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Synthesis, structures and some chemical and electrochemical properties of *E*-1,2-diferrocenyl-3-methylthioprop-2-enone and its ketals

Tatiana Klimova Berestneva [a,*], Marcos Martínez García [b], Luis Ortiz-Frade [a], Simon Hernández Ortega [b], Ruben A. Toscano [b], Elena Klimova [a]

[a] *Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Coyoacán, C.P. 04510, México D.F., Mexico*
[b] *Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Coyoacán, C.P. 04510, México D.F., Mexico*

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Abstract

2,3-Diferrocenyl-1-methylthiocyclopropenylium iodide reacts with water, metal alkoxides, phenolates and with alcohols in the presence of Et_3N to give *E*-1,2-diferrocenyl-3-methylthioprop-2-enone or its ketals. Their structures were established based on data from ^1H and ^{13}C NMR spectroscopy and X-ray diffraction analysis. The mechanistic aspects of these reactions are discussed. Electrochemical properties of **8** and **13b** have been studied. The compounds present two oxidation processes (**I**–**II**), attributed to the oxidations of the ferrocenes groups, $E^{0'}$(**I**), $E^{0'}$(**II**), $\Delta E^{0'}$(**II**–**I**) and comproportionation constant K_{com} are reported.

Keywords: Ferrocene; Diferrocenyl(methylthio)cyclopropenilium; 3,3-Dimethylthio-cyclopropene; 1,2-Diferrocenyl-3-methylthioprop-2-enone; Three-membered ring opening

1. Introduction

It is well known, that one of the basic reactions of carbocations is the cation–anion combination reaction [1,2]. Thus, the reactions of cyclopropenylium cation (**1a**) with various carbon nucleophiles (RMgX, RLi, R_2Cd) result in high yields (~70–95%) of the corresponding 3,3-disubstituted cyclopropenes (**2a**) and (**2b**) [2–4] (Scheme 1).

At the same time, the Grignard reaction of 1-methylthio-substituted cyclopropenylium cation (**1b**) involves the attack of the anionic reagents at the carbon atom bearing the phenyl group to give 1-methylthiocycloprop-1-ene derivatives (**2c**) [5–7], which afford metylthio-substituted indene derivatives (**3**) in good yields upon thermolysis (Scheme 2).

Diferrocenylcyclopropenylium cations with heterosubstituents in the small ring have recently been described [8–10]. These include 1-ethoxy-, 1-diethylamino-, 1-morpholino-, 1-piperidino-2,3-diferrocenylcyclopropenylium tetrafluoroborates (**4a-d**) and 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide (**4e**). Their chemical properties are being currently investigated. Thus, it was established that the tetrafluoroborate (**4a**) reacts with organolithium compounds to yield 3,3-dialkyl-1,2-diferrocenylcyclopropenes (**5a**,**b**) [8] (Scheme 3).

Analogous compounds (**5a**,**c–e**) are obtained in low yields (~10–20%) in reactions of the iodide (**4e**) with RLi and RMgX, the major products being diferrocenyl-substituted (methylthio)polyenes (**6a**,**c–e**) (~60–70%) [10] (Scheme 4).

Thus, the nucleophilic attacks of the anionic reagents on 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide (**4e**) are directed at both C-1 and C-2 centers of the three-carbon ring, which allows the use of di(ferrocenyl)alkylthiocyclopropenyl cations as the starting material for the preparation of different classes of diferrocenyl-containing

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[*] Corresponding author. Tel./fax: +52 55 56225371.
E-mail address: klimova@servidor.unam.mx (T.K. Berestneva).

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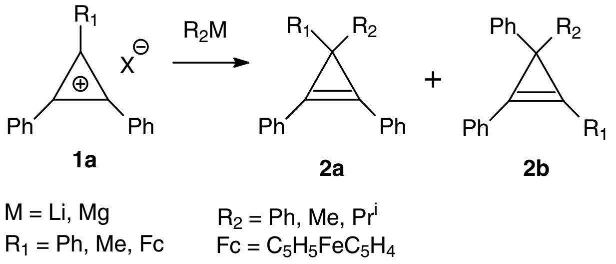
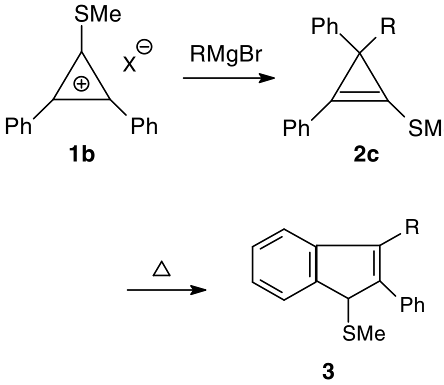
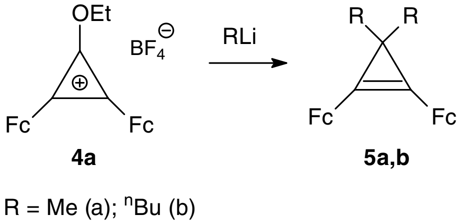


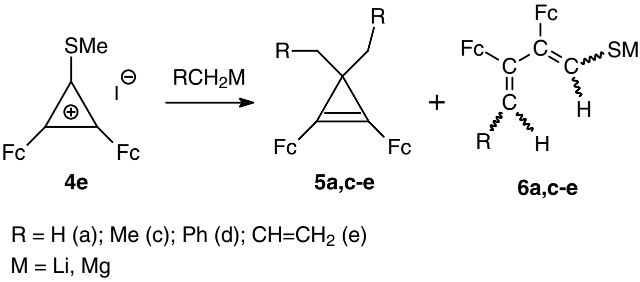
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

compounds both with retention of the alkylthio-substituents and devoid of them.

In the present work, we studied the reactions of 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide (**4e**) with water, metal alkoxides and aryloxides, and alcohols and investigated some chemical and electrochemical properties of the reaction products.

2. Results and discussion

2,3-Diferrocenyl-1-methylthiocyclopropenylium iodide **4e** was prepared [10] starting from 2,3-diferrocenylcyclopropenone according to Scheme 5.

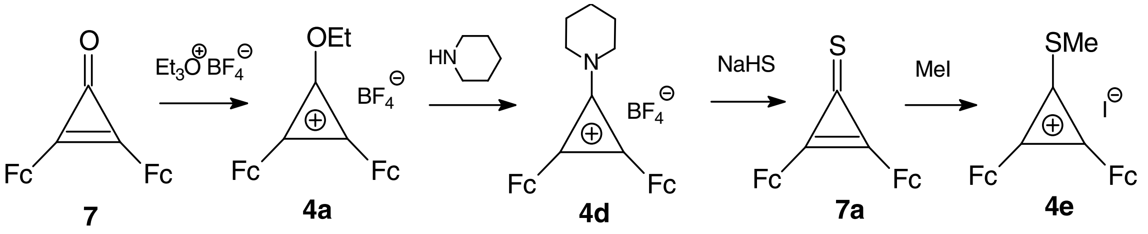
This is sedimented as a red-violet precipitate upon treatment of a solution of cyclopropenethione (**7a**) in benzene with methyl iodide, its ^{1}H and ^{13}C NMR spectroscopic characteristics are given in the Experimental section. The iodide **4e** is stable when stored in a dry inert atmosphere. In a contact with water or moist solvents this is transformed into 2,3-diferrocenylcyclopropenone **7**, 1,2-diferrocenyl-3-methylthioprop-2-enone (**8**) as a single geometric isomer, presumably with *E*-configuration, 2,3-diferrocenyl-1,1-dimethylthiocyclopropene (**9**) and 1,2-diferrocenyl-1,1,3-trimethylthio-2-propene (**10**) (Scheme 6).

The structure of this enone **8** was established based on the data from ^{1}H and ^{13}C NMR spectra and X-ray diffraction analysis. Thus, the ^{1}H NMR spectrum contained signals for two ferrocenyl substituents, a signal for the methyl group, and one signal for the olefinic proton. The presence in the ^{13}C NMR spectrum of compound **8** of signals for one methyl group, two ferrocenyl fragments, one CH= and C=O groups, and two C_{ipso}Fc carbon atoms corroborates completely the suggested structure. X-ray diffraction analysis of a single crystal of compound **8** obtained by crystallization from CH_2Cl_2 allowed elucidation of its spatial structure. The general view of the molecule **8** is shown in Fig. 1a and the crystal packing is shown in Fig. 1b. Selected bond lengths and bond angles are given in the legends to these figures.

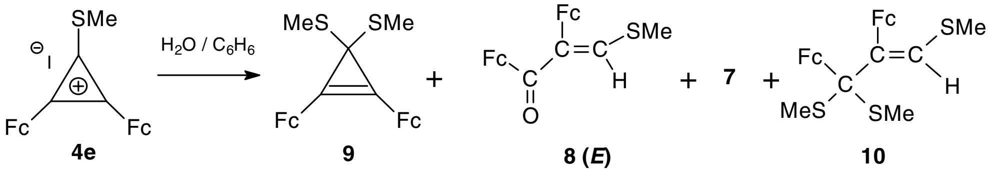
A tentative mechanism of this transformation is outlined in Scheme 7. The nucleophilic attack by water on the C-1 and C-2 atoms of the three-membered ring results in an unstable intermediate addition products, viz., 2,3-diferrocenyl-1-hydroxy-1-methylthio- and 2,3-diferrocenyl-3-hydroxy-1-methylthiocyclopropenes **A** and **B**, respectively. Intramolecular transformation of **A** affords diferrocenylcyclopropenone **7** and methanethiol, intramolecular transformation of **B** occurs with opening of the small ring into a carbenoid intermediate **C** and results in the final enone **8**. The methanethiol molecule as a nucleophile attack on the carbon atoms C-1 and C-2 of the iodide **4e** results in the dimethylthiocyclopropene **9** and dithioketal **10** (Scheme 7).

We also found that diferrocenylpropenone **8** also formed upon reaction of the iodide **4e** with metal alkoxides derived from alcohols containing a β hydrogen atom. The alkoxides tested comprised potassium *tert*-butoxide, sodium ethoxide, lithium 1-ferrocenylethoxide, and lithium 1-ferrocenylisobutoxide (Scheme 8 and 9).

In all cases, compound **8** was isolated in high yields (∼75–90%). In addition to the enone **8**, each reaction afforded the corresponding olefins (**11a**–**d**). The evolution of gaseous isobutylene **11a** and ethylene **11b** (Scheme 8) was proved by identification of the respective dibromides, which were obtained upon passing the evolving gases through bromine water. Vinylferrocene **11c** and isopropenylferrocene



Scheme 5.



Scheme 6.

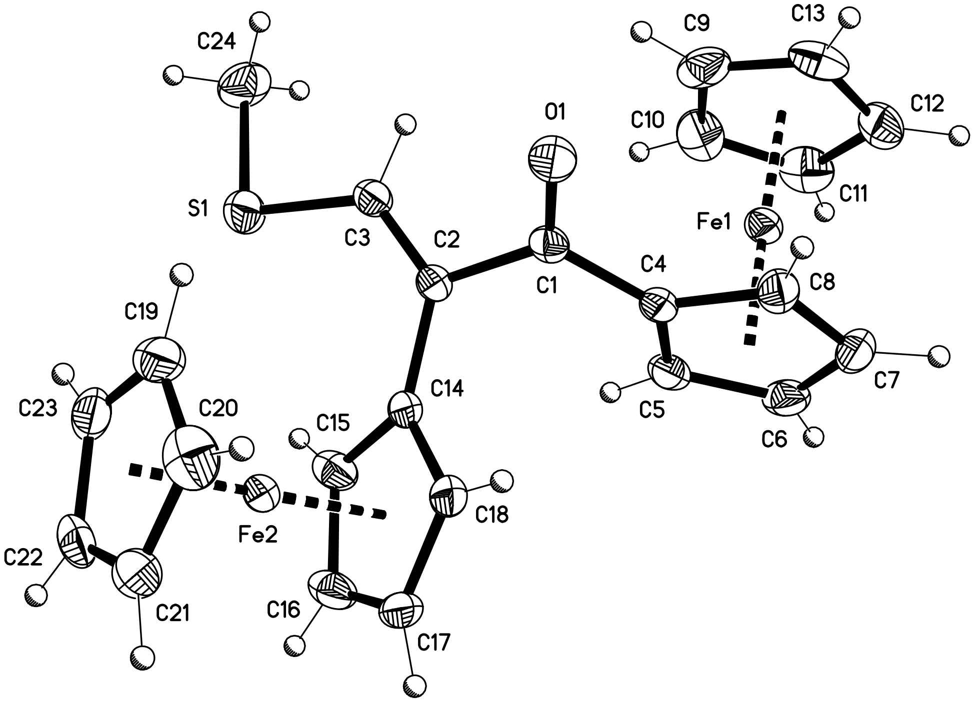


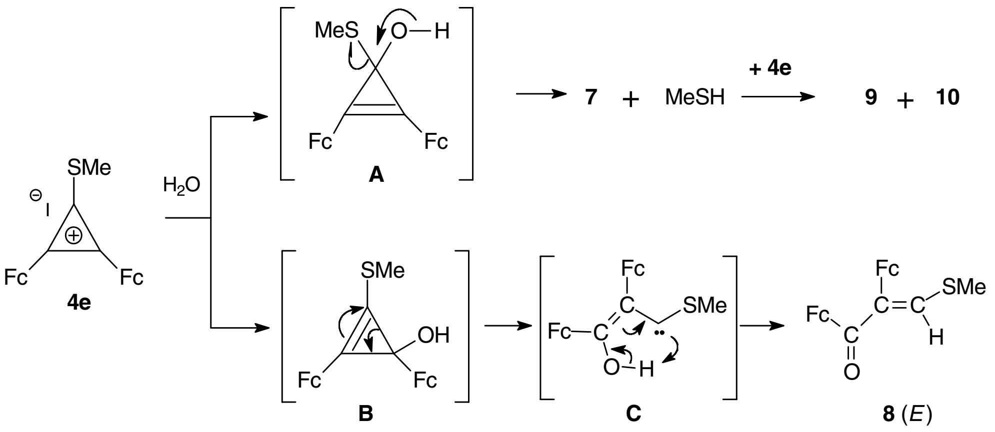
Fig. 1. Molecular structure of **8**. Selected bond lengths (Å): C(1)–C(4) = 1.472(2), C(1)–O(1) = 1.217(2), C(1)–C(2) = 1.497(2), C(2)–C(3) = 1.340(2), C(3)–S(1) = 1.7288(18), S(1)–C(24) = 1.789(2), C(2)–C(14) = 1.472(2), C(4)–C(5) = 1.427(3), C(14)–C(15) = 1.423(3). Selected bond angles (°): C(4)–C(1)–C(2) = 117.39(16), C(1)–C(2)–C(3) = 115.17(15), C(2)–C(3)–S(1) = 127.11(14), C(3)–S(1)–C(24) = 100.44(10), O(1)–C(1)–C(2) = 121.19(17), O(1)–C(1)–C(4) = 121.39(17), C(1)–C(2)–C(14) = 117.06(15); C(1)–C(4)–C(5) = 127.42(17).

11d were isolated in individual states by chromatography, their m.p.'s and ^{1}H NMR spectroscopic characteristics coincided with the literature data [11,12].

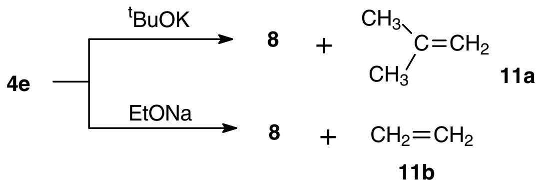
A tentative mechanism of the reaction of the salt **4e** with metal alkoxides (Scheme 10) should include intramolecular transformations of carbene-like intermediates (**12a–d**) (Scheme 10).

Metal alkoxides derived from alcohols devoid of β hydrogen atoms react with the iodide **4e** only in the presence of the corresponding alcohols. Thus, sodium methoxide and sodium benzyloxide form ketals (**13a**) and (**13b**), respectively (Scheme 11).

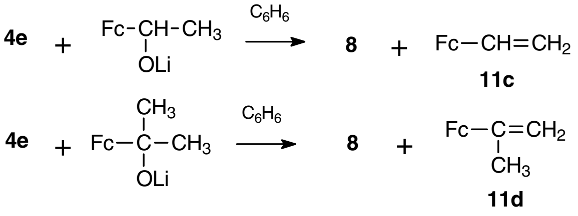
The structures of the ketals **13a** and **13b** were established based on the data from ^{1}H and ^{13}C NMR spectroscopy, and X-ray analysis (for **13b**). The ^{1}H MMR spectrum of compound **13a** contained two singlets for the protons of three methyl groups in a ratio 1:2, one singlet for the olefinic proton and signals for the protons of the ferrocenyl substituents. There were one singlet for the methyl group, one singlet for the protons of two methylene groups and



Scheme 7.



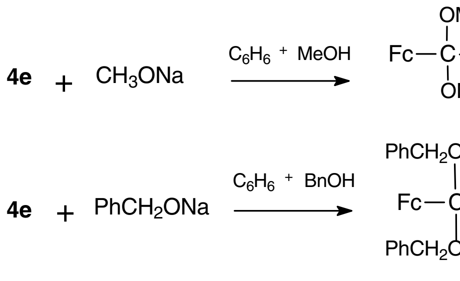
Scheme 8.



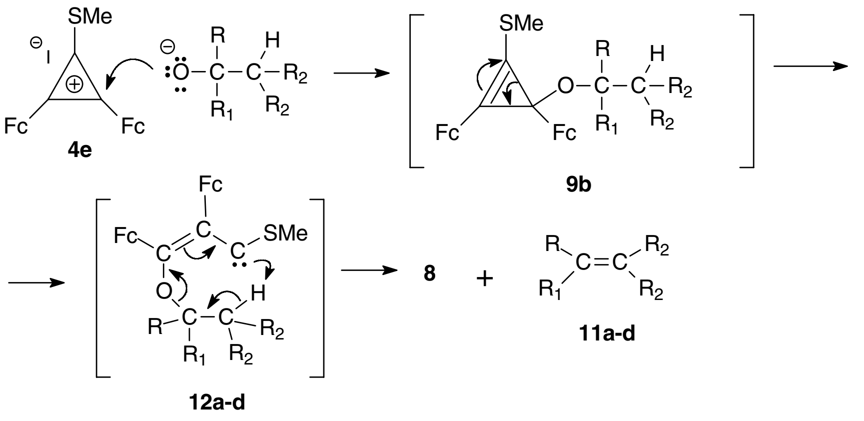
Scheme 9.

signals for the protons of two ferrocenyl and two phenyl substituents in the ^{1}H NMR spectrum of the ketal **13b**. ^{13}C NMR spectra of the ketals **13a** and **13b** corroborate completely their structures.

NMR spectroscopic data suggested that these ketals represented single geometric isomers. The results of X-ray diffraction analysis of a single crystal of compound **13b** obtained by crystallization from chloroform show that the double bond in this ketal has *E* configuration. Presumably, this holds for compound **13a** as well. The general view of the molecule **13b** is shown in Fig. 2a and the crystal packing is shown in Fig. 2b. Selected bond lengths and bond angles are given in the legends to these figures.



Scheme 11.



R= R_1 = CH_3, R_2 = H (a); R = R_1 = R_2 = H (b); R= R_2 = H, R_1 = Fc (c); R= H, R_1 = Fc, R_2 = CH_3 (d)

Scheme 10.

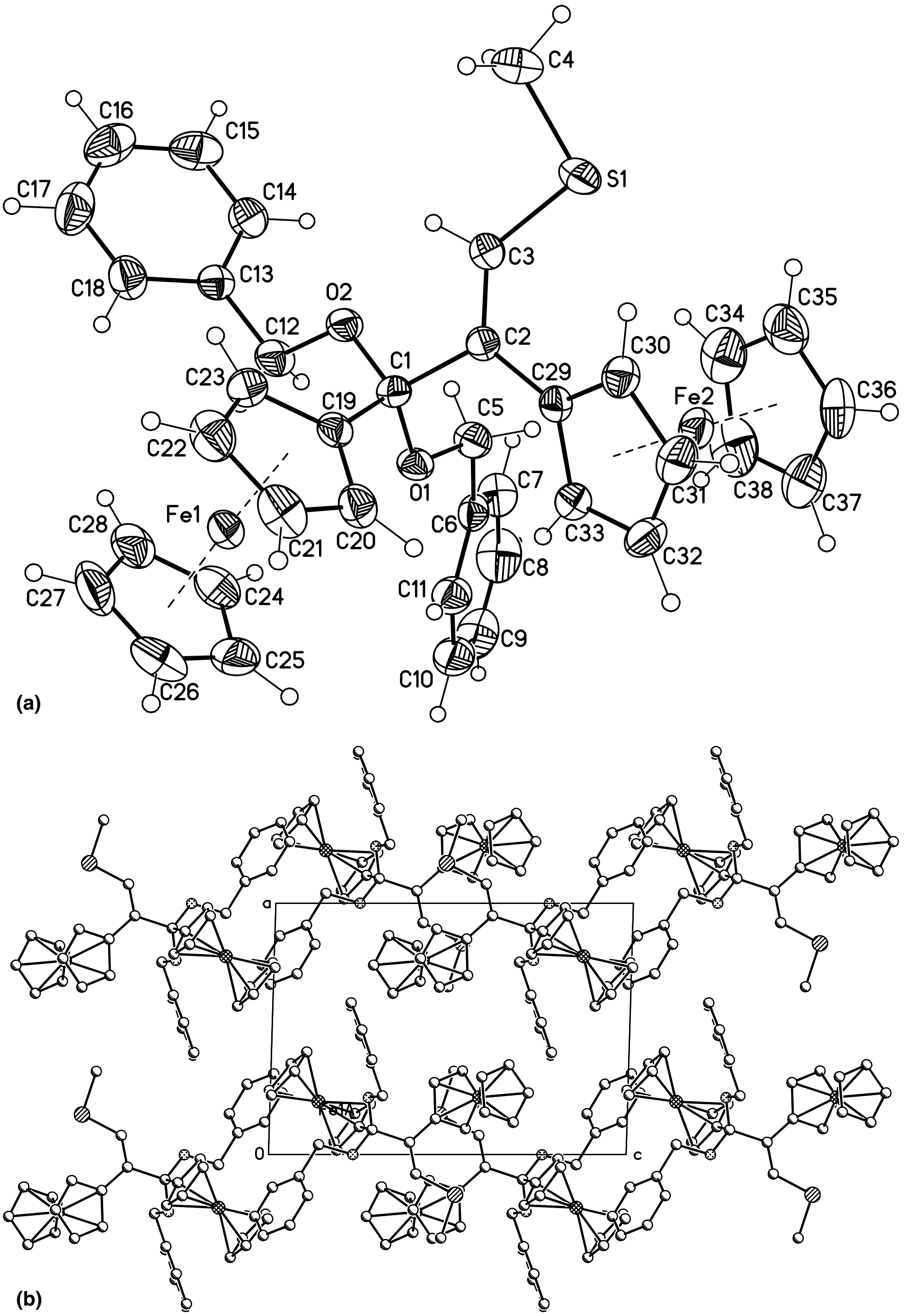


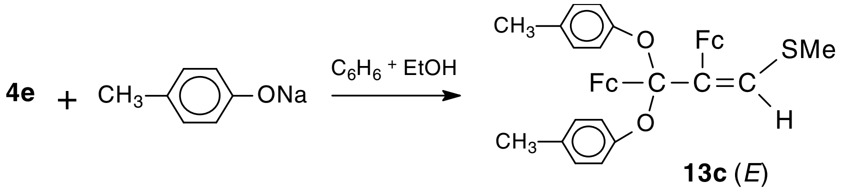
Fig. 2. (a) Molecular structure of **13b**. Selected bond lengths (Å): C(1)–O(1) = 1.414(2), C(1)–O(2) = 1.419(2), O(1)–C(5) = 1.427(2), C(12)–O(2) = 1.440(2), C(1)–C(2) = 1.544(3), C(2)–C(29) = 1.485(3), C(2)–C(3) = 1.331(3), S(1)–C(3) = 1.739(2), S(1)–C(4) = 1.791(2). Selected bond angles (°): C(4)–S(1)–C(3) = 99.94(11), S(1)–C(3)–C(2) = 128.13(17), C(3)–C(2)–C(1) = 117.87(17), C(2)–C(1)–O(2) = 106.79(15), C(2)–C(1)–O(1) = 112.25(15), C(1)–O(1)–C(5) = 114.29(14), C(1)–O(2)–C(12) = 116.07(14). (b) Crystal packing of **13b**.

The reactions of the iodide **4e** with metal phenolates occur analogously. Thus, sodium *p*-cresolate opens the three-membered ring to give compound **13c** (Scheme 12).

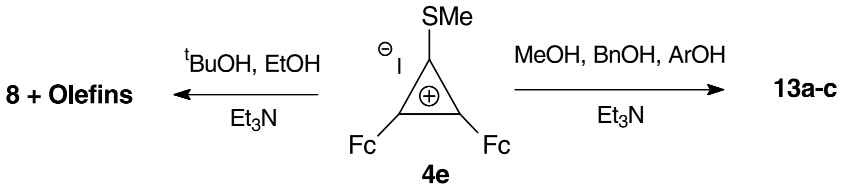
It was found further that di(ferrocenyl)methylthiocyclopropenylium iodide **4e** reacted with various alcohols in the presence of triethylamine (Scheme 13).

In these cases, the reactions seem to follow the mechanisms involving intermolecular transformations of carbene-like intermediates (**14a–c**) and (**12a–d**) (Scheme 14).

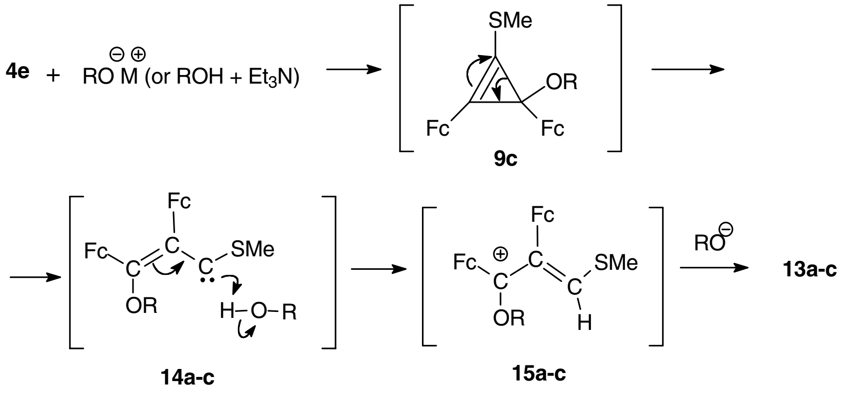
Compounds **8** and **13a–c** were found to react with hydrazine hydrate on heating to yield 3,4-diferrocenylpyrazole (**15**) (Scheme 15).



Scheme 12.

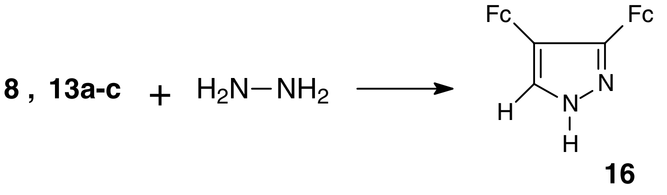


Scheme 13.



R = Me (a); R = Bn (b); R = p-$CH_3C_6H_4$ (c)

Scheme 14.



Scheme 15.

Its structure was established based on the data from elemental analysis and ^1H and ^{13}C NMR spectroscopy.

Thus, di(ferrocenyl)methylthiocyclopropenylium iodide reacts with O-nucleophiles in a stereospecific manner to give the three-membered ring-opening products, viz., propenone and its ketals, with trisubstituted *E* olefinic fragments.

3. Electrochemistry

The electrochemical behaviour of compounds **8** and **13b** was investigated by cyclic voltammetry. In all experiments, a 1.0×10^{-3} mol dm^{-3} solution of each compound in supporting electrolyte (0.1 M $TBABF_4$ in acetonitrile) was used. Fig. 3 shows a typical voltammogram of compound **8** obtained in a platinum electrode. When the potential scan was initiated in the positive direction, two oxidation signals ($\mathbf{I}_a$ and $\mathbf{II}_a$) were observed, and when the potential scan was reversed $E_{+\lambda}$ two reduction signals ($\mathbf{I}_c$ and $\mathbf{II}_c$) were detected. On the other hand, when the potential scan was started in the negative direction, the same behaviour is presented. The independence of the oxidation signals ($\mathbf{I}_a$ and $\mathbf{II}_a$) was established by modifying the switching potentials ($E_{+\lambda}$). Each oxidation signal has, respectively, a corresponding reduction signal ($\mathbf{I}_c$ and $\mathbf{II}_c$).

The anodic peak potential value $E_{pa}(\mathbf{I})$ obtained for signal $\mathbf{I}_a$ was 0.049 V/Fc–Fc$^+$, and the corresponding cathodic peak potential value $E_{pc}(\mathbf{I})$ for signal $\mathbf{I}_c$ was −0.010 V/Fc–Fc$^+$; a reversible electrochemical behaviour is presented. The ΔE_p was 0.059 V and independent of scan rate (0.1–1 V s^{-1}), the cathodic peak current was proportional to $v^{1/2}$, indicating that process **I** is a diffusion-controlled process [13].

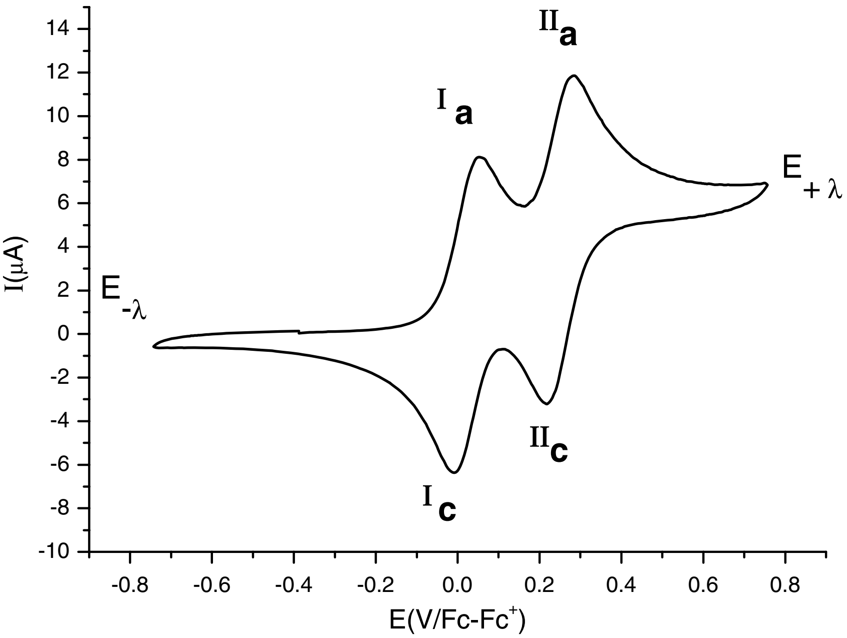


Fig. 3. Cyclic voltammograms for a solution 1.0×10^{-3} mol dm^{-3} of compound **8** in the presence of 0.1 M TBABF$_4$ in acetonitrile. The scan potential was initiated from E_{ocp} to positive direction. Scan rate 0.1 V s^{-1}. The working electrode used was platinum.

The anodic and cathodic peak potential values for signals **II**$_a$ and **II**$_c$ E_{pa}(**II**) and E_{pc}(**II**) are 0.277 and 0.215 V/Fc–Fc$^+$, respectively. The ΔE_p was also independent of scan rate (0.1–1 V s^{-1}), and the cathodic peak current was proportional to $v^{1/2}$. Process **I** and **II** are attributed for a two consecutives one-electron transfer. A similar behaviour was reported for diferrocenyl compounds [14–16].

The formal electrode potential was evaluated with the half sum of the anodic and cathodic peak potentials, $E^{0'} = (E_{pa} + E_{pc})$, for the electrochemical processes **I** and **II**. The values obtained were $E^{0'}$ (**I**) = 0.019 V/Fc–Fc$^+$ and $E^{0'}$(**II**) = 0.246 V/Fc–Fc$^+$, $\Delta E^{0'}$ (**II**–**I**) = 0.227 V. The value of comproportionation constant K_{com} evaluated according to the literature for a EE mechanism [13–16] was 7038.

The electrochemical behaviour for compounds **13b** is very similar to that observed for **8**, though there are slight changes in the values of peak potentials. The formal electrode potential of processes **I** and **II**, were $E^{0'}$(**I**) = 0.007 V/Fc–Fc$^+$ and $E^{0'}$(**II**) = 0.237 V/Fc–Fc$^+$. The values of $\Delta E^{0'}$(**II**–**I**) and comproportionation constant K_{com} were 0.230 V and 70912, respectively.

The similar values of ΔE^0 (**II**–**I**) and K_{com} for compounds **8** and **13b** can be attributed for the same stability of the mixed valence state Fc–Fc$^+$ in both compounds [17]. The values of K_{com} suggests that the electronic charge is slightly delocalized in the mixed valence compound generated electrochemically, according to the Robin-Day classification (class II) [16,17].

4. Conclusion

Thus, the results of this study support our previous conclusion [10] that, depending on whether the nucleophile attacks at the C-1 or C-2 positions of **4e**, the initially formed intermediates **A** and **B** (Scheme 7) usually from products that retain the original tree-membered ring or undergo C—C bond cleavage to give ring-opened products. Note that obtained products (the main process) that retain the methylthio-substituent dominate in the reaction products. This behavior of diferrocenyl(methylthio)cyclopropenylium **4e** is substantially different to that of its ethoxy analog **4a** [9].

5. Experimental

All the solvents were dried according to the standard procedures and were freshly distilled before use. IR spectra of compound **8** was obtained for samples as KBr pellets on a Specord IR-75 instrument. UV spectra of compound **8** was recorded on a Specord UV–Vis spectrophotometer. The mass spectrum of compounds **8**, **13a-c**, **15** were obtained on a Varian-MAT CH-6 instrument (EI, 70 eV). The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CDCl$_3$ and CD$_2$Cl$_2$ with Me$_4$Si as the internal standard. Chemical shifts are given in ppm and J values in Hz. An Elemental Analysis System GmbH was used for elemental analyses. Columns chromatography was carried out on alumina (Brockmann activity III).

The unit cell parameters and the X-ray diffraction intensities were recorded on a Bruker Smart Apex CCD area detector/ω diffractometer. The crystallographic data, the experimental conditions, and corrections are given in Table 1. The structures of compounds **8** and **13b** were solved by direct method (SHELXS) and refined using full-matrix least-squares on F^2.

Table 1
Crystal data and structure refinement parameters for compounds **8** and **13b**

Data	**8**	**13b**
Molecular formula	$C_{24}H_{22}Fe_2OS$	$C_{38}H_{36}Fe_2O_2S$
Formula weight (g mol^{-1})	470.18	668.43
Temperature (K)	293(2)	291(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.6252(4)	10.5927(6)
b (Å)	10.6547(6)	11.1169(6)
c (Å)	12.9373(7)	14.0025(8)
α (°)	85.724(1)	85.042(1)
β (°)	74.659(1)	86.678(1)
γ (°)	79.913(1)	68.941(1)
V ($Å^3$)	997.52(9)	1532.4(2)
Z	2	2
D_{calc} (Mg mm^{-3})	1.565	1.449
Absorption coefficient (mm^{-1})	1.571	1.049
$F(000)$	484	696
Radiation, λ(Mo Kα) (Å)	0.71073	0.71073
Monochromator	Graphite	Graphite
θ range (°)	1.94–25.01	1.97–25.00
Reflections collected	13850	12710
Reflections independent	7053	5411
R_{int}	0.0385	0.0314
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.0718$	$R_1 = 0.0318$, $wR_2 = 0.0641$
R indices (all data)	$R_1 = 0.0725$, $wR_2 = 0.0768$	$R_1 = 0.0424$, $wR_2 = 0.0665$
Refinable parameters	254	389
Goodness-of-fit	1.009	0.895
Refinement method	Full-matrix-least-squares on F^2	Full-matrix-least-squares on F^2
Minimum/maximum residual electron density (e $Å^{-3}$)	−0.366/0.716	−0.207/0.321

The following reagents were purchased from Aldrich: ferrocene, 98%; aluminum chloride, 99.99%; tetrachlorocyclopropene, 98%; triethyloxonium tetrafluoroborate, 1.0 M solution in dichloromethane; piperidine, 99%; potassium *tert*-butoxide, 95%; sodium ethoxide, 96%; sodium methoxide, 95%; sodium benzyloxide, 1.0 M solution in benzyl alcohol; *p*-cresol, 99%; iodomethane, 99.5%; sodium hydrosulfide hydrate $NaHS \cdot xH_2O$.

All electrochemical measurements were performed in acetonitrile (HPLC grade) solution containing 0.1 M tetra-*N*-butylammonium tetrafluoroborate ($TBABF_4$) as supporting electrolyte. A potentiostat/galvanostat EG&G PAR model 263 controlled by a PC software was used. A typical three-electrode array was employed for all electrochemical measurements: platinum disk as working electrode, platinum wire as counter-electrode, and a pseudo reference electrode of silver wire immersed in an acetonitrile solution with 0.1 M tetra-*N*-butylammonium chloride (TBACl). All solutions were bubbled with nitrogen prior to each measurement. All voltammograms were initiated from open circuit potential (E_{ocp}) and the scan potential was obtained in both positive and negative directions. All potentials were reported versus the couple Fc–Fc^+ according to IUPAC convention [18]. The formal electrode potential for (Fc–Fc^+) redox pair, determined by voltamperometric studies, was 0.743 V versus Ag|AgCl (MeCN).

Lithium 1-ferrocenylethoxide and lithium 2-ferrocenylisopropoxide were prepared by treating solutions of 1-ferrocenylethanol and 2-ferrocenylpropanol, respectively, in benzene with equivalent amounts of *n*-bytyllithium. 2,3-Diferrocenylcyclopropenone was obtained from the ferrocene and tetrachlorocyclopropene in the presence of $AlCl_3$ according to the standard procedure [19,20]. Ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate **4a** was obtained from the 2,3-diferrocenylcyclopropenone **7** in the presence of triethyloxonium tetrafluoroborate (1.0 M solution in dichloromethane) [8].

*5.1. Diferrocenyl(piperidino)cyclopropenylium tetrafluoroborate (**4b**)*

Piperidine (4.0 ml) was added dropwise to a solution of salt **4a** (0.54 g, 1 mmol) in dichloromethane (50 ml) and the mixture was stirred for 2 h at 20 °C in an inert atmosphere. Then dry ethanol (100 ml) was added, the mixture was stirred for 30 min, concentrated in vacuo to 30 ml, and left overnight at 20 °C. Then dry ethanol (100 ml) was added, the mixture was stirred for 30 min, concentrated in vacuo to 30 ml, and left overnight at 20 °C. The precipitate that formed was filtered off, washed with dry ethanol, and dried in a vacuum desiccator **4b** that formed was filtered off, washed with dry ethanol, and dried in a vacuum desiccator, yield 77%, red-violet crystals, m.p. 204–205 °C (lit. [8]: 204–205 °C). ^1H NMR: (CD_2Cl_2): δ 1.76 (2H, m, CH_2), 2.75 (2H, m, CH_2), 2.95–3.41 (4H, m, $2CH_2$), 3.64 (2H, m, CH_2), 4. 26 (10H, s, $2C_5H_5$), 4.31 (2H, m, C_5H_4), 4.49 (2H, m, C_5H_4), 4.69 (2H, m, C_5H_4), 4.87 (2H, m, C_5H_4). ^{13}C NMR (CD_2Cl_2): δ 30.87, 43.58, 48.93 ($5CH_2$), 60.31

(2C$_{ipso}$Fc), 70.72 (2C$_5$H$_5$), 71.68, 74.20 (2C$_5$H$_4$), 130.19 (2C), 138.89 (C–N). Anal. Calc. for $C_{28}H_{28}BF_4Fe_2N$: C, 58.28; H, 4.89; F, 13.17; Fe, 19.36; N, 2.43. Found: C, 58.44; H, 4.68; F, 13.29, Fe 19.18; N, 2.59%. MS *m*/*z* (%): 577 (89), 491 (100).

5.2. 2,3-Diferrocenylcyclopropenethione (7*a*)

A solution of $NaHS \cdot xH_2O$ (1.0 g) in water (10 ml) was added to a stirred suspension of salts **4b** (5 mmol) in ethanol (100 ml) at 20 °C and stirred for 6 h. The precipitate that formed was filtered off, washed with water, and dried in air. The yield of the title compound was ~2.0 g (91%), dark red fine crystals, m.p. 208–209 °C. Following purification by chromatography on alumina (hexane–dichloromethane, 5:1), thione **7a** had m.p. 209–210 °C. ^{1}H NMR (CDCl$_3$): δ 4.27 (10H, s, 2C$_5$H$_5$), 4.69 (4H, m, C$_5$H$_4$), 4.98 (4H, m, C$_5$H$_4$). ^{13}C NMR (CDCl$_3$): δ 63.25 (2C$_{ipso}$Fc), 70.14 (2C$_5$H$_5$), 71.29, 72.95 (2C$_5$H$_4$), 152.66 (2C), 171.15(C=S). Anal. Calc. for $C_{23}H_{18}Fe_2S$: C, 63.05; H, 4.14; Fe, 25.49. Found: C, 62.83; H, 4.19; Fe, 25.57%. MS: *m*/*z* 438 [M]$^+$.

5.3. Diferrocenyl(methylthio)cyclopropenylium iodide (4*e*)

Methyl iodide (0.5 ml) was added dropwise to a solution of cyclopropenethione **7a** (0.88 g, 2.0 mmol) in dry benzene (50 ml) and the mixture was stirred in an inert dry atmosphere for 3 h. The red-violet precipitate of the salt **4e** was filtered off, washed with benzene, and dried in a vacuum-dessicator. The yield of the iodide **4e** was 0.93 g (80%), m.p. 248–250 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.25 (3H, s, CH$_3$), 4.49 (10H, s, 2C$_5$H$_5$), 5.09 (8H, m, 2C$_5$H$_4$). ^{13}C NMR (CD$_2$Cl$_2$): δ 21.26 (CH$_3$), 58.79 (2C$_{ipso}$Fc), 72.26 (2C$_5$H$_5$), 74.32, 77.50 (2C$_5$H$_4$), 151.27 (2C), 152.30(C–S). Anal. Calc. for $C_{24}H_{21}Fe_2IS$: C, 49.69; H, 3.65; Fe, 19.24; I, 21.88%. Found: C, 49.48; H, 3.71; Fe, 19.17; I 21.97%.

5.4. Reactions of salt (4*e*) with water

Salt **4e** (0.58 g, 1.0 mmol) was refluxed in a mixture of water (0.5 ml) and benzene (50 ml) for 2 h. The solvent was evaporated in vacuo and the residue was chromatographed on alumina (hexane–diethyl ether, 4:1) to afford 0.025 g (5%) of the 2,3-diferrocenyl-1,1-dimethylthiocyclopropene (**9**), orange crystals, m.p. 136–137 °C. MS: *m*/*z* 500 [M]$^+$. Anal. Calc. for $C_{25}H_{24}Fe_2S_2$: C, 60.03; H, 4.84; Fe, 22.33; S, 12.80. Found: C, 59.88; H, 4.82; Fe, 22.47; S, 12.89%. δ_H (300 MHz, CDCl$_3$): 2.31 (6H, s, 2CH$_3$), 4.29 (10H, s, 2C$_5$H$_5$), 4.43 (4H, m, C$_5$H$_4$), 4.55 (4H, m, C$_5$H$_4$); 0.29 g (61%) of the 3-methylthio-1,2-diferrocenylpropenone (**8**), red-brown crystals, mp 157–159 °C. ν_{max} (KBr)/cm^{-1}: 473, 486, 522, 742, 756, 822, 846, 1002, 1027, 1043, 1104, 1219, 1270, 1371, 1442, 1565, 1638, 1720, 1859, 2925, 3026, 3079; λ_{max} (CHCl$_3$, 20°)/nm: 207, 251, 298, 449, 455. ^{1}H NMR (CDCl$_3$): δ 2.50 (3H, s, CH$_3$), 4.18 (5H, s, C$_5$H$_5$), 4.19 (5H, s, C$_5$H$_5$), 4.27 (2H, m, C$_5$H$_4$), 4.48 (2H, m, C$_5$H$_4$), 4.68 (2H, m, C$_5$H$_4$), 4.73 (2H, m, C$_5$H$_4$), 7.05 (1H, s, CH=).^{13}C NMR (CDCl$_3$): δ 18.86 (CH$_3$), 69.38, 70.10 (2C$_5$H$_5$), 68.33, 68.80, 71.34, 71.84 (2C$_5$H$_4$), 79. 25, 80.06 (2C$_{ipso}$Fc), 135.16 (CH=), 135.59 (C), 197.57(C=O). Anal. Calc. for $C_{24}H_{22}Fe_2OS$: C, 61.30; H, 4.72; Fe, 23.75; S, 6.83. Found: C, 59.88; H, 4.82; Fe, 22.47; S, 12.89%. MS: *m*/*z* 500 [M]$^+$. 0.063 g (15%) of the diferrocenylcyclopropenone (**7**), m.p. 182–183 °C (lit. [19]: m.p. 182–183 °C) and 0.033 g (6%) of the 1,2-diferrocenyl-1,1,3-trimethylthio-2-propene (**10**), red-brown powder, m.p. 193–194 °C. ^{1}H NMR (CDCl$_3$): δ 2.60 (6H, s, 2CH$_3$), 2.77 (3H, s, CH$_3$), 4.08 (5H, s, C$_5$H$_5$), 14.10 (5H, s, C$_5$H$_5$), 4.03 (2H, m, C$_5$H$_4$), 4.14 (2H, m, C$_5$H$_4$), 4.28 (2H, m, C$_5$H$_4$), 4.39 (2H, m, C$_5$H$_4$), 6.31 (1H, s, CH=). Anal. Calc. for $C_{26}H_{28}Fe_2S_3$: C, 56.96; H, 5.15; Fe, 20.38; S, 17.51. Found: C, 57.09; H, 5.21; Fe, 20.42; S, 17.40%. MS: *m*/*z* 548 [M]$^+$.

5.5. Reactions of salt (4*e*) with potassium tert-butoxide

Salt **4e** (0.58 g, 1.0 mmol) was refluxed in a mixture of potassium *tert*-butoxide (0.34 g, 3.0 mmol) and benzene (50 ml) for 3 h. The solvent was evaporated in vacuo and the residue was chromatographed on alumina (hexane–diethyl ether, 4:1) to afford 0.39 g (82%) of the 3-methylthio-1,2-diferrocenylpropenone (**8**), red crystals, m.p. 157–159 °C. MS: *m*/*z* 470 [M]$^+$.

5.6. Reactions of salt (4*e*) with sodium ethoxide

Salt **4e** (0.58 g, 1.0 mmol) was refluxed in a mixture of sodium ethoxide (0.2 g, 3.0 mmol) and benzene (50 ml) for 3 h. The solvent was evaporated in vacuo and the residue was chromatographed on alumina (hexane–diethyl ether, 4:1) to afford 0.37 g (79%) of the 3-methylthio-1,2-diferrocenylpropenone (**8**), red-brown crystals, m.p. 158–159 °C. MS: *m*/*z* 470 [M]$^+$.

5.7. Reactions of salt (4*e*) with lithium ferrocenylethoxide

This was carried out analogously using salt **4e** (1.16 g, 2.0 mmol), lithium ferrocenylethoxide (0.6 g, 2.5 mmol) and benzene (50 ml). The reaction mixture was worked up as described above, subsequent chromatography on Al$_2$O$_3$ (hexane–diethyl ether, 6:1) gave vinylferrocene (**11c**), yield 0.29 g (72%), and 3-methylthio-1,2-diferrocenylpropenone (**8**), yield 0.75 g (80%).

Compound **11c**, yield 0.29 g (72%), orange crystals, m.p. 62 °C (lit. [14]: 62 °C). MS: *m*/*z* 212 [M]$^+$.

Compound **8**, yield 0.75 g (80%), red-brown powder, m.p. 158–159 °C. MS: *m*/*z* 470 [M]$^+$.

5.8. Reactions of salt (4*e*) with lithium ferrocenylisopropoxide

Analogous treatment of salt **4e** (1.16 g, 2.0 mmol) in dry benzene (50 ml) with lithium ferrocenylisopropoxide

(0.75 g, 3 mmol) afforded isopropenylferrocene **11d**, yield 0.34 g (75%), and 3-methylthio-1,2-diferrocenylpropenone (**8**), yield 0.79 g (83%).

Compound **11d**, yield 0.34 g (75%), orange crystals, m.p. 64–65 °C (lit. [14]: 64–66 °C). ^{1}H NMR ($CDCl_3$): δ 2.05 (3H, bs, CH_3), 4.18 (5H, s, C_5H_5), 4.21 (2H, m, C_5H_4), 4.38 (2H, m, C_5H_4), 4.82 (1H, bs, CH_2=), 5.12 (1H, bs, CH_2=). MS: *m*/*z* 226 $[M]^+$.

Compound **8**, yield 0.79 g (83%), red-brown crystals, m.p. 157–159 °C. MS: *m*/*z* 470 $[M]^+$.

5.9. 1,1-Dimethoxy-3-methylthio-1,2-diferrocenylpropene (**13a**)

Salt **4e** (0.58 g, 1.0 mmol) was refluxed in a mixture of sodium methoxide (0.22 g, 4.0 mmol), 2 ml methanol and benzene (50 ml) for 2 h. The solvent was evaporated in vacuo and the residue was chromatographed on alumina (hexane–diethyl ether, 5:1) to give compound **13a**, yield 0.42 g (80%), orange powder, m.p. 164–165 °C. ^{1}H NMR ($CDCl_3$): δ .47 (3H, s, CH_3), 3.25 (6H, s, $2CH_3$), 4.08 (5H, s, C_5H_5), 4.21 (5H, s, C_5H_5), 4.07 (2H, m, C_5H_4), 4.19 (2H, m, C_5H_4), 4.23 (2H, m, C_5H_4), 4.73 (2H, m, C_5H_4), 6.75 (1H, s, CH=). ^{13}C NMR ($CDCl_3$): δ 19.20 (SCH_3), 49.76 ($2OCH_3$), 69.08, 69.26 ($2C_5H_5$), 66.80, 67.36, 68.37, 69.61 ($2C_5H_4$), 82.11, 91.61 ($2C_{ipso}$Fc), 128.99 (CH=), 103.74, 131.33 (2C). Anal. Calc. for $C_{26}H_{28}Fe_2O_2S$: C, 60.49; H, 5.47; Fe 21.64. Found: C, 60.64; H, 5.38; Fe, 21.47%. MS: *m*/*z* 516 $[M]^+$.

5.10. 1,1-Dibenzyloxy-3-methylthio-1,2-diferrocenylpropene (**13b**)

This was carried out analogously using salt **4e** (0.58 g, 1.0 mmol), sodium benzyloxide (1.0 M solution in benzyl alcohol, 7.0 ml) and benzene (50 ml). The reaction mixture was worked up as described above, subsequent chromatography on Al_2O_3 (hexane–diethyl ether, 3:1) gave compound **13b**, yield 0.48 g (71%), as a orange crystals, m.p. 174–176 °C. ^{1}H NMR ($CDCl_3$): δ 2.33 (3H, s, CH_3), 4.12 (5H, s, C_5H_5), 4.18 (5H, s, C_5H_5), 4.10 (2H, m, C_5H_4), 4.19 (2H, m, C_5H_4), 4.35 (2H, m, C_5H_4), 4.82 (2H, m, C_5H_4), 4.67 (4H, bs, $2CH_2$), 6.86 (1H, s, CH=), 7.25–7.42 (10H, m, 2Ph). ^{13}C NMR ($CDCl_3$): δ 19.14 (SCH_3), 63.95 ($2CH_2$), 69.17, 69.28 ($2C_5H_5$), 66.99, 67.49, 68.39, 69.77 ($2C_5H_4$), 82.10, 91.70 ($2C_{ipso}$Fc), 129.04 (CH=), 104.23, 131.34 (2C), 126.91, 127.08, 128.33 (2Ph), 138.91 ($2C_{ipso}$). Anal. Calc. for $C_{38}H_{36}Fe_2O_2S$: C, 68.28; H, 5.43; Fe, 16.71. Found: C, 68.41; H, 5.32; Fe, 16.88%. MS: *m*/*z* 668 $[M]^+$.

5.11. Reactions of salt (**4e**) with sodium p-tolyloxide

A solution 0.33 g (3 mmol) *p*-cresol, 0.17 g (2.5 mmol) EtONa in benzene (70 ml) was added 0.58 g (1.0 mmol) of compound **4e**. The mixture was refluxed for 3 h and quenched by addition of water (100 ml). The organic layer was separated, washed with water (2 × 20 ml) and solvent was evaporated in vacuo. The residue was chromatographed on Al_2O_3 (hexane–diethyl ether, 2:1) to give 1,1-bis-*p*-tolyloxy-3-methylthio-1,2-diferrocenylpropene (**13c**), yield 0.45 g (67%), as a orange powder, m.p. 183–184 °C. ^{1}H NMR ($CDCl_3$): δ 2.24 (6H, s, $2CH_3$), 2.33 (3H, s, CH_3), 4.09 (5H, s, C_5H_5), 4.30 (5H, s, C_5H_5), 4.19 (1H, m, C_5H_4), 4.42 (1H, m, C_5H_4), 4.47 (1H, m, C_5H_4), 4.50 (1H, m, C_5H_4), 4.63 (2H, m, C_5H_4), 5.01 (2H, m, C_5H_4), 7.86 (1H, s, CH=), 6.79–7.17 (8H, m, 2Ar). Anal. Calc. for $C_{38}H_{36}Fe_2O_2S$: C, 68.28; H, 5.43; Fe 16.71. Found: C, 68.09; H, 5.51; Fe, 16.67%. MS: *m*/*z* 668 $[M]^+$.

5.12. Reactions of salt (**4e**) with 2-methyl-2-propanol, ethanol, 1-ferrocenylethanol, 2-ferrocenyl-2-propanol

Salt **4e** (0.58 g, 1.0 mmol) was refluxed in a mixture of 2-methyl-2-propanol (3.0 ml), triethylamine (5.0 ml) and benzene (50 ml) for 3 h. The solvent was evaporated in vacuo and the residue was chromatographed on alumina (hexane–diethyl ether, 4:1) to afford 0.38 g (81%) of the 3-methylthio-1,2-diferrocenylpropenone **8**, red crystals, m.p. 157–159 °C. MS: *m*/*z* 470 $[M]^+$.

Analogous treatment of salt **4e** (1.0 mmol) in dry benzene (50 ml) with ethanol, 1-ferrocenylethanol or 2-ferrocenyl-2-propanol afforded 3-methylthio-1,2-diferrocenylpropenone (**8**), yield 76–83% and olefins **11c** and **11d**.

Analogous treatment of salt **4e** (1.0 mmol) in dry benzene (50 ml) with methanol, benzyl alcohol or *p*-cresol afforded ketals **13a**–**c**, yield 66–72%.

5.13. 3,4-Diferrocenylpyrazole (**15**)

This was obtained according to the known procedure [21] by reactions of the compounds **8** and **13a**–**c**, respectively, with hydrazine hydrate in ethanol. The reaction product that precipitated was collected by filtration, washed with ethanol and dried in vacuo. The yield ranged from 62% to 71%, m.p. 238–239 °C, orange powder. ^{1}H NMR ($CDCl_3$): δ 4.09 (5H, s, C_5H_5), 4.14 (5H, s, C_5H_5), 4.21 (2H, m, C_5H_4), 4.31 (2H, m, C_5H_4), 4.39 (2H, m, C_5H_4), 4.53 (2H, m, C_5H_4), 6.40 (1H, bs, NH), 7.69 (1H, s, CH=). ^{13}C NMR ($CDCl_3$): δ 69.20, 69.30 ($2C_5H_5$), 67.68, 68.27, 68.49, 68.59 ($2C_5H_4$), 78.74, 78.40 ($2C_{ipso}$Fc), 116.52 (CH=), 139.20, 140.34 (2C). Anal. Calc. for $C_{23}H_{20}Fe_2N_2$: C, 63.34; H, 4.62; Fe, 25.62; N, 6.42. Found: C, 68.29; H, 4.70; Fe, 25.78; N, 6.31%. MS: *m*/*z* 436 $[M]^+$.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 292194 for compound **8** and CCDC No. 235195 for compound **13b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44 1223

336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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