

Electron transfer in *trans*-[Pt(PPh₃)₂(-C≡C-Fc)₂] and related compounds[☆]

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Abstract

The electrochemical behaviour of the title complex shows two reversible 1e oxidations centred on the ferrocenyl moieties, indicating a moderate electronic communication between such redox units through the organic chain and the Pt hinge. Moreover, two irreversible 1e reductions are detected, and assigned to the stepwise Pt^{II} → Pt⁰ process. The transient Pt^I intermediate is somewhat stabilized by the electronic delocalization over the external ferrocenyl units. The assignment of the redox processes is carried out by comparison of the electrochemical behaviour of several model complexes, which represent the building blocks of the overall molecule.

Keywords: Electron transfer; Electrochemistry; Platinum complexes; Acetylide complexes; Ferrocenyl complexes

1. Introduction

Transition metal polyacetylide complexes [1] represent an interesting class of rigid, linear molecules in virtue of their potential as non-linear optical (NLO) [2] and low-dimensional conducting (LDC) materials [3]. Because of the introduction of the metal moieties into the poly-yne backbone, these compounds show enhanced performances compared to the conventional organic polymers (i.e. polyacetylene). The metal centres can act both in transferring electron density to/from the chain and ensuring suitable bulk properties (i.e. 'rigid rod' behaviour). Evidence from optical spectra suggest that the π system of these polymers extend over the organometallic fragments [4]. This interaction has been confirmed by photoelectron spectroscopy of metal-d π -butadiynyl derivatives [5]. Ferrocene derivatives represent the prototypes of redox-active molecules, and their properties have been the object of many interesting investigations [6]. Covalently bonded ferrocene-tetrathiafulvalene derivatives show interesting electrochemical behaviour, involving charge transfer

reactions between the organic and the organometallic moieties [7]. Finally, bis-acetylide Pt^{II} complexes exhibit both second- and third-order NLO properties [8].

Whatever molecular hyperpolarizability or inter- and intramolecular conductivity is desired, the necessary (but not sufficient) requirement is a highly electronic delocalization through the chain. A simple qualitative method to evaluate these features may consist of an electrochemical measurement of the degree of electronic communication between two redox centres linked by the chain under study [9]. The title complex, namely *trans*-[Pt(PPh₃)₂(-C≡C-Fc)₂] (Fc = ferrocenyl), is ideally suited for such electrochemical studies. Indeed, this complex contains two reversible redox centres (the Fc moieties) bonded by the conjugate '-C≡C-Pt-C≡C-' chain (which may be considered the model of a repeating unit in an organometallic polymer); moreover, the Pt^{II} centre is itself electroactive.

2. Results and discussion

In order to obtain a detailed assignment of the redox processes occurring in *trans*-[Pt(PPh₃)₂(-C≡C-Fc)₂], we first investigated the electrochemistry of the following derivatives: ethynylferrocene, HC≡CFc (**1**), *trans*-

[☆]Dedicated to the memory of Dr Mauro Arbrun, a clever research student and dear friend.

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[Pt(PPh₃)₂(-C≡C-Ph)₂] (2), *trans*-[Pt(PPh₃)₂(R)(-C≡C-Fc)] (R = -C≡C-Ph (3), R = H (4)). Each of them represents a building block of the overall molecule and then provides information on the specific electron transfer process undergone by a given redox centre of *trans*-[Pt(PPh₃)₂(-C≡C-Fc)₂] (5) (Fig. 1).

Fig. 2 shows the cyclic voltammetric (CV) response of a tetrahydrofuran (THF) solution of **1**, 0.2 M in [NBu₄][PF₆], at a hanging mercury drop electrode (HMDE). An electrochemically and chemically reversible 1e oxidation process (peak system A/B) is

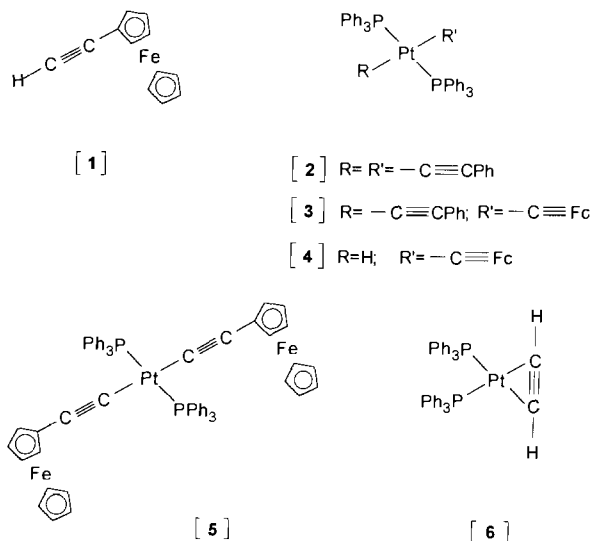


Fig. 1. Sketch of the structure of complexes 1-6.

observed at a formal electrode potential $E^{\circ'} = (E_p(A) + E_p(B))/2 = +0.70$ V versus SCE [10], as expected for a ferrocenyl redox centre. The $E^{\circ'}$ value of ethynylferrocene is more anodic than that observed for ferrocene in the same experimental conditions (i.e. +0.56 V versus SCE [11]), indicating the ability of the Fc moiety to inject electron density into the acetylenic chain.

A single reduction process (peak C) is observed in the cathodic sweep of a THF solution of **2** ($E_p(C) = -2.19$ V versus SCE at scan rate 0.2 V s^{-1}), together with some small peaks (due to reoxidation of electrogenerated fragments) in the reverse scan (Fig. 3). The electrochemical features for the reduction peak C are the following: (i) the peak current, $i_p(C)$, increases linearly with $v^{1/2}$ and concentration, indicating a diffusion-controlled process; (ii) the breadth of the peak measured at the half-width, $E_p - E_{p/2}$, increases from 48 to 86 mV as the scan rate increases from 0.05 to 5.00 V s^{-1} ; (iii) the plot of E_p versus $\log v$ is linear with a slope of ~ 50 mV. All these data are consistent with an electrochemically (slow electron transfer step) and chemically (short living reduction product) irreversible $2e$ reduction process, assigned to the $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^0$ reduction. The stoichiometry of such a reduction has been confirmed by comparison with the electrochemical response of ferrocene added in equimolar amount and correct for the diffusion coefficient and the degree of reversibility of the processes, and by potential controlled coulometry ($E_{\text{appl}} = -2.25$ V). This agrees with the usual electrochemical behaviour of Pt^{II} complexes [12].

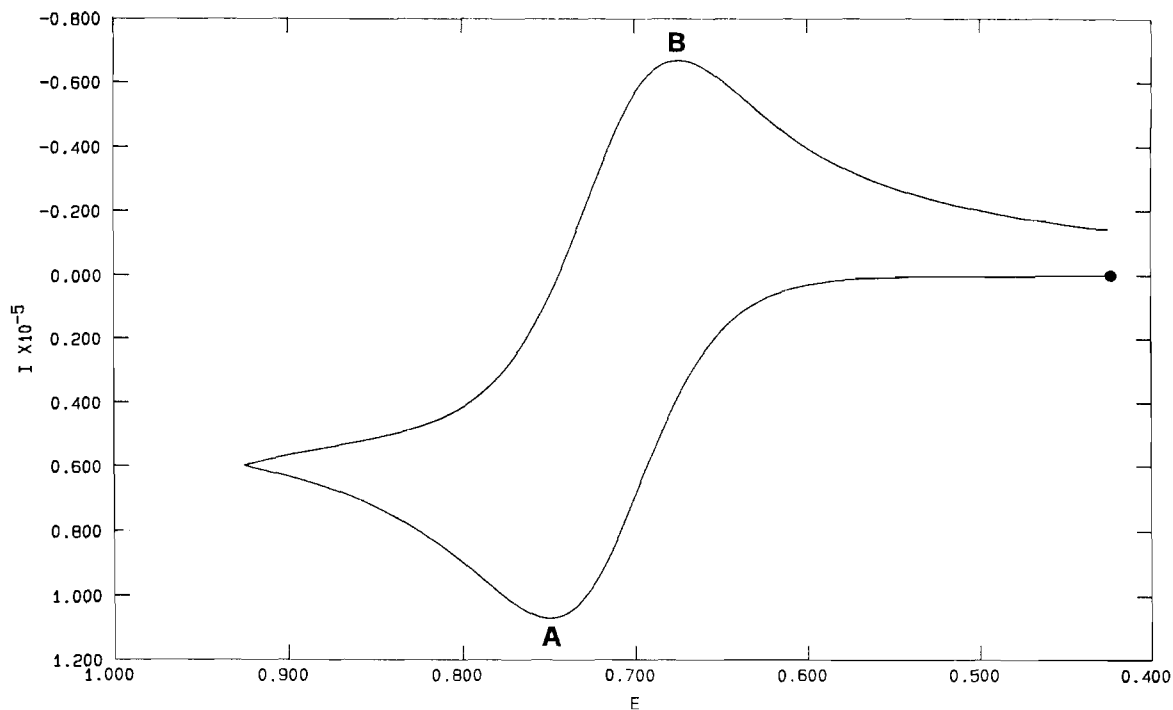


Fig. 2. CV response of a THF solution of **1** at a HMDE, scan rate 0.2 V s^{-1} , temperature 25°C .

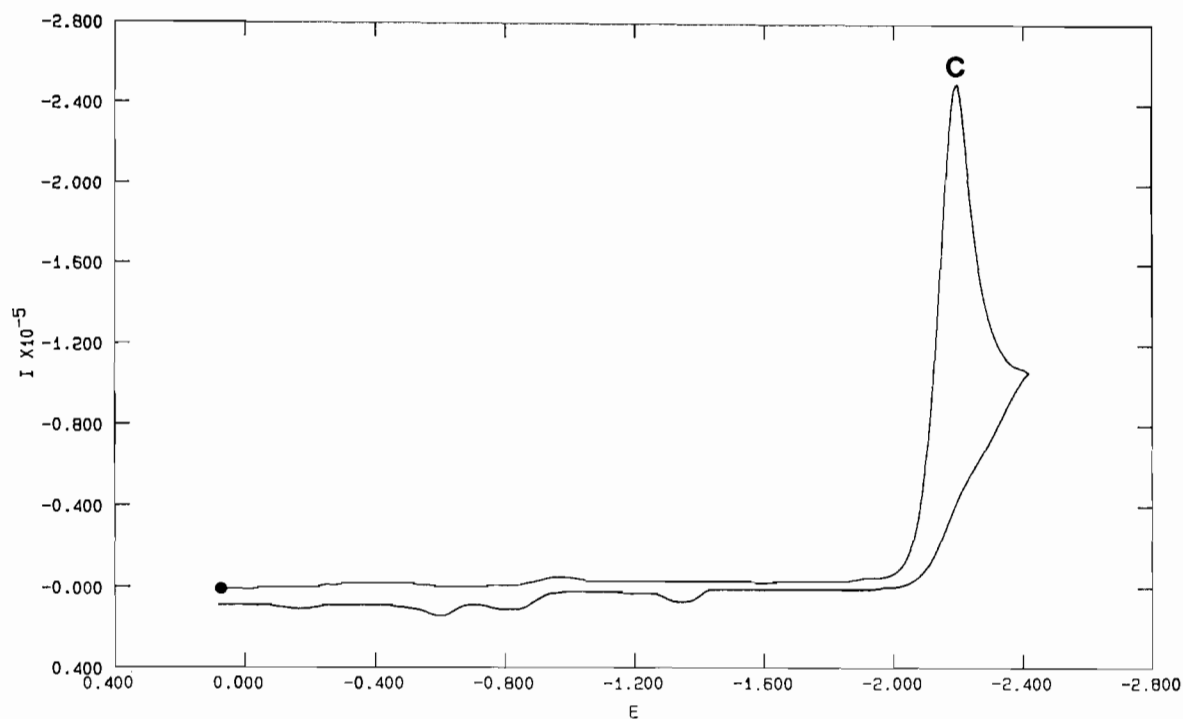


Fig. 3. CV response of a THF solution of **2** at a HMDE, scan rate 0.2 V s^{-1} , temperature $25 \text{ }^\circ\text{C}$.

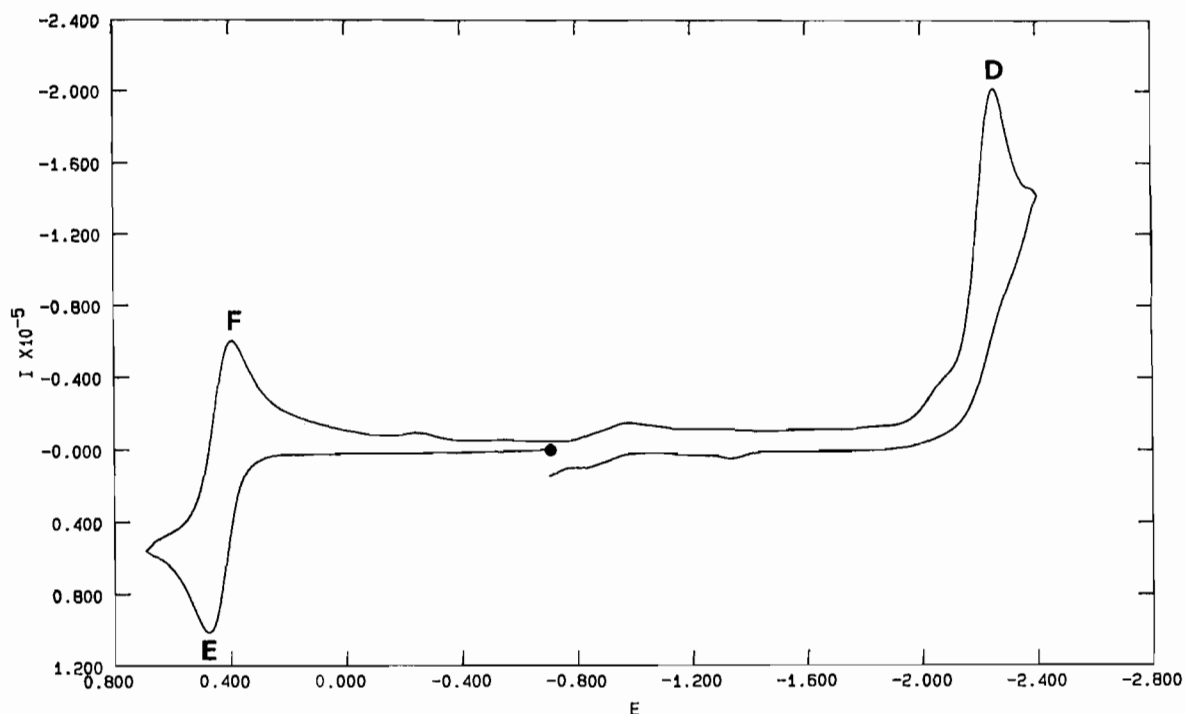


Fig. 4. CV response of a THF solution of **3** at a HMDE, scan rate 0.2 V s^{-1} , temperature $25 \text{ }^\circ\text{C}$.

The CV response of a THF solution of **3** (Fig. 4) shows a reduction peak (D) ($E_p(\text{D}) = -2.25 \text{ V}$ versus SCE, scan rate 0.2 V s^{-1}), together with the $1e$ oxidation process (peak system E/F) of the ethynylferrocenyl fragment ($E^{o'} = +0.43 \text{ V}$ versus SCE). The electrochemical parameters for peak D are very similar to

those of peak C, so the former can also be assigned to the irreversible $2e$ reduction $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^0$. The electrochemical features of the E/F couple are: (i) $i_{pc}(\text{C})/i_{pa}(\text{D})$ ratio varies from 0.85 to 1 in the scan rate range $0.05\text{--}5.00 \text{ V s}^{-1}$; (ii) $\Delta E_p = E_p(\text{F}) - E_p(\text{E})$ varies from 70 to 90 mV; these data are consistent with an elec-

trochemically and chemically quasi-reversible 1e process. The oxidation of the ethynylferrocenyl fragment in **3** is shifted toward less positive potential with respect to the oxidation of ethynylferrocene itself ($\Delta E^{\circ'} = -270$ mV), and shows a somewhat decreased degree of reversibility. This feature has been previously observed for ferrocenyl derivatives bearing bulk and rigid substituents on the cyclopentadienyl rings [6].

The i_p ratio between peaks D (Pt) and E (Fc) is 2.2:1, as expected on the basis of the Randles–Sevcik equation taking into account the lower degree of electrochemical reversibility of the reduction process (peak D) with respect to the oxidation one (peak E), i.e. $2^{3/2} \times 0.78$. Obviously the diffusion coefficient is the same, the two redox centres being part of the same molecule.

The polarographic response confirms the 2:1 ratio of the electronic stoichiometry of the two processes. In fact the reduction wave D ($E_{1/2} = -2.18$ V versus SCE; E versus $\log [(i_d - i)/i]$ slopes 65 mV) is twice as high as the Fc oxidation ($E_{1/2} = +0.45$ V versus SCE; E versus $\log [(i_d - i)/i]$ slopes 67 mV). The electrochemical scenario for compound **4** is very similar to that of **3** (Table 1).

Finally, the CV response of the title compound **5** (Fig. 5) exhibits in the cathodic sweep two chemically irreversible 1e processes (peaks G and H) at $E_p(G) = -1.51$ V and $E_p(H) = -2.24$ V versus SCE. Reversing the sweep at the potential $E_\lambda = -2.00$ V, peak G is still irreversible. In the anodic scan two separated 1e processes (peaks I/L and M/N) are observed at $E^{\circ'}(0/1+) = +0.48$ V and $E^{\circ'}(1+/2+) = +0.75$ V versus SCE. In multiscan CV the pattern remains practically unchanged.

Both the oxidations are electrochemically quasi-reversible (ΔE_p up to 100 mV) and the second is also chemically semi-reversible.

The polarographic response, in the negative scan, shows two well-shaped waves at $E_{1/2}(G) = -1.44$ V (E

versus $\log [(i_d - i)/i]$ slopes 125 mV) and $E_{1/2}(H) = -2.18$ V (E versus $\log [(i_d - i)/i]$ slopes 71 mV).

There is no evidence of the rearrangement of **5** to $\text{Pt}(\text{PPh}_3)_2(\pi\text{-HC}\equiv\text{CPh})$ (**6**), as assessed by comparison with the CV response of an authentic sample. In fact **6** shows only an ill-defined reduction peak very near the solvent discharge. The electrochemical feature is unchanged by deliberate addition of PPh_3 and $\text{HC}\equiv\text{CPh}$, respectively, indicating that no exchange of ligand occurs in **5**, at least in the CV time scale.

For all the Pt-containing compounds **2–5**, no further oxidation attributable to the $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$ process is observed on a Pt or glassy carbon (GC) electrode in the available anodic window.

The complete electrochemical scenario for complex **5** is depicted in Fig. 6.

3. Conclusions

The striking features of the electrochemical behaviour of **5** are as follows.

(i) A moderate electronic interaction exists between the two Fc moieties through the organic chain and the Pt hinge ($\Delta E^{\circ'} = 260$ mV). A precedent for charge delocalization through a metallic hinge can be found in the redox behaviour of cyanomanganesecarbonyl complexes [13].

(ii) The formation during the reduction of a Pt^I intermediate (even as a transient species) which is somewhat stabilized by the electronic delocalization over the external Fc units. A precedent of stabilization of an unusual Pt oxidation state is found for the $[(\text{NC})_5\text{Fe}^{\text{II}}(\mu\text{-CN})\text{Pt}^{\text{IV}}(\mu\text{-NC})\text{Fe}^{\text{II}}(\text{CN})_5]^{4-}$ complexes, where optical excitation leads to a transient $\text{Fe}^{\text{III}}/\text{Pt}^{\text{III}}/\text{Fe}^{\text{II}}$ intermediate [14].

4. Experimental

The complexes **1–6** were synthesized according to the literature procedures [15,16]. Their purity were checked by IR and ¹H NMR spectroscopy.

Electrochemical measurements were performed using an EG&G PAR 273 electrochemical analyser interfaced to a microcomputer, employing PAR M270 electrochemical software. A standard three-electrode cell was designed to allow the tip of the reference electrode (SCE) to closely approach the working electrode. All measurements were carried out under Ar in anhydrous deoxygenated THF; solutions were 1×10^{-3} M with respect to the compounds under study and 2×10^{-1} M with respect to the supporting electrolyte $[\text{Bu}_4\text{N}][\text{PF}_6]$. The temperature of the solution was kept constant within 1 °C by circulation of a thermostatted water–ethanol mixture through the double wall of the cell.

Table 1

Redox potentials (V vs. SCE) for the following complexes: ethynylferrocene, $\text{HC}\equiv\text{CFc}$ (**1**) $[\text{Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C}-\text{Ph})_2]$ (**2**), $[\text{Pt}(\text{PPh}_3)_2(\text{R})(-\text{C}\equiv\text{C}-\text{Fc})]$ ($\text{R} = -\text{C}\equiv\text{CPh}$ (**3**), H (**4**)), $[\text{Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C}-\text{Fc})_2]$ (**5**) in THF solution (0.2 M $[\text{Bu}_4\text{N}][\text{PF}_6]$) at an hanging mercury drop electrode

Compounds	$E_p(0/2-)^a$		$E^{\circ'}(0/1+)^b$	
1			+ 0.70	
2		- 2.19		
3		- 2.25	+ 0.43	
4		- 2.47	+ 0.43	
	$E_p(0/1-)^a$		$E^{\circ'}(1+/1+)^b$	
5	- 1.51	- 2.24	+ 0.49	+ 0.75

^aMeasured at 0.2 V s⁻¹.

^b $E^{\circ'} = (E_{pa} + E_{pc})/2$.

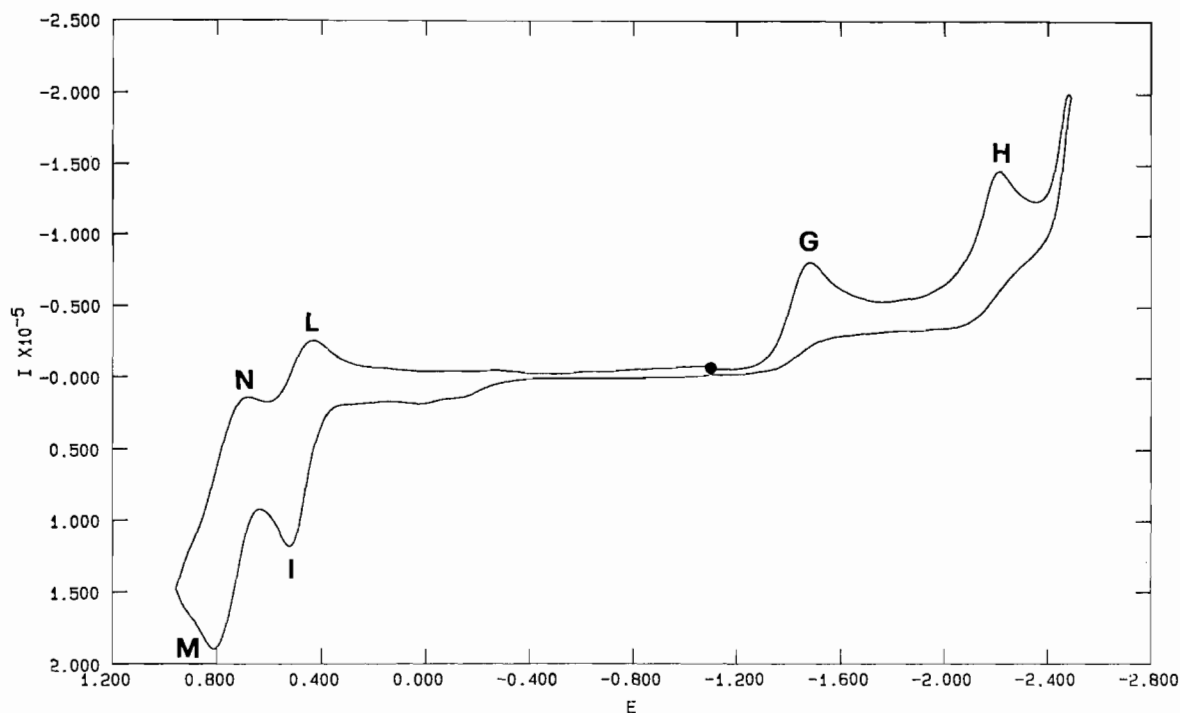


Fig. 5. CV response of a THF solution of **5** at a HMDE, scan rate 0.2 V s^{-1} , temperature $25 \text{ }^\circ\text{C}$.

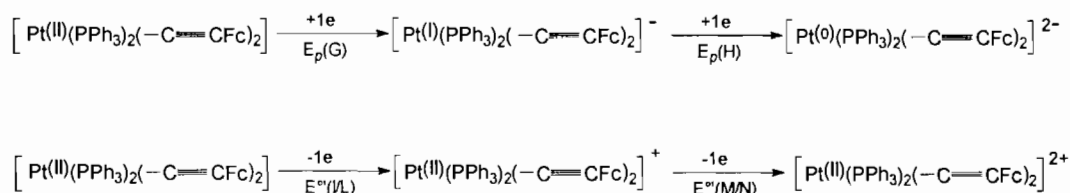


Fig. 6. Proposed mechanism of the overall electrochemical behaviour of **5**.

Although positive feedback iR compensation was applied routinely, some iR drop distortion is present in the high resistance THF medium. Then, the peak-to-peak separation, ΔE_p , as function of the CV scan rate, was always compared to that of the [ferrocene] $^{0/1+}$ couple, recorded in the same experimental conditions. Therefore, the statement ‘electrochemically reversible’ indicates a redox process as reversible as the oxidation of ferrocene is [11]. The working electrode was an HMDE. The reference electrode was an AgCl-coated silver wire dipped in a $2 \times 10^{-1} \text{ M}$ solution of $[\text{Bu}_4\text{N}][\text{PF}_6]$ in THF 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 versus the pseudo-reference electrode and then versus an aqueous SCE, to which all data are referred.

Under the actual experimental conditions the ferrocene/ferrocenium couple is located $+0.56 \text{ V}$ versus SCE in THF [11]. The number of electrons transferred (n) in a particular redox process was determined by controlled potential coulometry at a mercury pool; all experiments were done in duplicate.

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