

Preliminary communication

ELECTROCHEMICAL STUDIES ON ORGANOMETALLIC COMPOUNDS

**XIV *. ELECTROGENERATION OF THE
 BIS(PHENYLETHYNYL)DICYCLOPENTADIENYL TITANIUM(III) ANION**

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Summary

The one-electron reduction of $(C_5H_5)_2Ti^{IV}(C\equiv CC_6H_5)_2$ is reversible and gives the anion which is very stable at $-30^\circ C$. At $25^\circ C$, the anion undergoes a slow transformation with loss of a cyclopentadienyl anion.

The electrochemical one-electron reduction of $Cp_2TiR'_2$ ($Cp = C_5H_5$; $R' = CH_3$, C_6H_5 , o -2,2'- C_6H_4) [1] resulting in the formation of the corresponding anion, is generally followed by a more or less rapid loss of Cp rather than loss of a carbanion [2]; on the voltammetric time scale the anion ($R' = o$ -2,2'- C_6H_4) is stable enough to give an anodic peak, but after a controlled potential electrolysis the anion is no longer observed by cyclic voltammetry. Instead an anodic peak, at about -0.2 V relative to an aqueous saturated calomel electrode (SCE), corresponding to the oxidation of the free Cp anion, is observed.

In this communication we report on the electrochemical behaviour of Cp_2TiR_2 (**1**, $R = C\equiv CC_6H_5$) prepared by a known procedure [3]. A stabler anion was expected owing to the presence of the triple bonds. All the experiments were carried out in the dark, since **1** is light-sensitive in solution.

In tetrahydrofuran between -30 and $25^\circ C$ (0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte) the cyclic voltammogram of **1** at a platinum electrode exhibits a system of reversible peaks AA' at -1.10 V (Fig. 1), followed by an irreversible reduction peak at more negative potentials. Only the first reduction stage is considered here.

* Part XIII see ref. 11.

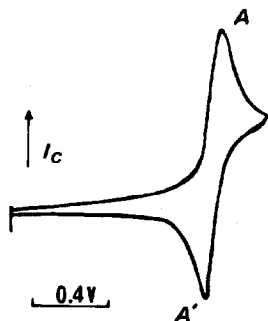


Fig. 1. Voltammogram of $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$. Starting potential: 0V sweep rate: 200 mV s^{-1}

An exhaustive controlled potential electrolysis at -1.40 V/SCE consumes 1F when carried out at -30°C , and a little more than 1F at room temperature. At -30°C , the voltammetry of the electrolysis solution on a rotating disk electrode shows only an anodic wave A' , which appears at the same potential as that of wave A and has the same height. At 25°C , a very small and ill-defined wave appears at about -0.30 V (wave A'_1 , Fig. 2) and wave A' is smaller than the initial wave A. At 25 and -30°C , the ESR spectra recorded directly for the electrolysis solutions consist of one main line, attributable to the ^{48}Ti isotope, with g value = 1.9913 (DPPH was used as internal reference). A set of weaker lines comes from the ^{49}Ti isotope.

In view of the results at low temperature it might be concluded that the uptake of an electron is reversible and leads to the anion species $\text{Cp}_2\text{TiR}_2^-$ (2) (Scheme 1, path a). However, as we have shown previously, the same overall reversible behaviour is also obtained when the addition of the electron is followed by the rapid loss of one of the ligands which turns during the backward sweep (pseudo-reversibility [4–6]). In the present case this would correspond either to path ab (and ba) or ab' (and $b'a$) of Scheme 1.

The two types of mechanisms are not easy to distinguish. We first studied the influences of the sweep rate and the temperature on the cyclic voltammograms. For a pseudo-reversible system, as the temperature decreases or the sweep rate increases a new oxidation peak at potentials less negative than A' should appear. It

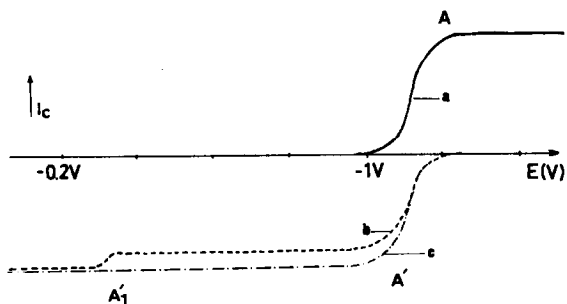
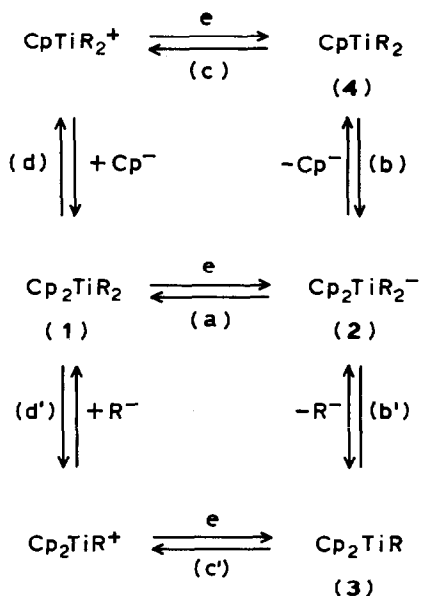


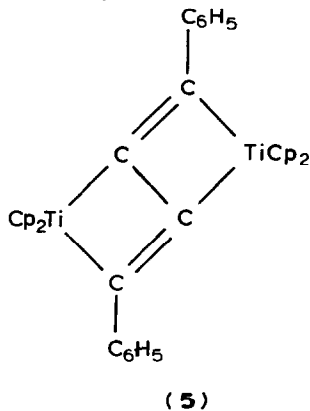
Fig. 2. Voltammograms of $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ on a rotating disk electrode. (a) Before electrolysis; (b) after electrolysis at -1.40 V and at 25°C ; (c) after electrolysis at -1.40 V and at -30°C .



SCHEME 1.

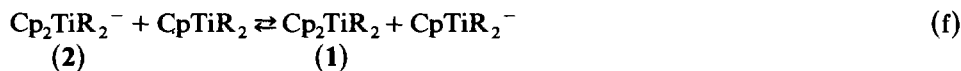
corresponds to the oxidation of the neutral species 3 or 4 (Scheme 1, path c, c' or cd, c'd'). Whatever the sweep rate between 0.01 and 100 V s⁻¹ and the temperature within the range -30 to 25°C, no change in the cyclic voltammogram is observed: in particular no wave A₁' appears.

It has been shown [3,7] that the complex Cp₂TiR (3) is rapidly converted into the dimeric green titanium(IV) complex 5.



We have prepared 5 chemically [3,7]; it is reduced [8] at -1.75 V/SCE. In an independent experiment we have shown [9] that Cp₂TiR₂ is reduced to Cp₂TiR₂⁻ by R⁻. The voltammograms of the solution show peaks A' and A₁'. Therefore if path ab' was followed, less than 1F would be consumed during the electrolysis, since part of Cp₂TiR₂ would disappear by this reaction.

As mentioned above, during a controlled potential electrolysis of 1 at 25°C and at -1.40 V, two anodic waves A' and A₁' appear at -0.3 V/SCE. When the



SCHEME 2.

resulting solution is left under argon the height of wave A_1' increases and that of wave A' decreases, whereas the cathodic wave A slowly reappears. We have shown that wave A_1' is due to the oxidation of Cp^- , by adding CoBr_2 to the solution, which leads to the formation of cobaltocene $\text{Co}(\text{C}_5\text{H}_5)_2$ [10]. This shows that the anion $\text{Cp}_2\text{TiR}_2^-$ is formed after the uptake of the electron (reversible system A/A'), and that it slowly loses a Cp^- to give CpTiR_2 .

In view of the above results CpTiR_2 would be expected to give an anodic wave and an ESR spectrum different from that of $\text{Cp}_2\text{TiR}_2^-$. As mentioned previously we observed neither this wave nor the spectrum. This can be rationalized in terms of Scheme 2, with reaction (f) faster than reaction (b). This would account for the absence of CpTiR_2 during the electrolysis, the slow disappearance of $\text{Cp}_2\text{TiR}_2^-$, and the regeneration of $\text{Cp}_2\text{TiR}_2^-$. The species $\text{CpTi}^{\text{II}}\text{R}_2^-$ is probably unstable.

As expected, the anion $\text{Cp}_2\text{TiR}_2^-$ is much more stable than the anions $\text{Cp}_2\text{TiR}'_2^-$; at room temperature, reaction (b) does not go to completion during one day, whereas it takes only a few minutes with R' as substituents.

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