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Electrochemical Oxidation of the Dithiophosphate Complexes η-Cp*Fe(CO)$_2$(η^1-SP(S)(OR)$_2$), (Cp* = η-C$_5$H$_5$, η-C$_5$H$_4$Me, η-C$_5$Me$_5$; OR = OEt, O^{i}Pr)

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Abstract

The oxidation of the dicarbonyl dithiophosphate cyclopentadienyl iron complexes Cp*Fe(CO)$_2$(η^1-SP(S)(OR)$_2$), (Cp* = η-C$_5$H$_5$, η-C$_5$H$_4$Me, η-C$_5$Me$_5$; OR = OEt, O^{i}Pr), in CH$_2$Cl$_2$ and CH$_3$CN has been examined using the techniques of cyclic voltammetry and controlled potential electrolysis. In CH$_3$CN, by using a combination of electrochemical, IR and EPR techniques, it has been possible to study in detail the oxidation mechanism of these complexes. According to the results obtained, the products of the one-electron oxidation are labile.

Introduction

In a previous work [1] we have described the synthesis and characterization of the dithiophosphate complexes, η-Cp*Fe(CO)$_2$(η^1-SP(S)(OR)$_2$). In order to establish the reactivity of these complexes, their electrochemical oxidation in various solvents has been studied. The results obtained are described in this paper.

Experimental

The electrochemical measurements were carried out under a nitrogen atmosphere. The cyclic voltammetry measurements were carried out with an Amel Model 4881 A, in conjunction with a Hewlett-Packard 7040 A X-Y recorder. The coulometric experiments were carried out with a Beckman Electroscan-30. The reference electrodes were an Ag wire/AgNO$_3$ (1.0×10^{-2} mol dm^{-3}) in acetonitrile or a standard calomel electrode (SCE) in dichlorometane.

Cyclic voltammetry experiments were made at a platinum working electrode. In the coulometry, the working electrode was a 9 cm^2 platinum plate which was separated from the auxiliary platinum electrode by a glass frit. All the electrochemical measurements were carried out at 25 °C.

The solvents CH$_3$CN and CH$_2$Cl$_2$ were purified by the standard methods used in electrochemical studies. Tetra-n-butylammonium hexafluorophosphate (Fluka) was recrystallised from ethanol and dried *in vacuo*; it was deoxygenated and dehydrated by melting under vacuum before use.

spectrometer, using a liquid cell with NaCl windows. In all cases the solvent absorptions were substracted by use of the software of the spectrophotometer.

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The complexes η-Cp*Fe(CO)$_2$(η^1-SP(S)(OR)$_2$) were obtained by published method [1].

Results and Discussion

The electrochemistry of the compounds η-Cp*Fe(CO)$_2$(η^1-SP(S)(OR)$_2$), (Cp* = η-C$_5$H$_5$, η-C$_5$H$_4$Me, η-C$_5$Me$_5$; OR = OEt, O^{i}Pr), was investigated in acetonitrile and dichloromethane with hexafluorophosphate as supporting electrolyte. Electrochemical parameters of the complexes are summarized in Table I. In acetonitrile, the cyclic voltammograms show an anodic and cathodic peaks, but they are not associated with a reversible oxidation–reduction process, because of a large peak separation and an ip_c/ip_a value much smaller than unity (Fig. 1).

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TABLE I. Cyclic Voltammetry at the Sweep Rate of 0.25 V s^{-1}

Complexes	CH_3CN[a]					CH_2Cl_2[b]	
	A	B′	B′$_1$	B	C′	A	B′$_1$
(η-C_5H_5)Fe(CO)$_2$[η^1-SP(S)(OEt)$_2$]	+0.86	−0.92	−0.46				
(η-C_5H_5)Fe(CO)$_2$[η^1-SP(S)(O^{i}Pr)$_2$]	+0.82	−0.92	−0.53			+1.22	−0.32
(η-C_5H_4Me)Fe(CO)$_2$[η^1-SP(S)(O^{i}Pr)$_2$]	+0.75	−0.94	−0.51			+1.12	−0.30
(η-C_5Me_5)Fe(CO)$_2$[η^1-SP(S)(OEt)$_2$]	+0.66	−1.27	−0.68			+0.93	−0.45
(η-C_5Me_5)Fe(CO)$_2$[η^1-SP(S)(O^{i}Pr)$_2$]	+0.56	−1.27	−0.70				
[(η-C_5H_5)Fe(CO)$_2$]$_2$		−0.93		+0.29	−1.31		
[(η-C_5H_4Me)Fe(CO)$_2$]$_2$		−0.93		+0.17	−1.33		
[(η-C_5Me_5)Fe(CO)$_2$]$_2$		−1.27		+0.12	−1.66		
NaSP(S)(O^{i}Pr)$_2$	+0.35						

[a] Potential peaks vs. Ag/Ag$^+$, volt. [b] Potential peaks vs. SCE, volt.

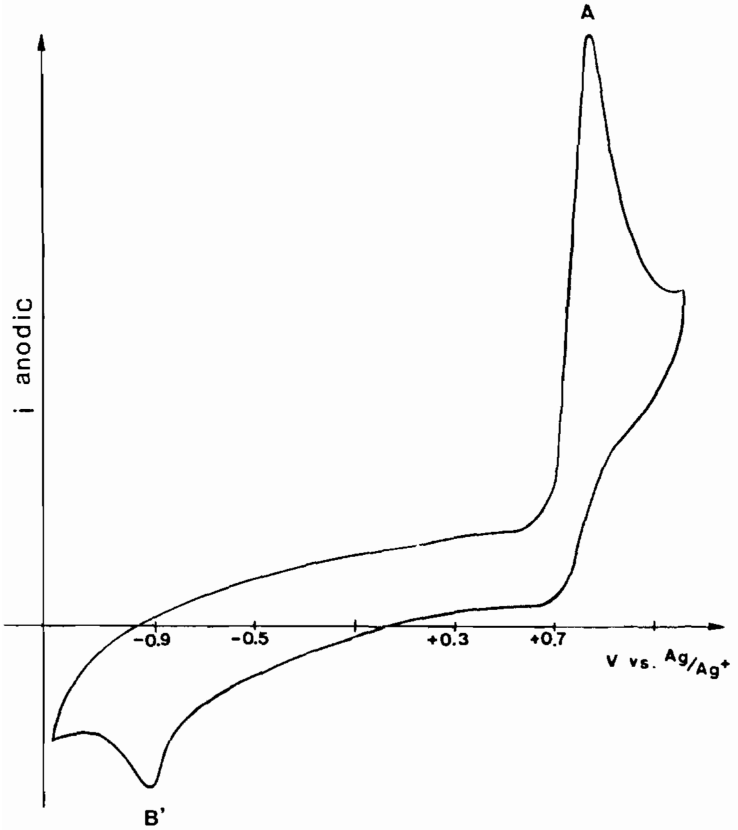


Fig. 1. Cyclic voltammogram of (η-C_5H_5)Fe(CO)$_2$(η^1-SP(S)(OEt)$_2$) in acetonitrile, at platinum electrode, containing 0.1 M Bu_4NPF_6, scan rate 0.1 V s^{-1}.

The anodic oxidations are irreversible at scan rates as high as 5 V/s.

The second cyclic run gives a new peak (B), at lower potentials than the first one (A). With repeating cyclization, another new cathodic peak (B′$_1$) at higher potentials than the original one (B′) can be observed. The current of these peaks increases gradually while that of peak A decreases (Fig. 2).

At slow scan rates it is possible to note the cathodic wave B′$_1$ in the first sweep. The multicyclic voltammograms recorded in dichloromethane exhibit only peaks A and B′$_1$. The peak potentials varied with sweep rate in both acetonitrile and dichloromethane.

Bulk oxidation of the complexes, carried out at more positive 100 mV than the anodic potentials, results in the removal of 1.0 electron/molecule.

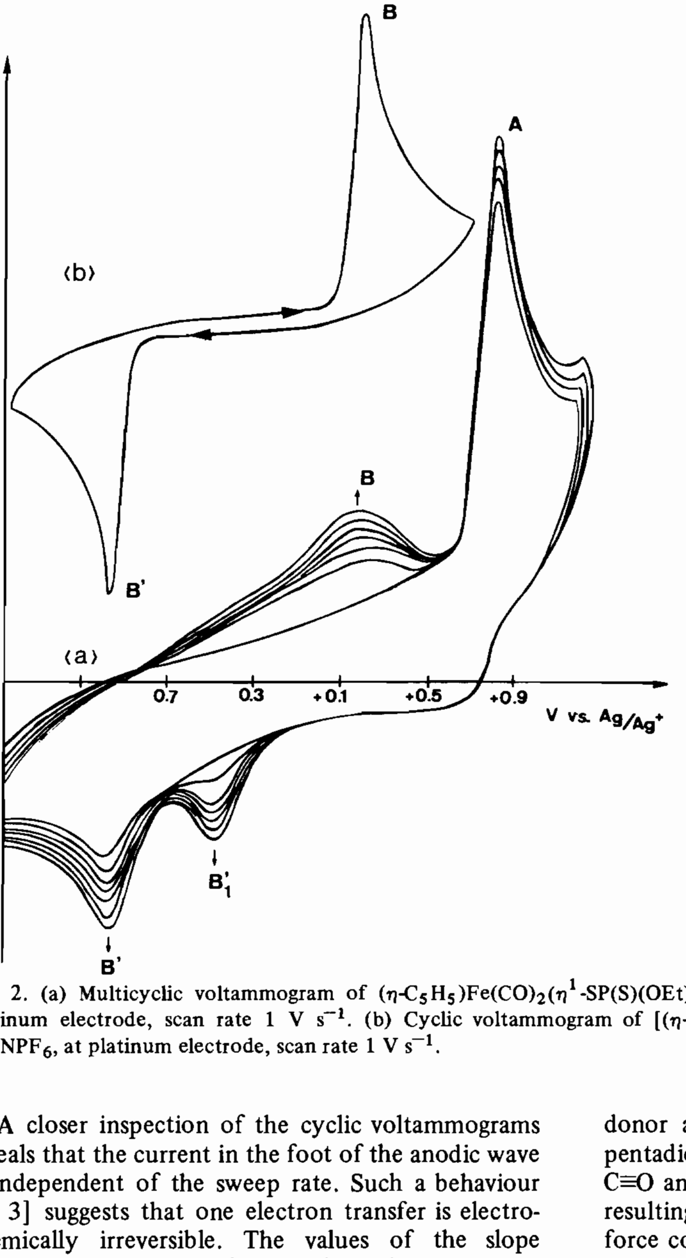


Fig. 2. (a) Multicyclic voltammogram of (η-C_5H_5)$Fe(CO)_2$(η^1-SP(S)$(OEt)_2$), in acetonitrile containing 0.1 M Bu_4NPF_6, at platinum electrode, scan rate 1 V s^{-1}. (b) Cyclic voltammogram of [(η-C_5H_5)$Fe(CO)_2$]$_2$, in acetonitrile, containing 0.1 M Bu_4NPF_6, at platinum electrode, scan rate 1 V s^{-1}.

A closer inspection of the cyclic voltammograms reveals that the current in the foot of the anodic wave is independent of the sweep rate. Such a behaviour [2, 3] suggests that one electron transfer is electrochemically irreversible. The values of the slope observed in the plots of *Ep vs.* log ν (ν = CV sweep rate) are approximately 60 mV per decade (Fig. 3). These results provide evidence of an irreversible electron-transfer process.

The infrared spectra of the complexes η-Cp*$Fe(CO)_2$(η^1-SP(S)$(OR)_2$), (Cp* = η-C_5H_5, η-C_5H_4Me, η-C_5Me_5; OR = O^iPr), show the ν(CO) bands at 2047, 2001; 2043, 1997; and 2025, 1978 cm^{-1}, respectively. From these data the stretching force constants, *K*, of the C≡O bond were calculated by the Cotton–Kraihanzel method [4]. A plot of the *K* values against the anodic peak potentials of these complexes in CH_2Cl_2 is depicted in Fig. 4, which indicates that the *K* values increase with increasing anodic peak potentials. Due to the greater electron donor ability of the methyl and pentamethylcyclopentadienyl rings, electron densities flow into the C≡O antibonding π^* orbitals through the iron center, resulting in lowering of the C≡O bond order and force constants. The anodic potential values decrease with increasing electron density of the metallic atom. The observed relation between K_{CO} and the anodic peak potentials is similar to the one found for these anodic potentials and the chemical shift, δCO, of ^{13}C NMR spectra [1].

The following scheme indicates the origin of the observed electrochemical reactions:

$$Cp^*Fe(CO)_2L \xrightarrow{-e^-} [Cp^*Fe(CO)_2L]^+A \qquad (1)$$

$$[Cp^*Fe(CO)_2L]^+ + MeCN \longrightarrow [Cp^*Fe(CO)_2MeCN]^+ + L^{\bullet} \qquad (2)$$

$$\begin{tikzcd}
2[Cp^*Fe(CO)_2MeCN]^+ \arrow[r, "+2\,e^-"] & 2Cp^*Fe(CO)_2^{\bullet} + 2MeCN\ B' \arrow[d] \\
 & {[Cp^*Fe(CO)_2]_2} + 2MeCN\ B \arrow[ul, "-2\,e^-"]
\end{tikzcd} \qquad (3)$$

$L = \eta^1 - SP(S)(OR)_2$

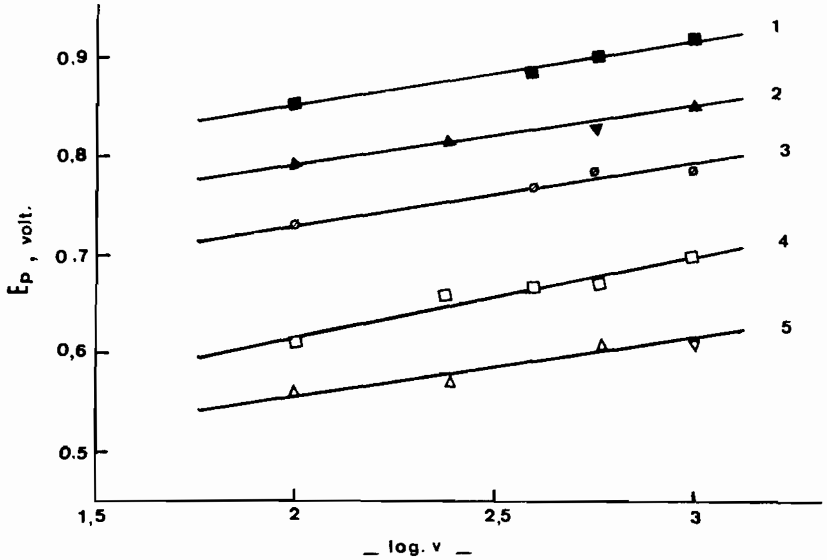


Fig. 3. Variation of the anodic peak potential with the log of scan rate, in acetonitrile, containing 0.1 M Bu_4NPF_6 and 10^{-3} of: (1) $(C_5H_5)Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$; (2) $(C_5H_5)Fe(CO)_2(\eta^1\text{-}SP(S)(OEt)_2)$; (3) $(C_5H_4Me)Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$; (4) $(C_5Me_5)Fe(CO)_2(\eta^1\text{-}SP(S)(OEt)_2)$; (5) $(C_5Me_5)Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$.

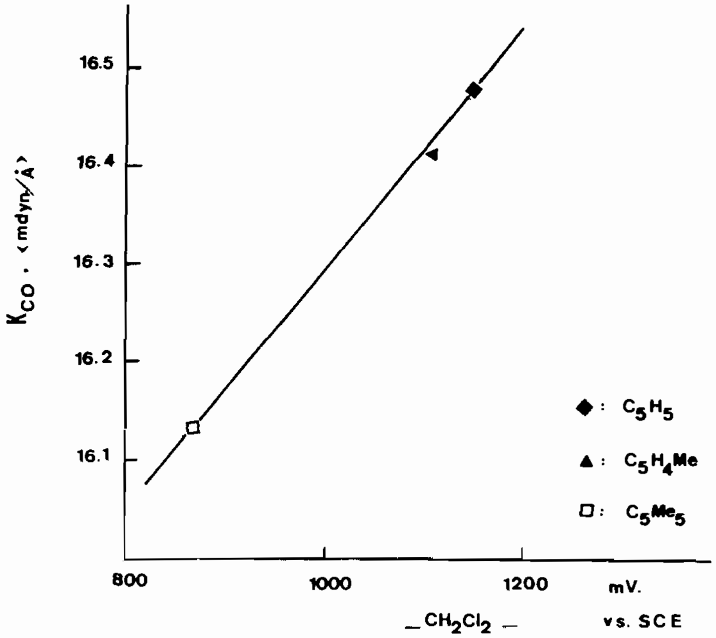


Fig. 4. Plot of the carbonyl force constant, K_{CO}, against the anodic oxidation potential for the complexes $\eta\text{-}Cp^*Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$, ($Cp^* = \eta\text{-}C_5H_5, \eta\text{-}C_5H_4Me, \eta\text{-}C_5Me_5$).

TABLE II. EPR and IR Data of the Studied Compounds

Complexes	g_{iso}	νCO^a
$(\eta\text{-C}_5\text{H}_5)\text{Fe(CO)}_2[\eta^1\text{-SP(S)(O}^i\text{Pr)}_2]$		2043, 1997
$(\eta\text{-C}_5\text{H}_5)\text{Fe(CO)}_2[\eta^1\text{-SP(S)(OEt)}_2]$		2043, 1998
$(\eta\text{-C}_5\text{H}_4\text{Me)Fe(CO)}_2[\eta^1\text{-SP(S)(O}^i\text{Pr)}_2]$		2039, 1994
$(\eta\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2[\eta^1\text{-SP(S)(O}^i\text{Pr)}_2]$		2021, 1973
$(\eta\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2[\eta^1\text{-SP(S)(OEt)}_2]$		2021, 1975
$[(\eta\text{-C}_5\text{H}_5)\text{Fe(CO)}_2[\eta^1\text{-SP(S)(O}^i\text{Pr)}]^+$	1.997	2013
$[(\eta\text{-C}_5\text{H}_5)\text{Fe(CO)}_2[\eta^1\text{-SP(S)(OEt)}_2]^+$	1.992	2014
$[(\eta\text{-C}_5\text{H}_4\text{Me)Fe(CO)}_2]\,[\eta^1\text{-SP(S)(O}^i\text{Pr)}_2]^+$	1.992	2010
$[(\eta\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2]\,[\eta^1\text{-SP(S)(O}^i\text{Pr)}_2]^+$	1.997	2033, 1986
$[(\eta\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2]\,[\eta^1\text{-SP(S)(OEt)}_2]^+$	1.996	2030, 1985
$[(\eta\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{NCCH}_3]^{+\,b}$		2079, 2032
$[(\eta\text{-C}_5\text{H}_4\text{Me)Fe(CO)}_2\text{NCCH}_3]^+$		2028
$[(\eta\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2\text{NCCH}_3]^{+\,c}$		2012
$[(\eta\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$		1990, 1790
$[(\eta\text{-C}_5\text{H}_4\text{Me)Fe(CO)}_2]_2$		1987, 1789
$[(\eta\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2]_2$		1936, 1763

^{a}Frequencies in cm^{-1}. ^{b}Ref. 8. ^{c}2065 and 2010 cm^{-1}, ref. 7.

The formation of the cation $[\text{Cp}^*\text{Fe(CO)}_2\text{L}]^+$ is supported by the EPR and IR spectra.

When the complexes were electrochemically oxidized (at $E > Ep_A$) *in situ* in the cavity of an EPR spectrometer at room temperature, the EPR spectra obtained showed a single signal, which is typical of the Fe(III) compounds [5]. The g_{iso} values calculated from these spectra are summarized in Table II. When the potentiostat was turned off, the signal decayed slowly to one or more EPR silent species.

After exhaustive bulk electrolysis, the IR spectra of resulting solutions show new bands corresponding to ν(CO) stretching vibrations. In the case of the anodic oxidation of the complex $\eta\text{-C}_5\text{Me}_5\text{Fe(CO)}_2(\eta^1\text{-SP(S)(O}^i\text{Pr)}_2)$, ($\nu$(CO): 2021 and 1973 cm^{-1}), two bands are observed at 2033 and 1986 cm^{-1} that can be assigned to the stretching vibration modes A$'$ and A$''$, respectively, of the CO group; these bands are displaced towards higher frequencies owing to the higher oxidation state of the metal atom.

For the complex $\eta\text{-C}_5\text{H}_5\text{Fe(CO)}_2(\eta^1\text{-SP(S)(O}^i\text{Pr)}_2)$, ($\nu$(CO): 2043 and 1927 cm^{-1}), it is possible to observe the band corresponding to the vibration mode A$'$ of the cation generated by electrolysis. This band will appear at frequencies above 2043 cm^{-1}, being masked by the solvent. The other ν(CO) band of $[\eta\text{-C}_5\text{H}_5\text{Fe(CO)}_2(\eta^1\text{-SP(S)(O}^i\text{Pr)}_2)]^+$ is observed at 2013 cm^{-1}. Analogous results are obtained with all the complexes investigated (Table II).

In the IR spectra of the solutions obtained by electrolitic oxidation, other bands are observed that suggest the presence of cations like $[\text{Cp}^*\text{Fe(CO)}_2\text{MeCN}]^+$ [6, 7] in these solutions. The frequencies are 2032 cm^{-1} ($\text{Cp}^* = \eta\text{-C}_5\text{H}_5$), 2028 cm^{-1} ($\text{Cp}^* = \eta\text{-C}_5\text{H}_4\text{Me}$) and 2012 cm^{-1} ($\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$), respectively.

Cyclic voltammograms of the iron dimer $[\eta\text{-Cp}^*\text{Fe(CO)}_2]_2$ ($\text{Cp}^* = \eta\text{-C}_5\text{H}_5$, $\eta\text{-C}_5\text{H}_4\text{Me}$, $\eta\text{-C}_5\text{Me}_5$) in acetonitrile have a pair of anodic and cathodic peaks which correspond exactly to the potentials of peak B and B$'$ of the respective compounds (Fig. 2).

The reduction of the $[\eta\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{L}]^+$ (L = PPh$_3$, CO, MeCN) complexes to $[\eta\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2$ in various solvents has been observed by several authors [8, 9]. Likewise, it is known that the oxidation of $[\eta\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2$ gives a short-lived intermediate which is rapidly attached by the solvent to give $[\eta\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{MeCN}]^+$ [10]. These processes explain the origin of peak B in the second cyclic run.

The formation of the iron dimers was proved by IR spectroscopy and electrochemical control of the solutions obtained by bulk electrolytic oxidation followed by an exhaustive reduction electrolysis. This reduction was carried out at potentials more negative than the cathodic peak B$'$. In the IR spectra of these solutions obtained by reduction, bands are observed which are characteristic of the dimers in acetonitrile solutions, $[\eta\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2$: ν(CO): 1990, 1790 cm^{-1}; $[\eta\text{-C}_5\text{H}_4\text{MeFe(CO)}_2]_2$: ν(CO): 1987, 1789 cm^{-1} and $[\eta\text{-C}_5\text{Me}_5\text{Fe(CO)}_2]_2$: ν(CO): 1936, 1763 cm^{-1} (Table II).

The voltammetric behaviour of these solutions is like that of the iron dimer solutions. When positive potentials are scanned, oxidation peaks corresponding to process B are observed. In the cathodic sweep reduction, peaks are found which arise from the reaction:

$[Cp^*Fe(CO)_2]_2 \xrightarrow{+2\,e^-} 2\,[Cp^*Fe(CO)_2]^-$ C′ [8].

The second process (2) in the proposed scheme is the oxidatively induced reductive elimination (OXIRE) of the ligand $L^{\bullet}$, which can produce L_2. Such OXIRE reactions of a σ-bound ligand should occur whenever the central metal atom has a reasonably accessible higher oxidation state and if the σ-bond is unstable in that higher oxidation state. In our case the ratios of cathodic to anodic peak currents $ip_{B'}/ip_A < 1$ suggest a slow rate for the OXIRE reaction.

As was previously mentioned, the peak B'_1 appears in the first run at very slow rate or in multicyclic sweep. However, if in repeating cycles the potential sweep was reversed at any point before the foot of the anodic wave A, the peak B'_1 was not observed, whilst B and B′ remained practically unchanged. From this fact it seems clear that the process responsible for peak B'_1 involves cations like $[Cp^*Fe(CO)_2L]^+$.

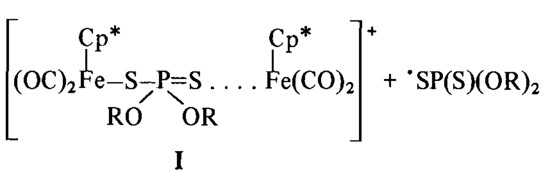
One possible statement for the origin of B'_1 should be the coordination of the ligand dimer through products originating from OXIRE:

$$[Cp^*Fe(CO)_2(SP(S)(OR)_2)]^+ + {}^{\bullet}SP(S)(OR)_2 \longrightarrow [Cp^*Fe(CO)_2((RO)_2(S)PS{-}SP(S)(OR)_2)]^+$$

These results have been reported in the one-electron oxidation of cyclopentadienyl iron(II) thiolates [11] which gives compounds of the type $[CpFe(CO)_2\text{-}\mu\text{-}Ph{-}S{-}S{-}Ph{-}Fe(CO)_2Cp]^{2+}$; in acetonitrile the dimer decomposed to $[CpFe(CO)_2(PhSSPh)]^+$ and $[CpFe(CO)_2MeCN]^+$.

Another possibility to explain the peak B'_1 consists of a reaction between the parent compound and the cation resulting from the oxidation reaction in competition with the solvent in an OXIRE reaction:

$$Cp^*Fe(CO)_2(SP(S)(OR)_2) + [Cp^*Fe(CO)_2(SP(S)(OR)_2)]^+ \longrightarrow$$



$$\left[(OC)_2\overset{Cp^*}{Fe}{-}S{-}\underset{RO\ \ OR}{P}{=}S\cdots\overset{Cp^*}{Fe}(CO)_2\right]^+ + {}^{\bullet}SP(S)(OR)_2$$

I

Similar compounds have been obtained by Catheline *et al.*, such as the bridged ligand dithiocarbamate, $SC(S)NR_2$ [7].

Unfortunately, although we tried very intensively, we could not isolate any defined compound from solutions obtained by electrolytic oxidation. However, we have observed in the IR spectra of these solutions the presence of the notably broadened ν(CO) bands of the initial compounds. These bands suggest the formation of above-mentioned type **I** compounds because in this case the electronic environment of the two metal atoms is similar, and the ν(CO) bands should appear at frequencies close to those of the initial complexes. Therefore, we believe that $[Cp^*Fe(CO)_2\text{-}\mu\text{-}SP(S)(OR)_2Fe(CO)_2Cp^*]^+$ is the most apropiate candidate for explaining the ocurrence of the peak B'_1.

Conclusion

As expected [12], the case of the oxidation of the compounds $\eta\text{-}Cp^*Fe(CO)_2L$ ($L = \eta^1\text{-}SP(S)(OR)_2$) tends to parallel the electron-donating ability of the ligands, while the number of electrons abstracted from each dicarbonyl compound is unity. The initial products all of the oxidations are labile, as the cyclic voltammetric experiments showed.

In all cases the reductive elimination is an important step. Such reactions are highly important in organometallic chemistry and metal-catalyzed reactions [13–15]; however, the mechanisms of such reactions have been thoroughly studied in only a few instances, such as the $CpFe(CO)_2R$ systems [15].

One final point of interest concerns the detection of a species we suspect to be the dithiophosphate-bridge dimer. This finding is parallel to the known formation of thiolate and dithiocarbamate bridged dimers by an OXIRE process [12, 16, 17]. This behaviour has been related to the instability observed in 17-electron d^5 complexes, such as those described here. The reactivity of these complexes is associated with the loss of an electron from a sulphur lone-pair orbital, assumed to be the HOMO orbital, giving a radical site located at the sulphur [11].

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