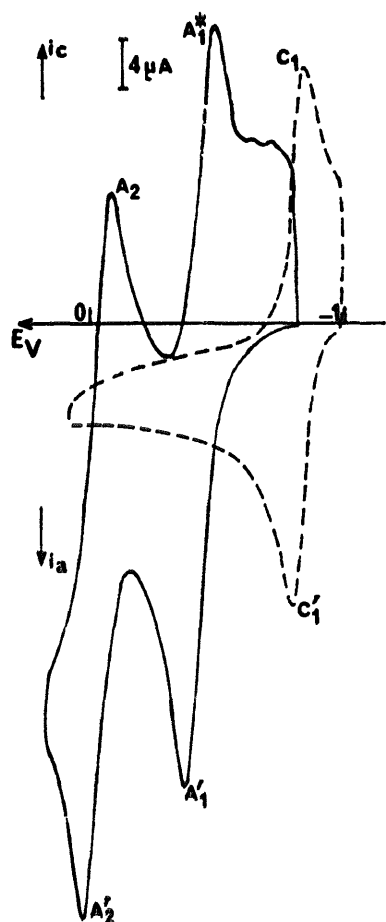
Fig. 4. Cyclic voltammogram of electrogenerated Cp'_2NbCl **2** complex in THF–NaBPh₄ (0.2 M) solution. Sweep rate 0.2 V s⁻¹. Starting potential: (a) = 0.8 V; (b) = 1 V. (a) Initial cyclic voltammogram; (b) after addition of one equivalent of Na_2CO_3 in water.

5′ was identified by ESR spectroscopy. The ESR spectra of **5′** are related to those previously found for several paramagnetic niobocene complexes with different unsaturated molecules, such as ketenimines [10], ketenes [11], acetylenes [12], aldehydes [13], and nitrosoarenes [14]. The small values of the coupling constants found in these complexes indicate an appreciable delocalization of the unpaired spin density onto the ligands. Extended Hückel calculations performed for some of our complexes [15] containing a ligand coordinated in an η^2-fashion give an insight into the role of the ligand electronic properties in the electron delocalization onto the carbonato ligand in **5′**. Theoretical studies concerning chelate niobocene complexes are presently in progress [16].

In addition, the IR spectrum of **5′** shows two bands at 1578 and 1482 cm⁻¹ which suggest the presence of bidentate carbonato ligand [17]. In $[(Cp_2Ti)_2CO_3]_2$ the $\nu(CO)$ appears at 1475 and 1425 cm⁻¹ [9].

Similar electrochemical results are obtained from the complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2(Cp'_2NbCl_2)$ **1**. Fig. 4 shows the cyclic voltammogram of the electrogenerated

niobium complex Cp'_2NbCl **2**. In a THF 0.2 M NaBPh₄ solution two systems A_1/A'_1 and A_2/A'_2 are displayed [18]. The addition of CO_3^{2-} (Na_2CO_3 in water) causes another reversible system C'_1/C_1 to appear and the colour of the solution changes from brown to green. The oxidation of this electrolyzed green solution at the potential of peak C'_1 yields the orange carbonato complex $Cp'_2Nb(OC(O)O\text{-}O,O')$ **5** which shows in ESR spectroscopy a well-defined ten line signal ($\langle g \rangle$ = 2.037, $\langle a_{Nb} \rangle$ = 56.7 G).

System C'_1/C_1 is also obtained by addition of CO_3^{2-} to the electrogenerated anionic niobium(III) complex $Cp'_2NbCl_2^-$, which can be prepared from one-electron reduction of **1** at low temperature in a THF 0.2 M Bu₄NPF₆ solution [19]. This reaction also causes a reduction wave ($E_{1/2}$ = −1.7 V) to appear which is characteristic of the formation of the oxo complex $Cp'_2Nb(O)Cl$ **4** [20].

A similar mechanism to the one cited above can also be postulated for the formation of complexes **3** and **5**.
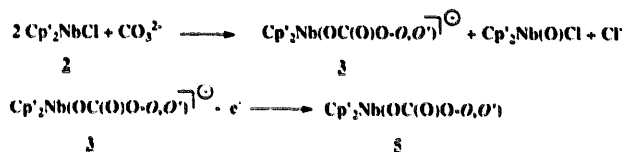
2.2. Electrosynthesis of the carbonato complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(OC(O)O\text{-}O,O')]$ **3** from electroreduction of niobocene oxo complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O)Cl$ in the presence of carbon dioxide

The carbonato derivative **3** can also be obtained according to the following process. Fig. 5 shows the cyclic voltammogram of complex **4**, $Cp'_2Nb(O)Cl$, in a THF 0.2 M NBu₄PF₆ solution: reduction peak B is observed in the cathodic scan; inversion of the potential scan after peak B causes several ill-defined oxidation peaks to appear. In the presence of carbon dioxide the height of peak B increases and a well-defined oxidation peak C'_1 is observed. During the second cathodic scan a peak C_1, which forms a reversible system with C'_1, appears.

The electrolysis of the resulting complex **3** in the presence of carbon dioxide consumes two equivalents of electrons. No signal is detected by ESR spectroscopy. In cyclic voltammetry the well-defined system C'_1/C_1 is observed, and by polarography the corresponding wave C'_1 appears according to the proposed formation of the anionic carbonato complex **3**.

We suggest that the one-electron reduction of **4** yields initially the corresponding anionic species **4′**
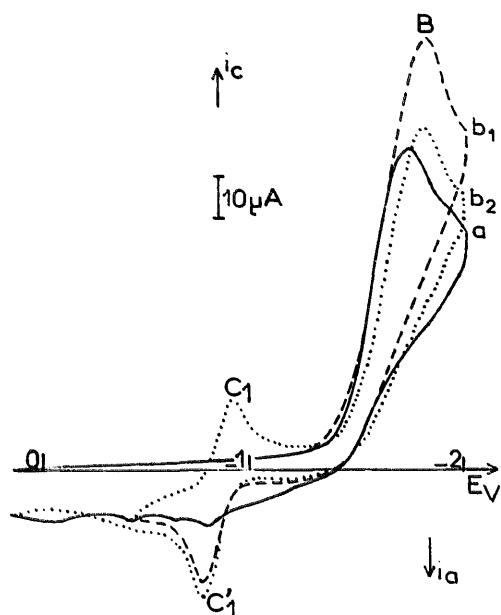
Fig. 5. Cyclic voltammogram of $Cp'_2Nb(O)Cl$ in $THF-NBu_4PF_6$ (0.2 M) solution. Sweep rate: 0.2 V s^{-1}. Starting potential: 0 V. (a) Under argon; (b$_1$) first scan under carbon dioxide; (b$_2$) second scan.

which evolves by loss of the chloride anion to give the neutral derivative **4"** (a complete report of the electrochemical behaviour of the oxo complex **4** will be published in a future paper). In the presence of carbon dioxide **4"** gives complex **5** through the insertion reaction of CO_2 into the niobium–oxygen bond. Similar reactions have previously been postulated [5]. Afterwards, complex **5** is reduced to give **3** which is oxidized at the potential of peak C'_1:

$$Cp'_2Nb(O)Cl + e^{-} \rightleftharpoons Cp_2Nb(O)Cl^{-\ominus}$$
$$\mathbf{4} \qquad\qquad\qquad \mathbf{4'}$$

$$Cp'_2Nb(O)Cl^{-\ominus} \longrightarrow \text{"} Cp'_2Nb(O)\text{"}$$
$$\mathbf{4'} \qquad\qquad\qquad \mathbf{4''}$$

$$\text{"} Cp'_2Nb(O)\text{"} + CO_2 \longrightarrow Cp'_2Nb(OC(O)O\text{-}O,O')$$
$$\mathbf{4''} \qquad\qquad\qquad\qquad \mathbf{5}$$

$$\mathbf{5} + e^{-} \xrightarrow{C_1} \mathbf{3}$$
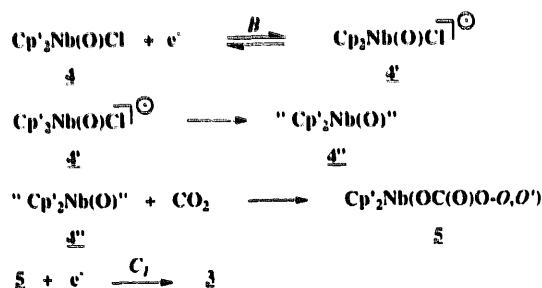
2.3. Reactivity of the carbonato niobocene complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(OC(O)O\text{-}O,O')]^-$ **3**
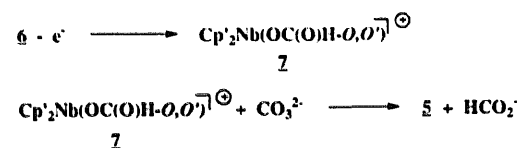
We have studied the reactivity of the carbonato complex **3** towards anionic substrates. The addition of an excess of HCO_2^- (HCO_2Na in water) on the electrogenerated complex **3** causes the oxidation wave C'_1 to disappear and a new oxidation wave F'_1 is observed. As mentioned previously [3], F'_1 corresponds to the oxida-

tion of the neutral formato complex $Cp'_2Nb(OC(O)H\text{-}O,O')$ **6**. In cyclic voltammetry, the height of peak C'_1 decreases relative to that of peak F'_1 by adding HCO_2^-. By inversing the potential scan after peak F'_1, peak C_1 is obtained (Fig. 6).

The addition of the HCO_2^- anion to the complex **3** yields the neutral formato complex according to the following reaction.

$$Cp'_2Nb(OC(O)O\text{-}O,O')^{-\ominus} + HCO_2^- \longrightarrow Cp'_2Nb(OC(O)H\text{-}O,O') + CO_3^{2-}$$
$$\mathbf{3} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{6}$$
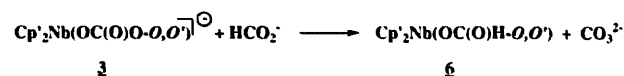
Under the influence of carbonate anion the oxidation of **6** gives the neutral carbonato complex **5** (see Fig. 6).

$$\mathbf{6} - e^{-} \longrightarrow Cp'_2Nb(OC(O)H\text{-}O,O')^{\ominus}$$
$$\qquad\qquad\qquad\qquad \mathbf{7}$$

$$Cp'_2Nb(OC(O)H\text{-}O,O')^{-\ominus} + CO_3^{2-} \longrightarrow \mathbf{5} + HCO_2^-$$
$$\mathbf{7}$$

The above results can be rationalized according to the square Scheme 1; one electron is exchanged horizontally and formiate or carbonate ion vertically.

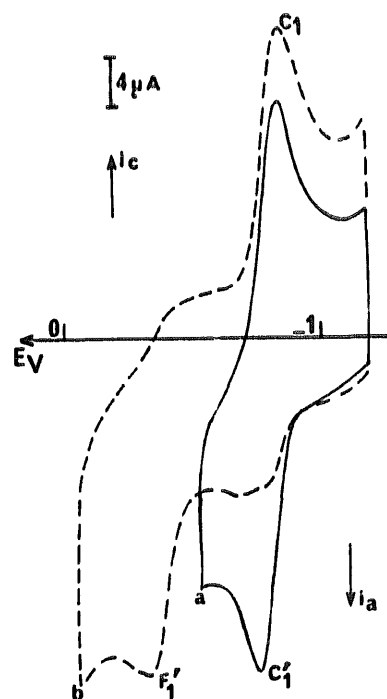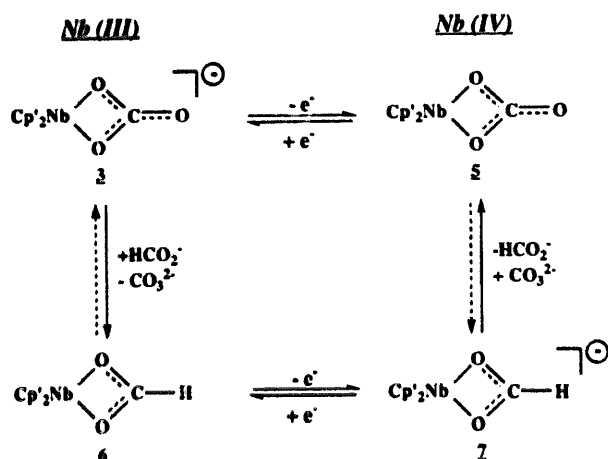Fig. 6. Cyclic voltammogram of the carbonato anionic complex $Cp'_2Nb(OC(O)O\text{-}O,O')^-$ **3** in $THF-NaBPh_4$ (0.2 M) solution. Sweep rate: 0.2 V s^{-1}. Starting potential: −1.2 V. (a) Initial cyclic voltammogram; (b) after addition of an excess of HCO_2Na in water.

Nb (III)   **Nb (IV)**

Scheme 1.

It is noteworthy that the substitution of CO_3^{2-} by HCO_2^- occurs in the case of niobium (III) complexes and that the reverse reaction is observed in the case of niobium (IV) complexes; in both oxidation states, the neutral derivative is the most stable species.

3. Experimental section

3.1. Electrochemical equipment and cells

Cyclic voltammetry was carried out in a standard three-electrode Tacussel UAP$_4$ unit cell. The reference electrode was a saturated calomel electrode (SCE), separated from the solution by a sintered-glass disk. The auxiliary electrode was a platinum wire. For all voltammetric measurements the working electrode was a vitreous carbon electrode. For the polarograms, a three-electrode Tacussel Tipol polarograph was used. The dropping-mercury electrode characteristics were $m =$ 3 mg s^{-1} and $\tau = 0.5$ s. For controlled-potential electrolysis, a mercury pool was used as the cathode and a platinum plate as the anode, the latter being separated from the solution by a sintered-glass disk. In all cases, the electrolyte was a 0.2 M solution of tetrabutylammonium hexafluorophosphate or sodium tetraphenylborate in THF. The electrolyses were performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator.

3.2. General procedures

All manipulations were performed by using standard Schlenk techniques in an atmosphere of dry, dioxygen-free dinitrogen or argon. Solvents were dried under N$_2$ and degassed before use.

IR spectra were recorded on Perkin-Elmer 881 and Nicolet 205 spectrometers in solution between NaCl plates. ESR spectra were recorded at room temperature

with a Bruker Esp 300 spectrometer. (NBu$_4$)PF$_6$ and NaBPh$_4$ were purchased from Fluka (puriss. p.a. for electrochemical grade), dried and deoxygenated before use.

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