

Diiodine complex of diferrocenyl(phenyl)phosphine sulfide: the structural and electrochemical behaviour of $\text{Fc}_2(\text{Ph})\text{PS} \cdot \text{I}_2$

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Abstract

The title compound, $\text{Fc}_2(\text{Ph})\text{PS} \cdot \text{I}_2$, has been prepared and characterised in both the solid state and solution. Single crystal X-ray crystallography reveals that the adduct adopts a molecular charge-transfer structure in the solid state. Mössbauer spectroscopy confirms the presence of low spin Fe^{2+} but also indicates the presence of ca. 24% of an Fe^{3+} species. The electrochemistry of $\text{Fc}_2(\text{Ph})\text{PS} \cdot \text{I}_2$, $\text{Fc}_2(\text{Ph})\text{PS}$ and $\text{Fc}_2(\text{Ph})\text{P}$ has been studied using a combination of cyclic voltammetry and differential pulse voltammetry. The data for $\text{Fc}_2(\text{Ph})\text{PS} \cdot \text{I}_2$ show two redox processes, consistent with the sequential oxidation of the ferrocenyl groups to ferrocenium species.

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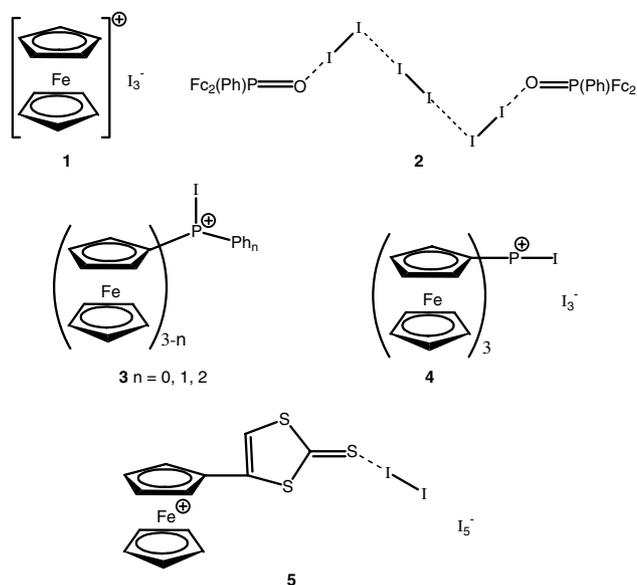
1. Introduction

Treatment of ferrocene with diiodine leads to oxidation of the iron yielding the ferrocenium triiodide salt **1** [1]. In contrast, treatment of substituted ferrocene derivatives, such as ferrocenyl phosphines or ferrocenyl phosphine oxides, with diiodine yields molecular charge-transfer complexes, **2**, or ionic species, **3**, **4**, without simultaneous oxidation of the iron [2,3]. We have recently reported the structural and magnetic properties of a remarkable ferrocenium–polyiodide

charge-transfer complex **5**, obtained by treating the parent ferrocene-substituted 1,3-dithiole-2-thione with diiodine. Rather than simply forming a molecular charge-transfer complex with the thiocarbonyl–sulfur, as one might have expected, the iron atom is simultaneously oxidised from Fe^{2+} to Fe^{3+} through a novel ‘double’ charge-transfer process [4]. The only previous report of simultaneous oxidation of the iron atoms and the heteroatoms in substituted ferrocenes was by Wei et al. [5] with the formation of mixed valence $\text{Fe}^{2+}/\text{Fe}^{3+}$ species. Herein, we report the first crystallographically characterised dihalogen complex of a ferrocenyl phosphine chalcogenide, $\text{Fc}_2(\text{Ph})\text{PS} \cdot \text{I}_2$ (**6**), together with investigations into the electrochemistry of $\text{Fc}_2(\text{Ph})\text{P}$, $\text{Fc}_2(\text{Ph})\text{PS}$ and **6**.

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2. Experimental

Diferrocenyl(phenyl)phosphine sulfide was prepared from diferrocenyl(phenyl)phosphine and sulfur using standard synthetic procedures [6]. Diiodine was purchased commercially (Aldrich) and used as received. Solvents were distilled from appropriate drying agents under nitrogen before use. Raman spectra were recorded on a Renishaw Ramascope 100 Raman Microscope using a 780 nm near IR laser. IR spectra were recorded on a ATI Mattson Genesis series spectrometer. NMR spectra were obtained using a Bruker AC250 spectrometer. Elemental analysis was performed by the staff of the Microanalysis Service, Department of Chemistry, University of Manchester. ^{57}Fe Mössbauer spectroscopy was performed at room temperature on a constant acceleration spectrometer. The spectrum was fitted using a Lorentzian software package [7] and calibration is relative to $\alpha\text{-Fe}$.

2.1. Synthesis of $\text{Fc}_2(\text{Ph})\text{PS} \cdot \text{I}_2$ (**6**)

A solution of diiodine (0.254 g, 0.1 mmol), dissolved in 20 ml CH_2Cl_2 , was added to a sample of $\text{Fc}_2(\text{Ph})\text{PS}$ (0.510 g, 0.1 mmol), dissolved in 20 ml of CH_2Cl_2 . An immediate color change from yellow to dark brown was observed. The mixture was heated under reflux, with stirring, for 30 min. After this time the solution was cooled and the solvent allowed to evaporate slowly over a period of three days, producing a small crop of black crystals which were separated by filtration (0.3 g, 32%). Anal. Calc. for $\text{C}_{26}\text{H}_{23}\text{Fe}_2\text{I}_2\text{PS}$: C, 40.87; H, 3.03. Found: C, 40.72; H, 3.08%. IR (KBr disc):

$\nu(\text{P-S})$ 597 (w), 618 (w); Raman: $\nu(\text{I-I})$ 171 (vs) cm^{-1} . MS *m/e* 510 Fc_2PhPS , 254 I_2 , 127 I.

2.2. Cyclic voltammetry

The measurements for compounds **6**, $\text{Fc}_2(\text{Ph})\text{PS}$, $\text{Fc}_2(\text{Ph})\text{P}$, and ferrocene were performed on a CHI660A electrochemical workstation with *iR* compensation, using anhydrous acetonitrile as the solvent, aqueous Ag/AgCl as the reference electrode and platinum wire and glassy carbon disk as the counter and working electrodes, respectively. All solutions were degassed (N_2) and contained the substrate in concentrations ca. 10^{-3} M, together with *n*- Bu_4NPF_6 (0.1 M) as the supporting electrolyte. Cyclic voltammograms were run at a scan rate of 25 mV s^{-1} .

2.3. X-ray crystal structure determination

Data were collected at low temperature on an Nonius KappaCCD area detector diffractometer located at the window of a Nonius FR591 rotating anode X-ray generator, equipped with a molybdenum target ($\lambda\text{Mo K}\alpha = 0.71073 \text{ \AA}$). Structures were solved and refined using the SHELX-97 suite of programs [8]. Data were corrected for absorption effects by means of comparison of equivalent reflections using the program SORTAV [9]. Non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were generally fixed in idealised positions with their thermal parameters riding on the values of their parent atoms. $\text{C}_{26}\text{H}_{23}\text{Fe}_2\text{I}_2\text{PS}$, Triclinic, $P\bar{1}$, $a = 11.140(2)$, $b = 11.235(2)$, $c = 11.426(2) \text{ \AA}$, $\alpha = 115.27(3)$, $\beta = 92.42(3)$, $\gamma = 100.23(3)^\circ$, $V = 1261.4(4) \text{ \AA}^3$, 150 K, $Z = 2$, $D_c = 2.011 \text{ mg/m}^3$, $\mu = 3.757 \text{ mm}^{-1}$, $\theta_{\text{max}} = 27.50^\circ$, 20234 measured and 5727 unique ($R_{\text{int}} = 0.0723$) reflections, R_1 (obs) = 0.0406 and wR_2 (all data) = 0.1119, $\rho_{\text{max}}/\rho_{\text{min}} = 1.313/-2.889 \text{ e \AA}^{-3}$. Supplementary data have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. 6: CCDC239428).

3. Results and discussion

Combining the phosphine sulfide donor $\text{Fc}_2(\text{Ph})\text{PS}$ with one molar equivalent of diiodine in dichloromethane yields the adduct $\text{Fc}_2(\text{Ph})\text{PS} \cdot \text{I}_2$ **6** after evaporation of the solvent. The X-ray crystal structure of **6** (Fig. 1) shows that the compound has a molecular charge-transfer structure. Kirss and coworkers [2] concluded that the diiodine complex of the analogous oxide donor, $\text{Fc}_2(\text{Ph})\text{PO}_2 \cdot (\text{I}_2)_3$ (**2**), forms a molecular adduct in which two donor molecules are bridged by three diiodine molecules. We have previously demonstrated that the nature of diiodine adducts of Ph_3PS and Ph_3PSe are very different to that of Ph_3PO [10]. Moreover, the nature of the

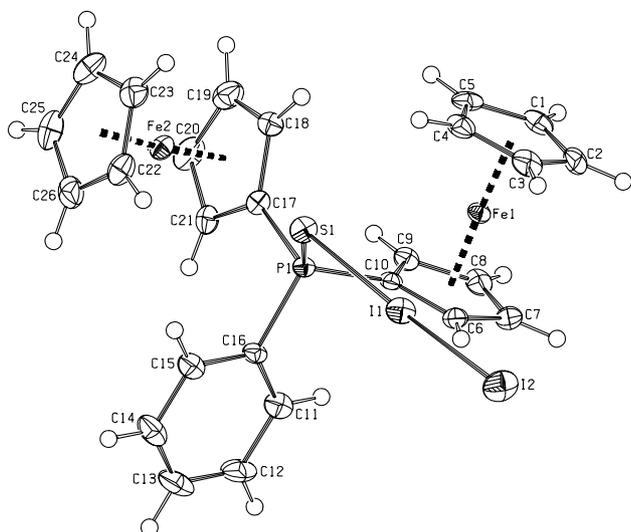


Fig. 1. The X-ray crystal structure of **6**, showing the atomic numbering scheme.

adduct is very much dependent upon the solvent and the relative quantities of donor and acceptor; Kirss studied the interaction of $\text{Fc}_2(\text{Ph})\text{PO}$ with an excess of I_2 in benzene, whereas the work reported here was carried out in dichloromethane.

Selected bond lengths and angles in **6** are presented in Table 1. The S–I–I bond angle [$176.31(2)^\circ$] is close to linear and the I–I bond length [$2.8233(9) \text{ \AA}$] is lengthened compared to the bond length of uncoordinated diiodine [2.681 \AA] [11], but is shorter than the van der Waals radius of diiodine (3.40 \AA) [12], and lies within the range observed for related compounds, $2.705\text{--}2.9818 \text{ \AA}$ [10,13–17]. The Raman spectrum of **6** displays an intense $\nu(\text{I-I})$ band at 171 cm^{-1} which, according to the classification developed by Deplano, corresponds to a strong charge-transfer adduct [18]. The S···I bond in **6** [$2.7607(12) \text{ \AA}$] has a similar length to those in diiodine complexes of other tertiaryphosphine sulfides, which lie in the range $2.591\text{--}3.204 \text{ \AA}$ [10,13–17]. The thiophosphoryl bond length is similar to that in other diiodine complexes of phosphine sulfides indicating that the ferrocenyl groups do not have any significant effect on the P = S moiety.

The Mössbauer spectrum of powdered crystals of **6** (Fig. 2), shows a major doublet with an isomer shift $\delta = 0.43 \text{ mm s}^{-1}$ and quadrupole splitting $\Delta E_Q = 2.27 \text{ mm s}^{-1}$. This result is consistent with low spin iron (II), which typically has an isomer shift in the range

Table 1
Selected bond lengths (\AA) and angles ($^\circ$) in **6**

I1–I2	2.8233(9)	S1–I1	2.7670(12)
P1–S1	2.0015(14)	P1–C16	1.814(3)
P1–C17	1.776(3)	P1–C10	1.778(3)
S1–I1–I2	176.31(2)	P1–S1–I1	109.71(5)

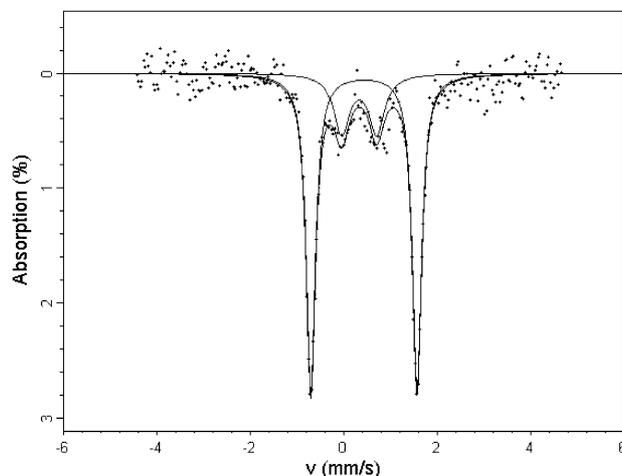


Fig. 2. The Mössbauer spectrum of a powdered sample of **6**.

$0.3\text{--}0.4 \text{ mm s}^{-1}$ and quadrupole splittings of $2.2\text{--}2.3 \text{ mm s}^{-1}$ [19]. For example, the related compound $(\text{Fc}_2(\text{Ph})\text{PO})_2 \cdot (\text{I}_2)_3$ has Mössbauer parameters of $\delta = 0.468$ and $\Delta E_Q = 2.371 \text{ mm s}^{-1}$, at 293 K [2].

The spectrum of **6** also revealed the presence of a small amount of a second component with $\delta = 0.33$ and $\Delta E_Q = 0.75 \text{ mm s}^{-1}$, typical of an iron (III) species [19]. The relative quantities of the iron(II)/(III) species are 76% and 24%, respectively. The formation of a mixed valence species in the reaction between diiodine and ferrocene-substituted donors, although unusual, is not without precedent, Wei et al. [5] having observed similar behaviour in a series of substituted ferrocene derivatives; for example, the oxidised ferrocenyl phosphine, $[\text{Fc}_2(\text{Ph})\text{P}]^+\text{I}_3^-$ comprised an iron (II) component ($\delta = 0.44$ and $\Delta E_Q = 2.4 \text{ mm s}^{-1}$) and an iron (III) component ($\delta = 0.38$ and $\Delta E_Q = 0 \text{ mm s}^{-1}$).

The redox behaviour of **6**, $\text{Fc}_2(\text{Ph})\text{PS}$ and $\text{Fc}_2(\text{Ph})\text{P}$ have been studied by cyclic voltammetry (Fig. 3). The substrates containing phosphine sulfide groups displayed two sequential reversible oxidation processes at almost identical values ($E_{1/2}^1 \approx +0.62$ and $E_{1/2}^2 \approx +0.76 \text{ V}$, Table 2). These peaks are assigned to the oxidation of the two ferrocenyl moieties to the corresponding ferrocenium species. The appearance of two separate redox processes proves that simultaneous oxidation of both metalocenes does not take place. The first oxidation is higher than that of unsubstituted ferrocene ($E_{1/2} = +0.43 \text{ V}$), due to the electron withdrawing nature of the phosphine sulfide functionality. Noticeably, the complexation of diiodine does not affect the redox properties of compound **6** (by direct comparison with $\text{Fc}_2(\text{Ph})\text{PS}$), indicating that the electron withdrawing ability of the phosphine sulfide groups in compounds **6** and $\text{Fc}_2(\text{Ph})\text{PS}$ are essentially identical (allowing for experimental error), and therefore independent of the dihalogen unit. The electrochemistry of the parent phosphine, $\text{Fc}_2(\text{Ph})\text{P}$, is very different from its sulfide

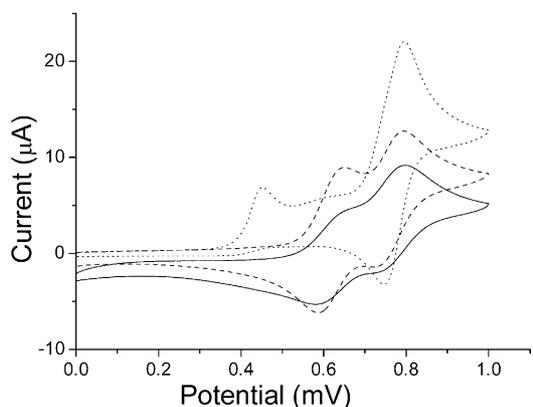


Fig. 3. Cyclic voltammograms of **6** (bold line), $\text{Fc}_2(\text{Ph})\text{PS}$ (dashed line) and $\text{Fc}_2(\text{Ph})\text{P}$ (dotted line).

derivatives. An irreversible oxidation process at +0.45 V and a second, reversible oxidation at +0.77 V were observed. The marked difference in the redox behaviour between $\text{Fc}_2(\text{Ph})\text{P}$ and compounds **6** and $\text{Fc}_2(\text{Ph})\text{PS}$, must be due to the oxidisable phosphine functionality, compared with the electrochemically stable phosphine sulfide group. The resulting radical cation from the first, irreversible oxidation could be delocalised over a phosphine–ferrocene fragment, rendering the latter electrochemically inert; the second, reversible oxidation is at a similar potential to those corresponding to $E_{1/2}^2$ for **6** and $\text{Fc}_2(\text{Ph})\text{PS}$ and is assigned to the second ferrocene unit. Kagan and coworkers [20] noted that the ferrocenyl phosphines, in which the phosphorus has a lone pair of electrons, show irreversible oxidation steps whereas analogous compounds containing oxidised phosphorus centres, such as ferrocenyl phosphine oxides, display a number of reversible, one-electron, oxidation waves equal to the number of ferrocenyl groups in the molecule. Thus, $\text{Fc}_2(\text{Ph})\text{PO}$ displays two reversible oxidation waves at +0.59 and +0.75 V that correlate well with the data reported here for **6** and $\text{Fc}_2(\text{Ph})\text{PS}$, whereas $\text{Fc}(\text{Ph})_2\text{P}$ has a reversible oxidation at +0.46 V and an irreversible step at +1.40 V.

Our electrochemical data for $\text{Fc}_2(\text{Ph})\text{P}$ are not in agreement with that reported previously for this compound by Kirss, who observed an irreversible oxidation at +0.18 V, followed by a second reversible oxidation

at +0.36 V, and a third irreversible oxidation at +0.51 V [2]. Kotz [21] reported that $\text{Fc}_2(\text{Ph})\text{P}$ displayed only two reversible oxidations at +0.62 and +0.705 V, but a third oxidation was not observed, whereas Wei et al. [5] reported two reversible oxidation steps for $\text{Fc}_2(\text{Ph})\text{P}$ at +0.582 and +1.062 V. These apparently contradictory cyclic voltammetry results prompted us to investigate these compounds by differential pulse voltammetry (DPV), which is a sensitive analytical technique and is a useful method for resolving ill-defined or broad redox-waves [22]. Our results from DPV (Fig. 4), confirm the conclusions made from CV studies; however, we also observed a broad peak at ca. +0.525 to +0.59 V for compound $\text{Fc}_2(\text{Ph})\text{P}$. This feature possibly represents the electrochemical behaviour of a by-product obtained by oxidation of the substrate and confirms the instability of the phosphine group towards oxidation.

In our electrochemical experiments on compound **6**, we did not observe any redox properties corresponding to diiodine, proving that the charge-transfer adduct is stable in acetonitrile solution. The UV–Vis spectrum of **6** in acetonitrile contains an intense peak at 328 nm, resulting from the charge-transfer complex, and a much weaker peak centred at 490 nm assigned to un-coordinated diiodine. There was no evidence for the presence

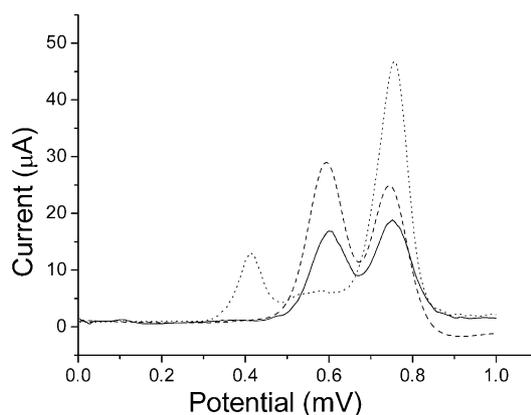


Fig. 4. Differential pulse voltammograms of **6**, $\text{Fc}_2(\text{Ph})\text{PS}$ and $\text{Fc}_2(\text{Ph})\text{P}$.

Table 2

Electrochemical data for compounds for **6**, $\text{Fc}_2(\text{Ph})\text{PS}$ and $\text{Fc}_2(\text{Ph})\text{P}$ and ferrocene; substrate ca. 10^{-3} M in acetonitrile, 0.1 M [$^t\text{Bu}_4\text{N}$][PF_6], vs. Ag/AgCl, glassy carbon working electrode, Pt counter electrode, scan rate 25 mV s^{-1}

Compound	Cyclic voltammetry		Differential pulse voltammetry (mV)
	$E_{1\text{ox}}$ (mV)	$E_{2\text{ox}}$ (mV)	
FcH	+431 (68)	–	+426
6	+617 (69)	+769 (57)	+601,+751
$\text{Fc}_2(\text{Ph})\text{PS}$	+618 (61)	+764 (62)	+595,+745
$\text{Fc}_2(\text{Ph})\text{P}$	+452 (irrev.)	+771 (49)	+413,+560 (br),+756

Numbers in parentheses represent the difference between peak maxima for oxidation and reduction processes in reversible redox waves, where applicable.

of the I_3^- ion which exhibits a pair of very strong bands at 360 and 294 nm [23].

4. Conclusion

Our studies of $Fc_2(Ph)PS$ and **6** indicate that the thiophosphoryl group is electrochemically stable but that the ferrocenyl moieties undergo partial oxidation upon treatment with iodine producing a mixed valence Fe^{2+}/Fe^{3+} species. The ease with which the ferrocenyl moieties in ferrocenes bearing heteroatom functionalities undergo chemical oxidation is clearly dependent upon the electroactivity of the substituents.

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