Preliminary communication

Electrochemical studies on organometallic compounds

XXXVII *. Unusual paramagnetic bis(silylated cyclopentadienyl)niobium(IV) cationic complexes

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Abstract

Electrochemical oxidation of Cp'_2NbHL ($Cp' = C_5H_4SiMe_3$, $L = P(OMe)_3$) yields Cp'_2NbHL^+ and $Cp'_2NbL_2^{2+}$, which have been characterized by ESR spectroscopy. These species represent the first niobium(IV) monocationic hydride and dicationic niobiocene complexes.

Transition metal hydrides are important intermediates and catalysts in a variety of reactions [1]. In particular the properties of the niobiocene trihydride $(C_5H_5)_2NbH_3$ have been of much interest for some years, and Tebbe and Parshall demonstrated its activation of carbon–hydrogen bonds in 1971 [2].

Recently, some of us reported the preparation of bissilylated cyclopentadienyl niobium trihydrides, which were characterized as "non-classical" hydrides on the basis of their anomalous ^1H NMR spectra [3]. In continuation of our studies of the reactivity of our niobium hydride complexes, we describe below the characterization by ESR spectroscopy of the bis(silylated cyclopentadienyl)niobium(IV) complexes Cp'_2NbHL^+ and $Cp'_2NbL_2^{2+}$ ($Cp' = C_5H_4SiMe_3$, $L = P(OMe)_3$), produced in solution by electrochemical oxidation of Cp'_2NbHL (**1**). To the best of our knowledge these species are the first niobium(IV) monocationic hydride and dicationic

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* For part XXXVI see ref. 9.
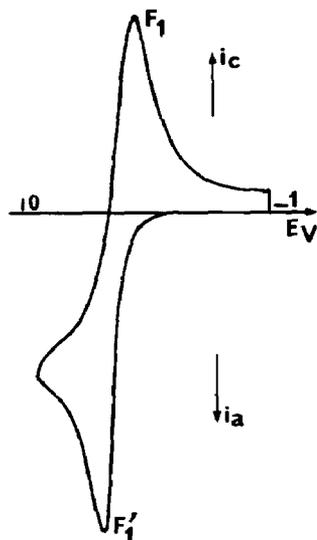
Fig. 1. Cyclic voltammogram of Cp'_2NbHL. Starting potential -1 V. Sweep rate 0.2 V/s.

niobiocene complexes. Only a few niobium(IV) cationic niobiocene compounds have been reported previously [4].

Complex **1** was prepared by a published method [5].

In tetrahydrofuran (THF) with 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, the voltammogram of **1** on a rotating glassy carbon disc electrode (r.d.e.) exhibits an anodic wave F'_1 at -0.35 V versus an aqueous saturated calomel electrode. Cyclic voltammetry of **1** reveals the peaks F'_1/F_1 (Fig. 1) which show all the characteristics of a reversible system [6].

No drastic modification of the cyclic voltammogram is observed within the temperature range $-40\,^\circ$C to $25\,^\circ$C at sweep rates varying from 0.01 to 100 V/s. No changes occur when triphenylphosphite is added to the solution. This is a strong indication that the system is reversible [7]. At room temperature controlled potential electrolysis (plateau of wave F'_1) on a carbon gauze electrode consumes approximately one faraday; the r.d.e. voltammogram shows the reduction wave F_1.

The ESR spectrum (centered at $g = 2.006$) of the electrolyzed solution is shown in Fig. 2 together with the computer-simulated spectrum. It reveals coupling of the electron to a niobium nucleus ($a_{Nb} = 32.4$ G), a phosphorus nucleus ($a_P = 38$ G) and a proton ($a_H = 10.3$ G). The electrochemical and spectroscopic data are in keeping with the formation of the cationic species Cp'_2NbHL^+. This complex is relatively stable at room temperature even in the presence of an excess of ligand. However, after heating ($60\,^\circ$C) of the electrolyzed solution, the reduction wave F_1 disappears from the r.d.e. voltammogram and a new oxidation wave F'_2 appears at $+0.49$ V (Fig. 3b). No signal can be detected by ESR spectroscopy.

Cyclic voltammetry gives a reversible system of peaks F'_2/F_2. After controlled potential electrolysis at $+0.75$ V, which consumes 1 F, the reduction wave F_2 is seen in the r.d.e. voltammogram of the electrolyzed solution (Fig. 3c). The ESR spectrum (centered at $g = 2.004$) of this solution is shown in Fig. 4. The hyperfine structure is due to a coupling of the electron with a niobium nucleus ($a_{Nb} = 78$ G) and two phosphorus nuclei ($a_P = 38.6$ G). Analysis of this ESR spectrum shows that

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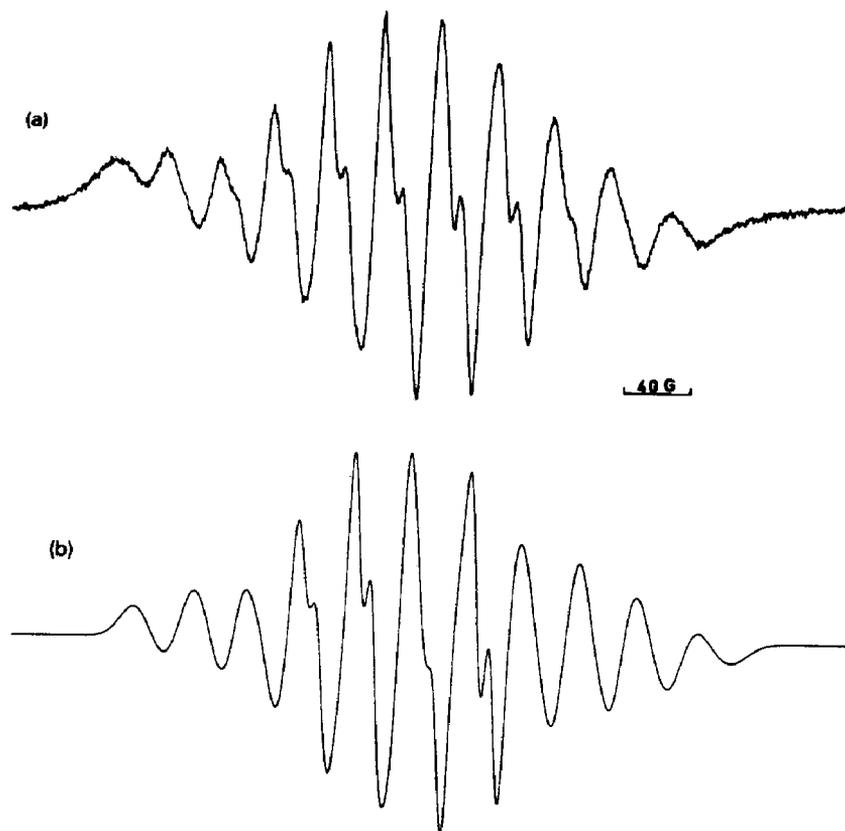Fig. 2. (a) ESR spectrum after one-electron oxidation of Cp'_2NbHL; (b) computer simulation.

the unpaired electron is localized mainly on the niobium nucleus and the electron density on the niobium is higher than in the cationic complex Cp'_2NbHL^+.

The electrochemical and spectroscopic data are consistent with the formation of the dicationic species $Cp'_2NbL_2^{2+}$. To our knowledge, it is the first dicationic complex of Nb(IV).
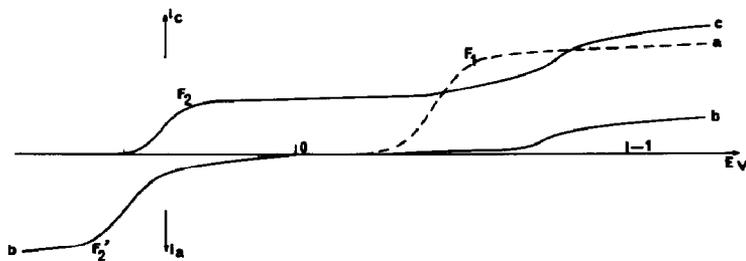

Fig. 3. (a) Rotating disc electrode voltammograms of Cp'_2NbHL^+ in THF; (b) after heating (60°C) in the presence of $P(OMe)_3$; (c) after one-electron oxidation on a carbon gauze electrode at 0.75 V.
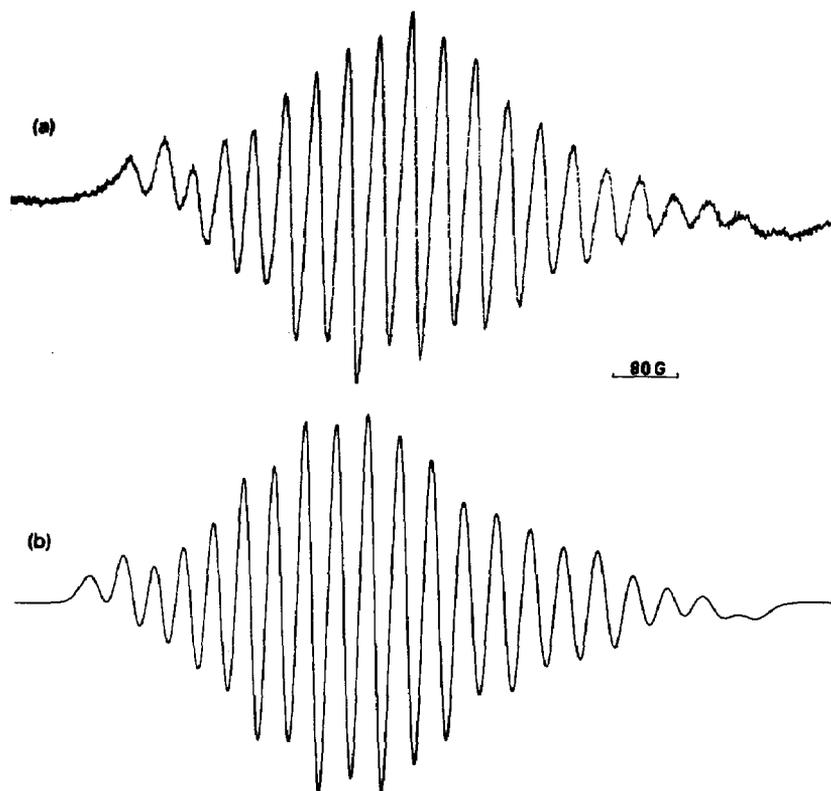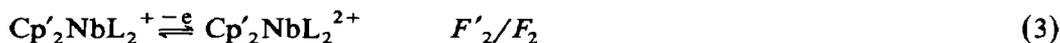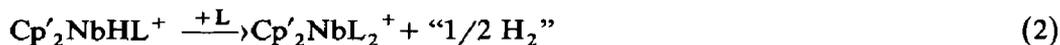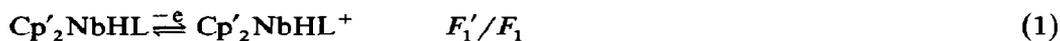
Fig. 4. (a) ESR spectrum of $Cp'_2NbL_2^{2+}$; (b) computer simulation.

The results can be rationalized in terms of the following mechanism:

$$Cp'_2NbHL \underset{}{\overset{-e}{\rightleftharpoons}} Cp'_2NbHL^+ \qquad F'_1/F_1 \tag{1}$$

$$Cp'_2NbHL^+ \xrightarrow{+L} Cp'_2NbL_2^+ + \text{``}1/2\ H_2\text{''} \tag{2}$$

$$Cp'_2NbL_2^+ \underset{}{\overset{-e}{\rightleftharpoons}} Cp'_2NbL_2^{2+} \qquad F'_2/F_2 \tag{3}$$

Reaction (2), which corresponds to reductive elimination with loss of dihydrogen, is an interesting step. In the case of niobiocene trihydride the abstraction of hydrogen with t-butoxy radical yields the paramagnetic $(C_5H_5)_2NbH_2$, which may play important catalytic roles [8].

We are currently investigating the chemical synthesis of these cationic species and their activity in catalytic reactions.

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