Electrochemical Studies on Organometallic Compounds. IV. Influence of the Substitution and of the Nature of the Ligands on the Products of the Electrochemical Reduction of Titanocene Mono and Dichlorides

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The $1e^-$ reduction of $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ and $(\eta^5\text{-}C_5H_5)$ $(\eta^5\text{-}C_5H_4(CH_2)_2P(C_6H_5)_2)TiCl_2$ in THF is followed by a fast loss of Cl^-. This reaction is much slower for $(\eta^5\text{-}C_5H_4CO_2CH_3)_2TiCl_2$. The uptake of an electron by the reduction product is examined by linear potential sweep voltammetry in THF in the presence of various ligands L. A pseudoreversible behaviour is observed with L=dimethylphenylphosphine. In the presence of cyclohexyl isocyanide, the reduction gives a stable Ti(II) species.
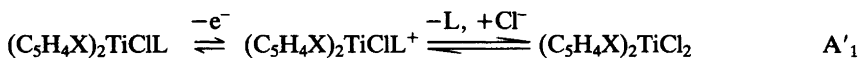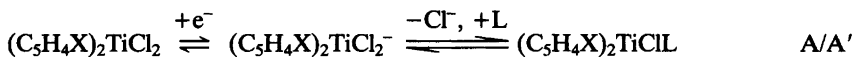
Titanocene dichloride $(\eta^5\text{-}C_5H_5)_2TiCl_2$ 1 is reduced electrochemically in three monoelectronic stages;[1,2] during the first, a Cl^- ion is lost very rapidly after the uptake of the electron. This phenomenon can be easily followed by studying the cyclic voltammograms (cf. Fig. 1).
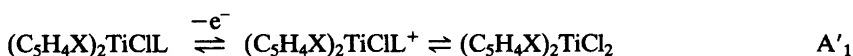
The reactions corresponding to the different peaks are given in Scheme 1 (X=H); L, a neutral ligand, can be added to the solution or can be a molecule of the solvent.

The relative magnitude of peaks A′ and A′₁ depends on the rate of recombination of Cl^- with the species Cp_2TiClL. If for a given sweep rate v, this rate is very large, A′ will appear alone; if it is very small, only A′₁ will be observed. On the other hand, if v increases, A′₁ grows relatively to A′, because the recombination reaction has less time to take place (cf. Fig. 1).

Compounds 1, 2, 3

$$(C_5H_4X)_2TiCl_2 \underset{}{\overset{+e^-}{\rightleftharpoons}} (C_5H_4X)_2TiCl_2^- \overset{-Cl^-,\ +L}{=\!=\!=\!=} (C_5H_4X)_2TiClL \qquad \text{A/A}'$$

$$(C_5H_4X)_2TiClL \underset{}{\overset{-e^-}{\rightleftharpoons}} (C_5H_4X)_2TiClL^+ \overset{-L,\ +Cl^-}{=\!=\!=\!=} (C_5H_4X)_2TiCl_2 \qquad \text{A}'_1$$

Compound 4

$$(C_5H_4X)_2TiCl_2 \underset{}{\overset{+e^-}{\rightleftharpoons}} (C_5H_4X)_2TiCl_2^- \qquad \text{A/A}''$$

$$(C_5H_4X)_2TiClL \underset{}{\overset{-e^-}{\rightleftharpoons}} (C_5H_4X)_2TiClL^+ \rightleftharpoons (C_5H_4X)_2TiCl_2 \qquad \text{A}'_1$$
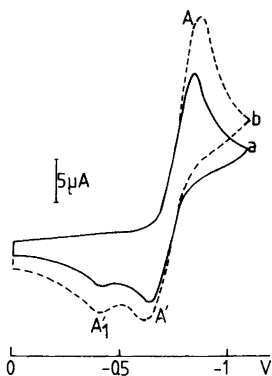
Scheme 1.

Fig. 1. Cyclic voltammograms of *1* in THF at −54 °C. Sweep rate: a, 50 mV/s; b, 100 mV/s. Starting potential: 0 V.

A priori, three factors can have an influence on the rate of recombination.

(a) The temperature. A decrease of the temperature should decrease the rate, *i.e.* A'_1 should increase. This was shown to be the case in a previous work.[2] In tetrahydrofuran at room temperature, only A' is seen; as the temperature decreases, A'_1 appears (*cf.* Fig. 1).

(b) The ligand L. The more strongly L is bound, the slower should the recombination become. From a previous study,[2] and from the results of the present investigation, it is found that the ligands are less and less strongly bound in the sequence cyclohexyl isocyanide (CHIC), *N,N*-dimethylformamide (DMF), 2,6-dimethylphenylisocyanide (DMPIC), pyridine, dimethylphenylphosphine (DMPP) and THF.

(c) A change in the structure of the molecule. Electron-attracting substituents should increase the rate of recombination, while electron-donating ones should decrease it. This effect, which

was not investigated earlier, is examined in this paper.

The electrochemistry of the second stage of the reaction has never been systematically investigated, although it is known that the formation of a complex with nitrogen requires that the metal should be in the +2 oxidation state.[3] We report here a few preliminary results on this problem.

RESULTS AND DISCUSSION

Influence of the substituents on the first stage. We have examined three titanocene dichloride derivatives, $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ *2*, $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4(CH_2)_2P(C_6H_5)_2TiCl_2$ *3* and $(\eta^5\text{-}C_5H_4CO_2CH_3)_2$ $TiCl_2$ *4*. The peak potentials of peak A (first stage), B (second stage) and C (third stage) are given in Table 1.

The peak potentials of *2* are shifted towards negative potentials, owing to the electron releasing character of the methyl groups. In THF at room temperature, peak A'_1 is well marked (Fig. 2) whereas for titanocene dichloride it did not appear under the same conditions.[2] This shows that the recombination rate is decreased, in accordance with the predictions presented above.

The peak potentials for compound *3* are practically the same as for titanocene dichloride; the substituent has neither electron-donating nor electron-releasing properties. The behaviour of this compound should thus be similar to that of *1*. In THF at room temperature, however, peak A'
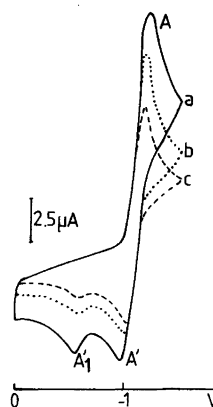
Table 1. Potential peaks (V) of titanocene derivatives.

	A	B	C
1	−0.8 [a]	−2.1	−2.4
	−0.85 [b]	−	−
2	−1 [a]	−2.18	−
3	−0.8 [b]	−2	−2.5
4	−0.25 [a]	−	−

[a] In THF. [b] In acetone.

Fig. 2. Cyclic voltammograms of *2* in THF. Sweep rate: a, 500 mV/s; b, 200 mV/s; c, 100 mV/s. Starting potential: 0 V.
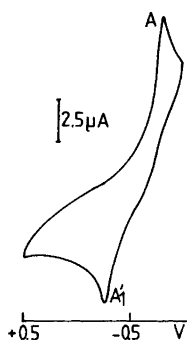
Fig. 3. Thin layer voltammogram of *3* in THF.
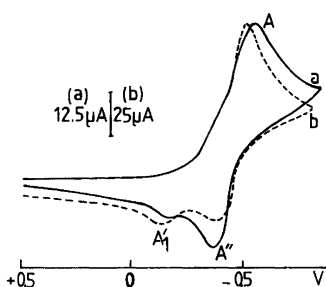Sweep rate: 50 mV/s. Starting potential: +0.5 V.

Fig. 4. Cyclic voltammograms of *4* in acetone at
+35 °C. Sweep rate: a, 1 V/s; b, 200 mV/s.
Starting potential: +0.5 V.

Fig. 5. (a) Cyclic voltammogram of *1* in THF in
presence of DMPP. Sweep rate: 10 mV/s. Start-
ing potential: +0.5 V. (b) Cyclic voltammogram
of *1* in THF in presence of DMPP. Sweep rate: 2
V/s. Starting potential: +0.5 V.

is completely absent (Fig. 3). This can be
attributed to an internal ligandation,[4] in which
the phosphine ligand chelates the metal after the
Cl⁻ ion separates.

For compound *4*, the peak potential is much
more positive than for *1*, which points to a strong
decrease of the electronic density on the metal.
The experiments were carried out in acetone,
because *4* is not soluble enough in THF.

In acetone, the voltammogram of *1* shows both
peaks A' and A'$_1$; an increase in the scan rate or
a decrease of the temperature causes an increase
of A'$_1$, as in THF.

Compound *4* also shows two peaks A" and A'$_1$;
however, A" increases when the sweep rate
increases, instead of decreasing (Fig. 4). This
points to a relative stability of the anionic species
(η^5-C$_5$H$_4$CO$_2$CH$_3$)$_2$TiCl$_2^-$ (*cf.* Scheme 1,
X=CO$_2$CH$_3$); the rate at which Cl⁻ leaves the
molecule would be much slower than for *1*,
because of the decreased electronic density on
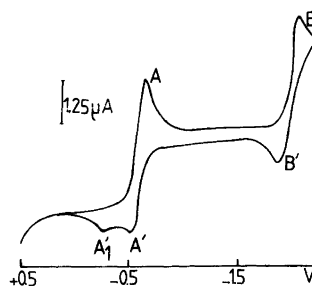the metal. At larger sweep rates, more of the

anionic species would be present, whence the
increase of A'.

The second reduction stage for Cp$_2$TiCl$_2$. In
THF, at sweep rates larger than a few V s⁻¹, a
reversible system B/B' is obtained. At slower
sweep rates, peak B' disappears. When DMPP is
added to the solution, a pseudo-reversible [2]
system B/B' is observed at slow sweep rates (Fig.
5a); peak B' decreases and a new peak B'$_1$
appears at higher sweep rates (Fig. 5b).

With CHIC, peak B' is never observed whatev-
er the sweep rate; only B'$_1$ and a new peak A'$_2$
appear (Fig. 6). If the scan is reversed again after
peak B'$_1$ (Fig. 7), a new peak B$_1$ is observed, the
system B$_1$/B'$_1$ being reversible. The same peaks
B'$_1$, A'$_2$ and B$_1$ are obtained by starting directly
from the chemically prepared [5] species (η^5-
C$_5$H$_5$)$_2$TiCl–CHIC.

These results show that the behaviour of the
species (η^5-C$_5$H$_5$)$_2$TiClL is in general analogous
to that of *1* and can be explained on the basis of
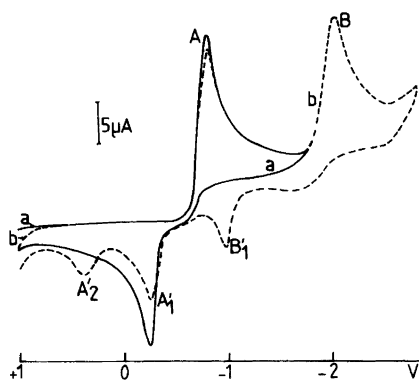Scheme 2.

Fig. 6. Cyclic voltammograms of *1* in THF in presence of CHIC. Sweep rate: 100 mV/s. a, first sweep; b, second sweep. Starting potential: +1 V.
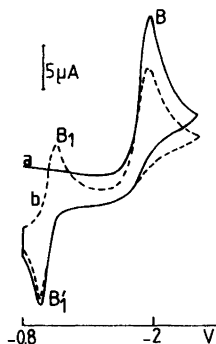

Fig. 7. Cyclic voltammograms of *1* in THF in presence of CHIC. Sweep rate: 100 mV/s. a, first sweep; b, second sweep.
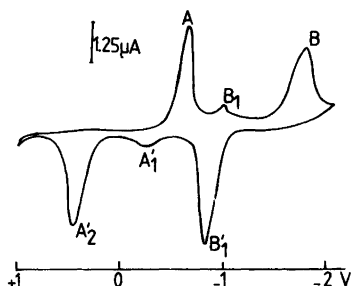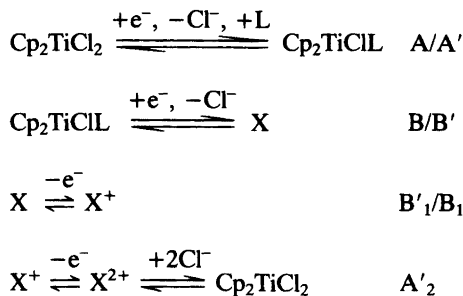

Fig. 8. Thin layer voltammogram of *1* in THF in presence of CHIC (second sweep). Sweep rate: 20 mV/s. Starting potential: +1 V.

$$Cp_2TiCl_2 \xrightleftharpoons[]{+e^-, \; -Cl^-, \; +L} Cp_2TiClL \quad A/A'$$

$$Cp_2TiClL \xrightleftharpoons[]{+e^-, \; -Cl^-} X \quad B/B'$$

$$X \xrightleftharpoons[]{-e^-} X^+ \quad B'_1/B_1$$

$$X^+ \xrightleftharpoons[]{-e^-} X^{2+} \xrightleftharpoons[]{+2Cl^-} Cp_2TiCl_2 \quad A'_2$$

Scheme 2.

As for the first stage, the uptake of an electron by the molecule (peak B) is followed by a fast loss of a Cl^- ion to give a titanium(II) complex, which we have designated as X. The structure of this compound, which is unstable, is now under investigation; according to our first results, X is probably a dimer in which only one molecule of CHIC per titanium atom is present. The species X^+, which is obtained by oxidation of X (peak B'_1, Scheme 2) is more stable than its analog [2] Cp_2TiClL^+, since it does not react with the Cl^- ions to regenerate Cp_2TiClL. Such a recombination, however, occurs after the oxidation of X^+ to X^{2+}, since Cp_2TiCl_2 is totally regenerated during this step (peak A'_2, followed upon a cathodic sweep by peak A in a thin-layer cell) (Fig. 8).

The stability of the Ti(II) complex depends on the ligand. The fact that in pure THF peaks B'_1 and A'_2 are not obtained points to a rapid decomposition, probably due to the fact that THF does not bind strongly enough to the molecule. In pyridine, the system B_1/B'_1 is visible only at high sweep rate or at low temperature; the behaviour is thus intermediate between that in pure THF and that in THF containing CHIC. In DMF, as in THF, the system B'/B'_1 is never observed.

All the above results were obtained under argon atmosphere. During preliminary experiments under nitrogen atmosphere, we did not find any difference in THF in the presence of strong ligands (DMPP, CHIC). Irreproducible changes in the second peak are observed in THF alone. In DMF, at low temperature on a mercury electrode, a highly reproducible modification of the second stage takes place. This shows the complexity of the reaction; it seems however that the presence of a too strongly coordinated ligand

prevents the reaction between nitrogen and the Ti(II) complex. We are currently investigating these phenomena by using differently substituted titanocene dichlorides.

EXPERIMENTAL

All manipulations were performed under argon. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon.

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 IG5 integrator were used.

The complexes $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ [6] 2 and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4(CH_2)_2P(C_6H_5)_2TiCl_2$ [4] 3 were prepared by literature methods. The carbomethoxy derivative 4 was obtained by the following procedure: A solution of $[C_5H_4CO_2CH_3]^-Na^+$ [7] (8.16 mM) in 30 ml of THF was added to $TiCl_4$ (4.08 mM) in THF at 0 °C. The solution was warmed slowly to room temperature and stirred for 2 h. A red precipitate was formed which was filtered off, then washed with 20 ml of cold THF (yield 50 %). ^1H NMR (CDCl$_3$): δ 7.17 (4 H, t, J 2.5 Hz), 6.56 (4 H, t, J 2.5 Hz), 3.90 (6 H, s). IR (KBr) $vc{=}o$ 1725 cm^{-1}. MS [IP 70 ev; m/e] 364 (M), 241 (M$-C_5H_4CO_2CH_3$).

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