

Synthesis of 1,2-diferrocenyl-3-(diacylmethylidene)cyclopropenes and 1,1-diacyl-2,3-diferrocenyl-4-methylsulfanylbuta-1,3-dienes, their structures and electrochemical properties

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Abstract

2,3-Diferrocenyl-1-morpholinocyclopropenylium tetrafluoroborate reacts with 1,3-diketones in the presence of triethylamine to give 3-diacylmethylidene-1,2-diferrocenylcyclopropenes (**8a–d**). Under similar conditions, 2,3-diferrocenyl-1-methylsulfanylcyclopropenylium iodide affords **8a–c** (~25–30%) and 1,1-diacyl-2,3-diferrocenyl-4-methylsulfanylbuta-1,3-dienes (**10a–c**) (~50–60%). The structures of the products obtained were established based on the data from ¹H (1D NOE) and ¹³C NMR spectra and X-ray diffraction analysis. Electrochemical properties of several (diacylmethylidene)diferrocenylcyclopropenes (**8a–c**) and 1,1-diacyl-2,3-diferrocenyl-4-methylsulfanylbuta-1,3-dienes (**10a–c**) are studied.

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1. Introduction

Diarylcyclopropenylium salts containing dialkylamino and alkylsulfanyl groups in the small ring have successfully been employed in organic synthesis as three-carbon-atom building blocks [1]. The reactions of this kind of compounds **1a, b** with carbon- and nitrogen-centered nucleophiles were shown [1–7] to produce selectively five- and six-membered carbo- and heterocycles.

Thus dialkylamino(diphenyl)cyclopropenylium tetrafluoroborates (**1a**) react with β -dicarbonyl compounds in the presence of triethylamine to yield 3-dialkylaminocyclopenta-2,4-dienol derivatives **2a** (Scheme 1). Under analo-

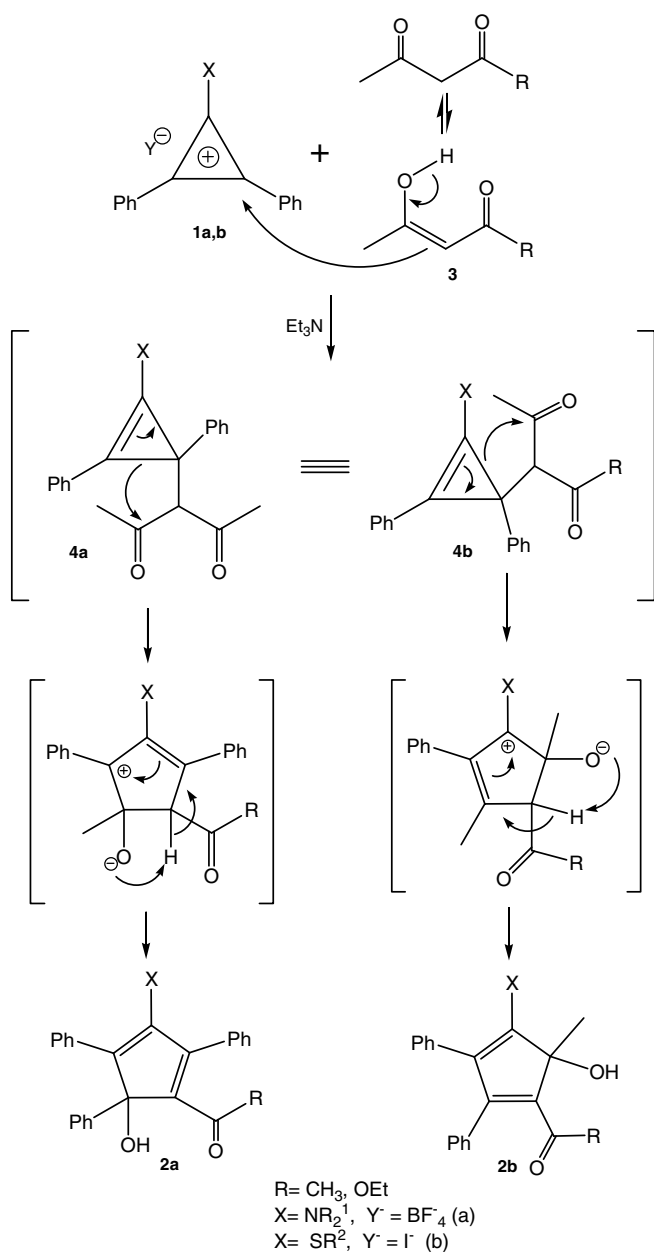
gous conditions, alkylsulfanyl(diphenyl)cyclopropenylium iodides afford cyclopenta-2,4-dienol derivatives (**2b**) with the alkylsulfanyl-substituent in position 2 of the five-membered ring [5] (Scheme 1).

Presumably [5], these reactions involve the initial attack of the nucleophile (**3**) on the carbon atom of the three-membered ring linked to a phenyl substituent to form tetrasubstituted cyclopropene intermediates **4a** or **4b**, which undergo ring extension (see Scheme 1).

The behavior of diferrocenyl analogs [8–10] of dialkylamino- or alkylsulfanyl-cyclopropenylium salts in reactions with 1,3-diketones has not been studied so far. In the present work, we studied the reactions of 2,3-diferrocenyl-1-morpholinocyclopropenylium tetrafluoroborate (**5a**) and 2,3-diferrocenyl-1-methylsulfanylcyclopropenylium iodide (**5c**) with 1,3-diketones and investigated some chemical and electrochemical properties of the reaction products.

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Scheme 1.

2. Results and discussion

The starting compounds, 2,3-diferrocenyl-1-morpholinocyclopropenylium tetrafluoroborate (**5a**) and 2,3-diferrocenyl-1-methylsulfanyl-cyclopropenylium iodide (**5c**), were prepared [11] from 2,3-diferrocenylcyclopropenone (**6**) according to Scheme 2.

We found that compound **5a** reacts with β -diketones (acetylacetone, dibenzoylmethane, dipivaloylmethane, and benzoylacetone (**7a–d**)) in the presence of triethylamine to afford high yields of 1,2-diferrocenyl-3-(diacylmethylidene)cyclopropenes (**8a–d**) (Scheme 3).

The cyclopropenes **8a–d** were isolated by column chromatography on alumina and recrystallized from ethanol.

Their structures were established by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

The formation of cyclopropenes **8a–d** can obviously be rationalized as the initial attack of a nucleophilic reagent on the C(1) atom of the cyclopropenylium cation resulting in cyclopropene intermediates (**9a–d**) followed by elimination of morpholine (Scheme 4).

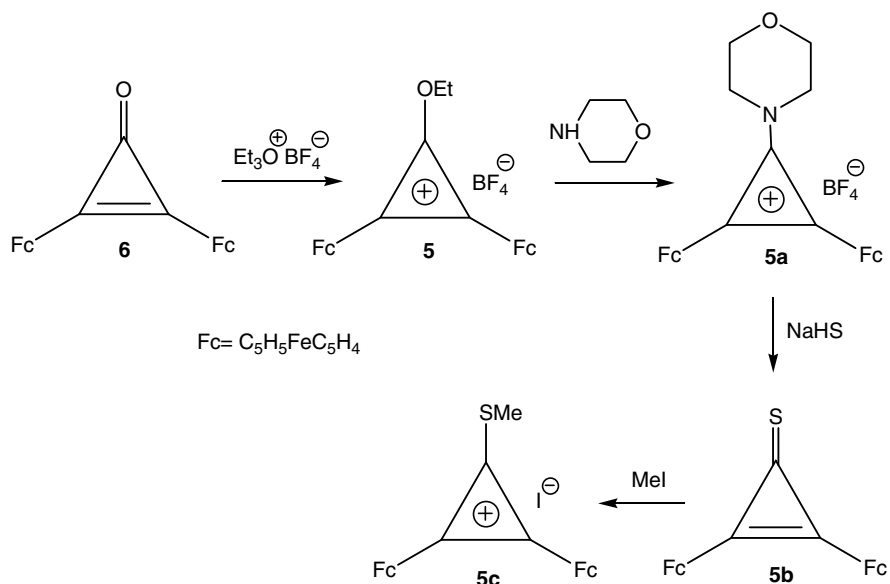
We found further that, unlike diferrocenyl(morpholino)cyclopropenylium tetrafluoroborate (**5a**), diferrocenyl(methylsulfanyl)cyclopropenylium iodide (**5c**) reacts with 1,3-diketones **7a–c** to give two products, *viz.*, (diacylmethylidene)diferrocenylcyclopropenes (**8a–c**) (~25–30%) and 1,1-diacyl-2,3-diferrocenyl-4-methylsulfanylbuta-1,3-dienes (**10a–c**) (~50–60%) separated by chromatography on alumina (Scheme 5).

The structures of compounds **10a–c** were established by mass spectrometry, ^{13}C and ^1H NMR (including 1D NOE) spectroscopy, and elemental analysis. The ^1H NMR spectra of compounds **10a–c** contain signals for the protons of the acyl substituents, of two ferrocenyl fragments, a singlet of protons of the methylsulfanyl group, and a singlet of the olefinic proton. The ^{13}C NMR spectra of compounds **10a–c** contain signals for the carbon atoms of two carbonyl groups, of two ferrocenyl fragments with two signals for C_{ipso} , and the corresponding number of signals for other carbon atoms of the molecules. The ^1H NMR spectrum of compound **10c** suggests that this was isolated as a single geometric isomer; its absolute configuration has not been established. The position of a proton at the double bond adjacent to the MeS group in compounds **10a–c** was confirmed by NOE experiments: irradiation of the methyl protons gave a response at the vinylic proton.

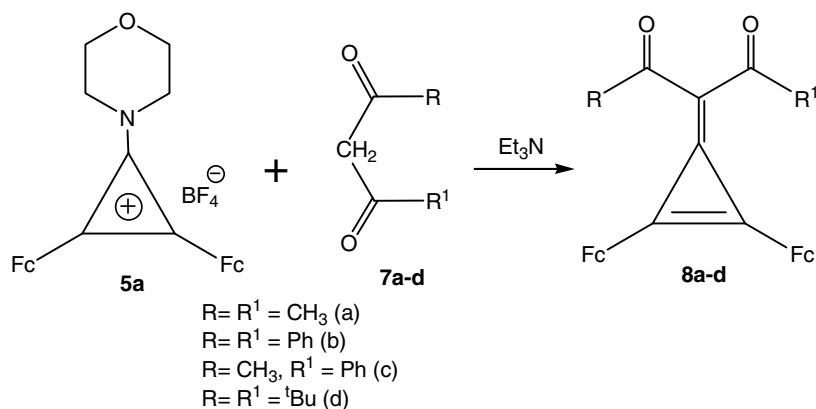
A putative mechanism for the formation of compounds **10a–c** is presented in Scheme 6.

The results obtained in the present study demonstrate that the nucleophilic attacks on the cation **5c** with a methylsulfanyl substituent are directed, contrary to the cation **5a**, on both the C(1) atom of the small ring and the C(2) atom. In the former case, cyclopropenes (**8a–c**) are formed according to Scheme 4. In the case of the attack on the C(2) atom linked to a ferrocenyl substituent, 3-ferrocenylcyclopropenes (**11a–c**) are formed as unstable intermediates [12–14]. These undergo spontaneous opening of the three-membered ring to yield vinylcarbenes (**12a–c**). The transformations of vinylcarbenes (**12a–c**) with intramolecular proton shift affords ultimately the linear products **10a–c**. The intramolecular character of the transformation of analogous vinylcarbenes was proved earlier for the reaction of the cation **5c** with diethyl [D_2]malonate [15].

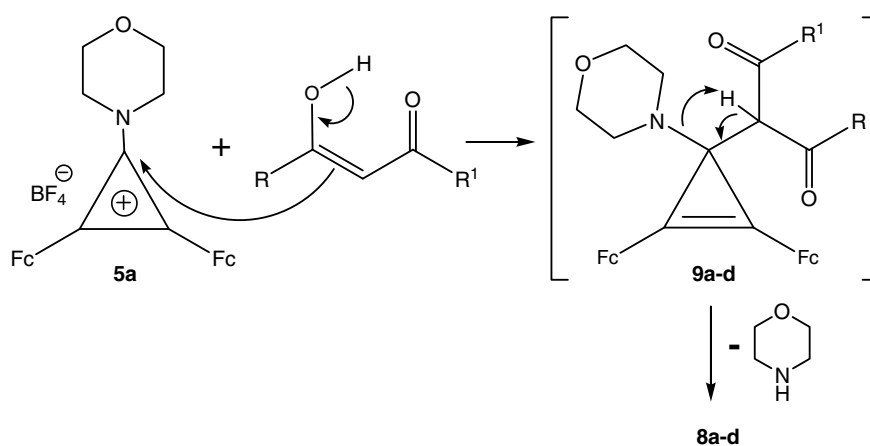
The formation of diacylmethylidene-cyclopropenes (**8a–d**) as sole reaction products of morpholino(diferrocenyl)cyclopropenylium tetrafluoroborate (**5a**) with 1,3-diketones should be stressed. This seems to be related to different distribution of the electron density deficiency in the three-membered rings of the amino **5a** and thio **5c** derivatives: $\text{N}-\text{C}_1^{\delta+} > \text{Fc}-\text{C}_2^{\delta+}$ for **5a**, $\text{Fc}-\text{C}_2^{\delta+} > \text{S}-\text{C}_1^{\delta+}$ for **5c**.



Scheme 2.



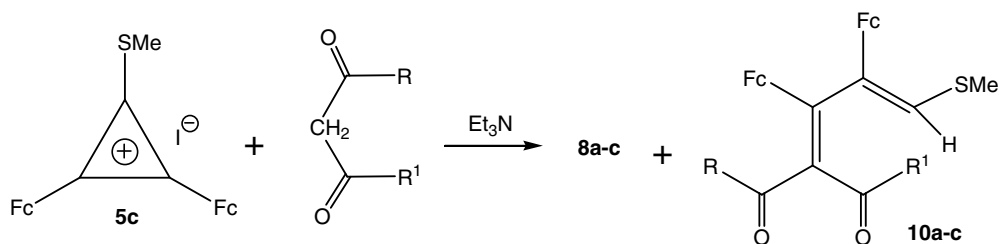
Scheme 3.



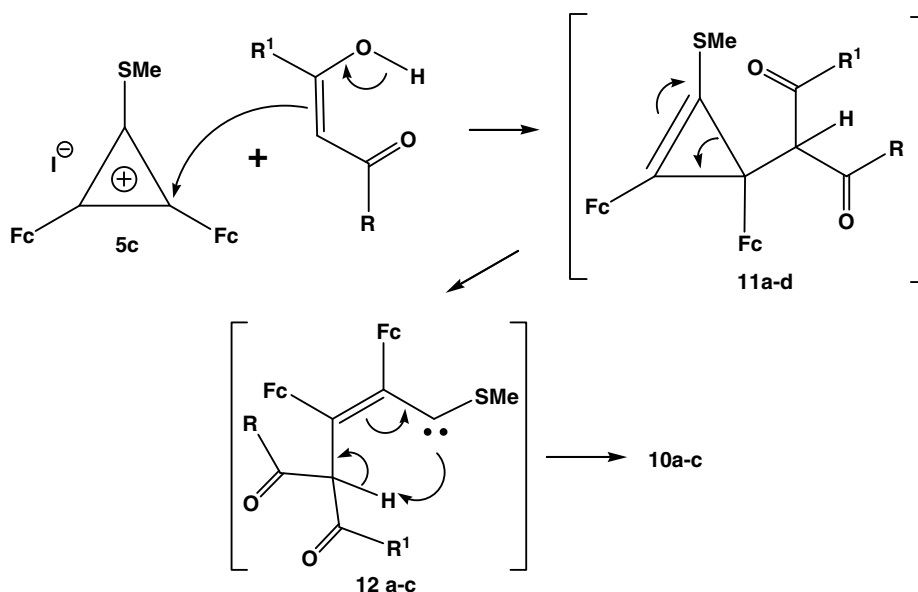
Scheme 4.

The structure of compound **8a** was confirmed by X-ray diffraction analysis. X-ray analysis of a single crystal prepared by crystallization from dichloromethane proved its

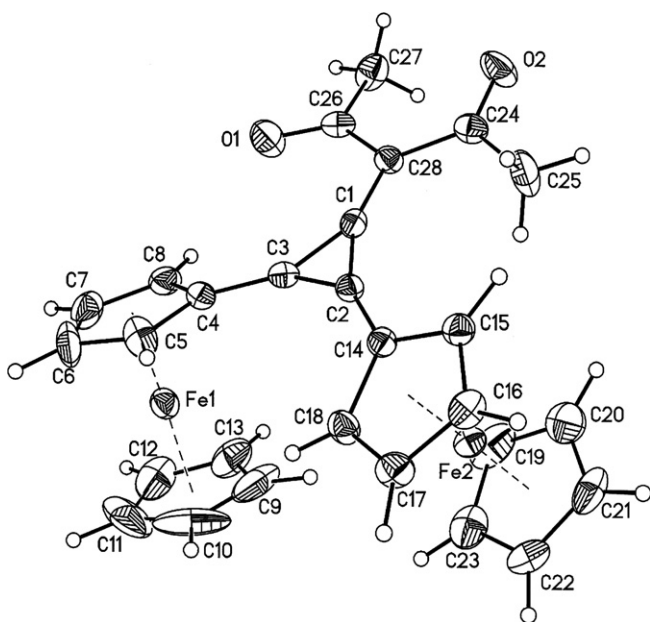
structure as 1,2-diferrocenyl-3-(diacetylmethylidene)cyclopropene. The general view of the molecule **8a** is shown in Fig. 1, the main geometrical parameters are given in Table 1.



Scheme 5.



Scheme 6.

Fig. 1. Molecular structure of **8a**.

The central fragment of the molecule **8a** is a flat three-membered ring. Data from the X-ray analysis show that the C(1)–C(2) and C(1)–C(3) bonds in the cyclopropene

Table 1
Selected bond lengths and bond angles for **8a**

Bond lengths, <i>r</i> (Å)		Bond angles, ω (°)	
C(1)–C(2)	1.409(4)	C(3)–C(1)–C(2)	57.3(2)
C(1)–C(3)	1.404(4)	C(1)–C(2)–C(3)	61.1(2)
C(2)–C(3)	1.348(4)	C(2)–C(3)–C(1)	61.6(2)
C(1)–C(28)	1.377(4)	C(1)–C(28)–C(26)	115.3(3)
C(24)–C(28)	1.455(4)	C(28)–C(1)–C(2)	155.3(3)
C(26)–C(28)	1.466(40)	C(28)–C(1)–C(3)	147.4(3)
C(24)–O(2)	1.213(4)	C(1)–C(28)–C(24)	122.3(3)
C(26)–O(1)	1.223(4)	C(26)–C(28)–C(24)	122.3(3)

ring are somewhat shorter ($r = 1.409(4)$ and $1.404(4)$ Å, respectively) than the standard values of 1.483 Å [16] and the C(1)–C(28), C(24)–C(28) and C(26)–C(28) bonds are somewhat longer [$r = 1.377(4)$, $1.455(4)$ and $1.466(4)$ Å, respectively] than the standard values of 1.34 and 1.42 Å [17], indicating a small contribution of the dipolar form and the pseudoaromatic character [18,19] of compound **8a**, as well as of compounds **8b,c**.

The lengths of the C–Fe and C–C bonds in the ferrocenyl substituents as well as the geometrical parameters of the ferrocene sandwiches are close to the standard values [12].

The pseudoaromatic character of 3-diacylmethylidene-1,2-diferrocenylcyclopropenes (**8a-c**) are manifested in

theirs stability towards thermolysis ($\sim 200^\circ\text{C}$) and upon the action of acids (HCl, AcOH). These compounds do not form Diels-Alder adducts with dienes such as cyclohexa-1,3-diene, 1,3-diphenylisobenzofuran, tetraphenylcyclopentadiene.

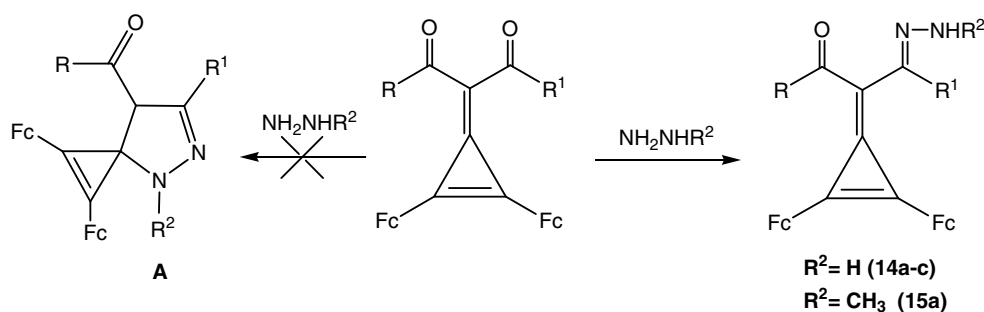
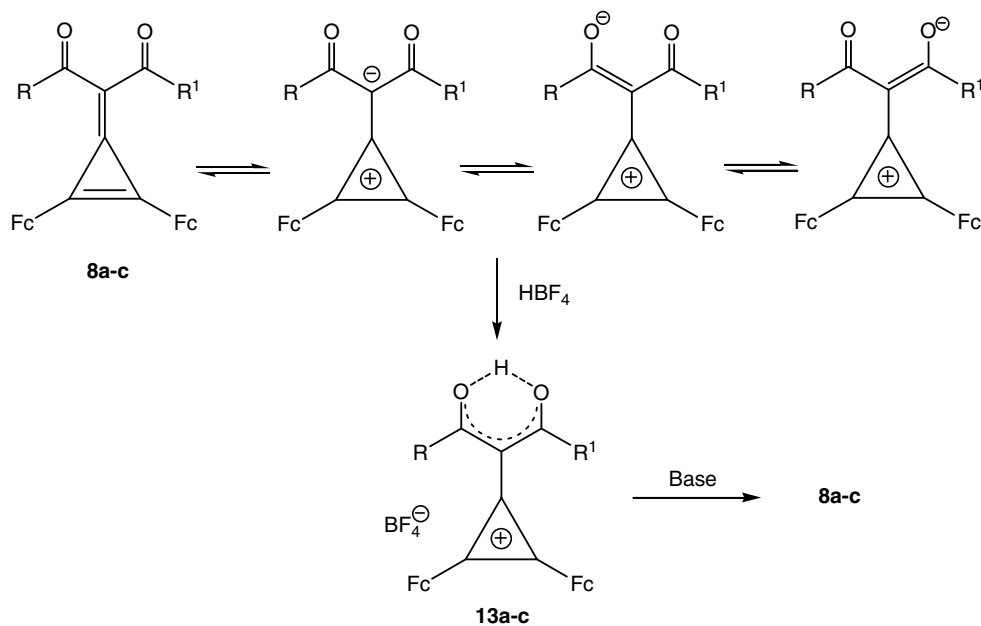
Treatment of the diacylmethylidene(diferrocenyl)cyclopropenes (**8a–c**) with tetrafluoroboric acid diethyl etherate affords crystalline salts (**13a–c**), which can be stored in a dry inert atmosphere (Scheme 7).

The structure of the salts **13a–c** was confirmed by ^1H and ^{13}C NMR spectroscopic data. The signals for the protons of the cyclopentadienyl rings of ferrocene in the ^1H NMR spectrum of the salts **13a–c** are noticeably shifted to lower fields ($\delta_{\text{C}_5\text{H}_5} = 4.37; 4.45; 4.26$ and 4.41 ppm; $\delta_{\text{C}_5\text{H}_4} = 4.85, 5.36; 4.91, 5.37; 4.49, 4.63, 4.98, 5.59$ ppm, respectively) relative to those of the original cyclopropenes (**8a–c**) ($\delta_{\text{C}_5\text{H}_5} = 4.24; 4.23; 4.15$ and 4.27 ppm; $\delta_{\text{C}_5\text{H}_4} = 4.71, 5.20; 4.65, 5.08; 4.32, 4.48, 4.72, 5.37$ ppm). In addition, the ^1H NMR spectra of compounds **13a–c** contain signals for the protons of the acyl substituents and broad signals for the one proton ($\delta_{\text{H}} = 5.43, 5.66$ and 5.74 ppm, respec-

tively). Data from the ^{13}C NMR spectrum corroborate the structures of the salts **13a–c**. They each contained three, four, or five signals for carbon atoms bearing no hydrogen atoms, one (**13a, b**) or two (**13c**) signals for the carbon atoms of groups $-\text{C}-\text{O}-$, one or two carbon atoms $\text{C}_{\text{ipso}}\text{Fc}$ of the ferrocene units. The number of signals for the C_5H_5 , C_5H_4- , C_6H_5- and Me groups and their chemical shifts correspond completely to the structures **13a–c**.

Unlike aryl- and ferrocenylcyclopropenyl cations, which give 3-substituted cyclopropenes upon the action of nucleophiles [19], the cations **13a–c** undergo deprotonation upon treatment with bases (*N,N*-dimethylaniline, pyridine) with the formation of the starting diacylmethylidene(diferrocenyl)cyclopropenes **8a–c** (Scheme 7).

The compounds **8a–c** are ferrocene-containing α, β -enediones, which could be expected to react with hydrazines giving derivatives of the diferrocenylcyclopropenylidene-4,5-dihydropyrazoles analogous to these obtained from ferrocenyl- α, β -enones [20–22]. However, our studies demonstrate that compounds **8a–c** do not form heterocycles of the type **A** (Scheme 8). The only reaction products



are monohydrazones **14a–c** and **15a** obtained in high yields (Scheme 8).

The structures of compounds **14a–c** and **15a** were established based on their ^1H (including 1D NOE) and ^{13}C NMR spectroscopic and elemental analysis data.

3. Electrochemistry

Fig. 2 shows the voltammetry of compound **8a** in acetonitrile solution containing 0.1 M $\text{Bu}_4\text{N}^+\text{BF}_4^-$. When the potential scan was initiated in positive direction and when the cycle was completed two oxidation signals (I_a and II_a) and two reduction signals (I_c and II_c) were observed. The obtained values of anodic and cathodic peak potentials $E_{\text{pa}}(\text{I})$ and $E_{\text{pc}}(\text{I})$ for signal I_a and I_c were 0.280 V/ Fc-Fc^+ and 0.221 V/ Fc-Fc^+ , respectively. The ΔE_p was 0.059 V and independent of the scan rate (0.1–1 V s^{-1}). A reversible electrochemical behavior is presented [23]. The anodic and cathodic peak potential values for signals II_a and II_c $E_{\text{pa}}(\text{II})$ and $E_{\text{pc}}(\text{II})$ are 0.398 and 0.338 V/ Fc-Fc^+ , respectively. The ΔE_p was also independent of the scan rate (0.1–1 V s^{-1}). It can be suggested a two-step reversible oxidation of ferrocene moieties for process I and II.

The formal electrode potential was evaluated with the half sum of the anodic and cathodic peak potentials, $E^0 = (E_{\text{pa}} + E_{\text{pc}})$. The values for processes I and II, were $E^0(\text{I}) = 0.250$ V/ Fc-Fc^+ and $E^0(\text{II}) = 0.368$ V/ Fc-Fc^+ . The value of $\Delta E^0(\text{II-I})$ for processes I and II was 0.118 V and the corresponding value of comproportionation constant K_{com} was 100 [23,24]. The electrochemical response of compounds **8b** and **8c** is very similar than the presented in compound **8a**.

Cyclic voltammetry experiment of compound **10b** also indicates a two consecutive electron transfer mechanism EE, Fig. 3.

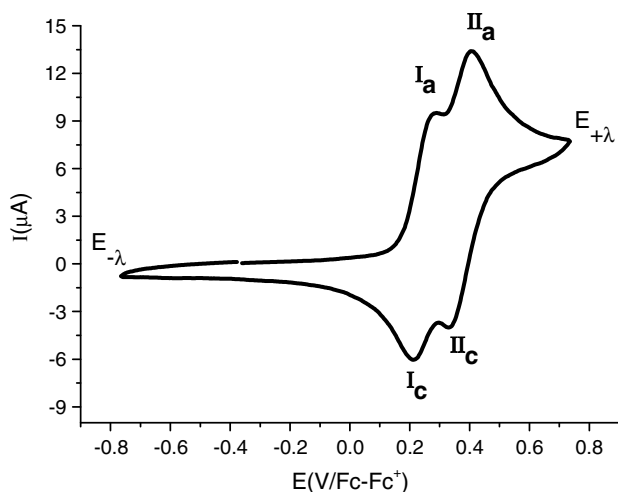


Fig. 2. Cyclic voltammogram for a 2.0×10^{-3} mol dm^{-3} solution of compound **8a** in acetonitrile in the presence of 0.1 M $\text{Bu}_4\text{N}^+\text{BF}_4^-$. The scan potential was initiated from E_{ocp} to positive direction. Scan rate 0.1 V s^{-1} . The working electrode used was platinum.

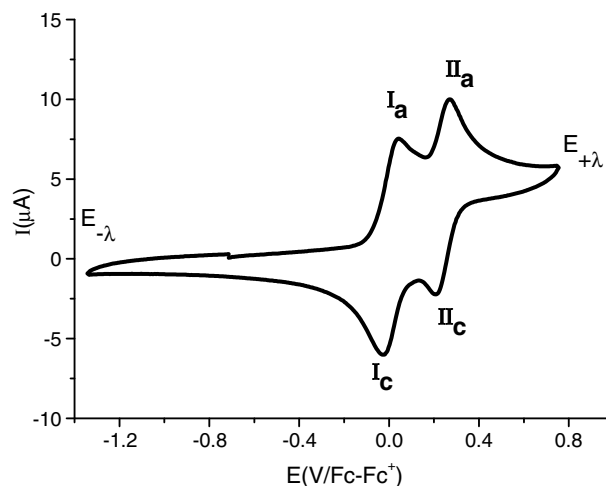


Fig. 3. Cyclic voltammogram for a 2.0×10^{-3} mol dm^{-3} solution of compound **10b** in acetonitrile in the presence of 0.1 M $\text{Bu}_4\text{N}^+\text{BF}_4^-$. The scan potential was initiated from E_{ocp} to positive direction. Scan rate 0.1 V s^{-1} . The working electrode used was platinum.

Table 2

Formal electrode potentials $E^0(\text{I})$, $E^0(\text{II})$ and $\Delta E^0(\text{II-I})$, and constant K_{com} for compounds **8a–c** and **10a–c**

Compound	$E^0(\text{I})$	$E^0(\text{II})$	$\Delta E^0(\text{II-I})$	K_{com}
8a	0.250	0.368	0.118	100
8b	0.249	0.362	0.113	82
8c	0.250	0.362	0.112	80
10a	0.006	0.241	0.235	9617
10b	0.007	0.240	0.233	8895
10c	0.011	0.239	0.228	7318

$E^0 = (E_{\text{pa}} + E_{\text{pc}})/2$, reported vs. ferrocene in 0.1 M $\text{Bu}_4\text{N}^+\text{BF}_4^-$ -acetonitrile. Scan rate 0.10 V s^{-1} .

A summary of the obtained values of $E^0(\text{I})$, $E^0(\text{II})$ and K_{com} for all the compounds studied by cyclic voltammetry is presented in Table 2.

The calculated values of K_{com} for all compounds suggests that the electron charge is slightly delocalized in the mixed valence state generated electrochemically, according to the Robin-Day classification (class II) [24,25]. The similar values of K_{com} for compounds **8a** and **8b**, **8c** suggest no effect of the substituent in the mixed valence state.

The values obtained for compounds **10a–c** suggest no differences in the electronic communication between ferrocene moieties in these compounds. The largest values of K_{com} for compounds **10a–c** compared with **8a–c** can be attributed to the presence of a sulfur atom close to one ferrocene moiety. The electronic communication in compounds **10a–c** cannot be neglected but probably with a minor effect compared with the presence of sulfur, which increases the value of $\Delta E^0(\text{II-I})$.

4. Conclusion

Thus, the results of the present study support our previous conclusion [8–10], that, depending on whether the nucleophile attacks C(1) or C(2) of the cations **5a** or **5c**,

the initially formed intermediates **9a–d** or **11a–c** (see Schemes 4 and 6) usually form the products that retain the original three-membered ring or undergo C–C bond cleavage to give ring-opened products. Diferrocenyl(morpholino)cyclopropenylum tetrafluoroborate (**5a**) reacts with 1,3-diketones to afford solely the products with retention of the three-membered ring – 3-diacylmethylidene-1,2-diferrocenylcyclopropenes (**8a–d**), while diferrocenyl(methylsulfanyl)cyclopropenylum iodide (**5c**) affords preferentially linear products (1,1-diacyl-2,3-diferrocenyl-4-methylsulfanylbuta-1,3-dienes (**10a–c**)) resulted from the opening of the small ring. This behavior of **5c** is substantially different from its morpholino analog **5a**. No cyclic products similar to cyclopentadienols **2a** and **2b** were observed in the reactions of compounds **5a** and **5c** with 1,3-diketones, which distinguishes diferrocenylcyclopropenylum salts from their diaryl-substituted analogs.

At the same time, it is known [26] that the presence of ferrocenyl substituents in molecules of organic compounds imparts new properties to these compounds that are absent, as a rule, in their alkyl/aryl analogs. This statement seems to concern also diferrocenylcyclopropenylum salts, which may prove to be appropriate synthons for the preparation of various classes of functionalized compounds with ferrocenyl substituents in molecules, of substances with valuable properties such as electrical conductivity, nonlinear optical effects, pharmacological activity, magnetic behavior, thermal stability, etc.

5. Experimental

All the solvents were dried according to the standard procedures and were freshly distilled before use. The ^1H and ^{13}C NMR spectra of compounds **8a–d** and **10a–c** were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz for ^1H and ^{13}C , respectively) of solns in CDCl_3 with Me_4Si as the internal standard. Chemical shifts are given in ppm and J values in Hz. The IR spectra of samples prepared as KBr pellets were measured on a Specord IR-75 instrument. The mass spectrum were obtained on a Varian-MAT CH-6 instrument (EI, 70 eV). 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 3. The structure of compound **8a** was solved by direct method (SHELXS-97 [27]) and refined using full-matrix least-squares on F^2 .

All electrochemical measurements were performed in acetonitrile solution containing 0.1 M tetra-*N*-butylammonium tetrafluoroborate ($^+\text{Bu}_4\text{N}^+\text{BF}_4^-$). A potentiostat/galvanostat EG&G PAR model 263A controlled by a PC software was used. A three-electrode array was employed. A platinum disk was used as working electrode, and a plat-

Table 3

Crystal data and structure refinement parameters for compound **8a**

Data	8a
Molecular formula	$\text{C}_{28}\text{H}_{24}\text{Fe}_2\text{O}_2$
Formula weight (g mol^{-1})	504.17
Temperature (K)	291(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.6648(6)
b (Å)	11.0139(6)
c (Å)	18.3080(10)
α (°)	90
β (°)	94.7870(10)
γ (°)	90
V (Å ³)	2143.0(2)
Z	4
D_{calc} (Mg mm^{-3})	1.563
Absorption coefficient (mm^{-1})	1.378
$F(000)$	1040
Radiation, λ (Å)	Mo $K\alpha$, 0.71073
Monochromator	Graphite
θ range (°)	2.16–25.00
Reflections collected	17171
Reflections independent	3779
R_{int}	0.0606
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0444$, $wR_2 = 0.0849$
R indices (all data)	$R_1 = 0.0617$, $wR_2 = 0.0908$
Refinable parameters	291
Goodness-of-fit	1.000
Refinement method	Full-matrix-least-squares on F^2
Minimum/maximum residual electron density (e Å^{-3})	–0.275/0.389

inum wire as counter-electrode. A pseudo reference electrode of silver wire immersed in a 0.1 M tetra-*N*-butylammonium chloride ($\text{Bu}_4\text{N}^+\text{Cl}^-$) in acetonitrile was also employed. All solutions were bubbled with nitrogen prior each measurement. In all experiments, a $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ solution of each compound in supporting electrolyte was used. 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 [28].

The following reagents were purchased from Aldrich: ferrocene, 98%; aluminum chloride, 99.99%; tetrachlorocyclopropene, 98%; triethyloxonium tetrafluoroborate, 1.0 M solution in dichloromethane; morpholine, 99+%; sodium hydrosulfide hydrate $\text{NaHS} \cdot x\text{H}_2\text{O}$; triethylamine, 99+%; 2,4-pentanedione, 99+%; dibenzoylmethane, 98%; 1-benzoylacetone, 99%; 2,2,6,6-tetramethyl-3,5-heptanedione, 98+%; iodomethane, 99.5%; hydrazine monohydrate, 98%; methylhydrazine, 98%. Tetrafluoroboric acid etherate, 50–52%, was purchased from Alfa AESAR.

2,3-Diferrocenylcyclopropenone (**6**) was obtained from the ferrocene and tetrachlorocyclopropene in the presence of AlCl_3 according to the standard procedure [29]. Ethoxy(diferrocenyl)cyclopropenylum tetrafluoroborate (**5**) was obtained from the 2,3-diferrocenylcyclopropenone (**6**)

in the presence of triethyloxonium tetrafluoroborate (1.0 M solution in dichloromethane) [8]. Differrocenyl(morpholino)cyclopropenylium tetrafluoroborate (**5a**) was obtained from ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate and morpholine in dichloromethane [8,9]. 2,3-Diferrocenylcyclopropenethione (**5b**) was obtained by treating ethanolic differrocenyl(morpholino)cyclopropenylium tetrafluoroborate [10] with an aqueous solution of NaSH [10], yield 91%, m.p. 208–209 °C. 2,3-Diferrocenyl(methylsulfanyl)cyclopropenylium iodide (**5c**) was obtained from the 2,3-diferrocenylcyclopropenethione and iodomethane [10].

5.1. Reaction of differrocenyl(morpholino)cyclopropenylium tetrafluoroborate (**5a**) with β -diketones (**7a–d**)

β -Diketones **7a–d** (6 mmol) and Et₃N (10 ml) were added with stirring in a mixture of salt **5a** (1.75 g, 3 mmol) in dry benzene (50 ml). After stirring for 6 h at ambient temperature, the volatiles were removed *in vacuo*; chromatography of the residue on Al₂O₃ (hexane-ether, 10:1) gave compounds **8a–d**.

3-Diacetylmethylidene-1,2-diferrocenylcyclopropene (**8a**), yield 1.07 g (71%), orange crystals, m.p. 168–169 °C. IR (KBr): $\nu = 486, 574, 661, 730, 818, 948, 1001, 1027, 1057, 1105, 1171, 1268, 1291, 1331, 1356, 1392, 1452, 1479, 1510, 1549, 1594, 1649, 1709, 1851, 2920, 2955, 3086 \text{ cm}^{-1}$. ¹H NMR: δ 2.59 (6H, s, 2CH₃), 4.25 (10H, s, 2C₅H₅), 4.71 (4H, m, C₅H₄), 5.20 (4H, m, C₅H₄). ¹³C NMR: δ 30.61 (2CH₃), 64.61 (C), 70.42 (2C₅H₅), 72.53, 73.00 (2C₅H₄), 100.99, 105.08 (2C_{ipso}Fc), 139.34(C), 140.89 (2C), 191.30, 195.65 (2C=O). Anal. Calc. for C₂₈H₂₄Fe₂O₂: C, 66.70; H, 4.80; Fe, 22.15. Found: C, 66.49; H, 4.91; Fe, 21.97%. MS: m/z 504 [M]⁺.

3-Dibenzoylmethylidene-1,2-diferrocenylcyclopropene (**8b**), yield 1.29 g (68%), orange powder, m.p. 299–301 °C. IR (KBr): $\nu = 416, 477, 531, 587, 632, 698, 724, 754, 813, 946, 999, 1025, 1080, 1226, 1325, 1381, 1417, 1460, 1480, 1527, 1549, 1594, 1652, 1712, 1839, 2991, 3057 \text{ cm}^{-1}$. ¹H NMR: δ 4.23 (10H, s, 2C₅H₅), 4.65 (4H, m, C₅H₄), 5.08 (4H, m, C₅H₄), 7.15–7.24 (6H, m, C₆H₅), 7.61–7.65 (4H, m, C₆H₅). ¹³C NMR: δ 64.73 (C), 70.25 (2C₅H₅), 72.73, 73.11 (2C₅H₄), 94.15, 101.51 (2C_{ipso}Fc), 127.79, 127.87, 128.18, 128.82, 130.51, 131.53 (2C₆H₅), 138.48, 138.93, 139.46 (3C), 142.04 (2C), 184.77, 195.03 (2C=O). Anal. Calc. for C₃₈H₂₈Fe₂O₂: C, 72.64; H, 4.49; Fe, 17.78. Found: C, 72.73; H, 4.32; Fe, 17.91%. MS: m/z 628 [M]⁺.

3-Acetyl(benzoyl)methylidene-1,2-diferrocenylcyclopropene (**8c**), yield 1.19 g (70%), orange powder, m.p. 206–208 °C. IR (KBr): $\nu = 412, 488, 552, 631, 697, 746, 821, 946, 989, 1000, 1027, 1048, 1109, 1173, 1237, 1290, 1331, 1381, 1406, 1453, 1522, 1594, 1638, 1679, 1700, 1823, 2904, 3056 \text{ cm}^{-1}$. ¹H NMR: δ 2.33 (3H, s, CH₃), 4.15 (5H, s, C₅H₅), 4.27 (5H, s, C₅H₅), 4.32 (2H, m, C₅H₄), 4.48 (2H, m, C₅H₄), 4.72 (2H, m, C₅H₄), 5.37 (2H, m, C₅H₄), 7.39–7.52 (3H, m, C₆H₅), 7.77–7.80 (2H, m, C₆H₅). ¹³C NMR: δ 30.04 (CH₃), 64.05 (C), 70.07, 70.24 (2C₅H₅), 71.70, 72.71, 73.08, 73.17 (2C₅H₄), 99.84, 102.90

(2C_{ipso}Fc), 128.55, 129.26, 131.45 (C₆H₅), 137.45, 138.70, 140.10, 142.13 (4C), 186.20, 195.32 (2C=O). Anal. Calc. for C₃₃H₃₆Fe₂O₂: C, 70.00; H, 4.63; Fe, 19.73. Found: C, 69.84; H, 4.80; Fe, 19.59%. MS: m/z 566 [M]⁺.

3-Dipivaloylmethylidene-1,2-diferrocenylcyclopropene (**8d**), yield 1.28 g (72%), orange powder, m.p. 238–239 °C. IR (KBr): $\nu = 414, 465, 542, 580, 626, 698, 729, 753, 854, 952, 999, 1003, 1032, 1057, 1100, 1174, 1221, 1266, 1321, 1354, 1443, 1462, 1574, 1653, 1679, 1711, 1843, 2955, 3087 \text{ cm}^{-1}$. ¹H NMR: δ 1.07 (18H, s, 6CH₃), 4.20 (10H, s, 2C₅H₅), 4.45 (4H, m, C₅H₄), 4.73 (4H, m, C₅H₄). ¹³C NMR: δ 27.84 (6CH₃), 44.59 (2C), 64.48 (C), 70.31 (2C₅H₅), 72.21, 72.93 (2C₅H₄), 99.87, 101.70 (2C_{ipso}Fc), 139.31(C), 140.83 (2C), 190.32, 195.04 (2C=O). Anal. Calc. for C₃₄H₃₆Fe₂O₂: C, 69.40; H, 6.17; Fe, 19.00. Found: C, 69.52; H, 6.04; Fe, 18.87%. MS: m/z 588 [M]⁺.

5.2. Reaction of differrocenyl(methylsulfanyl)cyclopropenylium iodide (**5c**) with β -diketones (**7a–c**)

This was carried out analogously using salt **5c** (1.74 g, 3.0 mmol), β -diketones (**7a–c**) (5 mmol), Et₃N (10 ml) and benzene (50 ml). The reaction mixture was worked up as described above, subsequent chromatography on Al₂O₃ (hexane-diethyl ether, 4:1) gave compounds **8a–c** and **10a–c**.

1,1-Diacetyl-2,3-diferrocenyl-4-methylthio-1,3-butadiene (**10a**), yield 0.90 g (54%), orange crystals, m.p. 182–183 °C. IR (KBr): $\nu = 764, 807, 887, 971, 1018, 1047, 1079, 1121, 1147, 1228, 1285, 1380, 1421, 1442, 1614, 1661, 1691, 1813, 2926, 2987, 3095 \text{ cm}^{-1}$. ¹H NMR: δ 2.22 (3H, s, CH₃), 2.24 (3H, s, CH₃), 2.35 (3H, s, CH₃S), 4.09 (5H, s, C₅H₅), 4.24 (5H, s, C₅H₅), 4.31 (1H, m, C₅H₄), 4.33 (3H, m, C₅H₄), 4.34 (1H, m, C₅H₄), 4.48 (1H, m, C₅H₄), 4.61 (1H, m, C₅H₄), 4.63 (1H, m, C₅H₄), 6.54 (1H, s, CH=). ¹³C NMR: δ 16.49 (CH₃S), 29.85, 30.59 (2CH₃), 70.16, 70.54 (2C₅H₅), 68.70, 69.05, 69.33, 70.63 (1C₅H₄), 70.00, 70.75 (1C₅H₄), 83.33, 85.33 (2C_{ipso}Fc), 126.12 (CH=), 133.19, 138.20, 155.80 (3C), 197.69, 200.34 (2C=O). Anal. Calc. for C₂₉H₂₈Fe₂O₂S: C, 63.07; H, 5.11; Fe, 20.23; S, 5.79. Found: C, 63.18; H, 5.012; Fe, 20.37; S, 5.64%. MS: m/z 552 [M]⁺.

Compound **8a**, yield 0.31 g (20%), orange crystals, m.p. 168–169 °C. MS: m/z 504 [M]⁺.

1,1-Dibenzoyl-2,3-diferrocenyl-4-methylthio-1,3-butadiene (**10b**), yield 1.24 g (61%), orange crystals, m.p. 314–316 °C. IR (KBr): $\nu = 772, 821, 892, 948, 987, 1007, 1024, 1053, 1080, 1124, 1147, 1231, 1289, 1386, 1431, 1447, 1634, 1668, 1696, 1811, 2928, 2979, 3058 \text{ cm}^{-1}$. ¹H NMR: δ 2.11 (3H, s, CH₃S), 4.11 (5H, s, C₅H₅), 4.28 (5H, s, C₅H₅), 4.26 (1H, m, C₅H₄), 4.32 (1H, m, C₅H₄), 4.38 (2H, m, C₅H₄), 4.46 (1H, m, C₅H₄), 4.55 (1H, m, C₅H₄), 4.59 (1H, m, C₅H₄), 4.79 (1H, m, C₅H₄), 7.06(1H, s, CH=), 7.10–7.93 (10H, m, 2C₆H₅). ¹³C NMR: δ 16.02 (CH₃S), 69.80, 70.19 (2C₅H₅), 68.05, 68.30, 69.27, 69.64, 69.74, 69.87, 70.63, 71.48 (2C₅H₄), 84.18, 85.58 (2C_{ipso}Fc), 121.48 (CH=), 127.76, 128.03, 128.09, 129.70, 131.82,

132.93 (2C₆H₅), 128.82, 135.95, 138.15, 139.11, 158.08 (5C), 188.48, 192.50 (2 C=O). Anal. Calc. for C₃₉H₃₂Fe₂O₂S: C, 69.25; H, 4.77; Fe, 16.52; S, 4.73. Found: C, 69.34; H, 4.89; Fe, 16.39; S, 4.95%. MS: *m/z* 676 [M]⁺.

Compound **8b**, yield 0.34 g (18%), orange powder, m.p. 298–300 °C. MS: *m/z* 628 [M]⁺.

1-Acetyl-1-benzoyl-2,3-diferrocenyl-4-methylthio-1,3-butadiene (**10c**), yield 1.05 g (57%), orange crystals, m.p. 211–212 °C. IR (KBr): ν 769, 819, 890, 946, 991, 1004, 1022, 1051, 1078, 1125, 1147, 1228, 1283, 1377, 1430, 1444, 1635, 1663, 1691, 1802, 2929, 2969, 3041 cm⁻¹. ¹H NMR: δ 2.13 (3H, s, CH₃), 2.21 (3H, s, CH₃S), 3.89 (5H, s, C₅H₅), 4.31 (5H, s, C₅H₅), 4.15 (3H, m, C₅H₄), 4.21 (1H, m, C₅H₄), 4.36 (2H, m, C₅H₄), 4.62 (1H, m, C₅H₄), 4.73 (1H, m, C₅H₄), 6.30 (1H, s, CH=), 7.30–7.35 (2H, m, C₆H₅), 7.47 (1H, m, C₆H₅), 7.88 (2H, m, C₆H₅). ¹³C NMR: δ 16.26 (CH₃S), 70.34, 70.57 (2C₅H₅), 68.21, 68.34, 69.35, 69.53, 69.78, 69.79, 70.60, 71.42 (2C₅H₄), 83.26, 85.32 (2C_{ipso}Fc), 120.96 (CH=), 128.34, 129.38, 131.79 (C₆H₅), 128.88, 136.06, 139.03, 154.12 (4C), 192.67, 198.84 (2 C=O). Anal. Calc. for C₃₄H₃₀Fe₂O₂S: C, 66.48; H, 4.92; Fe, 18.18; S, 5.21. Found: C, 66.63; H, 5.08; Fe, 18.3; S, 5.29%. MS: *m/z* 614 [M]⁺.

Compound **8c**, yield 0.37 g (22%), orange powder, m.p. 206–207 °C. MS: *m/z* 566 [M]⁺.

5.3. The action of tetrafluoroboric acid diethyl etherate on 3-diacylmethylidene-1,2-diferrocenylcyclopropenes (**8a–c**)

Tetrafluoroboric acid diethyl etherate (0.5 ml) was added dropwise with stirring at 20 °C in an atmosphere of dry nitrogen to a solution of compounds **8a–c** (0.5 mmol) in dry dichloromethane (30 ml). The mixture was stirred for 1 h at 20 °C and then dry diethyl ether (150 ml) was added. The crystals that formed were filtered off, washed on a filter with several portions of dry diethyl ether, and then dried in a vacuum desiccator over CaCl₂. The yield of tetrafluoroborates (**13a–c**) were 80–87%, brown crystals.

Tetrafluoroborate (**13a**), yield 0.24 g (81%), m.p. ca. 237 °C (decomp.). ¹H NMR: δ 2.67 (6H, s, 2CH₃), 4.37 (10H, s, 2C₅H₅), 4.85 (4H, m, C₅H₄), 5.36 (4H, m, C₅H₄), 5.43 (1H, bs). ¹³C NMR: δ 31.06 (2CH₃), 65.47 (C), 70.82 (2C₅H₅), 73.21, 73.70 (2C₅H₄), 109.03 (2C_{ipso}Fc), 142.41(2C), 149.02 (C), 168.47 (2C=O···1H). Anal. Calc. for C₂₈H₂₅BF₄Fe₂O₂: C, 56.80; H, 4.26; B 1.83; F, 12.84; Fe, 18.87. Found: C, 56.62; H, 4.31; F, 12.98; Fe, 18.73%.

Tetrafluoroborate (**13b**), yield 0.31 g (87%), m.p. ca. 261 °C (decomp.). ¹H NMR: δ 4.45 (10H, s, 2C₅H₅), 4.91 (4H, m, C₅H₄), 5.37 (4H, m, C₅H₄), 5.66 (1H, bs), 7.34–7.51 (6H, m, C₆H₅), 7.76–7.89 (4H, m, C₆H₅). ¹³C NMR: δ 66.52 (C), 71.04 (2C₅H₅), 72.98, 73.76 (2C₅H₄), 109.43 (2C_{ipso}Fc), 128.03, 128.16, 128.45, 128.91, 131.19, 133.37 (2C₆H₅), 139.61, 139.72, 139.93 (3C), 144.87(2C), 174.14 (2C=O···1H). Anal. Calc. for C₃₈H₂₉BF₄Fe₂O₂: C, 63.73; H, 4.08; B 1.51; F, 10.61; Fe, 15.60. Found: C, 63.56; H, 4.11; F, 10.72; Fe, 15.43%.

Tetrafluoroborate **13c**, yield 0.27 g (84%), m.p. ca. 224 °C (decomp.). ¹H NMR: δ 4.26 (5H, s, C₅H₅), 4.41 (5H, s, C₅H₅), 4.49 (2H, m, C₅H₄), 4.63 (2H, m, C₅H₄), 4.98 (2H, m, C₅H₄), 5.59 (2H, m, C₅H₄), 5.74 (1H, bs), 7.47–7.71 (5H, m, C₆H₅). ¹³C NMR: δ 27.64 (CH₃), 66.43 (C), 70.79, 71.38 (2C₅H₅), 71.92, 73.12, 73.56, 73.89 (2C₅H₄), 108.03, 111.15 (2C_{ipso}Fc), 129.42, 129.69, 132.83 (C₆H₅), 138.81, 139.64, 142.16, 144.06 (4C), 171.02 (2C=O···1H). Anal. Calc. for C₃₃H₂₇BF₄Fe₂O₂: C, 60.60; H, 4.16; B 1.65; F, 11.62; Fe, 17.08. Found: C, 60.72; H, 4.06; F, 11.51; Fe, 16.93%.

5.4. Reaction of 3-diacylmethylidene-1,2-diferrocenylcyclopropenes (**8a–c**) with hydrazines (**16a,b**)

A solution of compounds **8a–c** (0.5 mmol) and hydrazine hydrate or methylhydrazine (1.5 ml) in ethanol (20 ml) was stirred for 3 h at 20 °C. The reaction mixture was evaporated *in vacuo*, and residue was chromatographed (Al₂O₃; hexane/ether, 4:1) to give hydrazones **14a–c** and **15a–c**.

Hydrazone **14a**, yield 0.16 g (62%), orange powder, p.m. 218–219 °C. IR (KBr): ν 495, 555, 691, 820, 879, 920, 958, 1001, 1025, 1081, 1106, 1159, 1234, 1269, 1332, 1355, 1373, 1389, 1412, 1446, 1518, 1584, 1672, 1703, 1725, 2889, 2924, 3090, 3430 cm⁻¹. ¹H NMR: δ 2.11 (3H, s, CH₃), 2.54 (3H, s, CH₃), 3.97 (2H, bs, NH₂), 4.14 (5H, s, C₅H₅), 4.22 (5H, s, C₅H₅), 4.00 (2H, m, C₅H₄), 4.06 (2H, m, C₅H₄), 4.51 (2H, m, C₅H₄), 5.03 (2H, m, C₅H₄). Anal. Calc. for C₂₈H₂₆Fe₂N₂O: C, 64.90; H, 5.06; Fe, 21.55; N, 5.40. Found: C, 64.78; H, 4.98; Fe, 21.64; N, 5.17%. MS: *m/z* 518 [M]⁺.

Hydrazone **14b**, yield 0.20 g (60%), orange powder, p.m. 305–307 °C. IR (KBr): ν 492, 561, 690, 819, 864, 926, 963, 1001, 1022, 1085, 1105, 1157, 1242, 1267, 1334, 1357, 1384, 1412, 1448, 1521, 1588, 1643, 1664, 1700, 1723, 2887, 2918, 3087, 3425 cm⁻¹. ¹H NMR: δ 4.04 (2H, bs, NH₂), 4.21 (5H, s, C₅H₅), 4.29 (5H, s, C₅H₅), 4.11 (2H, m, C₅H₄), 4.18 (2H, m, C₅H₄), 4.59 (2H, m, C₅H₄), 5.11 (2H, m, C₅H₄), 7.20–7.56 (10H, m, 2C₆H₅). Anal. Calc. for C₃₈H₃₀Fe₂N₂O: C, 71.05; H, 4.71; Fe, 17.39; N, 4.36. Found: C, 70.96; H, 4.83; Fe, 17.48; N, 4.28%. MS: *m/z* 642 [M]⁺.

Hydrazone **14c**, yield 0.18 g (63%), orange powder, p.m. 227–228 °C. IR (KBr): ν 489, 557, 689, 821, 863, 924, 962, 1002, 1021, 1082, 1103, 1155, 1241, 1264, 1336, 1356, 1383, 1412, 1446, 1520, 1587, 1640, 1663, 1703, 1720, 2883, 2921, 3090, 3430 cm⁻¹. ¹H NMR: δ 2.40 (3H, s, CH₃), 3.88 (2H, bs, NH₂), 4.00 (5H, s, C₅H₅), 4.20 (5H, s, C₅H₅), 3.99 (2H, m, C₅H₄), 4.19 (2H, m, C₅H₄), 4.48 (2H, m, C₅H₄), 5.06 (2H, m, C₅H₄), 7.23–7.62 (5H, m, C₆H₅). Anal. Calc. for C₃₃H₂₈Fe₂N₂O: C, 68.30; H, 4.86; Fe, 19.25; N, 4.83. Found: C, 68.42; H, 4.93; Fe, 19.32; N, 4.75%. MS: *m/z* 580 [M]⁺.

Hydrazone **15a**, yield 0.17 g (62%), orange powder, p.m. 207–209 °C. IR (KBr): ν 491, 557, 691, 818, 880, 921, 959, 1001, 1022, 1079, 1104, 1161, 1234, 1267, 1333, 1355, 1374, 1386, 1410, 1447, 1521, 1585, 1671, 1705, 1721, 2880, 2920, 3087, 3424 cm⁻¹. ¹H NMR: δ 1.84 (3H, s, CH₃), 2.44 (3H,

s, CH₃), 3.59 (3H, s, CH₃), 4.17 (1H, s, NH), 4.09 (5H, s, C₅H₅), 4.28 (5H, s, C₅H₅), 4.24 (2H, m, C₅H₄), 4.30 (2H, m, C₅H₄), 4.44 (2H, m, C₅H₄), 4.83 (2H, m, C₅H₄). Anal. Calc. for C₂₉H₂₈Fe₂N₂O: C, 65.43; H, 5.30; Fe, 21.00; N, 5.26. Found: C, 65.29; H, 5.41; Fe, 21.10; N, 5.32%. MS: *m/z* 532 [M]⁺.

6. Supplementary material

CCDC 665728 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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