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ELECTROCHEMICAL STUDIES OF ORGANOMETALLIC COMPOUNDS

I. ON THE REVERSIBILITY OF THE FIRST REDUCTION STAGE OF TITANOCENE DICHLORIDE

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Summary

The 1*e* reduction of titanocene dichloride (η^5-Cp_2TiCl_2) in various solvents has been examined in detail by polarography, voltammetry on a disk electrode, and linear potential sweep voltammetry. In all cases, the electron uptake is followed by a fast loss of Cl^-, which is replaced by a neutral ligand (which can be a solvent molecule). In tetrahydrofuran, whose binding ability is weak, a pseudo reversible behaviour is observed due to a return of Cl^- to the molecule. In dimethylformamide, which is strongly bonded, the reaction is irreversible. In pyridine, it can be reversible or irreversible according to the conditions.

Introduction

Despite a large number of investigations [1—10], the mechanism of the reduction of titanocene dichloride Cp_2TiCl_2 is far from being clear. The fact that the reversibility of the first 1*e* stage in aprotic media depends both on the solvent and on the supporting electrolyte [3—6,9,10] has not been explained. Most workers [3—5,9] have assumed that separation of a chloride ion occurs during the reduction, according to the scheme:

$$Cp_2TiCl_2 + e^- \rightleftharpoons Cp_2TiCl + Cl^-$$

In a recent paper however, El Murr et al. [10] have concluded, mainly on the basis of the reversible behaviour observed in tetrahydrofuran (THF) as solvent, that the uptake of the electron leads to the stable radical anion $[Cp_2TiCl_2]^-$. We represent here the results of a thorough examination of the first reduction stage of Cp_2TiCl_2, which disproves the existence of this radical anion. A study of the second and third reduction stages, and of the different species generated during the electrochemical processes will be described in a future paper in this series.

Experimental

All manipulations were performed under argon. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon. The ESR spectra were recorded on a Varian E4 spectrometer using DPPH ($g = 2.0036$) as reference. Cp_2TiCl [12] and $Cp_2TiClPMe_2C_6H_5$ [13] were prepared by known methods.

The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum disk electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 *M*) in all cases; the salt (Fluka) was dried and deoxygenated before use.

A Tacussel UAP4 unit connected to a Tektronix oscilloscope (linear potential sweep experiments), a three electrode Tacussel Tipol polarograph, an Amel 552 potentiostat and a Tacussel IG_5 integrator were used.

Results and discussion

In THF, on a platinum rotating disk electrode, Cp_2TiCl_2 gives three reduction waves A, B and C, whose half-wave potentials are respectively −0.80, −2.10 and −2.38 V. Three corresponding reduction peaks are found in linear potential sweep voltammetry; studies of waves B and C will be described in another paper in this series. When the potential sweep is reversed after peak A, an anodic peak A′ is obtained; as previously reported [10], A/A′ presents all the characteristics of a reversible system: in particular, the peak separation is not very different from the theoretical value, 56 mV [11] (Fig. 1).

After a complete electrolysis of Cp_2TiCl_2 at −1 V on the plateau of wave A, 1 F has been consumed, and a green-yellow solution is obtained. The polaro-

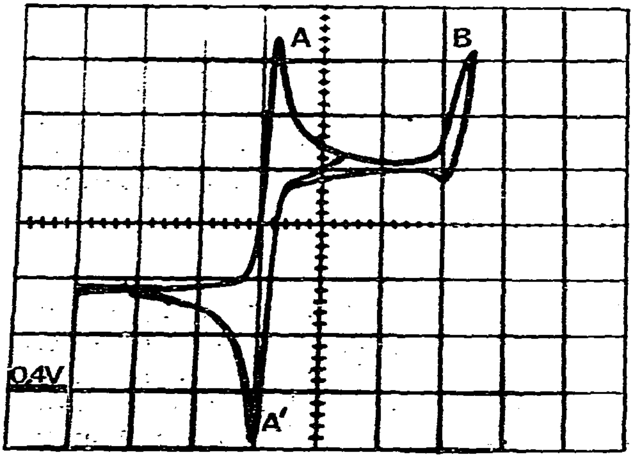

Fig. 1. Voltammogram of η^5-Cp_2TiCl_2 in THF. Starting potential: +0.5. Sweep rate: 0.020 V s^{-1}.

gram consists of an anodic wave A′, whose half-wave potential is equal to that of wave A, and of the two cathodic waves B and C. After a controlled potential reoxidation on the plateau of wave A′, 1 F has been consumed, and wave A is obtained.

A voltammetric study in dimethylformamide (DMF) shows the same three reduction peaks at —0.63, —1.8 and —2.37 V. In contrast with what is observed in THF, however, the first reduction stage A is not reversible: whatever the sweep rate (from 50 mV s^{-1} to 100 V s^{-1}) and the temperature (from —30°C to +25°C), there is no oxidation peak A′ corresponding to A; a peak A'_1, situated at a more positive potential appears instead. At high scan rates at room temperature, or at slower scan rates at low temperature, a peak A_1 can be seen during the second cycle, which indicates the formation of a new reversible redox couple (Fig. 2). After electrolysis on the plateau of wave A, no anodic wave A′ is found. These results confirm earlier findings [5,9] that the reduction is irreversible in DMF when the supporting electrolyte is not a chloride salt. With LiCl as supporting electrolyte, the reaction becomes reversible [4,5].

The behaviour of Cp_2TiCl_2 in pyridine is intermediate between that in DMF and that in THF. At slow sweep rates, the reversible system A/A′ can be observed at room temperature, and peak A'_1 appears only as a small shoulder anodic to peak A′. When the scan rate is increased, peak A′ decreases and peak A'_1 increases, until at high sweep rates A'_1 appears practically alone (Fig. 3).

The same type of voltammogram is obtained if we add DMF, pyridine or dimethylphenylphosphine to the solution of Cp_2TiCl_2 in THF (Fig. 4). At slow sweep rates, two anodic peaks A′ and A'_1 are obtained, whereas at high sweep rates, only peak A'_1 appears. For the same sweep rate and at the same temperature, peak A'_1 is more marked in the order DMF, dimethylphenylphosphine, pyridine.

The above results can be interpreted by considering the cyclic scheme depict-

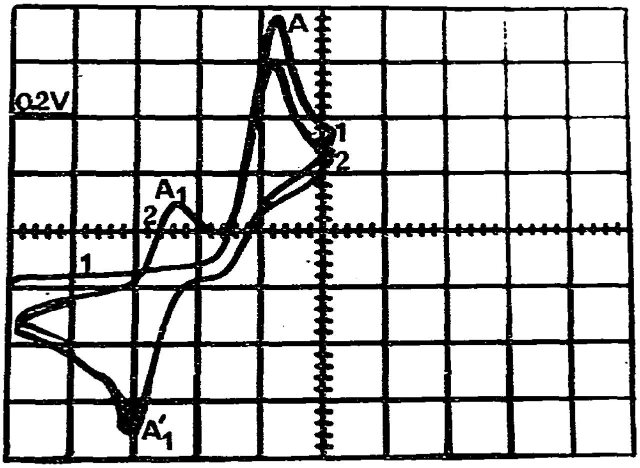

Fig. 2. Voltammograms of η^5-Cp_2TiCl_2 in DMF at —20°C. Starting potential: 0 V. Sweep rate: 2 V s^{-1}. 1, first sweep; 2, second sweep.

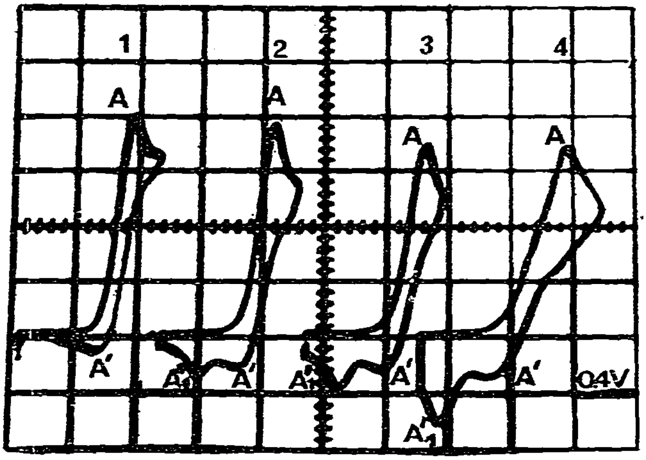

Fig. 3. Voltammograms of η^5-Cp_2TiCl_2 in pyridine. Starting potential: 0 V. Sweep rate (V s^{-1}): 1, 0.010; 2, 0.050; 3, 0.2; 4, 2.

ing the possible electron and ligand exchange reactions (Scheme 1).

SCHEME 1

$$\begin{tikzcd}
\mathrm{Cp_2TiCl_2} \arrow[r, shift left, "e^-"] \arrow[d, shift left, "(a)"] & (\mathrm{Cp_2TiCl_2})^- \arrow[l, shift left] \arrow[d, shift left, "{-\mathrm{Cl}^-,\ +\mathrm{L}}"] \\
\mathrm{Cp_2TiClL}^+ \arrow[u, shift left, "{+\mathrm{Cl}^-,\ -\mathrm{L}}"] \arrow[r, shift left, "e^-"] & \mathrm{Cp_2TiClL} \arrow[l, shift left] \arrow[u, shift left, "(b)"] \\
(c) & (d)
\end{tikzcd}$$

L represents a ligand which may be a solvent molecule.

Although is has been claimed [10], on the basis of the reversible behaviour observed in THF, that the electron uptake produces the species $(Cp_2TiCl_2)^-$ in that solvent, it can be concluded from our results and from the experiments described below that the reaction actually proceeds, whatever the solvent, to the species Cp_2TiClL, the electron uptake being followed by the ligand

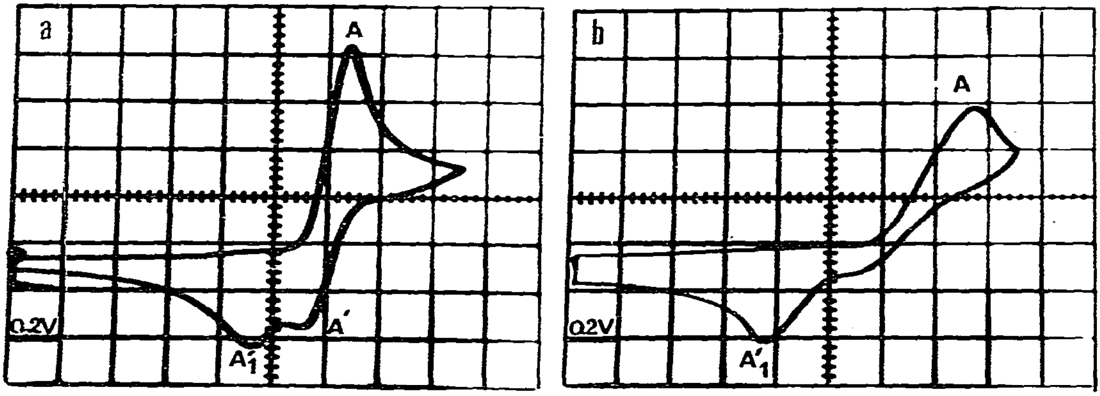

Fig. 4. Voltammograms of η^5-Cp_2TiCl_2 in THF containing 9% DMF in volume. Starting potential +0.5 V Sweep rate (V s^{-1}): 4a, 0.5; 4b, 50.

exchange $-Cl^-/+L$. The nature of L will be discussed below.

(1) The ESR spectrum of the product obtained after electrolysis of Cp_2TiCl_2 in THF on the plateau of the first wave (at —1 V) is identical to that of chemically prepared Cp_2TiCl in the same solvent ($g = 1.9770 \pm 0.0005$ and $g = 1.9775 \pm 0.0005$, respectively). If dimethylphenylphosphine is added to the electrolyzed solution, the ESR spectrum is identical to that of (Cp_2TiCl-dimethylphenylphosphine) prepared chemically ($g = 1.9863 \pm 0.0005$ and $g = 1.9869 \pm 0.0005$, respectively; coupling constant: $A_{^{31}P} = 20$ G). These experiments clearly show that Cl^- separates during the electrolysis; it is replaced either by a molecule of THF (L = THF) or by a molecule of Cp_2TiCl itself (L = Cp_2TiCl) to yield the pseudo-dimer $Cp_2TiClClTiCp_2$ (autoligandation). When dimethylphenylphosphine, which is a stronger ligand, is added to the solution, it replaces THF or Cp_2TiCl.

(2) Peak A′ can be interpreted as being due to the reaction $Cp_2TiClL \rightarrow Cp_2TiCl_2^- \rightarrow Cp_2TiCl_2$ (path d-b-a, Scheme 1). The Cl^- which separated after the electron uptake now returns to the metal; this reaction is slow, so that only peak A′ appears if the sweep rate is small enough. If the sweep rate is large, there is not enough time for reaction d-b to take place, and reaction d-c takes place (peak A'_1, see below). Reaction d-b is the slower the more strongly binding is the ligand L. The influence of the addition of ligands in THF, and study of the sequence in which they displace one other, indicates that DMF (and the phosphine) bind more strongly than pyridine, which in its turn is bound more strongly than THF. This explains why only wave A'_1 is observed in DMF, both A′ and A'_1 in pyridine, and only A′ in THF at room temperature. However, by decreasing the temperature to —30° C (which decreases the rate of reaction d-b, and by using a sweep rate of 50 V s^{-1}, we could observe peak A'_1 in THF (Fig. 5). This confirms our interpretation, and shows that the rate of the loss of Cl^- is very high.

Peak A'_1 corresponds to the reaction $Cp_2TiClL \rightarrow Cp_2TiClL^+$ (d-c, Scheme 1) and peak A_1 to the reverse reaction c-d. If the sweep rate is small enough, peak

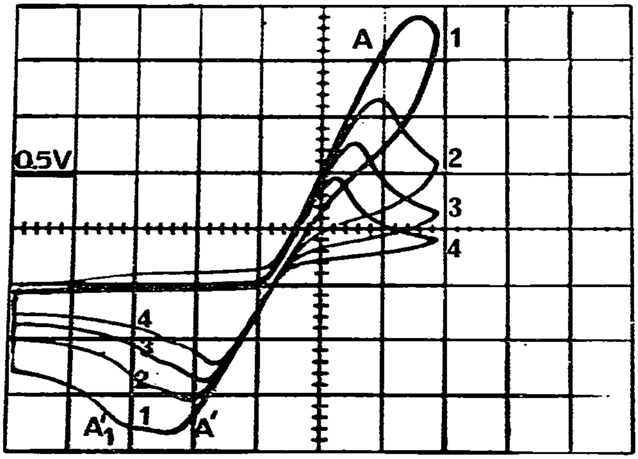

Fig. 5. Voltammograms of η^5-Cp_2TiCl_2 in THF at —30° C. Starting potential: +1.2 V. Sweep rate (V s^{-1}): 1, 50; 2, 20; 3, 10; 4, 5.

A_1 disappears, because of the reaction $Cp_2TiClL^+ \rightarrow Cp_2TiCl_2$ (c-a, Scheme 1) which regenerates Cp_2TiCl_2.

(3) In DMF, the half-wave potential of wave A varies linearly with $-\log Cl^-$ with a slope equal to -0.059 V/log-unit [4,5]. This confirms that the Cl^- is split off. If the reaction stopped at $(Cp_2TiCl_2)^-$, no variation of $E_{1/2}$ would be observed. If on the other hand, the reaction goes all the way to the species Cp_2TiClL, a linear variation, with a slope -0.059 V, should be obtained, which is the case. We tried unsuccessfully to apply the same criterion in THF, but the chloride salts remain practically undissociated in this medium, and a crown ether (Dibenzo-18-crown-6 (EGA)) which we used was not soluble enough.

(4) We have verified that Cp_2TiCl dissolved in THF, DMF or pyridine and that $Cp_2TiClPMe_2C_6H_5$ in THF yield peak A'_1 (and A_1 at high sweep rates).

Conclusion

Our results show that, contrary to the conclusions of a previous study [10], Cl^- is eliminated very rapidly after the uptake of the electron by the molecule of Cp_2TiCl_2, and demonstrate the instability of the species $(Cp_2TiCl_2)^-$. They also emphasize the importance of the ligandation of the diverse species by the solvent molecules, which was not taken into account in previous investigations [1—10].

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