Review

Unexpected fragmentation of phenyldithiobenzoate, formation and X-ray structure of [μ,η²(S,S)-1,2-(dithio)-1,2-(diphenylethylene)] diiron hexacarbonyl complex

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ABSTRACT

The reaction of $Fe_2(CO)_9$ with phenyldithiobenzoate $PhCS_2Ph$ **1** afforded four colored compounds: [(μ-η³(C,S,S)PhCS₂Ph)]Fe₂(CO)₆ **2**, (μ-S)₂Fe₃(CO)₉ **3**, (μ-SPh)₂Fe₂(CO)₆ **4** and [μ-η²(S,S)][PhC(S)C(S)Ph]Fe₂(CO)₆ **5**. Complex **5** was characterized by X-ray crystallography. The formation of complexes **4** and **5** was unexpected since it involved a fragmentation of the organic ligand **1** during its reaction with $Fe_2(CO)_9$. The electrochemical studies of **1**, complexes **2** and **3** were undertaken in order to get information about the chemical behaviors of the intermediates generated by electron transfer. The results of cyclic voltammetry studies of **2** and **1** suggested that the reaction of **1** with $Fe_2(CO)_9$ involved two competitive reactions: (i) a thermal reaction which led to the expected compounds **2** and **3** and (ii) an electron transfer reaction involving a fragmentation of starting ligand **1** led to the unexpected complex **5**. The required electrons may be provided by iron during the thermal decay of complexes **2** or **3** or $Fe_2(CO)_9$.

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Contents

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1. Introduction

The thermal reaction of $Fe_2(CO)_9$ with organic substrates that contain sulfur atoms is a general synthetic way to various hexacarbonyldiiron coordination compounds [1]. Some complexes containing a Fe_2S_2 core attract interest of chemists because they have a close resemblance to the diiron unit of the FeFe-hydrogenase [2,3]. These complexes are easily synthesized and have been studied as structural and functional mimics of enzyme active site [4]. Hydrogenase enzymes catalyze the oxidation of dihydrogen and the reduction of protons in nature. X-ray crystallography and IR spectroscopy of [Fe]-only hydrogenases have shown the active site to be comprised of a [2Fe–2S] subunit linked to a [4Fe–4S] cluster by a cysteinyl-S bridge [5–10]. The two iron atoms in the [2Fe–2S] subunit are linked by a bridging dithiolate ligand and are bound to the biologically uncommon ligands like carbon monoxide (CO) and cyanide (CN) [11]. Owing to the importance of [2Fe–2S] hydrogenase model it is interesting to investigate the coordination chemistry of organic compounds that contain several sulfur atoms.

The reaction of iron carbonyl with numerous sulfur containing compounds has been investigated. Dithioesters react with $Fe_2(CO)_9$ to afford binuclear iron carbonyl complexes with a σ metal–carbon bond in which the organic ligand gives 6 electrons to the $Fe_2(CO)_6$ skeleton [12]. The starting organic ligand is linked to the metal atoms without fragmentation and the overall reaction may be rationalized by a stepwise replacement of three CO ligand of $Fe_2(CO)_9$ by a six-electron ligand. X-ray structures of these complexes show that coordination imposes important geometrical constraints [13]. The reaction of $Fe_2(CO)_9$ with ethylene-trithiocarbonate [12,13], 1,2-dithiol-3-thiones [14] or 2,3-toluenedithiol and 1,3-propanedithiol [15] affords binuclear complexes without a ligand fragmentation. However, in some cases the thermal reaction of $Fe_2(CO)_9$ with sulfur containing substrates leads to the formation of binuclear compounds including one or several fragments arising from the organic substrates. For example, the reaction with xanthates [16], linear trithiocarbonates [17], S,S-substituted dithiocarbonates [18] or 1-thia-3-azabutadiene bearing a thiobenzyl group [19] involves in all cases the fragmentation of the substrate or an intermediate organometallic compound. S-Methyl O-methylene adamantane dithiocarbonate reacts with $Fe_2(CO)_9$ [20] like a dithioester ligand $[R^1CS_2R^2]$. At first, it leads to an intermediate which undergoes a rearrangement catalyzed by electron transfer and affords the final compound containing the fragmented organic ligand [20,21]. However, the reaction of $R^1CS_2R^2$ (R^1 = Me, R^2 = Et or R^1 = Ph, R^2 = Me) with $Fe(CO)_5$ or $Fe_2(CO)_9$ under UV irradiation gives three compounds [22]. In the first compound, the Fe atoms are doubly-bridged by a C–S unit and the original bivalent S atom of the intact dithioester in a well known structure [12]. The second one is a dimeric compound in which there is no metal–metal bond but each coordinated ligand forms an asymmetric dative S–metal bond to the other iron atom. The third compound is the result of carbonyl insertion into the C–SR^2 bond of the ligand [22]. The reaction of various O-alkyl aryl thioesters with diiron nonacarbonyl affords an isomeric oxygen sulfur–donor diiron hexacarbonyl complex as the major product [23].

It is remarkable that, despite some structural analogies with linear trithiocarbonates or xanthates, the dithioesters are generally stable during their thermal reaction with $Fe_2(CO)_9$ [12,13]. Surprisingly, we have observed an unusual fragmentation of phenyldithiobenzoate PhC(S)SPh (**1**) during its thermal reaction with $Fe_2(CO)_9$ leading to the expected complexes **2** and **3**, and to complexes **4** and **5** of which the formation involved a fragmentation reaction of the starting ligand (Scheme 1). In order to understand
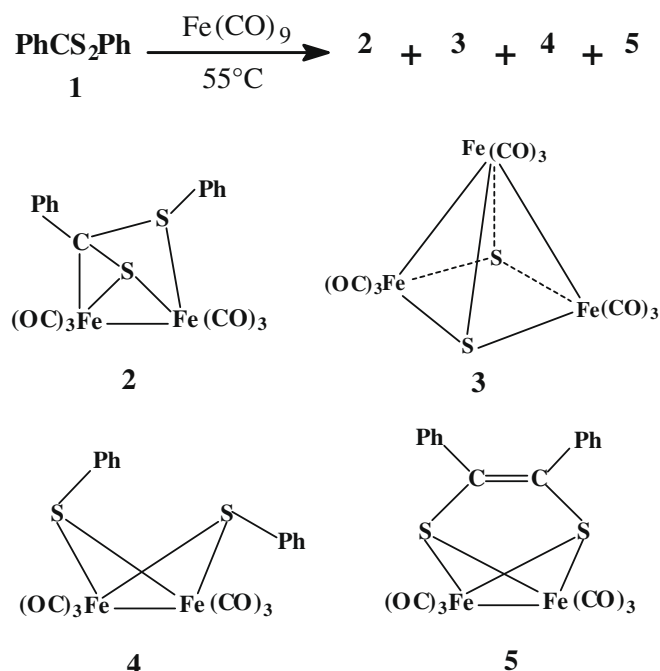
Scheme 1. Reaction and structures of isolated compounds.

this reaction, we investigated the electrochemical behavior of dithioester **1**, complexes **2** or **3** and **5** and we report here our results.

2. Experimental

2.1. Physical measurements

^1H and ^{13}C NMR spectra were recorded at 60 and 20.115 MHz, respectively, in $CDCl_3$ with TMS as internal standard. Mass spectra were recorded with a Varian MAT 311 spectrophotometer at 70 eV at CRMPO (Rennes, France). Elemental analyses were carried out by Service Central d'Analyse (Vernaison, France). The electrochemical experiments were carried out in a three-electrode thermostated cell with a PAR 362 potentiostat coupled to a Kipp and Zonen XY recorder. Pt micro disc and a saturated calomel electrode (SCE) were used as working and reference electrodes, respectively. Diffraction measurements of single crystals of complex **5** were made at 293 K on a kappa CCD diffractometer (Bruker AXS BV, 1997-2004) equipped with a graphite monochromatic using Mo Kα radiation (λ = 0.71073 Å). Crystal data collection, reduction and refinement were accomplished with COLLECT (Nonius, 1998), SCALEPACK and DENZO [24] programs. The structure was solved by SIR2002 [25] and refined by using SHELXL-97 [26]. The hydrogen atoms were located in Fourier maps but introduced in calculated positions and treated as riding on their parent C atom, with 0.95 (aromatic) and with Uiso(H) = 1.2 Ueq (aromatic C atoms). The molecular graphical was showed with ORTEP-3 [27] program and material for publication was prepared with WinGX 1.7 Software [28,29].

2.2. Reagents

The supporting electrolyte Bu_4NBF_4 (Fluka, Purum) was recrystallized in a mixture of methanol and water (1/1), dried at 120 °C and used at 0.1 M concentration. Diiron nonacarbonyl and triiron dodecarbonyl (Strem Chemical, 99%), trimethylphosphite (Fluka purum, 97%) and diphenylacetylene (Aldrich, 99%) were used as

received. Toluene, acetone, CH_2Cl_2 and DMF (SDS, analytical grade) were stored over 4 Å molecular sieves before use.

2.3. Preparations

2.3.1. Reaction of $PhCS_2Ph$ **1** with diiron nonacarbonyl

The organic substrate $PhCS_2Ph$ was prepared according to the literature [30]. $Fe_2(CO)_9$ (1.5 mmol) was added to $PhCS_2Ph$ (1.0 mmol) in dry toluene (40 mL). The mixture, in the dark and under nitrogen, was heated at 55 °C for 0.5 h. The progress of the reaction was followed by thin layer chromatography. After filtration and distillation of the solvent, the residue was dissolved in 10 mL of diethyl ether. The reaction products were separated by chromatography on thin layer of silica gel and elution with petroleum ether. The isolated complexes, with decreasing polarity were: **3** (6%), **4** (20%), **5** (24%) and **2** (43%). They were purified by crystallization from ethanol solution. All yields are based on $PhCS_2Ph$.

2.3.2. Reaction of $PhCS_2Ph$ (**1**) with triiron dodecarbonyl

$Fe_3(CO)_{12}$ (1.0 mmol) was added to $PhCS_2Ph$ (1.0 mmol) in dry toluene (40 mL). The mixture, in the dark and under nitrogen, was stirred at room temperature for 72 h or heated at 55 °C for 1 h. After filtration, distillation of the solvent and chromatography on silica gel the complexes **2** and **3** were isolated with 60% and 10%, respectively.

*2.3.2.1. Complex **2**.* $[\mu-\eta^3(C,S,S)PhCS_2Ph]Fe_2(CO)_6$, m.p. 152 °C. ^1H NMR δ: 7.25(m) ppm. ^{13}C NMR δ: 211.0; 208.5 (CO); 146.9; 139.2; 129.9; 129.6; 128.5; 127.5; 126.7; 122.2 (Ph); 69.1 (CS_2) ppm. IR (C_2Cl_4): ν CO = 1970; 1980; 2000; 2010; 2040; 2080 cm^{-1}. Mass spectrum: M^+ found 509.8622; M^+ calc. 509.8617. Anal. Calc. for $C_{19}H_{10}Fe_2O_6S_2$: C, 44.70; H, 1.96; S, 12.54; Fe, 21.95; O, 18.82. Found: C, 45.75; H, 1.88; S, 13.08; Fe, 20.83%. Cyclic voltammetry: EpC1: −1.00; EpC2: −1.55 V versus SCE EpC1: −0.85; EpC2: −1.40 V versus SCE.

*2.3.2.2. Complex **3**.* $(\mu-S)_2Fe_3(CO)_9$, m.p. 114 °C; (114 °C [31]). IR (Nujol): ν CO = 2040; 2060; 2080 cm^{-1}. Mass spectrum: M^+ found 483.7019; M^+ calc. 483.7031.

*2.3.2.3. Complex **4**.* $(\mu-PhS)_2Fe_2(CO)_6$, m.p. 130 °C. ^1H NMR δ: 7.4(m) ppm. IR (C_2Cl_4): ν CO = 2000; 2010; 2040; 2080; cm^{-1}. Mass spectrum: M^+ found 497.8599; M^+ calc. 497.8617.

*2.3.2.4. Complex **5**.* $[\mu-\eta^2(S,S)PhC(S)=C(S)Ph]Fe_2(CO)_6$, m.p. 140 °C. ^1H NMR δ: 7.2(m) ppm. ^{13}C NMR δ: 207.8 (CO); 150.2 (C=C); 135.2; 128.9; 128.4; 127.3 (Ph) ppm. IR (C_2Cl_4): ν CO = 2000; 2040; 2080 cm^{-1}. Mass spectrum: $(M-CO)^+$ found 493.867.; calc. 493.866.

3. Results and discussion

### 3.1. Reaction of **1** with $Fe_2(CO)_9$

An excess of $Fe_2(CO)_9$ reacted with $PhCS_2Ph$ (**1**) and afforded four colored compounds: **2** (43%); **3** (6%); **4** (20%) and **5** (24%). Compound **2** was the expected product containing the starting dithioester ligand linked to $Fe_2(CO)_6$. It was fully characterized by mass spectrometry and by spectroscopic methods. Trinuclear cluster **3** was frequently obtained in low yield by reaction of $Fe_2(CO)_9$ with organic substrates that contain thiono group [13,16,23,32,33]. This cluster has been obtained, from the reaction of organic sulfide with $Fe_3(CO)_{12}$ [34], the thienyl Schiff base with $Fe_2(CO)_9$ [35] and its molecular structure is well known [36]. To date, no fragmentation of a dithioester compound has been de-

scribed during its thermal reaction with $Fe_2(CO)_9$. The formation of **3** is the proof of both reagent fragmentations. The formation of binuclear compounds **4** and **5** is also the proof of a fragmentation of the phenyldithiobenzoate during its thermal reaction with $Fe_2(CO)_9$. During this reaction 93% of the phenyldithiobenzoate were transformed into iron carbonyl complexes. Complexes **4** and **5** or analogous one were unexpected compounds and were never observed during reaction of $Fe_2(CO)_9$ with dithioesters.

3.2. X-ray crystal analysis

Crystals of complex **5** were triclinic with space group $P\bar{1}$. The X-ray study of **5** established that it was a binuclear iron complex. The two iron atoms are maintained at a distance from 2.56 Å with a dithiodiphenylethylene group. It was identical to the compound
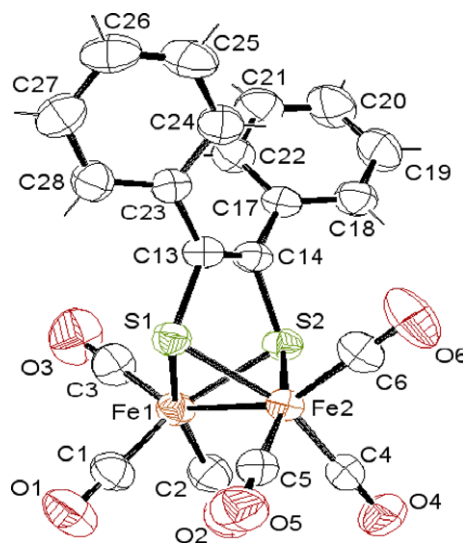
Fig. 1. Molecular structure of complex **5** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

Table 1
Crystal data and refinement details for X-ray structure determination of **5**.

Molecular formula	$C_{20}H_{10}Fe_2O_6S_2$
Formula weight (g mol^{-1})	522.1
T (K)	293 (2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.2280 (6)
b (Å)	14.9718 (10)
c (Å)	17.5488 (10)
α (°)	108.622 (3)
β (°)	91.688 (3)
γ (°)	107.939 (2)
V (Å^3)	2163.83 (34)
Z	4
Color	Red
ρ_{calc} (g cm^{-3})	1.60
μ (cm^{-1})	15.67
Θ_{min}–Θ_{max}	2.27–25.37
Measured data	13 748
Reflexions used	7431
F_{000}	1048
Radiation	Mo kα (graphite monochromated)
Wave length (Å)	0.71073
No. data with $I > 2\sigma$	4884
Number of parameters	542
R_{int}	0.0689
$R_1(I > 2\sigma)$	0.0397
$wR2$	0.0976
GOF	1.013

already described in the literature [37] which was synthesized by reaction of the tetraphenyldithine [38] or the diphenylthiirene-1-oxide [39] with $Fe_2(CO)_9$. The ORTEP plot is given in Fig. 1. Its crystal and collection parameters are shown in Table 1, and selected bond distances and angles are tabulated in Table 2.

3.3. Thermal studies

The reaction of **1** with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ in toluene or acetone gave a variety of results. The conditions and yields are listed in Table 3. When $Fe_2(CO)_9$ reacted with **1** at room temperature, **5** was not obtained. At 55 °C, the yield of **5** did not increase with longer reaction time or by using acetone instead of toluene solvent. At 110 °C, **4** and **5** were not isolated. When $Fe_3(CO)_{12}$ reacted with **1** at room temperature or at 55 °C, **4** and **5** were not obtained (Scheme 2). TLC analysis showed that **2** slowly decayed during its heating in toluene at 55 °C. After one day, trace amount of **5** was detected. After four days, the TLC analysis revealed the presence of free phenyldithiobenzoate, complex **3** and diphenylacetylene. These two last compounds suggest the occurrence of a fragmentation of **2** or **1** but the intermediate complex **5** was not isolated.

The main conclusion of these results was that **4** and **5** did not arise from a fast thermal reaction involving complex **2**. The formation of **4** and **5** during the reaction of $Fe_2(CO)_9$ with **1** at 55 °C was an indication of the occurrence of a more efficient activation than the thermal one. As for the fragmentation of xanthate ligand [12] we suggest that this efficient activation could be the result of an electron transfer involving **2** or **3** or **1**. The origin of the transferred electrons may be found in the decomposition of the iron carbonyl $Fe_2(CO)_9$ or one of complexes **2** or **3** leading to species containing iron at low oxidation state. The overall transformation of **2** implicated a fragmentation followed by a dimerization of mononuclear entities. It was very important to note that when the complexation of **1** was carried out at 55 °C with $Fe_3(CO)_{12}$, which is more reduc-

$$PhCS_2Ph \quad \xrightarrow[55°C]{Fe_3(CO)_{12}} \quad 2 \; + \; 3 \; + \; \ast \; + \; \ast$$
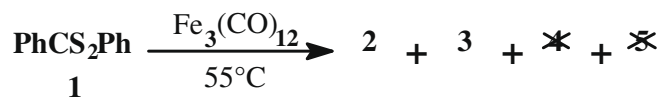
Scheme 2. Reaction of **1** with $Fe_3(CO)_{12}$.

ible than **2** and **1** [40], $Fe_3(CO)_{12}$ acted as an electron trap and inhibited the formation of **4** and **5**.

3.4. Voltammetric studies

In DMF solution, at room temperature, complex **2** underwent two one-electron reduction steps. The first one was quasi-reversible ($E_{1/2}$ = −0.75 V versus SCE) and gave the corresponding radical anion **2**[−], which was observed as a stable compound at the voltammetric time scale (Fig. 2a). The further reduction of **2**[−] to **2**[2−] due to the follow-up **2**[2−] chemical reaction's, was observed at −1.45 V versus SCE and was irreversible. The difference $\Delta Ep = Epa - Epc$ (0.5 V for the first reduction) showed a slow heterogeneous charge transfer. The heating of the solution increased the lability of **2**[−]. The voltammograms did not show the formation of complexes **4** or **5**. The relative peak currents and the loss of quasi-reversibility at 55 °C (Fig. 2b) suggest that the reduction of **2** followed an ECE mechanism, where the chemical step C occurring at **2**[−] allowed the transfer of a second electron at the same potential. The chemical reversibility of the reductions and the absence of following fragmentation led us to conclude that the extra electrons in **2**[−] and **2**[2−] were located on the metal atoms and not on the dithioester ligand.

However, the lability of **2**[−] may be disclosed in the presence of a donor ligand and confirm the electron localization on the metal center. When a ligand $P(OMe)_3$ was added into solution of **2** in DMF, the cyclic voltammogram (Fig. 3) showed the typical behavior of a ligand substitution catalyzed by an electron transfer which occurred at the cathode surface [13,18,41]. The cathodic peak C1 (Epc = −1.0 V versus SCE) of **2** decreased while the peak C3, corresponding to the reduction of the substituted complex [μ-η^3(C,S,S)PhCS_2Ph]Fe_2(CO)_5L (L = $P(OMe)_3$), appeared at more negative potentials (Epc = −1.2 V versus SCE).

Table 2
Selected bond lengths (Å) and angles (°) for complex **5**.

Bond lengths (Å)		Angles (°)	
Fe(1)–Fe(2)	2.4821(8)	Fe(1)–(S1)–Fe(2)	66.50(3)
Fe(1)–C(1)	1.772(5)	Fe(1)–S(2)–Fe(2)	66.44(3)
Fe(2)–C(4)	1.783(4)	C(1)–Fe(1)–Fe(2)	100.85(14)
C(1)–O(1)	1.146(5)	C(1)–Fe(1)–C(3)	100.6(2)
C(4)–O(4)	1.139(5)	C(5)–Fe(2)–Fe(1)	105.46(13)
Fe(1)–S(1)	2.2629(11)	C(5)–Fe(2)–C(4)	91.04(18)
Fe(1)–S(2)	2.2666(11)	S(1)–Fe(1)–S(2)	79.53(4)
Fe(2)–S(1)	2.2642(11)	S(1)–Fe(1)–C(1)	89.93(15)
Fe(2)–S(2)	2.2640(11)	S(1)–Fe(2)–S(2)	79.56(4)
S(1)–C(13)	1.816(4)	S(1)–Fe(2)–C(6)	104.47(13)
S(2)–C(14)	1.8144(4)	Fe(1)–S(1)–C(13)	102.85(13)
C(13)–C(14)	1.326(5)	Fe(2)–S(2)–C(14)	101.95(13)
C(13)–C(23)	1.481(5)	C(23)–C(13)–C(14)	129.2(3)
C(14)–C(17)	1.486(5)	C(13)–C(14)–C(17)	129.1(3)

Table 3
Reactions of $PhCS_2Ph$ with iron carbonyl.

Iron carbonyl	Temperature (°C)	Time (h)	Solvent	Yields of products (%)			
				2	3	4	5
$Fe_2(CO)_9$	55	0.5	Toluene	43	6	20	24
$Fe_2(CO)_9$	55	1	Toluene	35	8	25	30
$Fe_2(CO)_9$	110	1	Toluene	0	0	0	0
$Fe_2(CO)_9$	20–25[a]	1	Toluene	60	N.C.	N.C.	18
$Fe_2(CO)_9$	55	1	Acetone	30	N.C.	N.C.	18
$Fe_3(CO)_{12}$	20–25[a]	72	Toluene	65	0	0	0
$Fe_3(CO)_{12}$	55	1	Toluene	60	10	0	0
$Fe_3(CO)_{12}$	20–25[a]	4	Acetone	47	N.C.	0	0

[a] With ultrasonic activation; N.C.: not calculated.

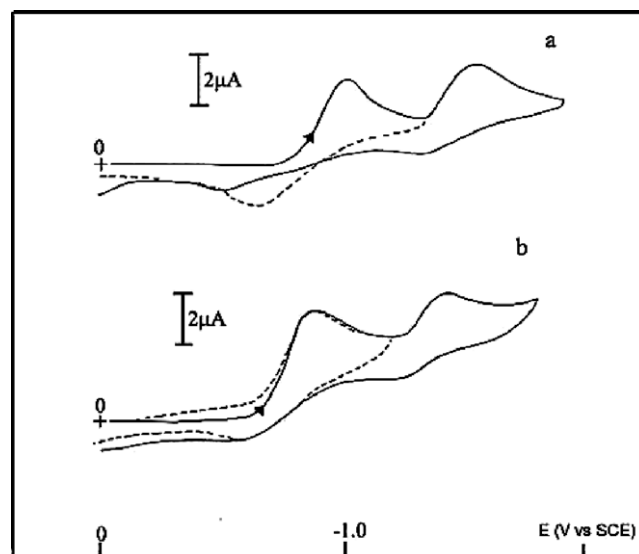**Fig. 2.** Cyclic voltammetry of 2 mM of complex **2** in DMF 0.1 M Bu_4N^+ BF_4^-; Pt electrode; scan rate 0.2 V s^{-1}. (a) At 20 °C; (b) at 55 °C; - - - - - reverse scan after the first reduction.

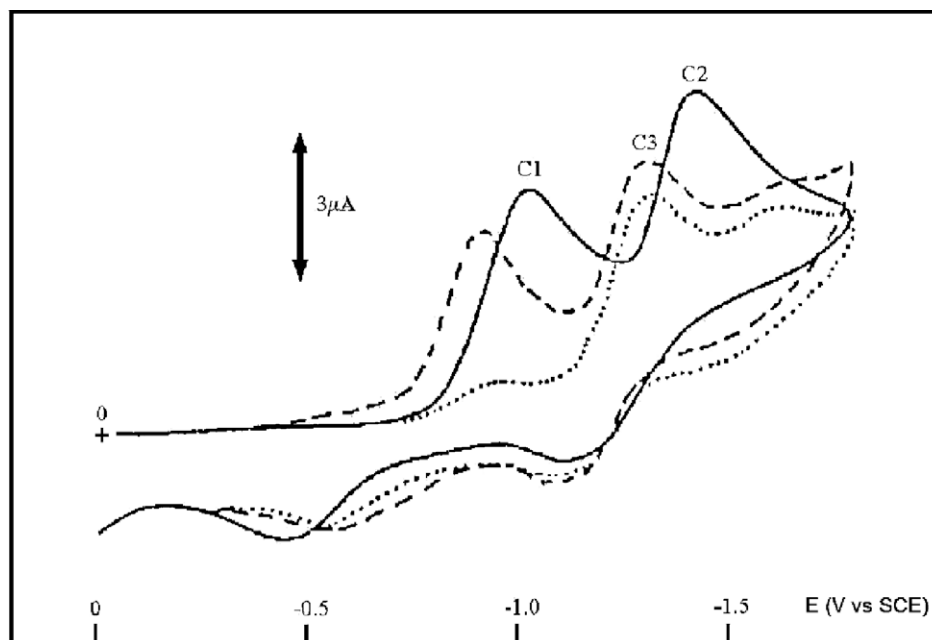**Fig. 3.** Cyclic voltammetry of 2 mM complex **2** in DMF 0.1 M Bu_4N^+ BF_4^-; Pt electrode; scan rate 0.5 V s^{-1}. — Complex **2** alone; - - - - - and ······ first and second scanning in the presence of an excess of P(OMe)$_3$.

The cyclic voltammetry of complex **5** was performed in CH_2Cl_2 solution (Fig. 4). The electronic effect of the bridging ligand influences the reduction potential which was observed at −0.99 V versus SCE, The reduction was a two-electron reversible process. For similar propane dithiolate iron carbonyl complex, the reduction is a two-electron quasi-reversible reaction [21].

The cyclic voltammetry of the phenyldithiobenzoate **1** showed three peaks. The first was attributed to the reduction of **1** leading to the corresponding anion **1**$^-$. The second was the reduction of anion **1**$^-$. The third was due to the reduction of phenylacetylene. As reported by Lund et al. [42], the first reduction (Epc = −1.12 V versus SCE) is irreversible and shows a heterogeneous electron transfer involving dimerization of anion radical **1**$^-$ followed by an elimination reaction (Scheme 3). We were able to confirm the
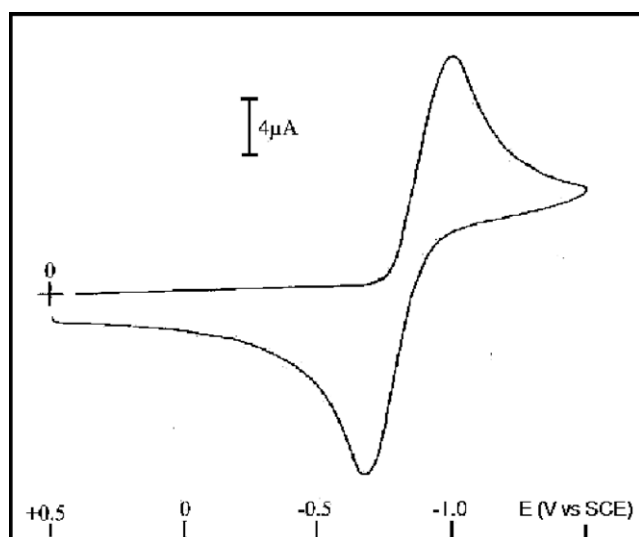
elimination of the PhC(S)S$^-$ by observing its irreversible oxidation at +0.4 V versus SCE.

### 3.5. Proposed mechanism for the formation of complexes **4** and **5**

The formation of **4** and **5** during the reaction of $Fe_2(CO)_9$ with **1** at 55 °C requires an activation more efficient than the thermal one. We suggest that the reaction involves an electron transfer mechanism. We propose that the reaction of **1** with $Fe_2(CO)_9$ follows two competitive pathways (Scheme 4). The first one would be a stepwise replacement of three carbonyls of $Fe_2(CO)_9$ by a ligand **1** with the formation of **2** and **3**. In this pathway 49% of the phenyldithiobenzoate have been transformed.

However the second pathway would be a reduction of **1** leading to the elimination of PhC(S) and PhS$^-$ fragments. These last two species or their dimerized forms would be trapped by $Fe_2(CO)_9$ and this reaction should consume 44% of PhCS$_2$Ph. The electrons required in the reduction of **1** may arise from the thermal decomposition of $Fe_2(CO)_9$, **2** or **3**. It is useful to recall that when the reaction of **1** was carried out with $Fe_3(CO)_{12}$ (Table 3), we obtained only complexes **2** and **3**. In the presence of $Fe_3(CO)_{12}$, this compound acted as an electron trap since it is more easy to reduce than **1**. So, complexes **4** and **5** could not be formed.

The mechanism of the second competitive pathway suggested above can be explained by the following reactions. First, the decomposition of iron carbonyl compounds ($Fe_2(CO)_9$, **2** or **3**) affords Fe(0) which reduces the starting dithioester **1**. Then, the reduced form of dithioester is involved in a cleavage leading to sulfur containing fragments or their dimers [42]. Finally, these compounds react with $Fe_2(CO)_9$ and lead to **4** and **5** (Scheme 4).

Fig. 4. Cyclic voltammetry of 2 mM of complex **5** in CH_2Cl_2 0.1 M Bu_4N^+ BF_4^-; Pt electrode; scan rate 0.5 V s^{-1}.

$$\mathbf{1} \underset{}{\overset{+\,e}{\rightleftharpoons}} \mathbf{1}^{\cdot-}$$

$$2\,\mathbf{1}^{\cdot-} \longrightarrow \text{PhC(S)C(S)Ph} + 2\,\text{PhS}^{\cdot-}$$

Scheme 3. Electrochemical reduction of **1**.
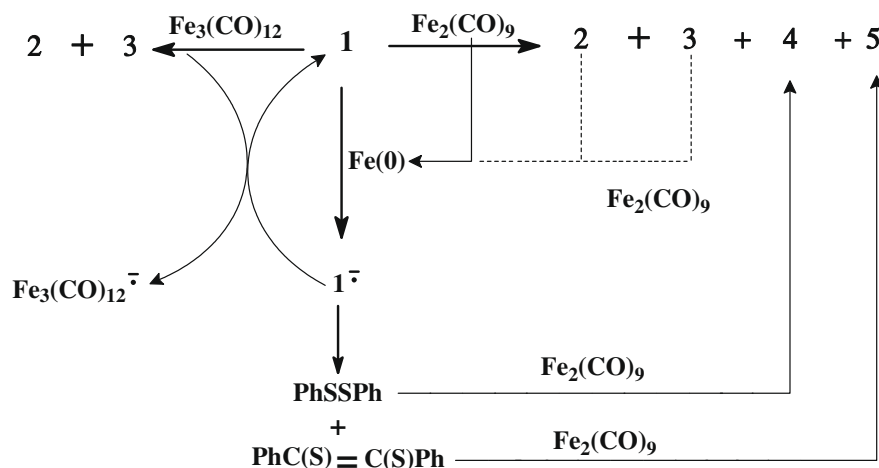
Scheme 4. Formation of complexes in reaction of **1** with iron carbonyl.

By taking into account the yields in each pathway, we can estimate that the kinetic constant ratio of the two competitive reactions (electron transfer and replacement of three carbonyls) is equal to 0.89.

4. Conclusion

The fragmentation occurring during the reaction of phenyldithiobenzoate is a new example of the intricacy of $Fe_2(CO)_9$ reactivity under thermal activation. Owing to the fact that the reaction of $Fe_3(CO)_{12}$ did not give the same products, we suggested the occurrence of an electron transfer that changes the nature of the organic ligand.

Acknowledgement

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