Electron Transfer Processes involving $[M(\eta^5\text{-}C_5H_5)_2X_2]$, M = Ti or Zr, X = Cl or Br. Electrogeneration of Unusual Anionic Species

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Summary $M(\eta^5\text{-}C_5H_5)_2X_2$ (M = Ti, X = Cl or Br, M = Zr, X = Cl) is reduced electrochemically in tetrahydrofuran to give, in successive electrochemical steps, $[M(\eta^5\text{-}C_5H_5)_2X_2]^-$, $[M(\eta^5\text{-}C_5H_5)_2X_2]^{2-}$, and $[Ti(\eta^5\text{-}C_5H_5)_2X_2]^{3-}$, $[Ti(\eta^5\text{-}C_5H_5)_2X_2]^-$ is stable in solution and reacts with $PPhMe_2$ while $[Ti(\eta^5\ C_5H_5)_2X_2]^{2-}$ dissociates into X^- and $[Ti(C_5H_5)_2X]^-$ which also reacts with $PPhMe_2$

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It has been suggested that the dihalides of bis(cyclopentadienyl)titanium, [Ti(η^5-C_5H_5)$_2$$X_2$], undergo two successive irreversible reduction steps.[1,2] Each one corresponds to a one-electron transfer reaction, leading successively to the cleavage of the two metal–halogen bonds.[3] It has further been claimed that the species formed after the first electron transfer step is Ti(η^5-C_5H_5)$_2$X (X = Cl), but the nature of the species generated after the addition of the second electron is still in dispute.[2,3] We now report an electrochemical examination of [Ti(η^5-C_5H_5)$_2$$X_2$], in which we demonstrate the generation of anionic titanium complexes, and settle the nature of the products obtained after each successive reduction step.

By working with an electrochemical cell under high-vacuum conditions, we have performed electrochemical experiments (cyclic voltammetry, polarography, coulometry, and preparative electrolysis) coupled with spectroscopic studies on [Ti(η^5-C_5H_5)$_2$$X_2$] (X = Cl or Br) and on [Zr(η^5-C_5H_5)$_2$$Cl_2$]. The use of high-vacuum methods, with pure solvents and supporting electrolytes, has enabled reproducible data to be obtained.

In tetrahydrofuran (THF) the polarogram (dropping mercury electrode) of Ti(η^5-C_5H_5)$_2$$X_2$ exhibits three reduction waves A, B, and C. A invariably corresponds to a one-electron transfer reaction. The height of B and C waves depends on the mercury drop time, τ; C decreases when τ increases. For τ = 2 s (X = Cl) or τ = 1 s (X = Br), the wave C disappears and the height of B is then equal to that of A.

The cyclic voltammogram of [Ti(η^5-C_5H_5)$_2$$X_2$] at a glassy carbon or Pt electrode, at a scan rate of 0·1 V s^{-1}, shows that the first electron transfer reaction is highly reversible‡ while the other two transfers are only slightly reversible (Figure 1). For scanning rates of 0·025 V s^{-1}, these last two electron transfers became completely irreversible, whereas the first wave is entirely reversible.

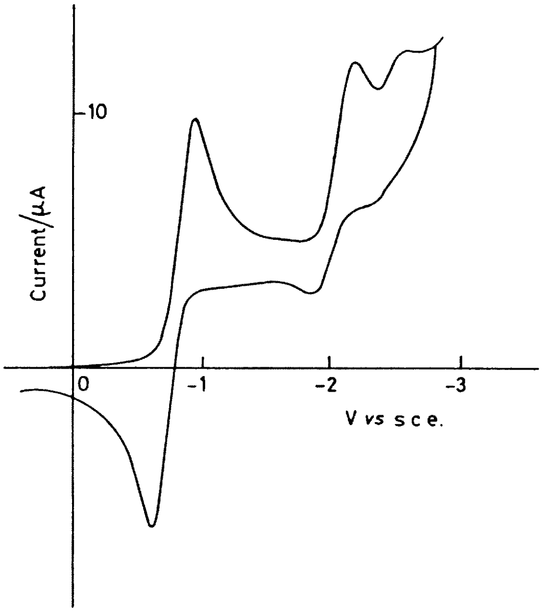

Figure 1. Cyclic voltammogram of Cp_2TiCl_2, in THF–Bu_4NPF_6, at glassy carbon electrode; scan rate = 0·1 V s^{-1}. S.c.e. = standard calomel electrode.

A thin layer linear potential sweep voltammogram shows that the wave A is completely reversible even for scan rates of 0·001 V s^{-1}, and this indicates that the one-electron reduction of [Ti(η^5-C_5H_5)$_2$$X_2$] affords a stable radical anion [Ti(η^5-C_5H_5)$_2$$X_2$]$^-$. The species [Ti($\eta^5$-$C_5H_5$)$_2$$X_2$]$^-$ were generated electrolytically at the potential equivalent to A over a mercury pool in THF using [Bu^n_4N][PF_6] as supporting electrolyte. These electrolyses gave solutions (X = Cl, yellow-green; X = Br, green) which had polarograms similar to those of the precursors, except that the wave A was anodic. Solutions containing [Ti(η^5-C_5H_5)$_2$$X_2$]$^-$ are stable for up to one day at room temperature in the absence of moisture or oxygen; no polarographic evidence could be obtained for the existence of free halide ions.

The e.s.r. spectra (25 °C) of solutions containing [Ti(η^5-C_5H_5)$_2$$X_2$]$^-$ exhibit one line when X = Cl (g = 1·9789, line width 10 G) and an ill-defined multiplet when X = Br (g = 1·9899, line width = 22 G). In both cases, satellite splittings due to ^{47}Ti and ^{49}Ti were observed. Addition of $PPhMe_2$ to solutions containing the titanium radical anion caused these signals to split into a doublet (22 G) owing to the interaction of the unpaired electron with ^{31}P (X = Cl, g = 1·9865; X = Br, g = 2·0017).

The addition of $PPhMe_2$ to [Ti(η^5-C_5H_5)$_2$$X_2$]$^-$ may give an adduct in which both rings are pentahapto and the metal in the reduced species has a 19-electron configuration. It is also possible however, that one or both rings in the reduced complex are no longer pentahapto, but have become tri- or even mono-hapto. E.s.r. and electrochemical techniques cannot, of course, reveal the true nature of this species.

A cyclic voltammogram of [Ti(η^5-C_5H_5)$_2$$X_2$]$^-$ in the presence of $PPhMe_2$ showed that the peak A had become irreversible, and a new oxidation peak D appeared at more positive potentials. Repetitive scanning showed that A and D are quasi-reversible; D corresponding to the regeneration of Ti(η^5-C_5H_5)$_2$$X_2$: Ti($\eta^5$-$C_5H_5$)$_2$$X_2$ + $PPhMe_2$ + e$^-$ $\rightleftharpoons$ [Ti(C_5H_5)$_2$$X_2$$PPhMe_2$]$^-$. This was confirmed by preparative electrolyses.

Electrolysis of [Ti(η^5-C_5H_5)$_2$$X_2$] at potentials corresponding to B gave, after the transfer of *two* electrons, blue-violet solutions which exhibited an e.s.r. signal (X = Cl, g = 1·9786; X = Br, g = 1·9801). When the reduction was carried out electrolytically in the presence of $PPhMe_2$, the e.s.r. signal was split (separation 22 G; X = Cl, g = 1·9781; X = Br, g = 1·99·6), again because of the interaction of the unpaired electron with ^{31}P.

Polarograms of solutions obtained after electrolyses at the potential of B in the presence or absence of $PPhMe_2$ revealed that C was absent and, furthermore, that one halide anion was liberated per mole of [Ti(η^5-C_5H_5)$_2$$X_2$]. No free cyclopentadienide ion was detected after electrolysis as was observed in the reduction of Ti(η^5-C_5H_5)$_2$$Q_2$ (Q = R, OAr, $OSiR_3$).[4]

No evidence could be obtained for the formation of [Ti(η^5-C_5H_5)$_2$] or a combination between a reduced titanium species and the base electrolyte after the addition of two electrons to [Ti(η^5-C_5H_5)$_2$$X_2$].

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‡ The cyclic voltammetry of Cp_2TiX_2 performed in the presence of Cp_2Fe shows an identical peak spread for this first step and the Cp_2Fe^+–Cp_2Fe system, which is known to be completely reversible in THF (J. D. L. Holloway and W. E. Geiger, Jr., *J. Am. Chem. Soc.*, 1979, **101**, 2038).

These results are not consistent with the formation of a Ti^{II} species, which must either be diamagnetic or have two unpaired electrons. However, here also, a chemical rearrangement of one or both rings has to be considered; no evidence concerning the exact nature of these species can be obtained using e.s.r. and electrochemical techniques.

Our new electrochemical results are fully consistent with the reaction (1). The subsequent electrochemical data can

$$Ti(\eta^5\text{-}C_5H_5)_2X_2 + e^- \rightleftharpoons [Ti(\eta^5\text{-}C_5H_5)_2X_2]^- \qquad (1)$$

$$[Ti(\eta^5\text{-}C_5H_5)_2X_2]^- + e^- \rightleftharpoons [Ti(C_5H_5)_2X_2]^{2-} \qquad (2)$$

$$\begin{tikzcd}[Ti(C_5H_5)_2X_2]^{2-} + e^- \arrow[r, phantom, "\rightleftharpoons"] & {[Ti(C_5H_5)_2X_2]^{3-}} \arrow[dl] & (3) \\ {[Ti(C_5H_5)_2X]^- + X^-} & & \end{tikzcd}$$

be interpreted in terms of the reactions (2) and (3). Reactions involving reduction of Ti species in the presence of $PPhMe_2$ could be interpreted electrochemically in terms of the steps (4) and (5). However, in the absence of full spectral and structural data, it is impossible to determine the exact nature of these reduced species.

$$\begin{tikzcd}Ti(\eta^5\text{-}C_5H_5)_2X_2 + PPhMe_2 + e^- \arrow[dr, Rightarrow] & \\ \text{or} & {[Ti(C_5H_5)_2\text{-}X_2PPhMe_2]^-} \quad (4) \\ {[Ti(\eta^5\text{-}C_5H_5)_2X_2]^- + PPhMe_2} \arrow[ur] & \end{tikzcd}$$

$$\begin{tikzcd}{[Ti(C_5H_5)_2X_2PPhMe_2]^- + e^-} \arrow[dr] & \\ \text{or} & {[Ti(C_5H_5)_2\text{-}XPPhMe_2]^- + X^-} \quad (5) \\ {[Ti(C_5H_5)_2X]^- + PPhMe_2} \arrow[ur] & \end{tikzcd}$$

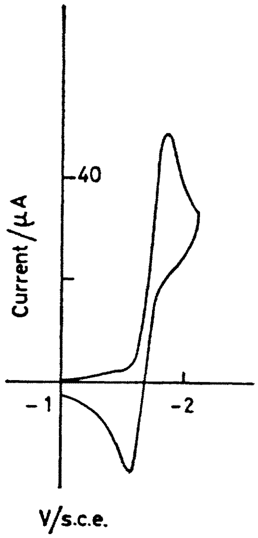

FIGURE 2. Cyclic voltammogram of $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$ in THF–Bu_4NPF_6, at a glassy carbon electrode; scan rate = 0·1 V s^{-1}.

In a related study of $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$ we have observed the electrochemically reversible generation of $[Zr(\eta^5\text{-}C_5H_5)_2\text{-}Cl_2]^-$ (Figure 2) but the subsequent behaviour of this species is different to that reported elsewhere[3a] and seems to be dependent on traces of moisture.

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