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Electrochemical studies on organometallic compounds

XXXIX *. Electrochemical behavior of bis-silylated cyclopentadienyl niobium trihydride. ESR spectroscopic characterization of the dimeric hydride niobium(IV) complex $[Nb(\eta^5\text{-}Me_3SiC_5H_4)_2H]_2(\mu\text{-}H)_2$

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Abstract

The one-electron oxidation of $NbCp'_2H_3$, **1** ($Cp' = Me_3SiC_5H_4$), has been found to give the dimeric niobium(IV) complex $(NbCp'_2H_2)_2$, **3**, which has been characterized by ESR spectroscopy. The cationic niobium(V) species $[NbCp'_2H_2(THF)]^+$, **4**, has been prepared through a two-electron oxidation of **1**. **3** can also be obtained by one-electron reduction of **4**. The same behaviour has been observed for $Nb(\eta^5\text{-}^tBuC_5H_4)_2H_3$.

Introduction

Polyhydrido transition metal complexes have attracted much interest in recent years, principally because of their great reactivity [1]. The activation of carbon–hydrogen bonds by niobocene trihydride, $NbCp_2H_3$ ($Cp = \eta^5\text{-}C_5H_5$) has been demonstrated by Parshall and Tebbe [2]. In 1975 Kochi and al. showed that the paramagnetic $Nb^{IV}(C_5H_5)_2H_2$ species, generated by abstraction of hydrogen from the diamagnetic trihydride $Nb(C_5H_5)_2H_3$ by a tert-butoxy radical can play an important role in the activation of the carbon–carbon double bond [3]. There are not many examples of stable paramagnetic hydride niobium(IV) complexes and in all cases they have phosphorus donor ligands around the niobium center [4]. We

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* For Part XXXVIII see ref. 14.

decided to examine the possibility of preparing a Nb^{IV} complex electrochemically from bis-silylated cyclopentadienyl niobium $Nb(Me_3SiC_5H_4)_2H_3$, **1** ($NbCp'_2H_3$).

Results

In tetrahydrofuran (THF) with Bu_4NPF_6 as supporting electrolyte, voltammetry of **1** on a glassy carbon rotating disk electrode (r.d.e.) exhibits two anodic waves E_1' and E_2'. The half wave potentials are respectively +0.15 V and +0.70 V versus an aqueous saturated calomel electrode. In cyclic voltammetry the inversion of the potential scan after peak E_1' causes a reduction peak A_3 to appear (Fig. 1a); when the scan is reversed after peak E_2', reduction peaks A_2 and A_3 are obtained (Fig. 1b).

After electrolysis at the potential of wave E_1' at −30 °C on a carbon gauze electrode, which consumes approximatively one faraday, the r.d.e. voltammogram at room temperature shows the reduction wave A_3 and the oxidation wave E_2'. A small oxidation wave D_1' appears at +0.43 V. After several minutes the oxidation wave D_1' increases whereas E_2' decreases (Fig. 2c). The ESR spectrum of the electrolyzed solution is rather complex and indicates that several paramagnetic species are formed. In cyclic voltammetry the inversion of the potential scan beyond peak E_2' induces the reduction peak A_1 (Fig. 3).

If the electrolysis is carried at +0.7 V r.d.e. voltammogram reduction waves A_1 and A_3 are observed (Fig. 2d). The same r.d.e. voltammogram is obtained when the electrolysis of **1** is carried out directly at the potential of wave E_2' with consumption of 2 F. No signal is observed by ESR spectroscopy. If the electrolysis is carried out

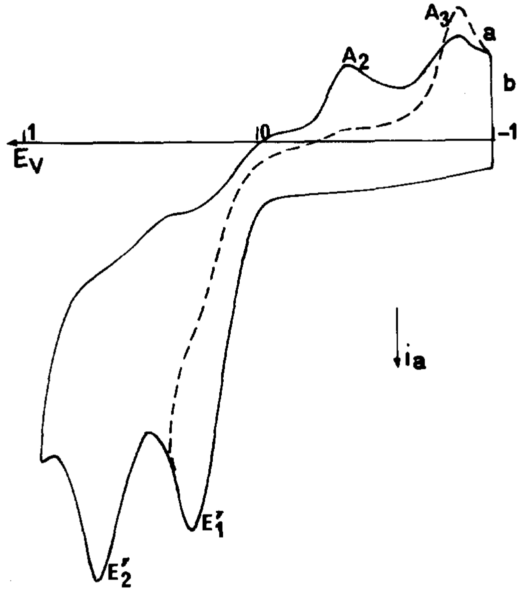


Fig. 1. Cyclic voltammograms of **1** in THF on a vitreous carbon electrode. Starting potential −1 V. Sweep rate 0.2 V s^{-1}.

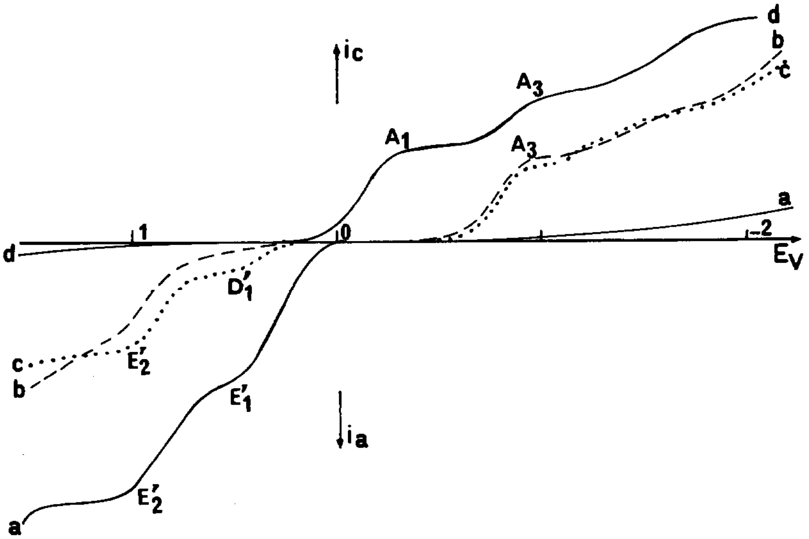


Fig. 2. Rotating disk electrode voltammograms of **1** in THF at room temperature: (a) before electrolysis; (b) after one-electron oxidation at +0.4 V at −30 °C; (c) after several minutes; (d) after electrolysis at +0.7 V.

at the potential of wave A_1, 1 F is consumed and the r.d.e. voltammogram exhibits the reduction wave A_3 and the oxidation wave D_1'.

The ESR spectrum centered at $g = 1.968$ is shown in Fig. 4, together with the computer-simulated spectrum. It consists of ten lines due to a coupling with niobium nucleus ($a_{Nb} = 113.8$ G). The hyperfine structure indicates a further coupling with a single proton ($a_H = 26$ G).

The oxidation wave D_1' ($E_{1/2} = +0.43$ V) and the reduction wave A_3 are obtained after electrolysis of **1** at room temperature at 0.1 V with consumption of 1 F (Fig. 5b). The ESR spectrum is complex; ill-defined lines are superimposed in the

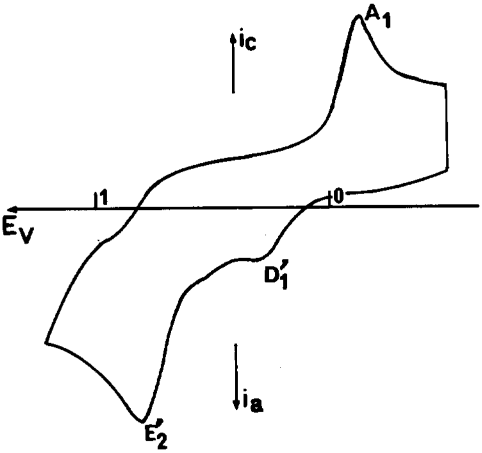


Fig. 3. Cyclic voltammogram of **1** after one-electron oxidation at +0.4 V. Starting potential −0.5 V. Sweep rate 0.2 V s^{-1}.

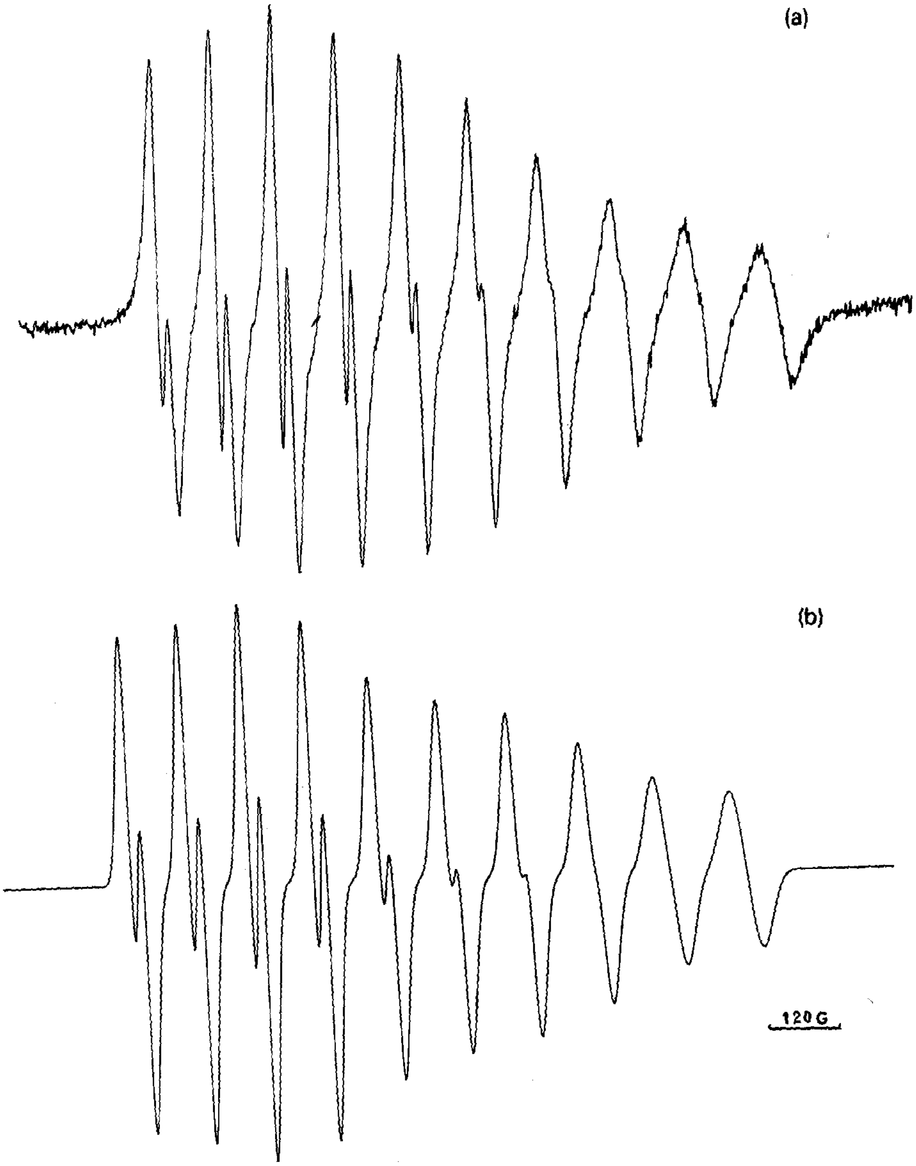


Fig. 4. (a) ESR spectrum of $(\text{NbCp}'_2\text{H}_2)_2$; (b) computer simulation.

spectrum of Fig. 4. In cyclic voltammetry after inversion of the potential scan after peak D'_1 peak A_1 appears. If the electrolysis is carried out at the potential of wave D'_1, 1 F is consumed and the r.d.e. voltammogram exhibits wave A_1 (Fig. 5c). Waves D'_1 and A_3 are obtained when **1** is added to the electrolyzed solution at 0.7 V.

We also studied the electrochemical oxidation of $\text{Nb}({}^t\text{BuC}_5\text{H}_4)_2\text{H}_3$ **1'**. The behavior is similar to that of complex **1**. After one electron oxidation of **1'** the ESR spectrum, centred at $g = 1.972$, of the electrolyzed solution is shown in Fig. 6, together with the computer-simulated spectrum. It results from coupling to a niobium nucleus ($a_{\text{Nb}} = 110.1$ G) and a single proton ($a_{\text{H}} = 24.2$ G). The same

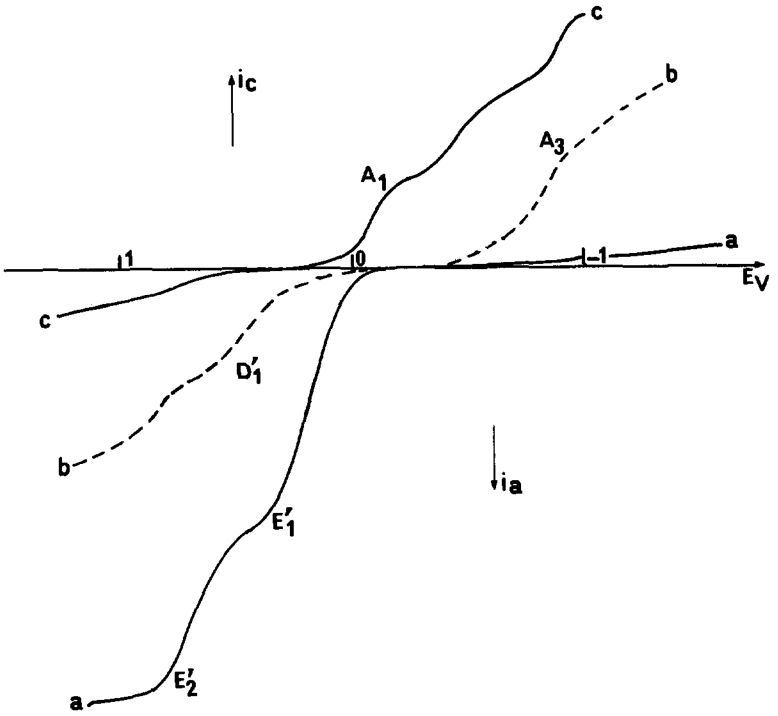


Fig. 5. Rotating disk electrode voltammograms of **1** in THF (a) before electrolysis; (b) after one-electron oxidation at +0.1 V; (c) after oxidation at +0.5 V and consumption of 2 F.

overall spectrum is obtained after two-electron oxidation of **1'** at 0.8 V (wave E_2') followed by one-electron reduction at 0.2 V (plateau of wave A_1).

Discussion

The results can be rationalized in terms of Scheme 1. The question of whether transition metal hydrides should be formulated as molecular hydrogen complexes $M(H_2)$ or "classical" hydrides (H–M–H) has attracted much interest [5]. Recently we reported the characterization of bis-silylated niobium trihydrides as "non-classical" hydrides on the basis of their anomalous ^1H NMR spectra [6]. Such anomalous NMR behavior has been also observed for other trihydrides [7]. Several authors have suggested that this anomalous behavior is not of magnetic origin but may be explained in terms of quantum mechanical exchange [8] rather than the equilibrium dihydrogen/hydride $\rightleftharpoons$ trihydride [6]. The electrochemical behavior of **1** is consistent with the formulation of a niobium(III) complex. Recently, Bianchini et al. [9] showed that electrochemistry provided a diagnostic tool for distinguishing between classical and non-classical hydride complexes.

The one-electron oxidation of **1** yields the cationic complex $[NbCp'_2H_3]^+$, which is very unstable even on the time scale of the cyclic voltammetry. A very fast loss of a proton occurs, to give $NbCp'_2H_2$, **2**, which is oxidized at the potential of wave E_2'. This neutral paramagnetic niobium(IV) complex can be obtained by electrolysis of **1** at −30 °C, but the ESR spectrum of the electrolyzed solution is rather complex and

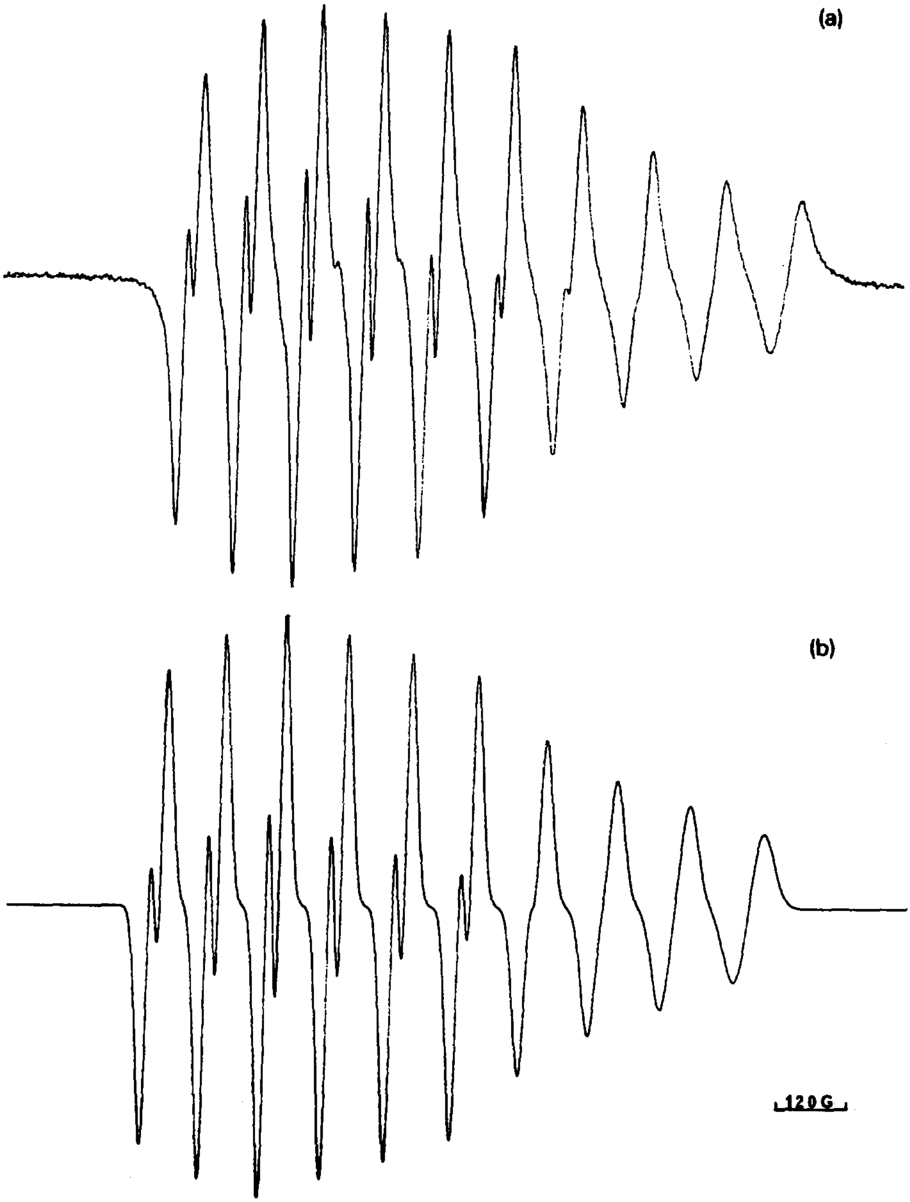
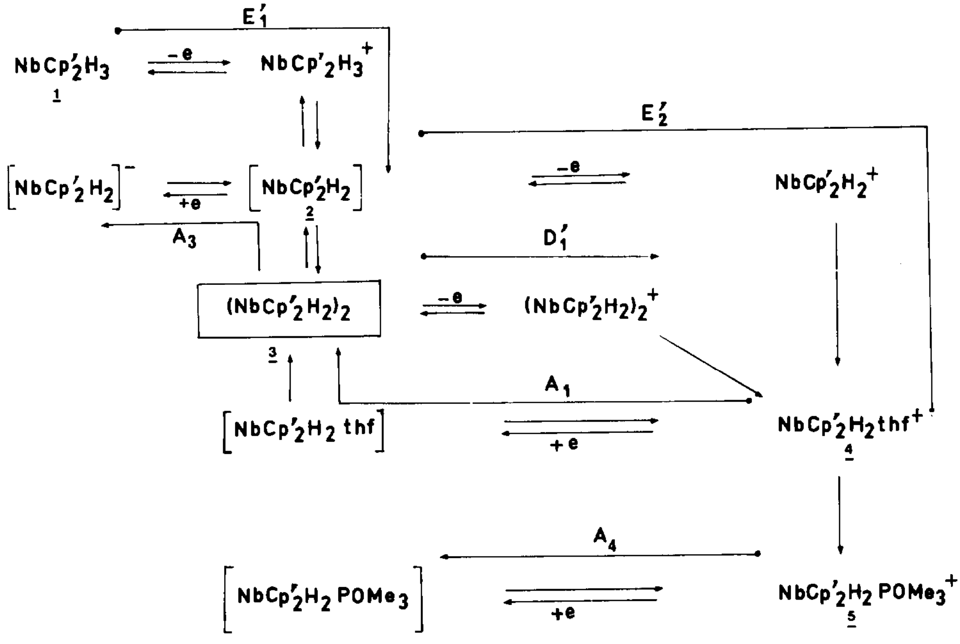


Fig. 6. (a) ESR spectrum of $[Nb(^tBuC_5H_4)_2H_2]_2$; (b) computer simulation.

arises from a mixture of compounds. However, the presence of triplets seems to indicate hyperfine splitting associated with two hydrogen atoms, probably in complex **2**. In the case of the unsubstituted derivative Kochi and al. [3] demonstrated that the complex $Nb(C_5H_5)_2H_2$ was stable in cyclopropane–benzene solution at −70 °C. This complex has now been fully characterized by ESR spectroscopy.

At room temperature **2** is rapidly transformed into the (suggested) dimeric complex $(NbCp'_2H_2)_2$, **3**, which is oxidized at the potential of peak D'_1. Complex **3**



Scheme 1

Table 1

Hyperfine coupling constants

Complex	$\langle a\rangle$Nb	$\langle a\rangle$Ht	$\langle a\rangle$Hb	g
$[Nb(Me_3SiC_5H_4)_2H]_2(\mu\text{-}H)_2$	113.8	26.04	≈ 6	1.968
$[Nb({}^tBuC_5H_4)_2H]_2(\mu\text{-}H)_2$	110.1	24.2	≈ 8	2.972

can also be obtained directly by one-electron oxidation of **1** at room temperature (see Fig. 5). The ESR spectrum of **3** consists of a decet of doublets, resulting from coupling with a niobium(IV) atom and a single hydrogen nucleus. On the basis of the data we suggest for **3** a dimeric structure with two bridging hydrogen atoms $[Nb(\eta^5\text{-}Me_3SiC_5H_4)_2H]_2(\mu\text{-}H)_2$. The bridging hydride coupling was not resolved, but introduction of a hydrogen bridge with a constant of about 6 G does not produce any significant change in the shape of the simulated ESR spectrum. The hyperfine coupling constants, isotropic g values, and line widths for our paramagnetic hydrides are given in Table 1. Such four-centered species have been suggested as intermediates in intramolecular exchange of hydride tungsten complexes [10].

Two other arguments may be advanced for the formation of **3**: (i) Addition of trimethylphosphite to **3** causes no change in the electrochemical and ESR properties; (ii) One-electron reduction of the diamagnetic niobium(V) complex **4** also gives **3** (*vide infra*). Unfortunately, it was not possible to isolate **3** from the solution [11*].

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* Reference number with asterisk indicates a note in the list of references.

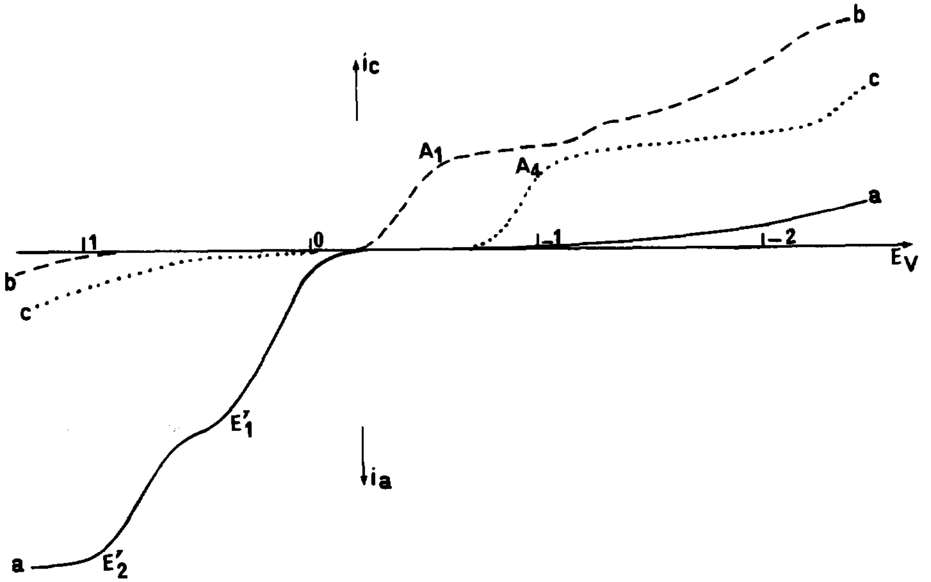

Fig. 7. Rotating disk electrode voltammograms of **1** in THF (a) before electrolysis; (b) after two-electron oxidation at 0.8 V; (c) after addition of POMe$_3$.

This dimeric complex **3** is reduced at peak A$_3$ by a C.E. mechanism:

$$\tfrac{1}{2}(\mathrm{NbCp'_2H_2})_2 \rightleftharpoons \mathrm{NbCp'_2H_2} \xrightarrow{+e^-} [\mathrm{Cp'_2NbH_2}]^-$$

Two-electron oxidation of **1** would give the coordinatively unsaturated cationic niobium(V) species [NbCp$'_2$H$_2$]$^+$ which would give the more stable complex [NbCp$'_2$H$_2$(THF)]$^+$ by coordination of a THF molecule to the metal center. It was not possible to isolate this cationic species free from the supporting salt. This type of cationic species has been mentioned previously [12].

The formulation of the cationic complex **4** is in keeping with the following experimental facts: the complex gives no ESR signal. (ii) One-electron reduction at the potential of peak A$_1$ gives the niobium(IV) complex **3**. (iii) Addition of trimethylphosphite to **4** causes reduction wave A$_1$ to disappear in favor of a more cathodic wave A$_4$ (Fig. 7).

These modifications are due to exchange between THF and trimethylphosphite ligands, which increases the electronic density on the niobium atom.

$$[\mathrm{NbCp'_2H_2(THF)}]^+ + \mathrm{POMe_3} \rightarrow [\mathrm{NbCp'_2H_2(POMe_3)}]^+ + \mathrm{THF}$$

Also we have prepared [13] complex **5** accordingly:

$$[\mathrm{NbCp'_2H(POMe_3)}] + \mathrm{HBF_4} \rightarrow [\mathrm{NbCp'_2H_2POMe_3}]^+\,\mathrm{BF_4^-}$$

In THF this cationic niobium complex exhibits an ill-defined wave A$_4$. Under our experimental conditions, in the absence of an excess of POMe$_3$ this complex is relatively unstable, and wave A$_4$ disappears within few minutes.

The cationic complex **4** reacts with **1** to give the species **3**:

$$\underset{(\mathbf{1})}{\mathrm{NbCp'_2H_3}} + \underset{(\mathbf{4})}{\mathrm{NbCp'_2NbH_2THF^+}} \xrightarrow[-\mathrm{THF}]{-\mathrm{H}^+} \underset{(\mathbf{3})}{(\mathrm{NbCp'_2H_2})_2}$$

Peak A_2, which appears only on the time scale of cyclic voltammetry of the starting material **1**, probably corresponds to the reduction of a dimeric complex obtained by condensation of $[NbCp'_2H_2]^+$ with **1**.

Conclusion

The main feature of the electrochemical behavior of **1** revealed by this study is that it involves formation of an unusual dimeric niobium(IV) complex that may play an important role in the activation of hydrogen–carbon bonds.

Experimental

All manipulations were performed under argon. Tetrahydrofuran was distilled from sodium benzophenone ketyl under argon. The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 *M*) in all cases; the salt (Fluka) was dried and deoxygenated before use. All the experiments were carried out under argon by Schlenk techniques. A Tacussel UAP4 unit connected to a Tektronix oscilloscope (linear potential sweep experimental), an Amel 552 potentiostat, and a Tacussel IG5 integrator were used.

$NbCp'_2H_3$ was prepared by published methods [6]. In cyclic voltammetry experiments the concentration of $NbCp'_2H_3$ was 3×10^{-3} *M*. ^1H NMR data for **5** are given in ref. 13*.

Acknowledgement

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