Synthesis, UV/vis spectra and electrochemical characterisation of arylthio and styryl substituted ferrocenes

Research Article

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Abstract: Two series of substituted ferrocenes were synthesised using either the Horner-Wadsworth-Emmons reaction or monolithiation of ferrocene. The series consist of arylthio- and styryl-ferrocenes with different substituents in the *para* position of the aryl rings of the systems. The electronic communication was investigated by comparing the substituent effects in absorption spectroscopy and in cyclic voltammetry. A small substituent effect was found in the electronic transitions of the styryl substituted ferrocenes. The oxidation of the ferrocene derivatives showed clear substituent effects as illustrated by the linear Hammett plots. The effect was shown to be an order of magnitude larger in the arylthio-systems than in the styryl systems. It is suggested that the reason behind the large effect is a direct sulfur-iron orbital overlap.

**Keywords:** Electrochemistry • Lithiation • Ligand effects • Ferrocene

1. Introduction

Ferrocene is a quite unique molecule. Among its many interesting properties some stand out, as they have been thoroughly investigated and exploited. Ferrocene is a stable yet easily oxidised molecule, which undergo chemical reactions like a simple organic aromatic compound. Therefore, advanced redox active molecular structures can be made using ferrocene as a building block. Of the many examples, where the facile synthesis of ferrocene derivatives has been used in combination with electrochemistry, the use of ferrocene as redox reporter in self-assembled monolayers and in biomolecule conjugates have received much attention [1-4]. Another special property of ferrocene is its structure. The molecular shape is that of a cylinder or barrel as shown in Fig. 1. A fact that has been exploited in chiral organometallic catalysis, where ligands incorporating ferrocene have high enantioselectivity and catalytic efficiency [5,6].

The synthesis of ferrocene derivatives has been widely explored. In this work, the focus is on direct monofunctionalisation of ferrocene, either from ferrocene itself or from ferrocenecarbaldehyde, which are both cheap starting materials. Direct functionalisation of ferrocene is possible by many methods, but few are so selective that only the monosubstituted derivative is obtained. Direct monolithiation of ferrocene has been reported by several groups, but no generally applicable method has so far been reported [7-10]. Here, we report a method for monolithiation of ferrocene that in our hands is shown to be reproducible with good to excellent yields upon quenching with electrophiles. This method of making monolithiumferrocene is used to synthesise arylthio-ferrocenes, a class of compounds which previously has been prepared using primarily organomercury chemistry [11]. The arylthio-ferrocenes, and the series of styrylferrocenes synthesised using the Arbuzov [12] and Horner-Wadsworth-Emmons [13] reactions, were investigated using UV/vis spectroscopy and cyclic voltammetry. The results show that the sulphur bridged compounds have a higher degree of electronic communication in the oxidation of ferrocene than the ethylene bridged compounds. On the other hand, the electronic transitions do not involve the ligand in the arylthio-ferrocenes, whereas the absorption spectra of the styryl-ferrocenes are highly perturbed by the ligand.

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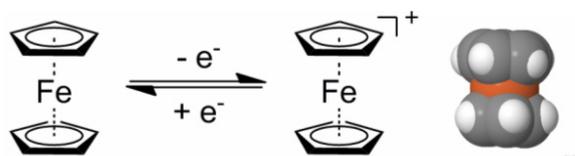
Figure 1. The ferrocene-ferrocenium redox couple and a spacefilling model of ferrocene.

2. Experimental Procedure

All compounds and solvents were used as received unless otherwise noted. THF was dried by distillation from Na/benzoephenone. NMR spectra were recorded on a Unity 400 MHz and are reported using the solvent residual peak as reference. Mass spectrometry was done on a HP GC-MS and a Micromass quadrupole-TOF ESI-MS, all compounds analysed by GC-MS were found to consist of only the desired product. Melting points were determined on a Kofler heat stage and are corrected with benzil (mp = 95°C) and phenacetin (mp = 134.5°C). Elementary analysis was performed for C, H and N on a FlashEA 1112. Electrochemistry was carried out in acetonitrile with a minimum of 100:1 electrolyte/analyte concentration on a CH-Instruments Model 400A potentiostat with a three electrode set-up using a platinum working and counter electrode and a silver/silver chloride reference electrode; the reference electrode was calibrated with the ferrocene/ferrocenium couple between each sample. Additional data can be found as supplemental information.

2.1. General procedure to phenyl disulfides (1)
The synthesis of disulphides **1a-d** was accomplished by a method adopted from Hirano *et al.* [14].

2.2. Phenyl-ferrocenyl sulphide [15-17]
Ferrocene 4.7 g (25 mmol) was dissolved in 30 mL dry THF and was cooled on an ice bath. *t*-butyllithium 13.3 mL (20 mmol, 1.5 M in hexane) was added drop-wise during a period of 10 min. The reaction mixture was stirred for 30 min at 0°C and a solution of 15 mmol diaryl disulphide (**1**) was added. The reaction mixture was allowed to warm to room temperature and after 2 hours of stirring the reaction was quenched with 15 mL of water, the phases were separated and the solvent was evaporated in vacuum. The crude product was dissolved in petrolether and flashed through a silica plug, with fractions of 50 mL of solvent. The fractions were investigated using TLC and the fractions containing a surplus of ferrocene were discarded. The remaining fractions were combined and evaporated onto a celite support and purified by vacuum flash chromatography with petrolether as the eluent. By removal of the solvent the product was isolated as an orange powder in a yield of 12% (450 mg). Mass Spectrometry: GC-MS m/z = 294. Elementary Analysis: Calculated C: 65.32; H: 4.80. Found: C: 65.40; H: 4.88. Mp: 110-111°C.

2.3. (4-chloro-phenyl)-ferrocenyl sulphide
The product was isolated as an orange powder in a yield of 40% (1.9 g). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.13 (d, *J* = 8.6, 2H), 6.96 (d, *J* = 8.6, 2H), 4.40 (s, 2H), 4.36 (s, 2H), 4.28 (s, 5H). Mass Spectrometry: GC-MS m/z = 328.

2.4. (4-bromo-phenyl)-ferrocenyl sulphide
The product was isolated as an orange powder in a yield of 68% (3.8 g). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.27 (m, 2H), 6.90 (m, 2H), 4.39 (s, 2H), 4.36 (s, 2H), 4.27 (s, 5H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ 7.34 (d, 2H), 6.96 (d, 2H), 4.40 (m, 4H), 4.27 (s, 5H). Mass Spectrometry: ESP+ (CH$_3$CN+TFA): m/z = 371.9 & m/z=373.9. MALDI-TOF+ (dithranol): m/z=372 & m/z=374. Elementary Analysis: Calculated C: 51.51; H: 3.51. Found: C: 51.87; H: 3.48. Mp: 134-136°C

2.5. 4-tolyl-ferrocenyl sulphide [17]
The product was isolated as a dark yellow powder in a yield of 70% (3.2 g). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 6.98 (m, 4H), 4.49 (s, 2H), 4.42 (s, 2H), 4.32 (s, 4H), 4.27 (s, 1H), 4.26 (s, 2H). Mass Spectrometry: GC-MS 100% of m/z = 308. Elementary Analysis: Calculated: C: 66.25; H: 5.23. Found: C: 66.52; H: 5.33. Mp: 94-96°C.

2.6. (4-carbonyl-phenyl)-ferrocenyl sulphide
20 mL of dry THF was cooled on an ice bath and *n*-butyllithium 0.45 mL (1.5 mmol, 2.5 M in hexane) was added. 4-Ferrocenylsulfanyl-brombenzene (**2c**) 0.5 g (1.3 mol) dissolved in 20 mL dry THF was added drop-wise and the reaction mixture was stirred for 15 min. 3 mL DMF (dried over molecular sieves) was then added and the ice bath was removed. After 75 min of stirring the reaction mixture was poured onto 100 mL of water and the product was extracted with two 100 mL portions of ethyl acetate. The combined extracts were washed with water and dried over magnesium sulphate. The product was isolated by dry column vacuum chromatography with methylene chloride as eluent in a yield of 75% (0.31 g). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 9.86 (s, 1H), 7.65 (m, 2H), 7.11 (m, 2H), 4.41 (s, 4H), 4.28 (s, 5H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ 191.0, 150.3, 132.9, 129.7, 124.7, 74.8, 73.1, 70.6, 69.7. Mass Spectrometry: GC-MS: m/z = 322. Elementary Analysis: Calculated: C: 63.37; H: 4.38. Found: C: 63.56; H: 4.22. Mp: 128-129°C.

2.7. General procedure to benzyl phosphonates (3) [18-27]

The benzyl bromide (Aldrich) 0.2 mol and triethylphosphite, 41.5 g (0.25 mol) were dissolved in 200 mL of 1,4-dioxane and heated to reflux under N_2. The reaction mixture was stirred at reflux for 20 hours. The product was isolated as a clear oil by kugelrohr distillation (airbath). The reaction is quantitative with a yield approaching 100%. The product dissociates on column materials. For use in HWE type reactions the surplus of triethylphophite does not have to be totally removed. The compound slowly hydrolyses when exposed to air resulting in the low values of the results of elementary analysis. Boiling points and analysis are given as supplemental information.

2.8. General procedure to styryl-ferrocenes 4a-h [28-34]

Ferrocenecarboxaldehyde 1.7 g (8 mmol) and benzylphosphonic acid diethyl ester (3a) 10 mmol were dissolved in 25 mL dry THF and cooled on an ice bath. Potassium *t*-butoxide 2 g (18 mmol) suspended in 30 mL dry THF was added drop-wise to the cooled solution with vigorous stirring. When the addition was complete, the ice bath was removed and the reaction mixture was stirred at ambient temperature for 2 hours. The reaction mixture was then poured onto 100 mL of water and the product was extracted with 3×40 mL portions of toluene. The combined extracts were washed with water and dried over magnesium sulphate. The solvent was removed in vacuum and the crude product was taken up in methylene chloride and flashed through a silica plug. Yields, appearance and analysis are given as supplemental information.

2.9. 4-((E)-2-ferrocenyl-vinyl)-benzaldehyde [28,29,35]

4-((E)-2-ferrocenyl-vinyl)-benzonitrile (4b) 1.5 g (5 mmol) was dissolved in 50 mL of dry THF and the solution was cooled on an ice bath. DIBAL 10 mL (10 mmol, 1 M in cyclohexane) was added and the reaction was stirred on the ice bath for 3 hours. The reaction was monitored with TLC (CH_2Cl_2). The reaction was quenched with 100 mL of 1 M HCl(aq) and the two phase system was stirred vigorously for 1 hour. The organic solvents were removed in vacuum and the product was extracted with 3 100-mL portions of ethyl acetate, the combined organic extracts were washed with brine and dried over magnesium sulphate. The product was isolated by dry column vacuum chromatography, using graduated elution from hexane to ethyl acetate, as red crystals in a yield of 14% (0.2 g). ^{1}H-NMR (400 MHz, CDCl$_3$)

δ 9.97 (s, 1H), 7.83 (d, 2H) 7.55 (d, 2H), 7.07 (d, 1H), 6.72 (d, 1H), 4.53 (s, 2H), 4.37 (s, 2H), 4.17 (s, 5H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ 191.5, 144.0, 134.6, 131.5, 130.3, 126.1, 124.7, 69.94, 69.60, 69.07, 67.47. Mass Spectrometry: MALDI-TOF: m/z = 316. Elementary Analysis: Calculated: C: 72.18; H: 5.10. Found: C: 72.12; H: 5.13. Mp: 162-166°C.

2.10. 4-*tert*-butylsulfanyl-β-(ferrocenyl)-styrene

Ferrocene-carboxaldehyde 200 mg (1 mmol) and (4-(*tert*-butylsulfanyl)-benzyl)-phosphonic acid diethyl ester (3h) 300 mg (1 mmol) were dissolved in THF and cooled on an icebath. Sodium hydride 160 mg (2.5 mmol, 60% in mineral oil) was added to the solution and the solution was stirred 1 hour at room temperature. The reaction mixture was poured onto 300 mL of water, the THF was removed in vacuum and the product was filtered off. The crude product was washed off the filter with acetone and dried over magnesium sulphate. Removal of the solvent and recrystallization from acetonitrile afforded the product as orange crystals in a yield of 27% (100 mg.). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.48 (s, 4H), 6.99 (d, 1H), 6.73 (d, 1H), 4.50 (s, 2H), 4.28 (s, 2H), 4.12 (s, 5H), 1.29 (s, 9H). Mass Spectrometry: ESP+ (CH$_3$CN+TFA): m/z=376. Elementary Analysis: Calculated: C: 70.21; H: 6.43. Found: C: 69.82; H: 6.40. Mp: 173-174°C

3. Results and Discussion

3.1. Synthesis

In the work presented here, five differently substituted arylthio-ferrocenes were prepared. The substituent *para* to the sulphur on the aryl ring was varied, and derivatives with *para* H, Cl, Br, CH$_3$ and CHO were synthesised. An analogues series of ten styryl substituted ferrocenes was prepared. In this series the groups *para* to the vinylene bridge in the styrene system were H, F, Cl, Br, CH$_3$, OCH$_3$, SCH$_3$, S^{t}Bu, CN and CHO respectively. The two series of compounds reported here have previously been synthesised. In the case of the arylthio-ferrocenes by using a similar route, with the key step being monolithiation of ferrocene [36]. In the case of the styryl-ferrocenes, they have previously been synthesised using both Wittig type chemistry and Heck coupling [29,35,37].

In this study, the monolithiation of ferrocene has been revisited. A method for preparing monolithium-ferrocene (**FcLi**) has been reported by several groups [8-10,17,36,38-40]. In this work, fourteen different

methods for preparing **FcLi** were tested [7-10,40], and the results were evaluated by quenching with DMF and *p*-bromophenyl disulfide (**1c**).

The two key issues in the preparation of monolithium-ferrocene are selectivity of the reaction and the stability of **FcLi** under the applied conditions. **FcLi** is under many conditions produced in a high yield, and it is the reaction time and the temperature of the following quenching with an electrophile that determines the yield. The half-life of **FcLi** is reported to be around 40 minutes in THF at -20°C, but it is considerably longer in ether [40]. This makes ether an attractive solvent. However, the problem is that the selectivity in ether is bad, as mostly dilithiated ferrocene is obtained. So, a compromise between selectivity and stability must be found. Here, **FcLi** was prepared using a method adopted from Kagan and co-workers [7]. Multiple solvent combinations, temperatures and reaction times were tested in order to find the best conditions for the reaction of **FcLi** with the two selected electrophiles. The result was tested multiple times with the two selected electrophiles and was found to give yields from 50-70% on up to a 2 gram scale. The reaction pathway used to obtain the arylthio-ferrocenes

(**2a**-**d**) is shown in Scheme 1. The reaction gives the yields shown in Table 1, the yield was low in case of **2a**, but this is believed to be due to the low vapour pressure of the disulphide. The diaryl disulphides were prepared using a method reported by Hirano *et al* [14].

The styryl-ferrocenes (or 1-aryl-2-ferrocenyl-ethenes, **4a**-**j**) were prepared as shown in Scheme 1. Earlier reported syntheses of similar compounds have used either Pd-coupling chemistry or the Wittig reaction to prepare the compounds [29,35,37]. Here, the Horner-Wadsworth-Emmons reaction was chosen for two reasons: i) the phophonate reagents are easily prepared on a large scale as they can be purified by distillation, and ii) where the Wittig reaction in most cases give a mixture of *cis* and *trans* isomers, the HWE reaction selectively gives the *trans* isomer in most cases [13]. The reactions to give **3** were performed on a 50-100 g scale and ran with complete conversion. The reaction from **3** to **4** was carried out with varying success. The yields of **4a**-**j** are reported in Table 1. As these easily obtained reagents were available in large quantities and the reactions were run on a gram scale, the reaction conditions were not further optimised.
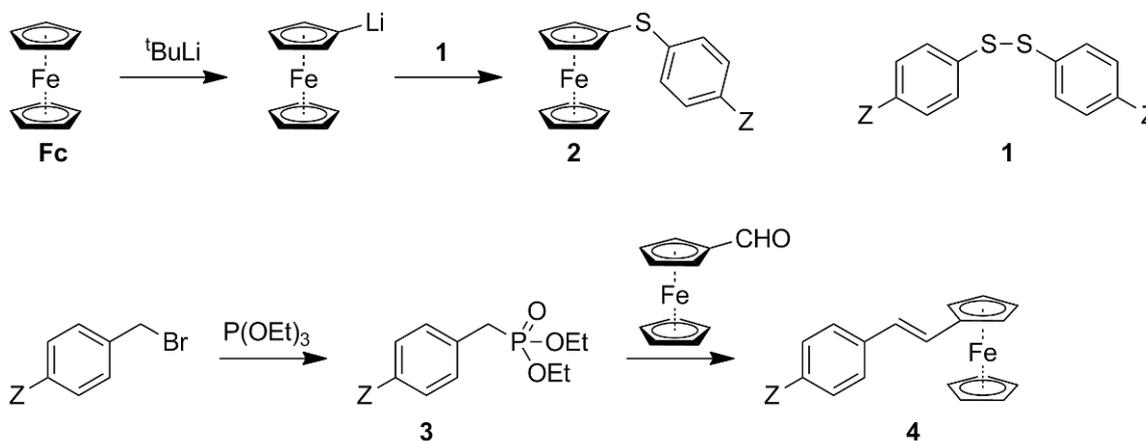
Scheme 1. Synthetic route to arylthio and styryl substituted ferrocenes.
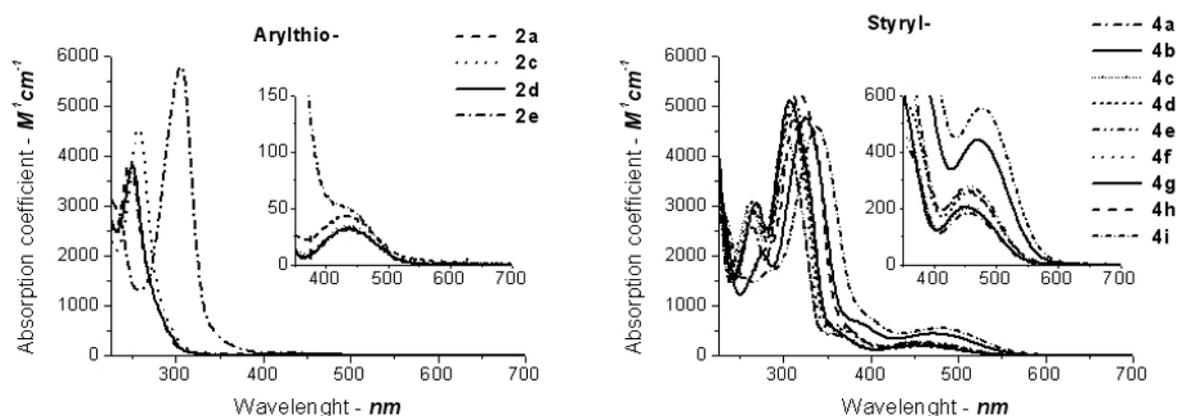
Figure 2. Absorption spectra of substituted ferrocenes in acetonitrile.

3.2. Absorption spectra

The absorption spectra of metallocenes have been treated extensively elsewhere [41]. For ferrocene the spectra consists of three main bands: two low intensity d-d transitions at 440 nm and 325 nm, with absorption coefficients of 96 and 55 $M^{-1} cm^{-1}$, respectively, and a third CT transition in the deep UV. The absorption spectra of the arylthio-ferrocenes (**2**) and styryl-ferrocenes (**4**) are shown in Fig. 2, and the data are compiled in Table 1. The two compound classes show very different absorption properties. The arylthio substituents affect the electronic transitions in ferrocene by lowering the intensity of the d-d transitions, whereas the energies of the transitions are not affected. Compared to ferrocene a new band is seen in the near UV, and this transition is ascribed to the local excitation of the arylthio substituent. On the other hand, the electronic transitions of styryl substituted ferrocenes differ significantly from those of ferrocene. Both the intensity and the energy of the d-d transitions are greatly affected by the addition of the styryl group and, to a lesser degree, by the nature of the *para*-group of the substituent. The styryl substituent increases the intensity of the first d-d transition by the factor of four and induces a redshift of 15 nm (750 cm^{-1}). There is a small increase in the absorption coefficient with the number of electrons in the system. The transition energy falls in the case of electron withdrawing groups and increases slightly for the electron donating groups. These effects are very small for all but the strong electron withdrawing groups. The cyano and carboxaldehyde substituted styryls show a marked increase in the transition intensity and a decrease in the transition energy. This can be a real effect, but can also be due to the intense π-π* transitions in the cyclopentadienyl-styryl system. The tail of the π-π* transition lifts the second d-d transition in all cases, but might, in the cyano and carboxaldehyde case, also lift the first d-d- transition. The π-π* transitions in the styrylferrocenes give rise to intense bands between 300 and 340 nm.

3.3. Electrochemistry

The electrochemistry of the substituted ferrocenes was investigated in acetonitrile using cyclic voltammetry. A platinum working and counter electrode were used with a silver/silver chloride reference electrode. Voltammograms were recorded with a minimum of three scan rates (*v*). The peak current was shown to depend linearly with $v^{\frac{1}{2}}$ and the peak separation was within the range expected for fully reversible redox processes [42]. In other words, the electrochemical behaviour of the alkylthio- and styryl-substituted ferrocenes was similar to that of ferrocene itself. Cyclic voltammograms of *p*-carboxaldehydephenylthio-ferrocene (**2e**) and *p*-cyanostyrylferrocene (**4b**) are shown in Fig. 3. The oxidation potentials of the compounds vary with both the bridge and the *para* substituent. The changes are shown in Fig. 4 and the electrochemical data are compiled in Table 2. The arylthio substituents clearly affect the oxidation potential more than the styryl substituents. Furthermore, the effect of changing the *para* substituent is larger in the arylthio systems than in the styryl systems. The phenylthio system is oxidised at 60 mV higher potential than ferrocene, whereas styryl-ferrocene is oxidised at basically the same potential as ferrocene. The change in the oxidation potential on going from hydrogen in the *para* position to carboxaldehyde is 118 mV for the sulphur bridge and only 40 mV for the ethylene bridge.

Table 1. The different substitution patterns, yields and characteristic electronic transitions of the synthesised ferrocenes, see Scheme 1 for the definition of Z and for the molecular structures.

| Compound	Bridge	Z	Yield	d-d transition		d-d transition		π-π* transition	
				λ, nm	ε, $cm^{-1} M^{-1}$	λ, nm	ε, $cm^{-1} M^{-1}$	λ, nm	ε, $cm^{-1} M^{-1}$
2a	S	-H	12%	440	96	325	55	-	-
2b	S	-Cl	40%	439	42	-	-	248	3914
2c	S	-Br	68%	439	35	-	-	257	4570
2d	S	-CH3	70%	439	35	-	-	250	3800
2e	S	-CHO	75%	443sh	48	-	-	306	5790
4a	-CH$_2$=CH$_2$-	-H	43%	455	183	361sh	410	306	3990
4b	-CH$_2$=CH$_2$-	-CN	80%	472	440	392sh	630	325	4770
4c	-CH$_2$=CH$_2$-	-F	55%	457	200	363sh	430	303	4400
4d	-CH$_2$=CH$_2$-	-Cl	54%	458	250	371sh	510	309	4800
4e	-CH$_2$=CH$_2$-	-Br	65%	458	280	372sh	560	310	5200
4f	-CH$_2$=CH$_2$-	-CH3	44%	455	211	367sh	440	307	4860
4g	-CH$_2$=CH$_2$-	-OCH3	22%	452	200	366sh	440	307	5100
4h	-CH$_2$=CH$_2$-	-SCH3	89%	454	262	-	-	320	5200
4i	-CH$_2$=CH$_2$-	-CHO	14%	480	550	400sh	760	338	4590
4j	-CH$_2$=CH$_2$-	-StBu	27%	440	96	325	55	-	-

Table 2. Electrochemical properties of the synthesised ferrocenes in 0.1 M TBAPF$_6$ in acetonitrile. The values are averages of three to four scans at four scanrates. The experiments were done at ambient pressure at 24°C. ΔE_p-values are obtained at $v = 1$ V s^{-1}.

| Compound	Bridge	Z	$\sigma_{Hammett}$	E_{red} vs NHE	E_{red} vs Fc	ΔE_p
				V	mV	mV
Fc	-	-	-	0.366	0	95
2d	S	-H	-0.17	0.425	59	117
2a	S	-Br	0	0.468	102	88
2c	S	-CH3	0.23	0.499	133	77
2e	S	-CHO	0.42	0.543	177	78
4a	-CH$_2$=CH$_2$-	-H	0	0.367	1	68
4b	-CH$_2$=CH$_2$-	-CN	0.66	0.402	36	91
4c	-CH$_2$=CH$_2$-	-F	0.06	0.362	-4	80
4d	-CH$_2$=CH$_2$-	-Cl	0.23	0.394	28	112
4e	-CH$_2$=CH$_2$-	-Br	0.23	0.379	13	75
4f	-CH$_2$=CH$_2$-	-CH3	-0.17	0.353	-13	105
4g	-CH$_2$=CH$_2$-	-OCH3	-0.27	0.34	-26	79
4h	-CH$_2$=CH$_2$-	-SCH3	0	0.364	-2	111
4i	-CH$_2$=CH$_2$-	-CHO	0.42	0.407	41	61
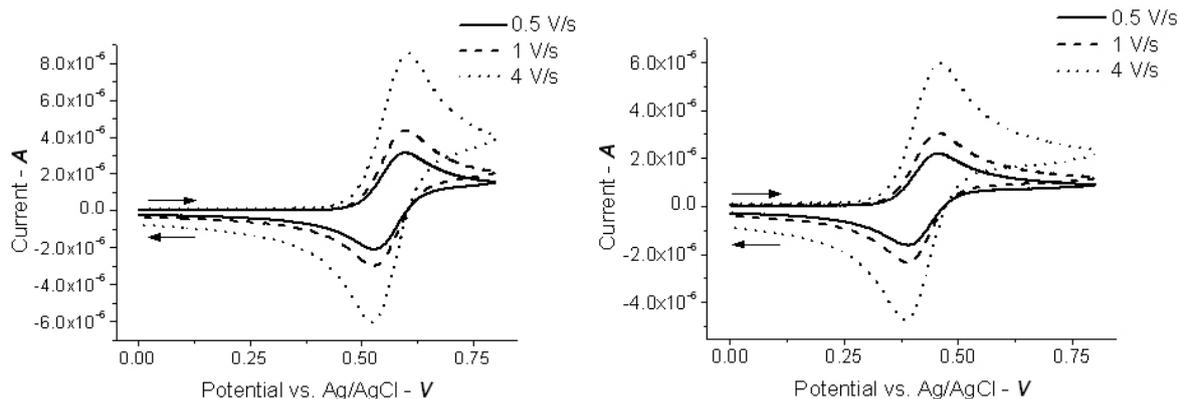
Figure 3. Cyclic voltammogram of 0.5 mM **2e** (right) and **4b** (left) in 0.1 M TBAPF6 in acetonitrile, recorded with a platinum working electrode.

It has previously been attempted to show linear correlations between the oxidation potentials of styryl-ferrocenes and other properties [15]. Fig. 5 shows plots of the oxidation potential of the arylthio- and styryl-ferrocenes versus the Hammett parameters for the different para-substituents. A good linear relationship is seen in both cases. The reaction constant quantifies the observation that the substituent effect is much larger in the arylthio systems than in the styryl systems. This can be due to i) a through bond effect where the communication in the arylthio system is superior to that of the styryl system or ii) a through space effect where the arylthio systems brings the electrons of aromatic system closer to the active iron center.

Nagy *et al.* have previously determined the reaction constant for the oxidation of phenyl-ferrocenes to 0.45 [43]. This value in combination with the two values determined here, gives a measure for the electronic communication from the ligand to the redoxcenter. The direct attachment in the phenyl-ferrocens has the largest effect, where the conjugated system of the
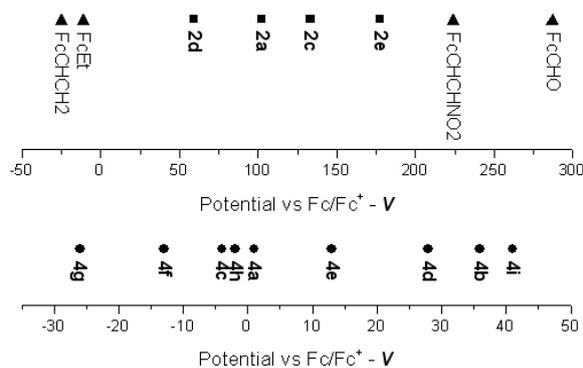
Figure 4. Electrochemical potentials for selected ferrocenes in 0.1 M TBAPF$_6$ in acetonitrile. ■ is arylthioferrocenes, ● is styrylferrocenes, and ▲ is litterature values from [45] and [46].

styryl-ferrocenes influences the oxidation less than the arylthio substituent. Interestingly, direct substitution onto the ferrocene system gives a lower reaction constant at only 0.38 [44]. Thus, supporting the notion that the through space communication is larger than the through bond communication.

$$\log\left(\frac{K}{K_0}\right) = \sigma \cdot \rho \; ; \; E_x - E_H = \sigma \cdot \rho$$
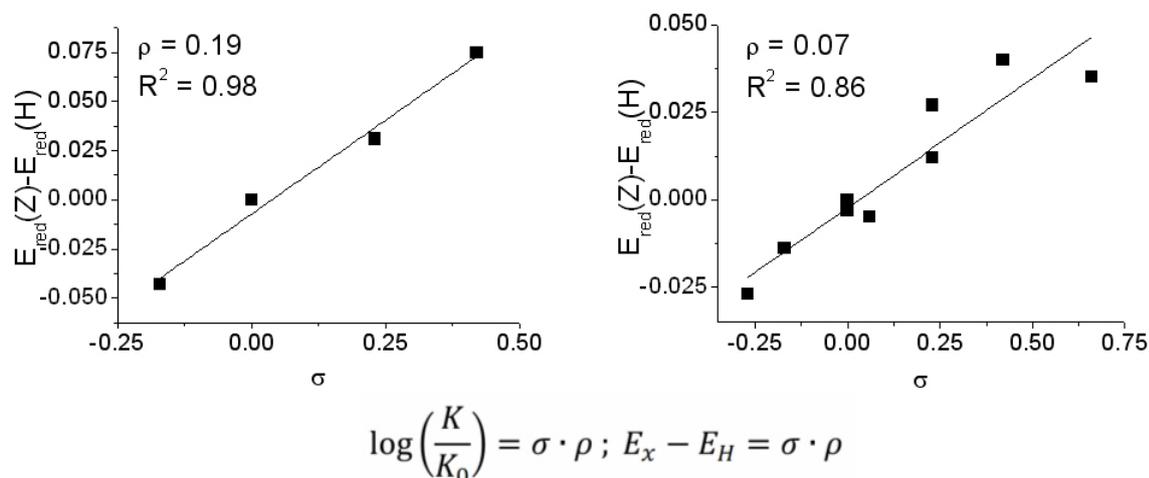
Figure 5. Hammett plots of the oxidation potential of the synthesised arylthio- (■) and styryl- (●) ferrocenes in 0.1 M TBAPF$_6$ in acetonitrile. The applied version of the Hammett equation, from [46], is given below. Sigma values from [47].

The styryl systems have a restricted geometry and a high degree of conjugation within the single π-system of the styryl-cyclopentadienyl ligand, *vide supra*. Thus, the effect of the para substituents working on the cyclopentadienyl ring through conjugation is believed to be larger in this system, than in the arylthio system. Therefore, a more direct mechanism of communication between the arylthio substituent and the iron core of ferrocene must be operating.

The ferrocene system is very compact, and sulphur is relatively large. The C-S-C bond angle in sulphides is around 103°, which in turn imply that the sulphur lone-pairs take up a large space. Thus, the better communication between the *para* groups in the arylthio derivatives can be due to either a close contact of the aryl group and the iron orbitals or communication through an overlap of the sulphur lone-pairs and empty iron orbitals. The latter is most likely due to the strict steric demands of the former. This conclusion is also supported by the fact that direct substitution of ferrocene has less influence than substitution on the phenyl ring of phenyl-ferrocene. The direct electronic communication between the phenyl substituent and the iron atom must be larger than the effect of the smaller substituent, which must be transmitted through the cyclopentadienyl ligand.

and transition energy was found in the styryl system only. The oxidation potentials of the arylthio- and styryl-ferrocenes were determined in acetonitrile. A substituent effect on the oxidation potential was found for both arylthio- and styryl-ferrocenes. The effect is an order of magnitude larger in the arylthio systems as shown directly by the oxidation potentials and *via* a Hammett plot. This is explained by a mechanism of direct communication between the arylthio-substituent and the iron core of ferrocene involving the sulphur atom lone-pairs and the iron orbitals. The absorption properties and the electrochemistry of the two series do not appear to be correlated. The conclusion is that the absorption properties are governed by the electronic properties of ferrocene, where the frontier orbitals are affected by electronic perturbations in the cyclopentadienyl ligands. On the other hand the oxidation potential is less sensitive to changes in the cyclopentadienyl ligand. Hence, it must be concluded that another communication mechanism is operating. In this work a through space mechanism, working on the empty d-orbitals of ferrocene is found to be the most likely. The conclusion is supported by the large substituent effect observed in phenyl-ferrocenes [43] and in arylthio-ferrocenes.

4. Conclusions

Arylthio- and styryl-ferrocenes were synthesised with many different *para*-groups in the aryl rings. The absorption spectra were obtained, and an effect of the *para*-substituent on the ferrocene d-d transition intensity

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