Iron–Xanthate Complexes [Fe(CO)₂(η-C₅R₅){SC(S)OEt}] and [Fe(CO)-(η-C₅R₅)(S₂COEt)] (R = H or Me). Synthesis and Electrochemistry

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Xanthate complexes of the type [Fe(CO)₂(η-C₅R₅){SC(S)OEt}] [R = H (1) or Me (2)] can be conveniently prepared by reaction between [{Fe(CO)₂(η-C₅R₅)}] and [SC(S)OEt]₂ in cyclohexane. U.v. photolysis of (1) and (2) causes decarbonylation and affords the chelate complexes [Fe(CO)-(η-C₅R₅)(S₂COEt)] [R = H (3) or Me (4)]. The electrochemical behaviour of these complexes has been studied both in acetonitrile and dichloromethane using cyclic voltammetry and coulometry. The monocarbonyl complexes (3) and (4) in dichloromethane exhibit a reversible oxidation–reduction process. In acetonitrile the oxidation reaction is accompanied by the co-ordination of solvent. The multicyclic voltammograms of the dicarbonyl complexes (1) and (2), in both solvents, reveal that the oxidation is followed by elimination of one molecule of carbon monoxide from iron, affording the corresponding chelate complexes (3) and (4).

The chemistry and structural aspects of xanthate complexes have been extensively studied.[1–5] However, organometallic complexes of xanthates are less numerous.[6–9] Only a very few complexes are known in which the mode of co-ordination of this ligand is monodentate,[9] and no carbonyl(cyclopentadienyl)iron xanthate complexes have been reported.

Mononuclear derivatives of carbonyl(cyclopentadienyl)-iron(II) with a terminal sulphur ligand are relatively rare, and in general this type of compound has been obtained by reaction between the halogenated derivatives [Fe(CO)₂X(η-C₅H₅)] (X = Cl or Br) and the sodium salt of the dithiocarbamate.[10,11] A recent method describes the preparation of [Fe(CO)₂(η-C₅H₅){SC(S)NR₂}] by treating [Fe(CO)₃(η-C₅H₅)]PF₆ or [Fe(CO)₂(thf)(η-C₅H₅)]PF₆ (thf = tetrahydrofuran) with NaSC(S)NR₂ (R = Me or Et).[12,13]

We have found that reactions between [{Feᴵ(CO)₂(η-C₅R₅)}₂] (R = H or Me) and O,O′-diethyl dithio-bis(thioformate), [SC(S)OEt]₂, give the stable, 18-electron, diamagnetic complexes with monodentate xanthate [Fe(CO)₂-(η-C₅R₅){SC(S)OEt}], via the oxidative cleavage of the Fe–Fe bond in the dimer and homolytic cleavage of the S–S bond in [SC(S)OEt]₂. We also considered the reactivity of the unco-ordinated sulphur atom in monodentate xanthate complexes and have induced chelation of the xanthate ligand by u.v. photolysis in the complexes [Fe(CO)₂(η-C₅R₅){SC(S)OEt}], which allow us to compare the properties of mono- and bidentate complexes in the same series.

Results and Discussion

Reactions between [{Fe(CO)₂(η-C₅R₅)}₂] (R = H or Me) and [SC(S)OEt]₂ in cyclohexane at 60 °C lead to formation of the red-orange crystalline complexes [Fe(CO)₂(η-C₅R₅){SC(S)-OEt}] [R = H (1) or Me (2)].

It is relevant to note that in these cases, independent of the ring substituent, complexes in which the xanthate behaves as a monodentate ligand are obtained. This result differs from those observed in the reactions of carbonyl(cyclopentadienyl)iron(II) complexes with dithiocarbamate and trithiocarbonate ligands, structurally and electronically similar to the xanthate, in which depending on the method used and the substituents on the ring,

complexes with a mono- or bi-dentate dithiocarbamate ligand are obtained.[10–12]

The decarbonylation and subsequent chelation of the xanthate ligand in both complexes (1) and (2) by a thermal reaction is a very difficult process, proceeding only at high temperatures (ca. 100 °C) and accompanied by extensive decomposition.

We attempted to synthesize the chelate compounds [Fe(CO)(η-C₅R₅)(S₂COEt)] using reagents that facilitate the chelation process in the dithiocarbamate complexes [Fe(CO)₂-(η-C₅H₅){SC(S)NR₂}],[13] for which chelation was easily induced by using PPh₃ + CS₂, [TiCl₂(η-C₅H₅)₂], or [Mo(CO)₆] in refluxing thf. However, in our case, the reactions between [Fe(CO)₂(η-C₅R₅){SC(S)OEt}] and PPh₃ + CS₂ (1:1) in refluxing thf do not give the chelates, but lead only to the formation of the substituted phosphine carbonyl complexes [Fe(CO)(PPh₃)(η-C₅R₅){SC(S)OEt}] (R = H or Me).

The different behaviour of the xanthate and dithiocarbamate complexes is probably due to the different reactivity of the free sulphur atom in the –SC(S)OR and –SC(S)NR₂ ligands, which in the dithiocarbamate has a strong driving force towards chelation through the entropy effect.[13] The xanthate ligand is more electronegative than the dithiocarbamate and thus reduces the capacity of the free sulphur atom for co-ordination of a metal centre.

However, we have found that u.v. photolysis of (1) and (2) in cyclohexane at room temperature causes decarbonylation and affords the desired chelates [Fe(CO)(η-C₅R₅)(S₂COEt)] [R = H (3) or Me (4)] (Scheme 1), in good yield after chromatographic purification on alumina. It is important to note that at a higher temperature of 25 °C, the reaction takes place with extensive decomposition and giving only very low yields of (3) and (4).

The xanthate ligand can act as a mono- or bi-dentate ligand and this different behaviour can be inferred from the i.r. spectra. However, the assignment of structures of metal xanthates from i.r. spectra has not always been reliable.[7,14–16] This is probably because both types of xanthate ligands exhibit three strong bands in the 1 200—1 100 cm⁻¹ region which are related to the vibrations of the SC(S)OR group, and these bands are highly coupled, and sensitive to environmental changes. A normal co-ordinate analysis of Niᴵᴵ(S₂COEt)₂[15] indicates that the band at

Table 1. Characteristic i.r. bands (cm^{-1}) for the iron–xanthate complexes

Complex	v(COC)	v(CO)	v(CS)	v(CO) $(A',A'')^a$	K^b	$K_i{}^b$
(1) [Fe(CO)$_2$(η-C$_5$H$_5$){SC(S)OEt}]	1 185vs	1 113s	1 042vs	2 042.5 1 998.0	16.5	0.38
(2) [Fe(CO)$_2$(η-C$_5$Me$_5$){SC(S)OEt}]	1 180vs	1 115s	1 042vs	2 021.3 1 973.4	16.1	0.37
(3) [Fe(CO)(η-C$_5$H$_5$)(S$_2$COEt)]	1 232vs	1 127s	1 039vs	1 950.8	15.3	
(4) [Fe(CO)(η-C$_5$Me$_5$)(S$_2$COEt)]	1 233vs	1 120s	1 039s	1 923.3	14.9	

^{a} In CH$_2$Cl$_2$. ^{b} K And K_i in mdyn Å^{-1} (dyn = 10^{-5} N), determined by the method of F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 1962, **84**, 4432.

Table 2. Cyclic voltammetric^a data for the complexes at 200 mV s^{-1}

Complex	E_p/V in CH$_3$CN^b				E_p/V in CH$_2$Cl$_2{}^c$		
	I	II	III	IV	I	I'	III
(1) [Fe(CO)$_2$(η-C$_5$H$_5$){SC(S)OEt}]	+0.41	+0.72	−0.42	−0.96	+0.82	+0.76	+1.04
(2) [Fe(CO)$_2$(η-C$_5$Me$_5$){SC(S)OEt}]	+0.16	+0.51	−0.74		+0.60	+0.53	+0.92
(3) [Fe(CO)(η-C$_5$H$_5$)(S$_2$COEt)]	+0.40		−0.43		+0.83	+0.76	
(4) [Fe(CO)(η-C$_5$Me$_5$)(S$_2$COEt)]	+0.18		−0.73		+0.59	+0.52	
[{Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$]				−0.95			
[Fe(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]$^+$				−1.30			

^{a} At a platinum electrode. ^{b} *Versus* Ag–Ag$^+$ electrode, ferrocene–ferrocenium couple E_{p_a} = +0.19 V, E_{p_c} = +0.12 V. ^{c} *Versus* an aqueous saturated calomel electrode; ferrocene–ferrocenium couple E_{p_a} = +0.55 V, E_{p_c} = +0.49 V.
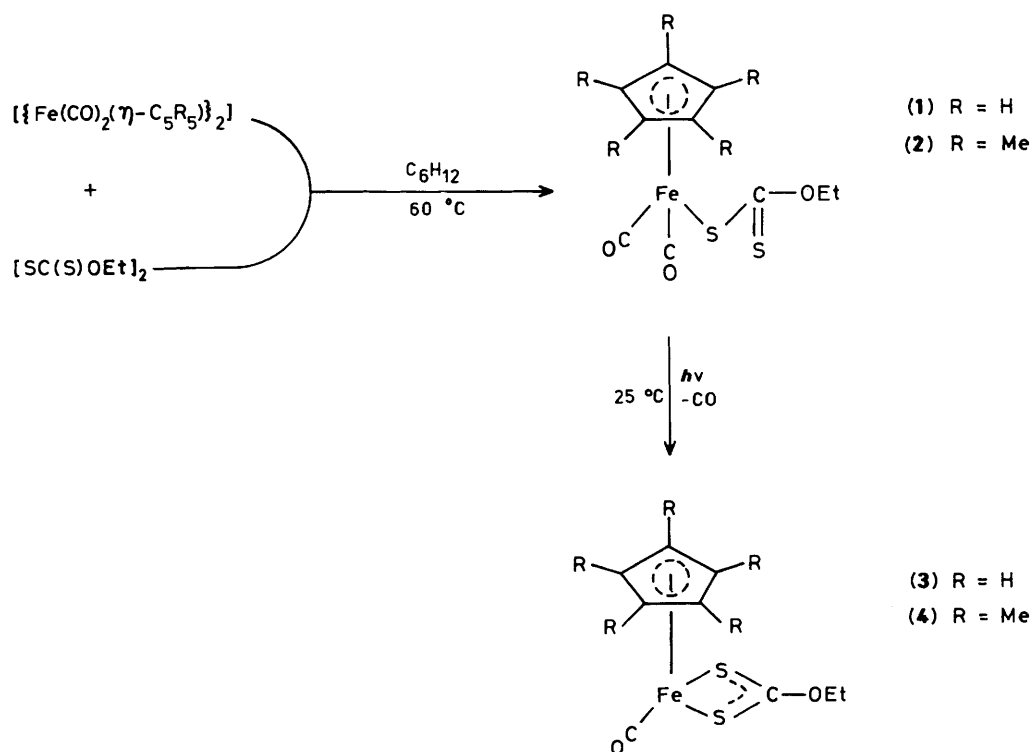
Scheme 1.

1 250 cm^{-1} has a *ca.* 90% contribution of C–OEt stretching, the band around 1 100 cm^{-1} is mainly a contribution of the v(C–O) mode, and the band around 1 060 cm^{-1} is entirely v(C=S).

In [Fe(CO)$_2$(η-C$_5$R$_5$){SC(S)OEt}] and [Fe(CO)(η-C$_5$R$_5$)(S$_2$COEt)] the characteristic xanthate bands in the 1 200—1 000 cm^{-1} region are listed in Table 1. The band assigned to the

v(C–OEt) mode appears at higher frequencies in the complexes with the bidentate ligand [v(COC) *ca.* 1 230 cm^{-1}]. This can be explained to be the result of the greatest contribution of the canonical form (C) to the structure of the bidentate xanthate complexes.[17]

In both [Fe(CO)$_2$(η-C$_5$R$_5$){SC(S)OEt}] and [Fe(CO)(η-
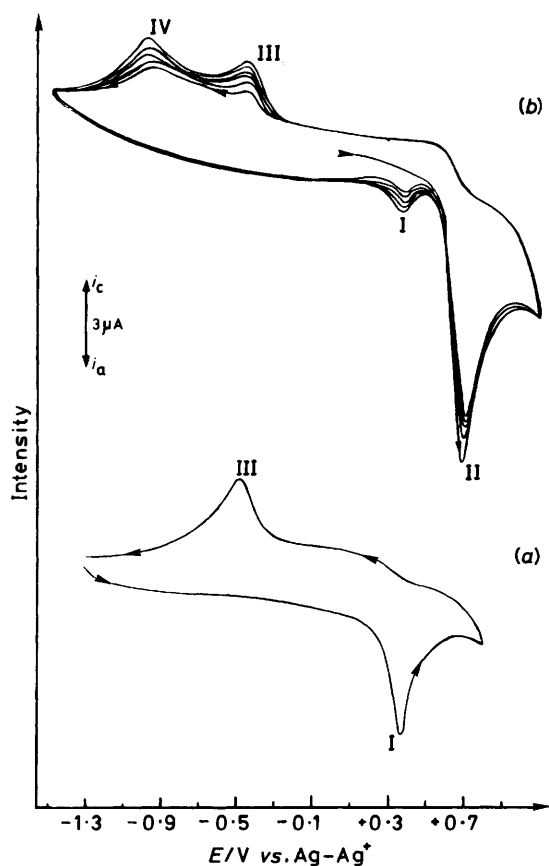
Figure 1(*a*) Cyclic voltammogram of $[Fe(CO)_2(\eta\text{-}C_5H_5)(S_2COEt)]$ (**3**) in CH_3CN at a Pt electrode; scan rate 0.2 V s^{-1}. (*b*) Multicyclic voltammogram of $[Fe(CO)_2(\eta\text{-}C_5H_5)\{SC(S)OEt\}]$ (**1**) in CH_3CN solution at a Pt electrode; scan rate 0.2 V s^{-1}

$C_5R_5)(S_2COEt)]$ the C=S stretching vibration appears at *ca.* 1 040 cm^{-1}. The ν(CS) values in Table 1 show that these frequencies are higher for $[Fe(CO)_2(\eta\text{-}C_5R_5)\{SC(S)OEt\}]$ than $[Fe(CO)(\eta\text{-}C_5R_5)(S_2COEt)]$ because in the latter complexes with bidentate xanthate, the C–S bond has less double-bond character.

The values of ν(CO) and *K* force constants in Table 1 show an important decrease in the ν(CO) frequencies on going from the complexes with C_5H_5 to the parent complexes with C_5Me_5, as a consequence of the higher electron donor capacity of the C_5Me_5 ligand.

Electrochemical Studies.—The oxidative electrochemistry of the synthesized compounds was investigated in acetonitrile and dichloromethane with $[NBu^n_4][PF_6]$ as supporting electrolyte. Electrochemical parameters of the complexes are summarized in Table 2.

$[Fe(CO)(\eta\text{-}C_5R_5)(S_2COEt)]$ [R = H (**3**) *or* Me (**4**)]. In acetonitrile, the cyclic voltammogram of (**3**) shows anodic (I) and cathodic (III) peaks, but they are not associated with a reversible oxidation–reduction process because of a large peak

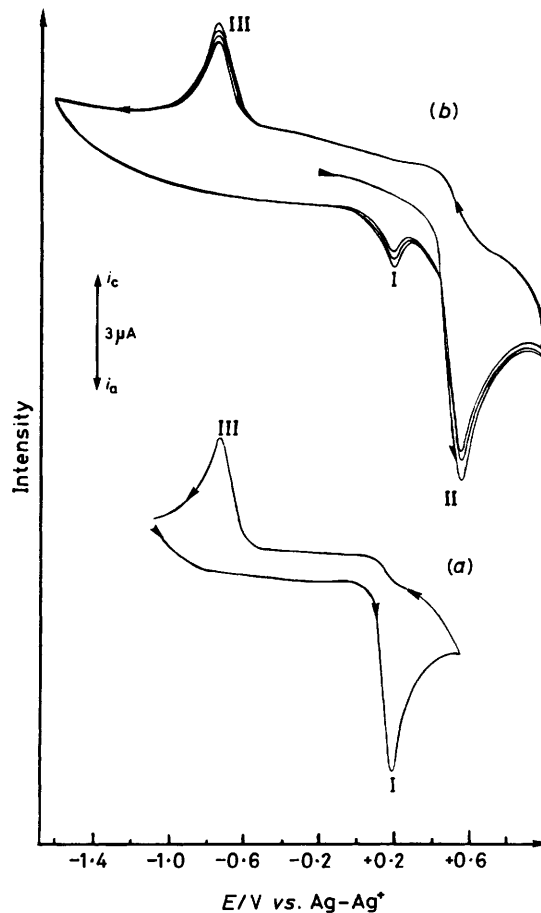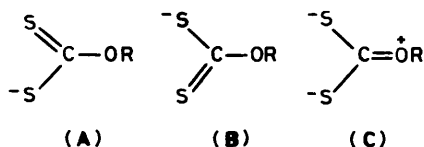**Figure 2.** Cyclic voltammogram in CH_3CN solution at a Pt electrode (scan rate 0.2 V s^{-1}) for: (*a*) $[Fe(CO)(\eta\text{-}C_5Me_5)(S_2COEt)]$ (**4**) and (*b*) $[Fe(CO)_2(\eta\text{-}C_5Me_5)\{SC(S)OEt\}]$ (**2**)

separation and a i_{pc}/i_{pa} value much smaller than unity [Figure 1(*a*)]. A similar result is found in the case of complex (**4**) [Figure 2(*a*)], although the anodic (I) and cathodic (III) peaks shift to more cathodic potentials in accordance with the greater donor ability of the C_5Me_5 ligand.

The electrochemical irreversibility of the process corresponding to peaks I and III is confirmed by the magnitude of the slopes in the plots of E_p *vs.* log v (v = scan rate),[18] which are significantly larger than those expected for a reversible process. These anodic oxidations are irreversible at scan rates as high as 5 V s^{-1}.

Bulk oxidation of complexes (**3**) and (**4**), carried out at a potential 100 mV more positive than the anodic potentials, results in the removal of 1.0 electron per molecule in both CH_3CN and CH_2Cl_2.

In CH_2Cl_2, however, (**3**) and (**4**) exhibit reversible cyclic voltammograms [Figure 3(*a*)] with $i/v^{\frac{1}{2}}$ independent of v and $i_{pc}/i_{pa} = 1$, which suggest chemical reversibility and the stability of $[Fe(CO)(\eta\text{-}C_5R_5)(S_2COEt)]^+$ species in this solvent. The existence of this cationic species has been proved by controlled potential electrolysis in the e.s.r. cavity. The species formed in the oxidation step show e.s.r. signals; in all cases simple one-line signals [g_{iso} = 2.010 for (**3**) and 1.998 for (**4**)] were found.

The results obtained suggest that the 17-electron oxidized species of (**3**) and (**4**), $[Fe(CO)(\eta\text{-}C_5R_5)(S_2COEt)]^+$ is unstable in CH_3CN and may be converted into a species co-ordinated by

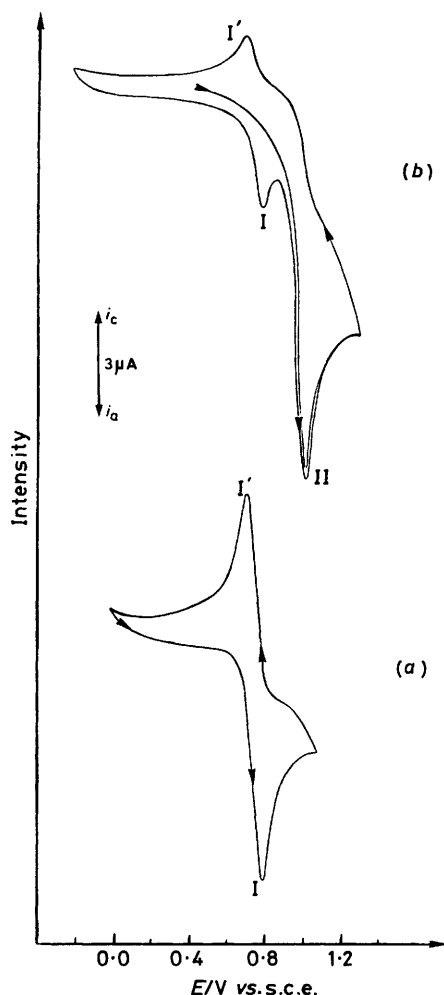**Figure 3.** Cyclic voltammogram in CH_2Cl_2 solutions at a Pt electrode (scan rate 0.2 V s^{-1}) for: (a) [Fe(CO)(η-C_5H_5)(S_2COEt)] (3) and (b) [Fe(CO)$_2$(η-C_5H_5){SC(S)OEt}] (1)

a solvent molecule. A similar behaviour has been reported previously in other cases.[19,20]

The experimental results are consistent with the electrochemical–chemical–electrochemical mechanism outlined in Scheme 2 (part B).

[Fe(CO)$_2$(η-C_5R_5){SC(S)OEt}] [R = H (1) or Me (2)]. In CH_2Cl_2, (1) and (2) display an anodic irreversible wave (II) [Figure 3(b)]. Repeating cyclization gives a pair of cathodic and anodic peaks corresponding to the reversible system (I,I') observed for complexes (3) and (4) [Figure 3(a)]. This result is consistent with the mechanism outlined in Scheme 3.

Cyclic voltammetry of (1) in CH$_3$CN at 200 mV s^{-1} [Figure 1(b)] shows an anodic peak (II) and two cathodic peaks (III, IV). The separation of the anodic and cathodic peak potentials is very large (see Table 2) and is dependent on scan rate; as the sweep rate is increased, all of the peaks shift (reduction peaks shift in a negative direction and oxidation peaks shift in a positive direction). These shifts in E_p indicate that the oxidation of (1) may be followed by a rapid chemical reaction.

However, the cyclic voltammogram of the pentamethylcyclopentadienyl derivative (2) displays an irreversible anodic peak (II) and only one cathodic peak (III) [Figure 2(b)]. The second cyclic run gives a new anodic peak (I) [Figures 1(b) and 2(b)]. With repeating cyclization, the electric current of peaks III, IV, and I increase, while that of peak II decreases.

The potentials of the new peaks I and III are identical to the anodic and cathodic peak potentials of (3) and (4) (see Table 2).

Complete electrolysis of all compounds, carried out at a potential 100 mV more positive than peak II, results in the removal of 1 electron per molecule.

In view of these results, the electrochemical processes of (1) and (2) in CH$_3$CN may be formulated as in Scheme 2. The complexes are oxidized to give electron-deficient dicarbonyliron(III) species, peak II, followed by the elimination of one CO ligand owing to decreasing π-back bonding from the Fe^{III} ion to the CO ligands. The elimination of CO ligands is probably assisted by nucleophilic attack of the solvent, yielding acetonitrile adducts of the electron-deficient iron(III) species.

The acetonitrile adducts may be formed also by the oxidation of (3) and (4), peak I, followed by co-ordination of the solvent accompanied by fission of a Fe–S bond. The adducts [Fe(CO)(CH$_3$CN)(η-C_5R_5){SC(S)OEt}]$^+$ may be reduced to give the Fe^{II} complexes that by elimination of CH$_3$CN regenerate (3) and (4), respectively.

It is known that electrochemical oxidation of [{Fe(CO)$_2$(η-C_5H_5)}$_2$] gives a short-lived intermediate which is rapidly co-ordinated by the solvent to give [Fe(CO)$_2$(CH$_3$CN)(η-C_5H_5)]$^+$.[21,22] This exhibits a cathodic peak which corresponds exactly to the potential of peak IV. Therefore the appearance in the cyclic voltammogram of this peak in the case of the cyclopentadienyl compound (Scheme 2, part A) can be attributed to the reduction of [Fe(CO)$_2$(CH$_3$CN)(η-C_5H_5)]$^+$, originating as a consequence of an oxidatively induced reductive elimination of the ligand SC(S)OEt, which takes place in addition to the cyclization reaction. This special behaviour of the cyclopentadienyl complex (1) may be related to the lower donor ability of the cyclopentadienyl ring.

When the oxidation of (1) is carried out in the presence of triphenylphosphine, the potential of peak IV changes and is identical to that observed in the electrochemical reduction of [Fe(CO)$_2$(PPh$_3$)(η-C_5H_5)]PF$_6$ solutions at −1.3 V; this confirms the partial elimination of the xanthate after oxidation.

Experimental

$[Fe(CO)_2(\eta-C_5R_5)\{SC(S)OEt\}]$

(1) R = H
(2) R = Me

$\downarrow$ $-e^-$
peak II

$[Fe(CO)_2(\eta-C_5R_5)\{SC(S)OEt\}]^{+\cdot}$

$\downarrow$ $-CO$ $+CH_3CN$ $\quad$ $\xrightarrow{CH_3CN}$ $\quad$ $[Fe(CO)_2(\eta-C_5R_5)(CH_3CN)]^+$ $\xrightarrow[peak\ IV]{+e^-}$ $\frac{1}{2}[\{Fe(CO)_2(\eta-C_5R_5)\}_2]$

$+$

$SC(S)OEt^{\cdot}$

Part A

[Fe(CO)(CH_3CN)(\eta-C_5R_5)\{SC(S)OEt\}]^{\cdot}

$\downarrow$ $+e^-$
peak III

$[Fe(CO)(CH_3CN)(\eta-C_5R_5)\{SC(S)OEt\}]$

$\downarrow$ $-CH_3CN$

$[Fe(CO)(\eta-C_5R_5)(S_2COEt)]$

(3) R = H
(4) R = CH_3

$\downarrow$ $-e^-$
peak I

$[Fe(CO)(\eta-C_5R_5)(S_2COEt)]^{\cdot}$

$+CH_3CN$

Part B

Scheme 2.

$[Fe(CO)_2(\eta-C_5R_5)\{SC(S)OEt\}] \xrightarrow[peak\ II]{-e^-} [Fe(CO)_2(\eta-C_5R_5)\{SC(S)OEt\}]^+$

$\downarrow -CO$

peak I'

$[Fe(CO)(\eta-C_5R_5)(S_2COEt)] \underset{peak\ I}{\overset{+e^-}{\underset{-e^-}{\rightleftharpoons}}} [Fe(CO)(\eta-C_5R_5)(S_2COEt)]^+$

Scheme 3.

A sample solution containing the metal complex (1×10^{-3} mol dm^{-3}) and a supporting electrolyte, $[NBu^n_4][PF_6]$ (1×10^{-1} mol dm^{-3}), was deaerated with nitrogen prior to measurements. Acetonitrile was purified by distillation over calcium hydride and dichloromethane was distilled over phosphorus pentoxide.

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

The e.s.r. spectra were recorded using a Varian E-12 spectrometer, at a microwave frequency of 9 GHz (X-band), equipped with a HP 5342 A frequency meter and a Bruker NMR gaussmeter, in a three-electrode cell specially constructed for *in situ* electrolysis.

Dicarbonyl(η-cyclopentadienyl)(O-ethyl dithiocarbonato-S)-iron(II), $[Fe(CO)_2(\eta-C_5H_5)\{SC(S)OEt\}]$ (1).—A mixture of $[\{Fe(CO)_2(\eta-C_5H_5)\}_2]$ (2.0 g, 5.6 mmol) and $[SC(S)OEt]_2$ (2.1 g, 8.6 mmol) in cyclohexane (60 cm^3) was kept between 50 and 60 °C. The formation of (1) was monitored by i.r. spectroscopy (the initial $\nu(CO)$ bands of $[\{Fe(CO)_2(\eta-C_5H_5)\}_2]$ at 2 004, 1 960, and 1 796 cm^{-1} (cyclohexane) give way to new bands at 2 046 and 1 998 cm^{-1}). An intense red solution was formed. After 4 h the reaction was complete and cooling to room temperature gave red crystals of (1). The solid was recrystallized from cyclohexane–hexane or CH_2Cl_2–hexane, yield 75% (Found: C, 39.9; H, 3.4; Fe, 18.5. $C_{10}H_{10}FeO_3S_2$ requires C, 40.2; H, 3.3; Fe, 18.0%); $\delta_H(CDCl_3)$ 1.42 (3 H, t, CH$_3$), 4.57 (2 H, q, CH$_2$), and 5.02 (5 H, s, C$_5$H$_5$); $\delta_C(CDCl_3)$ 14.0 (s, CH$_3$), 69.8 (s, CH$_2$), 86.92 (s, C$_5$H$_5$), and 213, 216 (s, CO, CS).

The compound $[Fe(CO)_2(\eta-C_5Me_5)\{SC(S)OEt\}]$ (2) was prepared similarly as orange crystals (Found: C, 48.5; H, 5.4; Fe, 14.9. $C_{15}H_{20}FeO_3S_2$ requires C, 48.9; H, 5.4; Fe, 15.1%); $\delta_H(CDCl_3)$ 1.41 (3 H, t, CH$_3$), 1.8 (15 H, s, C$_5$Me$_5$), and 4.55 (2 H, q, CH$_2$); $\delta_C(CDCl_3)$ 9.4 (s, C$_5$Me$_5$), 14.1 (s, CH$_3$), 69.6 (s, CH$_2$), 97.6 (s, C$_5$Me$_5$), and 215.8 (s, CO).

Carbonyl(η-cyclopentadienyl)(O-ethyl dithiocarbonato-S,S')-iron(II), $[Fe(CO)(\eta-C_5H_5)(S_2COEt)]$ (3).—A solution of (1) (2 g, 6.7 mmol) in cyclohexane (20 cm^3) was irradiated (u.v. light) at 25 °C and the reaction monitored by i.r. spectroscopy [the initial $\nu(CO)$ bands of (1) at 2 046 and 1 998 cm^{-1} (cyclohexane) give way to new band at 1 963 cm^{-1} corresponding to (3)]. Elimination of the solvent led to the isolation of an orange oil which was purified by column chromatography (alumina). Yield: 60% (Found: C, 39.9; H, 3.6; Fe, 20.3. $C_9H_{10}FeO_2S_2$ requires C, 40.0; H, 3.7; Fe, 20.6%); $\delta_H(CDCl_3)$ 1.40 (3 H, t, CH$_3$), 4.52 (2 H, q, CH$_2$), and 4.98 (5 H, s, C$_5$H$_5$); $\delta_C(CDCl_3)$ 13.8 (s, CH$_3$), 69.1 (s, CH$_2$), 87.0 (s, C$_5$H$_5$), and 220 (s, CO).

The pentamethylcyclopentadienyl analogue, $[Fe(CO)(\eta-C_5Me_5)(S_2COEt)]$ (4) was prepared similarly as brown crystals. Yield: 70% (Found: C, 49.1; H, 6.0; Fe, 16.1. $C_{14}H_{20}FeO_2S_2$ requires C, 49.4; H, 5.9; Fe, 16.4%); $\delta_H(CDCl_3)$ 1.38 (3 H, t, CH$_3$), 1.8 (15 H, s, C$_5$Me$_5$), and 4.51 (2 H, 1, CH$_2$), $\delta_C(CDCl_3)$ 9.3 (s, C$_5$Me$_5$), 14.1 (s, CH$_3$), 68.3 (s, CH$_2$), and 223 (s, CO).

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