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Electron-transfer-catalyzed ligand substitution of carboxylato niobocene complex induced by electrochemical oxidation

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Abstract

Electrochemical reduction of niobocene dichloride $(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl_2$ **1** formulated as Cp'_2NbCl_2 in the presence of 3,4-diaminobenzoic acid yields to the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^2\text{-}O,O\text{-}OOC(C_6H_3)(NH_2)_2)]$ **3**. When $CN(2,6\text{-}Me_2C_6H_3)$ formulated as xylylisonitrile (CNXylyl) is added to a complex **3** solution, a substitution reaction takes place to lead to the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-}O\text{-}OOC(C_6H_3)(NH_2)_2)(CN(2,6\text{-}Me_2C_6H_3))$ **4** after 3 h. An alternative way to yield quantitatively and nearly instantaneously **4** consists in a previous oxidation of **3** in the presence of CNXylyl. Hence, we present here a new example of electron-transfer-catalyzed (ETC) ligand substitution of carboxylato niobocene complex induced by electrochemical oxidation. The structure of the complexes, the formation mechanism are described using electrochemical and spectroscopic data. Electrochemical simulation have been done to verify experimental results and to complete them with a kinetic study.

Keywords: Niobocene; Electrochemistry; Carboxylato ligand; Isonitrile; Electron-transfer-catalyzed ligand substitution; Synthesis

1. Introduction

Electrocatalysis or electron-transfer chain (ETC) catalysis [1] first disclosed in organic chemistry by Kornblum [2] and Russell [3] was applied to ligand exchange reactions on a transition metal complex by Feldberg [4] in 1972. Almost all the examples with the ETC mechanism have an exergonic cross-ET propagation step and, thus fast and complete [5]. This can be performed for example by oxidative initiation in monomolecular complexes when the incoming ligand is less electron-donating than the displaced [3,6]. Few cases are known with an endergonic cross-ET step [7,8] but in those cases the catalytic efficiency is low.

Recently, we have prepared several paramagnetic dicarboxylato Nb(IV) complexes from electroreduction of niobocene dichloride $(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl_2$ or Cp'_2NbCl_2 **1** in the presence of suitable aliphatic acid such malonic acid, oxalic acid and succinic acid [9]. Continuing our studies in connection with the synthesis of new carboxylato niobocene complexes, we are currently interested in studying the reactivity of different niobocene moities towards aromatic acid and we report here a new example of ETC ligand substitution from

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Abbreviations: Cp′; $(\eta^5\text{-}C_5H_4SiMe_3)$; ETC; Electron-transfer-catalyzed; RDE; Rotating disk electrode; SCE; Saturated calomel electrode; ESR; Electron spin resonance; NMR; Nuclear magnetic resonance; THF; Tetrahydrofuran; $NaBPh_4$; Sodium tetraphenylborane; CNXylyl; 2,6-Dimethylphenylisocyanide.

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carboxylato niobocene complexes in the presence of xylylisonitrile.

2. Results and discussion

2.1. Electrochemical behaviour of **1** in the presence of 3,4-diaminobenzoic acid

Upon rotating disk electrode (RDE) voltammetry, in THF in the presence of 0.2 M $NaBPh_4$ as supporting electrolyte Cp'_2NbCl_2 **1** exhibits a reduction wave A and an oxidation wave E′ (Fig. 1(a)).

The wave A corresponds to the one electron reduction of **1** to give Cp'_2NbCl **2** as previously mentioned [10]. In the presence of 1 equivalent of 3,4-diaminobenzoic acid, no modification of this RDE voltammogram was observed; however when the electrolysis is performed on a carbon gauze electrode at −1.2 V (versus SCE electrode) corresponding to the plateau of wave A, a quantity of electricity close to 2 equivalents of electrons per mol of **1** was consumed. No signal was detected by ESR spectroscopy. The RDE voltammogram of the resulting solution showed one well defined oxidation wave F′ at −0.655 V (Fig. 1(b)). This electrogenerated product corresponds to the carboxylato niobocene complex **3** which has been characterized by NMR spectroscopy (see Section 4). The formation of Nb(III) **3** (18 electrons configuration) can be rationalized in accordance with the global reaction (1).

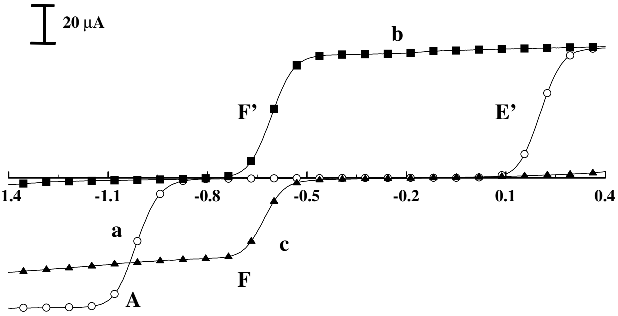
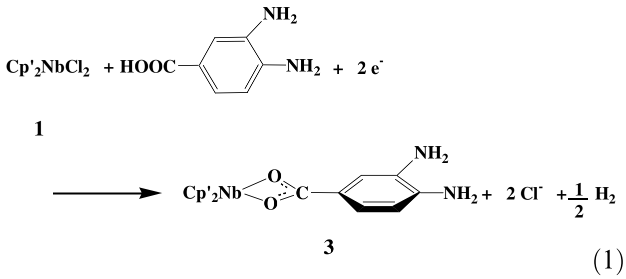


Fig. 1. RDE voltammogram of (a, ○) Cp'_2NbCl_2 **1** in THF containing 0.2 M $NaBPh_4$; (b, ■) after adding 1 equivalent of 3,4-diaminobenzoic acid and a 2 e^- reduction at −1.2 V on carbon electrode; (c, ▲) after 1 e^- oxidation at 0 V (scan rate: 20 mV s^{-1}).



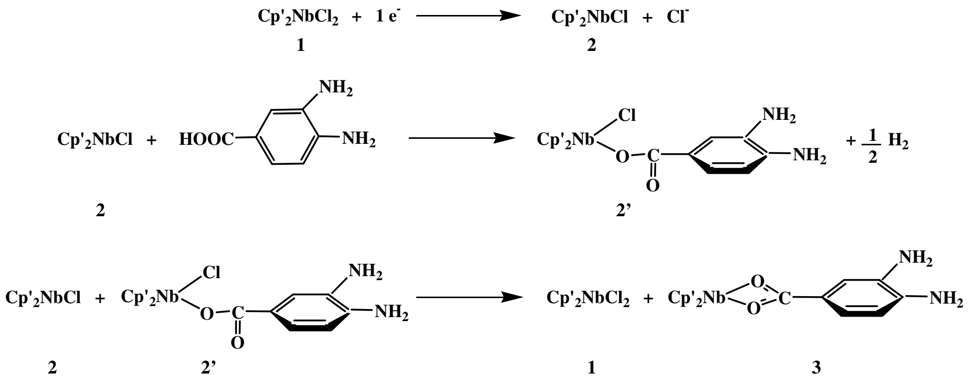
(1)

When 1 equivalent of 3,4-diaminobenzoic acid was added to a solution containing **2** (obtained from one electron reduction of Cp'_2NbCl_2 **1** in THF-0.2 M $NaBPh_4$) a fast reaction occurs giving **3** and regeneration of 50% of **1** (identified by its reduction wave A and by ESR spectroscopy). This result explained the consumption of two electrons from electrolysis of **1** in the presence of 1 equivalent of 3,4-diaminobenzoic acid. Theses electrochemical results can be rationalized with Scheme 1.

The complex **2** (Nb(III) – 16 electrons configuration) reacts with aromatic acid to give a paramagnetic niobium(IV) complex **2′** and elimination of dihydrogen (reaction (3)). This intermediate **2′** is then reduced by **2** yielding **3** and regeneration of **1** (yield 50%, reaction (4)). The results necessarily imply that reaction (4) should be strongly faster than reaction (3).

In cyclic voltammetry, **3** exhibits a system F′/F (Fig. 2); the current ratio $i_{p,a}/i_{p,c}$ is equal to unity (or very close to it) for sweep rates v between 20 and 200 mV s^{-1} and the peak current increases linearly with $v^{1/2}$. The half-wave potential is independent of the potential scan rate and the peak shape is characterized by $|E_{p,a} - E_{p,c}| \approx 60$ mV in agreement with a one-electron transfer controlled by diffusion [11,12].

This was verified by controlled potential electrolysis at −0.2 V (plateau of wave F′) which gave 1.0 ± 0.1 e^-. The



(2)

(3)

(4)

Scheme 1.

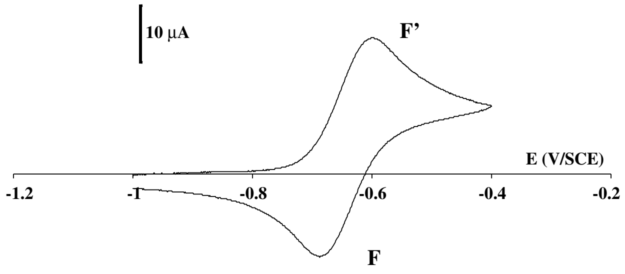
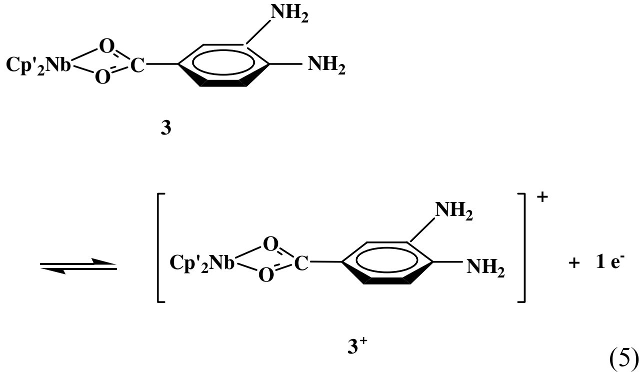


Fig. 2. Cyclic voltammogram of **3** on carbon electrode in THF containing 0.2 mol L^{-1} $NaBPh_4$ (scan rate: 50 mV s^{-1}; starting potential: −1 V).

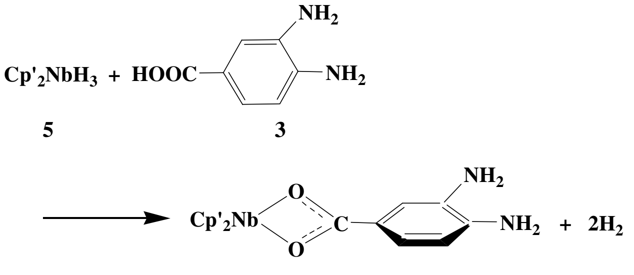
RDE voltammogram of the resulting solution exhibited one reduction wave F at −0.655 V (Fig. 1(c)). The electrogenerated paramagnetic cationic Nb(IV) complex $\mathbf{3}^+$ has been characterized by ESR spectroscopy (Fig. 3) and shows the characteristic 10-line spectrum (^{93}Nb nucleus, 100% natural abundance, $I = 9/2$, THF: $g_{iso} = 1.970$, $a_{iso,Nb} = 48.49$ G). The low value of the hyperfine splitting constant $a_{iso,Nb}$ denotes appreciable delocalization of the unpaired spin onto the carboxylato ligand while conventional $Cp_2Nb(IV)$ with two σ-donor ligands show $a_{iso,Nb}$ above 100 G [13,14]. This explanation may be related to that previously observed for the analogous dicarboxylato niobocene complexes [9]. Moreover, these results are in agreement with the reaction (5).



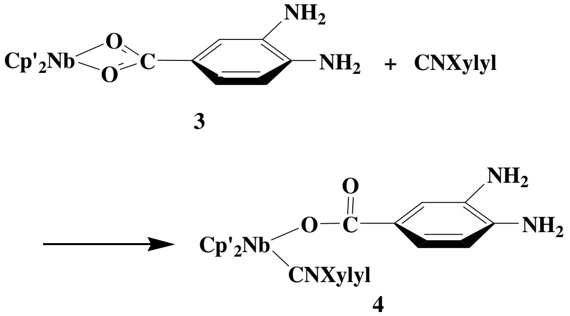
(5)

2.2. Chemical synthesis of complex 3

The reaction of the [Nb(η^5-$C_5H_4SiMe_3$)$_2H_3$] **5** with the 3,4-diaminobenzoic acid in THF at 60 °C, gave the corresponding carboxylate–niobocene complex [Nb(η^5-$C_5H_4SiMe_3$)$_2$(κ^2-*O*,*O*-OOC(C_6H_3)(NH_2)$_2$)] **3**.



The complex **3** was isolated as a green crystalline solid and characterized spectroscopically. The pseudo-C_{2v} symmetric of **3** gave in the ^{1}H NMR spectra two signals multiplets each assigned to two protons of the substituted cyclopentadienyl moiety together with three signals of the phenyl ring. The ^{13}C NMR spectra for **3** showed the expected signals for the different ligand systems present (see Section 4).



(6)

2.3. Electrochemical behaviour of 3 in the presence of isonitrile ligand

At room temperature, the addition of 1 equivalent of CNXylyl to a solution of **3** led to **4**. This electrogenerated product has been characterized on the spectroscopic features and corresponds to the diamagnetic Nb(III) complex **4** (18 electrons configuration). The involved reaction (6), followed by NMR analysis, is relatively slow and the quantitative transformation of **3** to **4** was achieved in 3 h (see Section 4).

In order to speed up the reaction, an electrochemical approach was proposed. This ligand substitution should be improved by a previous oxidation (initiation step) of the complex **3**. To realize this type of studies, to analyze the electrochemical results and to specify all kinetic and thermodynamic constants, the initial experimental conditions must be chosen as no chemical evolution of the complex **3** are observed, at least during a time lower than the time scale used for electrochemical technique.

At 0 °C, when 1 equivalent of CNXylyl was added to a complex **3** solution, no modification of the wave F was observed by RDE voltammetry even after several hours; however by cyclic voltammetry, an additional system G′/G with low intensity was detected at less cathodic potential than the system F′/F (Fig. 4). The height of peak G′ to that of peak F′ decreases when the sweep rate increases.

When electrolysis of **3** in the presence of CNXylyl was performed at the potential of peak F′, the current dropped to zero after the consumption of a low amount of electricity (0.1 electron) and the RDE voltammogram of this resulting solution exhibited the oxidation wave G′. By cyclic voltammetry, oxidation peak G′ and reduction peaks G and F were observed (Fig. 5).

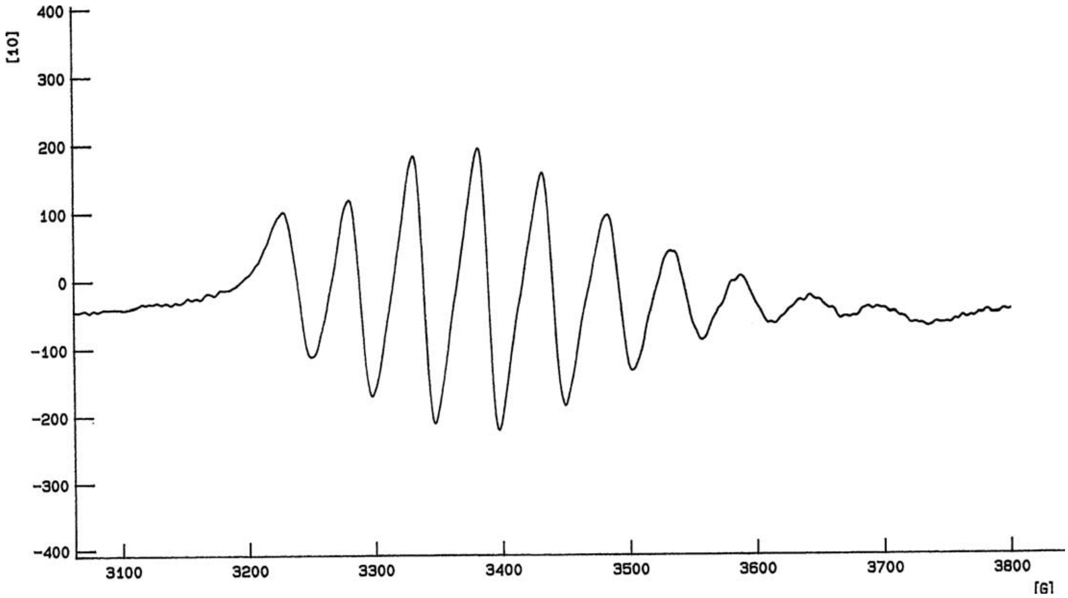


Fig. 3. ESR spectrum of 3^+ in THF at 293 K.

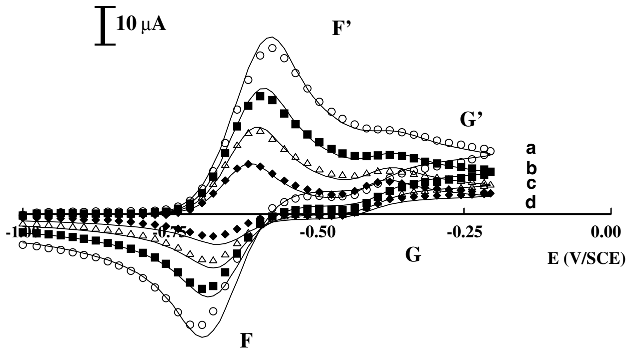


Fig. 4. Cyclic voltammogram of **3** (conc. = 4.02×10^{-3} mol L^{-1}) in presence of a slight excess of CNXylyl (conc. = 4.46×10^{-3} mol L^{-1}) on a carbon electrode in THF containing 0.2 mol L^{-1} $NaBPh_4$, starting potential: −1 V; (—) experimental and (○, ■, △, ◆) simulated curves; scan rate: (a) 200 mV s^{-1}; (b) 100 mV s^{-1}; (c) 50 mV s^{-1}; (d) 20 mV s^{-1}.

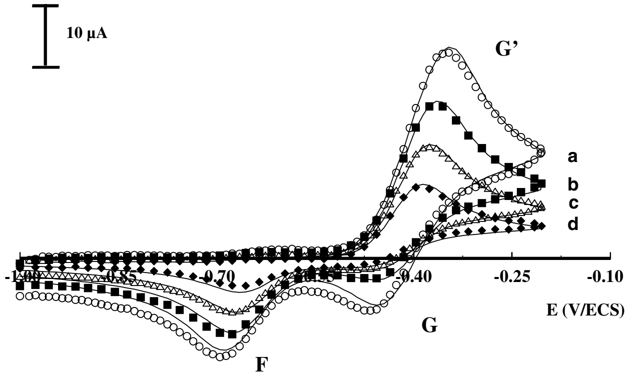
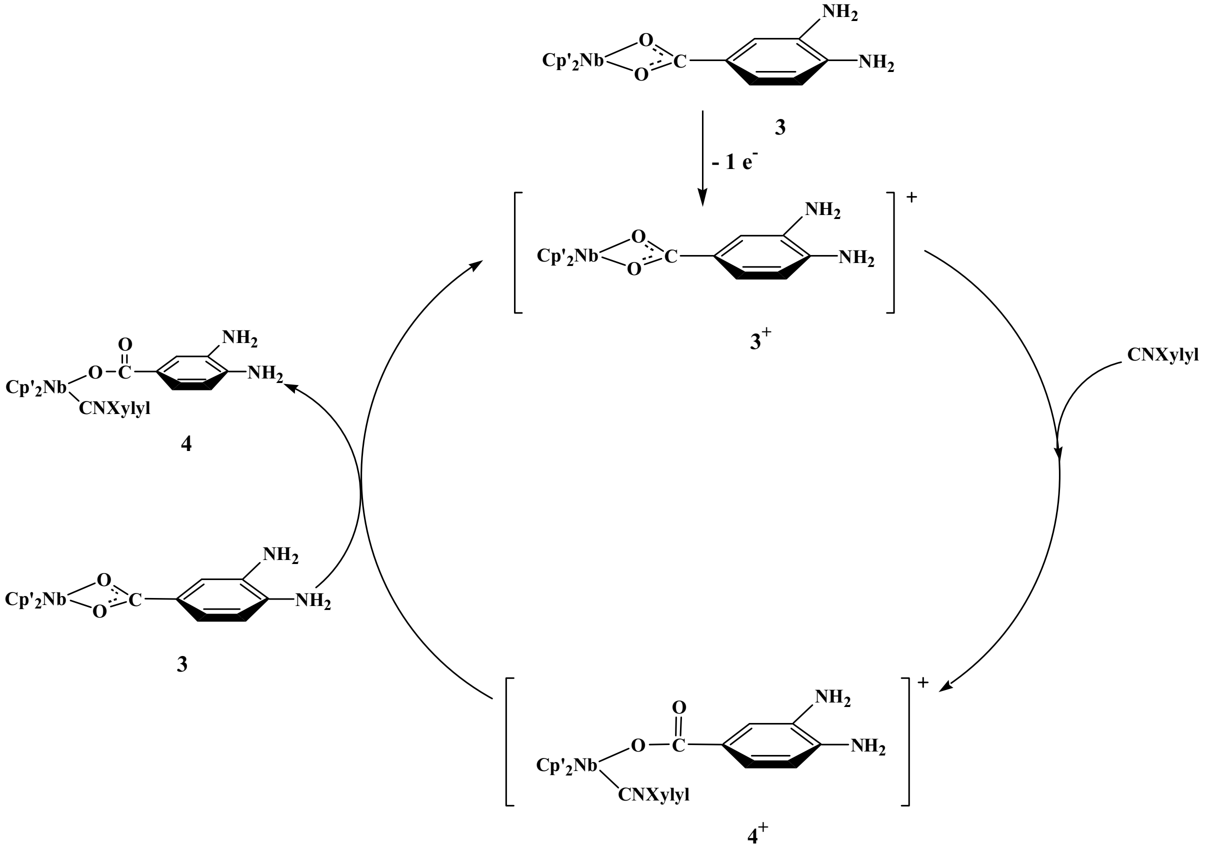


Fig. 5. Cyclic voltammogram of **4** (conc. = 4.02×10^{-3} mol L^{-1}) on a carbon electrode in THF containing 0.2 mol L^{-1} $NaBPh_4$, starting potential: −1 V; (—) experimental and (○, ■, △, ◆) simulated curves; scan rate: (a) 200 mV s^{-1}; (b) 100 mV s^{-1}; (c) 50 mV s^{-1}; (d) 20 mV s^{-1}.

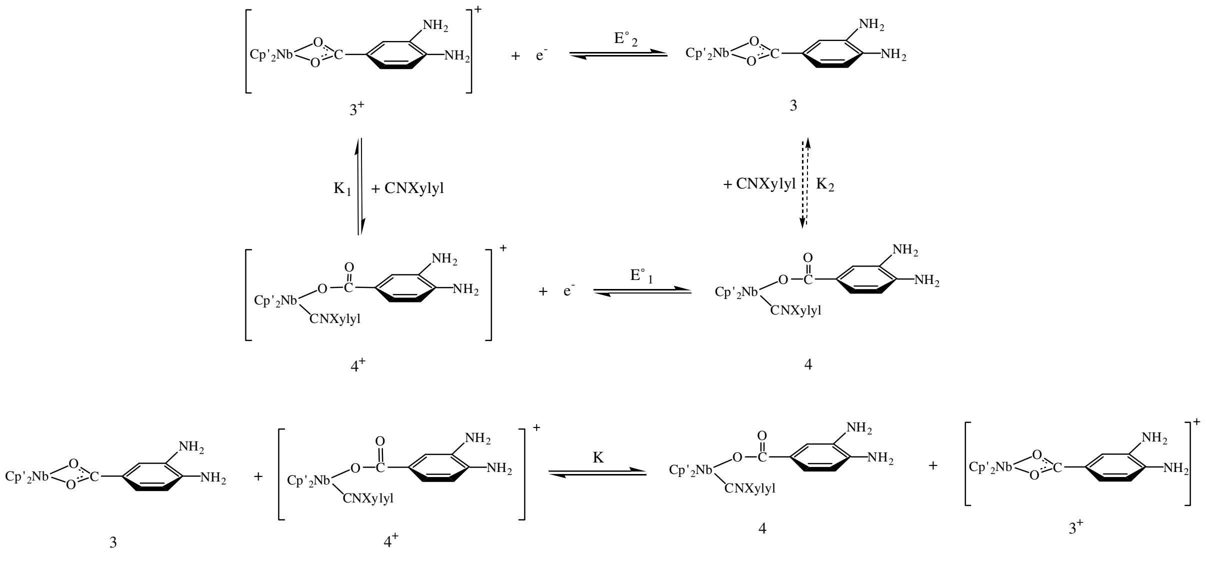
The ligand exchange reaction between **3** and **4** induced by electrochemical oxidation can be summarized as in Scheme 2.

From electrochemical oxidation of **3**, the corresponding cationic Nb(IV) complex $\mathbf{3}^+$ is obtained (initiation step). $\mathbf{3}^+$ reacts with CNXylyl to give the cationic derivative $\mathbf{4}^+$ (17 electrons configuration). This reaction is not in fact a classical ligand substitution since the bidentate carboxylate ligand remains on the complex but as a monodentate ligand (from κ^2 to κ^1). Reactivity of 17 electrons organometallic complex towards ligand substitution reaction is well-documented [15] and the associative and dissociative mechanisms for such exchanges are usually considered [16,17]. This cationic derivative $\mathbf{4}^+$ oxidized **3** with regeneration of $\mathbf{3}^+$ and formation of **4** (propagation step). The electron transfer between $\mathbf{4}^+$ and **3** is thermodynamically favorable ($\Delta E = -0.655 - (-0.41) = -0.245$ V) hence driving the catalytic cycle. It is interesting to note that by injecting a small amount of electricity (0.02 F mol^{-1} for 1 equivalent of CNXylyl for instance and stopping the electrolysis before the current reaches zero), we observe that the ligand substitution goes to completion giving **4** in quantitative yield. As a result, the turnover number for this specific example becomes equal to 49 (i.e., (1 − 0.02)/0.02) in comparison with 9 (i.e., (1 − 0.1)/0.1) for the more rapid exhaustive nonstop electrolysis. So the turnover number is a function of the initial amount of injected electricity.

At room temperature, the reaction of the complex **3** with 1 equivalent of CNXylyl gave the complex **4**. The substitution reaction is nearly instantaneous (few minutes) and quantitative if the induction is performed by oxidation of **3** at the plateau of wave F. Without induction, the substitution reaction is much more slower: to be



Scheme 2.



with $K_1=\frac{k_{f1}}{k_{b1}}=\frac{[4^+]}{[3].[CNXylyl]}$ $K_2=\frac{k_{f2}}{k_{b2}}=\frac{[4]}{[3].[\mathrm{CNXylyl}]}$ $K=\frac{k_f}{k_b}=\frac{[4].[3^+]}{[3].[4^+]}$

Scheme 3.

complete, the transformation reaction required 3 h. The final product **4** was isolated as a green crystalline solid and characterized spectroscopically. The C_s symmetric **4** gave in the ^{1}H NMR spectra, four signals assigned to the four protons of the substituted cyclopentadienyl moiety, one singlet signal at 2.36 ppm due to the two methyl

Table 1
Diffusion coefficients obtained from waves height in RDE voltammetry

Complex **3**	Complex **3**$^+$	Complex **4**	Complex **4**$^+$
2.1×10^{-6} cm^2 s^{-1}	0.9×10^{-6} cm^2 s^{-1}	1.1×10^{-6} cm^2 s^{-1}	0.6×10^{-6} cm^2 s^{-1}

At 0 °C, kinematic viscosity of THF is equal to $v = 0.0070$ cm^2 s^{-1}.

Table 2
Thermodynamic electrochemical and kinetic parameters at 0 °C for the reaction between **3** and CNXylyl (k_{hi}, heterogeneous charge transfer scan rate; α_i, charge transfer coefficient; K_i, k_{fi}, chemical reaction constants)

E_i^0 vs. SCE	k_{hi} (cm s^{-1})	α_i	K_i	k_{fi}
$E_1^0 = -0.41$	$k_{h1} = 0.01$	$\alpha_1 = 0.5$	$K_1 = 20$ mol^{-1} l	$k_{f1} = 40$ mol^{-1} l s^{-1}
$E_2^0 = -0.655$	$k_{h2} = 0.01$	$\alpha_2 = 0.5$	$K = 3.33\times10^4$	$k_f = 3000$ mol^{-1} l s^{-1}
			$K_2 = 6.66\times10^5$ mol^{-1} l	

group of the isocyanide ligand and several signals assigned to the phenyl rings. The ^{13}C NMR spectra for **4** showed the expected signals for the different ligand systems present (see Section 4).

2.4. Simulations

The CV and RDE voltammograms of **3** and **4** have been simulated in relation with the four-species square scheme [18–20] and with the Solution Electron-Transfer Red-Ox reaction (SET) between **4**$^+$ and **3**, as shown in Scheme 3. When the equilibrium is not established, the situation can be designated as catalytic. This is the case if **3** is only present initially and the reaction **3** → **4** is very slow (metastable equilibrium). In this case, at the potential where **3** is oxidized, the **4**$^+$ formed from **3**$^+$ can be reduced to **4**, either at the electrode or via SET reaction.

The computations were performed using the commercially available program called Digisim (Bioanalytical Systems) with disabled option of the equilibrium conditions. The uncompensated resistance is Ru = 500 Ω and the double-layer capacitance value was estimated as $C_{dl}/A = 3.04$ μF cm^{-2} using a blank solution prior to voltammetric measurements. The experimental curves were corrected for residual current, also determined using voltammetric measurement of blank solutions.

The first necessary input parameters for these simulations are the diffusion coefficients for the species **3**, **3**$^+$, **4**, and **4**$^+$. Using standard methodologies using RDE voltammograms at 0 °C, the values were listed in Table 1.

The knowledge of E_1^0 and E_2^0 is required and were identified using the half-wave potentials extracted from the RDE voltammograms for **4** (obtained after electrolysis at F′ peak potential and adduct of a slight CNXylyl excess and with knowing that the equilibrium **3**$^+$/**4**$^+$ is much in favor of **4**$^+$) and **3** (reaction (5)). The standard heterogeneous electron transfer rate constants k_{hi} and the transfer coefficients α_i were then obtained by simulation of the RDE voltammograms. The best fitting is obtained with $\alpha_i = 0.5$ and $k_{hi} = 0.01$ cm s^{-1} and confirms that the charge transfers are not very fast (Table 2).

Afterwards, the simulation results of CV voltammograms (Figs. 4 and 5) provide by fitting both the equilibrium constant K_1 and the rate constants k_{f1} and k. K was in relation with E_1^0 and E_2^0, and K_2 was calculated since $K = K_2/K_1$. K_1 is also equal to k_{f1}/k_{b1}, then k_{b1} is able to be obtained.

The square scheme is not in equilibrium, the rates of the reaction **3** $\rightleftharpoons$ **4** are very low at 0 °C. The chemical reaction constants k_{f2} and k_{b2} are not able to be deduct from voltammetric results. The simulated curves do not change anymore as soon as k_{f2} is inferior to 1 mol^{-1} L s^{-1}. Experimentally at 0 °C, when 1 equivalent of CNXylyl was added to complex **3** solution, no modification of the wave F was observed, even after several hours. This result means that k_{f2} is widly inferior to 1 mol^{-1} L s^{-1}. The reaction SET is fast but the value of k cannot be determined with great accuracy because the simulation gives an approximate value.

3. Conclusion

We have presented here a new electron-transfer-catalyzed ligand substitution of carboxylato niobocene complex induced by electrochemical oxidation. This reaction permits, via a previous oxidation of **3** to generate **4** nearly instantaneously and quantitatively. **3** was already obtained by reduction of **1**, in presence of 1 equivalent of 3,4-diaminobenzoic acid.

These two complexes have been obtained by two different ways: chemically or electrochemically. Their structure and their formation mechanism have been described using electrochemical and spectroscopic data. Electrochemical simulation have been done to verify experimental results and have been completed by a kinetic study.

4. Experimental

4.1. Chemical experiments

All reactions were carried out by using Schlenk techniques. Oxygen and water were excluded by the use of vacuum lines supplied with purified N_2. Toluene was distilled from sodium. Pentane was distilled from sodium/potassium alloy. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone. All solvents were deoxygenated prior to use. The complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ **5** was prepared as described in the literature [21]. Deuterated solvents were dried over 4 Å molecular sieves and degassed prior to use. 3,4-diaminobenzoic acid was used as purchased from Aldrich. NMR spectra were recorded on a Varian Unity 300 (300 MHz for ^1H, 75 MHz for ^{13}C) spectrometer. Chemical shifts were measured related to partially deuterated solvent peaks and reported relative to TMS IR spectra were recorded on a Perkin–Elmer 883 spectrometer in Nujol mulls over CsI windows.

4.2. Electrochemical experiments

All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon gas and using dry solvents. The supporting electrolyte was degassed under vacuum before use and then solubilized at a concentration of 0.2 mol L^{-1}. For cyclic voltammetry experiments, the concentration of the analyte was nearly 4×10^{-3} mol L^{-1}, CNXylyl was introduced in a slight excess. Voltammetric analyses were carried out in a standard three-electrode cell with a Princeton Applied Research, Model 263A. 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 ($\phi = 3$ mm). A CTV101 Speed Control unit was used to adjust the rotation speed ($\varpi = 500$ rpm) of the EDI101 electrode (Radiometer). In these conditions, when operating in THF, the formal potential for the ferrocene$^{+/-}$ couple is found to be +0.56 V versus SCE. The controlled potential electrolysis was performed with an Amel 552 potentiostat coupled with an Amel 721 electronic integrator. High scale electrolyses were performed in a cell with three compartments separated with fritted glasses of medium porosity. A carbon gauze was used as the working electrode, a platinum plate as the counter-electrode and a saturated calomel electrode as the reference electrode.

4.3. Synthesis of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^2\text{-}O,O\text{-}OOC(C_6H_3)(NH_2)_2)]$ **3**

A mixture of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3]$ **5** (0.28 g; 0.75 mmol) and the 3,4-diaminobenzoic acid $[3,4\text{-}(NH_2)_2\text{–}C_6H_3(COOH)]$, (0.12 g; 0.75 mmol) was stirred with 30 mL of dry THF, at 60 °C for 4 h. After that time, the solution become dark green colour, the solvent was evaporated under vacuum to dryness. The dark green oily residue was extracted with 10 mL of hexane. The resulting solution was filtered and evaporated to dryness. A dark green solid was isolated, yielding 90% of **3**: ^1H NMR (toluene-d^8): δ 0.22 (s, 18H, SiMe_3), 4.30, 5.80 (4H each a complex signal, $C_5H_4SiMe_3$), 6.15 (d, $^5J_{H\text{–}H} =$ 8.05 Hz, 1H, C_6H_3), 6.70 (s, 1H, C_6H_3). 7.68 (d, $^5J_{H\text{–}H} = 8.05$ Hz, 1H, C_6H_3), $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.4 (SiMe_3), 93.1 (C^1, $C_5H_4SiMe_3$), 104.1, 107.1 ($C^{2\text{–}5}$, exact assignment not possible, $C_5H_4SiMe_3$), 140.0, 133.1, 132.9, 132.1, 122.1 (C_6H_3), 191.2 (COO^-). Anal. Calcd. (Found) for $C_{23}H_{33}NbN_2O_2Si_2$: C, 56.22 (56.11); H, 6.72 (6.59); N, 5.70 (5.60)%.

4.4. Synthesis of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-}O\text{-}OOC\text{-}(C_6H_3)(NH_2)_2)(CN(2,6\text{-}Me_2C_6H_3))]$ **4**

A mixture of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^2\text{-}O,O\text{-}OOC(C_6H_3)(NH_2)_2)]$ **3** (0.13 g; 0.75 mmol), and the 2,6-dimethylphenylisocyanide $[CN(2,6\text{-}Me_2C_6H_3)]$ (0.06 g; 0.75 mmol) was stirred with 30 mL of dry THF, at room temperature for 3 h. After that time, the solution took a green colour, the solvent was evaporated under vacuum to dryness. The green oily residue was extracted with 10 mL of hexane. The resulting solution was filtered and evaporated to dryness. A green solid was isolated, yielding 80% of **4**: ^1H NMR (toluene-d^8): δ 0.06 (s, 18H, SiMe_3), 2.36 (s, 6H, $CN(2,6\text{-}Me_2C_6H_3)$), 4.95, 5.16, 5.42, 5.72 (2H each a complex signal, $C_5H_4SiMe_3$), 6.64 (s, 3H, $CN(2,6\text{-}Me_2C_6H_3)$), 6.30 (t, $^5J_{H\text{–}H} = 8.0$ Hz, 1H, C_6H_3), 7.13 (s, 1H, C_6H_3) 6.62 (d, $^5J_{H\text{–}H} = 8.0$ Hz, 1H, C_6H_3). $^{13}C\{^1H\}$ NMR (toluene-d^8): δ 0.2 (SiMe_3), 19.1 ($CN(2,6\text{-}Me_2C_6H_3)$), 92.9 ($C^1$ C_5H_4), 96.7, 101.5, 104.5, 110.2 ($C^{2\text{–}5}$, exact assignment not possible, $C_5H_4SiMe_3$), 126.5, 129.8, 130.3 and 130.7 ($CN(2,6\text{-}Me_2C_6H_3)$), 140.0, 133.1, 132.9, 132.1, 122.1 (C_6H_3), 174.6 (COO^-), 212.2 ($CN(2,6\text{-}Me_2C_6H_3)$). Anal. Calcd. (Found) for $C_{31}H_{42}NbN_3O_2Si_2$: C, 56.96 (56.85); H, 6.43 (6.39); N, 6.43 (5.35)%.

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