Cyclopentadienyliron Complexes with P=S Ligands; Synthesis and Electrochemical Behaviour

M. MORÁN, I. CUADRADO, C. PASCUAL, J. R. MASAGUER

Departamento de Química, Facultad de Ciencias, C-VIII, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

and J. LOSADA

Departamento de Química Inorgánica y Analítica, E.T.S. de Ingenieros Industriales, Universidad Politécnica de Madrid, 28001 Madrid, Spain

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Abstract

Reactions of $[\eta\text{-}C_5H_5Fe(CO)_2THF]^+PF_6^-$ with the P=S neutral ligands L = $SPMe_3$, $SPPh_3$, $SP(OEt)_3$, $SP(OPh)_3$ and $(S)PEt_2{-}P(S)Et_2$, lead to the formation of cationic complexes $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$, which were characterized by IR and NMR spectra. The electrochemical behaviour of these complexes has been studied in THF solution, using cyclic voltammetry and coulometry. According to the results obtained, the products of the one-electron reduction are labile and the reduced species lose the ligand L. The oxidation of the dimer $[\eta\text{-}C_5H_5Fe(CO)_2]_2$ in the presence of the ligands, indicates that electrochemical synthesis of the complexes $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$ is possible.

Introduction

One of the most thoroughly studied groups of organometallic complexes is that of the derivatives of the cyclopentadienyliron dicarbonyl, $(\eta\text{-}C_5H_5)Fe(CO)_2$ [1–4], probably because many routes are available for the synthesis of these complexes. One route is the oxidative cleavage of the Fe–Fe bond in $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, which has been used to synthesize the cationic complexes $[(\eta\text{-}C_5H_5)Fe(CO)_2L]^+$. Chemical oxidations with $AgBF_4$ [5], $FeCl_3$ [6], O_2/HBF_4 [7], Ph_3C^+ [8], as well as electrochemical oxidations [9] have also been used.

Recently, Catheline and Astruc [10] have found that the ferricinium cation is a very efficient and clean reagent for the oxidation of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$. This oxidation proceeds at room temperature, in various coordinating solvents, to give stable complexes, $[\eta\text{-}C_5H_5Fe(CO)_2S]^+PF_6^-$ (S = THF, CH_3CN, $(CH_3)_2CO$, py). The cation $[\eta\text{-}C_5H_5Fe(CO)_2THF]^+PF_6^-$ is shown as an excellent intermediate for the preparation of the complexes $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$ [10].

Although cationic complexes, $[\eta\text{-}C_5H_5Fe(CO)_2L]^+BF_4^-$ have been reported with some phosphorous and sulphur ligands such as $P(OR)_3$, $P(NR_2)_3$, SR_2 and RSSR [11–15], until now complexes with phosphines sulphides or tetraalkyldiphosphines disulphides as ligands have not been synthesized.*

We report here the preparation and spectroscopic data of the cationic complexes $[\eta\text{-}C_5H_5Fe(CO)_2(SPR_3)]^+PF_6^-$, (R = Me, Ph, OEt, OPh), and $[\eta\text{-}C_5H_5Fe(CO)_2(SPEt_2{-}P(S)Et_2)]^+PF_6^-$, which can be obtained by two different methods:

(i) Treatment of $[\eta\text{-}C_5H_5Fe(CO)_2THF]^+PF_6^-$ with the different neutral P=S donor ligands, and

(ii) Electrochemical oxidation of $[\eta\text{-}C_5H_5Fe(CO)_2]_2$ at a platinum electrode, in THF solution, in the presence of the donor ligands $SPMe_3$, $SPPh_3$, $SP(OEt)_3$, $SP(OPh)_3$ and $[Et_2P(S)]_2$, using tetra-n-butylammonium hexafluorophosphate as supporting electrolyte.

In addition, we have studied the electrochemical behaviour of the $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$ complexes synthesized.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry and oxygen-free dinitrogen. The complexes $[\eta\text{-}C_5H_5Fe(CO)_2]_2$ [17] and $[\eta\text{-}C_5H_5Fe(CO)_2THF]^+PF_6^-$ [10] and the ligands, $SPMe_3$ [18], $[Et_2P(S)]_2$ [19], $SPPh_3$ and $SP(OPh)_3$ [20], were prepared by literature methods.

Infrared spectra were recorded at 4000–200 cm^{-1} on a Nicolet 5DX FT-IR spectrometer using Nujol and hexachlorobutadiene mulls between CsI windows. The solution spectra were examined in a

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*While this work was in progress, BF_4^- salts of the $[\eta\text{-}C_5H_5Fe(CO)_2SPMe_3]^+$ and $[\eta\text{-}C_5H_5Fe(CO)_2SPPh_3]^+$ cations were prepared by others workers [16].

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liquid cell with CsBr windows. In all cases the solvent absorptions were subtracted by use of the software of the spectrometer.

The proton and carbon NMR spectra were recorded on a Bruker WH-500-2Y (200 MHz, FT mode) spectrometer.

Cyclic voltammetric measurements were carried out by the use of a Metrohm VA-Scanner, in conjunction with a Metrohm VA-detector and a Linseis LY-17100, X-Y recorder. Fast scan cyclic voltammograms are recorded on a Hitachi VC-6015 digital storage oscilloscope. The coulometric experiments were carried out with a Beckman Electroscan-30 instrument. The electrochemical measurements were performed in a three-electrode cell with a platinum disk working electrode, a platinum wire auxiliary electrode and aqueous satured calomel electrode (SCE) as reference electrode. The reference electrode was separated from the test solution by a Vycor frit and a bridge of $[n\text{-}Bu_4N][PF_6]$ (0.1 M) in THF. A sample solution containing a metal complex (1×10^{-3} M) and a supporting electrolyte, $[n\text{-}Bu_4N][PF_6]$, was dearated with nitrogen prior to measurements. Tetrahydrofuran was purified by the ketyl method.

In the coulometry, the working electrode was a platinum mesh.

The conductivity measurements were carried out in CH_3CN solutions with a Metrohm Conductometer E-518.

Preparation of Complexes

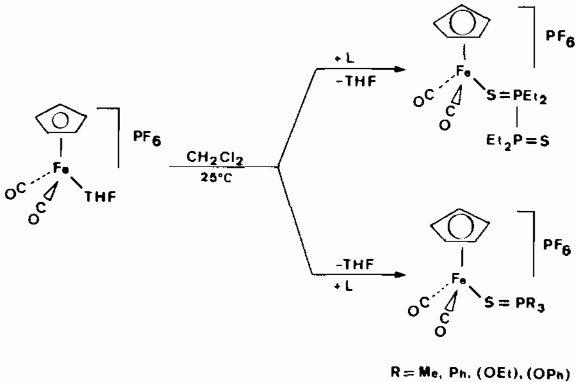
The preparation of $[\eta\text{-}C_5H_5Fe(CO)_2(SP(OEt)_3)]^+PF_6^-$ is described in detail below. The procedures for the synthesis of the other complexes were similar. The experimental details and analytical data are given in Table I.

$[\eta\text{-}C_5H_5Fe(CO)_2(SP(OEt)_3)]^+PF_6^-$

A mixture of $[\eta\text{-}C_5H_5Fe(CO)_2THF]PF_6$ (1.77 g, 4.5 mmol) and $SP(OEt)_3$ (1.78 g, 9.0 mmol) in CH_2Cl_2 (30 ml), was stirred at room temperature for 36 h. Ether (50 ml) was added. The orange solid which separated was filtered off, washed with ether, and dried *in vacuo*. The solid was recrystallized from CH_2Cl_2/ether. The yield was about 70%.

Results and Discussion

The cationic complexes $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$ (Scheme 1), were prepared in good yield by reaction of the neutral donor P=S ligands with $[\eta\text{-}C_5H_5Fe(CO)_2THF]^+PF_6^-$. The general method consisted of adding an excess (2:1) of the neutral ligand to a dichloromethane solution which contains the complex $[\eta\text{-}C_5H_5Fe(CO)_2THF]PF_6$, (previously synthesized from $[\eta\text{-}C_5H_5Fe(CO)_2]_2$ and $[(\eta\text{-}C_5H_5)_2Fe]^+PF_6^-$, see ref. 10). The mixture was kept at room temperature for a time period that depended on the ligand (usually 24 to 36 h, see data on Table I), a colour



Scheme 1.

TABLE I. Physical, Preparative and Analytical Data for the Complexes $[CpFe(CO)_2L]^+PF_6^-$

Complex	$[CpFe(CO)_2THF]PF_6$ g (mmol)	L g (mmol)	*t* (h)	Colour	Analysis, Found (calc.) (%)		
					C	H	Fe
$[CpFe(CO)_2(SPMe_3)]PF_6$	1.77(4.5)	0.97(9.0)	24	orange	27.9 (27.2)	3.2 (3.1)	12.9 (13.0)
$[CpFe(CO)_2((S)PEt_2P(S)Et_2)]PF_6$	1.77(4.5)	2.17(9.0)	24	orange	31.9 (31.6)	4.4 (4.4)	9.9 (9.8)
$[CpFe(CO)_2(SPPh_3)]PF_6$	1.77(4.5)	2.64(9.0)	36	orange	51.3 (50.9)	3.4 (3.3)	9.5 (9.9)
$[CpFe(CO)_2(SP(OEt)_3)]PF_6$	1.77(4.5)	1.78(9.0)	36	orange	30.0 (30.2)	3.8 (3.7)	10.7 (10.9)
$[CpFe(CO)_2(SP(OPh)_3)]PF_6$	1.77(4.5)	3.07(9.0)	36	orange	45.8 (45.1)	3.5 (3.0)	8.7 (8.3)

TABLE II. Characteristic IR[a] Spectra of the Compounds $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$

Ligand L =	ν(CO)				k[b]	k_i	δ(FeCO)[c]				ν(PS)[d]
	Nujol		CH_2Cl_2								
	A	A′	A	A′							
$SPMe_3$	2045	2002 1971sh	2048	2000	16.54	0.36	605s	595w	571s	526m	541s
$Et_2P(S)P(S)Et_2$	2058	1998 1951sh	2054	2010	16.65	0.38	605s	600w	572s	525m	540s
$SPPh_3$	2060 2049	2012 2004sh	2055	2012	16.70	0.35	612m	570s	532s		598vs
$SP(OEt)_3$	2061	2013 1983sh	2062	2018	16.80	0.34	600m	598sh	569s	532m	615m
$SP(OPh)_3$	2065	2018 1987sh	2068	2020	16.87	0.38	610m	600sh	570s	530m	618m

[a] Data in cm^{-1}. [b] In CH_2Cl_2, mdyn A^{-1}. [c] In Nujol. [d] ν(PS) for the free ligands: $SPMe_3$ = 564 cm^{-1}; $[Et_2P(S)]_2$ = 551 cm^{-1}; $SPPh_3$ = 636 cm^{-1}; $SP(OEt)_3$ = 640, 615 cm^{-1}; $SP(OPh)_3$ = 625 cm^{-1}.

change being observed. Addition of ether causes the precipitation of the complexes, which are isolated as orange crystalline solids. The analytical data (Table I), conductivity measurements, and IR and NMR data are in agreement with the formulation indicated in Scheme 1.

In the IR spectra of the free ligands, the ν(P=S) stretching mode increases from $SPMe_3$ to $SP(OEt)_3$ and $SP(OPh)_3$, according to the different electronegativity of the phosphorous substituents, as is indicated in the values shown in Table II. In the complexes, the formation of the Fe–S bond causes a decrease in the P=S bonding and consequently, we observe an important decrease in the ν(P=S) in the synthesized complexes (see Table II), which is consistent with the values found in complexes of these ligands with others metals [21–25].

For the complex with tetraethyldiphosphine disulphide, $[\eta\text{-}C_5H_5Fe(CO)_2(SPEt_2\text{–}P(S)Et_2)]^+PF_6^-$, the number and position in the IR spectra of some characteristic bands corresponding to the ligand, indicate the coordination behaviour of the $Et_2P(S)$–$P(S)Et_2$, which can act as a monodentate, with retention of the '*trans*' conformation characteristic for the free solid ligand [26], or on the contrary, it can adopt a '*cis*' or 'gauche' chelate structure. In the $Et_2P(S)$–$P(S)Et_2$ free ligand with a centrosymmetric *trans*-structure (C_{2h}) [26], the ν_{as}(PS) gives rise to a strong IR band at 551 cm^{-1}, while the other ν_s(PS) stretching mode is not IR active, but it is readily identified with a strong Raman line at 602 cm^{-1}. For a bidentate chelate structure, both ν_s and ν_{as}(PS) modes become strongly IR active, being thus observed as two strong bands at 595 and 530 cm^{-1} respectively in complexes of other metal ions [21]. Likewise, for compounds of this ligand, with a '*cis*' or 'gauche' chelate structure, four IR bands are expected between 670 and 740 cm^{-1}, which correspond to ν(PC) modes. In the free ligand, only two IR absorptions at 735 and 682 cm^{-1} are observed, which is consistent with a '*trans*' conformation [21, 26].

In our complex $[\eta\text{-}C_5H_5Fe(CO)_2(SPEt_2\text{–}P(S)\text{-}Et_2)]PF_6$, only one ν(PS) band at 540 cm^{-1} and two ν(PC) bands at 732 and 678 cm^{-1} are observed; these data are consistent with a '*trans*'-structural rearrangement of the ligand, similar to that found in the solid free ligand, and therefore, with a monodentate coordination.

In the IR spectrum of the triethyl-thiophosphate, $(EtO)_3P$=S, a doublet at 640 and 615 cm^{-1} due to ν(PS) is observed, which has been attributed to the presence of two different rotational isomers [24]. The coordination of this ligand to a metal atom prevents the existence of different rotameric forms, as being coordinated to metal is the more stable. Thus, in $[\eta\text{-}C_5H_5Fe(CO)_2(SP(OEt)_3)]PF_6$, only one ν(PS) band is observed at 615 cm^{-1}, which indicates the existence of only one rotational isomer in the complex.

The IR spectra of the obtained complexes in the carbonyl stretching region have been registered either in the solid form or in CH_2Cl_2 solution. The two expected ν(CO) stretching vibrations (corresponding to the A′ and A″ modes) are listed in Table II. The presence of shoulders and in some cases doublets in these ν(CO) bands in the IR spectra recorded in Nujol mulls, may be due to solid state interactions, because they disappear when the spectra are recorded in dichloromethane solutions, only two strong bands then

TABLE III. ^1H and ^{13}C NMR Spectra of the Complexes $[CpFe(CO)_2L]^+PF_6^-$ [a]

Complex	δ (^1H)	δ (^{13}C)
$[CpFe(CO)_2(SPMe_3)]^+$	2.15 (d, 9H, CH_3)J(PH) = 14 5.70 (s, 5H, C_5H_5)	18.7, 17.6 (d, CH_3)J(PC) = 50 87.7 (s, C_5H_5) 212.4 (s, CO)
$[CpFe(CO)_2(SPPh_3)]^+$	4.90 (s, 5H, C_5H_5) 7.75 (m, C_6H_5)	86.2 (s, C_5H_5) 129.9, 129.2 (d, m-C_6H_5)J(PC) = 12 132.9, 132.7 (d, p-C_6H_5)J(PC) = 10 134.2 (d, o-C_6H_5) 211.3 (s, CO)
$[CpFe(CO)_2(S)PEt_2-P(S)Et_2]^+$	1.20 (d of t, 10H, CH_3)J(PH) = 12 2.20 (m, br, 4H, CH_2) 5.47 (s, 5H, C_5H_5)	6.4 (d, CH_3)J(PC) = 10 25.3 (s, CH_2) 87.8 (s, C_5H_5) 212.6 (s, CO)
$[CpFe(CO)_2(SP(OEt)_3)]^+$	1.45 (t, 9H, CH_3) 4.42 (m, 6H, CH_2) 5.57 (s, 5H, C_5H_5)	15.5 (s, CH_3) 68.7 (s, CH_2O) 87.2 (s, C_5H_5) 213.7 (s, CO)
$[CpFe(CO)_2(SP(OPh)_3)]^+$	5.41 (s, 5H, C_5H_5) 7.38 (m, C_6H_5)	88.6 (s, C_5H_5) 150.2 (d, C(1)) 120.6 (d, o-C_6H_5) 130.2 (d, m-C_6H_5) 126.7 (d, p-C_6H_5) 214.2 (s, CO)

[a] Cp = η-C_5H_5; in $CDCl_3$ solution, δ in ppm, J in Hz.

being observed (Table II). The calculated values of k (stretching) and k_i (interaction) force constants, according to the Cotton–Kraihanzel method [27], are in the range 16.5–16.8 and 0.34–0.39 mdyn A^{-1} respectively (Table II); they are very similar to those found in other iron cyclopentadienyldicarbonyl complexes such as $[\eta$-$C_5H_5Fe(CO)_2L]^+$ (L = PPh_3, CH_3CN, CO, C_2H_4) [28, 29].

The different electron-donating capacity of the P=S ligands is reflected in the values of ν(CO) as shown in Table II. Thus for the Me_3P=S ligand, the greater electron-donor ability (due to the presence of methyl groups), increases the electronic density around the iron center and this flows into the C≡O antibonding π^* orbitals, resulting in lowering in the C≡O bond order, which is reflected in the lower values of the ν(CO) frequencies for the η-$C_5H_5Fe(CO)_2(SPMe)_3PF_6$ complex. Along with this decrease of the ν(CO), there is a corresponding decrease in the values of the carbonyl force constants k and k_i, indicated in Table II. On the contrary, the complexes $[\eta$-$C_5H_5Fe(CO)_2(SP(OEt)_3)]^+$ and $[\eta$-$C_5H_5Fe(CO)_2$-$(SP(OPh)_3)]^+$ exhibit the higher values of ν(CO) and force constants, according with the more electronegative character of the –OR groups.

The four expected bending vibrations of δ(FeCO) [30] appear in the 610–520 cm^{-1} range (Table II), along with the bands due to the ν(P=S) of the ligands, and one of the stretching bands of the PF_6^- anion. The presence of this anion PF_6^- in all these cationic complexes studied is easily identified by the strong and characteristic absorptions due to the ν(PF) at 557 and 850–820 cm^{-1} [31].

The signals observed in the ^1H and ^{13}C NMR spectra are shown in Table III. The signals due to the ligands appear as doublets, as a consequence of the coupling with the phosphorous atoms. In the ^1H NMR spectra of the complexes there is only one signal in the δ 5 (ppm) region, indicating the equivalence of the five protons of the cyclopentadienyl ring, as expected, since the phosphorous atom is not directly bonded to the metal. On the other hand, when the electronic density around the metal is increased as a consequence of the increase of electron donor ability of the ligand, an increase in the screening of the ^{13}C nucleus is expected, shifting the CO signals to higher δ values [28].

Electrochemical Studies

The electrochemistry of the synthesized compounds $[\eta$-$C_5H_5Fe(CO)_2L]^+PF_6^-$, (L = $SPMe_3$, $SPPh_3$, $SP(OEt)_3$, $SP(OPh)_3$ and $SPEt_2$–$P(S)Et_2$), was investigated in THF solution, at a platinum electrode, with tetra-n-butylammonium hexafluorophosphate

TABLE IV. Cyclic Voltammetry of $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$ Complexes at Pt Electrode, Sweep Rate 0.1 V s^{-1}, in THF Solution

Complex[a]	E_p(A)	E_p(A$_1$)	E_p(B)	E_p(B$_1$)
$[CpFe(CO)_2(SPMe_3)]PF_6$	−0.64	+0.80	−1.66	−0.94
$[CpFe(CO)_2((S)PEt_2P(S)Et_2)]PF_6$	−0.53	+0.80	−1.68	−0.94
$[CpFe(CO)_2(SPPh_3)]PF_6$	−0.51	+0.81	−1.67	−0.95
$[CpFe(CO)_2(SP(OEt)_3)]PF_6$	−0.44	+0.87	−1.67	−0.95
$[CpFe(CO)_2(SP(OPh)_3)]PF_6$	−0.39	+0.89	−1.68	−0.94
$[CpFe(CO)_2]_2$			−1.68	−0.92

[a] Cp = $\eta\text{-}C_5H_5$.

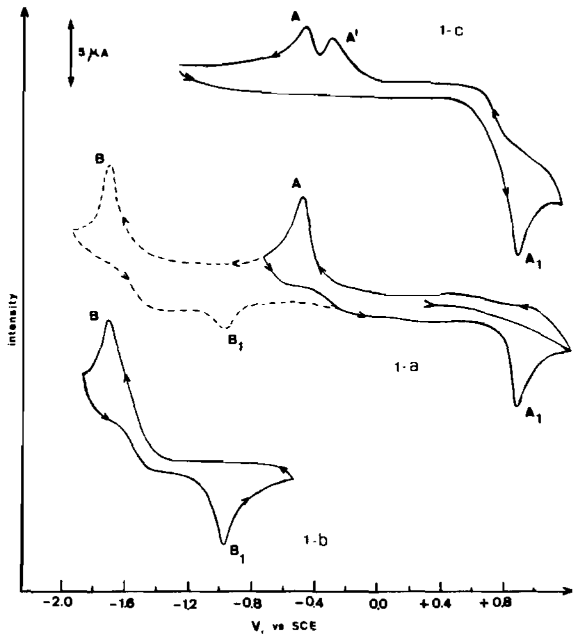


Fig. 1. Cyclic voltammograms in THF containing 0.1 M Bu_4NPF_6, at a Pt electrode, scan rate 0.1 V s^{-1} for: (a) 10^{-3} M $[\eta\text{-}CpFe(CO)_2(SPOEt)_3)]PF_6$; (b) 5×10^{-4} M $[\eta\text{-}CpFe(CO)_2]_2$; (c) 5×10^{-4} M $[\eta\text{-}CpFe(CO)_2]_2$ with 7.5×10^{-3} M of added $SP(OEt)_3$.

as supporting electrolyte. Electrochemical parameters of the complexes are summarized in Table IV. The cyclic voltammograms show a cathodic (A) and an anodic (A$_1$) peak, but they do not correspond to a reversible reduction–oxidation process, because of a large peak separation and ip_c/ip_a values much smaller than unity (Fig. 1a). The electrochemical irreversibility of the processes associated to peaks A and A$_1$ is confirmed by the magnitude of the slopes in the plots of E_p *versus* log ν (ν = scan rate) [32], which are significantly larger than those expected for a reversible process. These cathodic reductions are irreversible at scan rates as high as 5 V s^{-1}.

Complete electrolysis of all compounds, carried out at potentials 100 mV more negative than the peaks A, requires 1 Faraday/mole.

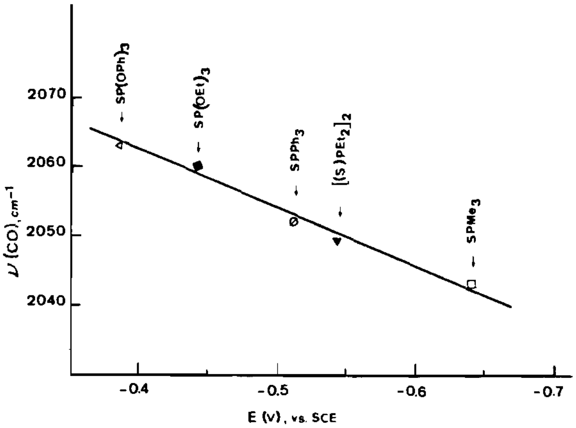


Fig. 2. Plot of $\nu(C\equiv O)$ against the cathodic peak potentials for the complexes $[\eta\text{-}CpFe(CO)_2L]^+PF_6^-$, (L = $SPMe_3$, $SPPh_3$, $(S)PEt_2\text{-}P(S)Et_2$, $SP(OEt)_3$, $SP(OPh)_3$; η-Cp = C_5H_5).

As expected the cathodic peak potentials shift to more negative values in accordance with the greater donor ability of the $R_3P{=}S$ ligands. A plot of ν(CO) (A' mode) values against the cathodic peak potentials of these complexes in THF is depicted in Fig. 2.

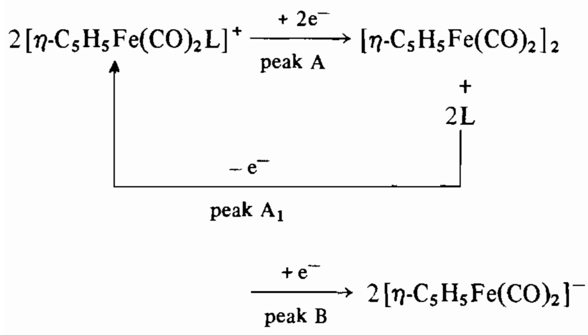
When the sweep range is extended about −2.0 V (*versus* SCE) the cyclic voltammogram displays another pair of cathodic and anodic peaks (B, B$_1$) (Fig. 1a). In all cases the potential value of the peak B is identical with the cathodic peak of the dimer $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ (Fig. 1b) and (Table III). A similar electrochemical behaviour is found in complexes of the type $[\eta\text{-}C_5H_5Fe(CO)_2PPh_3]PF_6$ at a Hg electrode [33].

On the other hand, it is known that oxidation of the dimer type $[\eta\text{-}Cp^*Fe(CO)_2]_2$ ($Cp^* = \eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$) gives cations $[\eta\text{-}Cp^*Fe(CO)_2S]^+$ (S = solvent) [9, 34]. The cyclic voltammogram of $[\eta\text{-}C_5H_5Fe(CO)_2]_2$ in THF exhibits an anodic peak (A$_1$) and a cathodic peak (A') corresponding to oxidation of the iron dimer and reduction of the reaction products, $[\eta\text{-}C_5H_5Fe(CO)_2THF]^+$. When this process is carried out in the presence of added nucleophiles L (L = $SPMe_3$, $(Et_2P(S))_2$, $SPPh_3$, $SP(OEt)_3$, $SP(OPh)_3$), the anodic peak shifts towards less positive potentials; the E_p values observed are identical with the peak A_1, previously mentioned, of the corresponding cations $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$. Furthermore, the intensity of the cathodic peak (A′) decreases and another cathodic peak appears, which is very close to peak A in all cases. As the relation L added/dimer increases the intensity of A increases, at the same time E_p for the second cathodic peak is closer to the respective peak A.

The amount of the added ligand necessary for the complete disappearance of the cathodic peak A′ due to the reduction of the cation $[\eta\text{-}C_5H_5Fe(CO)_2THF]^+$ increases with the decreasing electron donor ability of the ligands.

These facts suggest preparation of the cationic complexes $[\eta\text{-}C_5H_5Fe(CO)_2L]^+PF_6^-$, (L = $SPMe_3$, $(S)PEt_2\text{-}P(S)Et_2$, $SPPh_3$, $SP(OEt)_3$, $SP(OPh)_3$), by an electrochemical route from the dimer $[\eta\text{-}C_5H_5Fe(CO)_2]_2$ in the presence of ligands is possible.

The electrochemical processes observed can be explained as follows:



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