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The electrochemical reduction of Cp_2TiCl_2 in the presence of trimethylphosphine

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Abstract

The electrochemistry of the complexes $Cp_2TiCl_x(PMe_3)_{2-x}$ in anhydrous THF has been studied. The most stable complexes at the three oxidation states of titanium are Cp_2TiCl_2, $Cp_2TiCl(PMe_3)$ and $Cp_2Ti(PMe_3)_2$, and each of these species is readily formed by electrolysis. It has also been demonstrated that oxidation/reduction of these species is followed by facile and rapid ligand exchange to form the preferred species in the new oxidation state provided a stoichiometric concentration of the required ligand is present. The consequences of this redox and ligand exchange chemistry for the synthetic reactions catalyzed by lower oxidation states of Ti are discussed. Finally, the voltammetry of a titanocycle is reported, and it is shown that the corresponding Ti^{III} metallocycle is stable.

Key words: Titanium; Cyclopentadienyl; Phosphine; Voltammetry; Reduction; Electrochemistry

1. Introduction

In the previous paper [1], it was noted that a number of organic transformations of importance for synthesis may be carried out with Cp_2TiCl_2 in the presence of a reducing agent. A phosphine has usually been added to such systems to stabilize the lower oxidation states of titanium. Hence, in this paper we report a detailed electrochemical study of the reduction of Cp_2TiCl_2 in THF containing trimethylphospine, and also of the intermediates and the products that may be formed. The objectives were twofold: (i) to identify the key, reduced intermediates and to obtain a detailed knowledge of their thermodynamic and kinetic stabilities, and (ii) to define the conditions for the electrochemical preparation of those species of importance in synthesis.

The electrochemistry of Cp_2TiCl_2 remains the subject of some uncertainty [2–9]. The first reduction step appears on a voltammogram as a reversible $1e^-$ reduction, and controversy centres on the stability of the anion radical and whether this initial $1e^-$ reduction is followed by the rapid and reversible loss of chloride, *i.e.*

$$[Cp_2TiCl_2] + e^- \rightleftharpoons [Cp_2TiCl_2]^- \qquad (1)$$

$$[Cp_2TiCl_2]^- + \text{sol} \rightleftharpoons [Cp_2TiCl(\text{sol})] + Cl^- \qquad (2)$$

where sol denotes a solvent molecule. The shape of the voltammogram would not be influenced by the rapid and reversible loss of chloride ion from the anion radical. On the other hand, the coupled equilibrium will lead to a shift in both cathodic and anodic peaks positive to the formal potential of the $[Cp_2TiCl_2]/[Cp_2TiCl_2]^-$ couple, but this shift could only be recognized if the formal potential were independently known. It will be seen that when phosphines are present in solution, this uncertainty is not an important factor in the interpretation of the data. As part of this debate, however, there have been preliminary investigations of the electrochemistry of Cp_2TiCl_2/PR_3 systems [3,10–12], and a related study of the reduction Cp_2TiCl_2 in the presence of CO that showed it to be possible to prepare $Cp_2Ti(CO)_2$ [7].

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2. Experimental details

In systems involving Cp_2TiCl_2, clean voltammetry is only obtained if thorough precautions are taken to exclude water. Hence, all experiments were performed under argon using standard Schlenk techniques. These procedures, as well as the preparation of solvents and electrolyte, the instrumentation and the cells for voltammetry and electrolysis (designed to be used on a vacuum line) have been described previously [1].

The working electrode for voltammetry was a vitreous carbon disc (area 0.05 cm^2) sealed in a glass tube. The reference electrode was a silver wire in the solution under study. Where possible, potentials were calibrated by recording a cyclic voltammogram for ferrocene but the voltammograms for ferrocene were distorted in the presence of trimethylphosphine. In addition, the potential of the silver wire is shifted strongly by phosphines in solution. In general, therefore, potentials *versus* ferrocene were determined by the identification of a major peak in the voltammogram and measuring the potentials of other peaks from this pseudo reference point. This method is reliable to within 100 mV.

The Cp_2TiCl_2 (purity 97%) was supplied by Aldrich. The $Cp_2Ti(PMe_3)_2$ was prepared [13,14] by stirring a mixture of Cp_2TiCl_2 (0.5 g, 2 mmol), ground magnesium turnings (0.2 g, 8 mmol) and $HgCl_2$ (0.01 g, 0.02 equiv.) in THF (5 ml) for approximately 5 min. Trimethylphosphine as a 1 M solution in THF (8 ml, 8 mmol) was added, and the mixture was subjected to sonication until the colour changed from red to brown. The mixture was stirred at 30°C overnight, then the THF was removed from the black-brown solution *in vacuo*. The residue was extracted with hexane (10 + 5 ml), and after removal of the hexane from the extract *in vacuo*, black crystals of $Cp_2Ti(PMe_3)_2$ were obtained in 60% yield. The ^1H and ^{13}C NMR spectra were as reported [14]. The complex $Cp_2TiCl(PMe_3)$ has previously been prepared [15], but the method used here involved the addition of a solution of Cp_2TiCl_2 in THF (0.05 M) to one of $Cp_2Ti(PMe_3)_2$ in the some solvent until the colour changed from brown-black to blue-green (stoichiometric reaction was assumed). The THF was removed *in vacuo* to give blue-green crystals.

EI mass spec. *m/e* 213 ($M^+ - PMe_3$, 90%), 178 (Cp_2Ti^+, 22%), 148 ($CpTiCl^+$, 100%).

3,3-Bis(cyclopentadienyl)-2-^{n}butyl-3-titanabicyclo-[3.3.0]-oct-1-ene was prepared by the following procedure [13]. A solution of Cp_2TiCl_2 (0.5 g, 2 mmol) in THF (10 ml) was cooled to −70°C and ^{n}BuLi (2.2 ml of a 1.81 M solution in hexane, 2 equiv) and PMe_3 (4 ml of a 1.0 M solution in THF, 2 equiv) were added. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 1 h. To the resulting brown-black mixture was added 1-undecen-6-yne (0.3 g, 2 mmol), and the mixture was stirred for 1 h. The THF was removed *in vacuo* and the product extracted into hexane (8 ml). The hexane solution was transferred to another flask and the solvent removed *in vacuo* to give the desired compound in 75% yield (0.5 g) as dark red crystals.

^1H NMR (C_6D_6) δ 6.0 (5H, s), 5.95 (5H, s), 2.5–2.0 (7H, m), 1.9–1.7 (1H, m), 1.6–1.3 (5H, m), 1.3–0.9 (5H, m).

^{13}C NMR (C_6H_6) δ 113.5, 111.7, 58.4, 41.2, 40.0, 32.4, 30.3, 23.9, 22.7, 14.4.

The 1-undecene-6-yne was prepared as follows [16]. To a magnetically stirred solution of 1-hexyne (3.29 g, 40 mmol) in THF (20 ml) at −30°C was added ^{n}BuLi (22 ml of 1.8 M solution in hexane, 40 mmol). The mixture was stirred at −30°C for 1 hour, throughout which a faint white precipitate was evident. A solution of 5-bromo-pent-1-ene (5.96 g, 40 mmol) in HMPA (30 ml) was added dropwise during 30 min through a cannula to the mixture at 0°C. The resulting yellow solution was allowed to warm to room temperature, and stirred overnight, then poured onto H_2O (100 ml). After extraction with petroleum ether (100 + 50 ml), the extracts were combined, washed with water, and dried over $MgSO_4$, and the solvent was then removed by rotary evaporation. The crude product was a thick yellow liquid, which gave a colourless liquid upon Kugelrohr distillation. The title compound was obtained in 85% yield.

^1H NMR ($CDCl_3$) δ 5.80 (1H, ddt, $J = 17.2$, 10.0, 6.6 Hz), 5.08–4.93 (2H, m), 2.15 (6H, m), 1.70–1.29 (6H, m), 0.91 (3H, t, $J = 7.2$ Hz).

^{13}C NMR ($CDCl_3$) δ 138.2 d, 115.0 t, 80.6 s, 79.8 s, 33.0 t, 31.4 t, 28.5 t, 22.1 t, 18.6 t, 18.3 t, 13.8 q.

3. Results and discussion

3.1 The voltammetry of Cp_2TiCl_2

A cyclic voltammogram of Cp_2TiCl_2 (7.3 mM) in THF/Bu_4NBF_4 (0.2 M) at a vitreous carbon disc is shown in Fig. 1. Two reduction processes can be seen, at −1.32 V (peak A) and −2.52 V (peak B) *vs.* Cp_2Fe/Cp_2Fe^+, and there are coupled anodic processes (peaks A′ and B′ respectively). The first redox couple (A/A′) displays all the characteristics of a reversible $1e^-$ transfer. The peak separation is 60 mV and the ratio of peak currents, $I_p^{A'}/I_p^A$, is unity at all scan rates. A plot of I_p^A against the square root of the scan rate gives a straight line passing through the origin; the slope of this plot and the Randles-Sevčik equation give a value of $D = 1.3 \times 10^{-5}$ cm^2 s^{-1} assuming $n = 1$. This value of the diffusion coefficient is

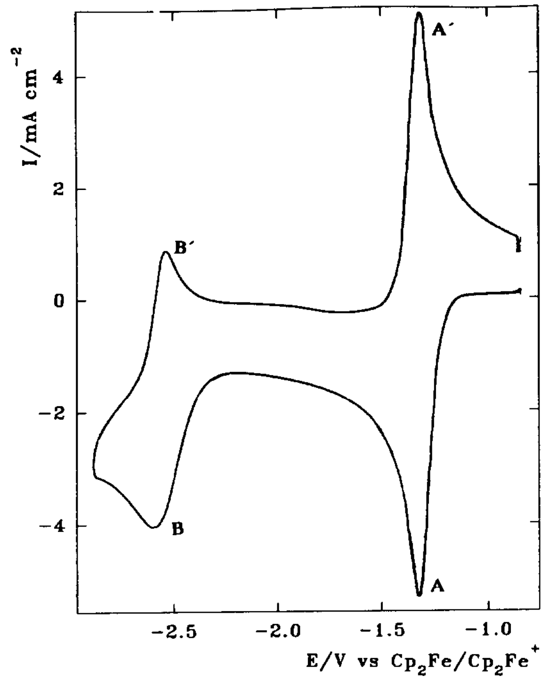


Fig. 1. Cyclic voltammogram for Cp_2TiCl_2 (7 mM) in THF/Bu_4NBF_4 (0.2 M). Vitreous carbon disc electrode. Potential scan rate 600 mV s^{-1}.

comparable to those for other similar titanium complexes in the THF medium [1].

The second reduction, represented by peak B, is only partially reversible, the anodic peak, B′ being smaller than peak B, although peak B′ does become larger at increasing scan rates. On the voltammogram, peak B is smaller than peak A, but it is again a 1e$^-$ reduction step. Because B/B′ is not a reversible process, the reduction peak is more drawn out along the potential axis; when allowance is made for its shape, and *n* assumed to be 1, the estimated diffusion coefficient from I_p^B is again 1.3×10^{-5} cm^2 s^{-1}.

This voltammetry for Cp_2TiCl_2 is, in general, consistent with earlier reports, although some authors reported the existence of a third cathodic process [3,8]. This reaction was never evident in this study, and we believe that it arises from coupled chemistry associated with the second reduction process under less anhydrous conditions.

3.2. *The voltammetry of Cp_2TiCl_2 in the presence of PMe_3*

Figure 2 shows cyclic voltammograms recorded at the vitreous carbon disc for Cp_2TiCl_2 (9 mM) in THF/Bu_4NBF_4 (0.2 M) also containing trimethylphosphine (50 mM). In Fig. 2(a), the potential scan is limited so that only the first reduction peak, A*, is seen (this peak is labelled A* since, although the reduction again corresponds to the addition of an electron to Cp_2TiCl_2, the coupled chemistry will cause a small positive shift in its potential; for the purposes of identifying other peaks, however, it was assigned a potential of −1.32 V *vs.* Cp_2Fe/Cp_2Fe^+, and the error is almost certainly small, see below). The current densities associated with the first reduction peak are almost unchanged upon the addition of the phosphine, and so the reduction remains a 1e$^-$ process. In the presence of the phosphine, however, coupled chemistry is clearly occurring; the reverse peak, A′, is absent, and a new

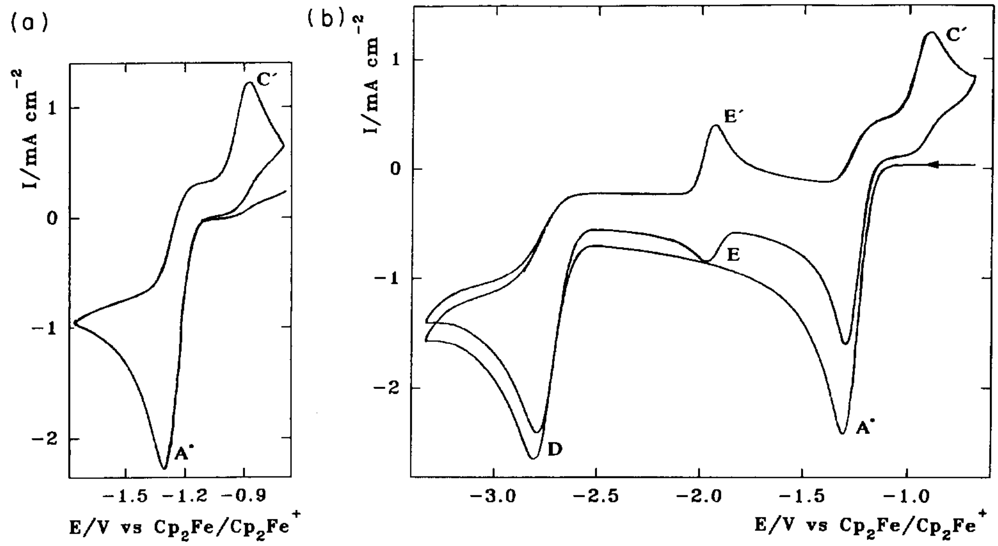


Fig. 2. Cyclic voltammograms for Cp_2TiCl_2 (9 mM) in THF/Bu_4NBF_4 (0.2 M) containing PMe_3 (50 mM). Vitreous carbon disc electrode. Potential scan rate 100 mV s^{-1}. Negative potential limits (a) −1.80 V (b) −3.3 V *vs.* Cp_2Fe/Cp_2Fe^+.

anodic peak, C′ at −0.92 V *vs.* Cp_2Fe/Cp_2Fe^+ is seen to replace it. The chemistry is likely to involve the reactions:

$$[Cp_2TiCl_2] + e^- \rightleftharpoons [Cp_2TiCl_2]^- \quad (3)$$

$$[Cp_2TiCl_2]^- + PMe_3 \rightleftharpoons [Cp_2TiCl(PMe_3)] + Cl^- \quad (4)$$

when peak C′ represents the reaction

$$[Cp_2TiCl(PMe_3)] - e^- \rightleftharpoons [Cp_2TiCl(PMe_3)]^+ \quad (5)$$

This cation may be shown to be unstable by continuing the voltammogram to a second cycle.

When the negative limit is extended, as in Fig. 2(b), a second irreversible $1e^-$ reduction peak is observed, peak D at −2.78 V *vs.* Cp_2Fe/Cp_2Fe^+. Peak D appears at 260 mV more negative than the second reduction seen with Cp_2TiCl_2 without phosphine present (peak B in Fig. 1). Furthermore, peak B is totally absent, a further indication that $[Cp_2TiCl_2]^-$ reacts rapidly with the phosphine. Therefore, it is consistent to propose that peak D is from reaction (6):

$$[Cp_2TiCl(PMe_3)] + e^- \rightleftharpoons [Cp_2TiCl(PMe_3)]^- \quad (6)$$

This anion is also unstable and probably undergoes reaction (7):

$$[Cp_2TiCl(PMe_3)]^- + PMe_3 \rightleftharpoons [Cp_2Ti(PMe_3)_2] + Cl^- \quad (7)$$

When the potential range includes peak D, the reverse scan leads to two anodic peaks peak E′, at −1.92 V, and peak C′ at −0.92 V. Peak E′ must be for the oxidation of a species formed in the reduction process D, probably

$$[Cp_2Ti(PMe_3)_2] - e^- \rightleftharpoons [Cp_2Ti(PMe_3)_2]^+ \quad (8)$$

Figure 2(b) also shows the second potential cycle, and it can be seen that the oxidation process, C′ is completely irreversible, and peak A* still represents the only reduction process in this potential region. A new cathodic process (E) is, however, now evident at −1.98 V, and it appears that E/E′ is for a reversible couple. The characteristics of these voltammograms do not change with sweep rates (25–300 mV s^{-1}).

3.3. *The voltammetry of $Cp_2Ti(PMe_3)_2$*

The voltammetry of $Cp_2Ti(PMe_3)_2$ is straightforward, (see Fig. 3(a)). At all potential scan rates, two oxidation processes are seen, at −1.95 V and −0.44 V *vs.* Cp_2Fe/Cp_2Fe^+; the first has the characteristics of a reversible $1e^-$ process and its presence confirms that the pair of peaks E′/E in the voltammetry of the solution containing $Cp_2TiCl_2 + PMe_3$ is, indeed, due to reaction (8). The cation is stable on the voltammetric timescale, and the second irreversible $1e^-$ oxidation (peak F′ in later voltammograms) must lead to an unstable dication.

When an excess of chloride ion (as anhydrous Bu_4NCl) was added to the THF/Bu_4NBF_4 solution of

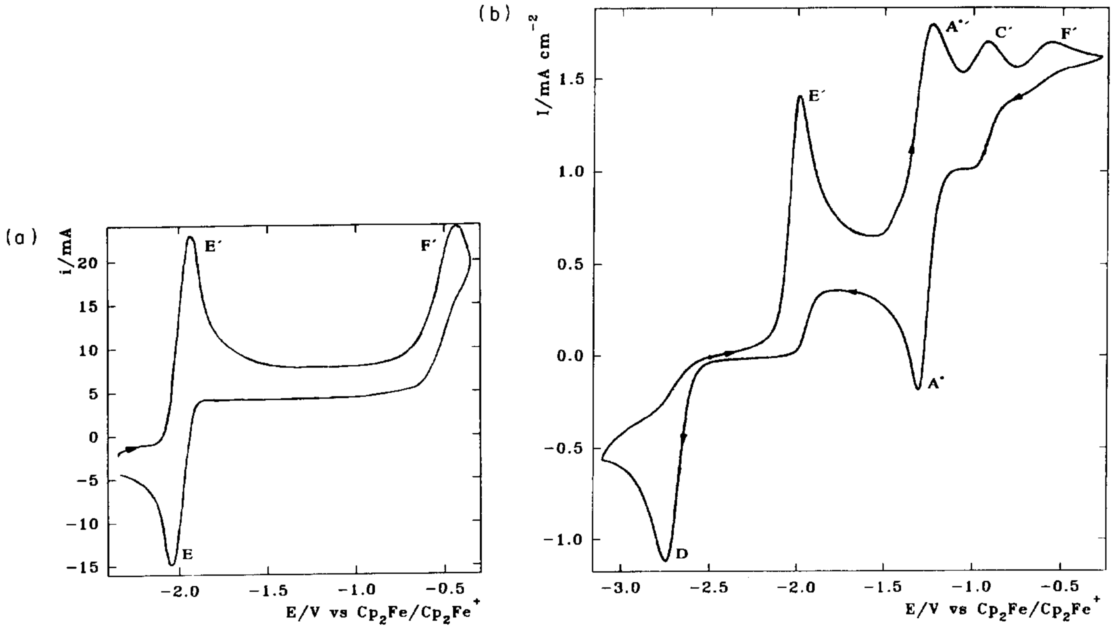


Fig. 3. Cyclic voltammograms for $Cp_2Ti(PMe_3)_2$ in THF/Bu_4NBF_4 (0.2 M). Vitreous carbon disc electrode. (a) before the addition of Bu_4NCl, potential scan rate 50 mV s^{-1} (b) after the addition of Bu_4NCl, potential scan rate 25 mV s^{-1}.

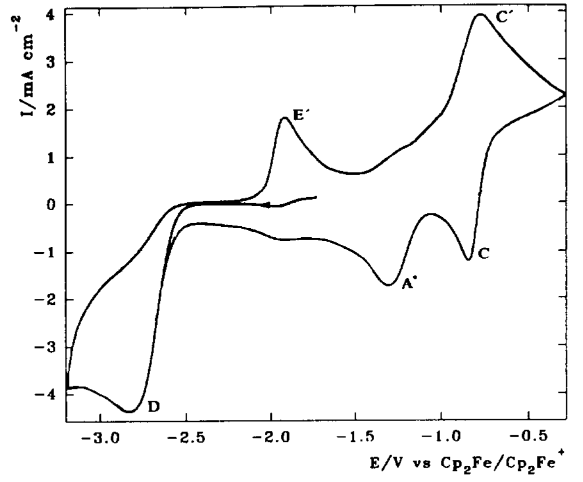


Fig. 4. Cyclic voltammograms for $Cp_2TiCl(PMe_3)$ in THF/Bu_4NBF_4 (0.2M). Vitreous carbon disc electrode. Potential scan rate 100 mV s^{-1}.

$Cp_2Ti(PMe_3)_2$, the voltammogram became more complex, (see Fig. 3(b)). The potential scan was scanned positive from −2.40 V, where no current flows; four anodic peaks are observed, as well as two cathodic peak on the reverse scan. The initial oxidation peak, E′, is now completely irreversible. Other important features are the appearance of the peaks A* and A*′ for a reversible process at a potential close to that A/A^- for the solution of Cp_2TiCl_2, the reduction peak, D, and the oxidation peak C′, previously identified as the reduction and oxidation of $Cp_2TiCl(PMe_3)$. Peak D is seen in the voltammogram for $Cp_2Ti(PMe_3)_2 + Cl^-$ even if the potential scan is reversed immediately positive to peak E′. Clearly, ligand substitution reactions are occurring at the Ti^{III} and Ti^{IV} oxidation levels. The oxidation, reaction (8), is followed by the coupled chemistry

$$[Cp_2Ti(PMe_3)_2]^+ + Cl^- \rightleftharpoons [Cp_2TiCl(PMe_2)] + PMe_3 \tag{9}$$

It is also noteworthy that the reaction

$$[Cp_2TiCl(PMe_3)] + Cl^- - e^- \rightleftharpoons Cp_2TiCl_2 + PMe_3 \tag{10}$$

is seen as the reversible pair of peaks, A*/A*′, whereas in the electrochemistry of $Cp_2TiCl_2 + PMe_3$, no oxidation peak was seen. This implies that, while the first step in reaction (10) is the formation of $[Cp_2TiCl(PMe_3)]^+$, it reacts rapidly with Cl^- and, indeed, all the coupled chemistry is rapid and in equilibrium, so that the couple $[Cp_2TiCl(PMe_2)]/Cp_2TiCl_2$ in chloride media appears as a reversible couple. Extensive simulations [17] of a system involving reversible electron transfer and a reversible chemical reaction show that, in all realistic situations, the potential shift resulting from the coupling chemistry is small, and seldom more than 100 mV.

3.4. *The voltammetry of $[Cp_2TiCl(PMe_3)]$*

A solution of $Cp_2TiCl(PMe_3)$ was prepared by a mixing equimolar amounts of Cp_2TiCl_2 and $Cp_2Ti(PMe_3)_2$ in THF. On mixing of the bright red solution of Cp_2TiCl_2 and the dark brown/black solution of $Cp_2Ti(PMe_3)_2$, a blue solution of $Cp_2TiCl(PMe_3)$ was obtained immediately. Blue/green crystals of $Cp_2TiCl(PMe_3)$ were isolated after evaporation of the THF under vacuum, and the product was characterized by mass spectrometry. The voltammetry of $Cp_2TiCl(PMe_3)$ was studied using the solution directly after the addition of electrolyte.

Figure 4 presents a voltammogram of $Cp_2TiCl(PMe_3)$ in THF/Bu_4NBF_4 (0.2 M). Starting the scan at −1.72 V *vs.* Cp_2Fe/Cp_2Fe^+ (a potential where no oxidation or reduction processes are occurring), a reduction peak is observed at −2.78 V, and this is clearly for the same process as found in the voltammetry of $Cp_2TiCl_2 + PMe_3$. This confirms that peak D is indeed for the reduction of $Cp_2TiCl(PMe_3)$, *i.e.* reaction (6). This reduction is again completely irreversible and, surprisingly, even in the absence of excess PMe_3, this coupled chemistry leads to the formation of some $Cp_2Ti(PMe_3)_2$ since the anodic peak, E′, for reaction (8) is clearly seen at −1.92 V. At the Ti^{II} level, ligand exchange reactions must be taking place. These also lead to Cp_2TiCl_2, since reduction peak A* (but not anodic peak A*′) is observed when the cycle is continued positive. The voltammogram also shows a reversible couple the potential of which matches that of C/C′. When the scan is initiated from −1.72 V and taken directly positive, only the C/C′ processes obtained as major peaks, and it appears that in the absence of chloride ion, $Cp_2TiCl(PMe_3)^+$ is stable, and reaction (5) is reversible.

When Bu_4NCl is added to the solution, the voltammetry is markedly simplified. As major peaks only the primary reduction peak, peak D, and the couple A*/A*′ are seen, with a much reduced oxidation peak E′. When cycled over the range −1.70 to 0.0 V, only the peaks A*/A*′ are seen. As expected from the discussion above, in the presence of an excess of chloride ion, the oxidation of $Cp_2TiCl(PMe_3)$ is seen as a reversible couple corresponding to $[Cp_2TiCl(PMe_3)]/Cp_2TiCl_2$.

3.5. *The products from electrolyses*

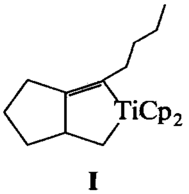
Controlled potential electrolyses was carried out on a solution of Cp_2TiCl_2 plus an excess of PMe_3 in

THF/Bu_4NBF_4 (0.2 M) first at −1.6 V and then at −3.2 V *vs.* Cp_2Fe/Cp_2Fe^+. The solution changed colour from bright red to blue/green at −1.6 V and then to dark brown at −3.2 V, as expected for the conversion of Cp_2TiCl_2 to $Cp_2TiCl(PMe_3)$ and finally $Cp_2Ti(PMe_3)_2$. The voltammetry of the solutions after the electrolysis, was similar, but not identical to that described above for solutions of the pure compounds. This is to be expected, since electrochemically-prepared solutions of $Cp_2TiCl(PMe_3)$ and $Cp_2Ti(PMe_3)_2$ must contain Cl^- formed in the cathode reactions, and in these experiments also contained free PMe_3, since the electrolyses were carried out in the presence of excess phosphine. The low concentration of chloride ion and the high concentration of phosphine had the expected effects on the chemistry coupled to the electron transfer reactions of $Cp_2TiCl(PMe_3)$ and $Cp_2Ti(PMe_3)_2$.

An anodic oxidation of a solution of $Cp_2TiCl(PMe_3)$ in THF/Bu_4NBF_4 containing Cl^- at −0.6 V led to a change in colour from blue/green to bright red. After electrolysis, the voltammetry of the product solution is very simple. Only the reversible couple $A^*/A^{*\prime}$ and the reduction peak D are seen. This is the voltammetry expected for Cp_2TiCl_2 in the medium containing Cl^- and PMe_3. Since the only phosphine in the solution is that formed during the anodic oxidation, it demonstrates that a stoichiometric concentration of phosphine is sufficient to trap all the $[Cp_2TiCl_2]^-$ formed at the electrode.

3.6. The voltammetry of a titanocycle

Since one objective of the programme was to use the electrogenerated reduced titanium compounds in synthesis, it was decided to investigate the voltammetry of a titanocycle, a typical product of reaction between Ti^{II} species and an enyne [18]. The titanocycle, I, was therefore prepared by the reaction between $Cp_2Ti(PMe_3)_2$ and the enyne, 1-undecene-6-yne.



I

The solution of the titanocycle (26 mM) in THF/Bu_4NBF_4 (0.2 M) had a dark red colour. Cyclic voltammograms recorded for this solution showed a single reversible $1e^-$ reduction at peak, at −2.44 V *vs.* Cp_2Fe/Cp_2Fe^+, at all potential scan rates studied. The diffusion coefficient was estimated to be 9.2×10^{-6} cm^2 s^{-1}. Hence, this reduction appears to be a very simple process leading to a stable Ti^{III} metallocycle; this is the first report of a stable Ti^{III} titanocycle. On the other hand, the Ti^{IV} titanocycle is certainly difficult to reduce since the Ti^{IV}/Ti^{III} couple has a very negative formal potential; it is > 1 V more negative than the $Cp_2TiCl_2/[Cp_2TiCl_2]^-$ couple. No further reduction processes and no oxidations were observed when the potential limits of the voltammogram was extended. The Ti^{III} titanocycle should, however, be a good nucleophile and this was confirmed by recording the voltammetry in a solution saturated with CO_2. The reduction peak became completely irreversible.

4. Discussion

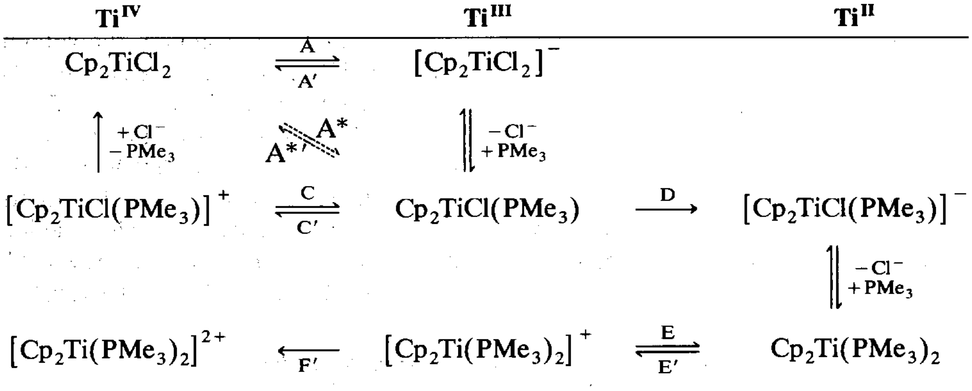
In the $Cp_2TiCl_2/PMe_3/Cl^-$ system in THF, three oxidation states of the metal are stable but the preferred ligands at each oxidation level are different. The most stable complexes are:

Ti^{IV} Cp_2TiCl_2

Ti^{III} $Cp_2TiCl(PMe_3)$

Ti^{II} $Cp_2Ti(PMe_3)_2$

Each of these species is stable enough to allow isolation of the solids and prolonged storage of their solu-



Scheme 1.

TABLE 1. Formal potentials for the Ti^{IV}/Ti^{III} and Ti^{III}/Ti^{II} couples in THF estimated by cyclic voltammetry. In brackets, the letter reports the label for the peaks on the cyclic voltammograms

Ti^{IV} species	E^0 for Ti^{IV}/Ti^{III} (V *vs.* Cp_2Fe/Cp_2Fe^+)	E^0 for Ti^{III}/Ti^{II} (V *vs.* Cp_2Fe/Cp_2Fe^+)
Cp_2TiCl_2	-1.29 (A)	-2.49 (B)
$[Cp_2TiCl(PMe_3)]^+$	-0.95 (C)	-2.75 [a] (D)
$[Cp_2Ti(PMe_3)_2]^{2+}$	-0.47 [a] (F)	-1.95 (E)

[a] Estimated since the voltammetric peak is irreversible.

tions provided there is protection from oxygen and water.

After any change in the oxidation state of the titanium, ligand substitution reactions appear to be facile and fast. Equilibrium is rapidly established following reduction or oxidation with the most stable species at the new oxidation state predominating provided the solution contains the stoichiometric concentration of the required ligand. The electrode reactions and the complex coupled chemistry are summarized in Scheme 1. As a result of this facile interchange of ligands, the redox chemistry of these Ti complexes will also be strongly influenced by the presence of a small excess of chloride ion or phosphine. For example, it was noted above the chemistry of $Cp_2Ti(PMe_3)_2$ might be markedly affected by the Cl^- formed during the electrolytic preparation from Cp_2TiCl_2, and hence the reactivity of such solutions may not be the same as that of solutions formed from crystalline $Cp_2Ti(PMe_3)_2$. For example, yields from synthetic reactions using the Ti^{II} complex may not be the same. It is also possible to envisage ligand substitution reactions induced by catalytic quantities of electrons or redox reagents.

The formal potentials for the Ti^{IV}/Ti^{III} and Ti^{III}/Ti^{II} couples with the various combinations of ligands are summarized in Table 1. It can be seen that successive replacement of Cl^- by PMe_3 always makes the reduction of Ti^{IV} to Ti^{III} easier by 300–400 mV. The effect of this substitution on the Ti^{III}/Ti^{II} couple is more complex. Two phosphine ligands lead to a strong positive shift in the formal potential compared to two chlorides; *i.e.* the phosphines provide thermodynamic stabilization of Ti^{II}. On the other hand, the replacement of one Cl^- by PMe_3 appears to make the reduction of Ti^{III} to Ti^{II} more difficult, and this is consistent with $Cp_2TiCl(PMe_3)$ being the most stable Ti^{III} species. It is also noteworthy that the metal centre in titanocycles can be reduced, and that the Ti^{III} metallocycle is stable, at least on a voltammetric timescale (10–100 s).

We believe that the results in this paper provide a valuable insight into the redox chemistry and ligand substitution reactions of a type of titanium species widely used in organic synthesis. The paper includes the first examples of the voltammetry of a Ti^{II} complex as well as of a titanocycle. Moreover, it has been demonstrated that both $Cp_2TiCl(PMe_3)$ and $Cp_2Ti(PMe_3)_2$ can be prepared electrochemically, and this could be the first step in the development of new electrosynthetic procedures.

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