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)cyclopentadienylium 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

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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-methylsulfanylcy clopropenylium 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-methylsulfanylcy clopropenylium tetrafluoroborate with organolithium compounds are regioselective to yield diferrocenylcycloropenes 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.

\[
\text{Fc= C}_2\text{H}_5\text{FeC}_5\text{H}_4; \quad X= Y= \text{COOEt (a), X= COCH}_3, Y= \text{COOEt (b); X= Bz, Y= COOEt (c)}
\]
Elimination of morpholine from cyclopropenes 2a–c then resulted in 1,2-diferrocenyl-3-(disubstituted)methylidencyclopropenes 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).

\[
\text{Scheme 2. Reaction of 2,3-diferrocenyl-1-morpholino(piperidino)cyclopropenylium tetrafluoroborates 1a,b with 1-methylprop-2-enylmagnesium chloride 5.}
\]

According to a standard procedure [5-7], 2,3-diferrocenylcyclopropenone [9] was first converted into 1-ethoxy-2,3-diferrocenylcyclopropenylum 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 $^1$H- 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 C₅H₄ groups are observed at higher field than the singlets from the protons of the C₅H₅ groups [10]; the $^1$H-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 C₅H₄ moieties of the ferrocenyl substituents. The $^{13}$C-NMR spectra of compounds 8a and 8b each contained two signals for CipsoFc 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 (CH₃) from 8a, and δ 12.92, 20.26 (2CH), 21.34 ppm (CH₃) 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 $^1$H-NMR spectra with a one-dimensional NOE experiment, which showed the interaction of the protons of the two CH groups with the 2-CH₂-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 CH₂Cl₂. 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 $^1$H-NMR spectra of trienes 10a and 10b, they are formed as single isomers. The spectra contained each signals for the olefinic protons of the –CH= fragments and the protons of the terminal –CH₂ group, singlets for the CH₃– group and two C₅H₅ 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) | 117.9(3) |
| C(24)-C(25)               | 1.541(4)                 | C(21)-C(22)-C(27) | 122.9(3) |
| C(25)-N(1)                | 1.473(4)                 | C(22)-C(23)-C(27) | 117.9(3) |
| C(26)-C(2)                | 1.514(4)                 | C(23)-C(24)-C(25) | 122.9(3) |
| C(24)-C(11)               | 1.506(4)                 | C(23)-C(24)-C(25) | 122.9(3) |
| **10a**                   |                          |                  |           |
| C(21)-C(22)               | 1.317(6)                 | C(21)-C(22)-C(23) | 122.8(4) |
| C(22)-C(23)               | 1.459(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(25)-C(26)-C(27) | 115.8(3) |
| C(23)-C(27)               | 1.495(5)                 | C(23)-C(24)-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(24)-C(23)-C(22) | 115.8(2) |
| C(24)-C(25)               | 1.468(3)                 | C(27)-C(24)-C(23) | 122.1(2) |
| C(25)-C(26)               | 1.343(3)                 | C(24)-C(23)-C(22) | 121.3(2) |
| C(21)-C(22)               | 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) | 113.9(3) |
| 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 2](image)

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

![Figure 3](image)

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 $^1$H and $^{13}$C-NMR spectra of each of them contain signals for two ferrocenyl, one methyl, and one heterocyclic substituents, two olefinic –CH= and one terminal CH$_2$= 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-heterarylallylcarbenes 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-heteryl-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 (Ia and IIa) with its complementary reduction signals (Ic and IIc) 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 $E^{0'}$ (I) = 0.004 V/Fc-Fc$^+$ and $E^{0'}$ (II) = 0.232 V/Fc-Fc$^+$ with its corresponding difference $\Delta E^{0'}$ (II-I) = 0.228 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.

![Cyclic voltammograms](image)

**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.

![Square wave voltammetry](image)

The estimated values of E₀' (I) and E₀' (II) were 0.058 and = 0.159 V/Fc-Fc⁺ with ΔE₀' (II-I) = 0.101 V and K_{com}= 51.4. The highest value of ΔE₀' (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 an electron donating effects must be consider. Also, the difference in the conjugation manner in compounds 7 and 8a could be the reason for the difference in ΔE₀' (II-I) values. Figure 6 presents cyclic voltammoamperometric response of compound 10a. When the potential scan was initiated in the positive direction, three oxidation signals (Iₐ, IIₐ, and II''ₐ) were observed, and when the potential scan was reversed, two reduction signals (Iₐ and II'ₐ) were also observed. We propose that the electrochemical process I with its corresponding oxidation and reduction signals, Iₐ and Iₐ, are attributed to electron transfer ferronece/ferricium⁺ 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_0cp 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”a 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_0cp in the positive direction. The working electrode used was a platinum disc.
The values for $E^{0'}$ (I), $E^{0'}$ (II), and $E^{0'}$ (II*) were $-0.260$, $0.152$, and $0.256$ V/Fc-Fe$^+$, 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 $E^{0'}$ (I), $E^{0'}$ (II) and $\Delta E^{0'}$ (II-I), and constant $K_{com}$ for compounds 7, 8a, 10a, and 10b.

| Compound | $E^{0'}$ (I) | $E^{0'}$ (II) | $E^{0'}$ (II*) | $E^{0'}$ (II*) |
|----------|--------------|--------------|--------------|--------------|
| 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 $^1$H and $^{13}$C-NMR spectra of the compounds 6, 7, 8a, 10a, 11a, b were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CDCl$_3$, with Me$_4$Si 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 Elementar Analysensysteme was used for elemental analyses.

Electrochemical measurements were carried out in acetonitrile containing 0.1 M tetra-$n$-butylammonium tetrafluoroborate (TBABF$_4$) 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/Fe$^+$ couple, according to the IUPAC convention [23].

The following reagents were purchased from Aldrich: Tetrachlorocyclopropene, 98%; ferrocene, 98%; triethylxonium tetrafluoroborate, 1.0 M solution in dichloromethane; morpholine, 99.5%; piperidine, 99%; 1-methyl-2-propenylmagnesium chloride, 0.5M solution in tetrahydrofuran. Ethoxy-(diferrocenyl)cyclopropenylum tetrafluoroborate was obtained by treating 2,3-diferrocenylcyclopropenone [2] in dichloromethane with triethylxonium tetrafluoroborate. Diferrocenyl(morpholino)- or (piperidino)cyclopropenylum tetrafluoroborates 1a,b were obtained from ethoxy(diferrocenyl)cyclopropenylum 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 (2CipsoFc), 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 (2CipsoFc), 126.54, 131.24, 131.87 (C6H3), 134.28, 134.93, 136.99 (3Cipso); 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), 1.75 (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, 2CH2), 3.48 (m, 4H, 2CH2), 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 (2C5H3), 67.21, 67.42, 67.61, 67.89, 68.52, 68.91, 69.54, 69.71 (2C5H4), 82.80, 83.14 (2CipsoFc), 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.
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(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 (3CipsoFc), 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. λmax (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, 3047, 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), 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 (C5H4), 84.96, 85.23 (2CipsoFc), 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, 68.09; 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%). λmax (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), 4.28 (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 (2CipsoFc), 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, 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, CH2), 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 (2CH2), 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, 69.32, 69.34 (2C5H4), 82.54, 82.87 (2CipsoFc), 132.62, 133.91 (2C); MS: m/z 545 [M]+. Anal. Calcd. for C32H35Fe2N: C, 67.87; H, 6.01; Fe, 20.31; N, 2.24.

7-Ferrocenyl-3,4-ferroceno-6-methyl-1-piperidinobicyclo[3.1.0]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), 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 (3CipsoFc), 131.42, 141.58 (2C); MS: \[m/z\] 545 [M]+. Anal. Calcd. for C₃₂H₃₅Fe₂N: C, 70.48; H, 6.47; Fe, 20.53; N, 2.57.

E,E-1,3-Diferrocenyl-4-methyl-2-piperidinohexa-1,3,5-triene (10b). Orange crystals, yield: 0.57 g (21%), m.p. 206–207 °C; λmax (CHCl₃, 20 °C) 211, 293 nm; IR (KBr): 492, 819, 903, 1004, 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), 4.01 (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); 13C-NMR: 16.48 (CH₃), 24.76 (CH₂), 25.86, 37.86 (4CH₂), 68.98, 69.39 (2C₅H₅), 67.03, 67.43, 67.53, 67.69, 67.90, 69.37, 70.88, 71.78 (2C₅H₅), 85.43, 85.91 (2CipsoFc), 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, 70.57; H, 6.47; Fe, 20.53; N, 2.49.

Z,E-1,2-Diferrocenyl-4-methyl-3-piperidinohexa-1,3,5-trienes (11b). Orange oil, yield: 0.43 g (16%); λmax (CHCl₃, 20 °C) 211, 294 nm; IR (KBr): 489, 812, 818, 860, 896, 1006, 1021, 1103, 1163, 1224, 1301, 1385, 1434, 1625, 1648, 2037, 2191, 2855, 2952, 3081, 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, 2CH₂), 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: 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 (2C₅H₅), 85.43, 85.91 (2CipsoFc), 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.

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, \(a = 10.5528(9), b = 10.3965(9), c = 22.8882(2)\) Å, \(α = 90°, β = 93.605(10), γ = 90°\), \(V = 2506.1(4)\) Å³, \(T = 130(2)\) K, \(Z = 4\), \(ρ = 1.445\) Mg/m³, \(λ (Mo – Ka) = 0.71073\) Å, \(F(000) = 1144\), absorption coefficient \(9.429\) mm⁻¹, crystal size \(0.444 \times 0.2658 \times 0.1397\) mm³, index ranges \(-12 \leq h \leq 12, -12 \leq k \leq 8, -27 \leq l \leq 27\), scan range \(3.87 \leq θ \leq 68.09°\), 4574 independent reflections, \(R_{int} = 0.0757\), 14354 total reflections,
318 refinable parameters, final R indices [I > 2σ(I)] R₁ = 0.0487, wR₂ = 0.1299, R indices (all data) R₁ = 0.0588, wR₂ = 0.1388, goodness-of-fit on F² 1.083, largest difference peak and hole 0.482/−0.915 eÅ⁻³.

Crystal data for C₃₁H₃₃Fe₂NO (10a): M = 547.28 g mol⁻¹, monoclinic P2₁/c, a = 15.602(1), b = 10.598(2), c = 15.362(1) Å, α = 90, β = 95.844(5), γ = 90°, V = 2526.9(5) Å³, T = 298(2) K, Z = 4, ρ = 1.439 Mg/m³, λ (Mo − Kα) = 0.71073 Å, F(000) = 1144, absorption coefficient 1.73 mm⁻¹, crystal size 0.6003 × 0.4151 × 0.0545 mm³, index ranges −15 ≤ h ≤ 19, −13 ≤ k ≤ 9, −19 ≤ l ≤ 18, scan range 3.25 ≤ θ ≤ 26.62°, 5270 independent reflections, R[int] = 0.0456, 11939 total reflections, 317 refinable parameters, final R indices [I > 2σ(I)] R₁ = 0.0551, wR₂ = 0.1644, R indices (all data) R₁ = 0.0715, wR₂ = 0.1781, goodness-of-fit on F² 1.090, largest difference peak and hole 1.348/−0.600 eÅ⁻³.

Crystal data for C₃₂H₃₅Fe₂N (10b): M = 545.31 g mol⁻¹, monoclinic P2₁/c, a = 15.5360(5), b = 10.2960(2), c = 16.8430(5) Å, α = 90, β = 110.613(3), γ = 90°, V = 2521.70(12) Å³, T = 130(2) K, Z = 4, ρ = 1.436 Mg/m³, λ (Mo − Kα) = 0.71073 Å, F(000) = 1144, absorption coefficient 1.172 mm⁻¹, crystal size 0.5175 × 0.1764 × 0.1143 mm³, index ranges −15 ≤ h ≤ 19, −11 ≤ k ≤ 12, −20 ≤ l ≤ 20, scan range 3.43 ≤ θ ≤ 26.06°, 4978 independent reflections, R[int] = 0.0442, 18609 total reflections, 317 refinable parameters, final R indices [I > 2σ(I)] R₁ = 0.0382, wR₂ = 0.0979, R indices (all data) R₁ = 0.0502, wR₂ = 0.1020, goodness-of-fit on F² 0.990, largest difference peak and hole 0.830/−0.498 eÅ⁻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 1EZ, UK (Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk or www: 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.

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