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The synthesis and electrochemistry of $CpTiCl_2(OR)$ ($R = $ alkyl, aryl) complexes

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Abstract

The syntheses of several new $CpTiCl_2(OR)$ (R = alkyl, aryl) complexes are described. It was possible to isolate pure product when the R group is substituted such as to cause steric crowding at the metal centre; for example, particularly good yields of the phenolate complexes were obtained when there were isopropyl substituents in the 2 and 6 positions of the phenolate. Electrochemical studies of the complexes in dry THF show that the Ti^{III} complexes are relatively stable, but only a diol complex could be reduced further to a Ti^{II} species. In general, the Ti^{IV} complexes undergo a reversible $1e^-$ reduction reaction. The chemistry is more complex if the electrolyte contains added water: both the Ti^{IV} and Ti^{III} complexes can react with water, the OR group being replaced by OH. The reaction is particularly rapid for the Ti^{III} alkoxide complexes.

Key words: Titanium; Cyclopentadienyl; Synthesis; Reduction; Electrochemistry

1. Introduction

Cyclopentadienyl titanium complexes have been investigated as catalysts for a wide range of reactions, including the polymerization of alkenes [1–3], the hydrogenation and isomerization of alkenes [4,5], the coupling of carbonyl compounds [6–8], Wittig type reactions [9,10], radical cyclizations [11], the formation of metallocycles [12–15] and nitrogen fixation [16–19]. Commonly, some of these reactions are thought to occur via titanium in a lower oxidation state, and various authors postulate the involvement of the oxidation states +3, +2 and 0. In general, however, there is little experimental evidence to support the oxidation state involved.

Electrochemical experiments provide a rapid and reliable method of determining the stability of transition metal complexes in lower oxidation states as well as the formal potentials for the couples involved. Up to now studies of the electrochemistry of cyclopentadienyl titanium complexes have been limited. The most intensively studied complex is Cp_2TiCl_2 [20–26], and even with this simple species, the literature is complicated by the discussion about whether or not the initial $1e^-$ reduction is followed by the rapid and reversible loss of chloride, i.e.

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

$$[Cp_2TiCl_2]^- + sol \rightleftarrows [Cp_2TiCl(sol)] + Cl^- \qquad (2)$$

where sol is a solvent molecule or Lewis base. The various authors have provided compelling evidence both for the stability of the initial anion radical and for rapid substitution of chloride, and, indeed, this may indicate that the rate of the substitution depends strongly on the experimental conditions; for example, the water content of the medium. Reports of the electrochemistry of $CpTiCl_3$ and its derivatives are particularly limited [27]. Hence, there remains a need for electroanalytical studies of a broader range of cyclopentadienyl titanium complexes.

In this paper, we report the synthesis and electrochemistry of a family of complexes with the formula $CpTiCl_2(OR)$ (R = alkyl, aryl) (see Fig. 1). The starting material was always $CpTiCl_3$ and the preparations therefore involved the substitution of a chlorine by the

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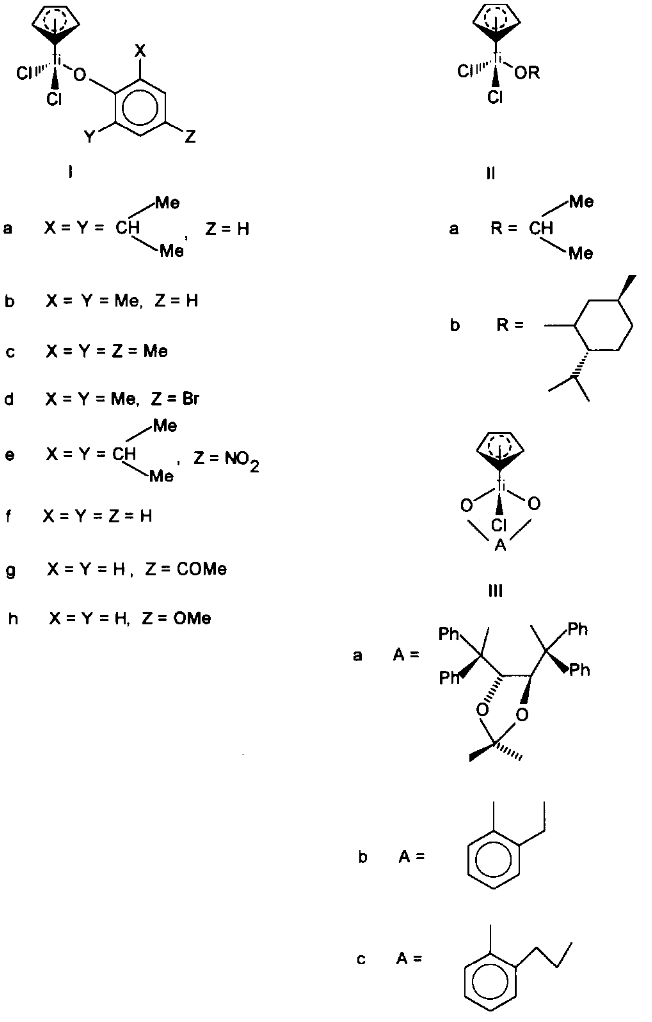

Fig. 1. Structures of the titanium(IV) complexes synthesized and studied in this paper.

OR group. Few CpTiCl$_2$(OR) compounds have previously been reported. During the course of this work, Höhlein and Schobert [28] described the preparation of a series of such complexes where OR is a secondary alkoxy group (including **IIb**); they used Cp$_2$TiCl$_2$ as the source of titanium and displaced a cyclopentadienyl ring by an alkoxy group by heating with a stoichiometric amount of the secondary alcohol in benzene in the presence of triethylamine, and the yields of CpTiCl$_2$(OR) were good (40–90%). An earlier paper [29] describes similar reactions of Cp$_2$TiCl$_2$ with simple primary alcohols such as ethanol, but diverse products including Cp$_2$TiCl(OC$_2$H$_5$), CpTiCl$_2$(OC$_2$H$_5$) and CpTiCl(OC$_2$H$_5$)$_2$ were reported and the yields were poor. Duthaler and co-workers [30–32] recently described the reaction of CpTiCl$_3$ with carbohydrate derivatives in the presence of triethylamine and application in synthesis of the resulting CpTiCl(OR)$_2$ complexes. Another method for the introduction of OR groups has been described by Kalirai *et al.* [33]; they formed sodium phenoxide by reaction of the phenol with sodium hydride before the addition of Cp$_2$TiCl$_2$, yielding Cp$_2$Ti(OAr)$_2$ complexes.

2. Experimental details

2.1. Synthesis

All reactions were performed under argon by use of standard Schlenk techniques; the argon was passed through a column of molecular sieves before entering the reaction vessel and all glassware was dried in an oven at 150°C for at least 12 h prior to use. Evacuation of apparatus to 0.05–0.2 mbar was achieved with an Edwards two-stage oil pump connected *via* a vacuum line, and pressures were measured with an Edwards vacustat 2 gauge.

The ^{1}H and ^{13}C NMR were recorded on a JOEL GX 270 FT nmr spectrometer. Mass spectra were obtained with a VG Analytical 70-250-SE Normal Geometry Double Focusing mass spectrometer. All electron ionisation (EI) data were recorded at 6 kV at 70 eV with a source temperature of 200°C.

Most reagents were supplied by Aldrich, including Cp$_2$TiCl$_2$ in 97% purity. The 2,6-di-isopropylphenol and 2-isopropyl alcohol were distilled before use. All solvents were dried and distilled. Diethyl ether, benzene and THF were distilled from Na/benzophenone with tetraglyme. Hexane was dried with concentrated H$_2$SO$_4$ and MgSO$_4$ before distillation from Na/benzophenone. Dichloromethane, xylene, and triethylamine were distilled from CaH$_2$. THF was used straight from the still; all other solvents were stored in sealed glass vessels under argon and transferred by syringe.

The synthetic procedures are described below.

2.1.1. Monocyclopentadienyl titanium trichloride, CpTiCl$_3$ [34]

TiCl$_4$ (14.7 ml, 130 mmol) was added to a solution of Cp$_2$TiCl$_2$ (12 g, 48 mmol) in xylene (100 ml) and the mixture was refluxed for 3 h and allowed to cool room temperature. Large dirty yellow crystals separated and the solvent was carefully decanted off with a constant stream of argon passing through the flask. The crystals were washed with hexane (3 × 30ml) then heated in benzene (110 ml) with some decolourizing charcoal (3 small spatula heads). The mixture was filtered hot through a large glass in-line sinter. A clear yellow solution emerged, and this was set aside overnight to allow for CpTiCl$_3$ to crystallize out, giving a first crop of 8.3 g of bright yellow crystals (78% yield). A second crop was obtained by concentrating the remaining solution. A total yield of 97% was obtained.

^1H NMR ($CDCl_3$): δ 7.05 (s). ^{13}C NMR ($CDCl_3$): δ 123.6. Melting point: 108–110°C (literature [34] 110°C).

2.1.2. Preparation of (2,6-di-isopropyl)-4-nitrophenol [35]

2,6-Di-isopropylphenol (5 ml, 27 mmol) was dissolved in 2,2,4-trimethylpentane (10 ml) and 50% aqueous nitric acid (1.6 ml, 0.4 equivalents) added dropwise at such a rate as to keep the temperature less than 30°C. After *ca.* 30 min stirring, the colour of the mixture changed from pale yellow to orange and a precipitate formed. Stirring was continued for another 1.5 h, and the mixture then cooled and filtered and the residue washed thoroughly with water. This residue was recrystallized from 2,2,4-trimethylpentane (10 ml), to give a cream-coloured product (yield 18%).

^1H NMR ($CDCl_3$) δ 8.0 (2H, s); 5.50 (1H, s); 3.18 (2H, septet, $J = 6.76$ Hz); 1.31 (12H, d, $J = 6.76$ Hz). ^{13}C NMR ($CDCl_3$): δ 155.9, 134.7, 120.2, 27.5, 22.5.

2.1.3. Preparation of substituted cyclopentadienyl titanium dichloride complexes, $CpTiCl_2[OR]$

The complexes were prepared by two methods each involving use of 3–5 mmol of starting materials. The procedures are illustrated by the synthesis of **Ia**.

2.1.3.1. Method A. The complex $CpTiCl_3$ (0.66 g, 3 mmol) was dissolved in diethyl ether (60 ml) to give a clear yellow solution. 2,6-Di-isopropylphenol (0.55 ml, 3 mmol) was added, the solution was stirred for approximately 2 min and triethylamine (0.46 ml, 3.3 mmol) was then added dropwise. An immediate white precipitate was observed, along with a colour change of the solution to orange. The mixture was stirred overnight then filtered through an in-line glass sinter. The residue was washed twice with Et_2O (2 × 20 ml), the washings were combined with the filtrate, and the solvent was removed *in vacuo* to leave an orange/red solid. This was recrystallized from hexane (25 ml) to give compound **Ia** in 70% yield.

2.1.3.2. Method B. Sodium hydride (0.6 g of a 60% suspension in oil, 15 mmol) was washed with petroleum ether (5 ml) to remove the oil, then dried under vacuum. Toluene (40 ml) and 2,6-di-isopropylphenol (0.9 ml, 5 mmol) were added and the mixture was stirred for 0.5 h at 100°C (oil bath). A solution of $CpTiCl_3$ (1.1 g, 5 mmol) in toluene (40 ml) was added, the mixture changing colour from yellow to orange. The mixture was left stirring at 100°C overnight, allowed to cool to room temperature, and then filtered through a glass sinter packed with kieselguhr. The toluene was removed *in vacuo* and the resulting orange/red solid recrystallized from hexane (40 ml). Compound **Ia** was isolated in 63% yield.

2.1.4. Analytical data for the $CpTiCl_2[OR]$ complexes

*Compound **Ia***: Colour, orange/red; m.p. 128–129°C. ^1H NMR ($CDCl_3$): δ 7.04–7.16 (3H, m); 6.72 (5H, s); 3.25 (2H, septet, $J = 6.8$ Hz); 1.25 (12H, d, $J = 6.8$). ^{13}C NMR ($CDCl_3$): δ 164.6 (s); 138.3 (s); 124.7 (d); 123.5 (d); 120.9 (d); 27.1 (d); 23.7 (q). EI mass spec.: *m/e* 360 (M^+, 85%); 345 ($M^+ - CH_3$, 22%); 309 ($M^+ - CH_3 - HCl$, 100%); 288 ($M^+ - 2HCl$, 70%); 273 ($M^+ - 2HCl - CH_3$, 16%); 183 ($M^+ - C_{12}H_{17}O$, 15%); 177 ($C_{12}H_{17}O^+$, 20%).

*Compound **Ib***: Colour, orange/red; m.p. 114–115°C. ^1H NMR ($CDCl_3$): δ 6.90–7.10 (3H, m); 6.73 (5H, s), 2.30 (6H,s). ^{13}C NMR ($CDCl_3$): δ 128.6, 127.6, 124.2, 121.0 (d); 17.4 (q). EI mass spec.: *m/e* 305 (M^+, 90%), 268 ($M^+ - HCl$, 20%); 232 ($M^+ - 2HCl$, 100%); 203 ($M^+ - HCl - Cp$, 25%); 183 ($M^+ - C_8H_9O$, 24%); 148 ($M^+ - C_8H_9O - Cl$, 23%); 121 ($C_8H_9O^+$, 24%).

*Compound **Ic***: Colour red; m.p. 108–110°C. ^1H NMR ($CDCl_3$): δ 6.81 (2H, s); 6.72 (5H, s); 2.27 (9H, s). ^{13}C NMR ($CDCl_3$): δ 133.9, 129.1, 127.4, 120.9, 21.0, 17.4. EI mass spec.: *m/e* 318 (M^+, 90%); 282 ($M^+ - HCl$, 12%); 246 ($M^+ - 2HCl$, 54%); 217 ($M^+ - Cp - HCl$, 17%); 183 ($M^+ - C_9H_{11}O$, 10%); 135 ($C_9H_{11}O^+$, 100%).

*Compound **Id***: Colour, orange/red; m.p. 136–138°C. ^1H NMR ($CDCl_3$): δ 7.20 (2H, s); 6.73 (5H, s); 2.25 (6H, s). ^{13}C NMR ($CDCl_3$): δ 131.2 (s); 129.7 (s); 122.4 (s); 121.2 (d); 120.7 (d); 17.3 (q). EI mass spec.: *m/e* 382 (M^+, 100%), 309 ($M^+ - 2HCl$, 27); 266 ($M^+ - Cp - HCl - CH_3$, 24%); 182 ($M^+ - C_8H_9OBr$, 30%).

*Compound **Ie***: Colour, yellow/orange; m.p. decomposes above 200°C. ^1H NMR ($CDCl_3$): δ 8.03 (2H, s); 6.77 (5H, s); 3.21 (2H, septet, $J = 6.8$ Hz); 1.28 (12H, d, $J = 6.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 167.5 (s); 143.6 (s); 139.8 (s); 121.6 (d); 119.9 (d); 27.5 (d); 23.4 (q). EI mass spec.: *m/e* 405 (M^+, 90%); 390 ($M^+ - CH_3$, 15%); 354 ($M^+ - CH_3 - HCl$, 100%); 333 ($M^+ - 2HCl$, 15%); 304 ($M^+ - HCl - Cp$, 57%).

*Compound **IIa***: Colour, yellow; m.p. 104–105°C. ^1H NMR ($CDCl_3$): δ 6.70 (5H, s); 4.97 (1H, septet, $J = 6.2$ Hz); 1.38 (6H, d, $J = 6.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 119.0 (d); 87.3 (d); 25.0 (q). EI mass spec.: *m/e* 242 (M^+, 20%); 227 ($M^+ - CH_3$, 100%); 200 ($M^+ - C_3H_6$, 16%); 183 ($M^+ - C_3H_7O$, 67%); 164 ($M^+ - C_3H_6 - HCl$, 40%); 148 ($M^+ - C_3H_6O - HCl$, 32%).

*Compound **IIb***: Colour, yellow; m.p. 89–90°C. ^1H NMR ($CDCl_3$): δ 6.66 (5H, s); 4.50 (1H, dt, $J = 4.2$, 10.5 Hz); 2.27 (1H, double septet, $J = 15$, 6 Hz); 2.13 (1H, m); 1.55–1.70 (2H, m); 1.35–1.70 (2H, m); 1.27 (1H, q, $J = 7$ Hz); 0.96 (3H, d, $J = 6.4$ Hz); 0.92 (3H, d, $J = 7$ Hz); 0.90 (2H, m); 0.83 (3H, d, $J = 7$ Hz). ^{13}C

NMR ($CDCl_3$): δ 119.0 (d); 95.9 (d); 50.6, 44.6 (t); 34.1 (t); 32.0, 25.9, 22.8 (t); 22.2, 21.0, 15.8. EI mass spec.: *m/e* 338 (M^+, 12%); 302 ($M^+ - HCl$, 100%); 266 ($M^+ - 2HCl$, 18%); 253 ($M^+ - 2HCl - CH$, 45%); 183 ($M^+ - C_{10}H_{19}O$, 30%).

2.2. Electrochemical experiments

The THF was distilled under nitrogen from Na/benzophenone before use. The supporting electrolyte, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), was prepared by mixing aqueous solutions of tetrabutylammonium hydrogen sulphate, Bu_4NHSO_4 (200 g, 0.5 mol) and sodium tetrafluoroborate (55 g, 0.5 mol). A thick white precipitate formed immediately. The aqueous mixture was filtered and the residue heated in a vacuum oven to remove the majority of the water. The white solid was then dissolved in ethyl acetate and the small water layer removed. The ethyl acetate layer was heated to dissolve all of the crude Bu_4NBF_4, and the solution was dried over $MgSO_4$ and filtered. Petroleum ether was added to the filtrate, which was then cooled to afford light white crystals. These were dried thoroughly in a vacuum oven and stored in a desiccator. Isolated yield 85%; m.p. 160–162°C (literature 162°C).

Electrochemical experiments were carried out in a sealed cell under conditions designed to minimize interference from water. All cell parts were dried in an oven at 150°C for at least 12 h prior to use and the cell was assembled hot. A weighed sample of the electroactive compound, along with a magnetic stirrer bead, was placed in the cell and the whole apparatus evacuated for 3–5 h with refilling with dried argon at intervals. The supporting electrolyte was melted in a separate flask under vacuum; after cooling, recently distilled THF was introduced into to this flask *via* a cannula. Once the Bu_4NBF_4 had dissolved, a cannula was again used to transfer the solution to the top of the drying column attached to the cell. The electrolyte solution passed through the activated alumina column (Woelm neutral, super 1 grade [36,37]) into the working compartment, and stirring was applied until all the solid active compound had dissolved. After the study of the compound of interest, ferrocene was added through a solid addition arm and another cyclic voltammogram was recorded.

The cell for voltammetry was designed to be operated on a vacuum line. A vitreous carbon disc (area = 0.05 cm^2), sealed in a glass tube, acted as the working electrode. The counter electrode was a platinum wire hoop while a silver wire, placed inside a Luggin capillary was used as a pseudo reference electrode (its potential was determined by the voltammetry of ferrocene, see above). The Luggin tip was placed close to, but not touching, the working electrode. The positions of both the working electrode and the Luggin capillary could be adjusted and, if essential, removed for cleaning by means of Young's greaseless sliding joints. The pear-shape of the main body of the cell was chosen in order to minimize the volume of electrolyte solution, hence reducing the amount of complex needed. A pressure-equalizing funnel was fitted to the top of the cell. A rotatable, bent, sealed glass tube was fitted to one side of the cell, this was used to add ferrocene to the electrolyte solution at the end of an experiment as an internal reference. Attachment to the vacuum line was *via* a vacuum tap connected on the other side of the cell. Elastic bands were used to hold all the Quickfit joints tightly together.

A modified cell allowed electrolyses to be carried out in similar conditions. The counter electrode was a cylindrical platinum gauze placed in a glass column separated from the working compartment by a glass sinter. The working electrode was a Pt gauze (area 4 cm^2) placed parallel to the sinter, and in order to minimize the cell resistance, the working and counter electrodes were each positioned close to the two sides of the sinter. The counter electrode compartment and the electrode itself were mounted on Young's greaseless sliding joints. The Luggin capillary tip could be manoeuvered so that its tip was close to the working electrode. The reference electrode was again a silver wire placed inside the Luggin capillary. Cyclic voltammograms were recorded both before and after electrolyses. This cell required 10 cm^3 of electrolyte and electrolyses could be completed within 30 min.

Voltammetry and electrolyses were carried out with a Hi-Tek Instruments potentiostat (model DT 2101) and waveform generator (model PPR1). The response was recorded on a Gould x-y recorder (model 60000).

3. Synthesis

Two procedures for the preparation of the $CpTiCl_2(OR)$ complexes were used. Method A was based on a procedure for the preparation of other cyclopentadienyl titanium complexes described by Riediker and Duthaler [30]; the $CpTiCl_3$ was treated with the alcohol or phenol in diethyl ether and triethylamine was used to remove the HCl as it was formed. In method B, the phenoxide was first formed by reaction of the phenol with NaH and then treated with $CpTiCl_3$; this procedure was adapted from a method described by Kalirai *et al.* [33].

In early experiments, method A was used in an attempt to prepare complex **If**, starting from unsubstituted phenol. On mixing of the reactants, the expected colour change from yellow to dark orange was ob-

TABLE 1. Isolated yields (%) of the $CpTiCl_2(OR)$ complexes

Compound	Method A	Method B
Ia	70	63
Ib	76	–
Ic	–	40
Id	50	42
Ie	–	86
IIa	50	–
IIb	70	–
IIIa	36	–

served and ^1H NMR of the product showed a large singlet for the cyclopentadienyl protons at $\delta = 6.71$ (*i.e.* at the chemical shift expected for the complex $CpTiCl_2(OC_6H_5)$). However, this spectrum also showed significant peaks which could not be assigned to this complex, clearly showing the product to be a mixture. All attempts to obtain crystals from the thick orange oil were unsuccessful. Similarly, reactions designed to lead to **Ig** and **Ih** gave mixtures of products. In contrast several complexes in which the aromatic ring had substituents in the 2,6-positions, *e.g.* **Ia**, **Ib** and **Id**, were isolated in good yields as pure crystalline products, as reported in Table 1. Similarly, although straight chain alcohols gave mixtures of products, secondary alcohols again gave satisfactory yields of a single product (see Table 1), **IIa** or **IIb**. This result is consistent with the outcome of previous syntheses [28,29] starting from Cp_2TiCl_2 and it appears that steric hindrance at the Ti centre is important for obtaining a single product, maybe preventing further substitution reactions.

Method A was unsuccessful for the preparation of **Ie**, and so method B was developed, and, gave an excellent yield of **Ie**. It also proved to be suitable for the preparation of the the other phenoxide complexes (see Table 1).

The synthesis of the diol complex **IIIa**, previously reported by Riediker and Duthaler [30] was successfully repeated. On the other hand, attempts to apply method A to the preparation of complexes **IIIb** and **IIIc** with bidentate diol ligands gave thick red oils that would not yield crystals. The ^1H NMR spectrum indicated that some **IIIb** had indeed, been formed but other products were also present. The NMR spectrum of the other reaction product was less promising, and there was little evidence for **IIIc** amongst the products. It should be noted that neither of these diol ligands is branched at the carbon bonded to the oxygen.

4. Electrochemistry

4.1. Dry solutions

Figure 2 shows a set of cyclic voltammograms recorded over the potential range -0.8 V to -1.6 V vs. the Cp_2Fe/Cp_2Fe^+ couple at a vitreous carbon disc electrode in a solution of complex **Id** (11 mM) in THF/Bu_4NBF_4 (0.2 M). It can be seen that over a range of potential scan rates, a well formed reduction peak is observed at -1.23 V and there is a coupled oxidation peak at -1.17 V. In addition, the peak currents are proportional to the square root of the potential scan rate and the ratio, I_p^{ox}/I_p^{red} is unity. Hence, it would appear that the complex undergoes a

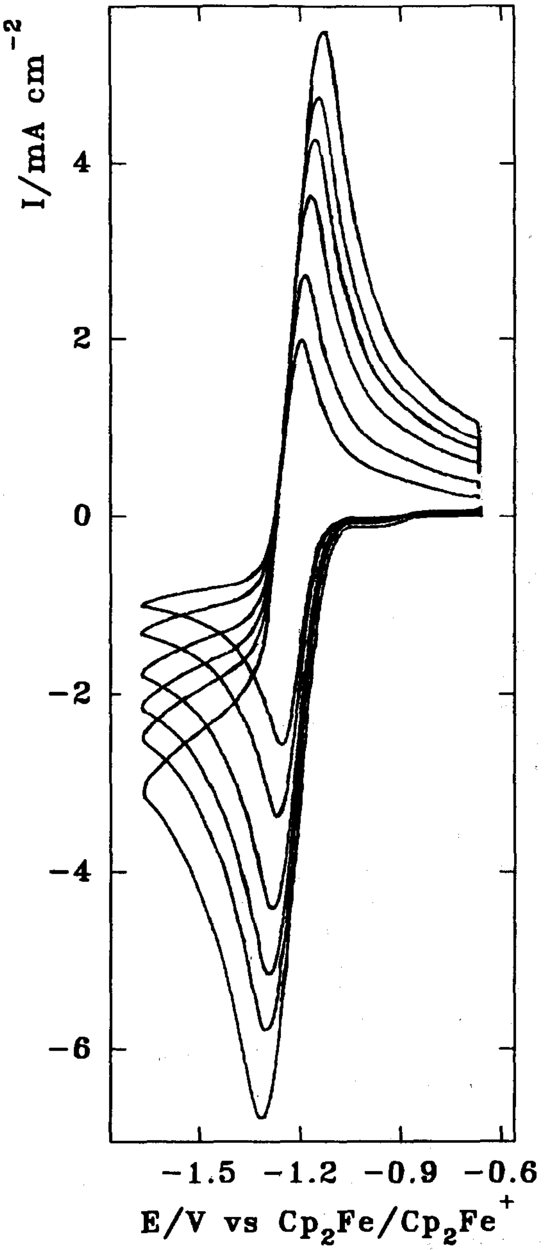

Fig. 2. Cyclic voltammograms for the complex **Id** (11 mM) in THF/Bu_4NBF_4 (0.2 M). Vitreous carbon disc electrode. Potential scan rates are 50, 100, 200, 300, 400 and 600 mV s^{-1}.

reversible $1e^-$ reduction and the reduced complex is fully stable. Confirmation that the reduction involves a single electron was obtained by recording voltammograms at a Pt microdisc electrode (diameter 10 μm); a well formed S-shaped reduction wave was observed at $E_{1/2} = -1.20$ V and there was little hysteresis between forward and back scans. Analysis of the mass-transport-controlled, limiting current at the microdisc leads to nD [38], and the slope of the I_p *vs.* $\nu^{1/2}$ plot from the cyclic voltammograms in Fig. 2 allows calculation of a value for n^3D [39]. Therefore, combining these two measurements allows n and D to be estimated independently; the values found were $n = 1.1$ and $D = 1.1 \times 10^{-5}$ cm^2 s^{-1}.

The only other feature of the voltammograms in Fig. 2 is a very small reduction wave at about -0.92 V, and this is discussed further below. Extension of the potential limits do not disclose any further redox processes within the limits imposed by oxidation/reduction of the THF/Bu_4NBF_4. Hence, the redox chemistry is limited to the reaction

$$\mathbf{Id} + e^- \rightleftarrows \mathbf{Id}^-$$

Electrolysis of a solution of complex **Id** (10 mM) in THF/Bu_4NBF_4 (0.2 M) at -1.6 V led to a change in the colour of the solution from orange to blue. A cyclic voltammogram at the end of the electrolysis showed only the response for the reversible oxidation of $\mathbf{Id}^-$. Hence, the titanium(III) complex is completely stable in dry THF even over a period of 1 h.

The cyclic voltammograms of the complexes **Ia**, **Ib** and **Ic** are very similar to that of **Id**. All show reversible $1e^-$ reduction processes. Moreover, electrolysis of **Ia** led to a colour change from red/orange to green and the product solution gave simple voltammetry for the oxidation of $\mathbf{Ia}^-$. Hence, these Ti^{III} complexes with phenoxide substituents all appear to be very stable in dry THF. It can be seen from the data in Table 2, taken from the voltammograms, that the formal potentials for the Ti^{IV}/Ti^{III} couples are insensitive to the substituents on the aromatic ring. The substitution of one chlorine of $CpTiCl_3$ by the phenoxide groups has made reduction more difficult by some 350 mV. The diffusion coefficients for the complexes were also estimated from the variation of the peak current densities with potential scan rate and the resulting values are also reported in Table 2. In fact, we believe that the values should all be approximately 1×10^{-5} cm^2 s^{-1}, and the lower values from some experiments result from uncertainties in the concentration of the electroactive species in work with the closed system on the vacuum line; for example, incomplete dissolution of the complex could be the problem.

TABLE 2. Data taken from cyclic voltammograms for the $CpTiCl_2(OR)$ complexes in THF/Bu_4NBF_4

Complex	E° (V) *vs.* Cp_2Fe/Cp_2Fe^+ [a]	10^5D (cm s^{-1})
$CpTiCl_3$	-0.86	0.9
Ia	-1.18	0.6
Ib	-1.20	1.0
Ic	-1.18	1.1
Id	-1.20	1.1
Ie	-1.00 [b]	1.1
IIa	-1.28 [c]	
IIb	-1.38	1.2
IIIa	-1.82	

[a] Formal potentials for the couple $CpTiCl_2(OR)/[CpTiCl_2(OR)]^-$.

[b] This is a reduction potential since the couple is irreversible.

[c] Again, this couple is only partially reversible.

The voltammetry of complex **Ie** is quite different. A reduction peak is observed at -1.00 V *vs.* Cp_2Fe/Cp_2Fe^+, but at slow potential scan rates it is totally irreversible, and only at scan rates above 0.3 V s^{-1} is there evidence for a coupled oxidation peak (see Fig. 3). At all scan rates, the peak current densities are similar to those for complexes **Ia**–**Id**, indicating that the reduction is probably still a $1e^-$ transfer process. A

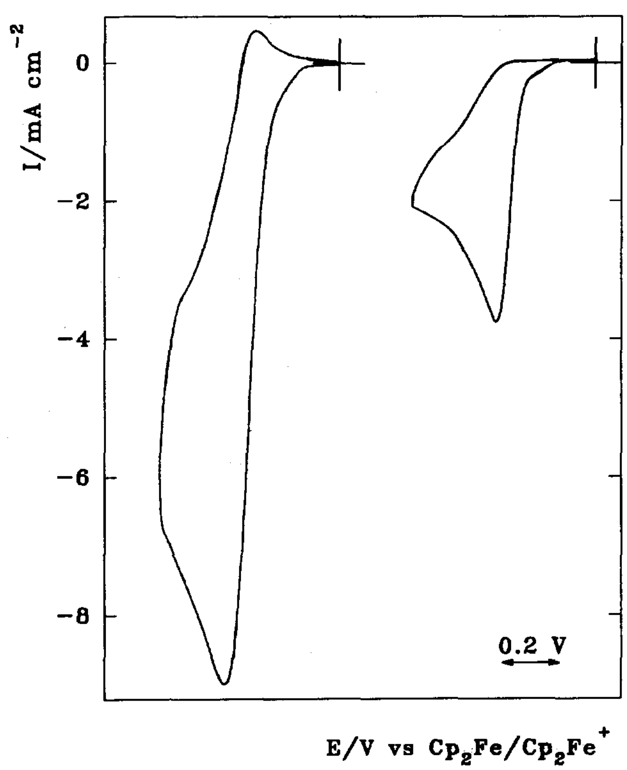

Fig. 3. Cyclic voltammograms for the complex **Ie** (14 mM) in THF/Bu_4NBF_4 (0.2 M). Vitreous carbon disc electrode. Potential scan rates are 100 and 800 mV s^{-1} and the scans were each commenced from -0.66 V.

second reduction process, also irreversible, is seen at -2.02 V. The low stability of **Ie**$^-$ was confirmed by electrolysis; after complete reduction, the voltammogram showed no oxidation or reduction peaks. The shift in the reduction potential probably indicates that reduction occurs, not at the Ti centre but rather at the nitro group, a readily reduced group in aprotic media. The resulting anion radical is, however, unusually unstable (the anion radicals of nitroaromatic molecules are normally very stable); one possibility is that cleavage of the Ti–O bond occurs, to form the phenoxide and $CpTiCl_2$ or its dimer.

Figure 4 shows a set of voltammograms for the alkoxy derivative, **IIa**. A reduction peak is always seen at -1.32 V, but at slow potential scan rates this reduction process is completely irreversible. An important anodic peak is, however, observed at -0.86 V. At higher scan rates, the reduction process at -1.32 V becomes more reversible, since the anodic peak at -1.25 V grows in importance while that at -0.86 V shrinks relative to the other peaks. The peak current for the reduction process is proportional to the square root of the potential scan rate and its magnitude indicates that it is a 1e$^-$ reaction. Hence, the reduced species decays by a chemical reaction (with a half life ≈ 10 s) and the product of the chemical change is reoxidized at -0.86 V. The nature of this chemistry is discussed further below.

The voltammetry of complex **IIb** is similar, although it is evident that the reactions of the reduced intermediate are much slower. At potential scan rates > 0.5 V s^{-1}, a clean response for a reversible reduction is seen, but at slower scan rates the peak current ratio drops below one and another anodic peak grows at -0.86 V. It can be seen from the data in Table 2 that the alkoxy derivatives are more difficult to reduce than the aromatic derivatives.

A cyclic voltammogram for the diol complex **IIIa** shows two reduction processes; the first is reversible but the second appears to be irreversible. The formal potential for the Ti^{IV}/Ti^{III} couple has at a substantially larger negative value than those for the $CpTiCl_2(OR)$ complexes, *i.e.* -1.85 V.

Overall, it is clear that titanium(III) is the dominant, and often the only, reduced oxidation state with these cyclopentadienyl titanium complexes. Moreover, the reduced species have considerable stability, although the stability of the Ti^{III} species does depend on its structure. The studies of the synthesis of the Ti^{IV} complexes suggests that resistance of the products to further substitution requires steric protection of the Ti centre. The results of the electrochemical experiments

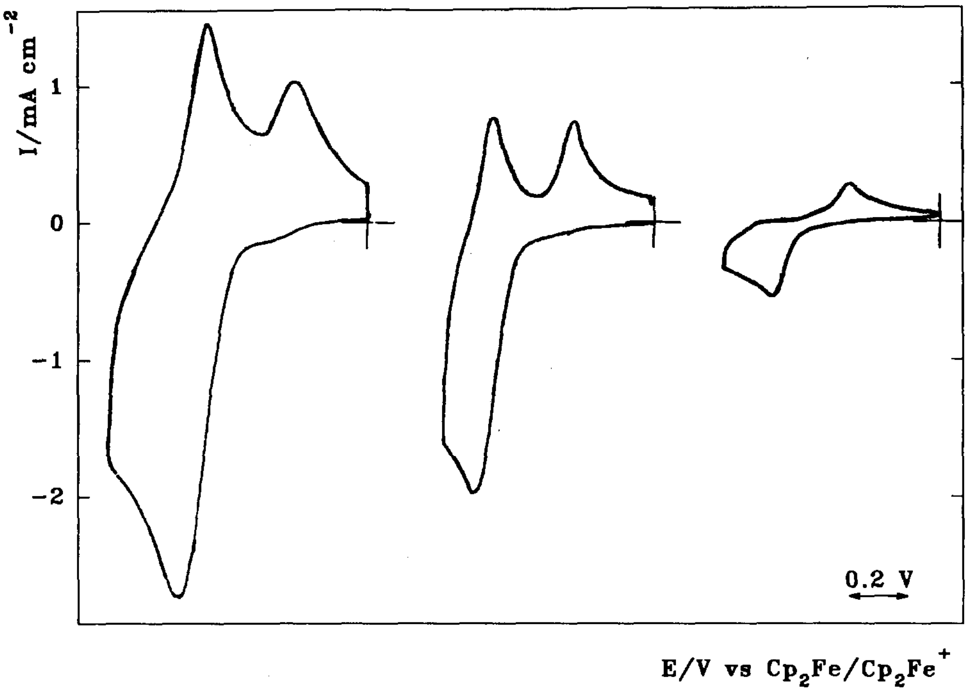

Fig. 4. Cyclic voltammograms for the complex **IIa** (7 mM) in THF/Bu_4NBF_4 (0.2 M). Vitreous carbon disc electrode. Potential scan rates are 36, 225 and 400 mV s^{-1}. The initial potential for each scan was -0.60 V.

are consistent with the same factors determining the stability of the reduced complexes. The Ti^{III} complexes are, however, less stable than the Ti^{IV} complexes. The formal potential for the Ti^{IV}/Ti^{III} couple is influenced by whether the substituent is an alkoxide, aryloxide, or diol, but not by the nature of substituents in the aromatic ring.

4.2. The influence of added water

It should be emphasized that, in order to obtain the electrochemical responses described above, it is necessary to work with carefully dried chemicals and to take stringent precautions to avoid contamination by water during the experiments. Indeed, it took considerable time and effort to develop the procedures described in the Experimental section. During this programme, it became clear that the concentration of water in solution influenced the results strongly. The behaviours of the aryloxide and the alkoxide complexes towards water are different.

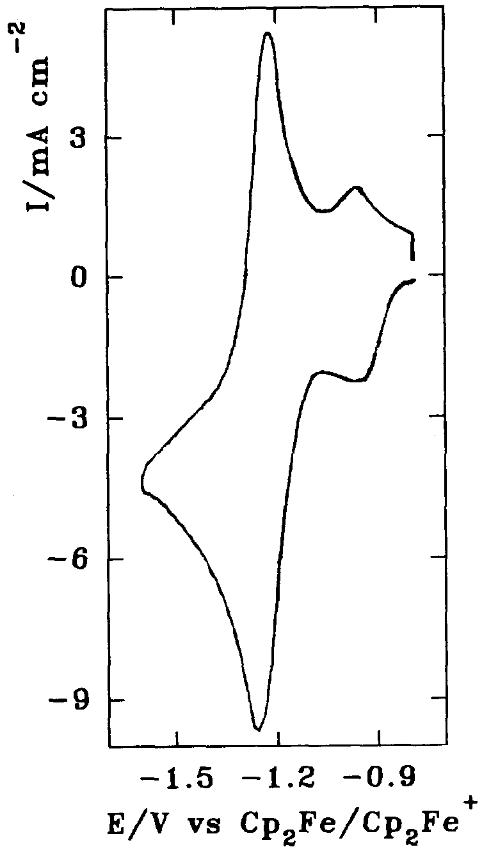

Fig. 5. Cyclic voltammograms for the complex **Id** (21 mM) in THF/Bu$_4$NBF$_4$ (0.2 M) where the Bu$_4$NBF$_4$ has been poorly dried and hence the medium contains some water. Vitreous carbon disc electrode. Potential scan rate is 400 mV s^{-1}.

Figure 5 reports a voltammogram recorded at 0.4 V s^{-1} for a typical aryloxide complex, **Id**, in a solution containing some water (in fact, the Bu$_4$NBF$_4$ was not melted under vacuum before use). There are clearly two cathodic and two anodic processes and comparison of this response with that in Fig. 2 shows that the reduction peak at −0.92 V is much larger, although still a small fraction of the total current. The peak current density for this process is proportional to the square root of the potential scan rate and hence there is no limitation from homogeneous kinetics. Indeed, the response is that for two reversible 1e$^-$ reductions, and it would appear that the two processes arise from two different species in solution (with no interconversion of the species on the timescale of the voltammetric experiment). The first peak only arises when water is present. Hence, it is logical to assume that the first peak arises from substitution of a ligand of CpTiCl$_2$(OR) in a reaction involving water. Several experiments suggest that it is -OR group that is displaced; for example, (a) the potentials of the additional cathodic/anodic peaks are the same for all the complexes studied (both aryloxide and alkoxide complexes), and (b) addition of free chloride ion does not effect the data. Hence, a likely reaction is

$$\mathrm{CpTiCl_2(OR) + H_2O \rightleftarrows CpTiCl_2(OH) + ROH}$$

The anodic and cathodic peaks close to −0.90 V are for the process

$$\mathrm{CpTiCl_2(OH) + e^- \rightleftarrows [CpTiCl_2(OH)]^-}$$

The processes associated with the two pairs of peaks are apparently totally independent, and therefore there is no interconversion of CpTiCl$_2$(OR) and CpTiCl$_2$(OH) on the timescale of a voltammetric experiment (10 s) when R = aryl.

For the alkoxide complexes, however, the anodic peak at −0.86 V is always much larger than the corresponding cathodic peak at −0.92 V if the potential range includes the reduction of the CpTiCl$_2$(OR) complex (see for example, in Fig. 4, the responses for complex **IIa**). Moreover, the importance of the anodic peak at −0.86 V grows as the reduction peak for CpTiCl$_2$(OR) becomes irreversible, i.e. as the potential scan rate is lowered or more water is added. Figure 6 reports some voltammograms for complex **IIa** in incompletely dried solutions where the potential range is limited to exclude reduction of CpTiCl$_2$(OR). Firstly, it can be seen that the reduction peak at −0.92 V is much larger in the wetter solution. Secondly, with the restricted potential scan, it can be seen that this reduction process is reversible. To explain the large anodic peaks in Fig. 4, the electroactive species for this anodic peak must also be formed by decomposition of the

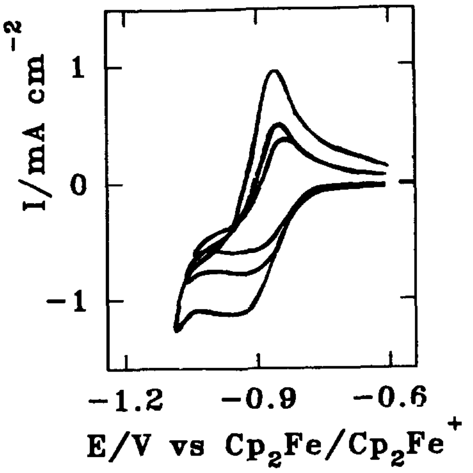

Fig. 6. Cyclic voltammograms for the complex **IIa** (19 mM) in THF/Bu_4NBF_4 (0.2 M) where the Bu_4NBF_4 has been poorly dried and hence the medium contains some water. Vitreous carbon disc electrode. Potential scan rates are 75, 100 and 600 mV s^{-1}. The negative potential limit is restricted so that $CpTiCl_2(OH)$ but not $CpTiCl_2(OR)$ is reduced.

reduced species formed in the main cathodic process at −1.32 V. This implies a reaction mechanism best described in a 'scheme of squares'

$$\begin{tikzcd} CpTiCl_2(OR) + e^- \arrow[r, shift left] \arrow[d, shift left] & {[CpTiCl_2(OR)]^-} \arrow[l, shift left] \arrow[d, shift left, "H_2O\text{-}ROH"] \\ CpTiCl_2(OH) + e^- \arrow[u, shift left, "ROH\text{-}H_2O"] \arrow[r, shift left] & {[CpTiCl_2(OH)]^-} \arrow[l, shift left] \arrow[u, shift left] \end{tikzcd}$$

OR = alkoxide

Even when the anodic peak at −0.86 V is very pronounced (see *e.g.* Fig. 3), the corresponding cathodic peak does not grow on the second potential cycle and hence the Ti^{IV} complex interacts more strongly with the OR group than with OH. Indeed, on the timescale of voltammetry, $CpTiCl_2(OH)$ is converted back to $CpTiCl_2(OR)$. With the Ti^{III} complexes, the competition between OR and OH is more favourable to OH, and depends on the concentration of water and the structure of OR.

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