Electrochemical behaviour of some polyoxo clusters

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Abstract

We describe the redox behaviour in non-aqueous solvents of some cyclopentadienyl(oxo)titanium derivatives. The derivative $[Ti_4\{\eta^5\text{-}C_5H_4(SiMe_3)\}_4(\mu\text{-}O)_6]$ shows an electrochemically and chemically reversible 1e reduction process, followed by a multi-electron, chemically complicated reduction at a fairly cathodic potential. On the basis of the overall electrochemical features and the comparison with the redox behaviour of the quasi-planar compound $[[Ti\{\eta^5\text{-}C_5H_4(SiMe_3)\}Cl(\mu\text{-}O)]_4]$, we propose an EECCEE mechanism for the first derivative, where the second electron-transfer induces a cascade of chemical reactions giving rise to irreversible cluster breakdown. The electrochemically induced fragmentation can be viewed as a retrosynthetic pathway. The heterometallic derivative $[\{Ti(\eta^5\text{-}C_5H_4Me)_2(\mu_2\text{-}MoO_4)_2\}_2]$ shows two consecutive reduction processes; the first is chemically reversible, and the second quasi-reversible. The molybdate bridges apparently increase the stability of the electrogenerated anions. However none of these poly-oxo clusters can be considered as good models of electron 'sinks'.

Keywords: Polyoxo clusters; Electrochemistry; Titanium; Reaction mechanisms

1. Introduction

Polyoxo clusters are attractive as model systems for metal oxides in solution. Provided that the presence of organic ligands guarantees enough solubility in non-aqueous solvents, it is possible to perform catalytic reactions in a homogeneous phase [1]. Discrete poly-oxo-bridged derivatives of titanium(IV) can be synthesized either by controlled oxidation of suitable Ti^{III} precursor or by controlled hydrolysis of titanium(IV) compounds under acidic or basic conditions. Hydrolysis of $[Ti(\eta^5\text{-}C_5R_5)Cl_3]$ (R = H, Me, $SiMe_3$, etc.) is an efficient method to produce dinuclear μ-oxo-complexes, together with trimers and tetramers, depending upon the nature of Cp-substituents and reaction conditions [2] (Fig. 1). We have studied the tetramer $[Ti_4\{\eta^5\text{-}C_5H_4(SiMe_3)\}_4(\mu\text{-}O)_6]$, 1, (Fig. 2) because of its reasonable solubility and stability in organic solvents, especially tetrahydrofuran (THF). Its electronic structure has been studied using extended-Hückel molecular-

orbital (EHMO) calculations which show that the HOMO set is mainly localized on the Cp, with little contribution from the metal d orbitals, and that the LUMO set essentially corresponds to non-bonding Ti d orbitals [2].

Compounds which also contain oxo-bridges between different metals could be of interest in this context. For instance, Carofiglio et al. reported the complexation of molybdate anions with cyclopentadienyltitanium(IV) cations to produce $[\{Ti(\eta^5\text{-}C_5H_4Me)_2(\mu_2\text{-}MoO_4)_2\}_2]$ (Fig. 2) [3].

In this work, cyclic voltammetry (CV), d.c. polarography, and square wave voltammetry (SWV) have been used to elucidate the redox properties of such compounds.

2. Results and discussion

Fig. 3 shows the CV response of a THF solution of $[Ti_4\{\eta^5\text{-}C_5H_4(SiMe_3)\}_4(\mu\text{-}O)_6]$, 1, containing $[Bu_4N][PF_6]$ (0.2 M) as the supporting electrolyte, at a hanging mercury-drop electrode (HMDE). The cathodic sweep reveals two reduction processes (peaks A and C), the

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[CpTiCl$_3$]+ H$_2$O ────────► [Cp$_2$Ti$_2$(μ-O)Cl$_4$] (linear)

│ + H$_2$O

────────► [Cp$_4$Ti$_4$(μ-O)$_4$Cl$_4$] (quasi-planar)

│ + H$_2$O

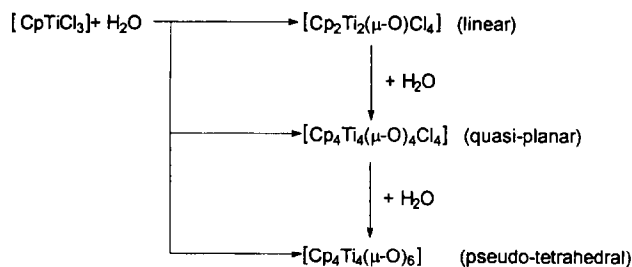────────► [Cp$_4$Ti$_4$(μ-O)$_6$]   (pseudo-tetrahedral)

Fig. 1. Sketch of the hydrolysis leading to the compounds under study.

latter peak being much larger than the former, and their ratio depending upon scan rate. The lack of an associated reoxidation peak in the reverse scan, as well as the appearance of extra peaks at less negative potentials shows the instability of the anion electrogenerated at the potential of peak C. If the cathodic scan is limited to the first reduction process (peak A) by reversing the scan at the potential $E_\lambda = -1.95$ V (dotted line in Fig. 3), a well-behaved associated reoxidation peak B can be observed. Under these experimental conditions, the relevant electrochemical data for the A/B peak couple are as follows.

(1) A plot of $i_p(A)$ vs. $v^{1/2}$ is linear through the origin indicating a diffusion-controlled process.

(2) A comparison of the trend of $\Delta E_p = E_p(B) - E_p(A)$ at various scan rate (0.05–50.00 V s^{-1}) with that of ferrocene added as an internal standard indicates that this reduction is electrochemically reversible (see Experimental).

(3) The ratio $i_p(B)/i_p(A)$ is unity in the above interval of scan rate showing that the process is chemically reversible.

(4) The value of $[E_p(B) + E_p(A)]/2$ is independent of scan rate and corresponds very well to the formal electrode potential of the process, $E^{o\prime}(0/1 -) = -1.55$ V vs. SCE.

The $(0/1 -)$ process undergone by 1 is therefore electrochemically and chemically reversible and implies a fast 1e transfer without important structural rearrangements of the cluster framework [4].

As far as the second reduction is concerned, $E_p(C) = -2.31$ V vs. SCE at 0.2 V s^{-1}, the $E_p-E_{p/2}$ breadth is not consistent with a multi-electron-transfer process. The width $E_p-E_{p/2}$ is almost independent of scan rate and its average value (65 mV) is close to that deduced for a 1e Nernstian process (57 mV) [4]. A plot of $E_p(C)$ vs. log v is linear with a slope of 37 mV and reasonably consistent with the theoretical cathodic shift of 29 mV per decade for a first-order chemical reaction following a 1e reduction process [5].

In order to reconcile the current behaviour (indicating a multi-electron process) with the potential behaviour (indicating a fast 1e transfer) of the second reduction process (peak C), we suppose an overall EEC$_n$EE mechanism [6]. The second 1e reduction step is followed by a cascade of fast chemical reactions (C$_n$) generating fragments electroactive at the potential of peak C (up to a further addition of 2e). Indeed, the ratio $i_p(C)/i_p(A)$ is dependent on the scan rate, being approximately 3 at 0.05 V s^{-1}, but drops to 1 at 50 V s^{-1},
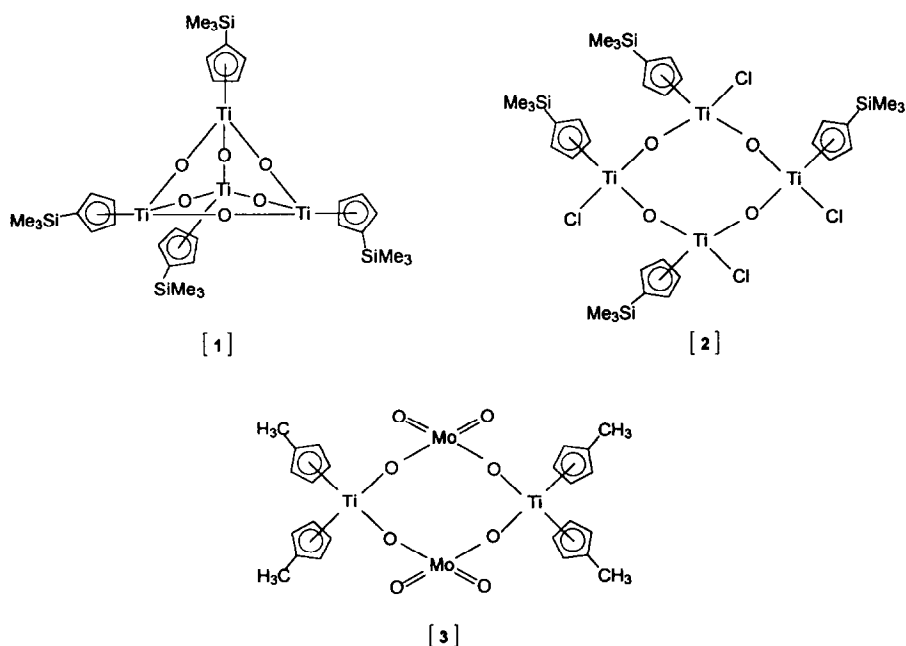
Me$_3$Si

[1]

Me$_3$Si

[2]

[3]

Fig. 2. Sketch of the structure of [Ti$_4${η^5-C$_5$H$_4$(SiMe$_3$)}$_4$(μ-O)$_6$], 1, [[Ti{η^5-C$_5$H$_4$(SiMe$_3$)}Cl(μ-O)]$_4$], 2, and [{Ti(η^5-C$_5$H$_4$Me)$_2$(μ$_2$-MoO$_4$)$_2$}$_2$], 3.
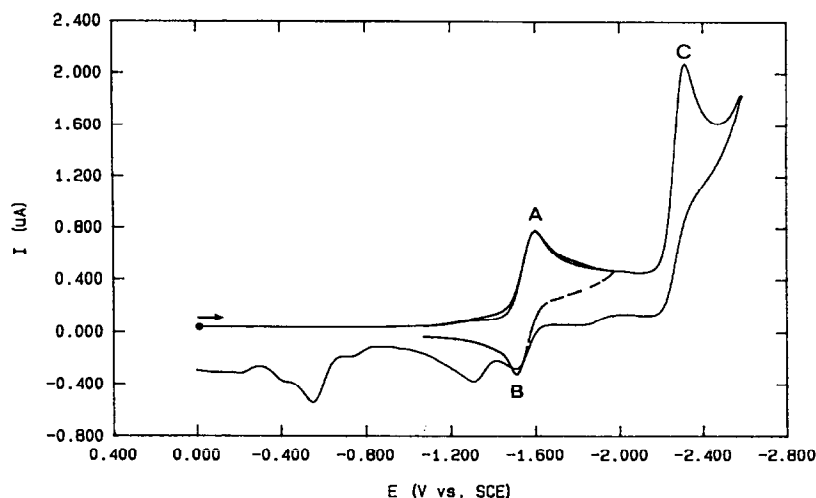
Fig. 3. Cyclic voltammogram of 1 in THF 0.2 M [Bu$_4$N][PF$_6$] at an HMDE, scan rate $v = 0.2$ V s^{-1}.

confirming that when the chemical complications are suppressed by the short time scale of the experiment, the mechanism simplifies to an EE process.

The polarographic response confirms the electrochemically reversible character for both processes, and the electron stoichiometry. Two well-resolved waves are observed, having half-wave potentials $E_{1/2}(A) = -1.55$ and $E_{1/2}(C) = -2.24$ V vs. SCE. Both plots of E vs. log $[(i_d - i)/i]$ have a slope of 60 mV, as expected for a 1e Nernstian (fast electron-transfer) process. The ratio between the two limiting currents, $i_d(C)$ and $i_d(A)$, is 2.8.

Finally, the SWV response of a THF solution of 1 exhibits two reduction maxima, having E_{su} values of -1.55 and -2.50 V [7]. The summit current ratio $i_{su}(C)/i_{su}(A)$ is lower than the peak current ratio

$i_p(C)/i_p(A)$ obtained from CV experiments. This confirms that the fast chemical complications are entirely associated with the second reduction process. The plots of i_{su} vs. the square root of frequency (in the range 10–400 Hz) are linear through the origin for both reductions, and the peak widths $W_{1/2}$ are almost independent of frequency and close to the value expected for a Nernstian one-electron process (99 mV at 25°C) [8].

The closeness of potentials obtained by CV, polarography, and SWV, confirms once again the electrochemical reversibility of both processes. The cathodic shift of the second reduction maximum in SWV can be associated with rapid chemical complications [8].

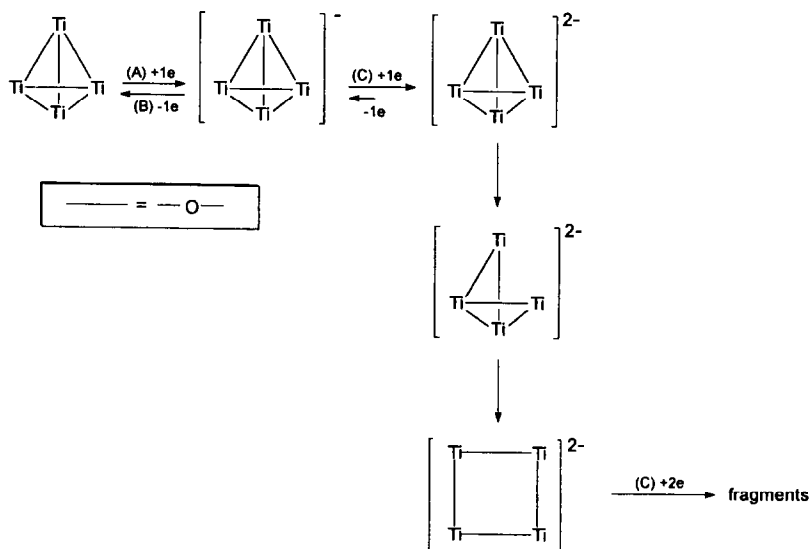Any mechanism proposed must explain that while peak A is always a 1e, electrochemically and chemi-

Fig. 4. Proposed mechanism for the electrochemical reduction of 1.

cally reversible, reduction, peak C suggests a multi-electron transfer (up to 3e) in slow techniques (polarography or CV at low scan rate). However, peak C is consistent with a simple 1e-process in fast techniques (SWV or high-speed CV). The proposed EECCEE mechanism is shown in Fig. 4. Compound 1 undergoes the first electron-transfer (peak couple A/B) generating a moderately stable and chemically unmodified monoanion 1^-. The second electron-transfer, although fast, induces a cascade of chemical reactions from 1^{2-}. The species produced by such a decomposition may be similar to the intermediates found in the synthesis of 1 by controlled hydrolysis [2]. The sequence of geometrical rearrangements from tetrahedral to 'butterfly' and finally to planar has been found experimentally in the reaction of the parent cluster 1 with $TiCl_4$ [9]. The decomposition pattern induced by electrochemical reduction can be considered as a retrosynthetic pathway, such as those often postulated in organic chemistry based upon analysis of mass spectra fragmentation patterns [10].

A coulometric experiment performed using a Pt basket was hampered by the moderate solubility of the compound in THF. However, at $E_{appl} = -1.7$ V vs. SCE, about 1 F $mole^{-1}$ was consumed smoothly. The electrogenerated anion 1^- is unstable at room temperature on the electrolysis time-scale (about 1 h). The initial yellow solution turns deep blue during the electrolysis, but the degree of decomposition is very high, as confirmed by in situ CV tests. After complete electrolysis, the solution no longer exhibits the anodic peak B, associated with 1^-, but there are two other chemically irreversible reductions at $E_p = -1.87$ V and -2.09 V vs. SCE, together with a strong reoxidation peak at $E_p = -0.18$ V vs. SCE (scan rate 0.2 V s^{-1}). This anodic peak is consistent with the presence of $C_5H_4(SiMe_3)^-$ in solution [11]. The EPR spectrum of a

partially-electrolyzed (0.5 F $mole^{-1}$) solution of 1, frozen to liquid nitrogen temperature, shows a very sharp axial signal with $g_{\parallel} = 2.0034$ and $g_{\perp} = 2.0025$ ($\Delta H_{pp} \simeq 2$–3 G). At ambient temperature, the isotropic spectrum is completely lost in the baseline. The position and the shape of the EPR signal are consistent with the presence of an organic radical. However the lack of any hydrogen hyperfine coupling does not permit further elucidation.

To gain insight into the proposed reaction sequence (Fig. 4), we studied the electrochemistry of the quasi-planar compound $[[Ti\{\eta^5\text{-}C_5H_4(SiMe_3)\}Cl(\mu\text{-}O)]_4]$, 2 (Fig. 2). The presence of chlorine ligands causes strong adsorption phenomena and perturbation of double-layer characteristics, giving rise to poor CV responses (Fig. 5). The cathodic sweep reveals two reduction processes (peaks D and F), the latter being stronger than the former. If the cathodic scan is limited to the first reduction (peak D) by reversing the scan at the potential $E_\lambda = -1.0$ V, a well-behaved associated reoxidation peak E can be observed (dotted line in Fig. 5). Apart from the presence of a polarographic maximum associated with the second wave, the polarographic response gives better results. Two reduction waves are observed, at $E_{1/2}(D) = -0.76$ V and $E_{1/2}(F) = -1.39$ V. Wave D corresponds to a 1e, Nernstian process (plot of E vs. log $[(i_d - i)/i]$ slopes 60 mV). The relative ratio $i_d(F)/i_d(D)$ is about 1.8. If we interpret the CV response on the basis of the polarographic data, we infer that a chemically reversible 1e process at $E^{o\prime}(0/1 -)$ $= [E_p(D) + E_p(E)]/2 = -0.77$ V vs. SCE, is followed by a 2e chemically irreversible reduction, $E_p(F) = -1.53$ V vs. SCE at 0.2 V s^{-1} scan rate. The reduction of 2^- [$E_p(F) = -1.53$ V] occurs at less cathodic potentials than that of reduction of 1^- [$E_p(C) = -2.31$ V]. These features support the proposed mechanism. If 1^{2-} becomes quasi-planar upon geometrical reorganization
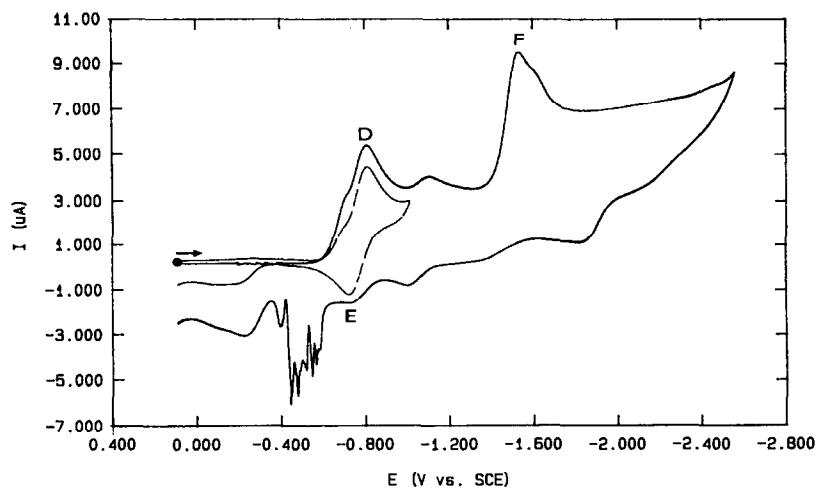

Fig. 5. Cyclic voltammogram of 2 in THF 0.2 M [Bu$_4$N][PF$_6$] at an HMDE, scan rate $v = 0.2$ V s^{-1}.

(Fig. 4), it should be able to take up two further electrons at the same potential, thus explaining the multi-electron character of peak C, with its electron stoichiometry dependent upon the scan rate.

If the EHMO results on the neutral parent **1** are still applicable to its electrogenerated anion, i.e. the LUMO set corresponds to non-bonding Ti d orbitals, we conclude that two Ti atoms, are no longer able to stabilize the μ-oxo bridge when both are reduced to the oxidation state III. Thus, the progressive reduction of **1** quickly destabilizes the oxo-bridges, and after the addition of 2e, total breakdown of the cluster framework occurs (possibly through intermediates having 'butterfly' and quasi-planar structures, as depicted in Fig. 4).

The heterometallic compound [{$(\eta^5$-MeC$_5$H$_4)_2$Ti-(μ_2-MoO$_4)_2\}_2$], **3**, has a molecular geometry similar to that of **2**. Fig. 6 shows the CV response of a dichloromethane solution of **3**, at an HMDE at different scan rates. The cathodic sweep reveals two reduction processes (peaks G and I). The weakness of the associated reoxidation peaks (H and L respectively) in the reverse scan, as well as the appearance of extra peaks, proves the instability of the electrogenerated anions upon reversing the potential at $E_\lambda = -1.1$ V, so that the cathodic scan is limited to the first reduction (peak G), the i_p(H)/i_p(G) ratio becomes unity. The formal reduction potentials are $E^{o\prime}$(G/H) = -0.87 V, and $E^{o\prime}$(I/L) = -1.39 V vs. SCE. The analysis of the electrochemical data for the G/H and I/L couples indicates that both processes are diffusion-controlled and electrochemically reversible, the former being chemically reversible and the latter quasi-reversible. The ratio i_p(I)/i_p(G) is about 1.5 at scan rate 0.2 V s^{-1}, but reaches unity at higher scan rates, so that when chemical complications are quenched, both reductions correspond to 1e processes as confirmed by the comparison with the oxidation peak of ferrocene, added as internal standard in equimolar concentration.

The polarographic response is consistent with the CV data. Two well-resolved waves with the same limiting current are observed. The half-wave potentials $E_{1/2}$ are -0.87 and -1.36 V vs. SCE. Both plots of E vs. log [$(i_d - i)/i$] have slope 60 mV, as expected for a 1e Nernstian process.

A coulometric experiment performed at a Hg pool confirms the stoichiometry of the reduction. At $E_{appl} = -1.1$ V, 1 F mole^{-1} is consumed. The electrogenerated anion **3**$^-$ is not stable at room temperature on the coulometric time scale. The initial orange solution turns to a green one during the electrolysis. After complete electrolysis, the reduced solution does not exhibit the anodic peak H, but there are two partially overlapping peaks at -1.37 V and -1.45 V vs. SCE at 0.2 V s^{-1}, potentials near that of E_p(I). This could explain why peak I is stronger than peak G at low scan rates. The fragments produced after the first reduction are reduced at the same potential as **3**$^-$. The anion **3**$^-$ is stable on the short CV time scale, but not in the electrolysis time scale. The EPR spectrum of the green solution frozen to liquid nitrogen temperature shows an axial signal with $g_\parallel = 1.93$ and $g_\perp = 1.90$ ($\Delta H_{pp} = 40$ G). At ambient temperature, the isotropic spectrum completely vanishes. The EPR data are consistent with those obtained by Chaloyard et al. revealing the existence of a Ti^{III} species after the first reduction [11]. Thus, the molybdate bridge is more robust toward Ti$^{IV} \rightarrow$ Ti^{III} reduction than the oxo-bridge.

For these polyoxo-clusters the concept of 'electron reservoir' or 'electron sponge', coined for transition metal compounds such as cubane-like systems, is not fully applicable [12].

3. Experimental section

The oxo-clusters **1**, **2** and **3** were synthesised by published procedures [2,3]. Electrochemical measure-
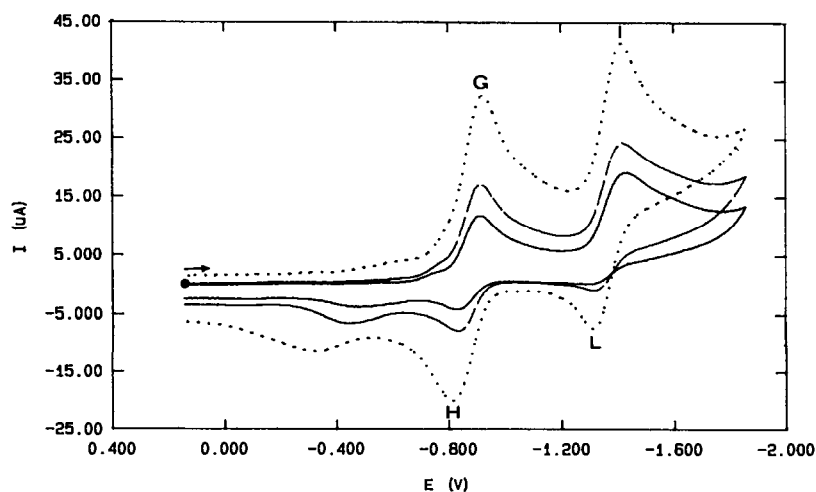

Fig. 6. Cyclic voltammogram of **3** in THF 0.2 M [Bu$_4$N][PF$_6$] at an HMDE, scan rates $v = 1, 2$ and 10 V s^{-1}.

ments were performed using both EG&G PAR 273 and EG&G PAR 263 electrochemical analysers interfaced to personal computers, employing EG&G PAR M270 electrochemical software. A standard three-electrode cell was designed to allow the tip of the reference electrode to approach closely the working electrode. Positive feedback iR compensation was applied routinely. All measurements were carried out under N_2 in anhydrous deoxygenated solvents. The temperature of the solution was kept constant to within $1°C$, by circulation of a thermostatically controlled water–ethanol mixture through the double wall of the cell. Since some iR drop distortion is present in the highly resistive THF and dichloromethane media, the peak-to-peak separation ΔE_p as a function of the CV scan rate, was compared with that of ferrocene (added as internal standard). Therefore, electrochemically reversible or Nernstian indicates that an electron-transfer process is as fast as that of the oxidation of ferrocene [13]. The working electrode was an HMDE (Metrohm Mod. 6.0335). The reference electrode was a AgCl-coated silver wire dipped in a 0.2 M solution of $[Bu_4N][PF_6]$ in the solvent used in the electrochemical cell, and separated from the cell solution by a Vycor frit. At the end of each experiment, the potential of the ferrocene $(0/1 +)$ couple was measured vs. the pseudo-reference electrode and then vs. an aqueous SCE, to which all data are referred. Under the actual experimental conditions the ferrocene/ferrocenium couple is at $+0.56$ V in THF and $+0.46$ V vs. SCE in dichloromethane.

The EPR spectra were recorded on a Varian E-109 instrument operating in the X-band mode equipped with a variable-temperature accessory. Varian pitch $(g = 2.0028)$ was use a reference standard for g value calibration.

Acknowledgements

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