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ELECTROCHEMICAL STUDIES ON ORGANOMETALLIC COMPOUNDS

II. THE OXIDATION OF TITANOCENE MONOCHLORIDE

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Summary

The electrochemical oxidation of titanocene monochloride, Cp_2TiClL (L = tetrahydrofuran or dimethylphenylphosphine), has been studied by voltammetry on a disc electrode, by linear potential sweep voltammetry and by controlled potential electrolysis. A first one electron step yields Cp_2TiClL^+, which then reacts with Cp_2TiClL to give Cp_2TiCl_2 and $Cp_2TiL_2^+$. The latter is oxidized to $Cp_2TiL_2^{2+}$.

Introduction

It was shown in a previous paper [1] that Cl^- is eliminated very rapidly after the uptake of one electron by the molecule of titanocene dichloride, Cp_2TiCl_2, so that titanocene monochloride Cp_2TiClL is obtained; L is a ligand which can be a solvent molecule. The reoxidation of Cp_2TiClL was also studied; this was complicated, however, by the fact that return of Cl^- to the molecule can take place. In order to avoid this we have studied the anodic behaviour of chemically prepared Cp_2TiClL, with L = tetrahydrofuran (THF) or dimethylphenylphosphine (DMPP) in a solution which does not contain chloride ions.

Experimental

The experimental conditions and the preparation of the products have been described in ref. 1.

Results

1. Cp_2TiCl in THF

Cp_2TiCl was dissolved in THF. In this case L is probably a molecule of THF,

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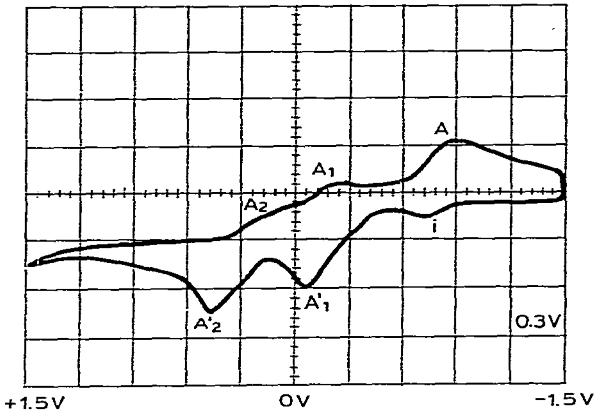

Fig. 1. Voltammogram of Cp_2TiClL (L = THF) in THF. Starting potential —1.5 V. Sweep rate: 0.500 V s^{-1}.

although an autoligation (L = Cp_2TiCl) cannot be completely excluded. On a rotating platinum electrode, two cathodic and two anodic waves are observed. The two cathodic waves B and C, whose $E_{1/2}$ are respectively —2.12 and —2.42 V, correspond to the second and third reduction waves of Cp_2TiCl_2 [1]. (Throughout this paper, we use the same notations as in ref. 1 for the waves and for the voltammetric peaks, in order to facilitate comparisons). Waves B and C will be studied later. The $E_{1/2}$ of the two oxidation waves A'_1 and A'_2 are —0.25 and +0.25 V, respectively. As deduced from a comparison with the one-electron wave B, the oxidation of each of waves A'_1 and A'_2 involves 0.5 *e*.

In cyclic voltammetry, two anodic peaks A'_1 and A'_2 corresponding to the waves are observed (Fig. 1). On reversing the scan, three cathodic peaks are obtained. Peaks A_2 and A_1 form reversible systems with A'_2 and A'_1, respectively, their heights are however much smaller than those of the cathodic peaks. Peak A is situated at the same potential as the peak of Cp_2TiCl_2 [1]; it appears

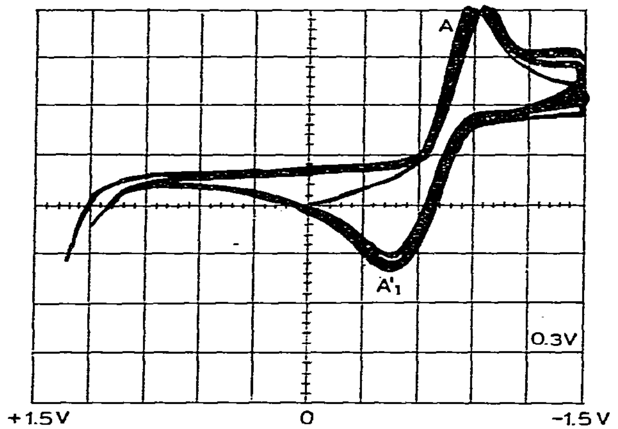

Fig. 2. Voltammogram of Cp_2TiClL (L = THF) in THF containing LiCl. Starting potential —1.5 V. Sweep rate: 0.2 V s^{-1}.

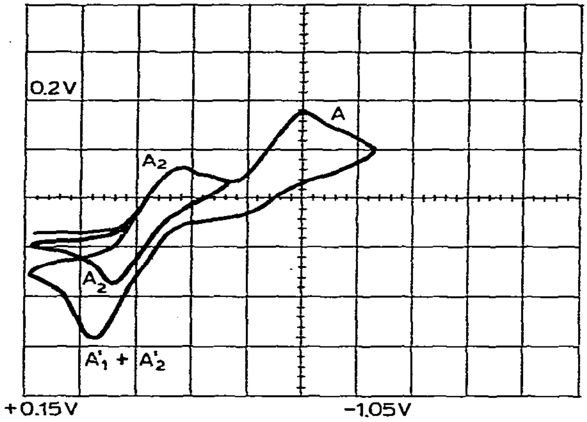

Fig. 3. Voltammogram of $Cp_2Ti(DMPPL)$ in THF. Starting potential +0.15. Sweep rate: 0.2 V s^{-1}.

only if peak A'_1 is scanned. Peak I is due to an impurity. After addition of Cl^- ions to the solution, peaks A'_2, A_2 and A_1 disappear, and peak A'_1 is shifted towards negative potentials (Fig. 2). During an exhaustive controlled potential oxidation of Cp_2TiClL on the plateau of wave A'_1 (E = —0.1 V), 0.5 F are consumed, and a red solution, giving an ESR signal, is obtained. Air oxidation of the solution causes the signal to disappear. Cp_2TiCl_2 can be isolated from the solution in about 50% yield.

2. *Cp_2TiCl dimethylphenylphosphine*

In THF, on a rotating disc electrode, only one reduction wave B ($E_{1/2}$ = —2.12 V) and one oxidation wave A'_1 ($E_{1/2}$ = —0.23 V) are obtained. Wave B, corresponding to a one electron (1*e*) process, has already been observed during the reduction of Cp_2TiCl_2 in the presence of DMPP [1]. Wave A'_1 also corresponds to a 1*e* process.

When the potential is scanned cathodically, starting from a potential on the plateau of wave A'_1, a cathodic peak A_2 is observed (Fig. 3).

Upon reversing the scan after this peak, a symmetrical anodic peak A'_2 appears. If the switching potential is negative enough, peak A is observed, and the height of peak A'_2 doubles (peak A'_1 + A'_2). Peak A does not appear if the cathodic scan is started at a potential more negative than that of peak A'_2.

After an exhaustive controlled potential oxidation on the plateau of wave A'_1 (E = —0.1 V), one Faraday has been consumed and a red orange solution is obtained. From this solution, Cp_2TiCl_2 is isolated in a yield of about 50%. After completion of the electrolysis, the voltammogram shows only peaks A, A′ and A'_1; the system A_2/A'_2 has disappeared.

Discussion

The results can be interpreted as follows:

Wave A'_1 corresponds to the oxidation of Cp_2TiClL according to:

$$Cp_2TiClL - e^- \rightleftharpoons Cp_2TiClL^+ \tag{1}$$

followed by the fast reaction:

$$Cp_2TiClL^+ + Cp_2TiClL \rightarrow Cp_2TiCl_2 + Cp_2TiL_2^+ \tag{2}$$

Overall, the process involves only 0.5 e, since reaction 2 causes half of the Cp_2TiCl to disappear chemically to form Cp_2TiCl_2, so that only half of it is oxidized to $Cp_2TiL_2^+$.

Wave A'_2 corresponds to the process:

$$Cp_2TiL_2^+ - e^- \rightleftharpoons Cp_2TiL_2^{2+} \tag{3}$$

The process here also involves only 0.5 e per molecule of Cp_2TiClL, since only half a mole of $Cp_2TiL_2^+$ results from the oxidation of one mole of Cp_2TiClL (eq. 2).

This scheme accounts for the experimental results obtained for Cp_2TiCl(THF), viz. the two 0.5 e oxidation waves, the appearance of the peak of Cp_2TiCl_2 when peak A'_2 is scanned, the formation of Cp_2TiCl_2 after a controlled potential electrolysis, and the observation of an ESR spectrum, showing that a Ti^{III} species ($Cp_2TiL_2^+$) has been formed. In the case of Cp_2TiCl(DMPP), the only difference is that wave A'_2 appears at the same potential as wave A'_1, and that the product of the oxidation of $Cp_2Ti(DMPP)L^+$ is unstable, since after the electrolysis, peaks A'_2/A_2 have disappeared.

Conclusion

An earlier study of the electrochemical behaviour of Cp_2TiCl_2 showed that reactions of ligand exchange between the complex and the solution (or between the complex and a ligand present in the solution) have to be considered when the degree of oxidation of the metal changes. The results in the present paper show that during the electrochemical reaction of organometallic compounds the possibility of ligand exchange between two molecules of the complex must also be taken into account.

Reference

1. Y. Mugnier, C. Moise and E. Laviron, J. Organometal. Chem., 204 (1981) 61.