

Coupled Redox Reactions, Linkage Isomerization, Hydride Formation, and Acid–Base Relationships in the Decaphenylferrocene System

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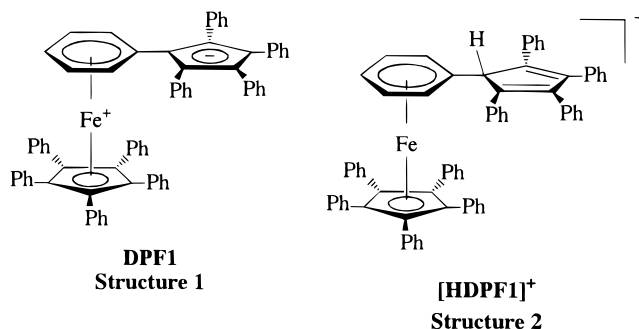
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Decaphenylferrocene (DPF) exists in two isomeric forms, blue $\text{Fe}(\eta^6\text{-C}_6\text{H}_5\text{-C}_5\text{Ph}_4)(\eta^5\text{-C}_5\text{Ph}_5)$ (DPF1), which is known to readily protonate on the ligand giving orange $[\text{Fe}(\eta^6\text{-C}_6\text{H}_5\text{-C}_5\text{HPh}_4)(\eta^5\text{-C}_5\text{Ph}_5)]^+$, [HDPF1]⁺, and insoluble pink $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)_2$ (DPF2). The redox chemistry is unusually complex for a ferrocene system because acid–base chemistry, formation of the hydride $[\text{HFe}(\eta^5\text{-C}_5\text{Ph}_5)_2]^+$, [HDPF2]⁺, together with isomerization and radical abstraction reactions are coupled with the electron-transfer processes. The use of a wide range of voltammetric techniques, time domains, and temperatures and the application of techniques which identify the species in bulk solution enable the reversible half-wave potentials of at least five-electron-transfer processes to be identified. These are $[\text{DPF2}]^+ + e^- \rightleftharpoons \text{DPF2}$ ($E_{1/2} = -40$ mV); $[\text{HDPF2}]^+ + e^- \rightleftharpoons \text{HDPF2}$ ($E_{1/2} = -220$ mV at -60 °C), $[\text{DPF1}]^+ + e^- \rightleftharpoons \text{DPF1}$ ($E_{1/2} = -170$ mV), $[\text{HDPF1}]^{2+} + e^- \rightleftharpoons [\text{HDPF1}]^+$ ($E_{1/2} = 710$ mV), $[\text{HDPF1}]^+ + e^- \rightleftharpoons \text{HDPF1}$ ($E_{1/2} = -1480$ mV), and additionally, C_5HPh_5 is reversibly oxidized at 765 mV (all potentials vs Fc^+/Fc ($\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$) at 20 °C. Only the first two processes are metal based, while the other processes are believed to have considerable ligand character. The wide range of reversible potentials, in particular the similar potentials of the $[\text{HDPF2}]^{+/0}$ and $[\text{DPF1}]^{+/0}$ processes, enable an extensive series of cross-redox reactions to accompany the electron-transfer processes which occur either at the electrode surface or in the bulk solution. The reaction pathways identified include the following: in the presence of acid, DPF1 is protonated on the ligand to give [HDPF1]⁺, DPF2 forms a Fe(IV) hydride, [HDPF2]⁺, which rearranges to [HDPF1]⁺, thereby providing a route for isomerization. In very strong acid, DPF2 is oxidized to $[\text{DPF2}]^+$, which in turn may be converted back to DPF2 by addition of base. Additionally, chemical oxidation or bulk electrolysis of DPF1 gives [HDPF1]⁺ via formation of $[\text{DPF1}]^+$, which is followed by a hydrogen radical abstraction reaction. The electrochemical and chemical redox studies have been supported by NMR, ESR, and UV–vis spectroscopies and electrospray mass spectrometry.

Introduction

Decaphenylferrocene (DPF) has been characterized in two structural forms. In 1990 Brown, Field, and co-workers¹ reported the synthesis of deep blue $\text{Fe}(\eta^6\text{-C}_6\text{H}_5\text{-C}_5\text{Ph}_4)(\eta^5\text{-C}_5\text{Ph}_5)$ (DPF1) from $\text{Fe}(\text{CO})_5$, Zn, and $\text{C}_5\text{Ph}_5\text{Br}$ in boiling benzene. The zwitterionic structure proposed for this compound is shown in structure 1 and was deduced from mass spectrometric and ¹H, ¹³C NMR, UV–vis, and IR spectroscopic data. Under the conditions of conventional cyclic voltammetry, only a single reversible one-electron oxidation process was reported for DPF1, which was assumed to produce $[\text{DPF1}]^+$. However, electrochemical oxidation of DPF1 under bulk electrolysis conditions gave an unidentified red product



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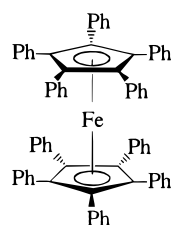
[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

(1) Brown, K. N.; Field, L. D.; Lay, P. A.; Lindall, C. M.; Masters, A. F. *J. Chem. Soc., Chem. Commun.* 1990, 408.

rather than $[\text{DPF1}]^+$, which implies that $[\text{DPF1}]^+$ is unstable on the longer time scale. It was demonstrated that DPF1 is readily protonated to give orange [HDPF1]⁺, for which structure 2 was determined by NMR spectroscopy.

Schumann et al.² in 1994 described the synthesis of extremely insoluble pink $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)_2$ (DPF2) from $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{Ph}_5)\text{Br}$ in refluxing xylene. The highly

symmetric structure 3 was determined for the solid by X-ray crystallography, solid-state ^{13}C NMR, IR, and Raman spectroscopies. DPF2 was oxidized by NOBF_4

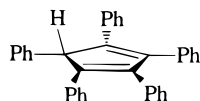


DPF2
Structure 3

to give orange red $[\text{DPF2}]^+$, which in contrast to $[\text{DPF1}]^+$, is stable and could be isolated as its tetrafluoroborate salt. An X-ray structural determination of this salt showed that the cation $[\text{DPF2}]^+$ retains the structural features of neutral DPF2. Under cyclic voltammetric conditions in acetonitrile solution, $[\text{DPF2}]^+$ was reported to show a reversible one-electron reduction to DPF2, but the redox process could not be observed starting with DPF2 due to its extreme insolubility.²

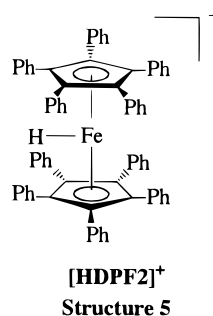
Also in 1994, Field et al.,³ in a paper devoted to titanium chemistry, made brief mention of DPF2. In 1995 this group reported⁴ in more detail that their DPF1 could be converted to DPF2 by heating in xylene solution. They examined the product by X-ray powder crystallography, and the unit-cell parameters determined were very similar to those of the single-crystal determination of $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)_2$, so there seems little doubt that they had succeeded in interconverting the linkage isomers of decaphenylferrocene.

In this paper, we report extensive electrochemical studies of $[\text{DPF2}]^+$, DPF2, $[\text{HDPF1}]^+$, and DPF1. The investigations are augmented by UV-vis, NMR, ESR, and electrospray mass spectrometric (ESMS) studies and studies on C_5HPh_5 (structure 4). It transpires that



C_5HPh_5
Structure 4

the solution chemistry and electrochemistry of both the DPF1 and DPF2 isomeric systems are much more complex than indicated in the previous short communications^{1,2} and involve both isomerization and acid-base reactions coupled with the electron transfer process. In particular, the insolubility of DPF2 and the existence of a hydride $[\text{HDPF2}]^+$ (structure 5) coupled with square schemes involving structural rearrangements⁵ introduce novel features not found in other ferrocene systems.



$[\text{HDPF2}]^+$
Structure 5

Experimental Section

Chemicals and Solvents. $(\eta^5\text{-Pentaphenylcyclopentadienyl})\{1-(\eta^6\text{-phenyl})-2,3,4,5\text{-tetraphenylcyclopentadienyl}\}\text{-iron(II)}$, DPF1, and $(\eta^5\text{-pentaphenylcyclopentadienyl})\{1-(\eta^6\text{-phenyl})-1H-2,3,4,5\text{-tetraphenylcyclopentadiene}\}\text{-iron(II)}$, $[\text{HDPF1}]^+$, were prepared as described in the literature.¹ $\text{Bis}(\eta^5\text{-pentaphenylcyclopentadienyl})\text{iron(II)}$, DPF2, was prepared as described in the literature² or quantitatively from DPF1 by briefly heating in a hexamethylbenzene melt followed by washing with diethyl ether and drying *in vacuo*. $[\text{DPF2}]\text{-BF}_4$ was prepared by oxidation of DPF2 with NOBF_4 . 1,2,3,4,5-pentaphenylcyclopentadiene (structure 4) was prepared as described elsewhere.⁶

Trifluoromethanesulfonic acid (triflic acid) and deuterated triflic acid were obtained from Aldrich and were used as supplied. All other reagents were of analytical reagent or electrochemical grade purity. For experiments in dichloromethane, HPLC grade dichloromethane was passed through a column of basic alumina. All other solvents were of at least HPLC grade and were used as received.

Electrochemical Studies. Electrochemical experiments were undertaken via use of (i) voltammetric systems consisting of either a MacLab 4/e Interface and PO15 Potentiostat with EChem version 1.3 software (all ADI Instruments, Sydney, Australia) or a Cypress Electrochemical Analyzer 1090 (Cypress Systems Inc., Kansas); (ii) a BAS 100 Electrochemical Analyzer, for bulk electrolyses, (Bioanalytical Systems, Lafayette, IN); (iii) a BAS CV-27 instrument was used in conjunction with a Houston Instruments $x-y$ recorder, for *in-situ* ESR/electrochemical experiments.

Solutions to be investigated by voltammetry typically contained 1 mM analyte and 0.1 M Bu_4NPF_6 in dichloromethane, acetone, or acetonitrile, saturated with high-purity nitrogen. The working electrodes used were either Pt disk electrodes with a radius of 5 μm , 12.5 μm , 0.25 mm, 0.5 mm, or 0.8 mm or glassy carbon disk electrodes with a radius 6 μm or 1.5 mm. Pt gauze or wire served as the auxiliary electrode. Several reference electrodes, such as a Ag/AgCl electrode containing a chloride salt and solvent or Ag/Ag^+ (0.02 M AgNO_3 in acetonitrile), were employed in this study. The reversible ferrocene oxidation process, Fc^+/Fc , was recorded with the same experimental arrangement, and all potential values are quoted relative to this potential ($\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)$).

Bulk electrolysis experiments were performed using a platinum basket working electrode, an appropriate Ag/AgCl reference electrode, and a platinum gauze auxiliary electrode separated from the test solution by a salt bridge.

ESR Spectroscopy. ESR studies on oxidized solutions of DPF1 and solutions of $[\text{DPF2}]^+$ were undertaken in dichloromethane in conventional 4 mm (o.d.) ESR quartz tubes. For simultaneous electrochemical ESR (SEESR) experiments, solutions of DPF1 were prepared as described in the solution voltammetry section, with dichloromethane as solvent. Approximately 0.2 mL of solution was then placed into the

(2) Schumann, H.; Lentz, A.; Weimann, R.; Pickardt, J. *Angew. Chem.* **1994**, *106*, 1827; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1731.

(3) Field, L. D.; Lindall, C. M.; Maschmeyer, T.; Masters, A. F. *Aust. J. Chem.* **1994**, *47*, 1127.

(4) Field, L. D.; Hambley, T. W.; Humphrey, P. A.; Lindall, C. M.; Gainsford, G. J.; Masters, A. F.; Pierre, T. G. St.; Webb, J. *Aust. J. Chem.* **1995**, *48*, 851.

(5) (a) Bond, A. M.; Colton, R.; McCormick, M. J. *Inorg. Chem.* **1977**, *16*, 155. (b) Bond, A. M.; Carr, S. W.; Colton, R. *Inorg. Chem.* **1984**, *23*, 2343. (c) Bond, A. M.; Colton, R.; Feldberg, S. W.; Mahon, P. J.; Whyte, T. *Organometallics* **1991**, *10*, 3320.

(6) Field, L. D.; Ho, K. M.; Lindall, C. M.; Masters, A. F.; Webb, A. G. *Aust. J. Chem.* **1990**, *43*, 281.

SEESR cell described elsewhere.⁷ The reference system in the SEESR experiments was a Ag/AgCl electrode.⁷ Studies were undertaken within the TE₁₀₂ resonant cavity of a Bruker ECS106 ESR spectrometer operated in the X band mode. ESR studies were also conducted on dichloromethane solutions of DPF1 after irradiation with the unfiltered light of a Spindler and Hoyer (Göttingen, Germany) HBO 50 W medium-pressure mercury lamp within the cavity of the ESR spectrometer.

The ESR spectrum of solid [DPF2]BF₄ at 4 K was measured over a sweep width of 400 mT using a Bruker ESP-300 ESR spectrometer.

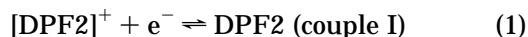
NMR Spectroscopy. Proton NMR spectra were recorded at 400.13 MHz on a Bruker DRX-400 spectrometer in deuterio-dichloromethane solution and referenced against TMS at 0 ppm (TMS = tetramethylsilane).

Electrospray Mass Spectrometry (ESMS). Samples of 20 μL of a 1 mM solution of analyte in acetonitrile were diluted with 170 μL of either H₂O/MeOH/CH₃CO₂H or H₂O/MeOH. Twenty microliters of the resulting solution was then injected into a Bio-Q triple-quadrupole electrospray mass spectrometer (VG Bio-Tech, Altrincham, Cheshire, U.K.). Either acidic (H₂O/MeOH/CH₃CO₂H), neutral (H₂O/MeOH), or basic (H₂O/MeOH/KOH) carrier phases were used.

UV-Vis Absorption Spectroscopy. Spectra were recorded in dichloromethane solution on a Hitachi 150-20 spectrophotometer.

Results

[DPF2]⁺. (i) Voltammetric Reduction in Dichloromethane. Figure 1a shows cyclic voltammograms over the potential range from 160 to -250 mV at various scan rates for the reduction of [DPF2]BF₄ in dichloromethane at 20 °C at a platinum macroelectrode. Only one diffusion-controlled redox couple is observed, and there are no other reductive responses before the solvent limit of -2100 mV. At all scan rates, over the range from 100 to 1000 mV s⁻¹, the redox couple is fully reversible with equal peak currents for the reduction (process I') and oxidation (process I) response. Throughout this paper, reduction responses will be designated with a prime symbol. The reversible half-wave potential ($E'_{1/2}$), calculated as the average of the reduction (E_p^{red}) and oxidation (E_p^{ox}) peak potentials, is closely related to the formal reversible potential E° and has a value of -40 mV. The peak-to-peak separation (ΔE_p) is very similar to that of the ferrocene redox couple (a known reversible one-electron process) under the same conditions, and the data are summarized in Table 1. These observations, together with the known stabilities of both DPF2 and [DPF2]⁺, confirm that the redox couple I (consisting of processes I and I') may be assigned to the reversible reaction



The shape of the reduction response corresponds to the formation of a soluble species, even though DPF2 is insoluble in dichloromethane. The conclusion is that the rate of precipitation is slow in this solvent compared with the voltammetric time scale. Voltammetric results at a glassy carbon working electrode are essentially the same as at platinum.

The steady-state reductive voltammogram for process I' in dichloromethane at a platinum microdisk electrode

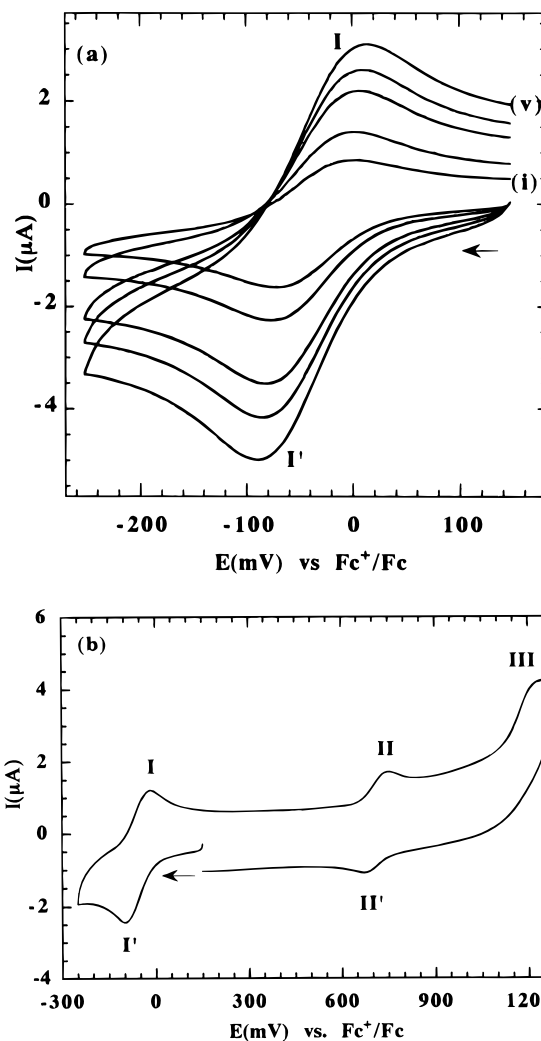


Figure 1. Cyclic voltammograms for a 1 mM solution of [DPF2]⁺ in dichloromethane (0.1 M Bu₄NPF₆) at a platinum disk electrode (radius 0.8 mm). (a) Dependence of reduction process I' at 20 °C on scan rate at (i) 100, (ii) 200, (iii) 500, (iv) 700, and (v) 1000 mV s⁻¹. (b) Low-temperature (-70 °C) voltammogram at a scan rate of 100 mV s⁻¹ over a potential range which encompasses reduction process I' and oxidation processes II and III.

(radius 5 μm) is also fully reversible in terms of the shape of the response. Thus, a plot of E versus $\log[(i_d - i)/i]$ derived from the sigmoidal-shaped response is linear with a slope of RT/F , as expected for a reversible one-electron process.

A reductive bulk electrolysis of [DPF2]BF₄ in dichloromethane was carried out at a constant potential of -200 mV at 20 °C. As the electrolysis proceeds, the initially orange-red solution gradually becomes colorless. A small amount of a light colored precipitate is observed in the solution, but the bulk of the product adheres to the electrode. At the end of the electrolysis, the voltammogram of the solution is indistinguishable from that of the solvent and supporting electrolyte alone. The solid product has properties identical to those of an authentic sample of DPF2. This result confirms that insoluble DPF2 is produced by reduction of [DPF2]⁺ in dichloromethane on the synthetic time scale.

(ii) Voltammetric Oxidation in Dichloromethane.

A series of oxidative cyclic voltammograms at a platinum macrodisk electrode were recorded at 20 °C using

(7) Fiedler, D. A.; Koppenol, M.; Bond, A. M. *J. Electrochem. Soc.* **1995**, *142*, 862.

Table 1. Voltammetric Data Obtained at a Platinum Macrodisk Electrode in Dichloromethane Solution

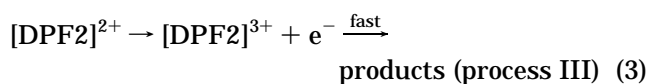
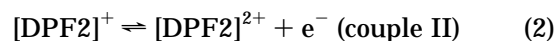
starting material	process (or couple)	scan rate (mV s ⁻¹)	$E_{1/2}$ (mV) ^{a,b}	ΔE_p (mV)	E_p^{ox} or E_p^{red} (mV) ^a	
[DPF2] ⁺	I	100	-40	75	1250	
		200		80		
		500		90		
		700		95		
		1000		100		
	II	100	745	125		
		200		110		
		500		125		
		700		125		
III	1000		130			
	200					
	200					
[HDPF1] ⁺	IV	200	710	100		
	V	200	-1480	90		
	VI	200			1260	
DPF1	VII	100	-170	70	1265	
		200		80		
		500		90		
		700		95		
	VIII	1000		105		
		100		-30		75
		200		75		
		500		85		
	IX	700	740	90		
		1000		100		
	X	200				
		200				
	XI'	200				
		200				
C ₅ HPh ₅	XII	200	765	100		
	XIII	200			1300	
[HDPF2] ⁺	XIV	200	-220 ^c			

^a Referenced vs Fc⁺/Fc. ^b Calculated as $(E_p^{\text{ox}} + E_p^{\text{red}})/2$. ^c Value obtained at -65 °C.

scan rates in the range from 100 to 1000 mV s⁻¹ for a solution of [DPF2]BF₄ in dichloromethane. An oxidation process, process II, and a corresponding reduction, process II', are observed, with a reversible potential of 745 mV being calculated for process II. Another irreversible oxidation wave (process III) is observed at more positive potentials, with a peak potential of 1250 mV. However, at potentials more positive than process I, there is a steadily increasing current instead of the usual relatively flat base line, although the total current from the true base line to the peak maximum is similar to that for process I. The sloping base line means that the oxidation peaks for processes II and III are not as well defined as the peaks for process I. Data are summarized in Table 1.

At platinum (radius 5 μm) or glassy carbon (radius 6 μm) microdisk electrodes under steady-state conditions (scan rate 10 mV s⁻¹), the height of the reversible reduction process I' is equal to the total limiting current for the oxidation process II. However, there is a finite positive current at all potentials between processes I' and II, which is consistent with the sloping base line seen in the cyclic voltammograms.

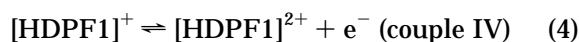
At low temperatures, problems with the sloping base line are minimized. Figure 1b is a low temperature (-70 °C) voltammogram over a potential range which encompasses all processes. The redox couple I is still completely reversible, and couple II is now clearly chemically reversible and has a well defined peak-shaped response. Process III remains irreversible. Although considerable uncertainty exists in the reaction nuances, couple II and process III are conveniently written as



(iii) Voltammetry in Acetonitrile. The voltammetry of [DPF2]⁺ in acetonitrile is complicated by adsorption, and also numerous electrode, concentration, and scan rate dependent processes were found. Consequently, no voltammetric data relevant to the chemistry of interest in this paper could readily be obtained in acetonitrile. Close examination of the cyclic voltammogram in acetonitrile published previously² actually shows that it exhibits a nondiffusion-controlled shape. Furthermore, the midpoint potential (average of E_p^{ox} and E_p^{red}) of 743 mV vs Ag/AgCl using an aqueous agar (saturated KCl) salt bridge was not calibrated against ferrocene. The inevitable junction potentials generated by this nonstandard reference electrode arrangement and the presence of surface-based reactions make the significance of the potential measurement reported in the earlier work somewhat uncertain.

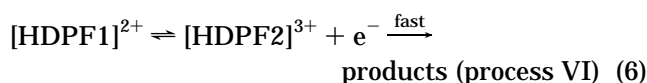
(iv) Electropray Mass Spectrometry. The electropray mass spectrum of a solution of [DPF2]BF₄ gives a strong peak for the intact ion [DPF]⁺ at *m/z* 946, but the technique does not give information on the isomeric form of the cation.

[HDPF1]⁺. (i) Voltammetric Studies in Dichloromethane. Figure 2a shows a cyclic voltammogram of an orange solution of [HDPF1]⁺ in dichloromethane at a scan rate of 200 mV s⁻¹ at a platinum macrodisk electrode at 20 °C over the potential range from -1700 to 900 mV. Two chemically reversible redox couples (processes IV,IV' and V,V') are observed at reversible potentials of 710 and -1480 mV, respectively. Very small additional responses due to other unidentified processes are always apparent. Processes IV and V' were shown by steady-state voltammetry at a platinum microdisk electrode (radius 12.5 μm) to correspond to a one-electron oxidation and a one-electron reduction, respectively (shape of wave and limiting current). Thus, the redox reactions associated with couples IV and V are



In these equations, it is assumed that the molecular structure is unchanged upon oxidation and reduction. The compounds [HDPF1]²⁺ and HDPF1 have not been reported before, but they are respectively a strong oxidant and strong reductant. Redox couple V being well-removed from the other processes is extremely useful to confirm the presence of [HDPF1]⁺ in bulk solution for various reaction mixtures (see later discussions).

Figure 2b shows a cyclic voltammogram over a more positive potential range, which shows that an irreversible process VI is present at a similar potential to that observed for process III for a solution of [DPF2]⁺ (Figure 1b). Process VI is, therefore, analogously described as



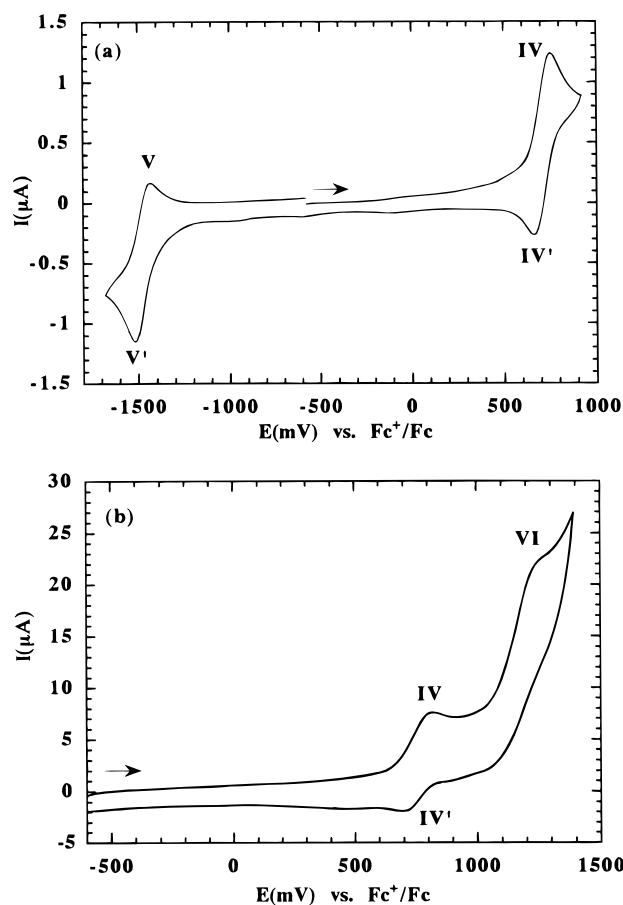
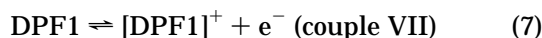


Figure 2. (a) Cyclic voltammogram of 1mM [HDPF1]⁺ in dichloromethane (0.1 M Bu₄NPF₆) at a Pt disk electrode (radius 0.5 mm, scan rate 200 mV s⁻¹, 20 °C) over the potential range from -1700 to 900 mV vs Fc⁺/Fc. (b) Similar conditions but scanned over the potential range from -500 to 1500 mV vs Fc⁺/Fc.

DPF1. (i) Voltammetric Oxidation in Dichloromethane. The original report¹ on the voltammetry of DPF1 mentioned only a single oxidative response, but we find the electrochemistry to be much more complicated with many electrochemical responses being observed.

Figure 3a shows an oxidative cyclic voltammogram at 20 °C for DPF1 in dichloromethane at a platinum macrodisk electrode at a scan rate of 200 mV s⁻¹. Four oxidative processes are observed, labeled VII, VIII, IX, and X, and the data are summarized in Table 1.

Process VII is the process reported in the original communication,¹ and Figure 3b shows that it has many of the characteristics of a reversible one-electron oxidation process. This couple, therefore, can be assigned to the reaction



The reversible potential for couple VII is about -170 mV, which is significantly more negative than the value of -40 mV previously established for the [DPF2]⁺⁰ redox couple. Figure 3c shows the effect of the scan rate on couples VII and VIII. Both couples show an almost linear dependence of peak height on the square root of the scan rate, implying they are close to diffusion controlled. Despite the similarity of the potentials for couples I and VIII, couple VIII cannot result from the

oxidation of DPF2 present in the bulk solution as this material is completely insoluble in dichloromethane. Furthermore, couples VII and VIII also are observed under short time steady-state voltammetric conditions at a microdisk electrode (Figure 4a). However, couple VIII is absent when voltammetric oxidation of DPF1 in dichloromethane is undertaken in the presence of the base NEt₃ at -65 °C, implying that a protonation step is associated with the observation of process VIII. Voltammetric monitoring of the experiments involving addition of small amounts of NOBF₄ to a dichloromethane solution of DPF1 (22 °C) leads to the observation that couple VII disappears while couple VIII remains. Addition of more NOBF₄ eventually leads to the disappearance of couple VIII. Voltammetric monitoring of the oxidative bulk electrolysis of DPF1 at a potential between couples VII and VIII initially leads to the loss of couple VII, with retention of the majority of couple VIII. However, eventually couple VIII also disappears. Voltammetric responses consistent with formation of [HDPF1]⁺ are observed after chemical (NOBF₄) or electrochemical oxidation of DPF1.

Further processes are observed for the voltammetric oxidation of a solution of the blue compound DPF1. When the potential is scanned to more positive values, the multielectron oxidation process IX (Figure 3d) appears in a similar potential region as that for couples II and IV found in the oxidations of [DPF2]⁺ and [HDPF1]⁺, respectively. Process X (Figure 3a), which is observed close to the solvent limit, is irreversible under all conditions. It appears at a potential similar to those for processes III (Figure 1b) and VI (Figure 2b). The interrelationships of the processes at positive potentials will be discussed later.

The half-wave potential (versus Fc⁺/Fc) of couple VII is slightly solvent dependent (Figure 4), with values of -170 mV in dichloromethane, -110 mV in acetone, and -90 mV in acetonitrile. In acetone and acetonitrile, couple VIII is barely discernable (Figure 4) but its potential appears to be almost independent of solvent.

(ii) Voltammetric Reduction in Dichloromethane. Reductive cyclic voltammograms for freshly prepared solutions of DPF1 in dichloromethane at a platinum macrodisk electrode at 20 °C exhibit a small reduction process with an *E*_p value of about -1520 mV. Switching the potential immediately after the response reveals the oxidative half of the redox couple. This small reversible oxidation couple (couple V) can be assigned to the presence of [HDPF1]⁺ in the solution. The height of this reduction process relative to the oxidation processes VII, VIII, and IX is dependent on the age of the solution and the number of voltammetric experiments performed, but no solution could be prepared in which couple V was absent. A further reduction process XI' is detected at a very negative potential of -2180 mV. The current magnitude associated with this reduction process appears to be directly related to that for couple VII. Consequently, process XI' is assigned to the reduction of DPF1. This reduction process is chemically irreversible at room temperature and gives rise to a small product signal at *E*_p = -680 mV on reverse scans of the cyclic voltammetry. Kläui et al.⁸ observed the oxidation of the free [C₅Ph₅]⁻ ligand in dichloromethane at -350

(8) Kläui, W.; Huhn, M.; Herbst-Irmer, R. *J. Organomet. Chem.* **1991**, *415*, 133.

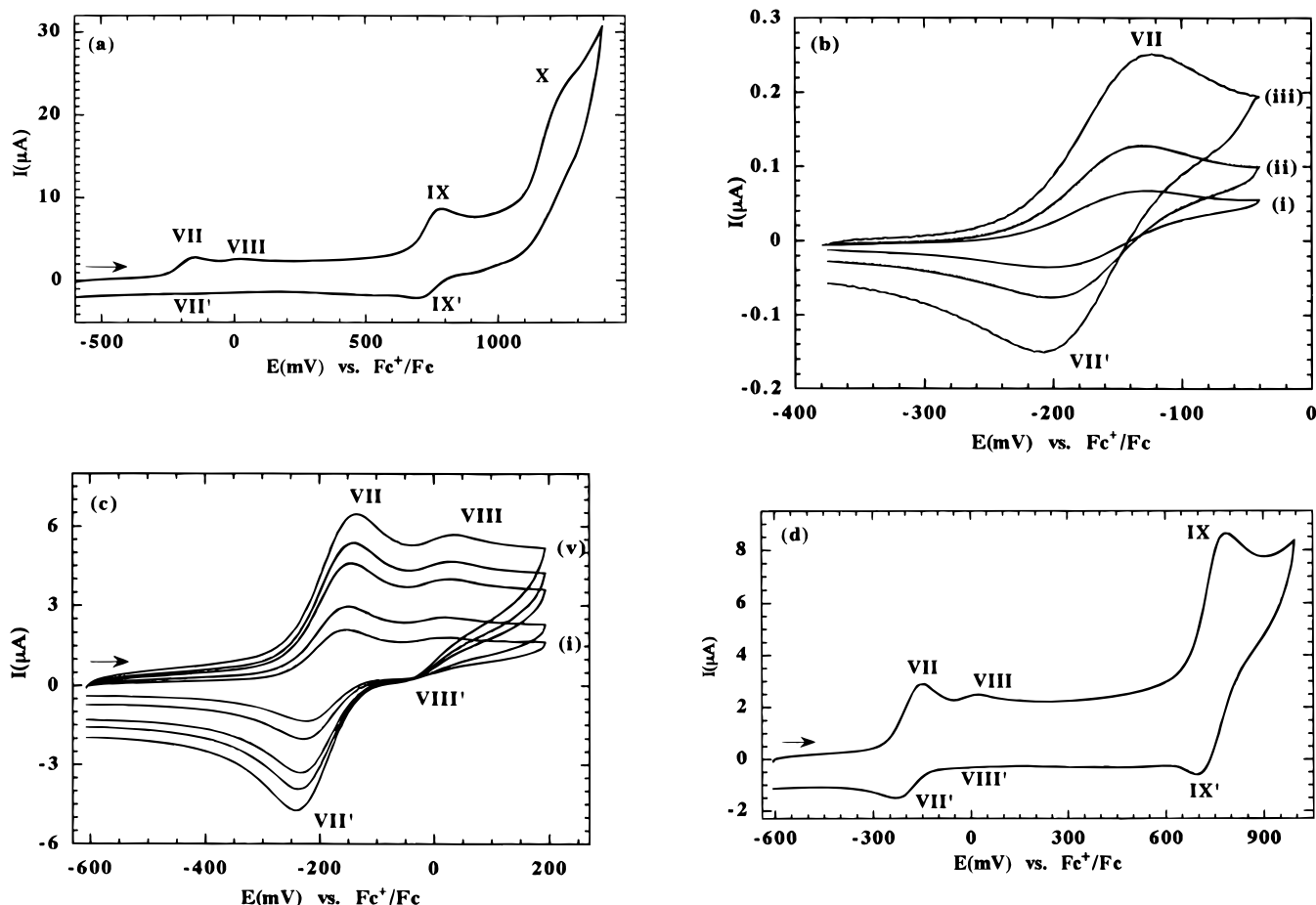
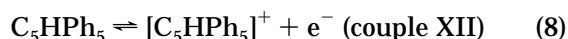


Figure 3. Oxidative cyclic voltammograms for a 1 mM solution of DPF1 in dichloromethane (0.1 M Bu₄NPF₆) at 20 °C at a platinum disk electrode (radius 0.8 mm): (a) over the approximate potential range from -600 to 1500 mV vs Fc⁺/Fc and scan rate of 200 mV s⁻¹; (b) over the potential range from -420 to -50 mV vs Fc⁺/Fc (couple VII) and scan rates of (i) 25, (ii) 100, and (iii) 400 mV s⁻¹; (c) over the potential range from -600 to 200 mV vs Fc⁺/Fc (couples VII and VIII) and scan rates of (i) 100, (ii) 200, (iii) 500, (iv) 700, and (v) 1000 mV s⁻¹; (d) over the potential range from -600 to 1000 mV vs Fc⁺/Fc and a scan rate of 200 mV s⁻¹.

mV vs SCE which, after conversion of the reference scale, is in close agreement with the potential of the observed product signal. Therefore, a plausible scheme for process XI' would indicate the loss of a [C₅Ph₅]⁻ ligand after the reduction of DPF1.

C₅HPh₅. Voltammetric oxidation in dichloromethane of C₅HPh₅ (structure 4), which is closely related to the ligand in DPF1, exhibits a chemically reversible oxidation couple XII, which has an *E*_{1/2} value of 765 mV and an irreversible response (process XIII) at 1300 mV (Table 1 and Figure 5). Thus, for all of the DPF complexes and for free C₅HPh₅, oxidation processes are present in the potential regions 710–765 and 1250–1300 mV. Over the scan rate range from 100 to 1000 mV s⁻¹, couple XII is diffusion controlled and is, therefore, described by eq 8.



This behavior is in contrast to the oxidation of C₅HPh₅ in acetonitrile which is irreversible.⁹

Acid–Base Studies. The experiments described above indicate that even adventitious amounts of proton sources have a profound effect upon the DPF species present in dichloromethane. The effects of deliberately

added acids and bases to solutions of the various complexes in the DPF system were, therefore, investigated.

(i) DPF2. When a 50-fold molar excess of triflic acid is added to a dichloromethane suspension of DPF2, the major product is [DPF2]⁺, as determined by examination of the UV–vis spectrum and a voltammogram at a microelectrode (reduction current associated with process I observed). A similar oxidation of ferrocene to the ferrocenium cation is commonly observed in acid media in the presence of oxygen.¹⁰

When a slight molar excess of a dilute solution of triflic acid in dichloromethane is added to a suspension of DPF2 in dichloromethane, a bright red coloration develops immediately in the solution, but it rapidly (10–20 s) changes to orange. The UV–vis spectrum of the orange solution is essentially identical to that of a solution of [HDPF1]⁺. That is, protonation with a small amount of acid after causing dissolution of insoluble DPF2 leads to isomerization in the coordination of one of the pentaphenylcyclopentadienyl ligands. Thus, at room temperature, a mixture of [HDPF1]⁺ and [DPF2]⁺ results from the addition of excess acid to a suspension of DPF2, with the proportion of the products depending

(9) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2872.

(10) Mueller-Westerhoff, U. T.; Haas, T. J.; Swiegers, G. F.; Liepert, T. K. *J. Organomet. Chem.* **1994**, *472*, 229.

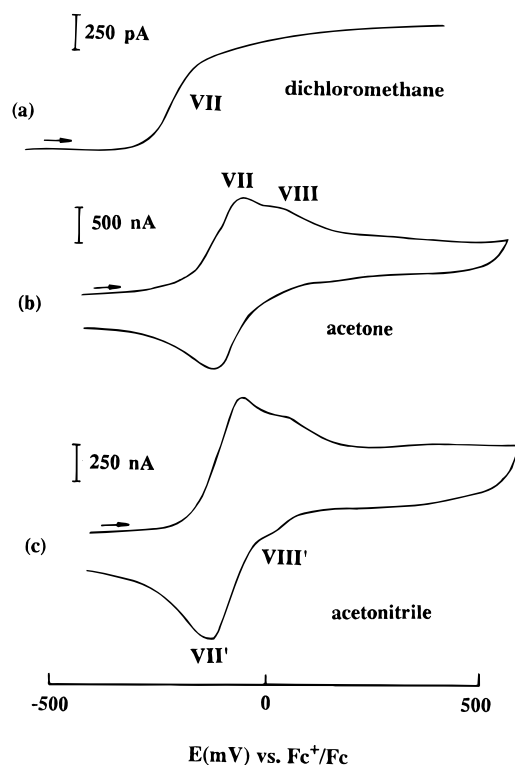


Figure 4. Cyclic voltammograms for the oxidation (processes VII and VIII) of DPF1 in (a) dichloromethane at a Pt microdisk electrode (radius 5 μm) and a scan rate of 10 mV s^{-1} , (b) acetone at a Pt disk electrode (radius 0.5 mm) and a scan rate of 100 mV s^{-1} , and (c) acetonitrile, same conditions.

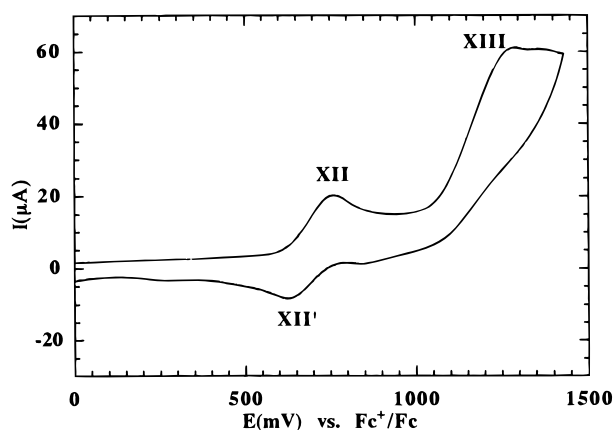
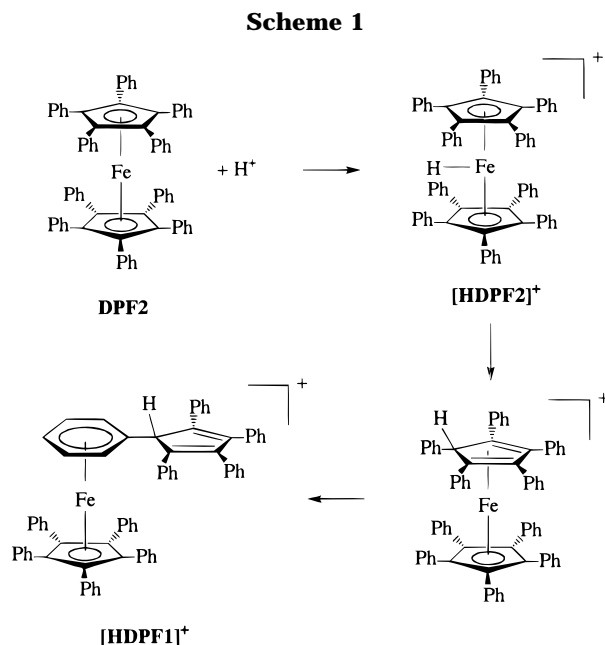


Figure 5. Cyclic voltammogram for the oxidation of 1mM C_5HPh_5 in dichloromethane (0.1 M Bu_4NPF_6) at a Pt disk electrode (radius 0.8 mm) and a scan rate of 200 mV s^{-1} .

critically upon the acidity of the solution and the concentration of oxygen present.

The red-colored species formed at lower acid concentrations is readily studied at low temperature, where high concentrations can be obtained for considerable periods of time. Triflic acid was added to a suspension of DPF2 in deuterodichloromethane in an NMR tube, and the tube was then immediately transferred to the precooled ($-60\text{ }^\circ\text{C}$) NMR probe. The proton NMR spectrum displayed a small peak at $\delta -0.77$ ppm, which is assigned to a metal-hydride signal. Hydrides are unique with respect to their proton chemical shifts being negative relative to TMS. Ferrocene itself and many of its derivatives may also be protonated,¹¹ if oxidation can be avoided, and the chemical shifts of their hydrides



are all at similar values to that found after addition of acid to DPF2. Thus, the initially formed product of the protonation of DPF2 is identified as the formally Fe(IV) hydride $[\text{HDPF2}]^+$, eq 9, the expected structure of which is shown in structure 5. Of course, the reaction may



be regarded as a simple acid-base reaction and the metal oxidation state assigned to this species is somewhat arbitrary. It is postulated that $[\text{HDPF2}]^+$ may subsequently undergo a proton shift from iron to one cyclopentadienyl ring, which then loses its aromatic character, as shown in Scheme 1. Isomerization to the protonated arene-bonded form (i.e., $[\text{HDPF1}]^+$) may occur via this mechanism. Ligand-slip rearrangements similar to that proposed are known,¹² but in these cases the five- and six-membered rings are fused rather than separated by a C-C bond.

The stability of $[\text{HDPF2}]^+$ at low temperatures also allows its voltammetry to be investigated. Triflic acid only reacts very slowly with DPF2 in dichloromethane at $-78\text{ }^\circ\text{C}$. Consequently, in order to form $[\text{HDPF2}]^+$ in sufficient concentrations to obtain well-defined voltammograms, a small excess of triflic acid was added at room temperature to a suspension of DPF2 in dichloromethane (0.1 M Bu_4NPF_6) in an electrochemical cell and the cell was then immediately cooled in an acetone/dry ice bath to $-65\text{ }^\circ\text{C}$. The cyclic voltammogram at a platinum macrodisk electrode at a scan rate of 200 mV s^{-1} showed a new dominant chemically reversible couple (processes XIV, XIV') at -220 mV, together with couples IV and V which arise from the presence of $[\text{HDPF1}]^+$. Microelectrode experiments showed the current for process XIV' to be completely

(11) (a) Cerichelli, G.; Illuminati, G.; Ortaggi, G.; Giuliani, A. M. *J. Organomet. Chem.* **1977**, *127*, 357. (b) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1977**, *141*, 355. (c) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4814. (d) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1972**, *40*, 197.

(12) (a) Nicholas, K. M.; Kerber, R. C.; Steifel, E. I. *Inorg. Chem.* **1971**, *10*, 1519. (b) Treichel, P. M.; Johnson, J. W. *J. Organomet. Chem.* **1975**, *88*, 207. (c) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749. (d) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 688.

reductive. Analysis of the steady-state current–voltage wave shape confirmed that this is a diffusion-controlled reversible one-electron process, and therefore, the redox couple XIV is assigned to the process

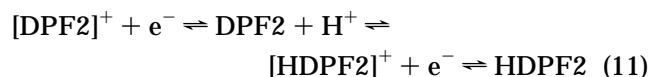


where the structure of HDPF2 is assumed to be the same as that of $[\text{HDPF2}]^+$ and is, therefore, formally regarded as a Fe(III) hydride.

The potentials of couples XIV and VII are almost the same, so that mixtures of $[\text{HDPF2}]^+$ and DPF1 are difficult to distinguish voltammetrically. When the solution is warmed toward room temperature, couple XIV diminishes and couple IV becomes dominant, but a small response (couple I) due to the presence of $[\text{DPF2}]^+$ also is evident. When the solution is recooled to -65°C , couple IV is still dominant, with a small response for $[\text{DPF2}]^+$, but couple XIV assigned to the hydride is not significantly regenerated. These electrochemical observations support the proposal that $[\text{HDPF2}]^+$ may be converted to $[\text{HDPF1}]^+$.

(ii) $[\text{DPF2}]^+$. $[\text{DPF2}]^+$ does not protonate. The UV–vis spectrum of $[\text{DPF2}]^+$ in dichloromethane is rich, and no change occurs on addition of a 10-fold molar excess of triflic acid. This is consistent with the visual observation of no color change after addition of acid. The electro spray mass spectrum of a solution of $[\text{DPF2}]^+$ obtained from an acidic mobile phase of $\text{H}_2\text{O}/\text{MeOH}/\text{HOAc}$ (50:50:1) shows only the molecular ion $[\text{DPF}]^+$ at m/z 946, with no evidence for a peak due to $[\text{HDPF}]^{2+}$ at m/z 473.5.

Under voltammetric conditions with a 50-fold molar excess of triflic acid, the reductive cyclic or steady-state voltammograms of $[\text{DPF2}]^+$ show processes XIV' and I', in contrast to the situation without acid, when the simple reduction process I' is observed. Process XIV' occurs due to protonation of the DPF2 generated at the electrode surface (but not in the bulk solution) and results from a combination of a modified version of couple I and eq 9 as follows:



Addition of excess base (NEt_3) to a solution of $[\text{DPF2}]^+$ in dichloromethane leads to rapid decolorization of the solution and precipitation of a pink solid. The solution gives no voltammetric responses for any DPF species. The solid shows all of the properties of DPF2, including its dissolution in acid solutions (see above). The result of this experiment is phenomenologically equivalent to the bulk electrolytic reduction of $[\text{DPF2}]^+$ described earlier. Thus, acid–base and redox reactions are intimately related. Redox interconversion reactions involving acid–base and redox chemistry in the presence of oxygen have been previously reported in studies of metal carbonyl complexes.¹³

(iii) DPF1. UV–vis spectroscopic studies show that addition of a slight molar excess of triflic acid to DPF1 causes complete removal of DPF1, since the characteristic absorption at 600 nm disappears, and the product

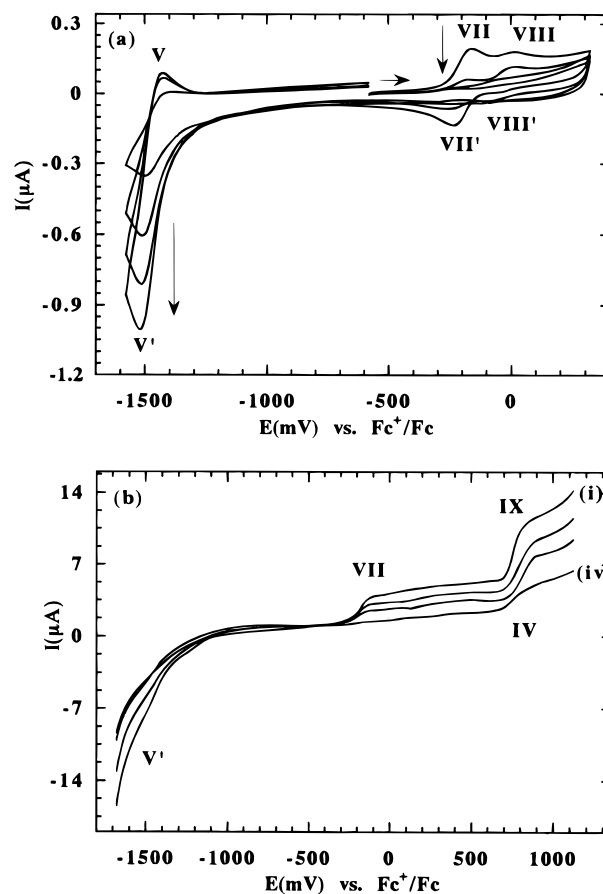


Figure 6. Voltammograms obtained during stepwise addition of triflic acid to a solution of DPF1 in dichloromethane (0.1 M Bu_4NPF_6) at (a) a Pt disk electrode (radius 0.25 mm) and scan rate of 200 mV s^{-1} and (b) a Pt microdisk electrode (radius $12.5 \mu\text{m}$) and a scan rate of 10 mV s^{-1} ; curve i, no acid; curve iv, equimolar DPF1 and acid; curves ii and iii are intermediate between i and iv.

is identified as $[\text{HDPF1}]^+$, agreeing with earlier observations¹ that DPF1 is readily protonated.

Figure 6a shows a series of cyclic voltammograms of a solution of DPF1 in dichloromethane to which successive amounts of triflic acid, beginning with sub-equivalent amounts and progressing to an equimolar quantity, were added. Process V' is used to monitor the formation of $[\text{HDPF1}]^+$, rather than process IV, because it occurs in a potential region free from other overlapping processes. Unfortunately, process V' cannot be observed at platinum electrodes in solutions containing excess acid due to the presence of the overlapping hydrogen ion reduction wave. Upon addition of acid, couple VII decreases in height before couple VIII is noticeably affected and process V' grows immediately. After addition of approximately an equimolar amount of acid, the complete cyclic voltammogram closely resembles that shown in Figure 2a for $[\text{HDPF1}]^+$. Monitoring the experiments by microelectrode voltammetry over a wider potential range allows other features to be detected. Figure 6b shows microelectrode voltammograms for (curve i) a solution of DPF1 without added acid, displaying the large response of process IX. As dilute acid is added (curves ii and iii), processes VII, VIII, and IX all decrease. At the molar equivalence point (curve iv), processes VII and VIII have disappeared and the multielectron process IX has changed into the reversible one-electron process IV. At the

(13) (a) Crossing, P. F.; Snow, M. R. *J. Chem. Soc. A* **1971**, 610. (b) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 2526.

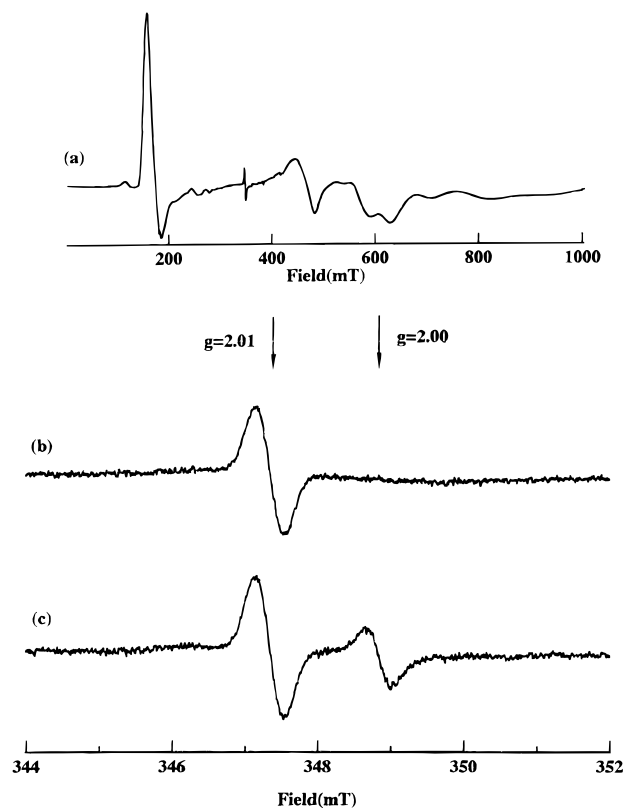


Figure 7. (a) ESR signal for solid $[\text{DPF2}]\text{BF}_4$ obtained at 4 K. (b and c) ESR signals obtained upon *in situ* SEESR electrochemical oxidation of DPF1 in dichloromethane (0.1 M Bu_4NPF_6) using an applied potential of (b) 0.2 V vs Fc^+/Fc and (c) 1.0 V vs Fc^+/Fc .

equivalence point, the limiting current for process IV is now equal to the sum of the original processes VII and VIII, within the limits of experimental error. Thus, these voltammograms confirm that the sum of processes VII and VIII is a one-electron process.

ESR Studies. All attempts to observe an ESR signal for the paramagnetic cation $[\text{DPF2}]^+$, either as the solid or a 0.5 mM solution in dichloromethane, were unsuccessful over the temperature range of 100–300 K and g -value range of 1–10. Paramagnetic iron d^5 sandwich complexes commonly require very low temperatures for ESR detection,¹⁴ so the absence of an ESR signal in this temperature range is not unexpected. However, at 4 K, a powder sample of $[\text{DPF2}]\text{BF}_4$ gave a highly anisotropic ESR spectrum (Figure 7a) consistent with that commonly obtained¹⁵ for low-spin Fe(III) (d^5) complexes. The spectrum exhibits a dominant signal at $g = 3.97$ with a line width at half-height of approximately 20 mT. A series of weaker signals over the g value range 1–1.5 is also observed. These features are all typical for ferrocenium and related low-spin Fe(III) compounds. A small sharp signal in the $g = 2.0$ region also is present, which would appear not to be related to a low-spin Fe(III) system. Rather, this appears to have the characteristics of a radical spectrum and may be due to an impurity.

(14) Elschenbroich, C.; Bilger, E.; Ernst, R. D.; Wilson, D. R.; Kralik, M. S. *Organometallics* **1985**, *4*, 2068 and references cited therein.

(15) (a) Inniss, D.; Soltis, S. M.; Strouse, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 5644. (b) Walker, F. A.; Huynh, B. H.; Scheidt, W. R.; Osvald, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 5288. (c) Walker, F. A.; Reis, D.; Balke, V. L. *J. Am. Chem. Soc.* **1984**, *106*, 6888. (d) Migita, C. T.; Iwaizumi, M. *J. Am. Chem. Soc.* **1981**, *103*, 4378. (e) Ammeter, J. H.; Swalen, J. D. *J. Chem. Phys.* **1972**, *57*, 678.

Vastly different ESR spectra to that in Figure 7a are observed following oxidation of DPF1. The *in-situ* electrochemical oxidation of a solution of blue decaphenylferrocene, DPF1, in dichloromethane solution using a SEESR cell⁷ by setting the potential of the Pt coil electrode to a value of 200 mV allows detection of a paramagnetic species with a g value of 2.01 (Figure 7b). Chemical oxidation of DPF1 in dichloromethane solution using $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{PF}_6$ also generates the same strong sharp signal with $g = 2.01$. This sharp signal decays on the minutes time scale and, therefore has a half-life consistent with the intermediate paramagnetic species $[\text{DPF1}]^+$ being converted to diamagnetic $[\text{HDPF1}]^+$, as was deduced from the bulk electrolysis experiments. Both the small line width of 0.4 mT and the position of the signal indicate the formation of a species with considerable radical character. Certainly, the ESR characteristics are not those of a low-spin Fe(III) compound, such as $[\text{DPF2}]^+$, where very low temperatures are required to observe the very weak and broad signal. When the electrolysis is conducted at the much more positive potential of 1000 mV (where process IX occurs), an additional ESR signal with $g = 2.00$ is detected (Figure 7c). This signal also corresponds to generation of a species with considerable radical character, which possibly could be the pentaphenylcyclopentadienyl radical.¹⁶ The same radical species with $g = 2.00$ also is generated in dichloromethane solution via a photochemical reaction of either DPF1 or $[\text{HDPF1}]^+$, using the unfiltered light of a mercury lamp. There is no sign of a photochemical isomerization to DPF2, and the fragmentation reaction which is believed to generate the signal at $g = 2.00$ is in agreement with similar reactions reported in the literature.¹⁷ If this interpretation is correct, then the partial irreversibility of process IX described above can be attributed to fragmentation of $[\text{DPF1}]^{2+}$, which then generates the observed radical species.

Electrospray Mass Spectrometry. ESMS cannot distinguish between the isomers of the DPF compounds examined. However, data obtained from other techniques enable the isomeric form to be determined, and structures assumed on this basis are used in the following section. An electrospray mass spectrum of the orange protonated compound $[\text{HDPF1}]^+$ generated by addition of triflic acid to a solution of blue DPF1 in acetonitrile gives a strong peak at m/z 947, and the isotope pattern is consistent with the empirical formula $[\text{HFe}(\text{C}_5\text{Ph}_5)_2]^+$. The mass spectrum of a similar solution obtained by using deuterated triflic acid shows two overlapping spectra having m/z values of 947 and 948, representing the protonated $[\text{HFe}(\text{C}_5\text{Ph}_5)_2]^+$ and the monodeuterated $[\text{DFe}(\text{C}_5\text{Ph}_5)_2]^+$ species, respectively. This implies that deprotonation of $[\text{HDPF1}]^+$ is slow, since if it were rapid the deuterated form would exchange with protons from the mobile phase and only one peak would be observed in the ES mass spectrum.

When a sample of DPF1 is oxidized with NOBF_4 and the solution injected into the electrospray mass spectrometer, the species observed is $[\text{HDPF1}]^+$ (m/z 947) rather than $[\text{DPF1}]^+$ (m/z 946). The time interval

(16) (a) Möbius, K.; Van Willigen, H.; Maki, A. H. *Mol. Phys.* **1971**, *20*, 289. (b) Kieslich, W.; Kurreck, H. *J. Am. Chem. Soc.* **1984**, *106*, 4328.

(17) McNair, A. M.; Schrenk, J. L.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 2633.

between injection and emergence of the sample at the ES ion source is about 2 min, and the conversion of $[\text{DPF1}]^+$ to $[\text{HDPF1}]^+$ within this time scale is consistent with the voltammetric results presented earlier. One way to reduce the time of reaction of $[\text{DPF1}]^+$ with the mobile phase is to generate the species electrochemically at the ion source nozzle just prior to transfer to the gas phase. This "tip oxidation" technique has been demonstrated for metal complexes by Van Berkel¹⁸ and Cole,¹⁹ and in the latter case, the compounds studied were ferrocenium and related cations. Using a neutral mobile phase of MeOH/H₂O, tip oxidation of DPF1 again gives an ES mass spectrum which showed only the peak due to $[\text{HDPF1}]^+$ (m/z 947). However, when the mobile phase is made basic (KOH added), then a mixture (about 1:3) of $[\text{DPF1}]^+$ and $[\text{HDPF1}]^+$ was detected. Thus, there are now three independent experiments (ESR, ESMS, and voltammetry) which confirm the transient existence of $[\text{DPF1}]^+$.

Discussion

We have established that there are at least five essentially reversible electron transfer couples associated with the DPF system in dichloromethane. The redox reactions and reversible half-wave potentials (approximately equal to E^0) are summarized in eqs 12a–e, but they commonly have coupled chemistry associated with them, which modifies the appearance of the voltammetry. The extent of the coupled chemistry is

couple I $[\text{DPF2}]^+ + e^- \rightleftharpoons \text{DPF2}$

$$E_{1/2}^r = -40 \text{ mV} \quad (12a)$$

couple XII $[\text{HDPF2}]^+ + e^- \rightleftharpoons \text{HDPF2}$

$$E_{1/2}^r = -220 \text{ mV} \quad (12b)$$

couple VII $[\text{DPF1}]^+ + e^- \rightleftharpoons \text{DPF1}$

$$E_{1/2}^r = -170 \text{ mV} \quad (12c)$$

couple IV $[\text{HDPF1}]^{2+} + e^- \rightleftharpoons [\text{HDPF1}]^+$

$$E_{1/2}^r = 710 \text{ mV} \quad (12d)$$

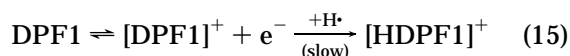
couple V $[\text{HDPF1}]^+ + e^- \rightleftharpoons \text{HDPF1}$

$$E_{1/2}^r = -1480 \text{ mV} \quad (12e)$$

associated with the acidity and basicity of the solution and the redox potential of the system. The acid–base equilibria that are important are



Additionally, interconversion of $[\text{HDPF1}]^+$ and $[\text{HDPF2}]^+$ may occur (Scheme 1), and chemical or bulk electrochemical oxidation of DPF1 gives $[\text{HDPF1}]^+$ rather than $[\text{DPF1}]^+$. Presumably a radical abstraction reaction gives rise to this conversion, as in eq 15. For



all of the compounds, there is an irreversible oxidation process between 1250 and 1300 mV at 200 mV s⁻¹ near the solvent limit, that is, process III for $[\text{DPF2}]^+$, process

VI for $[\text{HDPF1}]^+$, process X for DPF1, process XIII for C₅HPh₅ and also DPF2 in the presence of acid. Similarly, there is always a reversible couple in the 710–765 mV potential region: couple II for $[\text{DPF2}]^+$, couple IV for $[\text{HDPF1}]^+$, couple IX for DPF1, and couple XII for C₅HPh₅, although the appearances and relative peak heights in this potential region depend upon the acidity of the solution and the nature of the starting material. Since the $[\text{C}_5\text{HPh}_5]^{+/0}$ couple is observed in this potential region, these responses are believed to be ligand based rather than metal based.

Couples VII and VIII are also involved in coupled chemistry at the electrode surface, but their relative heights are dependent upon the starting material, the time scale of the voltammetric experiment, and the acidity or otherwise of the solution. Couple VIII occurs at essentially the same potential as couple I and is believed to be a result of the generation of transiently soluble DPF2 at the electrode surface. That is, couples I and VIII are both associated with the $[\text{DPF2}]^{+/0}$ redox couple. It will be recalled that both couples VII and VIII(I) may be observed for all solutions except those of $[\text{HDPF1}]^+$; that is, all other precursors in the bulk solution can generate couples VII and VIII(I) at the electrode surface under certain conditions. It is possible to observe both couples VII and VIII(I) (oxidation of DPF1), just couple VII (oxidation of DPF1 at low temperatures in the presence of base), just couple I (reduction of $[\text{DPF2}]^+$), or neither couple ($[\text{HDPF1}]^+$) and yet still observe the same electrochemical responses at more positive potentials.

Crystallographic data^{2,4} for DPF2 and $[\text{DPF2}]^+$ show them to be typical ferrocene and ferrocenium species. Not unexpectedly, therefore, the $[\text{DPF2}]^{+/0}$ electrochemistry is typical of ferrocene systems in that there is no further reduction beyond DPF2 up to the solvent limit, and the $E_{1/2}^r$ for the $[\text{DPF2}]^{+/0}$ couple is only 40 mV from that of Fc^{+/0}. Some substituted ferrocene systems have $E_{1/2}^r$ values much further removed from that of Fc^{+/0}, for example that of the $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{+/0}$ couple is -560 ± 10 mV.²⁰ The absence of an ESR signal at temperatures to 100 K for $[\text{DPF2}]^+$ but its presence at 4 K is also a typical behavior for a ferrocenium cation. Thus, it may be assumed that couple I is essentially a metal-based (Fe(II)/Fe(III)) redox process.

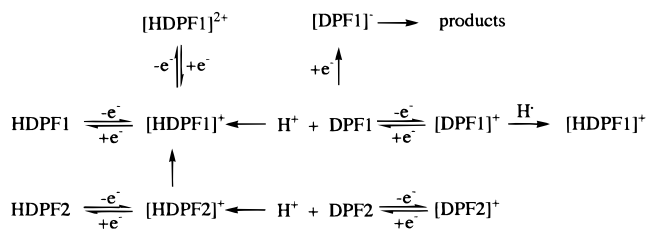
In contrast, ESR data suggest that $[\text{DPF1}]^+$ has significant radical character, which implies that the $[\text{DPF1}]^{+/0}$ redox chemistry is predominantly ligand based rather than metal based. The reversible oxidation of C₅HPh₅ is unambiguously an organic oxidation process. These ESR data support the suggestion that all processes in the DPF system at positive potentials are predominantly ligand based.

In the case of the voltammetric studies on DPF1, we never observe voltammetry completely free of responses due to the protonated form. Importantly, we have shown that $[\text{HDPF1}]^+$ is the orange product previously reported,¹ but not identified in that context, arising from the bulk oxidation of DPF1. The protonation to give

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Scheme 2



[HDPF1]⁺ is fast, but deprotonation back to DPF1 is never completely achieved using NEt₃ as the base. DPF2 can also be protonated, but the product is believed to be a Fe(IV) hydride and it provides a route to protonating the adjacent cyclopentadienyl ring and conversion to the linkage isomer [HDPF1]⁺.

The open circuit potential of the system, which depends on the oxygen and acid concentration, clearly is important in determining whether protonation or oxidation occurs and to a large extent determines the identities of species in the bulk solution. Similarly, the electrode potential is important in determining what happens at the electrode surface and, thus, which redox and acid–base reactions may be coupled. The complex combination of electron transfer and coupled chemical reactions can be summarized in Scheme 2, which is relevant to the voltammetric time scale. From the potentials of the various couples, several cross-redox reactions are thermodynamically favored, such as



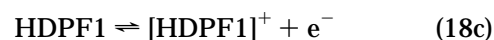
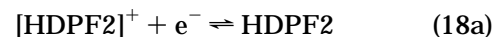
That is, many combinations of electron transfer and coupled chemical reactions are thermodynamically favored. In addition, because [DPF1]⁺ and its derivatives appear to have considerable radical character, reactions with solvent, water, or other adventitious impurities are highly likely, e.g., hydrogen atom abstraction is believed to give [HDPF1]⁺ which is the species observed after bulk oxidation of DPF1.

The very similar potentials of couples VII ([DPF1]⁺⁰) and XIV ([HDPF2]⁺⁰) probably account for the presence of small amounts of couple I (which requires interconversion of DPF1 to DPF2 at the electrode surface) as well as the expected large couple VII when DPF1 is

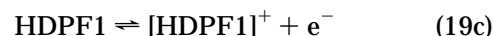
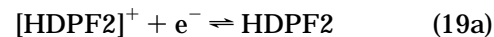
present in the bulk solution and when traces of acid are present. Dichloromethane invariably contains traces of hydrochloric acid, so that addition of DPF1 to dichloromethane leads to formation of trace amounts of [HDPF1]⁺ (always detected). Alternatively, small but variable amounts of [HDPF1]⁺ are formed during the synthesis of DPF1. Small amounts of the hydride [HDPF2]⁺ also are available via reaction of acid with traces of DPF2 present in DPF1 or from small equilibrium concentrations generated from the reaction



Under these circumstances, the following reaction sequence leads to interconversion of DPF1 and DPF2 at the electrode surface, with zero current flow, when DPF1 is placed in bulk solution:



Similarly, in the absence of DPF1 in the bulk solution, the zero current process sequence will occur at all potentials less negative than the reversible potential for couple V, under conditions where the interconversion reaction in equation 19b is fast.



Given the numerous pathways available, it is not possible to unambiguously specify a mechanism for the interconversion reactions. However, it is clear that isomerization, acid–base, and radical abstraction reactions are linked with redox chemistry in the novel decaphenylferrocene system.

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