

Article

Intramolecular Conversions of (Aminoferrocenylpenta-1,4-dienyl)-ferrocenylcarbenes: Synthesis of Diferrocenylmono-, bi-, tricycles and Amino(diferrocenyl)hexa-1,3,5-trienes

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Abstract: Synthesis of 3,4-diferrocenyltoluene (**7**), 1-morpholino- and 1-piperidino-2,3-diferrocenylbicyclo[3.1.0]hex-2-enes **8a**, **8b**, 1-morpholino- and 1-piperidino-7-ferrocenyl-3,4-ferrocenobicyclo[3.2.1]oct-6-enes **9a**, **9b**, 2- and 3-amino(diferrocenyl)-hexa-1,3,5-trienes **10a,b**, **11a,b** by reactions of amino(diferrocenyl)cyclopropenylium tetrafluoroborates with 1-methylprop-2-enylmagnesium chloride at 80 °C is described. The structures of the compounds obtained were determined by IR, ¹H- and ¹³C-NMR spectroscopy and mass spectrometry. X-ray diffraction data for 1-piperidino-7-ferrocenyl-3,4-ferrocenobicyclo[3.2.1]oct-6-ene (**9b**), 2-morpholino- and 2-piperidino-1,3-diferrocenyl-4-methylhexa-1,3,5-trienes **10a** and **10b** is presented. The electrochemical behaviour of compounds **7**, **8a**, **10a** and **10b** was investigated by means of cyclic voltammetry and square wave voltammetry. For **7** and **8a** two electrochemical processes (I-II), attributed to the oxidation of the ferrocene moieties were found. On the other hand for compounds **10a** and **10b** a

single electron transfer for both ferrocene groups and the electrochemical generation of the monocation and dication species were detected.

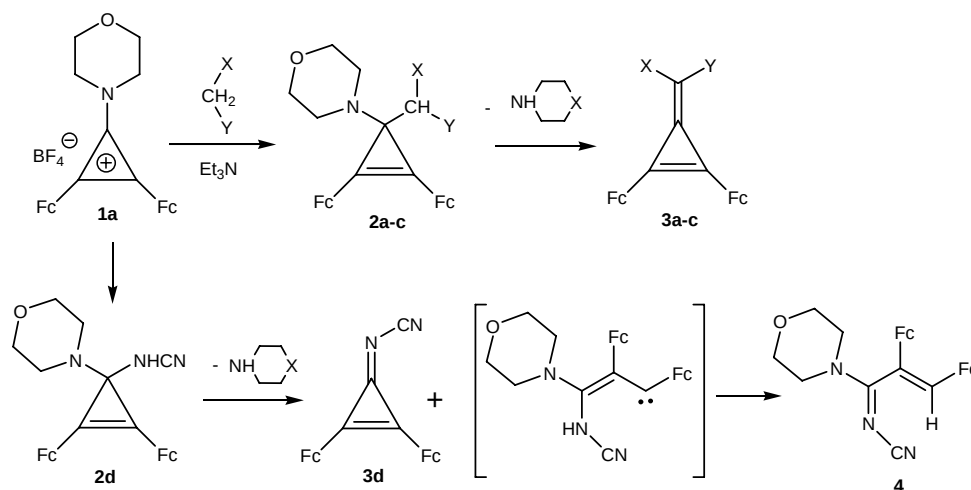
Keywords: amino(diferrocenyl)cyclopropenylium; cyclopropene ring opening; intramolecular conversion of aminoferrocenylpenta-1,4-dienyl(ferrocenyl)carbenes; 3,4-diferrocenyltoluene; amino(diferrocenyl)bicyclo-[3.1.0]hexanes; amino(ferrocenyl)-ferrocenobicyclo[3.2.1]octenes; amino(diferrocenyl)hexa-1,3,5-trienes; electrochemistry

1. Introduction

Diferrocenylcyclopropenylium cations with heterosubstituents in the small ring have recently been described [1–6]. These include 1-ethoxy-, 1-diethylamino-, 1-morpholino-, 1-piperidino-2,3-diferrocenylcyclopropenylium tetrafluoroborates and 2,3-diferrocenyl-1-methylsulfanylcyclopropenylium iodide. Thus, it was established that the reactions of 1-ethoxy-2,3-diferrocenylcyclopropenylium tetrafluoroborate with organolithium compounds are regioselective (the nucleophilic attacks of the anionic reagents on cyclopropenylium cation are directed at both C-1 centers of the three-carbon ring) to yield 3,3-dialkyl-1,2-diferrocenylcyclopropenes [1]. We have shown that the reactions of the 2,3-diferrocenyl-1-methylsulfanylcyclopropenylium iodide with RLi and RMgX are nonregioselective to yield diferrocenylcyclopropenes in low yields (~10%–20%), the major products being 2,3-diferrocenyl-1-methylsulfanyl-1,3-dienes and -1,3,5-trienes (~60%–70%) [4].

On the whole, salts of the 1-morpholino- or 1-piperidino-2,3-diferrocenylcyclopropenylium series are little studied in both the synthetic and practical aspects. Previously it has been shown that 2,3-diferrocenyl-1-morpholinocyclopropenylium tetrafluoroborate (**1a**) reacted with β -dicarbonyl compounds and sodium cyanamide to afford initially the adducts of the nucleophiles at the small ring, *i.e.*, tetrasubstituted diferrocenylcyclopropenes **2a–d** [5–7] (Scheme 1).

Scheme 1. Reaction of 2,3-diferrocenyl-1-morpholinocyclopropenylium tetrafluoroborate **1a** with β -dicarbonyl compounds.



Fc = $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$; X = Y = COOEt (a), X = COCH₃, Y = COOEt (b); X = Bz, Y = COOEt (c)

Elimination of morpholine from cyclopropenes **2a–c** then resulted in 1,2-diferrocenyl-3-(disubstituted)methylidenecyclopropenes **3a–c**. Under the reaction conditions, 3-cyanimino-1,2-diferrocenylcyclopropene (**3d**) and a linear conjugated product **4** formed from compound **2d**. In these reactions, the final products result from the regioselective attack of the nucleophiles on the C(1) atom of the three-membered ring of the cation **1a**.

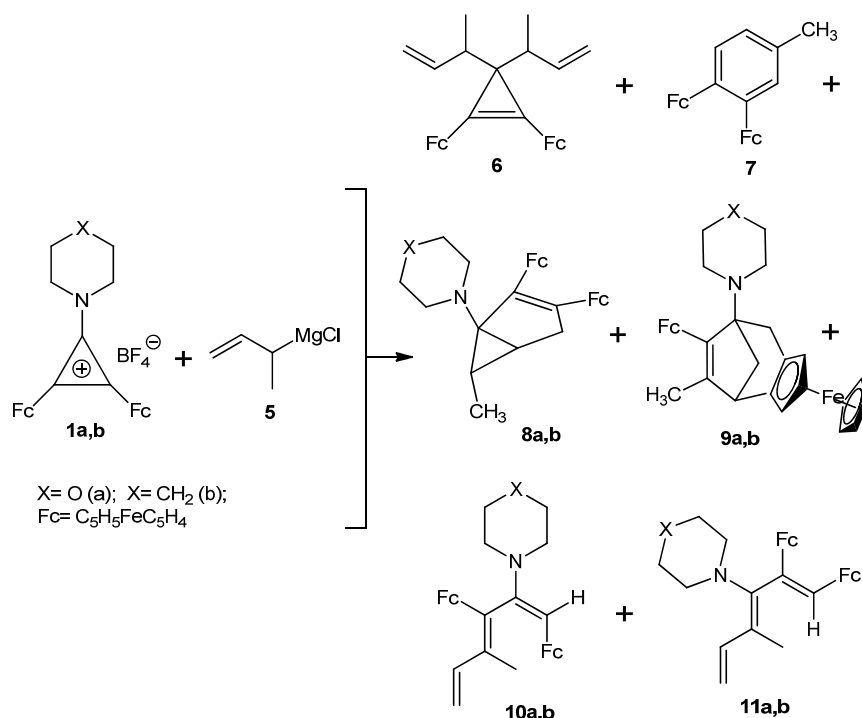
The interest in these compounds, especially with heteroaryl substituents in their molecules, may stem from the peculiarities of their chemical behavior due to the mutual effects of the ferrocene system and the heterocyclic fragment [8]. These effects may result in the emergence of diverse valuable properties, such as biological activity, dyeing ability, possible use as propellant additives or light-sensitive materials, redox switching receptors in supramolecular chemistry, *etc.*, which have previously been observed for a number of heteroarylferrocenes [8].

2. Results and Discussion

2.1. Synthesis of Diferrocenylmono-, bi-, tricycles and Amino(diferrocenyl)hexa-1,3,5-trienes

Here we report investigations into the reactions of 2,3-diferrocenyl-1-morpholino(piperidino)cyclopropenylium tetrafluoroborates **1a, b** with 1-methylprop-2-enylmagnesium chloride **5** (Scheme 2).

Scheme 2. Reaction of 2,3-diferrocenyl-1-morpholino(piperidino)cyclopropenylium tetrafluoroborates **1a,b** with 1-methylprop-2-enylmagnesium chloride **5**.



According to a standard procedure [5–7], 2,3-diferrocenylcyclopropenone [9] was first converted into 1-ethoxy-2,3-diferrocenylcyclopropenylium tetrafluoroborate and then to tetrafluoroborates **1a,b** [1,2], which served as the starting materials in the present study.

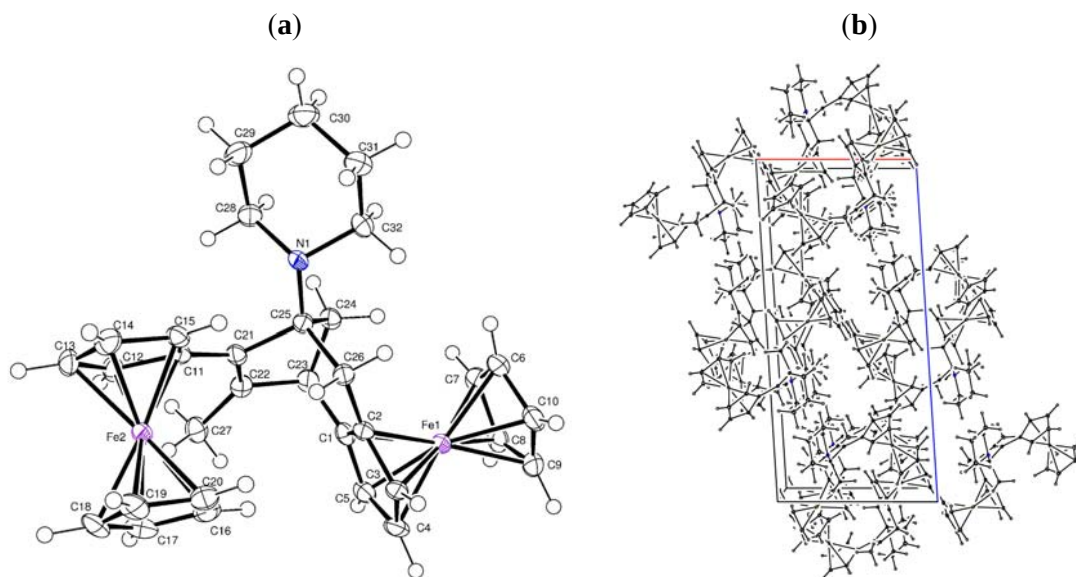
We found that tetrafluoroborate **1a** reacted with an excess of 1-methylprop-2-enylmagnesium chloride **5** to afford a complex mixture of reaction products, the main ones being 3,3-bis(1-

methylprop-2-enyl)-1,2-diferrocenylcyclopropene (**6**), 3,4-diferrocenyltoluene (**7**), 2,3-diferrocenyl-6-methyl-1-morpholinobicyclo[3.1.0]hex-2-ene (**8a**), 7-ferrocenyl-6-methyl-1-morpholino-3,4-ferrocenobicyclo-[3.2.1]oct-6-ene (**9a**), (*E,E*)-1,3-diferrocenyl-4-methyl-2-morpholinohexa-1,3,5-triene (**10a**), and (*Z,E*)-1,2-diferrocenyl-4-methyl-3-morpholinohexa-1,3,5-triene (**11a**) (Scheme 2). Analogously tetrafluoroborate **1b** reacted with the Grignard reagent **5** to give compounds **6**, **7**, **8b**, **9b**, **10b**, and **11b** (Scheme 2).

Both reaction mixtures were separated by column chromatography on alumina, and the structures of the isolated products were established based on the data from UV, IR, and ^1H - and ^{13}C -NMR spectroscopy, mass spectrometry, and elemental analysis. The physicochemical characteristics of compounds **6** and **7** corroborate completely their structures.

We attempted to assign *endo* forms of compounds **8a** and **8b** based on previously reported criteria [10–12]. Thus, compounds **8a** and **8b** were characterized as *endo* isomers based on the fact that the signals from three of the protons of the C_5H_4 groups are observed at higher field than the singlets from the protons of the C_5H_5 groups [10]; the ^1H -NMR spectra of compounds **8a** and **8b** each contain characteristic doublets for the protons of the methyl group (δ 1.04 and 0.97 ppm), two doublets of doublets for the methylene fragment, two multiplets for the methine fragments (δ 0.94 and 1.77; 0.89 and 1.76 ppm) [11], signals for the protons of the morpholine or piperidine substituents, two singlets for unsubstituted cyclopentadienyl rings and the appropriate number of multiplet signals for two substituted C_5H_4 moieties of the ferrocenyl substituents. The ^{13}C -NMR spectra of compounds **8a** and **8b** each contained two signals for $\text{C}_{\text{ipso}}\text{Fc}$ belonging to two ferrocene fragments, as well as the necessary number of signals for cyclopropyl-fragments δ 13.12, 20.54 ppm (2CH), 20.63 (CH_3) from **8a**, and δ 12.92, 20.26 (2CH), 21.34 ppm (CH_3) from **8b** [12]. The position of the heterocyclic substituents at the C(1) carbon atom of the bicycles **8a,b** was established based on the data from ^1H -NMR spectra with a one-dimensional NOE experiment, which showed the interaction of the protons of the two CH groups with the 2- CH_2 -protons of the heterocycles, that completely corroborated their structures. Additional proof of the structures of compounds **9a** and **9b** was obtained from X-ray diffraction analysis of a single crystal of compound **9b**, which was grown by crystallization from CH_2Cl_2 . A general view of **9b** is shown in Figure 1a, the character of packing of molecules in a crystal is shown in Figure 1b, and the main geometrical parameters are given in Table 1. Data from the X-ray analysis proved the structure of **9b** as 7-ferrocenyl-3,4-ferroceno-6-methyl-1-piperidinobicyclo-[3.2.1]oct-6-ene.

As inferred from the ^1H -NMR spectra of trienes **10a** and **10b**, they are formed as single isomers. The spectra contained each signals for the olefinic protons of the $-\text{CH}=\text{}$ fragments and the protons of the terminal $=\text{CH}_2$ group, singlets for the CH_3- group and two C_5H_5 fragments, as well as multiplets for the protons of the heterocyclic substituents. The data from ^{13}C -NMR spectroscopy of these compounds are in full accord with the proposed structures; however, the positions of the ferrocenyl and heterocyclic substituents remained uncertain.

Figure 1. (a) X-ray crystal structure of **9b**; (b) Crystal packing of **9b**.**Table 1.** Selected bond lengths and bond angles for **9b**, **10a** and **10b**.

Selected bond lengths (Å)		Selected bond angles (°)	
9b			
C(21)-C(22)	1.346(4)	C(2)-C(1)-C(23)	117.9(3)
C(22)-C(23)	1.526(4)	C(1)-C(2)-C(26)	122.9(3)
C(23)-C(24)	1.530(4)	C(1)-C(23)-C(22)	105.8(2)
C(24)-C(25)	1.541(4)	C(23)-C(22)-C(21)	109.9(3)
C(25)-C(26)	1.561(4)	C(22)-C(21)-C(25)	109.4(3)
C(25)-N(1)	1.473(4)	C(21)-C(25)-C(26)	106.7(2)
C(26)-C(2)	1.514(4)	C(21)-C(22)-C(27)	130.0(3)
C(1)-C(2)	1.430(4)	C(27)-C(22)-C(23)	119.2(3)
C(22)-C(27)	1.506(4)	C(22)-C(23)-C(24)	101.1(2)
10a			
C(21)-C(22)	1.317(6)	C(21)-C(22)-C(23)	122.8(4)
C(22)-C(23)	1.469(5)	C(22)-C(23)-C(24)	121.8(3)
C(23)-C(24)	1.353(5)	C(23)-C(24)-C(25)	121.3(3)
C(24)-C(25)	1.518(4)	C(24)-C(25)-C(26)	123.2(3)
C(25)-C(26)	1.336(5)	C(22)-C(23)-C(27)	115.8(3)
C(23)-C(27)	1.495(5)	C(24)-C(23)-C(27)	122.4(3)
C(25)-N(1)	1.423(4)	C(24)-C(25)-N(1)	113.6(3)
C(26)-C(1)	1.475(5)	N(1)-C(25)-C(26)	122.7(3)
C(24)-C(11)	1.489(4)	C(25)-C(26)-C(1)	128.7(3)
10b			
C(22)-N(1)	1.414(3)	C(26)-C(25)-C(24)	125.9(2)
C(22)-C(23)	1.501(3)	C(25)-C(24)-C(23)	122.1(2)
C(23)-C(24)	1.343(3)	C(25)-C(24)-C(27)	115.8(2)
C(24)-C(25)	1.468(3)	C(27)-C(24)-C(23)	122.1(2)
C(21)-C(22)	1.343(3)	C(24)-C(23)-C(22)	121.3(2)
C(25)-C(26)	1.326(3)	C(23)-C(22)-C(21)	122.7(2)
C(24)-C(27)	1.510(3)	C(21)-C(22)-N(1)	123.1(2)
C(23)-C(1)	1.480(3)	N(1)-C(22)-C(23)	113.90(19)
C(21)-C(11)	1.462(3)	C(24)-C(23)-C(1)	125.7(2)

To address this issue, we performed X-ray diffraction analysis of their single crystals grown by crystallization from dichloromethane. The general views of the molecules **10a** and **10b** are shown in Figures 2a,b and Figures 3a,b, respectively, and the main geometrical parameters are given in Table 1. Data from the X-ray analysis demonstrated that **10a** is (*E,E*)-1,3-diferrocenyl-4-methyl-2-morpholino-hexa-1,3,5-triene, and **10b** is (*E,E*)-1,3-diferrocenyl-4-methyl-2-piperidino-hexa-1,3,5-triene.

Figure 2. (a) X-ray crystal structure of **10a**; (b) Crystal packing of **10a**.

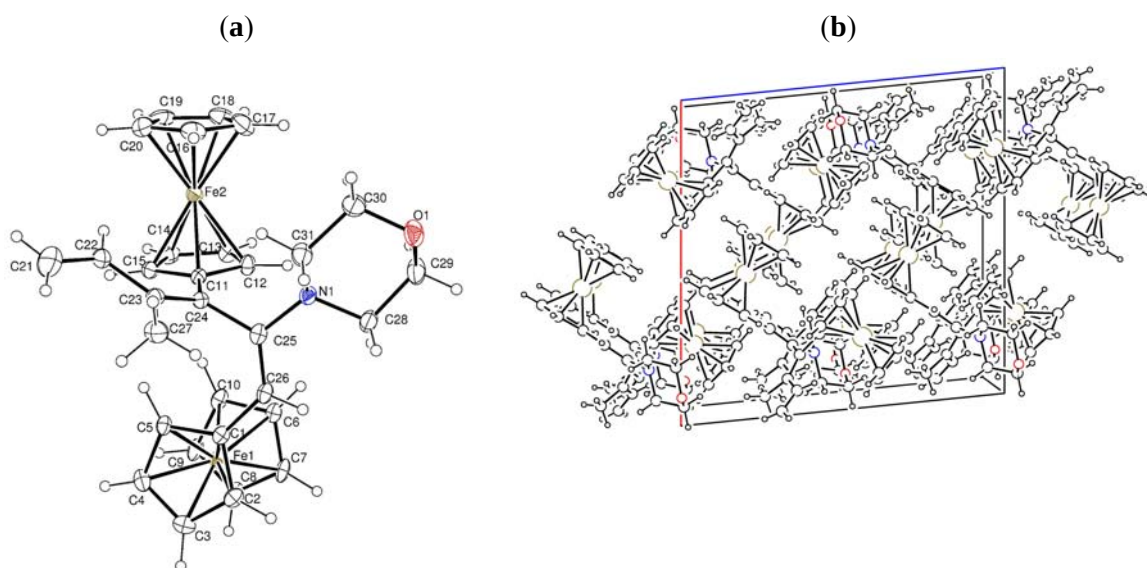
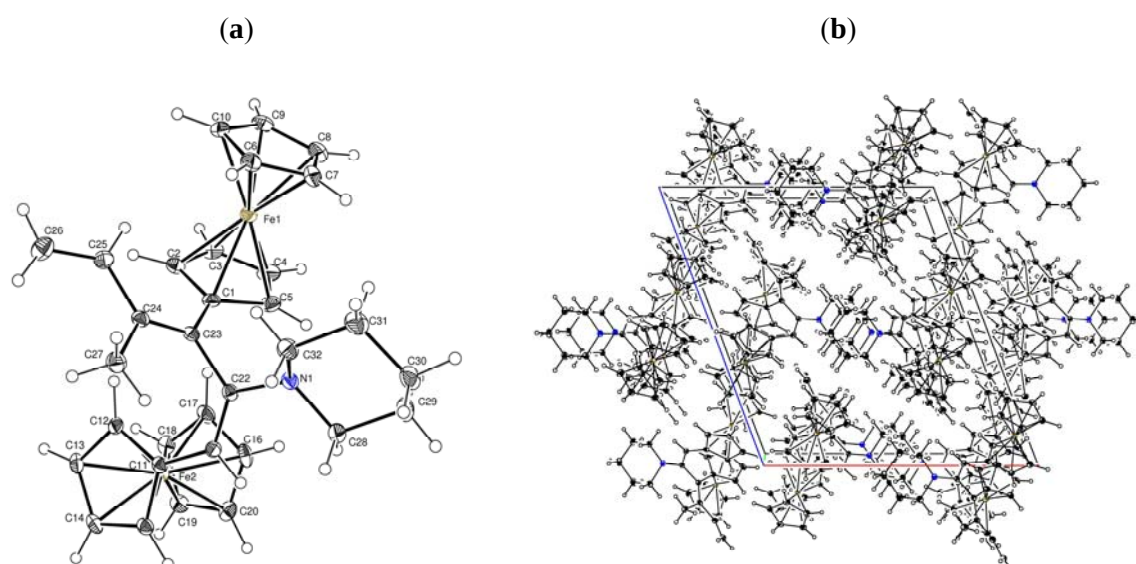


Figure 3. (a) X-ray crystal structure of **10b**; (b) Crystal packing of **10b**.

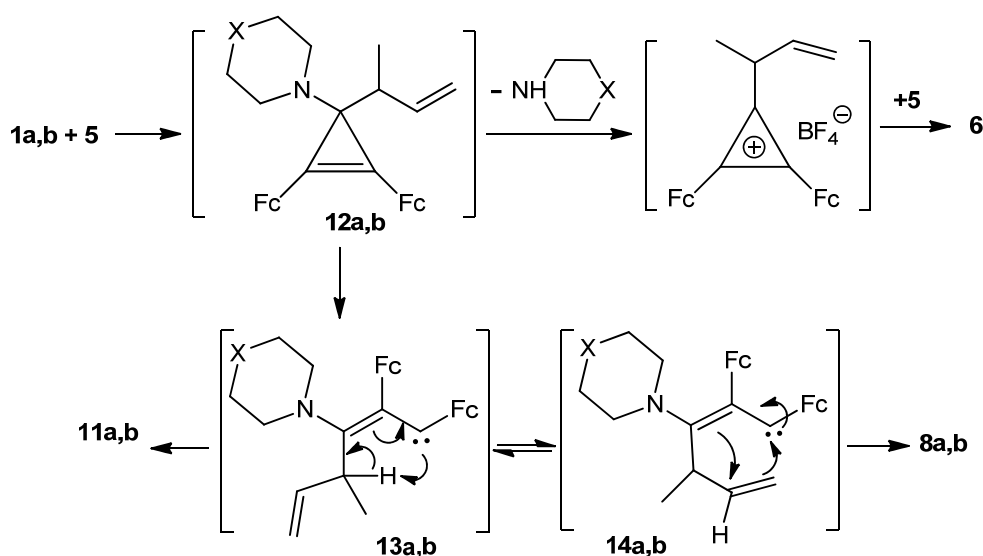


Compounds **11a** and **11b** were isolated as single geometrical isomers of (*Z,E*)-1,2-diferrocenyl-3-heteryl-4-methylhexa-1,3,5-trienes as inferred from the following data: the ^1H and ^{13}C -NMR spectra of each of them contain signals for two ferrocenyl, one methyl, and one heterocyclic substituents, two olefinic $-\text{CH}=\text{}$ and one terminal $\text{CH}_2=\text{}$ group. Presumably, the *Z*-arrangement of two ferrocenyl groups

at the C(2) = C(1) double bond was assigned based on comparison with *cis*-positions of two Fc-substituents in bicyclic products **8a,b**. The *E*-configuration of the C(3) = C(4) double bond was assigned based on comparison with *E*-configuration of the C(3) = C(4) in trienes **10a,b**.

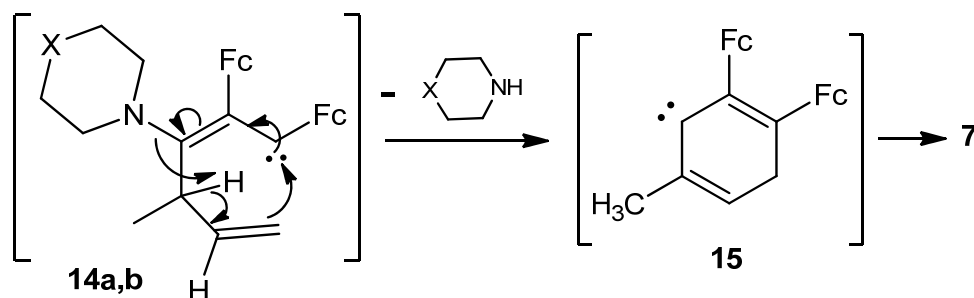
The most feasible mechanism of the formation of compounds **6**, **7**, **8a,b**, and **11a,b** involves the initial nucleophilic attack of the 1-methylprop-2-enyl anion on the heteroaryl-substituted carbon atom of the three-carbon ring of the cations **1a** and **1b** to afford unstable 1,2-diferrocenyl-3-heteroaryl-3-(1-methylprop-2-enyl)cyclopropenes **12a,b** (Scheme 3).

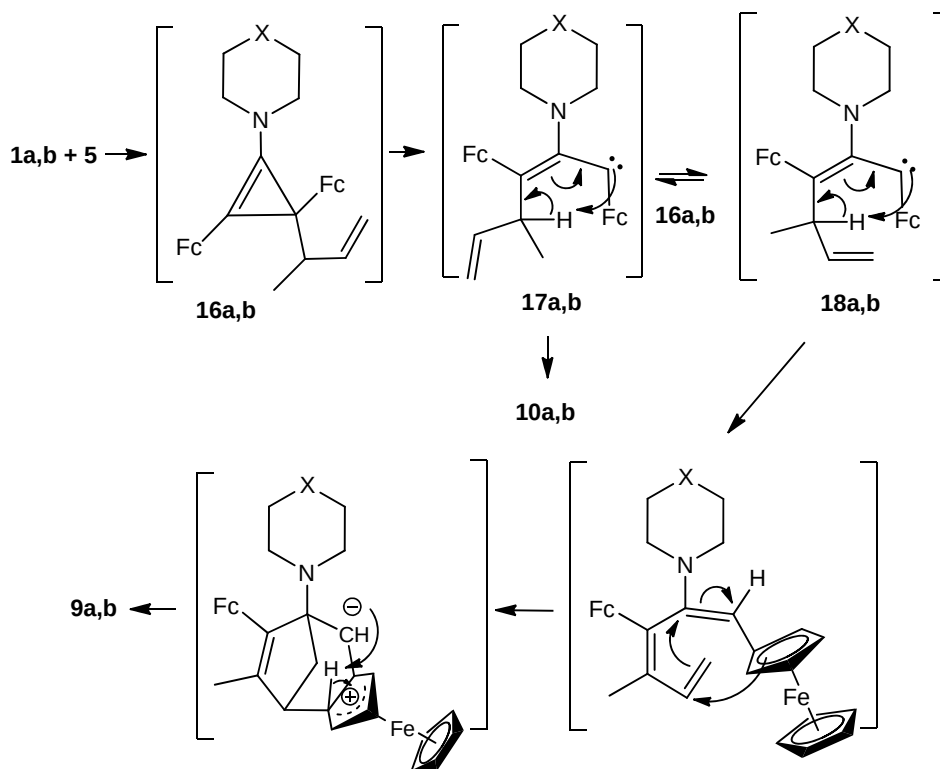
Scheme 3. Plausible mechanism of the formation of **6**, **8a,b** and **11a,b**.



The transformation of cyclopropenes with retention of the 3-membered ring and elimination of the heterocyclic substituents results in cyclopropene **6** (Scheme 3). Opening of the cyclopropene ring gives rise to bicyclic **8a,b** and linear triene products **11a,b** via 1,2-diferrocenyl-3-heteroaryl-3-(1-methylprop-2-enyl)carbenes **13a,b**. In our opinion, cyclization of carbenes in their configuration **13a,b** leads to bicyclic compounds **8a,b**, while it is the intramolecular transformation of these carbenes in the configuration **14a,b** results in (*Z,E*)-1,2-diferrocenyl-3-heteroaryl-4-methylhexa-1,3,5-trienes **11a,b** (Scheme 3). On the other hand, intramolecular transformation of carbenes **14a,b** with the loss of a heterocyclic substituent (Scheme 4) affords 3,4-diferrocenyltoluene **7** via transient 2,3-diferrocenyl-6-methylcyclohexa-2,5-dienylcarbene **15** (Scheme 4). Putative formation mechanisms of compounds **9a,b** and **10a,b** are depicted in Scheme 5.

Scheme 4. Plausible mechanism of the formation of **7**.



Scheme 5. Plausible mechanism of the formation of **9a,b** and **10a,b**.

The primary nucleophilic attack on the C(2) atom of cyclopropenylium cations **1a,b** affords unstable tetrasubstituted cyclopropenes **16a,b**. Small-ring opening in these transient species proceeds *via* 1,3-diferrocenyl-2-heterylallylcarbenes **17a,b** and **18a,b**, their intramolecular transformations result in tricyclic **9a,b** and linear **10a,b** final products. Compounds **9a,b** formed, like bicyclic products **8a,b**, from carbenes with configuration **18a,b**, while configuration **17a,b** of these carbenes gives rise to trienes **10a,b**.

2.2. Electrochemistry

In the framework of this work, we studied electrochemical behavior of compounds **7**, **8a**, **10a** and **10b** by means of cyclic voltammetry and square wave voltammetry. Figure 4 shows a typical voltammogram of compound **7** obtained in a platinum electrode. Two oxidation signals (**I_a** and **II_a**) with its complementary reduction signals (**I_c** and **II_c**) were detected. The anodic and cathodic peak potential values were independent of scan rate, which indicates the reversibility of the two processes. The logarithmic values of peak current and scan rate were linearly dependent, with a slope near 0.5; this behaviour is characteristic for a diffusion-controlled process. This evidence indicates that processes **I** and **II** are attributed to two consecutive electron transfers of ferrocene moieties.

In order to obtain the formal electrode potential for both processes, square wave voltammetry experiments were carried out (Figure 5). The obtained values were $E^{0'}(\text{I}) = 0.004 \text{ V/Fc-Fc}^+$ and $E^{0'}(\text{II}) = 0.232 \text{ V/Fc-Fc}^+$ with its corresponding difference $\Delta E^{0'}(\text{II-I}) = 0.228 \text{ V}$ and comproportionation constant K_{com} of 7151.3 [13,14]. The electrochemical response of **8a** was similar than those described above for **7**.

Figure 4. Cyclic voltammograms obtained for **7** in the presence of 0.1 M TBABF₄ in acetonitrile. Scan rate 0.5 V s⁻¹. The scan potential was initiated from E_{ocp} in the positive direction. The working electrode used was a platinum disc.

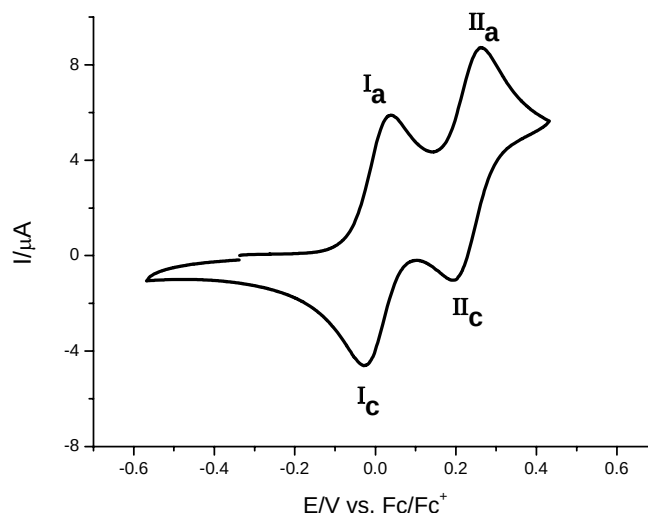
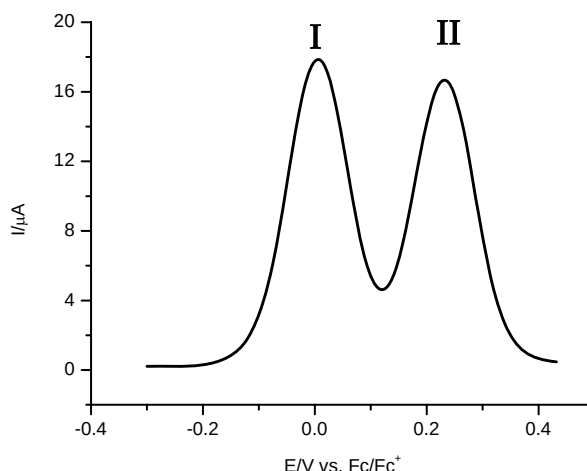


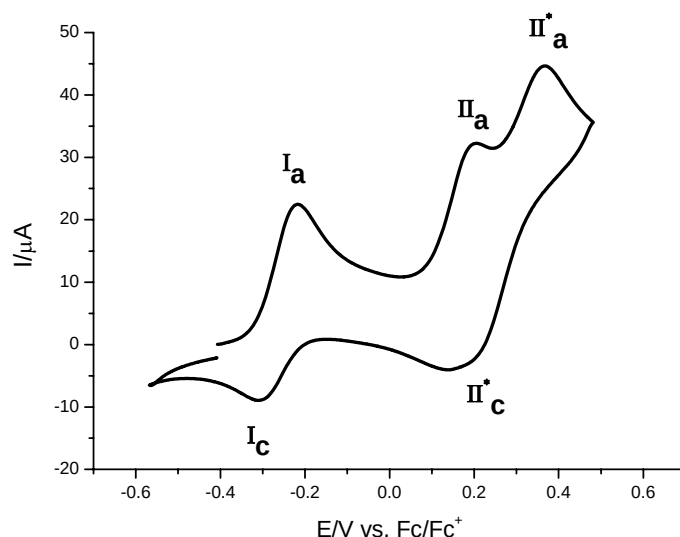
Figure 5. Square wave voltammetry obtained for **7** in the presence of 0.1 M TBABF₄ in acetonitrile. Amplitude of 50 mV with a frequency of 10 Hz and initiated from E_{ocp} in the positive direction. The working electrode used was a platinum disc.



The estimated values of E^{0'} (**I**) and E^{0'} (**II**) were 0.058 and = 0.159 V/Fc-Fc⁺ with ΔE^{0'} (**II-I**) = 0.101 V and K_{com} = 51.4. The highest value of ΔE^{0'} (**II-I**) for **7**, compared with the obtained value for **8a**, can be explained in terms of an increase in the electron density in ferrocene moieties due to the presence of an aromatic ring and the activating properties of the methyl substituent in **7**. This fact suggests that in the K_{com} values electron withdrawing and electron donating effects must be considered. Also, the difference in the conjugation manner in compounds **7** and **8a** could be the reason for the difference in ΔE^{0'} (**II-I**) values. Figure 6 presents cyclic voltamperometric response of compound **10a**. When the potential scan was initiated in the positive direction, three oxidation signals (**I**_a, **II'**_a, and **II''**_a) were observed, and when the potential scan was reversed, two reduction signals (**I**_c and **II'**_c) were also observed. We propose that the electrochemical process **I** with its corresponding oxidation and reduction signals, **I**_a and **I**_c, are attributed to electron transfer ferrocene/ferricinium⁺ for both moieties.

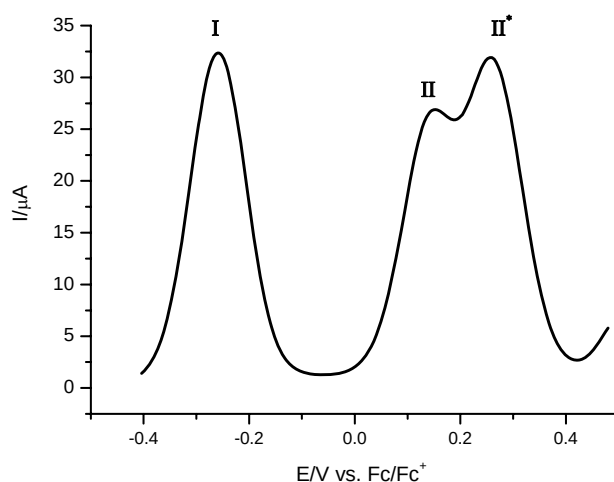
This is in agreement with the fact that a single electrochemical process is observed when there is no electronic communication between two redox centers, due to the long distance within a molecule, as occurs in compound **10a** (Figure 6).

Figure 6. Cyclic voltammograms obtained for **10a** in the presence of 0.1 M TBABF₄ in acetonitrile. Scan rate 0.5 V s⁻¹. The scan potential was initiated from E_{ocp} in the positive direction. The working electrode used was a platinum disc.



On the other hand, based on studies reported previously for molecules with conjugated double bonds, the processes II_a' and II_c' can be related to electrochemical generation of the monocation and dication species [15-21]. Controlled potential coulometry experiments acquired at potential step corresponding to anodic peak potential values for processes I, and II, led us to calculate the value of two electrons transferred for each process. The formal electrode potential values were evaluated also using square wave voltammetry experiments (Figure 7).

Figure 7. Square wave voltammetry obtained for **10a** in the presence of 0.1 M TBABF₄ in acetonitrile. Amplitude of 50 mV with a frequency of 10 Hz and initiated from E_{ocp} in the positive direction. The working electrode used was a platinum disc.



The values for $E^{0'}(\text{I})$, $E^{0'}(\text{II})$, and $E^{0'}(\text{II}^*)$ were -0.260 , 0.152 , and 0.256 V/Fc-Fc⁺, respectively. The electrochemical response of compound **10b** is similar that obtained for **10a**. However, different values of formal electrode potentials were observed. Table 2 shows a summary of electrochemical behaviour of compounds **7**, **8a**, **10a** and **10b**.

Table 2. Formal electrode potential $E^0(\text{I})$, $E^0(\text{II})$ and $\Delta E^0(\text{II-I})$, and constant K_{com} for compounds **7**, **8a**, **10a**, and **10b**.

Compound	$E^0(\text{I})^a$	$E^0(\text{II})^a$	$E^0(\text{II}^*)^b$	$E^0(\text{II}^*)^c$
7	0.004	0.232		
8a	0.058	0.101V		
10a	-0.260^d		0.152	0.256
10b	-0.328^d		0.136	0.240

3. Experimental

3.1. General

All the solvents were dried according to standard procedures [22] and were freshly distilled before use. Column chromatography and TLC were carried out on alumina (Brockmann activity III). The ¹H and ¹³C-NMR spectra of the compounds **6**, **7**, **8a,b**, **11a,b** were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CDCl₃, with Me₄Si as the internal standard. The IR spectra were measured with an FTIR spectrophotometer (Spectrum RXI Perkin-Elmer instruments) using KBr pellets. UV spectra were recorded on a Specord UV-VIS spectrophotometer. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). A LECO CHNS-900 Elemental Analysensysteme was used for elemental analyses.

Electrochemical measurements were carried out in acetonitrile containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) with sample concentration c.a. 1 mM. An Epsilon-BAS potentiostat/galvanostat was used for all experiments. A typical three-electrode array was employed; using a platinum disk as working electrode and a platinum wire as counter-electrode. A silver wire immersed in acetonitrile solution with 0.1 M tetra-*n*-butylammonium chloride (TBACl) was used as a pseudo reference electrode. Before each measurement all solutions were bubbled with nitrogen. Cyclic voltammetry experiments were acquired from the open circuit potential (E_{ocp}) to positive direction, at different scan rates (from 0.1 to 0.5 V s^{−1}). Square wave voltammetry experiments using amplitude of 50 mV with a frequency of 10 Hz were also performed. All potentials were reported versus the Fc/Fc⁺ couple, according to the IUPAC convention [23].

The following reagents were purchased from Aldrich: Tetrachlorocyclopropene, 98%; ferrocene, 98%; triethyloxonium tetrafluoroborate, 1.0 M solution in dichloromethane; morpholine, 99.5%; piperidine, 99%; 1-methyl-2-propenylmagnesium chloride, 0.5M solution in tetrahydrofuran. *Ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate* was obtained by treating 2,3-diferrocenylcyclopropenone [2] in dichloromethane with triethyloxonium tetrafluoroborate. *Diferrocenyl(morpholino)- or (piperidino)cyclopropenylium tetrafluoroborates 1a,b* were obtained from ethoxy(diferrocenyl)-cyclopropenylium tetrafluoroborate and morpholine or piperidine in dichloromethane [1].

Reactions of *diferrocenyl(morpholino)- or (piperidino)cyclopropenylium tetrafluoroborates 1a,b* with 1-methyl-2-propenylmagnesium chloride (5). 1-Methyl-2-propenylmagnesium chloride (5, 20.0 mL of a 0.5 M solution in tetrahydrofuran) was added to a suspension of salt **1a** or **1b** (5.0 mmol) in dry benzene (100 mL) and the mixture was stirred in an inert dry atmosphere (~70–80 °C) until complete dissolution of the salts **1a,b** occurred (~6–8 h). The excess of the organometallic compound was quenched with water (20 mL), the organic layer was separated, concentrated, and the residue was chromatographed on alumina (Brockmann activity III, hexane-dichloromethane, 7:1) to give compounds **6**, **7**, **8a–11a** and **8b–11b**.

1,2-Diferrocenyl-3,3-di-(3-buten-2-yl)cyclopropene (6). Orange powder, yield: 0.18–0.26 g (7%–10%), m.p. 103–104 °C (hexane); ¹H-NMR: 0.88 (d, 3H, CH₃, *J* = 6.9 Hz), 1.11 (d, 3H, CH₃, *J* = 6.9 Hz), 2.65 (m, 2H, 2CH), 4.19 (s, 5H, C₅H₅), 4.21 (s, 5H, C₅H₅), 4.34 (m, 3H, C₅H₄), 4.36 (m, 3H, C₅H₄), 4.52 (m, 2H, C₅H₄), 4.97–5.04 (m, 4H, 2CH₂=), 5.84–5.98 (m, 2H, 2CH=); ¹³C-NMR: 18.63, 18.81 (2CH₃), 42.66, 43.19 (2CH), 45.06 (C), 69.32, 69.37 (2C₅H₅), 68.91, 69.00, 69.04, 69.08, 69.27, 69.42, 69.44, 69.46 (2C₅H₄), 76.04 (2C_{ipso}Fe), 112.58, 112.88 (2CH₂=), 144.87, 144.95 (2CH=), 144.56 (2C); MS: *m/z* 516 [M]⁺. Anal. Calcd. for C₃₁H₃₂Fe₂: C, 72.11; H, 6.25; Fe, 21.64%. Found: C, 72.23; H, 6.17; Fe, 21.81.

3,4-Diferrocenyltoluene (7). Orange powder, yield: 0.12–0.18 g (5%–8%), m.p. 124–125 °C; ¹H-NMR: 2.40 (s, 3H, CH₃), 4.00 (s, 5H, C₅H₅), 4.02 (s, 5H, C₅H₅), 4.04 (m, 2H, C₅H₄), 4.06 (m, 2H, C₅H₄), 4.09 (m, 4H, C₅H₄), 7.03 (d, 1H, C₆H₃ *J* = 8.4 Hz), 7.55 (s, 1H, C₆H₃), 7.62 (d, 1H, C₆H₃ *J* = 8.4 Hz); ¹³C-NMR: 21.17 (CH₃), 69.32, 69.37 (2C₅H₅), 67.08, 67.15, 70.56, 70.65 (2C₅H₄), 87.81, 87.83 (2C_{ipso}Fe), 126.54, 131.24, 131.87 (C₆H₃), 134.28, 134.93, 136.99 (3C_{ipso}); MS: *m/z* 460 [M]⁺. Anal. Calcd. for C₂₇H₂₄Fe₂: C, 70.47; H, 5.26; Fe, 24.27. Found: C, 70.36; H, 5.40; Fe, 24.15.

2,3-Diferrocenyl-6-methyl-1-morpholinobicyclo[3.1.0]hex-2-ene (8a). Orange oil, yield: 0.27 g (10%); IR (KBr): 484, 755, 817, 876, 906, 969, 1002, 1031, 1044, 1106, 1119, 1172, 1220, 1263, 1302, 1360, 1449, 1614, 1714, 2250, 2734, 2851, 2955, 3093 cm⁻¹; ¹H-NMR: 0.94 (m, 1H, CH), 1.04 (d, 3H, CH₃, *J* = 6.9 Hz), 1.77 (m, 1H, CH), 2.35 (dd, 1H, CH₂, *J* = 4.8, 16.5 Hz), 2.63 (dd, 1H, CH₂, *J* = 6.6, 16.5 Hz), 2.78 (m, 4H, 2 CH₂), 3.48 (m, 4H, 2 CH₂), 3.91 (s, 5H, C₅H₅), 4.00 (s, 5H, C₅H₅), 3.84 (m, 2H, C₅H₄), 3.89 (m, 2H, C₅H₄), 3.94 (m, 2H, C₅H₄), 4.04 (m, 2H, C₅H₄); ¹³C-NMR: 13.12, 20.54 (2CH), 20.63 (CH₃), 34.23 (CH₂), 40.38, 50.13 (4CH₂), 65.09 (C), 68.43, 68.75 (2C₅H₅), 67.21, 67.42, 67.61, 67.89, 68.52, 68.91, 69.54, 69.71 (2C₅H₄), 82.80, 83.14 (2C_{ipso}Fe), 133.45, 135.12 (2C); MS: *m/z* 547 [M]⁺. Anal. Calcd. for C₃₁H₃₃Fe₂NO: C, 68.03; H, 6.08; Fe, 20.41; N, 2.56. Found: C, 67.96; H, 6.13; Fe, 20.55; N, 2.60.

7-Ferrocenyl-3,4-ferroceno-6-methyl-1-morpholinobicyclo[3.2.1]oct-6-ene (9a). Orange crystals, yield: 0.82 g (30%), m.p. 167–168 °C; IR (KBr): 497, 802, 809, 820, 998, 1025, 1106, 1153, 1304, 1390, 1442, 1465, 1630, 1715, 1768, 2184, 2793, 2918, 2952, 2976, 3075, 3107 cm⁻¹; ¹H-NMR: 1.75 (dd, 1H, CH₂, *J* = 5.7, 13.8 Hz), 1.85 (s, 3H, CH₃), 1.98 (dd, 1H, CH₂, *J* = 8.4, 13.8 Hz), 2.36 (d, 1H, CH₂, *J* = 12.6 Hz), 2.62 (d, 1H, CH₂, *J* = 12.6 Hz), 2.70 (m, 2H, CH₂), 2.93 (m, 1H, CH), 3.66 (m, 4H, 2CH₂), 3.88 (m, 4H, 2CH₂), 3.93 (s, 5H, C₅H₅), 4.04 (s, 5H, C₅H₅), 3.41 (m, 1H), 3.82 (m, 1H), 4.06 (m, 1H), 4.28 (m, 2H), 4.35 (m, 1H), 5.30 (m, 1H) (C₅H₄, C₅H₃); ¹³C-NMR: 17.01 (CH₃), 35.16, 36.66

(2CH₂), 46.31 (CH), 57.42, 67.71 (4 CH₂), 68.95 (C), 68.68, 69.36 (2C₅H₅), 67.14, 67.29, 67.87, 69.49, 70.22, 70.87, 72.91 (C₅H₄, C₅H₃), 76.83, 80.06, 93.47 (3C_{ipso}Fc), 136.22, 139.37 (2C); MS: m/z 547 [M]⁺. Anal. Calcd. for C₃₁H₃₃Fe₂NO: C, 68.03; H, 6.08; Fe, 20.41; N, 2.56. Found: C, 68.14; H, 5.97; Fe, 20.32; N, 2.41.

E,E-1,3-Diferrocenyl-4-methyl-2-morpholinohexa-1,3,5-triene (**10a**). Orange crystals, yield: 0.62 g (22%), m.p. 174–176 °C. $\lambda_{\max}$ (CHCl₃, 20 °C) 211, 282 nm; IR (KBr): 490, 817, 906, 1000, 1026, 1044, 1106, 1119, 1166, 1220, 1276, 1374, 1444, 1581, 1615, 1819, 2049, 2185, 2730, 2816, 2853, 2947, 3079, 3091 cm⁻¹; ¹H-NMR: 1.77 (s, 3H, CH₃), 2.92 (m, 4H, 2CH₂), 3.68 (m, 4H, 2CH₂), 4.00 (s, 5H, C₅H₅), 4.14 (s, 5H, C₅H₅), 4.05 (m, 2H, C₅H₄), 4.17 (m, 1H, C₅H₄), 4.22 (m, 1H, C₅H₄), 4.24 (m, 1H, C₅H₄), 4.33 (m, 1H, C₅H₄), 4.35 (m, 1H, C₅H₄), 4.37 (m, 1H, C₅H₄), 5.11 (s, 1H, CH=), 5.29 (dd, 1H, CH₂=, J = 1.2, 11.1 Hz), 5.35 (dd, 1H, CH₂=, J = 1.2, 17.4 Hz), 7.89 (dd, 1H, CH=, J = 11.1, 17.4 Hz); ¹³C-NMR: 16.60 (CH₃), 48.17, 67.15 (4CH₂), 69.01, 69.39 (2C₅H₅), 67.18, 67.30, 67.62, 67.66, 67.95 (2C), 70.95, 71.52 (2C₅H₄), 84.96, 85.23 (2C_{ipso}Fc), 113.86 (CH₂=), 100.24, 137.15 (2CH=), 132.68, 134.15, 147.82 (3C); MS: m/z 547 [M]⁺. Anal. Calcd. for C₃₁H₃₃Fe₂NO: C, 68.03; H, 6.08; Fe, 20.41; N, 2.56. Found: C, 68.09; H, 6.14; Fe, 20.53; N, 2.38.

Z,E-1,2-Diferrocenyl-4-methyl-3-morpholinohexa-1,3,5-trienes (**11a**). Orange oil, yield: 0.33 g (12%). $\lambda_{\max}$ (CHCl₃, 20 °C) 211, 292 nm; IR (KBr): 493, 815, 822, 865, 896, 1000, 1026, 1106, 1119, 1163, 1226, 1249, 1301, 1386, 1446, 1625, 1651, 2298, 2852, 2956, 3091 cm⁻¹; ¹H-NMR: 1.95 (s, 3H, CH₃), 3.17 (m, 4H, 2CH₂), 3.60–3.73 (m, 4H, 2CH₂), 4.01 (s, 5H, C₅H₅), 4.08 (s, 5H, C₅H₅), 3.97 (m, 2H, C₅H₄), 4.20 (m, 2H, C₅H₄), 4.28 (m, 2H, C₅H₄), 4.37 (m, 2H, C₅H₄), 5.15 (dd, 1H, CH₂=, J = 0.9, 11.4 Hz), 5.36 (dd, 1H, CH₂=, J = 0.9, 16.8 Hz), 6.25 (s, 1H, CH=), 7.03 (dd, 1H, CH=, J = 11.4, 16.8 Hz); ¹³C-NMR: 15.87 (CH₃), 45.84, 65.13 (4CH₂), 68.88, 69.12 (2C₅H₅), 68.46, 68.81, 69.34, 70.12 (2C₅H₄), 80.76, 82.60 (2C_{ipso}Fc), 116.72 (CH₂=), 128.62, 134.06 (2CH=), 132.42, 133.74, 148.13 (3C); MS: m/z 547 [M]⁺. Anal. Calcd. for C₃₁H₃₃Fe₂NO: C, 68.03; H, 6.08; Fe, 20.41; N, 2.56. Found: C, 67.87; H, 6.01; Fe, 20.31; N, 2.24.

2,3-Diferrocenyl-6-methyl-1-piperidinobicyclo[3.1.0]hex-2-ene (**8b**). Orange oil, yield: 0.22 g (8%); IR (KBr): 487, 761, 815, 874, 906, 966, 1001, 1017, 1024, 1103, 1117, 1175, 1214, 1263, 1303, 1360, 1444, 1617, 1716, 2247, 2723, 2867, 2909, 3093 cm⁻¹; ¹H-NMR: 0.89 (m, 1H, CH), 0.97 (d, 3H, CH₃, J = 6.9 Hz), 1.49 (m, 2H, CH₂), 1.76 (m, 1H, CH), 2.27 (dd, 1H, CH₂, J = 4.5, 16.2 Hz), 2.46 (dd, 1H, CH₂, J = 6.6, 16.2 Hz), 2.63 (m, 4H, 2CH₂), 3.04 (m, 4H, 2CH₂), 3.87 (s, 5H, C₅H₅), 3.98 (s, 5H, C₅H₅), 3.82 (m, 2H, C₅H₄), 3.92 (m, 2H, C₅H₄), 4.00 (m, 2H, C₅H₄), 4.02 (m, 2H, C₅H₄); ¹³C-NMR: 12.92, 20.46 (2CH), 21.34 (CH₃), 32.45 (CH₂), 47.56 (5CH₂), 33.87, 40.19 (5CH₂), 64.17 (C), 68.36, 68.59 (2C₅H₅), 67.19, 67.40, 67.54, 67.82, 68.73, 68.99, 69.32, 69.34 (2C₅H₄), 82.54, 82.87 (2C_{ipso}Fc), 132.62, 133.91 (2C); MS: m/z 545 [M]⁺. Anal. Calcd. for C₃₂H₃₅Fe₂N: C, 70.48; H, 6.47; Fe, 20.48; N, 2.57. Found: C, 70.32; H, 6.54; Fe, 20.31; N, 2.35.

7-Ferrocenyl-3,4-ferroceno-6-methyl-1-piperidinobicyclo[3.2.1]oct-6-ene (**9b**). Orange crystals, yield: 0.84 g (31%), m.p. 198–199 °C; IR (KBr): 498, 801, 810, 819, 999, 1024, 1105, 1153, 1307, 1394, 1439, 1464, 1629, 1715, 1764, 2184, 2797, 2912, 2941, 2971, 3075, 3103 cm⁻¹; ¹H-NMR: 0.87 (m, 2H, CH₂), 1.44 (m, 4H, 2CH₂), 1.85 (s, 3H, CH₃), 2.11 (m, 4H, 2CH₂), 2.21 (dd, 1H, CH₂, J = 5.1, 9.6 Hz),

2.33 (d, 1H, CH₂, $J = 9.6$ Hz), 2.69 (d, 1H, CH₂, $J = 15.6$ Hz), 2.92(d, 1H, CH, $J = 5.1$ Hz), 3.27 (d, 1H, CH₂, $J = 15.6$ Hz), 3.74 (s, 5H, C₅H₅), 4.08 (s, 5H, C₅H₅), 3.94 (m, 1H), 3.97 (m, 2H), 4.07 (m, 2H), 4.31 (m, 1H), 4.97 (m, 1H), 5.30 (C₅H₄, C₅H₃); ¹³C-NMR: 15.99 (CH₃), 25.65, 29.96, 36.54 (3CH₂), 45.00 (CH), 26.99, 48.44 (4CH₂), 68.82 (C), 68.68, 69.36 (2C₅H₅), 63.14, 64.61, 66.58, 67.12, 67.37, 67.78, 75.07 (C₅H₄, C₅H₃), 80.34, 83.90, 91.81 (3C_{ipso}Fe), 131.42, 141.58 (2C); MS: m/z 545 [M]⁺. Anal. Calcd. for C₃₂H₃₅Fe₂N: C, 70.48; H, 6.47; Fe, 20.48; N, 2.57. Found: C, 70.57; H, 6.32; Fe, 20.53; N, 2.65.

E,E-1,3-Diferrocenyl-4-methyl-2-piperidino-hexa-1,3,5-triene (**10b**). Orange crystals, yield: 0.57 g (21%), m.p. 206–207 °C; $\lambda_{\max}$ (CHCl₃, 20 °C) 211, 293 nm; IR (KBr): 492, 819, 903, 1004, 1024, 1046, 1106, 1121, 1163, 1225, 1277, 1375, 1444, 1580, 1621, 1820, 2037, 2191, 2728, 2815, 2839, 2952, 3081, 3093 cm⁻¹; ¹H-NMR: 1.53 (m, 6H, 3CH₂), 1.74 (s, 3H, CH₃), 2.96 (m, 4H, 2CH₂), 3.97 (s, 5H, C₅H₅), 4.15 (s, 5H, C₅H₅), 4.01 (m, 2H, C₅H₄), 4.12 (m, 1H, C₅H₄), 4.20 (m, 1H, C₅H₄), 4.22 (m, 1H, C₅H₄), 4.34 (m, 1H, C₅H₄), 4.36 (m, 1H, C₅H₄), 4.37 (m, 1H, C₅H₄), 5.05 (s, 1H, CH=), 5.24 (dd, 1H, CH₂=, $J = 1.5$, 11.1 Hz), 5.31 (dd, 1H, CH₂=, $J = 1.5$, 17.4 Hz), 7.84 (dd, 1H, CH=, $J = 11.1$, 17.4 Hz); ¹³C-NMR: 16.48 (CH₃), 24.76 (CH₂), 26.35, 44.86 (4CH₂), 68.98, 69.39 (2C₅H₅), 67.03, 67.43, 67.53, 67.69, 67.90, 69.37, 70.88, 71.78 (2C₅H₄), 85.43, 85.91 (2C_{ipso}Fe), 113.35 (CH₂=), 99.29, 137.44 (2CH=), 133.50, 133.79, 148.87 (3C); MS: m/z 545 [M]⁺. Anal. Calcd. for C₃₂H₃₅Fe₂N: C, 70.48; H, 6.47; Fe, 20.48; N, 2.57. Found: C, 70.37; H, 6.58; Fe, 20.61; N, 2.49.

Z,E-1,2-Diferrocenyl-4-methyl-3-piperidino-hexa-1,3,5-trienes (**11b**). Orange oil, yield: 0.43 g (16%). $\lambda_{\max}$ (CHCl₃, 20 °C) 211, 294 nm; IR (KBr): 489, 812, 818, 860, 896, 1006, 1021, 1103, 1121, 1163, 1224, 1251, 1302, 1385, 1443, 1625, 1648, 2294, 2855, 2962, 3093 cm⁻¹; ¹H-NMR: 1.02–1.21 (m, 2H, CH₂), 1.34–1.45 (m, 4H, 2CH₂), 1.90 (s, 3H, CH₃), 2.35 (m, 4H, 2 CH₂), 4.00 (s, 5H, C₅H₅), 4.09 (s, 5H, C₅H₅), 3.85 (m, 2H, C₅H₄), 3.93 (m, 2H, C₅H₄), 4.13 (m, 2H, C₅H₄), 4.22 (m, 2H, C₅H₄), 5.12 (dd, 1H, CH₂=, $J = 1.2$, 11.1 Hz), 5.24 (dd, 1H, CH₂=, $J = 1.2$, 17.4 Hz), 6.18 (s, 1H, CH=), 6.97 (dd, 1H, CH=, $J = 11.1$, 17.4 Hz); ¹³C-NMR: 15.63, (CH₃), 20.67 (CH₂), 25.95, 37.86 (4CH₂), 68.47, 69.02 (2C₅H₅), 68.17, 68.23, 69.25, 70.01 (2C₅H₄), 81.04, 82.47 (2C_{ipso}Fe), 116.74 (CH₂=), 126.63, 130.13 (2CH=), 131.65, 134.01, 147.29 (3C); MS: m/z 545 [M]⁺. Anal. Calcd. for C₃₂H₃₅Fe₂N: C, 70.48; H, 6.47; Fe, 20.48; N, 2.57. Found: C, 70.55; H, 6.34; Fe, 20.60; N, 2.61.

3.2. Crystal structures of **9b**, **10a** and **10b**

Crystals of **9b**, **10a** and **10b** were obtained from dichloromethane. The unit cell parameters and the X-ray diffraction intensities of **10a** were recorded on a Siemens P4 diffractometer, of **9b** and **10b** on a Gemini (detector Atlas CCD, Cryojet N₂) diffractometer. The structure of compounds **9b**, **10a** and **10b** were solved by the direct method (SHELXS [24]) and refined using full-matrix least-squares on F^2 .

Crystal data for C₃₂H₃₅Fe₂N (**9b**): $M = 545.31$ g mol⁻¹, monoclinic P2₁/n, $a = 10.5528(9)$, $b = 10.3965(9)$, $c = 22.888(2)$ Å, $\alpha = 90$, $\beta = 93.605(10)$, $\gamma = 90^\circ$, $V = 2506.1(4)$ Å³, $T = 130(2)$ K, $Z = 4$, $\rho = 1.445$ Mg/m³, λ (Mo – K α) = 0.71073 Å, $F(000) = 1144$, absorption coefficient 9.429 mm⁻¹, crystal size 0.444 × 0.2658 × 0.1397 mm³, index ranges $-12 \leq h \leq 12$, $-12 \leq k \leq 8$, $-27 \leq l \leq 27$, scan range $3.87 \leq \theta \leq 68.09^\circ$, 4574 independent reflections, $R_{\text{int}} = 0.0757$, 14354 total reflections,

318 refinable parameters, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0487$, $wR_2 = 0.1299$, R indices (all data) $R_1 = 0.0588$, $wR_2 = 0.1388$, goodness-of-fit on F^2 1.083, largest difference peak and hole $0.482/-0.915 \text{ e}\text{\AA}^{-3}$.

Crystal data for $C_{31}H_{33}Fe_2NO$ (10a): $M = 547.28 \text{ g mol}^{-1}$, monoclinic P21/c, $a = 15.602(1)$, $b = 10.598(2)$, $c = 15.362(1) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 95.844(5)$, $\gamma = 90^\circ$, $V = 2526.9(5) \text{ \AA}^3$, $T = 298(2) \text{ K}$, $Z = 4$, $\rho = 1.439 \text{ Mg/m}^3$, $\lambda (\text{Mo} - K\alpha) = 0.71073 \text{ \AA}$, $F(000) = 1144$, absorption coefficient 1.173 mm^{-1} , crystal size $0.6003 \times 0.4151 \times 0.0545 \text{ mm}^3$, index ranges $-15 \leq h \leq 19$, $-13 \leq k \leq 9$, $-19 \leq l \leq 18$, scan range $3.25 \leq \theta \leq 26.62^\circ$, 5270 independent reflections, $R_{\text{int}} = 0.0456$, 11939 total reflections, 317 refinable parameters, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0551$, $wR_2 = 0.1644$, R indices (all data) $R_1 = 0.0715$, $wR_2 = 0.1781$, goodness-of-fit on F^2 1.090, largest difference peak and hole $1.348/-0.600 \text{ e}\text{\AA}^{-3}$.

Crystal data for $C_{32}H_{35}Fe_2N$ (10b): $M = 545.31 \text{ g mol}^{-1}$, monoclinic P21/c, $a = 15.5360(5)$, $b = 10.2960(2)$, $c = 16.8430(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 110.613(3)$, $\gamma = 90^\circ$, $V = 2521.70(12) \text{ \AA}^3$, $T = 130(2) \text{ K}$, $Z = 4$, $\rho = 1.436 \text{ Mg/m}^3$, $\lambda (\text{Mo} - K\alpha) = 0.71073 \text{ \AA}$, $F(000) = 1144$, absorption coefficient 1.172 mm^{-1} , crystal size $0.5175 \times 0.1764 \times 0.1143 \text{ mm}^3$, index ranges $-15 \leq h \leq 19$, $-11 \leq k \leq 12$, $-20 \leq l \leq 20$, scan range $3.43 \leq \theta \leq 26.06^\circ$, 4978 independent reflections, $R_{\text{int}} = 0.0442$, 18609 total reflections, 317 refinable parameters, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0382$, $wR_2 = 0.0979$, R indices (all data) $R_1 = 0.0502$, $wR_2 = 0.1020$, goodness-of-fit on F^2 0.990, largest difference peak and hole $0.830/-0.498 \text{ e}\text{\AA}^{-3}$.

CCDC-804034 (for **9b**), CCDC-804035 (for **10a**) and CCDC-804036 (for **10b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

4. Conclusions

The reactions of 1-amino-2,3-diferrocenylcyclopropenylum cations **1a,b** with strong C-nucleophiles are nonregioselective (unlike the reactions with β -dicarbonyl compounds). The carbanions attack the C(1) and C(2) atoms of the cyclopropenylum cations with equal probability to afford two types of tetrasubstituted cyclopropenes, viz., 3-amino-1,2-diferrocenyl- and 1-amino-2,3-diferrocenylcyclopropenes. Intramolecular transformations of the latter formed due to opening of the three-membered ring giving rise to two types of diferrocenylvinylcarbene species **13a,b**, **14a,b**, **15** and **17a,b**, **18a,b** differing in location of ferrocenyl, methyl, allyl and heteroaryl substituents in the carbon chain. Their intramolecular conversions to cyclic, bicyclic, tricyclic and linear final products certainly form the basis for further investigations in the fields of theoretical and synthetic organic chemistry, the search for new methods for an access to practically valuable materials.

The electrochemical behaviour of compounds **7**, **8a**, **10a** and **10b** was investigated by means of cyclic voltammetry and square wave voltammetry. For **7** and **8a** two electrochemical processes (I-II), attributed to the oxidation of the ferrocene moieties were found. On the other hand for compounds **10a** and **10b** a single electron transfer for both ferrocene groups and the electrochemical generation of the monocation and dication species were detected.

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Conflict of Interest

The authors declare no conflict of interest.

References and Notes

1. Klimova, E.I.; Klimova, B.T.; Hernández Ortega, S.; Méndez Iturbide, D.; García Marquez, A.; Martínez García, M. Diferrocenylcyclopropenyl cations. Synthesis, structures, and some chemical properties. *J. Organomet. Chem.* **2005**, *690*, 3332-3335.
2. Klimova, E.I.; Klimova, T.; Betanzos Lara, S.; Dominguez Chavez, J.; Hernández Ortega, S.; Toscano, A.; Martínez García, M. Synthesis of stable 1-ethoxy-2,3-diferrocenylcyclopropenylum tetrafluoroborate and its reactions with lithium reagent. *J. Organomet. Chem.* **2006**, *691*, 1-8.
3. Klimova, B.T.; Martínez García, M.; Ortiz-Frade, L.; Hernández Ortega, S.; Toscano, R.A.; Klimova, E.I. Synthesis, structures and some chemical and electrochemical properties of *E*-1,2-diferrocenyl-3-methylthioprop-2-enone and its ketals. *J. Organomet. Chem.* **2006**, *691*, 2872-2882.
4. Klimova Berestneva, T.; Klimova, E.I.; Méndez Stivalet, J.M.; Hernandez Ortega, S.; Martínez García, M. Diferrocenyl(methylthio)cyclopropenylum iodide in the synthesis of 2,3-diferrocenyl-1-methylthio-1,3-dienes and -1,3,5-trienes. *Eur. J. Org. Chem.* **2005**, 4406-4413.
5. Klimova, E.I.; Klimova Berestneva, T.; Hernandez-Ortega, S.; Ortiz-Frade, L.A.; Backinowsky, L.V.; Martínez García, M. 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. *J. Organomet. Chem.* **2008**, *693*, 1215-1224.
6. Klimova, E.I.; Mendez Stivalet, J.M.; Klimova Berestneva, T.; Flores Alamo, M.; Backinowsky, L.V.; Ortiz Frade, L.; Martínez García, M. Reactions of diferrocenylmorpholino- and methylsulfanyl-cyclopropenylum salts with β -dicarbonyl compounds and diethyl malonate. *Syn. Commun.* **2010**, *40*, 839-854.
7. Klimova, E.I.; Klimova, T.; Flores Alamo, M.; Backinowsky, L.V.; Martinez García, M. Intramolecular transformations of 3-cyanoamino- and 3-cyanoimino-1,2-diferrocenylcyclopropenes. *Molecules* **2009**, *14*, 3161-3175.
8. Schvekhgeimer, M.-G.A. Heterylferrocenes. *Russ. Chem. Rev.* **1996**, *65*, 80-112.
9. Klimova, E.I.; Klimova, T.; Ruiz Ramirez, L.; Cinquantini, A.; Corsini, M.; Zanello, P.; Hernandez Ortega, S.; Martinez Garcia, M. 2,3-Diferrocenylcyclopropenone: Synthesis, structure and some chemical and electrochemical properties. *Eur. J. Org. Chem.* **2003**, 4265-4275.
10. Klimova, E.I.; Ruiz Ramirez, L.; Martinez García, M.; Espinosa, R.G.; Meleshonkova, N.N. Synthesis of biologically active compounds based on 2-ferocenylmethylene-3-quinuclidone. *Russ. Chem. Bull.* **1996**, *45*, 2602-2609.

11. Klimova, E.I.; Sazonova, V.A.; Pushin, A.N. Reaction of 1,2-diferrocenylcyclopropanes with trityl tetrafluoroborate. *Zh. Obshch. Khim.* **1987**, *57*, 2336-2342.
12. Nesmeyanov, A.N.; Klimova, E.I.; Struchkov, Yu.T.; Postnov, V.N.; Andrianov, V.G.; Postnov, V.N.; Sazonova, V.A. Cyclopropanes with a ferrocenyl group. *J. Organomet. Chem.* **1979**, *178*, 343-348.
13. Bard, A.J.; Faulkner, L.R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley and Sons: New York, NY, USA, 2001; Chapter 5.
14. Zanello, P. *Inorganic Electrochemistry, Theory, Practice and Application*; The Royal Society of Chemistry: Cambridge, UK, 2003.
15. Ferguson, G.; Glidewell, C.; Opromolla, G.; Zakaria, C.M.; Zanello, P. The redox behavior of some bis-ferrocenyl compounds: Crystal and molecular structures of diferrocenylmethane and diferrocenylmethanol. *J. Organomet. Chem.* **1996**, *517*, 183-186.
16. Khaled, M.; Hadjipetrou, A.; Kispert, L. Electrochemical and electron paramagnetic resonance studies of carotenoid cation radicals and dications: effect of deuteration. *J. Phys. Chem.* **1990**, *94*, 5164-5169.
17. Khaled, M.; Hadjipetrou, A.; Kispert, L.D.; Allendoerfer, R.D. Simultaneous electrochemical and electron paramagnetic resonance studies of carotenoid cation radicals and dications. *J. Phys. Chem.* **1991**, *95*, 2438-2442.
18. Jeevarajan, A.S.; Khaled, M.; Kispert, L.D. Simultaneous electrochemical and electron paramagnetic resonance studies of carotenoids: Effect of electron donating and accepting substituents. *J. Phys. Chem.* **1994**, *98*, 7777-7781.
19. Gao, G.; Jeevarajan, A.S.; Kispert, L.D. Cyclic voltammetry and spectroelectrochemical studies of cation radical and dication adsorption behaviour for 7,7'-diphenyl-7,7'-diapocarotene. *J. Electroanal. Chem.* **1996**, *411*, 51-56.
20. Jeevarajan, A.S.; Kispert, L.D. Electrochemical oxidation of carotenoids containing donor-acceptor substituents. *J. Electroanal. Chem.* **1996**, *411*, 57-66.
21. Blanchard, P.; Brisset, H.; Riou, A.; Hierle, R.; Roncali, J. Bridged 1,6-dithienylhexa-1,3,5-trienes as highly photoluminescent and stable thiophene-based π -conjugated systems. *J. Org. Chem.* **1998**, *63*, 8310-8319.
22. Robin, M.B.; Day, P. Mixed valence chemistry. A survey and classification. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247-422.
23. Gritzner, G.; Kűta, J. Recommendations on reporting electrode potentials in nonaqueous solvents. *Pure Appl. Chem.* **1984**, *54*, 461-466.
24. Sheldrick, G.M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1994.

Sample Availability: Samples of the compounds **8a**, **9b**, **10a,b** are available from the authors.