Intramolecular Transformations of 3-Cyanoamino- and 3-Cyanoimino-1,2-diferrocenylcyclopropenes

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Abstract: 3-Cyanoamino-1,2- and -2,3-diferrocenylcyclopropenes 6a,b and 11a,b prepared by the reaction of diferrocenylcyclopropenyl salts with sodium cyanamide undergo smooth intramolecular transformations with both conservation of the three-membered ring [affording 3-cyanoimino-1,2-diferrocenylcyclopropene (8)] and its opening [affording Z-3-morpholino- and Z-3-piperidino-3-(cyanoimino)-1,2-diferrocenylprop-1-enes 7a,b and Z-3-cyanoimino-2,3-diferrocenyl-1-methylthioprop-1-ene (10)]. 3-Cyanoimino-1,2-diferrocenylcyclopropene (8) reacts with hydrazine to form 3-amino-6-ferrocenyl-5-ferrocenymethyl-1,2,4-triazine (12) and Z-2,3-diferrocenylacrylohydrazide N-cyanoimide (13) as a result of intramolecular transformations. The structures of the compounds obtained were determined by IR, 1H- and 13C-NMR spectroscopy and mass spectrometry. The structures of compounds 7a and 10 were additionally confirmed by their X-ray diffraction analysis data.
**Keywords:** diferrocenylcyclopropenylium salts; cyanoamino(diferrocenyl)cyclopropenes; [amino(cyanoimino)methyl]-1,2-diferrocenylethenes; 3-amino-6-ferrocenyl-5-ferrocenylmethyl-1,2,4-triazine

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**Introduction**

The range of natural compounds comprising cyclopropane or cyclopropene fragments is fairly broad. Many of them are of particular interest due to their peculiar inherent biological activities [1-5]. In synthetic practice, compounds with a three-membered ring represent both the target products and intermediates in various carbon skeleton transformations [6-8]. These processes include, as a rule, ring opening reactions [8] into intermediate allylic cations or vinylcarbenes that serve as “building blocks” in organic synthesis. The presence of ferrocenyl substituents in the three-membered ring greatly facilitates these ring opening reactions [9-13]. This allows the use of ferrocenylcyclopropanes/cyclopropenes prepared by directed synthesis for their subsequent transformation into long-chain conjugated systems [6,8] and carbo- and heterocycles [14-17] incorporating iron-containing fragments. The effect of the nature of other functional groups and hetero-substituents on the ease of the three-membered ring opening of ferrocenylcyclopropenes has been but scantily explored. In particular, it has been established that the small ring opening occurs very readily for 2,3-diferrocenyl-1-methylthiocyclopropenes 1a-d [15-19]. These are formed in the reaction of diferrocenyl(methylthio)cyclopropenylium iodide (2) with active methylene reagents (diethyl malonate, malononitrile, nitroalkanes) and are further converted via 2,3-diferrocenyl-1-methylthiovinylcarbenes 3a-d into diene systems 4a-d with ferrocenyl substituents and terminal functionalities as a result of intramolecular migration of a functional group (Scheme 1).

**Scheme 1.** Reaction of diferrocenyl(methylthio)cyclopropenylium iodide (2) with active methylene reagents.
Studies on this type of chemical transformations are of undoubted interest for specialists in theoretical, physical and synthetic organic chemistry, as well as to the search for compounds with such valuable properties. In the present work, we report the results of studies on the reactions of sodium cyanamide with diferrocenyl(morpholino)- and -(piperidino)cyclopropenylum tetrafluoroborates 5a,b and diferrocenyl(methylthio)cyclopropenylum iodide (2).

Results and Discussion

The starting diferrocenylcyclopropenylum salts 5a, 5b, and 2 (Figure 1) were prepared from 2,3-diferrocenyl-cyclopropenone as described earlier [16,20,21].

Figure 1. Starting diferrocenylcyclopropenylum salts 5a, 5b, and 2.

We found that diferrocenyl(morpholino)- and -(piperidino)cyclopropenylium tetrafluoroborates 5a,b) react regioselectively with sodium cyanamide at 20 ºC (Scheme 2) to yield the following reaction products, viz., 6a,b, 7a,b, and 8 in the ratio ~ 1:3:2 (see Experimental section).

Scheme 2. Syntheses of 6a,b, 7a,b and 8.

These compounds were separated by column chromatography on alumina. Eluted first were cyclopropenes 6a (6b). In solid state, they are orange powders that gradually decompose on storage. Their structures were established based on the data from 1H- and 13C-NMR spectroscopy and mass spectrometry. Thus, the corresponding 1H- and 13C-NMR spectra contain the necessary number of signals for the protons and carbon atoms corresponding to the methylene groups of the morpholine and piperidine substituents and to two ferrocenyl fragments. The 13C-NMR spectra also contain the signals
for the nitrile groups (6a, δ 120.56 ppm; 6b, δ 121.75 ppm), and the 1H-NMR spectra contain signals at δ = 5.37 and 5.52 ppm, respectively, typical of the -NH group.

Eluted next from the column were compounds 7a and 7b as single isomers, judging from their 1H-NMR spectra. Their structures were established by 1H- and 13C-NMR, IR, and UV spectroscopy. The 1H-NMR spectra of compounds 7a and 7b contain, in addition to the signals for the protons and carbon atoms corresponding to the methylene groups of the morpholine and piperidine substituents and to two ferrocenyl fragments, one singlet each for low-field protons at δ 6.45 ppm (7a) and δ 6.39 ppm (7b), which allowed assigning them tentative structures of 3-morpholino-3-(cyanoimino) and 3-piperidino-3-(cyanoimino)-1,2-diferrocenylprop-1-enes 7a and 7b, respectively. The structure of compound 7a followed also from X-ray diffraction analysis of a single crystal prepared by crystallization from dichloromethane [22], which proved its structure as Z-3-morpholino-3-(cyanoimino)-1,2-diferrocenylprop-1-ene. The general view of the molecule 7a is shown in Figure 2a, the packing of molecules in a crystal is shown in Figure 2b, and the main geometrical parameters are given in Table 1. Data from the X-ray analysis show that the N=C bond in the azadiene is somewhat longer [d = 1.314(3) Å] than the standard value of 1.29 Å [23,24]. The lengths of C-Fe and C-C bonds in the ferrocenyl substituents are close to the standard values [25]. By analogy, the structure of Z-3-piperidino-3-(cyanoimino)-1,2-diferrocenylprop-1-ene was ascribed to compound 7b.

Eluted last from the chromatographic column was 3-cyanoimino-1,2-diferrocenylcyclopropene (8). It is possibly the pseudoaromatic character of these structures (A ↔ B) (Scheme 3) that determines this order of elution.

### Table 1. Selected bond lengths and bond angles for compounds 7a and 10.

|                  | Selected bond lengths (Å) | Selected bond angles (°) |
|------------------|---------------------------|--------------------------|
|                  |                           | 7a                       |
| C(24)-N(2)       | 1.151(4)                  | N(2)-C(24)-N(1)          | 172.6(3)   |
| C(24)-N(1)       | 1.329(4)                  | C(23)-N(1)-C(24)         | 119.3(2)   |
| C(23)-N(1)       | 1.314(3)                  | N(1)-C(23)-N(3)          | 117.5(2)   |
| C(23)-C(22)      | 1.495(3)                  | N(1)-C(23)-C(22)         | 123.2(2)   |
| C(22)-C(21)      | 1.334(3)                  | C(23)-C(22)-C(21)        | 118.8(2)   |
| C(23)-N(3)       | 1.332(3)                  | C(22)-C(23)-N(3)         | 119.3(2)   |
| N(3)-C(25)       | 1.454(4)                  | C(21)-C(22)-C(11)        | 123.0(2)   |
| C(1)-C(21)       | 1.462(3)                  | C(23)-N(3)-C(27)         | 121.4(3)   |
|                  |                           | 10                       |
| N(1)-C(25)       | 1.338(6)                  | C(21)-N(1)-C(25)         | 120.1(4)   |
| N(2)-C(25)       | 1.145(6)                  | N(2)-C(25)-N(1)          | 172.1(5)   |
| C(21)-N(1)       | 1.303(5)                  | N(1)-C(21)-C(22)         | 122.7(3)   |
| C(21)-C(22)      | 1.499(5)                  | C(21)-C(22)-C(23)        | 115.8(3)   |
| C(22)-C(23)      | 1.350(5)                  | C(22)-C(23)-S(1)         | 126.9(3)   |
| C(23)-S(1)       | 1.739(4)                  | C(23)-S(1)-C(24)         | 100.6(2)   |
| S(1)-C(24)       | 1.789(5)                  | N(1)-C(21)-C(1)          | 118.5(4)   |
| C(22)-C(11)      | 1.459(5)                  | C(1)-C(21)-C(22)         | 118.8(3)   |
| C(1)-C(21)       | 1.442(5)                  | C(11)-C(22)-C(23)        | 127.8(3)   |
Figure 2. (a) Crystal structure of 7a; (b) Crystal packing of 7a.

Scheme 3. Pseudoaromatic character of 3-cyanoimino-1,2-diferrocenylcyclopropene 8.

The cationic part of this structure is cyclopropenylum with the Hückel aromaticity [26,27], which makes the contribution of structure B quite important [7]. Spectroscopic characteristics of cyclopropene 8 corroborate its structure.

We also found that the reactions of diferrocenylcyclopropenylium salts 5a (5b) with sodium cyanamide carried out in boiling acetonitrile (10-12 h) afforded compounds 7a (7b) and 8. The same products were formed upon prolonged boiling of cyclopropenes 6a (6b) in acetonitrile (Scheme 4).

Scheme 4. Synthesis of 7a, 7b and 8.

\[
\begin{align*}
5a,b + NaNHCN & \xrightarrow{1^0} CH_3CN 7a,b + 8 \\
6a,b & \xrightarrow{1^0} CH_3CN 7a,b + 8
\end{align*}
\]

It thus follows that azadienes 7a (7b) and cyanoiminocyclopropene 8 result from transformations of tetrasubstituted diferrocenylcyclopropenes 6a (6b). A plausible mechanism of the reaction includes
initial nucleophilic attack of the cyanamide anion on the C-1 atom of the three-membered ring of cyclopropenylium cations 5a (5b) with formation of 3-cyanoamino-1,2-diferrocenyl-3-morpholino- (or -3-piperidino)cyclopropanes 6a (6b) (Scheme 5).

Scheme 5. Plausible mechanism of the formation of 6a, 6b and 8.

Subsequent intramolecular transformation of tetrasubstituted cyclopropanes 6a (6b) with elimination of a molecule of morpholine (piperidine) (Scheme 6) affords cyanoiminocyclopropene 8. Compounds 6a (6b) undergo also three-membered ring opening [16-19] giving cyanoamino-diferrocenyl(morpholino)- or -(piperidino)]vinylcarbenes 9a (9b), which are stabilized as a result of proton migration (Scheme 6).

Scheme 6. Plausible mechanism of the formation of 7a and 7b.

Unlike cyclopropenylium salts 5a (5b), diferrocenyl(methylthio)cyclopropenylium iodide (2) reacts with sodium cyanamide at 20 °C to yield mainly two products, 10 and 8, and small amounts of cyclopropanes 11a and 11b (Scheme 7).

Scheme 7. Synthesis of 10, 11a and 11b.
The physicochemical characteristics of compound 8 were identical to those of the product prepared from diferrocenyl(morpholino)- and -(piperidino)cyclopropenylum salts 5a and 5b. The structure of compound 10 was established based on the data from IR, UV, $^1$H- and $^{13}$C-NMR spectroscopy and mass spectrometry. The structure of compound 10 was also confirmed by X-ray diffraction analysis of a single crystal prepared by crystallization from chloroform [22]. The perspective view of the molecule 10 is shown in Figure 3a, the crystal packing diagram is shown in Figure 3b, and selected bond lengths and bond angles are listed in Table 1.

According to the data from X-ray analysis, compound 10 is Z-3-cyanoimino-2,3-diferrocenyl-1-methylthioprop-1-ene. The length of the N=C bond in compound 10 [$d = 1.303(5)$ Å] is somewhat longer than the standard value of 1.29 Å [23,24].

In our opinion, the fact that the N=C bond in compounds 7a and 10 is longer than the standard value of 1.29 Å is due to the presence of a conjugated system of double bonds in these compounds. In addition, it can be observed from Table 1 that σ-bonds in these compounds are somewhat shorter than the corresponding standard values. We think that the latter observation is also due to the presence of the conjugated system of bonds.

Isomeric 3-cyanoamino(diferrocenyl)cyclopropenes 11a and 11b (yields ~10 and 6%, respectively) are unstable oily products that undergo rapid decomposition on storage under ordinary conditions. Their structures were established based on the data from IR, $^1$H- and $^{13}$C-NMR spectroscopy and mass spectrometry. Structures 11a and 11b were assigned to the isomers of methylthiocyclopropenes based on the position of the proton signals of the substituted cyclopentadiene rings in the $^1$H NMR spectra. In cyclopropene 11a, all signals for the protons of the C$_5$H$_4$ fragments are present in a lower field than the singlets of the protons of unsubstituted cyclopentadienyl groups. In cyclopropene 11b, the signals for the protons of one of the C$_5$H$_4$ fragments of the ferrocenyl substituent are upfield relative to the signals for the protons of the C$_5$H$_5$ group, which corresponds to the effect of electron-donating MeS-C=C-Fc fragment of the cyclopropene.

**Figure 3.** (a) Crystal structure of 10; (b) Crystal packing of 10.
Obviously, one of the reaction products of iodide 2 with sodium cyanamide, viz., cyanoiminocyclopropene 8, results from intramolecular transformation of cyclopropene 11a (Scheme 8) analogous to that of 3-cyanoamino-1,2-diferrocenyl-3-morpholino- (or -3-piperidino)cyclopropenes 6a (6b) (see Scheme 5). The other reaction product, compound 10, is formed upon three-membered ring opening [16-19] in 3-cyanoamino-2,3-diferrocenyl-1-methylthiocyclopropene 11b to vinylcarbene 9c, whose stabilization owing to the proton transfer to the carbine center affords azadiene 10 (Scheme 8).

**Scheme 8.** Plausible mechanism of the formation of 8 and 10.

\[
\begin{align*}
&\text{Scheme 8. Plausible mechanism of the formation of 8 and 10.} \\
&\text{The results obtained demonstrate different effects of the heterosubstituents on the regioselectivities of reactions of morpholino- (or piperidino-) and methylthio-diferrocenylcyclopropenylium salts with the cyanamide anion and on relative stabilities, i.e., proneness to opening of their three-membered rings. The reaction products of salts 5a,b are formed exclusively upon the attack of the cyanamide anion on the C-1 atom of the cyclopropenylium ring. Such a regioselectivity is uncharacteristic of the reaction of the 1-methylthio- analog; at the same time, transformations of tetrasubstituted cyclopropene intermediates 11a and 11b occur much more smoothly.} \\
&\text{Further, we observed that 3-cyanoimino-1,2-diferrocenylcyclopropene (8) as a pseudoaromatic compound reacts with hydrazine in boiling ethanol to give two reaction products, viz., compounds 12 and 13 (Scheme 9). The nucleophilic attack of the hydrazine nitrogen atom on the carbon atom of the nitrile group results in 3-amino-6-ferrocenyl-5-ferrocenylmethyl-1,2,4-triazine (12) via tentative intermediates 14, 15, and 16. The structure of compound 12 was established by IR, \textsuperscript{1}H- and \textsuperscript{13}C-NMR spectroscopic and mass spectrometric data. Thus the IR spectrum of compound 12 contains absorption bands of a free NH \textsubscript{2} group (ν 3487 cm\textsuperscript{-1}) and ferrocenyl substituents. The \textsuperscript{1}H-NMR spectrum contains signals for protons of two ferrocene fragments, a singlet of an FcCH\textsubscript{2} group (δ 4.32 ppm) and a broad singlet of protons of the NH\textsubscript{2} group (δ 6.94 ppm). Data from the \textsuperscript{13}C-NMR spectrum corroborate the structure of compound 12.} \\
&\text{The nucleophilic attack of hydrazine on the C-1 atom of the three-membered ring in 8B affords product 13 resulting from opening of the small ring in intermediate 17 to vinylcarbene 18 and its}
\end{align*}
\]
subsequent intramolecular transformation; the structure of the final product 13 followed from the spectroscopic data.

**Scheme 9.** Plausible mechanism of reaction of 3-cyanoimino-1,2-diferrocenyl-cyclopropene 8 with hydrazine.

![Mechanism Diagram]

**Experimental**

**General**

All the solvents were dried according to the standard procedures and were freshly distilled before use [28]. Column chromatography was carried out on alumina (Brockmann activity III). The $^1$H- and $^{13}$C-NMR spectra were recorded on a Unity Inova Varian spectrometer (at 300 and 75 MHz, respectively) for solutions in CDCl$_3$, with Me$_4$Si as the internal standard; chemical shifts $\delta$ are given in ppm. The IR spectra were measured on a Perkin Elmer FT-IR spectrophotometer (Spectrum RXI) using KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). Elementar Analysensysteme LECO CHNS-900 was used for elemental analyses. The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4 diffractometer. The
structures of compounds 7a and 10 were solved by the direct method (SHELXS -97 [29]) and refined using full-matrix least-squares on F².

Synthesis of diferroenylcyclopropenyl salts (5a, 5b, and 2)

Diferroenylcyclopropenyl salts 5a, 5b, and 2 were prepared from 2,3-diferroenylcyclopropenone as described earlier [16,20,21]: 2,3-diferroenylcyclopropenone was obtained from the ferrocene and tetrachlorocyclopropene in the presence of AlCl₃ according to the standard procedure [20]; Ethoxy(diferroenyl)cyclopropenylum tetrafluoroborate was obtained from 2,3-diferroenylcyclopropenone in the presence of triethyl-oxonium tetrafluoroborate (1.0 M solution in dichloromethane) [21]; Morpholino- and piperidino-(diferroenyl)cyclopropenylum tetrafluoroborates were obtained from ethoxy(diferroenyl)-cyclopropenylum tetrafluoroborate and morpholine or piperidine in dichloromethane [21]; Diferroenylcyclopropenethione was obtained by treating ethanolic diferroenyl(morpholino)-cyclopropenylum tetrafluoroborate with an aqueous solution of NaSH [16]; 2,3-Diferroenyl-(methyithio)cyclopropenylum iodide (2) was obtained from the 2,3-diferroenylcyclopropenethione and iodomethane [16]. Freshly prepared and thoroughly dried tetrafluoroborates 5a,b and iodide 2 were employed in the reactions with sodium hydrogencyanamide. Reactions were carried out in freshly distilled dry solvents.

Reaction of dialkylamino(diferroenyl)cyclopropenylum tetrafluoroborates with sodium hydrogencyanamide

Sodium hydrogencyanamide (0.64 g, 10 mmol) was added to a solution of 1-amino-2,3-diferroenylpropenylium tetrafluoroborate 5a, b (5 mmol) in dichloromethane (chloroform, acetone, or acetonitrile) (100 mL), and the mixture was stirred in a dry inert atmosphere at ~20 °C (~24-36 h) or under reflux (14-20 h). The solvents were removed in vacuo, and the residues were chromatographed on alumina (hexane-dichloromethane, 4:1) to give compounds 6a, b, 7a, b and 8.

3-Cyanoamino-1,2-diferroenyl-3-morpholinocyclopropene (6a): Yield 0.32 g (12%); red-violet powder; mp 174-175 °C; ¹H-NMR: δ 3.16 (m, 4H, 2CH₂), 3.56 (m, 4H, 2CH₂), 4.09 (s, 5H, C₅H₅), 4.24 (s, 5H, C₅H₅), 4.05 (m, 2H, C₅H₄), 4.15 (m, 1H, C₅H₄), 4.43 (m, 1H, C₅H₄), 4.68 (m, 2H, C₅H₄), 5.01 (m, 2H, C₅H₄), 5.37 (bs, 1H, NH); ¹³C-NMR: δ 61.23 (C), 65.21 (2CH₂), 66.34 (2CH₂), 69.24, 70.43 (2C₅H₅), 67.93, 68.05, 69.04, 69.37, 70.82, 71.10, 72.34, 72.47 (2C₅H₄), 80.22, 81.23 (2C₁₃₀Fe), 120.56 (CN), 139.11 (2C); MS: m/z 533 [M⁺]; Anal. Calcd. for C₂₈H₂₇Fe₂N₃O: C, 63.07; H, 5.10; Fe, 20.95; N, 7.88; Found: C, 62.91; H, 5.17; Fe, 21.06; N, 7.69.

Z-3-morpholino-3-(cyanoimino)-1,2-diferroenylprop-1-en (7a): Yield 1.01 g (37%); violet crystals; mp 229-230 °C; λ_max (CHCl₃, 20°C): 207.31, 207.80, 235.05, 235.55 nm; IR (KBr): 473, 483, 541, 723, 773, 824, 861, 898, 921, 930, 977, 1000, 1024, 1052, 1105, 1115, 1214, 1259, 1286, 1324, 1352, 1383, 1411, 1440, 1484, 1536, 1626, 2181, 2851, 2977, 3082 cm⁻¹; ¹H-NMR: δ 3.48-3.92 (m, 8H, 4CH₂), 4.27 (s, 5H, C₅H₅), 4.29 (s, 5H, C₅H₅), 4.04 (m, 1H, C₅H₄), 4.22 (m, 1H, C₅H₄), 4.25 (m, 1H, C₅H₄), 4.28 (m, 1H, C₅H₄), 4.32 (m, 1H, C₅H₄), 4.34 (m, 1H, C₅H₄), 4.41 (m, 1H, C₅H₄), 4.82 (m, 1H, C₅H₄), 6.45 (s, 1H, CH=); ¹³C-NMR: δ 66.22 (2CH₂), 66.52 (2CH₂), 69.53, 69.74 (2C₅H₄), 67.98, 68.15, 68.88, 68.95, 69.12, 70.01, 70.25, 71.29 (2C₅H₄), 78.18, 80.28 (2C₁₃₀Fe), 126.07 (CN), 133.89
3-Cyanoimino-1,2-diferrocenylcyclopropene (8): Yield 0.56 g (25%); orange crystals; mp 214-216 °C; IR (KBr): 472, 483, 540, 551, 558, 722, 772, 824, 861, 898, 920, 930, 977, 1000, 1024, 1052, 1104, 1115, 1214, 1258, 1286, 1323, 1352, 1381, 1411, 1439, 1494, 1534, 1626, 1864, 2179, 2850, 2892, 2977, 3082 cm⁻¹; ¹H-NMR: δ 4.28 (s, 10H, 2C₅H₅), 4.71 (m, 4H, C₅H₄), 4.93 (m, 4H, C₅H₄); ¹³C-NMR: δ 70.48 (2C₅H₅), 72.65, 73.31, 73.35, 73.38 (2C₅H₄), 88.36, 88.64 (2CipsoFc), 121.28 (CN), 132.64 (C), 145.51 (C=N); MS: m/z 533 [M]+; Anal. Calcd. for C₂₈H₂₇Fe₂N₃O: C, 63.07; H, 5.10; Fe, 20.95; N, 7.88; Found: C, 63.19; H, 4.98; Fe, 20.87; N, 7.99.

3-Cyanoimino-1,2-diferrocenyl-3-piperidinocyclopropene (6b): Yield 0.38 g (14%); red-violet powder; mp 172-173 °C; ¹H-NMR: δ 1.58 (m, 2H, CH₂), 1.74 (m, 4H, 2CH₂), 2.99-3.06 (m, 4H, 2CH₂), 4.05 (s, 5H, C₅H₅), 4.21 (s, 5H, C₅H₅), 3.99 (m, 1H, C₅H₄), 4.03 (m, 1H, C₅H₄), 4.05 (m, 1H, C₅H₄), 4.55 (m, 1H, C₅H₄), 4.71 (m, 2H, C₅H₄), 5.10 (m, 1H, C₅H₄), 5.52 (bs, 1H, NH); ¹³C-NMR: δ 23.95 (CH₂), 25.64 (2CH₂), 50.31 (2CH₂), 58.19 (C), 69.31, 70.52 (2C₅H₅), 68.04, 68.12, 69.29, 69.42, 71.02, 72.13, 72.85, 72.90 (2C₅H₄), 81.35, 81.41 (2CipsoFc), 121.75 (CN), 139.24 (2C); MS: m/z 531 [M]+; Anal. Calcd. for C₂₉H₂₉Fe₂N₃: C, 65.56; H, 5.50; Fe, 21.03; N, 7.91; Found: C, 65.63; H, 5.38; Fe, 21.15; N, 7.99.

Z-3-Piperidino-3-(cyanoimino)-1,2-diferrocenylprop-1-ene (7b): Yield 1.20 g (45%); violet crystals; mp 195-196 °C; λmax (CHCl₃, 20°C): 205.96, 207.43, 233.82, 237.03 nm; IR (KBr) 206, 207, 233, 237, 308 cm⁻¹; ¹H-NMR: δ 1.73-1.92 (m, 6H, 3CH₂), 3.15-3.72 (m, 4H, 2CH₂), 4.22 (s, 5H, C₅H₅), 4.23 (s, 5H, C₅H₅), 4.05 (m, 1H, C₅H₄), 4.12 (m, 1H, C₅H₄), 4.17 (m, 1H, C₅H₄), 4.20 (m, 1H, C₅H₄), 4.21 (m, 1H, C₅H₄), 4.30 (m, 1H, C₅H₄), 4.36 (m, 1H, C₅H₄), 4.78 (m, 1H, C₅H₄), 6.39 (s, 1H, CH=); ¹³C-NMR: δ 24.05, 24.38, 26.32, 45.19, 49.85 (SCH₂), 69.42, 69.63 (2C₅H₄), 67.92, 68.01, 68.64, 68.99, 69.09, 69.78, 70.62, 70.89 (2C₅H₄), 78.40, 80.92 (2CipsoFc), 126.07 (CN), 133.0 (CH=), 135.52 (C), 152 46 (C=N); MS: m/z 531 [M]+; Anal. Calcd. for C₂₉H₂₉Fe₂N₃: C, 65.56; H, 5.50; Fe, 21.03; N, 7.91; Found: C, 65.39; H, 5.61; Fe, 21.18; N, 7.79.

3-Cyanoimino-1,2-diferrocenylcyclopropene (8): Yield 0.57 g (26%); orange crystals; mp 214-216 °C.

Reaction of 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide (2) with sodium hydrogencyanamide

A solution of compound 2 (2.9 g, 5.0 mmol) in dichloromethane (chloroform, acetone, or acetonitrile) (100 mL) was stirred with sodium hydrogencyanamide (0.64 g, 10 mmol) at ~20 °C (9-12 h) or under reflux for 5 h. Subsequent work-up of the reaction mixtures as described above gave compounds 8, 10 and 11a,b.
Z-3-Cyanoimino-2,3-diferrocenyl-1-methylthioprop-1-ene (10): Yield 1.51 g (61%); violet crystals; mp 183-184 °C; \( \lambda_{\text{max}} \) (CHCl_3, 20°C): 245.09, 299.36, 299.70, 368 nm; IR (KBr): 474, 495, 540, 613, 677, 723, 774, 818, 829, 866, 889, 1000, 1030, 1048, 1106, 1123, 1216, 1295, 1304, 1338, 1376, 1408, 1432, 1464, 1517, 1567, 1635, 2178, 2919, 3103 cm^{-1}; \(^1\)H-NMR: \( \delta \) 2.59 (s, 3H, CH_3), 4.20 (s, 5H, C_5H_5), 4.28 (s, 5H, C_5H_5), 4.25 (m, 2H, C_5H_4), 4.30 (m, 2H, C_5H_4), 4.48 (m, 1H, C_5H_4), 4.62 (m, 2H, C_5H_4), 5.05 (m, 1H, C_5H_4), 6.71 (s, 1H, CH=); \(^{13}\)C-NMR: \( \delta \) 18.87 (CH_3), 69.83, 70.92 (2C_5H_5), 68.32, 68.74, 73.27, 73.68 (2C_5H_4), 93.22, 99.91 (2C_{ipso}Fc), 121.15 (CH=), 123.07 (CN), 132.48 (C), 155.91 (C=N); MS: \( m/z \) 494 [M]^+; Anal. Calcd. for C_{25}H_{22}Fe_2N_2S: C, 60.36; H, 4.50; Fe, 22.60; N, 5.66; S, 6.43; Found: C, 60.48; H, 4.33; Fe, 22.54; N, 5.72; S, 6.57.

3-Cyanoamino-1,2-diferrocenyl-3-methylthiocyclopropene (11a): Yield 0.25 g (10%); red-violet powder; mp 163-164 °C; \(^1\)H-NMR: \( \delta \) 2.48 (s, 3H, CH_3), 4.18 (s, 5H, C_5H_5), 4.19 (s, 5H, C_5H_5), 4.36 (m, 2H, C_5H_4), 4.45 (m, 1H, C_5H_4), 4.58 (m, 2H, C_5H_4), 4.69 (m, 1H, C_5H_4), 4.70 (m, 2H, C_5H_4), 4.91 (m, 1H, C_5H_4), 5.08 (bs, 1H, NH); \(^{13}\)C-NMR: \( \delta \) 16.23 (CH_3), 58.52 (C), 69.59, 70.13 (2C_5H_5), 68.57, 68.86, 69.42, 70.45 (2C_5H_4), 85.41, 87.74 (2C_{ipso}Fc), 122.83 (CN), 126.95, 133.21 (2C); MS: \( m/z \) 494 [M]^+; Anal. Calcd. for C_{25}H_{22}Fe_2N_2S: C, 60.36; H, 4.50; Fe, 22.60; N, 5.66; S, 6.43; Found: C, 60.42; H, 4.37; Fe, 22.73; N, 5.47; S, 6.58.

3-Cyanoamino-2,3-diferrocenyl-1-methylthiocyclopropene (11b): Yield 0.15 g (6%); red-violet powder; mp 158-159 °C; \(^1\)H-NMR: \( \delta \) 2.62 (s, 3H, CH_3), 4.07 (s, 5H, C_5H_5), 4.11 (s, 5H, C_5H_5), 4.01 (m, 2H, C_5H_4), 4.09 (m, 2H, C_5H_4), 4.18 (m, 2H, C_5H_4), 4.23 (m, 2H, C_5H_4), 5.31 (bs, 1H, NH); \(^{13}\)C-NMR: \( \delta \) 17.4 (CH_3), 63.14 (C), 69.46, 69.75 (2C_5H_5), 68.41, 68.54, 68.92, 70.04 (2C_5H_4), 80.01, 82.91 (2C_{ipso}Fc), 149.13, 152.36, 156.29 (3C); MS: \( m/z \) 494 [M]^+; Anal. Calcd. for C_{25}H_{22}Fe_2N_2S: C, 60.36; H, 4.50; Fe, 22.60; N, 5.66; S, 6.43; Found: C, 60.21; H, 4.67; Fe, 22.51; N, 5.72; S, 6.35.

Reaction of 3-cyanoimino-1,2-diferrocenylcyclopropene (8) with hydrazine

A solution of compound 8 (1.0 mmol) and hydrazine hydrate (2.0 mL) in ethanol (20 mL) was stirred for 6 h at 78 °C. The reaction mixture was evaporated in vacuo, and residue was chromatographed (Al_2O_3; hexane/ethyl ether, 4:1) to give compounds 12 and 13.

3-Amino-6-ferrocenyl-5-ferrocenylmethyl-1,2,4-triazine (12): Yield 0.17g (35%); orange powder; mp 236-238 °C; IR (KBr) 487, 534, 718, 821, 89, 934, 1002, 1038, 1101, 1171, 1244, 1302, 1360, 1456, 1507, 1586, 1599, 1612, 1651, 2890, 2934, 3091, 3421 cm^{-1}; \(^1\)H-NMR: \( \delta \) 4.12 (s, 5H, C_5H_5), 4.24 (s, 5H, C_5H_5), 4.01 (m, 2H, C_5H_4), 4.09 (m, 2H, C_5H_4), 4.18 (m, 2H, C_5H_4), 4.23 (m, 2H, C_5H_4), 5.31 (bs, 1H, NH); \(^{13}\)C-NMR: \( \delta \) 6.42 (C), 69.46, 69.75 (2C_5H_5), 68.41, 68.54, 68.92, 70.04 (2C_5H_4), 80.01, 82.91 (2C_{ipso}Fc), 125.24 (CN), 127.13, 131.84 (2C); MS: \( m/z \) 478 [M]^+; Anal. Calcd. for C_{25}H_{22}Fe_2N_4: C, 60.36; H, 4.50; Fe, 22.60; N, 5.66; S, 6.43; Found: C, 60.21; H, 4.67; Fe, 22.51; N, 5.72; S, 6.35.

Z-2,3-Diferrocenylacrylohydrazide N-cyanoimide (13): Yield 0.23 g (48%); violet powder; mp 304-305 °C; IR (KBr) 478, 498, 532, 614, 678, 720, 770, 821, 830, 869, 923, 1001, 1027, 1051, 1103,
1120, 1221, 1297, 1302, 1345, 1369, 1411, 1432, 1469, 1523, 1567, 1634, 2172, 2896, 3093, 3165, 3487 cm\(^{-1}\); \(^1\)H-NMR: \(\delta\) 4.09 (s, 5H, C\(_5\)H\(_5\)), 4.14 (s, 5H, C\(_5\)H\(_5\)), 4.21 (m, 2H, C\(_5\)H\(_4\)), 4.32 (m, 2H, C\(_5\)H\(_4\)), 4.39 (m, 2H, C\(_5\)H\(_4\)), 7.68 (s, 1H, CH=), 8.94 (bs, 3H, NH\(_2\)); \(^13\)C-NMR: \(\delta\) 69.12, 69.2 (2C\(_5\)H\(_5\)), 67.56, 67.84, 67.96, 68.32, 68.53, 69.02, 69.32, 69.75 (2C\(_5\)H\(_4\)), 86.91, 91.08 (2C\(_{ipso}\)Fe), 125.47 (CN), 134.21 (CH=), 142.08 (C), 158.51 (C=N); MS: \(m/z\) 478 [M]+; Anal. Calcd. for C\(_{24}\)H\(_{22}\)Fe\(_2\)N\(_4\): C, 60.29; H, 4.64; Fe, 23.36; N, 11.71; Found: C, 60.51; H, 4.70; Fe, 23.21; N, 11.79.

Transformation of 3-dialkylamino-, 3-methylthio-3-cyanamino-1,2-diferrocenylcyclopropenes 6a,b and 11a into 3-cyanimino-1,2-diferrocenylcyclopropene (8)

A solution of the compounds 6a, 6b or 11a (1 mmol) in ethanol (acetonitrile, benzene) (50 mL) was heated at reflux for 6 h and concentrated. The residue was chromatographed on Al\(_2\)O\(_3\) (hexane - dichloromethane, 4:1) to give 0.34 - 0.36 g (75 - 81%) (from 6a), 0.32 - 0.34 g (68 - 76%) (from 6b) or 0.32 - 0.33 g (71 – 73%) (from 11a) of compound 8, mp 214-216 °C.

Transformation of 3-cyanamino-2,3-diferrocenyl-1-methylthiocyclopropene (11b) into Z-3-cyanoimino-2,3-diferrocenyl-1-methylthio-prop-1-ene (10)

A solution of cyclopropene 11b (1 mmol) in benzene (50 mL) was heated at reflux for 6 h and concentrated. The residue was chromatographed on Al\(_2\)O\(_3\) (hexane - dichloromethane, 4:1) to give 0.39 g (79%) of compound 10, mp 183-184 °C.

Conclusions

3-Cyanoamino-1,2-diferrocenyl-3-morpholino- (piperidino- or methylthio)cyclopropenes 6a,b, 11a undergo smooth intramolecular transformations with conservation of the three-membered ring affording 3-cyanoimino-1,2-diferrocenylcyclopropene (8). Compounds 6a and 6b also undergo three-membered ring opening giving cyanoaminodiferrocenyl(morpholino)- or -(piperidino)vinylcarbenes 9a (9b) which allows the use of 1,2-diferrocenylpropene fragments in the synthesis of diferrocenylhetero-1,3-diene systems 7a and 7b. 3-Cyanoamino-2,3-diferrocenyl-1-methylthiocyclopropene (11b) is transformed upon three-membered ring opening into Z-3-cyanoimino-2,3-diferrocenyl-1-methylthioprop-1-ene (10). 3-Cyanoimino-1,2-diferrocenylcyclopropene (8) reacts with hydrazine to form 3-amino-6-ferrrocenyl-5-ferrocenylmethyl-1,2,4-triazine (12) and Z-2,3-diferrocenylacrylohydrazide-N-cyanoimide (13) as a result of intramolecular transformations of intermediates 14 and 17 with cyclopropene-ring opening. Thus, the reaction of diferrocenylcyclopropene 8 with hydrazine gives rise to aromatic 1,2,4-trizines with amino substituents in the heterocycle. This novel method of synthesis of 1,2,4-aminotrizines, obviously, requires more detailed studies aimed at extension of its potential for the application in organic synthesis.

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22. CCDC 72930 (for 7a) and 729319 (for 10) 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 DB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Sample Availability: Samples of the compounds 5a,b, 7a,b and 8 are available from the authors.

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