

## Preliminary communication

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### STUDY BY CYCLIC VOLTAMMETRY OF SOME CYCLOPENTADIENYL-CYCLOOCTATETRAENE COMPOUNDS OF TITANIUM

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#### Summary

Cyclopentadienylcyclooctatetraenetitanium and some other substituted cyclopentadienyl compounds of the same structure have been studied by cyclic voltammetry. They show a perfectly reversible one-electron oxidation wave at relatively low potentials. They are not reducible to 18-electron species.

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#### Results

( $\eta^5$ -Cyclopentadienyl)( $\eta^8$ -cyclooctatetraene)titanium and its substituted derivatives are among the somewhat rare organometallic compounds of titanium which have an authentic "sandwich" structure. They are remarkably stable under an inert atmosphere and react with nucleophiles to yield products of substitution on the cyclopentadienyl ring in which the metallocene structure is preserved [1]. For these reasons we deemed it of interest to study them by cyclic voltammetry in order to determine the stability of the species associated with the anodic or cathodic reactions.

Our studies were conducted on the series of compounds [Ti(cot)L] where (cot) = ( $\eta^8$ -C<sub>8</sub>H<sub>8</sub>) and L = cyclopentadienyl ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) (I), methylcyclopentadienyl ( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>) (II), indenyl ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>) (III) and fluorenyl\* ( $\eta^5$ -C<sub>13</sub>H<sub>9</sub>) (IV) ligands. The preparations and properties of all except II were previously reported [2-4].

In THF and with (NBu<sub>4</sub>)PF<sub>6</sub> as supporting electrolyte, I, II, III and IV exhibit

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\*In III and IV,  $\eta^5$  is related to bonding to the C<sub>5</sub> ring of the indenyl and fluorenyl ligands.

a one-electron oxidation wave situated at  $-0.50$ ,  $-0.56$ ,  $-0.42$  and about  $-0.30$  V (vs. saturated Ag/AgCl), respectively, Fig. 1; ( $[\text{Cp}_2\text{Fe}]/[\text{Cp}_2\text{Fe}]^+ = +0.45$  V in the same medium). A careful study of this wave with respect to scan speed and comparison with ferrocene under analogous conditions show that for I, II and III this oxidation is perfectly reversible. However, IV exhibits a badly distorted curve due to the very low stability of the compound in solution, so that the potential value lacks precision.

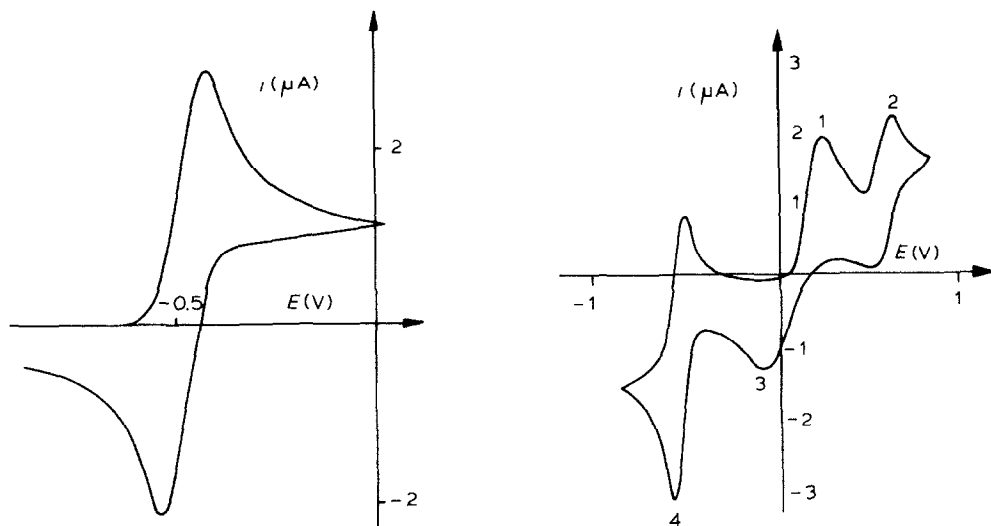
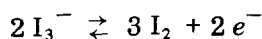
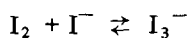
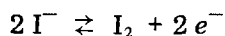


Fig. 1. Typical cyclic voltammogram scanned at  $100 \text{ mV s}^{-1}$ , of  $[\text{TiCp}(\text{cot})]$  in THF.

Fig. 2. Cyclic voltammogram of  $[\text{TiCp}(\text{cot})]\text{I}$  in THF scanned at  $100 \text{ mV s}^{-1}$  (I = iodide anion).

It is noteworthy that none of the compounds exhibit a cathodic wave, indicating that the 18-electron species expected from one-electron reduction is not readily accessible, at least in the solvent used.

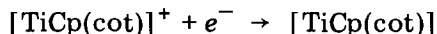
It has been demonstrated that I can be chemically oxidized by iodine to give the compounds  $[\text{TiCp}(\text{cot})]^+\text{X}^-$ , where  $\text{X} = \text{I}^-$  or  $\text{I}_3^-$  depending on the relative proportions of the reactants [5]. Electrochemical reduction of these species under the same conditions as above yielded the voltammogram shown in Fig. 2. This voltammogram exhibits two oxidations and two reductions 1, 2, 3 and 4 respectively. 1, 2 and 3 are attributable to the electrochemical system of  $\text{I}_2$  in THF and can be interpreted as follows:



This has been confirmed by a blank study on iodine alone in  $\text{THF}/(\text{NBu}_4)\text{PF}_6$ .

Reduction 4 is reversible and the value of the potential is the same as that at

which [CpTi(cot)] oxidizes. This reduction is therefore attributed to [TiCp(cot)]<sup>+</sup> according to the scheme:



This confirms that reduction of [TiCp(cot)] is chemically and electrochemically reversible.

In conclusion, it is shown in this study that the family of the 17-electron titanium compounds described above show easily accessible and perfectly reversible oxidation–reduction waves, at potentials which depend on the nature of the cyclopentadienyl moiety [6,7]. On the other hand, reduction to the 18-electron anions, if possible at all, does not fall within the electroactivity of the solvent used, and this reflects the highly negative potential of the Ti<sup>3+</sup>/Ti<sup>2+</sup> couple in this system.

## References

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