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ELECTROCHEMICAL STUDIES ON ORGANOMETALLIC COMPOUNDS

IX *. ELECTROGENERATION OF AN UNUSUAL SPECIES OF NIOBIUM(III)

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Summary

The one-electron reduction in THF/(Bu_4N^+ PF_6^-) of the complex Cp_2NbCl_2 ($Cp = \eta^5$-C_5H_5) at a low temperature (−30 °C) yields the anionic dimer $(Cp_2NbClCl_2NbCp_2)^-$ which remains stable for several hours.

Introduction

The chemical reduction of Cp_2NbCl_2 ($Cp = \eta^5$-C_5H_5) in the presence of various ligands L yields Cp_2NbClL [1]. These compounds can also be prepared electrochemically [2]. Without ligand, depending upon the experimental conditions, the chemical reduction gives $Cp_2NbClCl_2NbCp_2$ [3], Cp_2Nb [4] and Cp_2NbCl [5]. Only the first complex has been obtained as a crystallized product.

We present here the possibility of the electrogeneration at low temperature (−30 °C) of a new niobium(III) complex.

Experimental

Cp_2NbCl_2 [6] and $Cp_2NbClCl_2NbCp_2$ [3] were prepared by literature procedures. The electrochemical experiments were carried out under argon at −30 °C. Tetrahydrofuran was purified by distillation from sodium diphenylketyl under argon. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 *M*); the salt (Fluka) was recrystallized twice from ethanol, dried and deoxygenated before use.

The apparatus and technique have been described previously [7]. The reference electrode was a SCE separated from the solution by a sintered glass disk.

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* For part VIII see ref. 8.

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Results

On a platinum rotating disk electrode (RDE) at −30 °C, Cp_2NbCl_2 shows only a 1 *e* reduction wave A at −1.22 V *. In cyclic voltammetry, the corresponding peak A is obtained; during the reverse scan, a peak A′ is observed at −1.20 V (Fig. 1). At −30 °C, no modification of the cyclic voltammogram is observed at sweep rates varying from 0.01 to 100 V s^{-1}.

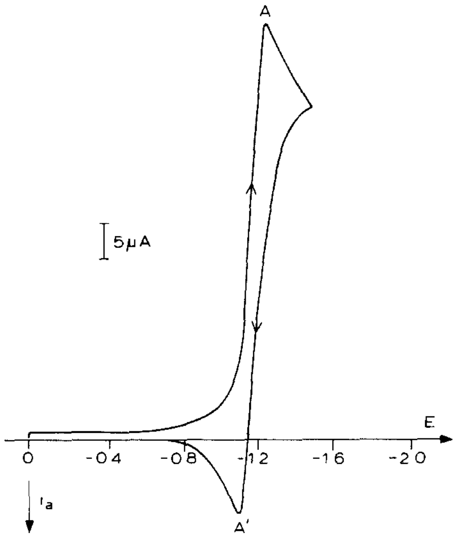

Fig. 1. Cyclic voltammogram of Cp_2NbCl_2 in tetrahydrofuran at −30 °C. Sweep rate 0.050 V s^{-1}. Starting potential 0 V.

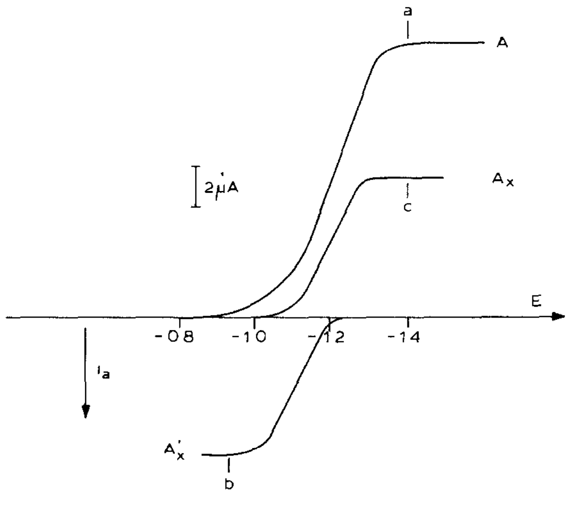

Fig. 2. Voltammogram on the RDE platinum electrode of Cp_2NbCl_2 in tetrahydrofuran at −30 °C (a) Before electrolysis; (b) after electroreduction at −1.5 V; (c) after reoxidation at −0.9 V.

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* One oxidation wave *E′* at +0.35 V is also observed.

After complete electrolysis (at −30 °C) of Cp_2NbCl_2 at −1.5 V (plateau of wave A) on a platinum electrode, 1 *F* has been consumed and an air sensitive brown solution is obtained. The voltammogram on the RDE platinum electrode of this solution consists of one oxidation wave A'_x at −1.12 V. The height of A'_x is half that of A. The electrochemical oxidation at −0.9 V (plateau of wave A'_x) consumes 0.5 *F* and a purple solution is obtained. (The initial solution of Cp_2NbCl_2 is pale green). The RDE voltammogram shows a reduction wave A_x at −1.20 V whose height is equal to that of A'_x (Fig. 2).

Discussion

The 1 *e* reduction of Cp_2NbCl_2 leads first to $Cp_2NbCl_2^-$ which is relatively stable (as shown by the reversibility of the voltammogram of Cp_2NbCl_2). This anion can react by one of the mechanisms (a) to (c):

(a) EC

$$\begin{tikzcd}
Cp_2NbCl_2 \arrow[r, "+1e"] & Cp_2NbCl_2^- \arrow[d, "-Cl^-"] \\
& \text{“}Cp_2NbCl\text{”}
\end{tikzcd}$$

Niobiocene monochloride is probably coordinated with a molecule of the solvent (THF). The fact that the half-wave potential of wave A'_x is nearly the same as that of wave A can be explained by a pseudo reversible behaviour due to a return of Cl^- to the molecule [7].

Since the oxidation consumes 0.5 *F*, the formation of a dimer is very likely and the following mechanism can be proposed.

(a_1)

$$\begin{tikzcd}
Cp_2NbCl \arrow[r, "-1e"] & Cp_2NbCl^+ \arrow[d, "Cl^-"] \\
& Cp_2NbCl_2 \arrow[d, "Cp_2NbCl"] \\
& Cp_2NbClCl_2NbCp_2
\end{tikzcd}$$

This process yields finally the dimer which can be prepared by chemical reduction of Cp_2NbCl_2 [3]. The mechanisms of reduction and of oxidation proposed above are compatible with the relative stability of the anion $Cp_2NbCl_2^-$. However they are not the most probable (vide infra).

(b) ECC

$$\begin{tikzcd}
Cp_2NbCl_2 \arrow[r, "1e^-"] & Cp_2NbCl_2^- \arrow[d, "-Cl^-"] \\
& Cp_2NbCl \arrow[d, "Cp_2NbCl_2^-"] \\
& (Cp_2NbClCl_2NbCp_2)^-
\end{tikzcd}$$

This implies that the loss of Cl^- is slower than the condensation of Cp_2NbCl on $Cp_2NbCl_2^-$.

(c) EC–CE

$$\begin{tikzcd}
Cp_2NbCl_2 \arrow[r, "1e"] & Cp_2NbCl_2^- \arrow[d, "-Cl^-"] & \\
& Cp_2NbCl \arrow[d, "Cp_2NbCl_2"] & \\
& Cp_2NbClCl_2NbCp_2 \arrow[r, "1e^-"] & (Cp_2NbClCl_2NbCp_2)
\end{tikzcd}$$

This mechanism could operate only if the chemical reactions were very fast and if the neutral dimer was reduced at the potential of Cp_2NbCl_2. Since the anion $Cp_2NbCl_2^-$ is relatively stable (voltammogram of Cp_2NbCl_2 at −30 °C), we can reject this mechanism.

Mechanism (b) is the most probable and the experimental results for the oxidation can be explained by the reversible reaction:

$$(Cp_2NbClCl_2NbCp_2)^- \overset{-1e}{\rightleftharpoons} (Cp_2NbClCl_2NbCp_2)$$

We have not been able to isolate the anionic dimer because this species is stable only at low temperature (−30 °C). At −20 °C, this dimer decomposes rapidly; however the nature of the complex is in good agreement with the following results.

By air oxidation of this dimer anion, we have obtained $Cp_2Nb(O)Cl$ [5]; this type of behaviour has already been observed for diverse complexes of niobium(III).

When we add trimethyl phosphite (TMP) to a solution of the product, wave A'_x disappears and is replaced by a new oxidation wave A'_1 at −0.4 V due to the complex $Cp_2NbCl(TMP)$ [2]. The height of the wave A'_1 is twice that of wave A'_x.

We have studied the electrochemical behaviour of the neutral dimer $(Cp_2NbClCl_2NbCp_2)$ prepared chemically [3]. This compound is reducible at A_x (at −30 °C). In cyclic voltammetry, when the potential scan is reversed after peak A_x, an anodic peak A'_x is obtained. Peaks A_x/A'_x present all the characteristics of a reversible system. Exhaustive electrolysis of $(Cp_2NbClCl_2NbCp_2)$ at −1.4 V consumes 1 *F* (0.5 *F* per atom of Nb). The solution which was originally purple becomes brown. The RDE voltammogram of this solution shows wave A'_x. The addition of TMP or air gives the same results as those described above.

We suggest that the most reasonable structure for the anionic dimer $(Cp_2NbClCl_2NbCp_2)^-$ contains a single bridge, as this places 18 electrons on the niobium(III) atoms, although other structures cannot be excluded.

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