Article

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4-(4-Nitrobenzyl)pyridine in Reaction with Diferrocenyl(methylthio)cyclopropenylium Iodide

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Abstract. Diferrocenyl(methylthio)cyclopropenylium iodide reacts with nitro compounds as CH-acids in the presence of triethylamine to yield both products with retention of the three-carbon ring and ring-opening products. Thus, 4-(4-nitrobenzyl)pyridine affords 1,2-diferrocenyl-3,3-dimethylthio- and 1,2-diferrocenyl-3-[(4-nitrophenyl)(4-pyridyl)methylidene]cyclopropenes and acyclic compounds: 2,3-diferrocenyl-1,3,3-tris(methylthio)propene and 2,3- diferrocenyl-1-methylthio-4-(4-nitrophenyl)-4-(4-pyridyl)buta-1,3-diene. Their structures were established based on data from ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction analysis. The mechanistic aspects of these reactions are discussed.
Key words: Ferrocene, cyclopropenylium iodide, cyclopropenes, diferrocenyl-1,3-butadiene.

Resumen. El yoduro de diferrocenil(metiltio)ciclopropenilo reacciona con los nitro-compuestos como CH-ácidos en presencia de trietilamina formándose los productos con la retención del anillo de tres miembros y con apertura del mismo. De esta manera, la 4-(4-nitrobencil)piridina produce los 1,2-diferrocenil-3,3-dimetiltio- y 1,2-diferrocenil-3-[(4-nitrofenil)(4-piridil)metiliden]ciclopropenos, así como los compuestos acíclicos: 2,3-diferrocenil-1,3,3-tris(metiltio)propeno y 2,3-diferrocenil-1-metiltio-4-(4-nitrofenil)-4-(4-piridil)buta-1,3-dieno. Sus estructuras fueron establecidas con base a la espectroscopia de RMN ^{1}H y de ^{13}C además de un análisis de difracción de rayos X. Se discuten los aspectos mecanísticos de estas reacciones.
Palabras clave: Ferroceno, yoduro de ciclopropenilio, ciclopropenos, diferrocenil-1,3-butadieno.

Introduction

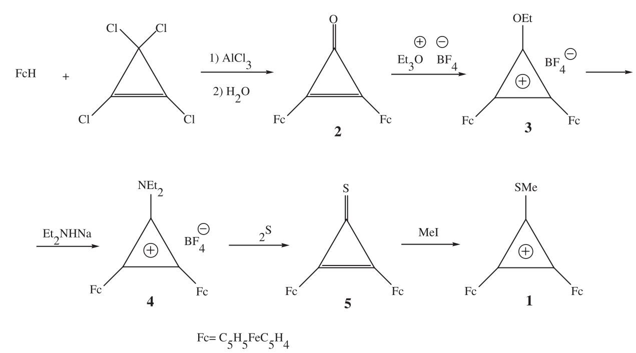
The ability of 2,3-diferrocenyl-1-methylthiocyclopropenylium cation **1** to undergo opening of the small ring in reactions with nucleophiles [1 - 3] makes it suitable for introducing the 1,2-diferrocenylpropene fragment, as a three-carbon building block, in organic compounds with the aim at preparing iron-containing carbo- and heterocycles as well as long-chain conjugated systems representing an important category of materials. The presence of ferrocene substituents in organic compounds, especially at multiple carbon–carbon bonds, imparts specific valuable properties, such as thermostability, magnetic behavior, electrical conductivity, even superconductivity, nonlinear optical effects, biological activities, *etc*. [4-8].

Studies aimed at estimating the feasibility of the use of diferrocenylcyclopropenylium cations as the sources of three-carbon ferrocenyl-substituted building blocks in the synthesis of novel types of organic compounds and materials are of indisputable practical interest.

In the present work, we studied the reactions of 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **1** with nitro compounds possessing CH-acidity, *viz*., 4-(4-nitrobenzyl)pyridine. So far, this type of reactions in the cyclopropenylium series has not been investigated.

Results and discussion

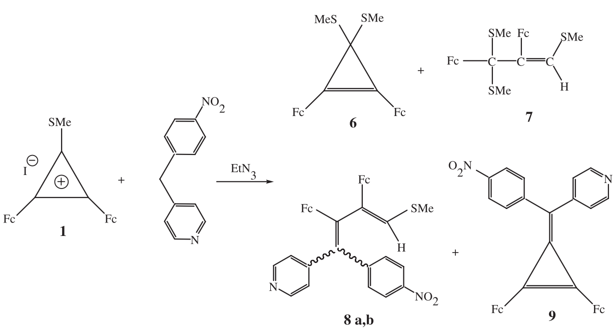
The starting 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **1** was prepared according to scheme 1 [1]:



Scheme 1

Alkylation of ferrocene with tetrachlorocyclopropene in the presence of $AlCl_3$ afforded 2,3-diferrocenylcyclopropenone **2** in quantitative yield; the yields of reaction products **3–5** in each of the subsequent steps were in the range of 75%-85%. In the couplings with nitro compounds, freshly prepared cyclopropenylium iodide **1** was employed.

We found that salt **1** reacted with 4-(4-nitrobenzyl)pyridine in the presence of triethylamine at 35-50 °C to afford the following products: 1,2-diferrocenyl-3,3-bis(methylthio)cyclopropene **6**, 2,3-diferrocenyl-1,3,3-tris(methylthio)propene **7**, 2,3-diferrocenyl-1-methylthio-4-(4-nitrophenyl)-4-(4-pyridyl)buta-1,3-diene **8** (the major product, yield 52%) and 1,2-diferrocenyl-3-(4-nitrophenyl)(4-pyridyl)methylidenecyclopropene **9** (Scheme 2):



Scheme 2

Table 1. Selected bond lengths and bond angles for **6**.

Selected bond lengths, r (Å)		Selected bond angles, w (o)	
C(21)-C(22)	1.307(6)	C(21)-C(23)-C(22)	52.7(3)
C(21)-C(23)	1.479(6)	C(23)-C(22)-C(21)	64.1(3)
C(22)-C(23)	1.467(6)	C(22)-C(21)-C(23)	63.2(3)
C(1)-C(22)	1.444(6)	C(22)-C(23)-S(2)	122.3(3)
C(11)-C(21)	1.446(6)	S(1)-C(23)-S(2)	108.9(2)
C(23)-S(1)	1.820(5)	C(23)-S(1)-C(25)	101.6(2)
C(23)-S(2)	1.826(4)	C(24)-S(2)-C(23)	101.9(3)
C(25)-S(1)	1.805(5)	C(21)-C(23)-S(1)	121.8(3)
C(24)-S(2)	1.796(7)	C(1)-C(22)-C(21)	152.5(4)

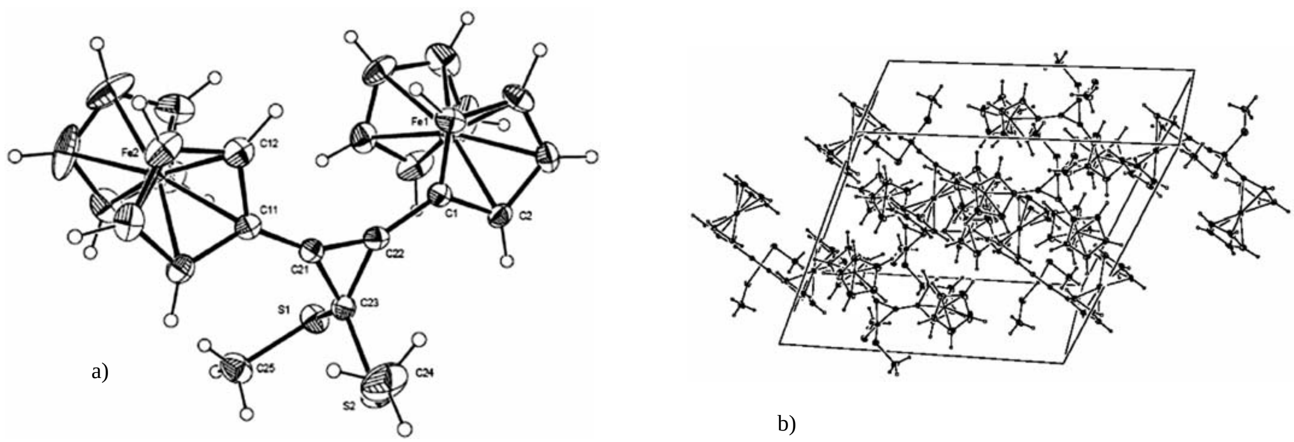


Fig. 1. (***a***) Crystal structure of compound **6**. (***b***) Crystal packing of **6**.

The structures of the compounds obtained were established based on the data from ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The ^{1}H NMR spectrum of cyclopropene **6** contained one six-proton singlet for two MeS groups, one singlet for protons of unsubstituted cyclopentadiene rings and two multiplets for protons of two substituted cyclopentadiene rings of the ferrocenyl fragments.

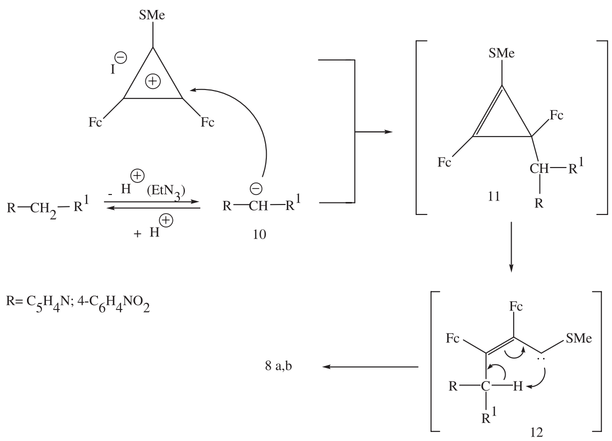
The spatial structure of compound **6** was established by X-ray diffraction of single crystals obtained by crystallization from hexane. The general view of the molecule of **6** is shown in Fig. 1a and the crystal packing, in Fig. 1b; selected geometric parameters are presented in Table 1. The three-membered ring containing two ferrocenyl and two methythio substituents is the central fragment of the molecule. The X-ray diffraction data confirmed the chemical structure of compound **6**. The length of the double C=C bond in the cyclopropene ring was equal to 1.307(6) Å and the lengths of the single C–C bonds, 1.479(6) Å; the acute angle at C(3) of the vertex of the three-membered ring was equal to 52.7(3)° [3, 9]. The lengths of the C–Fe and C-C bonds in the ferrocenyl substituents as well as the geometric parameters of the ferrocene sandwiches are close to the standard values [9].

The ^{1}H NMR spectrum of compound **7** contained two singlets for the protons of the methylthio groups with the ratio of integral intensities of 3:6, which corresponded to three MeS-substituents in the molecule, one singlet for the olefinic proton and signals for two ferrocenyl fragments. Based on these data as well as by analogy with the structures of *E*-1,2-diferrocenyl-3-methylthioprop-2-enone ketals established earlier [2], the structure of *E*-2,3-diferrocenyl-1,3,3- tris(methylthio)propene was ascribed to compound **7**.

According to data from ^{1}H and ^{13}C NMR spectra, compound **8** was formed as a ~1:1 mixture of two geometric isomers **8a** and **8b**, which probably differed in the spatial arrangement of the 4-nitrophenyl and 4-pyridyl substituents with the *cis*-orientation of the MeS and Fc fragments [1-3]. Our attempts to separate the isomeric butadienes **8a** and **8b** by TLC aimed at preparing crystals suitable for the spatial structural determination by X-ray diffraction analysis failed.

The ^{1}H and ^{13}C NMR spectroscopic characteristics of compound **9** corroborate completely its structure as 3-diarylmethylidene-1,2-diferrocenylcyclopropene.

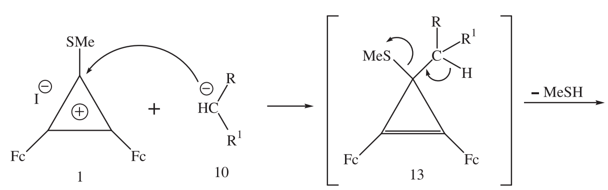
A conceivable mechanism of formation of compounds **8a,b** is presented in Scheme 3:



Scheme 3

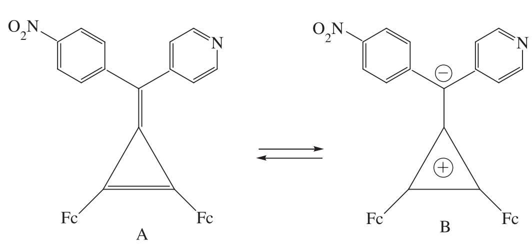
The reaction involves the initial attack of a carbanion species **10** on the ferrocenyl-substituted carbon atom of the three-membered ring resulting in unstable [9] 1,3-diferrocenylcyclopropene **11**. Opening of its small ring into a vinylcarbene intermediate **12** is followed by an intramolecular transformation leading to the isomeric diferrocenylbutadienes **8a** and **8b**.

The nucleophilic attack of the carbanionic species **10** on the carbon atom of the ring bearing the methylthio-substituent results in compound **9** (Scheme 4):



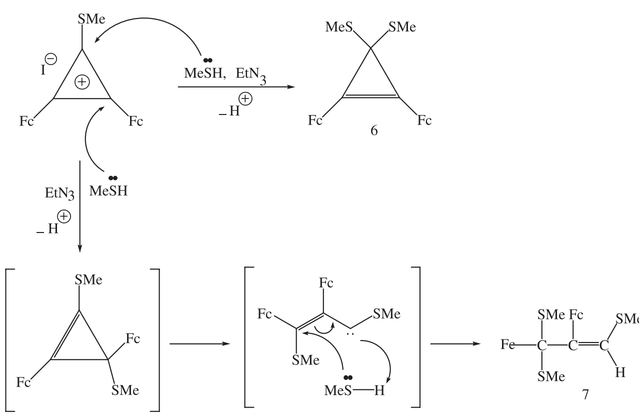
Scheme 4

1,2-Diferrocenyl-3-[(4-nitrophenyl)(4-pyridyl)methylidene]cyclopropene **9** was eluted last from the chromatographic column. It is possibly the pseudoaromatic character of their structures (A,B) (Scheme 5) that determines this order of elution.



Scheme 5

Methanethiol liberated upon the nucleophilic attack on the C(1) of the cyclopropenylium cation also reacts as the nucleophile with the starting compound **1** by pathways similar to those shown in schemes 3 and 4. Thus, the formation of dimethyl dithioketals **6** and **7** can be rationalized as follows (Scheme 6):



Scheme 6

The results obtained suggest that compounds **6**, **7**, and **9** formed upon addition of 4-(4-nitrobenzyl)pyridine to diferrocenyl(methylthio)cyclopropenylium iodide in low yields (6-12%) are the side reaction products. The major product, 2,3-diferrocenyl-1-methylthio-4-(4-nitrophenyl)-4-(4-pyridyl)buta-1,3-dienes **8a,b**, results from insertion of diferrocenylvinylcarbene, *i.e.*, the three-carbon building block, into the molecule of the starting nucleophile.

Experimental section

All the solvents were dried according to the standard procedures and were freshly distilled before use. IR spectra of compounds **4** and **5** was obtained for samples as KBr pellets on a Specord IR-75 instrument. UV spectra of compounds **4**, **5** were recorded on a Specord UV-VIS spectrophotometer. The mass spectrum of compounds **5 - 9** were obtained on a Varian-MAT CH-6 instrument (EI, 70 eV). The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ and CD_2Cl_2 with Me_4Si as the internal standard. Chemical shifts are given in ppm and *J* values in Hz. An Elemental Analysis System GmbH was used for elemental analyses. Columns chromatography was carried out on alumina (Brockmann activity III).

The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4 diffractometer. The| crystallographic data, the experimental conditions, and corrections are given in Table 2. The structures of compound **6** was solved by direct method (SHELXS) and refined using full-matrix least-squares on F^2.

Table 2. Crystal data, data collection and refinement parameters for **6**.

Data	6
Molecular formula	$C_{25}H_{24}Fe_2S_2$
Formula weight (g·mol-1)	500.26
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	P2(1)/a
a (Å)	18.169(3)
b (Å)	7.3990(9)
c (Å)	18.306(2)
α (o)	90.0
β (o)	114.316(12)
γ (o)	90.0
V (Å3)	2242.6(5)
Z	4
D calc.(Mg·mm^{-3})	1.482
Absorption coefficient (mm^{-1})	1.489
F(000)	1032
Radiation, λ(Å)	Mo-Kα, 0.71073
Monochromator	Graphite
θ range (o)	2.25-26.99
Reflections collected	6188
Reflections independent	4898
R int	0.0436
Final R indices [I > 2σ (I)]	R_1= 0.0561, wR_2 = 0.0944
R indices (all data)	R_1= 0.1285, wR_2 = 0.1154
Data / restraints / parameters	4898/0 / 264
Refinement method	Full-matrix-least-squares on F2
Goodness-of fit	1.006
Minimum/ maximum residual electron density (e Å-3)	-0.353 / 0.355

The following reagents were purchased from Aldrich: ferrocene, 98%; aluminum chloride, 99.99%; tetrachlorocyclopropene, 98%; triethyloxonium tetrafluoroborate, 1.0 M solution in dichloromethane; diethylamine, 99.5+%; iodomethane, 99.5%; sodium hydrosulfide hydrate NaHS·xH_2O, 4-(4-nitrobenzyl)pyridine, 98%.

2,3-Diferrocenylcyclopropenone 2 was obtained from the ferrocene and tetrachlorocyclopropene in the presence of $AlCl_3$ according to the standard procedure [10, 11].

Ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate 3 was obtained from the 2,3-diferrocenylcyclopropenone **2** in the presence of triethyloxonium tetrafluoroborate (1.0 M solution in dichloromethane) [12].

N,N-Diethylamino(diferrocenyl)cyclopropenylium tetrafluoroborate (4): Diethylamine (3.0 mL) was added dropwise to a solution of salt **3** (0.54 g, 1 mmol) in dichloromethane (50 mL) and the mixture was stirred for 2 h at 20 °C in an inert atmosphere. Then dry ethanol (100 mL) was added, the mixture was stirred for 30 min, concentrated *in vacuo* to 30 mL, and left overnight at 20 °C. The precipitate that formed was filtered off, washed with dry ethanol, and dried in a vacuum desiccator over P_4O_{10}. The yield of the title compound was 0.37 g (74%), red-violet crystals, mp 182 - 184 °C. IR (KBr): ν_{max} 751, 827, 900, 1033, 1049, 1069, 1146, 1313, 1360, 1388, 1450, 1503, 1560, 1910, 2880, 2939, 2982, 3032, 3110 cm^{-1}. UV ($CHCl_3$, 20°): λ_{max} 249, 284, 308, 349, 361, 419, 499 nm. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.50 (t, *J* = 7.2 Hz, 6 H,2 CH_3), 3.84 (q, *J* = 7.2 Hz, 4 H, 2 CH_2), 4. 35 (s, 10H, 2 C_5H_5), 4.83 (m, 4H, C_5H_4), 4.90 (m, 4H, C_5H_4) . ^{13}C NMR (75 MHz, CD_2Cl_2): δ 14.62 (2 CH_3), 49.04 (2 CH_2), 60.45 (2 C_{ipso}Fc), 70.82 (2 C_5H_5), 71.81, 74.39 (2 C_5H_4), 132.04 (2 C), 139.40 (C-N). Anal calc. for $C_{27}H_{28}BF_4Fe_2N$: C 57.39, H 5.00, F 13.45, Fe 19.77, N 2.48. Found C 57.54, H 4.73, F 13.61, Fe 19.63, N 2.52.

2,3-Diferrocenylcyclopropenethione (5): A solution of NaHS (1.0 g) in water (10 mL) was added to a stirred suspension of salt **4** (5 mmol) in ethanol (100 mL) at 20 °C and stirred for 6 h. The precipitate that formed was filtered off, washed with water, and dried in air. The yield of the title compound was ~ 2.0 g (91%), dark red fine crystals, mp 208 - 209 °C. Following purification by chromatography on alumina (hexane - dichloromethane, 5:1), thione **5** had m.p. 209 - 210 °C. IR (KBr): ν 480, 823, 898, 999, 1030, 1058, 1105, 1166, 1211, 1311, 1341, 1375, 1485, 1616, 1645, 1800, 2041, 2968, 3098 cm^{-1}. UV ($CHCl_3$, 20°): λ_{max} 248, 280, 298, 416, 475 nm. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27 (s, 10 H, 2 C_5H_5), 4.69 (m, 4 H, C_5H_4), 4.98 (m, 4 H, C_5H_4). ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.25 (2 C_{ipso}Fc), 70.14 (2 C_5H_5), 71.29, 72.95 (2 C_5H_4), 152.66 (2 C), 171.15(C=S). Anal calc. for $C_{23}H_{18}Fe_2S$: C 63.05, H 4.14, Fe 25.49, S 7.32. Found C 62.83, H 4.19, Fe 25.57. MS: *m/z* 438 $[M]^+$.

Diferrocenyl(methylthio)cyclopropenylium iodide (1): Methyl iodide (0.5 mL) was added dropwise to a solution of cyclopropenethione **5** (0.88 g, 2.0 mmol) in dry benzene (50 ml) and the mixture was stirred in an inert dry atmosphere for 3 h. The red-violet precipitate of the salt **1** was filtered off, washed with benzene, and dried in a vacuum-dessicator. The yield of the iodide **1** was 0.93 g (80%), mp 248 - 250 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.25 (s, 3H, CH_3), 4.49 (s, 10 H, 2 C_5H_5), 5.09 (m, 8 H, 2 C_5H_4). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 21.26 (CH_3), 58.79 (2 C_{ipso}Fc), 72.26 (2 C_5H_5), 74.32, 77.50 (2 C_5H_4), 151.27 (2 C), 152.30(C-S). Anal. calc. for $C_{24}H_{21}Fe_2IS$: C 49.69, H 3.65, Fe 19.24, I 21.88, S 5.54. Found C 49.48, H 3.71, Fe 19.17, I 21.97.

Reactions of salt 1 with 4-(4-nitrobenzyl)pyridine. 4-(4-Nitrobenzyl)pyridine (0.6 g, 3 mmol) and Et_3N (5.0 mL) were added with stirring to a mixture of salt **1** (1.74 g, 3 mmol) in dry benzene (50 mL). After stirring for 6 h at ambient temperature, the volatiles were removed *in vacuo*. The preparative TLC of the residue on Al_2O_3 (using hexane-ether, 6:1, as eluent) gave compounds **6**, **7, 8a,b** and **9**.

2,3-Diferrocenyl-1,1-dimethylthiocyclopropene 6, yield 0.075 g (5%), orange crystals, mp 136-137 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 2.31 (6 H, s, 2 CH_3), 4.29 (10 H, s, 2 C_5H_5), 4.43 (4 H, m, C_5H_4), 4.55 (4 H, m, C_5H_4). Anal. calc. for $C_{25}H_{24}Fe_2S_2$: C, 60.03; H, 4.84; Fe, 22.33; S, 12.80. Found: C, 59.88; H, 4.82; Fe, 22.47; S, 12.89. . MS: *m*/*z* 500 $[M]^+$.

***E*-2,3-Diferrocenyl-1,3,3- tris(methylthio)propene 7**, yield 0.1 g (6%) red-brown powder, mp 193-194 °C. ^{1}H NMR ($CDCl_3$) δ 2.60 (6H, s, 2CH_3), 2.77 (3H, s, CH_3), 4.08 (5H, s, C_5H_5), 4.10 (5H, s, C_5H_5), 4.03 (2H, m, C_5H_4), 4.14 (2H, m, C_5H_4), 4.28 (2H, m, C_5H_4), 4.39 (2H, m, C_5H_4), 6.31 (1H, s, CH=). Anal. calc. for $C_{26}H_{28}Fe_2S_3$: C, 56.96; H, 5.15; Fe, 20.38; S, 17.51. Found: C, 57.09; H, 5.21; Fe, 20.42; S, 17.40%. MS: *m*/*z* 548 $[M]^+$.

2,3-Diferrocenyl-1-methylthio-4-(4-nitrophenyl)-4-(4-pyridyl)buta-1,3-diene 8a,b, (~1:1), yield 1.04 g (52%), orange crystals, mp 235-237 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.65 (3H, s, CH_3), 2.79 (3H, s, CH_3), 4.12 (5H, s, C_5H_5), 4.23 (5H, s, C_5H_5), 4.26 (5H, s, C_5H_5), 4.31 (5H, s, C_5H_5), 4.39 (2H, m, C_5H_4), 4.43 (2H, m, C_5H_4), 4.58 (4H, m, C_5H_4), 4.63 (4H, m, C_5H_4), 4.66 (2H, m, C_5H_4), 4.68 (2H, m, C_5H_4), 7.32 (1H, s, CH=), 7.39 (1H, s, CH=). Anal. calc. for $C_{36}H_{30}Fe_2N_2O_2S$: C, 64.90; H, 4.54; Fe, 16.76; N, 4.20; S, 4.80. Found: C, 64.74; H, 4.63; Fe, 16.82; N, 4.03; S, 4.67%. MS: *m*/*z* 666 $[M]^+$.

1,2-Diferrocenyl-3-[(4-nitrophenyl)(4-pyridyl)methylidene]cyclopropene 9, yield 0.22 g (12%), red powder, mp 267-268 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26 (5H, s, C_5H_5), 4.29 (5H, s, C_5H_5), 4.64 (2H, m, C_5H_4), 4.68 (4H, m, C_5H_4), 4.70 (2H, m, C_5H_4), 7.40 (2H, d, *J* = 6.3 Hz, 4-Py), 7.59 (2H, d, *J* = 9.0 Hz, 4-C_6H_4 NO_2), 8.25 (2H, d, *J* = 9.0 Hz, 4-C_6H_4 NO_2) , 8.56 (2H, d, *J* = 6.3 Hz, 4-Py). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 66.28 (C), 70.15, 71.94 (2 C_5H_5), 72.03, 72.09, 72.55, 72.61 (2 C_5H_4), 90.45, 92.03 (2 C_{ipso}Fc), 122.10, 124.06, 127.76, 147.16 (4 Ar), 128.20, 129.83, 132.67, 148.04, 150.22, 154.05 (6 C). Anal. calc. for $C_{35}H_{26}Fe_2N_2O_2$: C, 68.00; H, 4.24; Fe, 18.07; N, 4.53. Found: C, 67.87; H, 4.29; Fe, 18.20; N, 4.47. MS: *m*/*z* 618 $[M]^+$.

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