Electrochemical and NMR spectroscopic studies of selenium- and tellurium-substituted ferrocenes I: ferrocenyl alkyl chalcogenides [Fe(η-C$_5$H$_5$)(η-C$_5$H$_4$ER)]

Mark R. Burgess, Christopher P. Morley *

Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea SA2 8PP, UK

Abstract

A series of 22 ferrocenyl alkyl selenides and tellurides has been prepared from the diferrocenyl dichalcogenides. The compounds have been characterised by mass spectrometry, multinuclear NMR spectroscopy, cyclic and differential pulse voltammetry. There is a close correlation between the ^{77}Se and ^{125}Te chemical shifts of analogous compounds, with $\delta(^{125}$Te$)/\delta(^{77}$Se$) = 1.60$. Other trends in the NMR data are also apparent. All the compounds studied undergo a one electron reversible oxidation at slightly more positive potentials than ferrocene itself. In addition, the tellurides exhibit a second quasi-reversible process at higher potentials, which appears to be chalcogen-based. There is no obvious correlation between the electrochemical results and the NMR spectroscopic data. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Selenium; Tellurium; Voltammetry; NMR spectroscopy

1. Introduction

Selenium- and tellurium-substituted ferrocenes have been of interest since the first practicable syntheses of diferrocenyl diselenide [1,2] and diferrocenyl ditelluride [2] were reported. Whilst the synthesis and reactivity of monosubstituted derivatives have been investigated previously [1–6], the reports of this work have included relatively little electrochemical and ^{77}Se/^{125}Te-NMR spectroscopic data, in stark contrast to the extensive electrochemical and spectroscopic studies of 1,2,3-trichalcogena[3]ferrocenophanes [7–9]. We have therefore performed a full-scale investigation into the electrochemistry of simple alkyl derivatives of general formula FcER, where Fc = ferrocenyl; R = alkyl; E = Se, Te. The synthesis of these two series of compounds should enable observation of any effect changes to the alkyl group have upon the electrochemistry of the ferrocenyl moiety and also reveal the effect upon the electrochemisty of changing the chalcogen atom. In addition, recording the ^{77}Se- or ^{125}Te-NMR spectrum of each compound has allowed us to study trends such as additivity and $\delta(^{77}$Se$)/\delta(^{125}$Te$)$ ratios, and to examine the possibility of there being a correlation between the electrochemical and NMR spectroscopic data.

2. Results and discussion

2.1. Synthesis and characterisation

Several straight chain ferrocenyl alkyl chalcogenides of formula FcER (E = Se, Te) were synthesised in excellent yield from the parent dichalcogenides using the reductive protocol of Nishibayashi et al. [3], as shown in (Eq. (1)), where R = Me, Et, ^{n}Pr, ^{n}Bu, ^{n}Pent, Hex, Oct. Three pairs of branched chain compounds (R = ^{i}Pr, ^{i}Bu, ^{i}Pent) were also synthesised by the same route, together with the benzyl derivatives FcECH$_2$Ph. Attempts to prepare the tertiary butyl derivatives FcEBu^t were, however, unsuccessful, with the only chalcogen-containing product isolated being the reformed dichalcogenide. The compounds were characterised by mass spectrometry, ^{1}H- and ^{13}C-NMR

* Corresponding author. Tel.: +44-1792-295273; fax: +44-1792-295747.

E-mail address: c.p.morley@swan.ac.uk (C.P. Morley).

spectroscopy, with a good match found between our results and literature data for FcEMe, FcE^{n}Bu [1,2,5,6] and FcTeCH$_2$Ph [3].

(1)
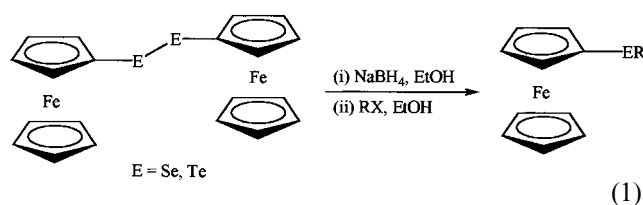
Each of the mass spectra of the new compounds contained prominent peak clusters due to the molecular ion and due to the fragments formed by sequential loss of the alkyl group and the chalcogen atom (see Table 1). The relative intensities of these three signals varied with the nature of both the chalcogen and the alkyl group, and with the ionisation technique employed. As expected, in general the molecular ion was more intense when fast atom bombardment (FAB) was used.

The ^{1}H-NMR spectra of the new compounds, summarised in Table 2, were generally unremarkable, with chemical shifts and coupling constants as expected. There is a number of small differences between the selenium derivatives and their tellurium analogues. In the spectra of the selenides the virtual triplet resonance for H-3 and H-4 has almost the same chemical shift as the resonance for the unsubstituted cyclopentadienyl ring. In the case of the tellurides, however, it is noticeably further downfield. Satellites associated with the peaks due to the group attached to the chalcogen atom are visible in the spectra of most of the tellurides, but only occasionally in the case of the selenides (see Table 3). The coupling constants $J(^1H-^{77}Se)$ are generally slightly less than half the corresponding value of $J(^1H-^{125}Te)$, as expected [10], and do not vary greatly with the nature of the alkyl group.

The ^{13}C-NMR spectra are summarised in Table 4. They are most notable for the 'heavy-atom effect', whereby the ^{13}C shifts of the carbon atoms bound to tellurium are shifted up to 35 ppm upfield of those in the analogous selenide [2]. This is observed in every case. Less dramatic changes are evident at the more distant carbon atoms when a selenium atom is replaced by tellurium. The resonances for the other carbon atoms in the substituted cyclopentadienyl ring are shifted downfield: C-3,4 by 1–2 ppm; C-2,5 by 4–5 ppm. As in the ^{1}H-NMR spectra, satellites were more frequently observed in the ^{13}C-NMR spectra of the tellurides. Unfortunately, the resonance for C-1 is particularly weak in the spectra of the selenides. As expected, however, in the telluride series the values of the coupling constant $^1J(^{13}C-^{125}Te)$ were significantly higher for this sp^2 carbon atom, than for coupling to the α-carbon of the alkyl chain. For example, in FcTe^{n}Pr the two values of $^1J(^{13}C-^{125}Te)$ are 307 and 152 Hz, respectively. Occasionally longer-range couplings were observed, but insufficient data are available for any trends to be discerned.

2.2. ^{77}Se/^{125}Te-NMR spectroscopy

The compounds were studied by ^{77}Se- or ^{125}Te-NMR spectroscopy as appropriate. The data obtained are summarised in Table 5. The relationship between

Table 1
Mass spectra of ferrocenyl alkyl chalcogenides, FcER

Compound	Method	RMM [a]	M$^+$ (%)	FcE$^+$ (%) [b]	FcH$^+$ (%) [c]
FcSeEt	EI	294	43	100	98
FcTeEt	EI	344	64	100	95
FcSe^{i}Pr	EI	308	47	71	100
FcTe^{i}Pr	FAB	358	77	47	100
FcSe^{n}Pr	FAB	308	100	26	37
FcTe^{n}Pr	FAB	358	100	42	58
FcSe^{i}Bu	FAB	322	100	43	68
FcTe^{i}Bu	FAB	372	100	51	78
FcSe^{i}Pent	FAB	336	100	34	73
FcTe^{i}Pent	FAB	386	100	85	84
FcSe^{n}Pent	FAB	336	100	15	30
FcTe^{n}Pent	FAB	386	100	33	67
FcSeHex	EI	350	81	100	54
FcTeHex	FAB	400	67	74	100
FcSeOct	EI	378	64	100	74
FcTeOct	FAB	428	100	37	70
FcSeCH$_2$Ph	FAB	356	100	85	41

[a] Calculated using ^{1}H, ^{12}C, ^{56}Fe, and ^{80}Se or ^{130}Te; expected isotope distribution patterns were observed.
[b] E = Se: $m/e = 265$; E = Te: $m/e = 315$.
[c] $m/e = 186$.

Table 2
^{1}H-NMR data for ferrocenyl alkyl chalcogenides, FcER [a]

Compound	C_5H_5	C_5H_4 (H-3,4) [b]	C_5H_4 (H-2,5) [b]	–EC*H*	–ECC*H*	–ECCC*H*	–EC$_n$C*H*$_3$
FcSeCH$_2$CH$_3$	4.16	4.17	4.28	2.58 (q)			1.32 (t)
FcTeCH$_2$CH$_3$	4.16	4.20	4.36	2.58 (q)			1.56 (t)
FcSeCH(CH$_3$)$_2$	4.10	4.12	4.22	2.92 (sept)			1.21 (d)
FcTeCH(CH$_3$)$_2$	4.12	4.18	4.26	3.20 (sept)			1.42 (d)
FcSe(CH$_2$)$_2$CH$_3$	4.10	4.11	4.24	2.50 (t)	1.55 (m)		0.88 (t)
FcTe(CH$_2$)$_2$CH$_3$	4.08	4.13	4.28	2.52 (t)	1.66 (m)		0.86 (t)
FcSeCH$_2$CH(CH$_3$)$_2$	4.18	4.18	4.25	2.53 (d)	1.77 (m)		0.88 (d)
FcTeCH$_2$CH(CH$_3$)$_2$	4.08	4.13	4.28	2.53 (d)	1.72 (m)		0.88 (d)
FcSe(CH$_2$)$_2$CH(CH$_3$)$_2$	4.12	4.12	4.22	2.60 (t)	1.43 (m)	1.59 (m)	0.78 (d)
FcTe(CH$_2$)$_2$CH(CH$_3$)$_2$	4.09	4.14	4.22	2.54 (t)	1.42 (m)	1.42 (m)	0.76 (d)
FcSe(CH$_2$)$_4$CH$_3$	4.11	4.11	4.24	2.51 (t)	1.50 (m)	1.18 (m) [c]	0.79 (t)
FcTe(CH$_2$)$_4$CH$_3$	4.08	4.12	4.23	2.55 (t)	1.58 (m)	1.20 (m) [c]	0.78 (t)
FcSe(CH$_2$)$_5$CH$_3$	4.17	4.17	4.26	2.60 (t)	1.54 (m)	1.20 (m) [d]	0.81 (t)
FcTe(CH$_2$)$_5$CH$_3$	4.08	4.13	4.26	2.54 (t)	1.59 (m)	1.20 (m) [d]	0.80 (t)
FcSe(CH$_2$)$_7$CH$_3$	4.17	4.17	4.26	2.60 (t)	1.54 (m)	1.20 (m) [e]	0.81 (t)
FcTe(CH$_2$)$_7$CH$_3$	4.08	4.14	4.28	2.53 (t)	1.60 (m)	1.20 (m) [e]	0.79 (t)
FcSeCH$_2$C$_6$H$_5$	4.12	4.11	4.11	3.64 (s)	7.00 (m) [f]	7.12 (m) [g]	

[a] s = singlet; d = doublet; t = triplet; q = quartet; sept = septet; m = multiplet.
[b] A virtual triplet for every compound.
[c] –E(CH$_2$)$_2$(C*H*$_2$)$_2$CH$_3$.
[d] –E(CH$_2$)$_2$(C*H*$_2$)$_3$CH$_3$.
[e] –E(CH$_2$)$_2$(C*H*$_2$)$_5$CH$_3$.
[f] *m*-C*H*.
[g] *o*-, *p*-C*H*.

$\delta(^{125}\text{Te})$ and $\delta(^{77}\text{Se})$ for analogous compounds is illustrated in Fig. 1, where a linear correlation was found for all members of the series except the ferrocenyl benzyl chalcogenides (where $\delta(^{125}\text{Te})/\delta(^{77}\text{Se}) = 1.74$). The gradient of the line gives a representative value for $\delta(^{125}\text{Te})/\delta(^{77}\text{Se})$, which was found to be 1.60, very much in accordance with what may have been expected based upon both previous theoretical calculations [10] of $\delta(^{125}\text{Te})/\delta(^{77}\text{Se})$, and also upon previous empirical investigations of the $\delta(^{125}\text{Te})/\delta(^{77}\text{Se})$ ratio. Indeed, the value of $\delta(^{125}\text{Te})/\delta(^{77}\text{Se})$ obtained for the ferrocenyl alkyl chalcogenides is actually closer to the theoretical value of between 1.5 and 1.6 than was obtained in previous empirical studies, where it was found to be 1.71 in the case of phenyl alkyl by O'Brien et al. [11], and 1.8 by McFarlane and McFarlane, who investigated a relatively broad range of chalcogen-containing compounds [12]. This 'normal' relationship between $\delta(^{125}\text{Te})$ and $\delta(^{77}\text{Se})$ for the ferrocenyl alkyl chalcogenides is in sharp contrast to the anomalous $\delta(^{125}\text{Te})/\delta(^{77}\text{Se})$ behaviour of the diferrocenyl dichalcogenides, diferrocenyl chalcogenides (vide infra) [13] and diphenyl dichalcogenides [14,15].

A number of authors have noted that the ^{77}Se or ^{125}Te chemical shifts of unsymmetrical chalcogenides may successfully be predicted by averaging the chemical shifts of the two symmetrical derivatives [10]. The chemical shifts predicted for the tellurides FcER on this basis, using data from the literature [11,12,16–18], are listed in Table 6. As can be seen, a good match exists

between the calculated and observed shifts for these compounds. However, when the process is repeated for the selenides the results are much further away from the observed data. This may be explained by the fact that the chemical shifts of the diferrocenyl chalcogenides are unusual in that they do not show the same $\delta(^{125}\text{Te}) = \delta(^{77}\text{Se}) \times 1.60$ relationship that is exhibited by the ferrocenyl alkyl chalcogenides [13]: the chemical shift for diferrocenyl selenide (275 ppm) appears to be anomalous. Based on the chemical shift of diferrocenyl telluride (350 ppm), the chemical shift of diferrocenyl selenide would be expected to be around 220 ppm. When this hypothetical figure is used to predict the ^{77}Se chemical shifts of the ferrocenyl alkyl selenides the match between observed and calculated values is considerably improved, as can be seen in Table 7.

Table 3
Chalcogen coupling in the ^{1}H-NMR spectra of ferrocenyl alkyl chalcogenides

Compound	E = Se: $^2J(^1\text{H}–^{77}\text{Se})$, Hz	E = Te: $^2J(^1\text{H}–^{125}\text{Te})$, Hz
FcEMe		22
FcEEt		37
FcE^{n}Pr	28	44
FcE^{i}Bu	23	29
FcE^{i}Pent		36
FcE^{n}Pent	21	44
FcEHex		43
FcEOct		42

Table 4
^{13}C-NMR data for ferrocenyl alkyl chalcogenides, FcER

Compound	C_5H_5	C_5H_4 (C-3,4)	C_5H_4 (C-2,5)	C_5H_4 (C-1)	–EC	–ECC	–ECCC	–ECCCC		–EC$_n$CH$_3$
FcSeCH$_2$CH$_3$	69.3	69.5	75.3	70.2	23.0					15.9
FcTeCH$_2$CH$_3$	69.2	71.1	79.4	43.0	0.7					17.5
FcSeCH(CH$_3$)$_2$	69.2	69.8	76.2	69.1	33.7					24.3
FcTeCH(CH$_3$)$_2$	69.2	71.3	80.0	43.6	15.2					26.7
FcSe(CH$_2$)$_2$CH$_3$	69.3	69.5	75.2	70.6	31.9	23.8				14.3
FcTe(CH$_2$)$_2$CH$_3$	69.2	71.0	79.3	43.3	11.5	25.5				16.5
FcSeCH$_2$CH(CH$_3$)$_2$	69.3	69.4	75.0	72.5	40.0	29.1				22.5
FcTeCH$_2$CH(CH$_3$)$_2$	69.3	70.9	79.2	43.7	21.3	29.9				23.8
FcSe(CH$_2$)$_2$CH(CH$_3$)$_2$	69.3	69.5	75.1	70.7	39.6	27.8	28.1			22.7
FcTe(CH$_2$)$_2$CH(CH$_3$)$_2$	69.2	71.0	79.2	43.8	6.1	41.1	30.0			22.0
FcSe(CH$_2$)$_4$CH$_3$	69.3	69.5	75.2	70.7	31.9	30.2	29.9	22.2		14.0
FcTe(CH$_2$)$_4$CH$_3$	69.2	71.0	79.2	43.4	9.1	34.0	31.6	22.0		14.0
FcSe(CH$_2$)$_5$CH$_3$	69.3	69.5	75.1	Not observed	31.3	30.5	29.9	29.4, 20.4		14.1
FcTe(CH$_2$)$_5$CH$_3$	69.2	71.0	79.2	43.4	9.2	32.0	31.6	31.5, 22.6		14.1
FcSe(CH$_2$)$_7$CH$_3$	69.3	69.5	75.2	Not observed	31.8	30.5	29.9	29.7, 29.2, 29.2, 22.6		14.1
FcTe(CH$_2$)$_7$CH$_3$	69.3	71.0	79.3	43.4	9.1	31.9	31.8	29.7, 29.2, 28.9, 22.7		14.1
FcSeCH$_2$C$_6$H$_5$	69.2	69.8	7.5	70.5	33.5	139.7	128.9 (*o*-)	128.5 (*m*-), 126.6 (*p*-)		

In both series of chalcogenides the chemical shifts of the higher members are identical. Substitution beyond the γ-carbon has a negligible effect. This phenomenon has been noted before for both selenides and tellurides [10]. The effect at the α-carbon of replacing a hydrogen by a methyl group can be seen in the series FcEMe, FcEEt, FcE^{i}Pr, where a deshielding of 160–190 ppm per methyl group is seen in the case of the tellurides and of 100–120 ppm in the case of the selenides. Similar values were observed in the series MeTeMe, MeTeEt, MeTe^{i}Pr [12] and MeSeMe, MeSeEt, EtSeEt [16].

Another point of interest is that in the spectra of the selenides there is a correlation between the ^{13}C chemical shifts of the cyclopentadienyl ring carbon attached to the selenium atom and the ^{77}Se chemical shifts, in that the compound with the most upfield ^{77}Se chemical shift (103 ppm), FcSeMe, has the most downfield ^{13}C peak, at 74.4 ppm. This is true for the entire series through to FcSe^{i}Pr, which has a ^{77}Se chemical shift of 321 ppm and a ^{13}C chemical shift of 69.1 ppm. This type of effect has been noticed once before in selenium-containing molecules by Wong et al. [19–21], in the course of their studies of selenoketones. No such correlation is seen in the data for the tellurides, where the ^{13}C-NMR chemical shifts of the *ipso*-carbon are nearly identical irrespective of substituent.

2.3. Electrochemistry

$E_{1/2}$ values from cyclic voltammetry and E_p values from differential pulse voltammetry are shown in Table 8. Cyclic voltammograms for FcE^{n}Pr are shown in Fig. 2 (E = Se) and Fig. 3 (E = Te). Each of the cyclic voltammograms of the ferrocenyl alkyl selenides showed a generally well-defined single electron wave that was reversible in nature, although the peak separations were generally somewhat greater than the 59 mV expected theoretically. Ferrocenyl $n$butyl selenide is the only ferrocenyl alkyl selenide to have been studied previously by cyclic voltammetry [1], and the behaviour observed then is generally in accordance with the results shown here. The value of $E_{1/2}$ relative to ferrocene was not reported, but it may be noted that the difference in $E_{1/2}$ between (FcSe)$_2$ and FcSe^{n}Bu was 125 mV, whereas the same $\Delta E_{1/2}$ calculation based on our results yields a value of 80 mV.

The $E_{1/2}$ and E_p values for the selenides are all positive, indicating as expected that oxidation of these compounds is slightly more difficult than that of ferrocene itself. There is no obvious correlation between

Table 5
^{77}Se and ^{125}Te chemical shifts of ferrocenyl alkyl chalcogenides, FcER

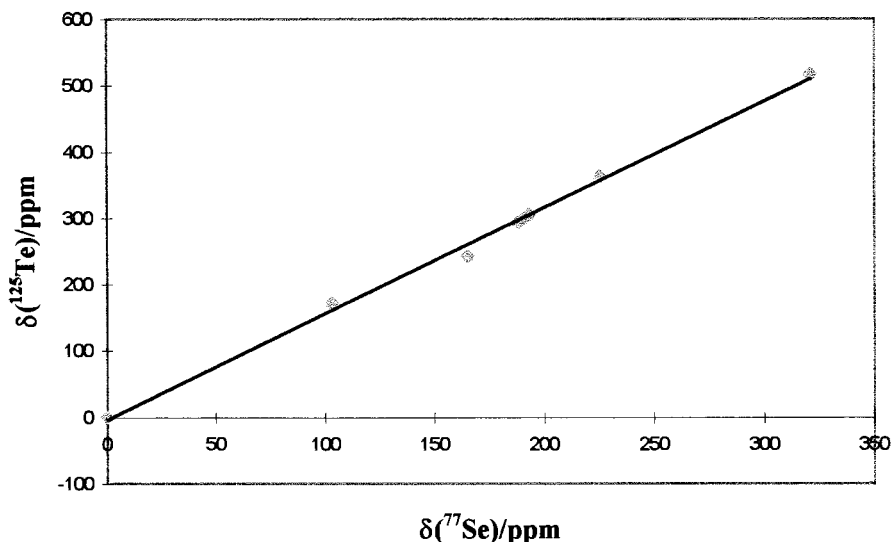| R	E = Se: $\delta(^{77}Se)$, ppm	E = Te: $\delta(^{125}Te)$, ppm
Methyl	103	172
Ethyl	225	363
iso-Propyl	321	517
Propyl	188	294
iso-Butyl	165	242
Butyl	191	300
iso-Pentyl	193	305
Pentyl	191	300
Hexyl	191	300
Octyl	191	300
Benzyl	287	500

Fig. 1. $\delta(^{77}Se)$ versus $\delta(^{125}Te)$ for ferrocenyl alkyl selenides.

the length of the alkyl chain and the $E_{1/2}$ and E_p values, which are all broadly similar. In their investigations of the electrochemistry of the chalcogena[3]ferrocenophanes, Ushijima et al. [7,8] noted that while they could not establish a correlation between the ^{77}Se-NMR spectroscopy data and the half-wave potentials, the compound with the higher oxidation potential gave an NMR signal for the ring-bound selenium atom at lower field. Analysis of the ^{77}Se-NMR spectroscopy data for the ferrocenyl alkyl chalcogenides shows that this trend is not repeated here over the very narrow range of values observed.

Ushijima et al. previously established [7,8] a linear relationship between the chemical shift of the *ipso*-carbon of the substituted cyclopentadienyl rings in the trichalcogena[3]ferrocenophanes and the $E_{1/2}$ values, a relationship that involved five of the six compounds studied. While the two most downfield shifts of the *ipso*-carbons are observed in the spectra of FcSeMe and FcSe^{i}Bu, which are in fact associated with the lowest $E_{1/2}$ and E_p values, there is clearly no correlation beyond that for data from either of the electrochemical techniques employed. This observation applies in the same way to the ^{77}Se-NMR spectra, where the same two compounds have the most upfield ^{77}Se shifts. Analysis of the chemical shifts of the alkyl carbon attached to selenium again shows that there is no correlation with the electrochemical data.

Considering the electrochemical data obtained for the ferrocenyl alkyl tellurides, each cyclic voltammogram showed two well-defined waves, the first of which was reversible, whilst the second was quasi-reversible in nature. This is in stark contrast with the selenides that showed a single reversible wave. Similarly, the DPV data showed two peaks, as opposed to the one observed for the analogous selenides.

The first wave can be easily assigned to the redox process at the iron centre of the ferrocene, analogous to the wave observed in the ferrocenyl selenides, since it is reversible. The $E_{1/2}$ values of this wave, shown together with the corresponding E_p values in Table 8, are broadly similar to those obtained for the ferrocenyl alkyl selenides. It is thus apparent that altering the chalcogen from selenium to tellurium has no significant effect upon the electrochemistry of the iron centre of the ferrocene moiety.

Table 6
Predicted and observed ^{125}Te chemical shifts of ferrocenyl alkyl tellurides

Compound	Prediction (ppm)	Observed (ppm)
FcTeMe	175	172
FcTeEt	353, 371 [a]	363
FcTe^{i}Pr	513	517
FcTe^{n}Pr	282	294
FcTe^{i}Bu	232	242
FcTe^{n}Bu	289	300
FcTeCH$_2$Ph		500

[a] Two different values of $\delta(TeEt_2)$ have been reported.

Table 7
Predicted and observed ^{77}Se chemical shifts of ferrocenyl alkyl selenides

Compound	Prediction (ppm)	Observed (ppm)	Hypothetical (ppm)
FcSeMe	137	103	109
FcSeEt	246, 255 [a]	225	218, 227 [a]
FcSe^{i}Pr	353, 355 [a]	321	325, 327 [a]
FcSe^{n}Bu	221	191	192
FcSeCH$_2$Ph	304	287	277

[a] Two different values of each of $\delta(SeEt_2)$ and $\delta(Se^iPr_2)$ have been reported.

Table 8
Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) results for ferrocenyl alkyl chalcogenides, FcER [a]

E =	Se		Te (E_1)		Te (E_2)	
R =	CV, $E_{1/2}$	DPV, E_p	CV, $E_{1/2}$	DPV, E_p	CV, $E_{1/2}$	DPV, E_p
Me	25	25	35	30	385	350
Et	40	30	50	60	380	365
^{i}Pr	70	65	70	65	370	350
^{n}Pr	80	75	70	70	435	420
^{i}Bu	20	30	45	45	325	330
^{n}Bu	50	45	55	65	420	405
^{i}Pent	35	30	45	30	340	325
^{n}Pent	75	70	55		320	
Hex	60		45	30	350	315
Oct	35	40	50	40	330	275
CH$_2$Ph	65	70				

[a] Relative to FcH (mV); values to ± 5 mV.
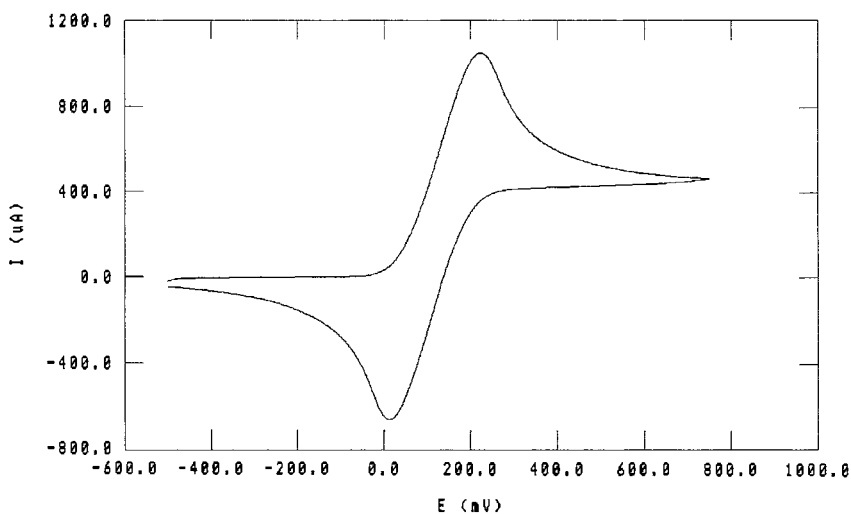
Fig. 2. Cyclic voltammogram of ferrocenyl *n*propyl selenide.
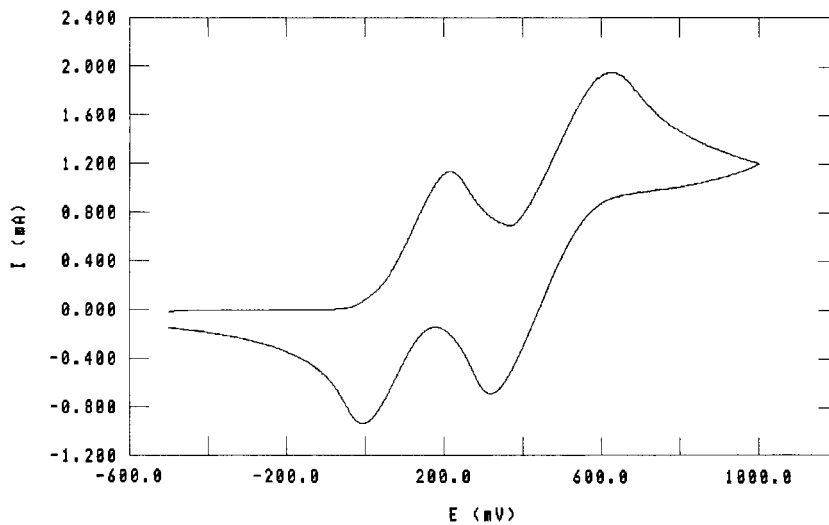
Fig. 3. Cyclic voltammogram of ferrocenyl *n*propyl telluride.

However, while the effect upon the iron centre may be minimal, there is still a major difference in the electrochemistry of the two analogous series, due to the presence of the second wave in the cyclic voltammograms of the ferrocenyl alkyl tellurides. This wave is highly likely to be due to the chalcogen acting as a redox centre, rather than the iron, given the potential at which the process occurs. Considering that the second wave was not initially observed in the case of the selenides, it was deemed prudent to run cyclic voltammograms of the ferrocenyl alkyl selenides over a much greater range in order to attempt to observe a similar effect occurring at an increased potential. The results of these additional experiments revealed that there was indeed a second feature in the cyclic voltammograms of the selenides. This feature, which was not particularly well defined, occurred at around 1.3–1.5 V, and was chemically irreversible, since there was no corresponding reduction down as far as -2.0 V. These observations fit the idea of the additional features being due to the chalcogen acting as a redox centre, with the selenium atom being more difficult to oxidise than the tellurium atom.

Good agreement is seen between the results obtained here and the reports by Singh et al. [5] of the cyclic voltammograms of FcTeMe, FcTe(p-C_6H_4OMe) and FcTeC$_6$H$_5$. Here, two single well-defined one electron waves were also observed. Singh et al. labelled the second wave as being reversible, but with larger peak separations than is theoretically allowed for a single reversible one electron process. With peak separations of the order of 300 mV, we prefer to consider the process quasi-reversible. This is not, however a major discrepancy since reversibility is a matter of degree and can disappear with increased scan rate.

Singh et al. also analysed the electrochemistry of the analogous 1,1′-disubstituted ferrocenyl telluride derivatives. These disubstituted derivatives each produced a single one electron wave which was quasi-reversible in nature, which demonstrated increased redox potential, and which it is reasonable to assume is associated with the iron centre. No second wave was observed. Although no comment on this difference was made at the time, this is a very interesting result, since there is no obvious reason for the second wave not to appear in the cyclic voltammograms of the disubstituted derivatives, the functional groups should be relatively independent of each other given their positions in the molecule.

Establishing correlations between NMR spectroscopic data and electrochemical data is as difficult with the tellurides as with the selenides, although it is noticeable that the *iso*-propyl derivative, which gives the most downfield peak in the ^{125}Te-NMR spectra, has the highest $E_{1/2}$ value. This is interesting when placed next to the fact that the two selenide derivatives with the

most upfield ^{77}Se resonances produced the lowest $E_{1/2}$ values, suggesting that there could indeed be a correlation between ^{77}Se/^{125}Te-NMR spectroscopy and the electrochemical behaviour at the iron centre, but that the precision of the electrochemical measurements is generally less than the variation related to the chemical shift. It may also be significant that one of the smallest values of $E_{1/2}$ for both E = Se and E = Te is for R = Me.

In a subsequent paper we will report the results of similar studies of compounds containing two ferrocene units: viz. diferrocenyl chalcogenides, diferrocenyl dichalcogenides and bis(ferrocenylchalcogeno)alkanes [13].

3. Experimental

All reactions were performed using standard Schlenk techniques and pre-dried solvents under an atmosphere of dinitrogen. ^{1}H(400.1 MHz)- and ^{13}C(100.6 MHz)-NMR spectra: Bruker AC400; tetramethylsilane as internal standard. ^{77}Se(47.7 MHz)- and ^{125}Te(78.9 MHz)-NMR spectra: Bruker WM250; dimethyl selenide or dimethyl telluride as external standard; solutions contained ca. 100 mg of analyte in ca. 0.5 cm^3 CDCl$_3$. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using electron impact (EI) or fast atom bombardment (FAB). Cyclic and differential pulse voltammetry: EG & G model 273 scanning potentiostat; Pt working and auxiliary electrodes; Ag│Ag$^+$ (0.1 M AgNO$_3$ in CH$_3$CN) as reference elec-

Table 9
Reagents used and yields obtained in the syntheses of ferrocenyl alkyl chalcogenides

Compound	Alkyl halide	Yield (%)
FcSeMe	Iodomethane	93
FcTeMe	Iodomethane	90
FcSeEt	Iodoethane	98
FcTeEt	Iodoethane	100
FcSe^{i}Pr	2-Bromopropane	92
FcTe^{i}Pr	2-Bromopropane	97
FcSe^{n}Pr	1-Iodopropane	
FcTe^{n}Pr	1-Iodopropane	97
FcSe^{i}Bu	1-Bromo-2-methylpropane	91
FcTe^{i}Bu	1-Bromo-2-methylpropane	99
FcSe^{n}Bu	1-Bromobutane	89
FcTe^{n}Bu	1-Bromobutane	91
FcSe^{i}Pent	1-Bromo-3-methylbutane	92
FcTe^{i}Pent	1-Bromo-3-methylbutane	91
FcSe^{n}Pent	1-Iodopentane	87
FcTe^{n}Pent	1-Iodopentane	89
FcSeHex	1-Bromohexane	
FcTeHex	1-Bromohexane	
FcSeOct	1-Bromooctane	93
FcTeOct	1-Bromooctane	91

trode; 0.1 M [NBu$_4$][ClO$_4$] in CH$_3$CN as supporting electrolyte; scan rates 100 mV s^{-1} (CV), 36 mV s^{-1} (DPV); under these conditions [Fe(C$_5$H$_5$)$_2$] | [Fe(C$_5$H$_5$)$_2$]$^+$ has $E_{1/2} = +0.035$ V, $E_p = +0.025$ V versus Ag | Ag$^+$. [Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$E)]$_2$ (E = Se, Te) were prepared from [Fe(η^5-C$_5$H$_5$)$_2$] via lithiation in THF with 0.9 equivalents of Li^{t}Bu, treatment with excess selenium or tellurium, and air oxidation, in a minor modification of a literature procedure [2,22].

The ferrocenyl alkyl chalcogenides were prepared using the reduction protocol of Nishibayashi et al. [3], as illustrated by the synthesis of FcSeEt which follows. The reagents used and the yields obtained are summarised in Table 9.

Diferrocenyl diselenide (0.19 g, 0.36 mmol) was dissolved in EtOH (100 cm^3) and an excess of NaBH$_4$ (0.07 g, 1.85 mmol) added. A distinct lightening of the solution was immediately observed, which was accompanied by bubbling, presumably of liberated H$_2$. After stirring at room temperature (r.t.) for 1 h, ethyl iodide (0.12 g, 0.77 mmol) was added to the mixture, where upon it became noticeably darker. The solution was left to stir for a further 3 h, and the solvent then removed by evaporation under reduced pressure. Extraction overnight into hexane was followed by filtration in air. A sticky orange–yellow solid, FcSeEt, which was air stable, was obtained from the filtrate after removal of the solvent by evaporation under reduced pressure. Yield: 0.21 g, 98%.

Mass spectral, ^{1}H- and ^{13}C-NMR data for the new compounds prepared are summarised in Tables 1–4. The ^{1}H- and ^{13}C-NMR spectra of the known compounds FcSeMe, FcTeMe, FcSe^{n}Bu, FcTe^{n}Bu, FcTeCH$_2$Ph corresponded to the data found in the literature [1–3,5,6]. The ^{13}C-NMR shift of the CH$_3$ group in FcTeMe, not previously observed, was found to be -0.2 ppm ($^2J(^1$H–^{125}Te$) = 22$ Hz).

The ^{77}Se- and ^{125}Te-NMR data and electrochemical results for all the compounds are listed in Tables 5 and 8, respectively.

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