

Short communication

Electrocatalytic process in the reduction of  
 $\{\text{Nb}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)]_2(\text{Cl})(\text{NHPH})\}\text{BF}_4$

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Abstract

Protonation of the biscyclopentadienyl imido niobium complex  $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{Cl})(=\text{NPh})$  affords the corresponding cationic amido complex  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{Cl})(\text{NHPH})]^+$ , **1**. Starting from **1**, an interesting amido group elimination reaction has been found to take place, reaction which must be electrochemically induced. © 1997 Elsevier Science S.A.

*Keywords:* Niobium; Protonation; Imido and amido complex; Electroreduction

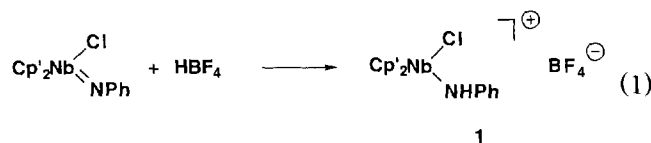
1. Introduction

Transition metal complexes having imido and oxo ligands are of continuing interest in organometallic chemistry [1–3]. An increasing number of early transition metal complexes having two-electron doubly-bonded oxo and imido ligands have been recently reported [4–9] which despite high reactivity and, in some cases, will even activate C–H [5–7].

Recently some of us described the synthesis of the imido niobocene complex  $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{Cl})(=\text{NPh})$  [10]. We now wish to present new features on the reactivity of that complex regarding protonation reaction together with a complete report of the electroreductive behaviour of the resultant cationic amido complex.

2. Results and discussion

Synthesis of the title compound,  $[\text{Cp}'_2\text{Nb}(\text{Cl})(\text{NHPH})]\text{BF}_4$  <sup>1</sup>, has been realized from protonation of the imido niobocene complex  $\text{Cp}'_2\text{Nb}(\text{Cl})(=\text{NPh})$  (see Section 3). Numerous reactions of imido complexes with electrophiles have been reported where the attacking electrophile is commonly a proton [11–13]. In our case  $\text{HBF}_4$  has been used as the proton donor according to the following reaction:



<sup>1</sup> The following abbreviations will be used within the text: THF: tetrahydrofuran; DCM: dichloromethane; TBAHFP: tetrabutylammonium hexafluorophosphate; STPB: sodium tetraphenylborate; Cp':  $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ ; SCE: saturated calomel electrode; ESR: electron spin resonance; M: mol l<sup>-1</sup>.

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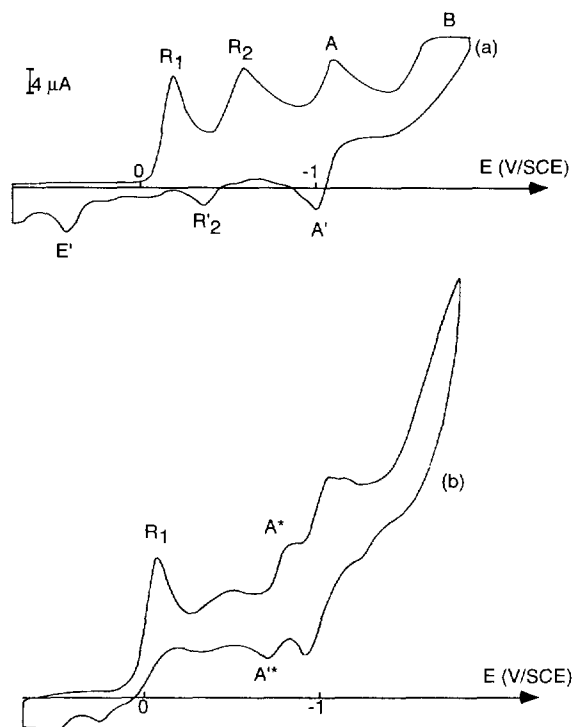
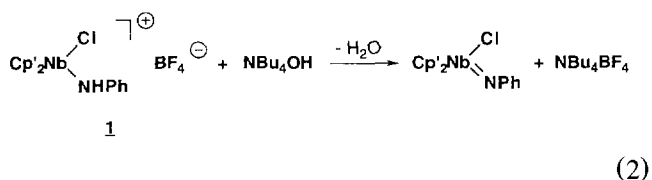


Fig. 1. Cyclic voltammogram of **1** ( $c = 2$  mM) in THF 0.2 M TBAHFP on carbon disk electrode. (a) at room temperature; (b) at 40°C. Sweep rate: 50 mV s<sup>-1</sup>. Initial potential: +0.7 V.

The reverse reaction can be readily achieved using a strong base like NBu<sub>4</sub>OH:



In THF 0.2 M TBAHFP the cyclic voltammogram of **1** on a carbon disk electrode at room temperature (see Fig. 1a) exhibits four reduction peaks  $R_1$ ,  $R_2$ ,  $A$  and  $B$  ( $E_{p,R_1} = -0.11$  V,  $E_{p,R_2} = -0.52$  V,  $E_{p,A} = -1.02$  V,  $E_{p,B} \approx -1.6$  V) on the cathodic scan. Three significant peaks  $A'$ ,  $R_2'$  and  $E'$  ( $E_{p,A'} = -0.92$  V,  $E_{p,R_2'} = -0.28$  V,  $E_{p,E'} = +0.5$  V) are seen on the reverse scan when the potential sweep is inverted after peak  $B$ ;  $A'$  and

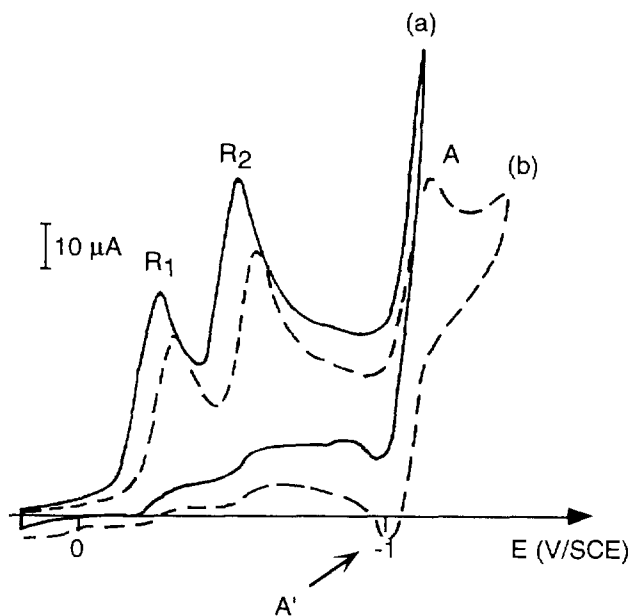


Fig. 2. Cyclic voltammogram of **1** ( $c = 2$  mM) in DCM 0.2 M TBAHFP on carbon disk electrode. (a) at room temperature; (b) at -25°C. Sweep rate: 200 mV s<sup>-1</sup>. Initial potential: +0.2 V.

peaks  $R_2'$  and  $E'$  are due to species generated along peaks  $A$  and  $R_2$ , respectively.  $A$  and  $E'$  are relevant to the reduction and oxidation of the well-known dichloro derivative Cp'<sub>2</sub>NbCl<sub>2</sub>, **2** [14,15].

Changes in the voltammetric profile are observed with the temperature: at 40°C  $R_2$  intensity is significantly reduced as a new reversible system  $A^*/A'^*$  ( $E_{p,A^*} = -0.83$  V,  $E_{p,A'^*} = -0.72$  V) appear which is situated at slightly less negative potentials than  $A/A'$  (see Fig. 1b).

In CH<sub>2</sub>Cl<sub>2</sub> 0.2 M TBAHFP **1** shows the cyclic voltammogram of Fig. 2.; compared to Fig. 1a peaks  $R_1$  and  $R_2$  are reencountered but with no associated anodic peaks on the reverse scan; in the place of peak  $A$  a continuously increasing current is registered due to the electrochemically catalysed reduction of the chlorinated solvent as previously mentioned [16]. At low temperature (-25°C) the latter process does not take place and the well-defined reversible system  $A/A'$  is observed.

Exhaustive electrolysis on mercury pool at the potential of -0.2 V and at room temperature in THF results in the consumption of less than 1 F per mol of initial

Table 1  
Coulometric data for the electrolysis of **1** on mercury pool (solute concentration: 2–3 mM)

Entry	Solvent/supporting electrolyte	$T$ (°C)	Potential (V versus SCE)	Q (F per mol of <b>1</b> )	Electrolysis product colour
1	THF 0.2 M TBAHFP	20	-0.2	0.66	brown
2	THF 0.2 M TBAHFP	40	-0.2	0.2	green
3	DCM 0.2 M TBAHFP	0	-0.4	0.55	orange
4	THF 0.2 M STPB	20	-0.45	0.1	orange

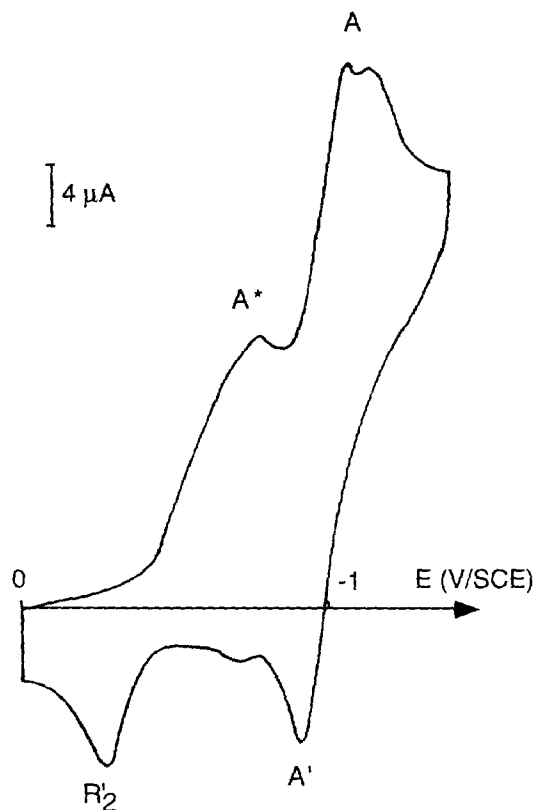


Fig. 3. Cyclic voltammogram of **1** ( $c = 2$  mM) in THF 0.2 M TBAHFP on carbon disk electrode after electrolysis on mercury pool at  $-0.2$  V. Sweep rate:  $100$  mV s $^{-1}$ . Initial potential:  $+0$  V.

complex (see Table 1, entry 1) as the solution colour turns from red to brown. The cyclic voltammogram of the electrolysed solution is depicted on Fig. 3 and exhibits two reduction peaks  $A^*$  ( $E_{p,A^*} = -0.78$  V) and  $A$  and two oxidation peaks  $A'$  and  $R'_2$  on the reverse scan. ESR analysis provides a signal which consists in the sum of two well-resolved ten-line spectra (see Fig. 4) corresponding to the presence in solution of two individual paramagnetic niobium (IV) complexes ( $g_{iso,+} = 1.995$ ,  $A_{iso,+} = 1.027 \cdot 10^{-2}$  cm $^{-1}$  and  $g_{iso,*} = 2.002$ ,  $A_{iso,*} = 1.074 \cdot 10^{-2}$  cm $^{-1}$ ). One of the ESR signal components has been clearly attributed to  $Cp'_2NbCl_2$ , **2** (marked \* on Fig. 4).

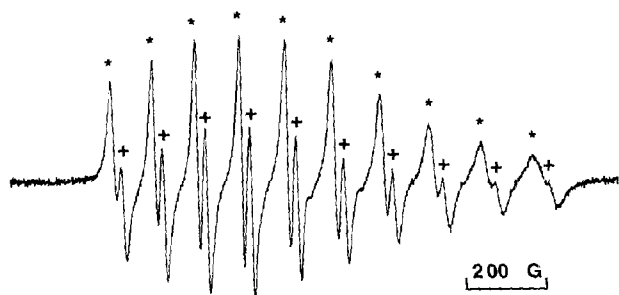


Fig. 4. ESR spectrum of **1** ( $c = 2$  mM) after reduction in THF 0.2 M TBAHFP on mercury pool at  $-0.2$  V.

When the electrolysis was carried out at higher temperature ( $40^\circ\text{C}$ ), coulometric consumption dropped to  $0.2$  F per mol of **1** (see Table 1, entry 2) and **2** was the only species observed by ESR analysis.

As indicated in Table 1 the coulometric consumption is highly dependent on the experimental conditions. However in each case **2** was identified as the major electrolysis product.

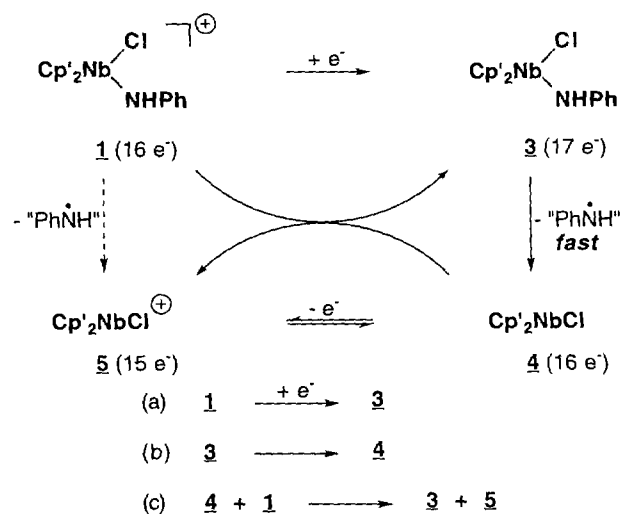
The above results can be rationalized according to Scheme 1.

This type of square scheme was first described by Jacq [17] and is often used to explain ligand exchange reactions in organometallic chemistry [17–36] [37–39]. Our mechanism would refer to the case where the electrocatalytic process is associated with an endergonic cross electron transfer propagation step [40,41].

In Scheme 1, the one-electron reduction of **1** (reaction a) affords the neutral amido niobium (IV) derivative **3** which is very unstable even in the time scale of cyclic voltammetry and rapidly dissociates into the niobium (III) complex  $Cp'_2NbCl$ , **4**, through elimination of the organic moiety formulated as 'PhNH·' with a change in the metal oxidation number from +IV to +III (b); **4** is oxidized at the potential of peak  $R'_2$ .

**4** reduces **1** according to reaction (c) which is driven by the irreversible fast reaction (b).

At the time scale of cyclic voltammetry cationic species **5**, generated from reaction (c), is reduced at the potential of peak  $R_2$ . As the system  $A/A'$  is seen on Fig. 1a we can suggest that formation of **2** arises from a chloro ligand exchange reaction between electrogenerated  $Cp'_2NbCl$  and  $Cp'_2NbCl^+$  formed along reaction (c) as it has been previously mentioned [42]. However, in the time scale of electrolysis  $[Cp'_2NbCl]^+$  evolves through Eq. (3) to give  $Cp'_2NbCl_2$ , **2**, and transient



Scheme 1.

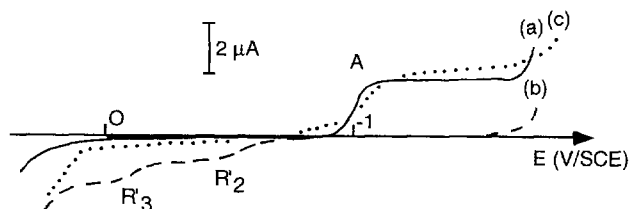
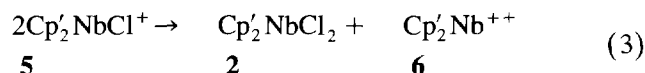


Fig. 5. Polarogram (average current) of **2** ( $c = 2.5$  mM) in THF 0.2 M STPB. (a) **2** alone; (b) after reduction on mercury pool at  $-1$  V; (c) immediately after addition of 1 molar equivalent of **1**.

species  $[\text{Cp}'_2\text{Nb}]^{++}$  **6**; indeed the peak  $R_2$  is not found after electrolysis:



At room temperature these two paramagnetic species are detected from ESR analysis of the electrolysed solution. Only four dicationic paramagnetic niobocene compounds,  $[\text{Cp}'_2\text{Nb}(\text{L})_2]^{2+}$  [ $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)$ ,  $\text{L} = \text{P}(\text{OMe})_3$  and  $\text{MeCN}$ ] [43] and  $[\text{Cp}_2\text{Nb}(\text{L})]\text{PF}_6$  [ $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ,  $\text{L} = \text{bipyridine}$  or  $o$ -phenanthroline] [44] and few monocationic analogues [45,46] have previously been reported.

At higher temperature ( $40^\circ\text{C}$ ) the only characteristic signal of  $\text{Cp}'_2\text{NbCl}_2$  is seen in ESR spectroscopy. Under these experimental conditions and in the absence of suitable ligands, **6** which is probably reduced at the potential of peak  $A^*$ , should be very unstable and its decomposition occurs.

The amido radical  $\text{PhNH}\cdot$  has been previously postulated as an intermediate in the reaction of decomposition of phenyl azide in aliphatic hydrocarbons leading to aniline, alkylamine, azobenzene and polymers [47,48]. The first step consists in the formation of a nitrene (singlet or triplet) which offers many reaction possibilities [49,50].

With the aim of proving reaction c, we have carried out the following experiment: **4** has been electrogenerated from one-electron reduction of **2** in THF 0.2 M  $\text{NaBPh}_4$  as supporting electrolyte [51]. In polarography **4** exhibits two oxidation waves  $R'_2$  and  $R'_3$  (Fig. 5b). The addition of cationic species **1** in equivalent amount causes  $R'_2$  and  $R'_3$  to disappear and reduction wave  $A$  to appear (Fig. 5c) indicating that  $\text{Cp}'_2\text{NbCl}_2$ , **2**, is effectively formed (also verified from ESR).

### 3. Experimental details

#### 3.1. Preparation of $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{NbCl}(\text{NPh})^+\text{BF}_4^-$ , **1**

To a solution of 0.50 g (1.00 mmol) of  $(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{NbCl}(\text{NPh})$  in 50 ml of diethyl ether,

0.18 ml (1.08 mmol) of  $\text{HBF}_4 \cdot \text{OEt}_2$  6 M was added dropwise at  $0^\circ\text{C}$  until complete precipitation of the title compound. Yield: 69%.

$^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 300 MHz):  $\delta$  0.23 (s, 18H,  $\text{SiMe}_3$ ), 6.90 (4H), 7.11 (4H)(m,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 7.20 (d, 2H), 7.30 (m, 1H), 7.49 (7, 2H)(phenyl ring), 12.79 (broad, 1H,  $\text{NHC}_6\text{H}_5$ )

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