Journal of Organometallic Chemistry, 212 (1981) C39—C42
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

ON THE REVERSIBILITY OF THE FIRST ELECTRON TRANSFER INVOLVING TITANOCENE DICHLORIDE

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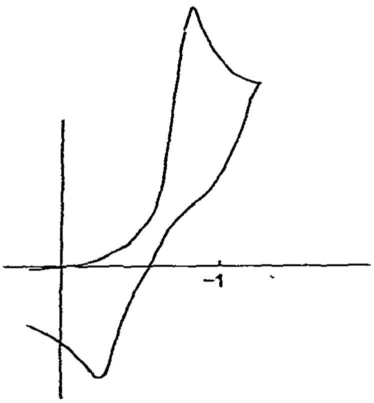
(Received January 22nd, 1981)

Summary

The 1*e* reduction of titanocene dichloride (Cp_2TiCl_2) in DMF has been examined in detail. The reaction is reversible, in contradiction of a recent report.

It has been suggested that dihalides of bis(cyclopentadienyl)titanium, Cp_2TiX_2, undergo a first one-electron transfer reaction, leading to the cleavage of the metal—halogen bond [1—9]. It was claimed that for Cp_2TiCl_2 the electrolytic electron transfer process is irreversible except when chloride ions are present in the solution [5,6]. Recently we reported new observations on the electrochemical behaviour of Cp_2TiX_2 and showed that in THF this first electron transfer is electrochemically and chemically reversible, and leads to the stable anionic species $Cp_2TiX_2^-$ [10]. In a recent paper [1] Mugnier, Moise and Laviron claimed that our findings were wrong, and that in the case of Cp_2TiCl_2 chloride ion is eliminated very rapidly after the uptake of the first electron. These authors judge $Cp_2TiCl_2^-$ to be unstable on the basis of cyclic voltammetry experiments. Although no preparative studies were described, Mugnier et al. proposed the following cyclic scheme to interpret their analytical experiments, which were mainly carried out in DMF:

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



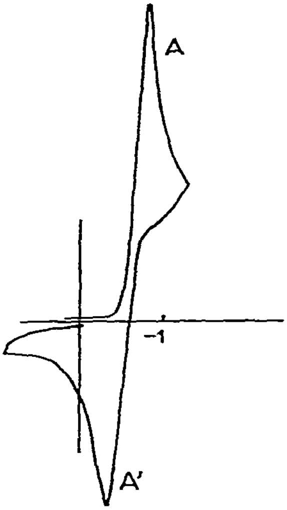


Fig. 1. Voltammogram of 0.002 *M* solution of Cp_2TiCl_2 in DMF. Starting potential 0 V. Sweep rate 0.1 V s^{-1}.

Fig. 2. Voltammogram of a 0.01 *M* solution of Cp_2TiCl_2 in DMF. Starting potential 0 V. Sweep rate 0.1 V s^{-1}.

We now describe below new results for the first electron transfer involving Cp_2TiCl_2 which show the observations by Mugnier et al. [1] to be inaccurate.

We first point out that, contrary to what Mugnier et al. claimed, our conclusions concerning the anions $Cp_2TiX_2^-$ were not reached only on "the basis of the reversible behaviour observed in THF". Polarography, coulometry, electrolyses of Cp_2TiX_2, reoxidation of the species thus formed and their identification, as well as evidence of the absence of free halide ion after reduction of Cp_2TiX_2 do, in our opinion, provide more than adequate proof [10]. Since Mugnier et al. [1] did much of their work in DMF we present briefly below our results for the electrochemical behaviour of Cp_2TiCl_2 in that solvent.

(a) Cyclic voltammetry of DMF solutions containing Bu_4NPF_6 as the supporting electrolyte and containing "low" concentration of Cp_2TiCl_2 (0.002 *M*), show voltammograms identical to those published by Mugnier et al. [1] (Fig. 1).

(b) When higher concentrations of Cp_2TiCl_2 are used (e.g. 0.01 *M*) there is a drastic change in the electrochemical behaviour. We detected a reversible system A/A′ (Fig. 2)* even at a scan rate of 25 mV s^{-1}, while Laviron et al. claimed that this electron transfer is irreversible even at 100 V s^{-1} [1,8]. The cyclic voltammogram represented in Fig. 2 confirms our findings on the formation of $Cp_2TiCl_2^-$.

(c) After the first electron transfer on Cp_2TiCl_2, we did not observe by cyclic voltammetry, any production of chloride ion even in DMF, which gave

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*Cyclic voltammetry of a 0.01 *M* solution of Cp_2TiCl_2 performed in the presence of Cp_2Fe (0.01 *M*) shows an identical peak-spread for the A/A′ system and the well known reversible Cp_2Fe/Cp_2Fe^+ system.

an oxidation peak (at platinum or glassy carbon electrodes) at around +1.3 V vs. S.C.E [11]; such a chloride ion peak appears if the potentials are swept until the second electron-transfer system of Cp_2TiCl_2 is reached.

(d) When a large amount of chloride ion (0.1 *M*) was added to an 0.01 *M* solution of Cp_2TiCl_2 there was no change in the potentials or in the reversibility of the A/A′ system.

(e) In the presence of a very large amount of dissociated bromide ion (0.2 *M* of Bu_4NBr) we again detected no change in the A/A′ system. No new peak, corresponding to $Cp_2TiClBr$, was observed after several sweeps on the same electrode surface. $Cp_2TiClBr$ was prepared in situ, using the method described by Lappert et al. [12], and its cyclic voltammogram in DMF shows, a reversible A/A′ system situated between those of Cp_2TiBr_2 and Cp_2TiCl_2.

(f) Electrolysis of a 0.01 *M* DMF solution of Cp_2TiCl_2 at a mercury pool at 0°C allowed us to detect, after consumption of one Faraday, the anodic wave corresponding to the peak A′ (oxidation wave of $Cp_2TiCl_2^-$) in 40% yield. This shows that, at least at 0°C, $Cp_2TiCl_2^-$ is stable enough on the time scale of electrolysis (40% after 2 h) to be detected by polarography.

All these results show clearly that the cyclic scheme depicted above is in error. It was probably based upon results obtained with concentrations of Cp_2TiCl_2 lower than 0.002 *M*. These concentrations in DMF are, in our opinion, too low to give accurate results, especially when very sensitive complexes are used or produced electrolytically. It is well known that DMF is very difficult to purify and always contains significant amounts of impurities [13]. Under our experimental conditions it is clear that a) Cl^- does not separate rapidly from $Cp_2TiCl_2^-$, b) the step d $\rightleftharpoons$ b in the above scheme does not take place even in the presence of a very large amount of halide ion, at least in the time scale of the cyclic voltammetry, c) when several cycles are run on the same electrode surface, no trace of new system A'_1/A_1 corresponding to the step d $\rightleftharpoons$ c is visible, and d) only the step a $\rightleftharpoons$ b, which we reported earlier [10] is, in fact, accurate in the scheme.

Our new results on the electrochemical behaviour of Cp_2TiCl_2 in DMF show without doubt that $Cp_2TiCl_2^-$ does exist, as we reported previously, and as was predicted [14] and that the proposals made by Mugnier et al. are invalid. Furthermore, $Cp_2TiX_2^-$ species have been made by M.C.R. Symons by γ-irradiation of titanocene dihalides [15].

Acknowledgement

The authors are indebted to Professor M.C.R. Symons for communicating information prior to publication.

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