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Electrochemical and spectroscopic studies on dicarboxylato niobocene complexes

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Abstract

Reaction of sodium oxalate or malonate onto the niobocene dichloride $Nb(\eta^5\text{-}C_5H_4SiMe_3)Cl_2$ (**1**) yields the dicarboxylato complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2$(*O,O′*-OCOOCO) (**4a**) and Cp'_2Nb(*O,O′*-$OCOCH_2OCO$) (**5a**) where the dicarboxylato ligand is proved to be chelating. An alternative way to yield the dicarboxylato niobium (IV) complexes consists in the electrochemical reduction of **1** in the presence of the corresponding carboxylic acid followed by the oxidation of the electrogenerated complex. In addition to **4a** and **5a** the latter method has been shown to yield the succinato and orthophtalato analogs $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2$(*O,O′*-$OCOCH_2CH_2OCO$) (**6a**) and $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2$(*O,O′*-$OCOC_6H_4OCO$) (**7a**). The structure of the complexes as well as the mechanism of their formation is discussed above electrochemical and spectroscopic data. A special emphasis is made on the ESR data which strongly depends on the length of the dicarboxylato chain. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Niobocene; Dicarboxylato ligand; Electrochemistry; ESR spectroscopy

1. Introduction

Metal-promoted transformations of carbon dioxide, which have stimulated widespread interest, constitute an attractive area of study. While a number of discrete CO_2 [1] containing complexes and their reactions have been described, few reactivity studies of co-ordinated CO_2 are known. Recently, in connection with our studies of carbon dioxide activation [2], the formation of formato niobocene complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2$(*O,O′*-OCOH) was achieved from carbon dioxide insertion into the niobium–hydrogen bond of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$. The formato complex can also be obtained from the two-electron reduction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ in the presence of formic acid [3]. More recently the paramagnetic carbonato niobocene complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2$(*O,O′*-OCOO) has been prepared from the insertion of carbon dioxide into the niobium–oxygen bond of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O)$ electrogenerated by the one-electron reduction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(O)$ in THF 0.2 M STPB solution. An alternative way for the preparation of carbonato niobocene complex consists in the addition of CO_3^{2-} dianion on the electrogenerated species $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ followed by the one-electron oxidation of the resulting anionic carbonato niobium (III) complex [4]. Although the formation of oxalate has been observed in the homogeneously catalyzed electrochemical reduction of CO_2, the catalysts were mainly organic

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Abbreviations: Cp′, $\eta^5\text{-}C_5H_4SiMe_3$; ESR, electron spin resonance; M, $mol\,l^{-1}$; SCE, saturated calomel electrode; STPB, sodium tetraphenylborate; TBAHFP, tetrabutylammonium hexafluorophosphate; THF, tetrahydrofuran.

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compounds [5]. Among the large family of complexes known to catalyze the electrochemical reduction of carbon dioxide [6], as far as we know, just two of them promote the transformation to oxalate [6e,6f]. Continuing our studies, in this paper we report our results on the electrosynthesis and synthesis of a paramagnetic oxalato niobocene complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O,O'\text{-}OCOOCO)$.

In addition we report the preparation and characterization of malonato, succinato and orthophtalato niobocene complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O,O'\text{-}OCOCH_2OCO)$, $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O,O'\text{-}OCOCH_2CH_2\text{-}OCO)$ and $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O,O'\text{-}OCOC_6H_4OCO)$ as well as several aspects of their formation mechanism.

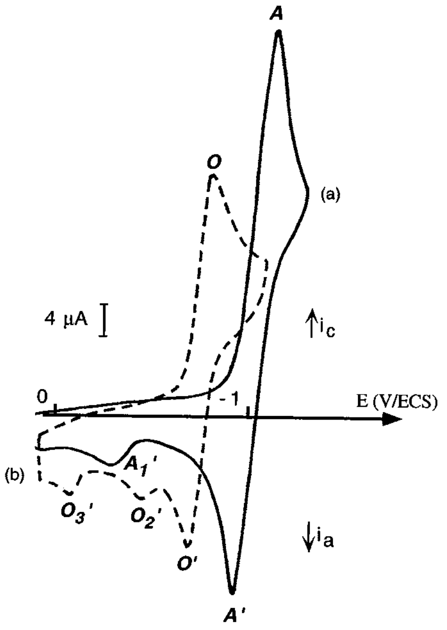


Fig. 1. (a) Cyclic voltammogram of Cp'_2NbCl_2, **1** ($c = 4.70$ mM), in THF 0.2 M TBAHFP. (b) After addition of 1.1 molar equivalents of sodium oxalate in water. Initial potential: +0.1 V. Scan rate: 50 mV s^{-1}.

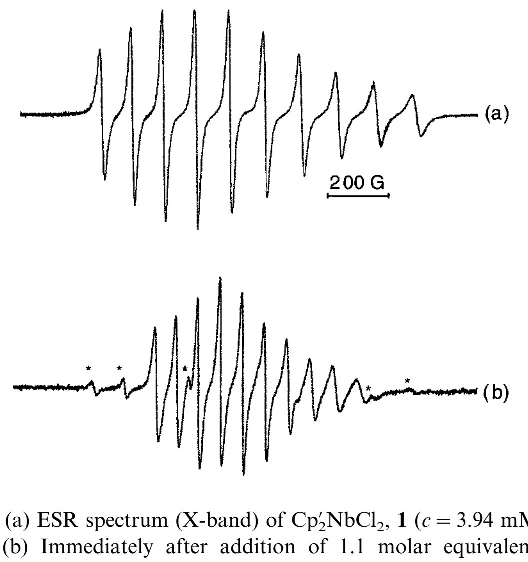
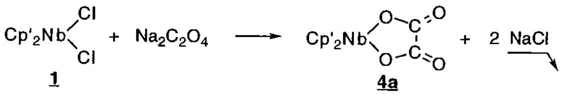


Fig. 2. (a) ESR spectrum (X-band) of Cp'_2NbCl_2, **1** ($c = 3.94$ mM), in THF. (b) Immediately after addition of 1.1 molar equivalents of sodium oxalate in water and stirring during 3 h (starred lines correspond to traces of unreacted **1**).

2. Results and discussion

Fig. 1a shows the cyclic voltammogram at room temperature of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$, **1** ($Cp'_2NbCl_2$) in THF 0.2 M TBAHFP on a vitreous carbon disk electrode. Two oxidation peaks A′ and A'_1 ($E_{p,A} = -1.13$ V, $E_{p,A'} = -0.93$ V, $E_{p,A'_1} = -0.93$ V) are observed when the potential is reversed after reduction peak A where A′ and A'_1 correspond to the oxidation of $Cp'_2NbCl_2^-$, **2** and Cp'_2NbCl, **3**, respectively [7]. An addition of nearly 1.1 molar equivalent of sodium oxalate in water results in complete replacement of peak A by a new cathodic peak O (see Fig. 1b) coupled on the reverse scan to O′ and two less intense peaks O'_2 and O'_3 ($E_{p,O} = -0.82$ V, $E_{p,O'} = -0.69$ V, $E_{p,O'_2} = -0.45$ V, $E_{p,O'_3} = -0.08$ V). Increasing the sweep rate or decreasing the temperature lowers the intensities of O'_2 and O'_3 which is indicative of chemical complications associated with heterogeneous electron transfer.

This drastic change induced by the salt addition is due to the formation of the oxalato chelate $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O,O'\text{-}OCOOCO)$, **4a**, through the following reaction (Eq. (1)):

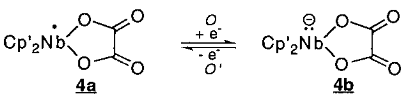


(1)

The reaction has been monitored independently by ESR spectroscopy in supporting electrolyte free solution. Fig. 2 shows the record as a function of time: the characteristic ten-line spectrum of **1** (THF: $g_{iso} = 1.9776$, $a_{iso,Nb} = 115.1$ G [8]) is gradually replaced by a less large signal ($g_{iso} = 1.9776$, $a_{iso,Nb} = 72.8$ G). Several experiments have been made varying the amount of water, the percentage of which must be equal to 10% at least for the reaction to be carried out. The reason is that the sodium oxalate salt must dissolve and appreciably dissociate to render the reaction feasible.

The low value of the hyperfine splitting constant $a_{iso,Nb}$ denotes appreciable delocalization of the unpaired spin onto the dicarboxylato ligand while conventional Cp_2Nb (IV) systems with two σ-donor ligands show $a_{iso,Nb}$ above 100 G [8,9]. This situation may be related to that previously observed for the analogous carbonato niobocene complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}(O,O'\text{-}OC(O)O)$ ($g_{iso} = 1.9776$, $a_{iso,Nb} = 54$ G) [4].

After an appropriate workup (Section 3) **4a** has been isolated and characterized from its infrared features. The OCO asymmetric and symmetric stretching fre-



Scheme 1.

quencies are particularly informative [10]. The usual approach is to relate the value of Δ [$\Delta = \nu(CO_2)_{asym} - \nu(CO_2)_{sym}$] with the carboxylate bonding mode (mono- or bi-dentate). In **4a**, in solid state, two close bands are found for the asymmetric vibration (1705, 1675 cm^{-1}) and one for the symmetric one (1341 cm^{-1}). The Δ value (349 cm^{-1}) is significantly larger than the ionic value ($\Delta = 201$ cm^{-1}) [11] which indicates that each carboxylate moiety acts as a monodentate group.

In addition the infrared spectrum of **4a** also exhibits the absorptions expected for the cyclopentadienyl and trimethylsilyl groups [12].

Voltammetric results (see Fig. 1) can be explained in the following terms.

One-electron reduction of **4a** initially yields the anionic species **4b** which is oxidized at O′. However, **4b** is not fully stable as peaks O'_2 and O'_3 must be issued from a chemical evolution of **4b**. **4b** is stabilized at low temperature. Indeed, by performing the voltammetric experiment at − 10°C, the intensities of O'_2 and O'_3 are reduced relatively to that of O′ (Scheme 1).

Reaction (1) has been extended to the malonato complex $Cp'_2Nb(OCOCH_2OCO$-*O*,*O*′) (**5a**) which has also been characterized by cyclic voltammetry, IR and ESR spectroscopies (see Tables 1 and 2) and the values are discussed below.

Fig. 3a displays the cyclic voltammogram of **5a** which is formed in situ by the reaction of sodium malonate with **1**. After the reduction peak M ($E_{p,M} = -0.9$ V), just two oxidation peaks, M′ ($E_{p,M'} = -0.76$ V) and M'_2 ($E_{p,M'_2} = -0.34$ V) are found on the reverse scan (no peak M'_3). Multicycle sweep experiments have also been experienced which shows that on the second cathodic scan no peak is observed except M.

The reduction mechanism of Scheme 2 can be postulated.

The electron transfer step gives the anionic complex **5b** which isomerizes to **5′b**. In **5b** the six-membered metallacycle implies that the two carboxylato groups are involved into ligation to the metal: the negative charge is localized on the metal center. In **5′b** the ligand is still chelating but via the two oxygen atoms of just one carboxylato group with the metal-free one bearing the charge. This would explain the lower oxidation potential of **5′b** (peak M'_2) compared with **5b** (peak M′) as the oxidation in the former concerns the *neutral* metallic core.

Oxidation of **5′b** leads to a zwitterionic species which is unstable at the voltammetric time scale since the corresponding reduction peak is not observed; this species rapidly reforms **5a**.

Addition of $NaBPh_4$ to **5a** (Fig. 3) results in the increase of M'_2 as simultaneously M′ decreases. The sodium salt favor the formation of the four-membered metallacycle **5′b** probably due to ion-pairing or chelation of Na^+ by the uncoordinated carboxylate group as it has been described in the field of metallocarboxylates [13]. On the other hand, Na^+ would have no stabilization effect on the metallate **5b**.

Unexpectedly, the addition of succinate or orthophtalate on **1** did not yield the corresponding dicarboxylato complexes probably due to the low solubility of the sodium salt in THF; furthermore, the reaction products are suspected of being unstable in the presence of water where the salt is soluble. So we have been looking for a new way of synthesis using reagents who do not need water to be solubilized; this can be achieved by starting from dicarboxylic acid. We will examine the method in the case of the succinato complex $Cp'_2Nb(OCOCH_2CH_2OCO$-*O*,*O*′) (**6a**).

The cyclic voltammogram of **1** in THF with $NaBPh_4$ as the supporting electrolyte is depicted in Fig. 4a. An addition of 1.2 molar equivalents of succinic acid causes (Fig. 4b) peak A to increase as appear a new reduction peak B ($E_{p,B} = -1.29$ V) and in the reverse scan an oxidation peak S*′ ($E_{p,S*'} = -0.37$ V). In these conditions an electrolysis on the mercury pool at the potential of A (− 1.3 V) consumes nearly two Faradays

Table 1
Spectroscopic data of dicarboxylato niobium (IV) complexes $Cp'_2Nb(O_2C(X)CO_2$-*O*,*O*′) [$X = (CH_2)_n$ with $n = 0$ (**4a**), 1 (**5a**) and 2 (**6a**); $X = o$-C_6H_4 (**7a**)]

Complex	ESR [a]			Infrared	
	Solvent	$a_{iso,Nb}$	g_{iso}	$\nu(CO)_{asym}$ (cm^{-1})	$\nu(CO)_{sym}$ (cm^{-1})
4a	THF	72.8	1.9721	1705, 1675	1341
5a	THF	93.5	1.9675	1675, 1646	1357
6a	THF	112.1	1.9654		
7a	THF	102.3	1.9719	1625, 1615	1345

[a] Hyperfine coupling constants and isotropic g factors are all corrected to second order using the Breit–Rabi equation.

Table 2
Cyclovoltammetric data of niobium (IV) and (III) complexes [a]

Complex	Solvent/electrolyte	$E_{p,red}$ (V)	$E_{p,ox}$ (V)
4a	THF/NBu_4PF_6	−0.84	
4c	THF/$NaBPh_4$		−0.4
5a	THF/NBu_4PF_6	−0.86	
5c	THF/$NaBPh_4$		−0.36
6a	THF/NBu_4PF_6	−0.96	
6c	THF/$NaBPh_4$		−0.36
7a	THF/NBu_4PF_6	−0.88	
7c	THF/$NaBPh_4$		−0.37

[a] Measured on vitreous carbon disk electrode. Potential reference: SCE. Scan rate: 0.2 V s^{-1}.

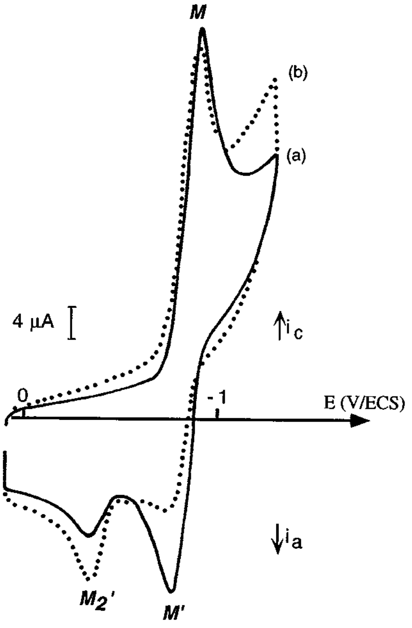


Fig. 3. (a) Cyclic voltammogram of $Cp'_2Nb(OCO–CH_2–OCO\text{-}O,O')$, **5a** ($c = 4.41$ mM), in THF/10% water 0.2 M TBAHFP. (b) After addition of 10 molar equivalents of sodium tetraphenylborate. Initial potential: + 0.1 V. Scan rate: 100 mV s^{-1}.

per mol of **1** and affords the cyclic voltammogram of Fig. 4c which exhibits a cathodic peak S* ($E_{p,S^*} = -0.48$ V) and S ($E_{p,S} = -0.96$ V) if the starting positive potential scan is inverted after S*′. At this stage the solution can be exhaustively oxidized ($Q_{exp} = 0.75$ F mol^{-1} of initially introduced) and the cyclic voltammogram of the electrolyzed solution (Fig. 4d) shows in the forward scan the cathodic peak S which is due to the presence in solution of the niobium (IV) succinato chelate $Cp'_2Nb(OCOCH_2CH_2OCO\text{-}O,O')$ (**6a**). Formation of the latter is also evidenced by ESR analysis which provided the characteristic ten-line signal ($g_{iso} = 1.9719$; $A_{iso,Nb} = 112.1$ G). Unfortunately, we have been unable to isolate **6a** to identify it by IR spectroscopy.

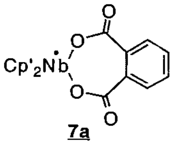
The formation of **6a** can be explained in terms of Scheme 3.

Two-electron reduction of **1** initially gives niobium (III) complex **6c** in which just one carboxylato group is involved into coordination. The same electrochemical reaction has been shown to be feasible with carboxylic monoacids (formic or acetic acid) [3]. It must be emphasized that the formato and acetato complexes have a close first oxidation potential to **6c** ($E_{1/2} = -0.34$ and -0.49 V, respectively, versus -0.425 V for **6c**) due to identical charge and coordination sphere for the metal. This first reaction is not elemental. As the chlorides cannot be eliminated at the same time, a chloro oxalato complex can be postulated as an intermediate which would be reducible at peak B. But we have no spectroscopic evidence for such a species. Finally, monoelectronic reduction of this intermediate would lead to **6c** after chloride elimination.

The second step consists in the oxidation of **6c**. The resulting metal-centered radical **6′c** is unstable at the time scale of electrolysis and leads to the chelate complex **6a** with the loss of one proton.[1]

With the aim of trapping **6′c** the electrolysis of **6c** has been performed at low temperature. After one-electron oxidation ESR analysis of the electrolyzed solution provided a narrow ten-line signal ($g_{iso} = 1.9685$; $A_{iso,Nb} = 49$ G) which we assigned to **6′c**. When the solution came back to room temperature this signal is gradually replaced by that of **6a**.

The same set of experiments has been realized with *o*-phtalic acid and led to similar results so that the same mechanism as that of Scheme 3 must apply. In addition, we have been able to isolate the dicarboxylato niobium (IV) complex **7a** which allowed its unequivocal identification.



7a

Finally the reduction/oxidation method to synthesize the chelate complexes has also been extended to oxalic and malonic acids.

All spectroscopic and electrochemical features are specified in Tables 1 and 2. In Table 2 **4c**, **5c**, **6c** and **7c** refer to the niobium (III) complexes where the dicarboxylato ligand is in its hemiacid form.

In the recent years, with the aim of finding substitutes to cisplatin, much work has been devoted to the synthesis of platinum (II) complexes with dicarboxylate ligands acting as chelates [14]. Similar infrared features

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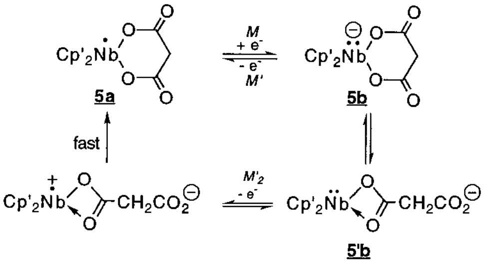
[1] When oxidizing **6c** the coulometric consumption is far less than 1 F mol^{-1}. Indeed, we have found that **6c** slowly evolves in solution to reform **6a** with the elimination of H_2. We are currently investigating the scope of this interesting reaction.



Scheme 2. Proposed mechanism for the reduction of **5a**.

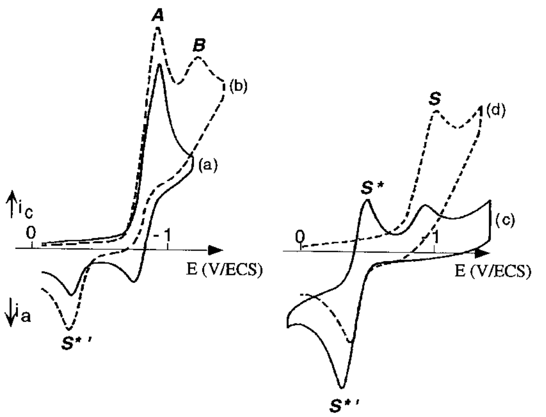


Fig. 4. (a) Cyclic voltammogram of Cp'_2NbCl_2, **1** ($c = 4.78$ mM), in THF 0.2 M STPB. (b) After addition of 2 molar equivalents of succinic acid. (c) Immediately after reduction at -1.3 V. (d) After oxidation at -0.4 V. Initial potential: -0.1 V (a, b and d) and -1.1 V (c). Scan rate: 200 mV s^{-1}.

are reported to us. Typically strong absorption is observed in the region 1570–1700 but it is unclear whether one or more bands are seen. One intense band for the symmetric stretch is always located between 1340 and 1410 cm^{-1}.

The most spectacular is the sequential growth of $a_{\mathrm{Nb},iso}$ (see Fig. 5) in the order **4a** < **5a** < **7a** < **6a** which seems to be directly reliable to the size of the metallacycle. It has been shown on theoretical basis that for a d^1 complex $[M(\eta\text{-}C_5H_5)_2L_2]$ the smaller the L–M–L angle the smaller will be the degree of metal character of the HOMO and consequently the value of the ^{93}Nb hyperfine splitting constant [15]. This can be extended to our chelate complexes where the O–Nb–O angle is forced to decrease with the number of atoms of the metallacycle because of steric congestion as evidenced by simply considering the planar molecular drawings:

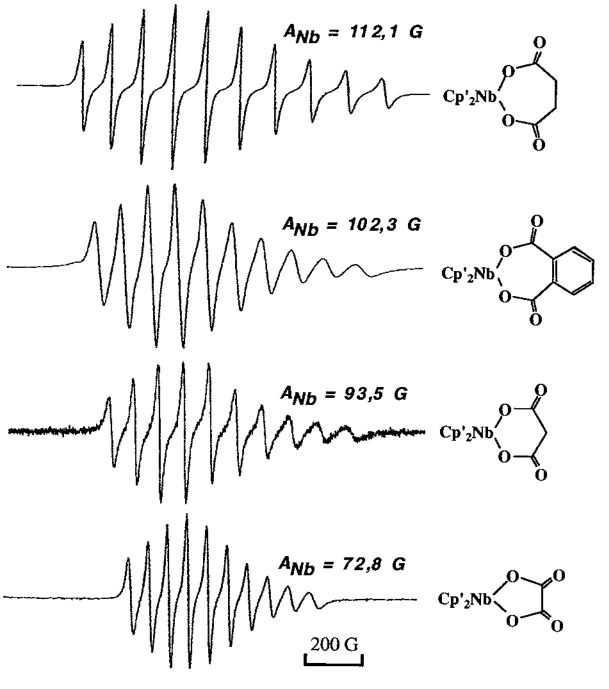
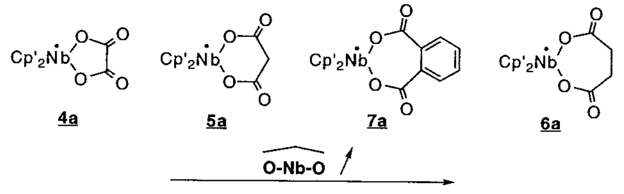
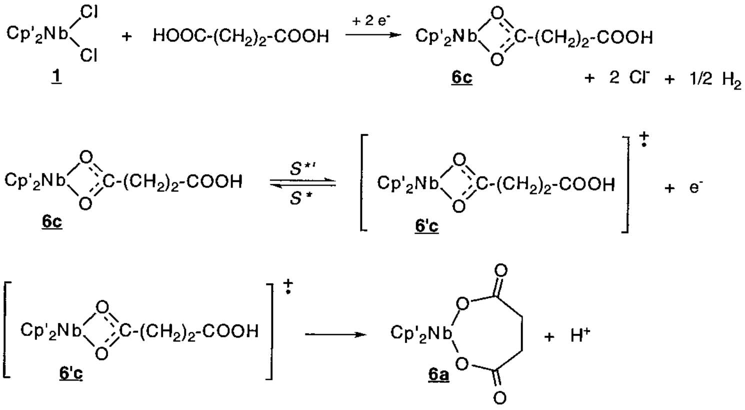


Fig. 5. ESR spectra (X-band) in THF of dicarboxylato niobium (IV) complexes **4a**, **5a**, **6a** and **7a**.





Scheme 3.

Comparing **6a** and **7a** (seven-member metallacycle) the C–C bond opposite to the metal shorter in **7a** (part of the phenyl ring) lowers the O–Nb–O angle being responsible for the weaker value of $a_{\mathrm{Nb},iso}$.

3. Experimental

3.1. General procedures

All manipulations were performed using standard Schlenck techniques in an atmosphere of dry, oxygen free argon. THF and toluene were distilled under argon from sodium and benzophenone and degassed before use. TBAHFP and sodium tetraphenylborate were purchased from Fluka (puriss p.a. for electrochemical grade), the salts being dried and deoxygenated under vacuum immediately before use.

Infrared spectra were obtained in the region 4000–400 cm^{-1} using a Nicolet 205 spectrophotometer. They were taken in the solid state as nujol mulls. Electron spin resonance spectra were recorded at room temperature (r.t.) with a Burker ESP 300 spectrophotometer.

Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode (SCE) separated from the analyzed solution by a sintered glass disk; the auxiliary electrode was a platinum wire. For all voltammetric measurements the working electrode was a carbon disk electrode initially polished with alumina. The controlled potential electrolysis was performed with an Amel 552 potentiostat coupled to an Amel 771 integrator. A mercury pool was used as the cathode, a platinum plate as the anode and an SCE as the reference electrode, each electrode being separated from the others by sintered glass disks **1** was prepared according to a published procedure [8].

3.2. Preparation of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(OCOOCO\text{-}O,O')$ **4a**

To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ (**1**, 32 mg, 73 μmol) in THF (10 ml) was added 11 mg of sodium oxalate (82 μmol) in 1 ml of H_2O and the mixture stirred for 1 h at r.t. after which the EPR analysis provided the signal of **4a**. The solution was then evaporated to dryness and the residue extracted with 10 ml of toluene. The resultant solution was evaporated to dryness to afford a green oily solid. ESR (THF): $g_{iso} = 1.9721$, $a_{iso,\mathrm{Nb}} = 72.8$ G. IR: $\nu(\mathrm{cm}^{-1}) = 1705$ and 1675 (CO, asymmetric stretching), 1341 (CO, symmetric stretching). Mass spectrometry (FAB): m/e = molecular ion peak unobserved, 383 ($M + 1\text{-}SiMe_3$), 368 ($M + 1\text{-}C_2O_4$).

Malonato complex **5a** was isolated in a similar way as a brown powder. ESR (THF): $g_{iso} = 1.9675$, $a_{iso,\mathrm{Nb}} = 93.5$ G. IR: $\nu(\mathrm{cm}^{-1}) = 1675$ and 1646 (CO, asymmetric stretching), 1357 (CO, symmetric stretching). FABMS; $m/e = 470$ ($M + 1$), 412 ($M + 1\text{-}CH_2CO_2$), 397 ($M + 1\text{-}SiMe_3$), 368 ($M + 1\text{-}O_2CCH_2CO_2$).

3.3. Preparation of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(OCO\text{–}C_6H_4\text{–}OCO\text{-}O,O')$ **7a**

A solution of **1** (20 mg, 46 μmol) and orthophtalic acid (9 mg, 54 μmol) in THF 0.2 M $NaBPh_4$ (10 ml) was electrolyzed on the mercury pool at -1.3 V until the current dropped to zero with a coulometric consumption close to 2 F mol^{-1} of initial complex. The potential was then set at -0.3 V where the solution was reoxidized with a charge of nearly 1 F mol^{-1}. The solvent was evaporated to dryness and the residue extracted with 10 ml of toluene. The extract was evaporated to dryness to leave a green oily solid identified to **7a**. ESR (THF): $g_{iso} = 1.9719$, $a_{iso,\mathrm{Nb}} = 102.3$ G. IR: $\nu(\mathrm{cm}^{-1}) = 1625$ and 1615 (CO, asymmetric stretching), 1345 (CO, symmetric stretching). FABMS; $m/e = 532$ ($M + 1$), 459 ($M + 1\text{-}SiMe_3$), 368 ($M + 1\text{-}O_2CC_6H_4CO_2$).

Succinato complex **6a** was synthesized according to a similar procedure but, owing to the poor stability of that compound, we were unable to collect infrared data. ESR (THF): $g_{iso} = 1.9654$, $a_{iso,\mathrm{Nb}} = 112.1$ G. FABMS; $m/e = 484$ ($M + 1$), 412 ($M + 1\text{-}CH_2CH_2CO_2$), 368 ($M + 1\text{-}O_2CCH_2CH_2CO_2$).

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