DOI: 10.1002/ejoc.200600413

Functional Group Migration in Reactions of 1,2-Diferrocenyl-3-(methylthio)-cyclopropenylium Iodide with CH Acids

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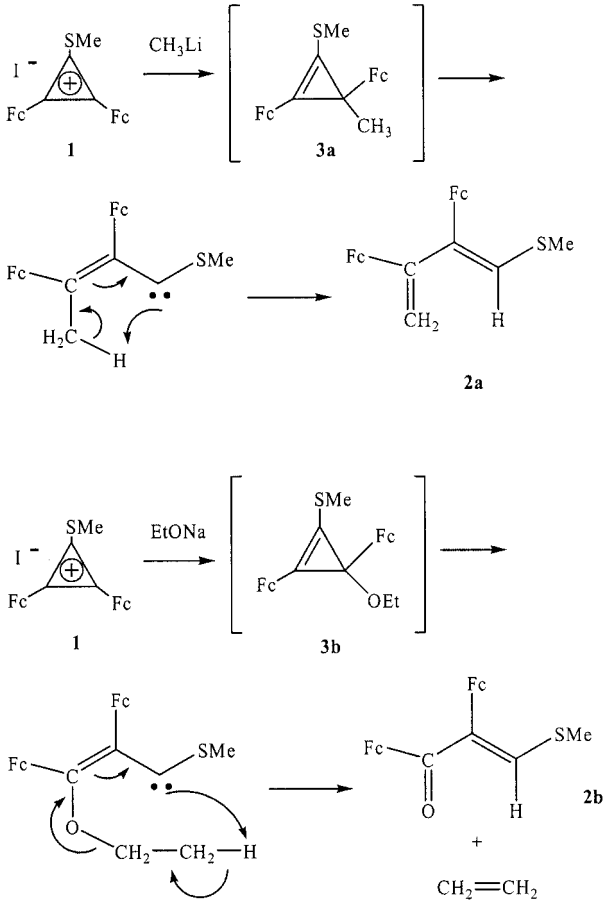
Keywords: 1,2-Diferrocenyl-3-(methylthio)cyclopropenylium / Cyclopropene / Cyclopropene ring opening / Migration of ethoxycarbonyl and cyano groups / Ferrocene

1,2-Diferrocenyl-3-(methylthio)cyclopropenylium iodide reacts with malonic acid derivatives (diethyl malonate and malononitrile as the active methylene compounds) to give mainly the corresponding 3,4-diferrocenyl-2-(methylthio)-hexa-2,4-dienedioic acid and 2,3-diferrocenyl-4-(methylthio)buta-1,3-diene-1,1-dicarboxylic acid derivatives as well as ethyl 2,3-diferrocenyl-4-(methylthio)-5-oxocyclo-1,3-pentadiene-1-carboxylate or 2-cyano-3,4-diferrocenyl-5-(methylthio)-2,4-cyclopentadien-1-imine. X-ray diffraction data for diethyl (2*Z*,4*E*)-3,4-diferrocenyl-2-(methylthio)hexa-2,4-dienedioate and 2,3-diferrocenyl-4-(methylthio)buta-1,3-diene-1,1-dicarbonitrile are presented.

Introduction

The presence of ferrocenyl substituents in molecules of organic compounds imparts new properties to these compounds which are absent, as a rule, in their alkyl and aryl analogues. In some cases, stabilities of compounds containing the ferrocenyl substituents are enhanced (α-ferrocenyl carbocations, ferrocenylalka-1,3-dienes, ferrocenylalkatrienes, etc.)[1–6] while in other cases, these compounds are less stable (ferrocenyl-*NH*-pyrazolines, ferrocenylcyclopropanes, 3-ferrocenyl-1-cyclopropenes, etc.).[7–12] Thus, ring opening of 3-ferrocenyl-1-cyclopropenes and 2,3-diferrocenyl-2-cyclopropen-1-one occurs at room temperature or on moderate heating to give intra- or intermolecular transformation products of the intermediate vinylcarbenes.[13–15] The presence of additional ferrocenyl fragments in the cyclopropane ring facilitates opening of the small ring[1,2,4] and isolation of 1,3-diferrocenyl-1-cyclopropene is often problematic.[4]

The transient formation of 1,3-diferrocenyl-1-cyclopropenes in the reactions of 1,2-diferrocenyl-3-(methylthio)cyclopropenylium iodide (**1**) with nucleophiles (RLi, RMgX, RONa, ROH/Et_3N)[4,16] was inferred from the linear structures of the main reaction products **2a**,**b** formed upon open-



Scheme 1.

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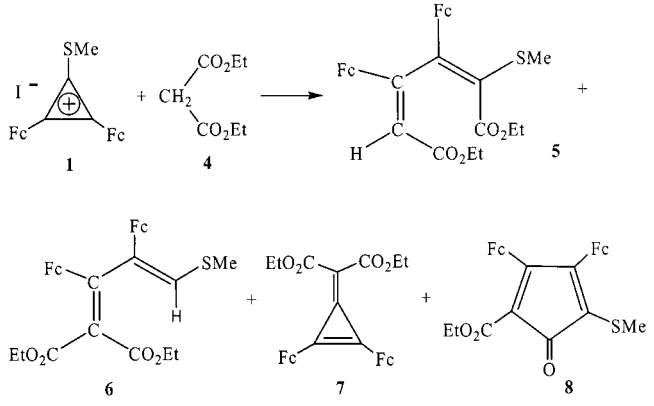
ing of the small ring of the intermediate cyclopropenes **3a**,**b** (Scheme 1).

The ability of 1,3-diferrocenyl-1-cyclopropenes to readily undergo cyclopropene ring opening can be efficiently exploited for the synthesis of diverse compounds of the ferrocene series, e.g. ketones, alcohols, olefins, carbo- and heterocycles etc. Of particular interest is the synthesis of unsaturated ferrocene-containing compounds with functional groups because of their exciting structures, chemical reactivities and potential for use as molecular building blocks and in the realm of supramolecular chemistry as redox switching receptors.[17–20] We herein present the results of studies of the reactions of 1,2-diferrocenyl-3-(methylthio)cyclopropenylium iodide (**1**) with CH acids, namely, diethyl malonate and malononitrile.

Results and Discussion

The starting 1,2-diferrocenyl-3-(methylthio)cyclopropenylium iodide (**1**) was prepared by treating 2,3-diferrocenyl-2-cyclopropene-1-thione with methyl iodide as described earlier.[4] A fine crystalline red-violet powder of the iodide **1**. It was found that it reacted with diethyl malonate (**4**) in the presence of Et_3N to give mainly diethyl 3,4-diferrocenyl-2-(methylthio)hexa-2,4-dienedioate (**5**) in ca. 45% yield (Scheme 2). In addition, the following products were isolated from the reaction mixture: diethyl 2,3-diferrocenyl-4-(methylthio)buta-1,3-diene-1,1-dicarboxylate (**6**, ca. 12%), 3-[1,1-bis(ethoxycarbonyl)methylene]-1,2-diferrocenyl-1-cyclopropene (**7**, ca. 9%) and ethyl 2,3-diferrocenyl-4-(methylthio)-5-oxo-1,3-cyclopentadiene-1-carboxylate (**8**, ca. 8%). The structures of the compounds obtained were established from the data from mass spectrometry, ^1H and ^{13}C NMR spectroscopy and elemental analysis. The spatial structure of compound **5** was also established by an X-ray analysis.



Scheme 2.

According to the NMR spectroscopic data, both **5** and **6** are formed as single geometric isomers. The ^1H NMR spectra of these compounds each contain two triplets and two quadruplets for the ethoxycarbonyl fragments, characteristic signals for two ferrocenyl substituents, one singlet for the methylthio group and one signal for the olefinic proton. An X-ray analysis of a single-crystal of compound **5** grown from diethyl ether confirmed its structure as diethyl (2*Z*,4*E*)-3,4-diferrocenyl-2-(methylthio)hexa-2,4-dienedioate. The general view of the molecule of **5** is shown in Figure 1, selected bond lengths and angles are given in Table 1. ^1H NMR spectroscopic studies of compound **6** allowed us to establish it as a structural isomer of compound **5**. Thus, a 1D NOE experiment revealed the proximity of the olefinic proton with the protons of the methylthio group.[4] Apparently, the methylthio group and a ferrocenyl substituent are (*Z*)-arranged, as in compound **5**.

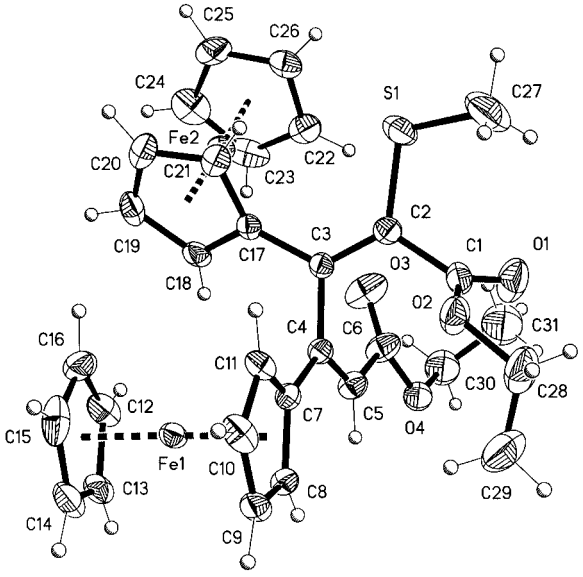
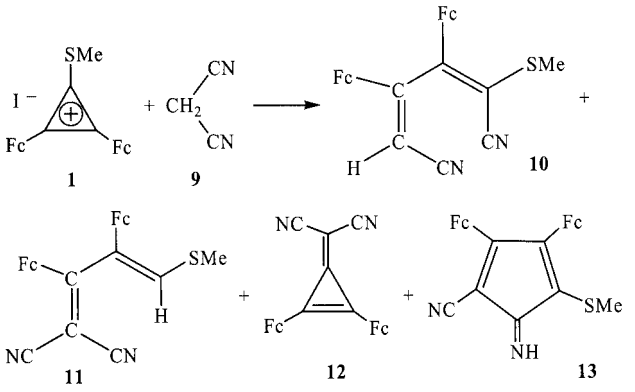


Figure 1. Molecular structure of **5** in the crystal.

Table 1. Selected bond lengths [Å] and bond angles [°] for compounds **5** and **11**.

5			
C(1)–O(1)	1.187(6)	O(2)–C(1)–C(2)	110.1(4)
C(1)–O(2)	1.335(6)	C(1)–C(2)–C(3)	120.0(4)
C(1)–C(2)	1.507(7)	C(2)–C(3)–C(4)	118.5(4)
C(2)–C(3)	1.344(6)	C(4)–C(5)–C(6)	125.0(5)
C(3)–C(4)	1.507(6)	C(5)–C(6)–O(3)	126.9(5)
C(4)–C(5)	1.332(7)	C(1)–C(2)–S(1)	116.2(4)
C(2)–S(1)	1.747(5)	C(2)–S(1)–C(27)	104.0(3)
C(5)–C(6)	1.466(7)	C(1)–O(2)–C(28)	117.6(5)
C(27)–S(1)	1.771(7)	C(4)–C(3)–C(17)	115.9(4)
11			
C(11)–C(12)	1.366(3)	C(14)–S(1)–C(25)	101.94(14)
C(12)–C(13)	1.484(3)	C(13)–C(14)–S(1)	125.35(19)
C(13)–C(14)	1.346(3)	C(14)–C(13)–C(12)	118.0(2)
C(14)–S(1)	1.730(3)	C(13)–C(12)–C(11)	117.3(2)
C(25)–S(1)	1.798(2)	C(12)–C(11)–C(26)	124.4(3)
C(11)–C(26)	1.442(4)	C(12)–C(11)–C(27)	122.5(2)
C(11)–C(27)	1.435(4)	C(11)–C(26)–N(1)	176.5(4)
N(1)–C(26)	1.129(4)	C(11)–C(27)–N(2)	175.8(3)
N(2)–C(27)	1.135(4)	C(26)–C(11)–C(27)	113.0(2)
C(31)–S(1)	1.794(3)	C(1)–C(12)–C(13)	117.2(2)

We found, further, that malononitrile (**9**) reacted with **1** in the presence of triethylamine in an analogous manner to give 3,4-diferrocenyl-2-(methylthio)hexa-2,4-dienedinitrile (**10**) as the major product (34%). In addition, compounds **11** (23%), **12** (10%) and **13** (11%) were isolated (Scheme 3). The structures of all these compounds were elucidated from their NMR (^{1}H and ^{13}C) and mass spectra and data from elemental analyses.



Scheme 3.

The spatial structure of compound **11** was determined by X-ray analysis of a single-crystal obtained by crystallisation from chloroform. The general view of the molecule of **11** is shown in Figure 2 with selected bond lengths and angles given in Table 1. Thus, compound **11** is 2,3-diferrocenyl-4-(methylthio)buta-1,3-diene-1,1-dicarbonitrile.

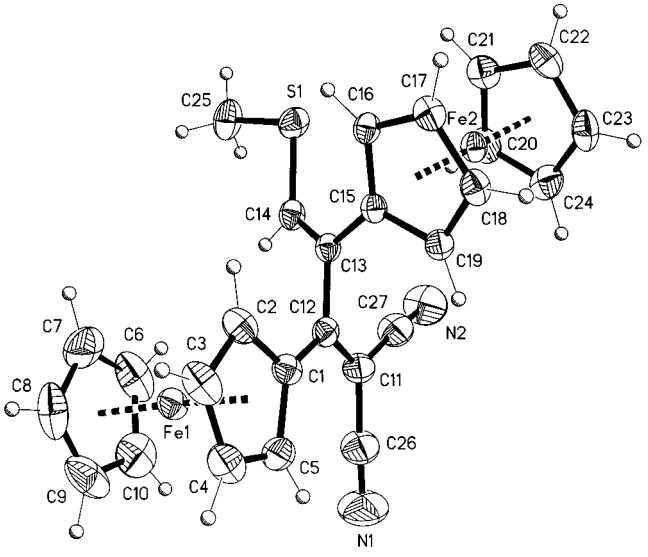
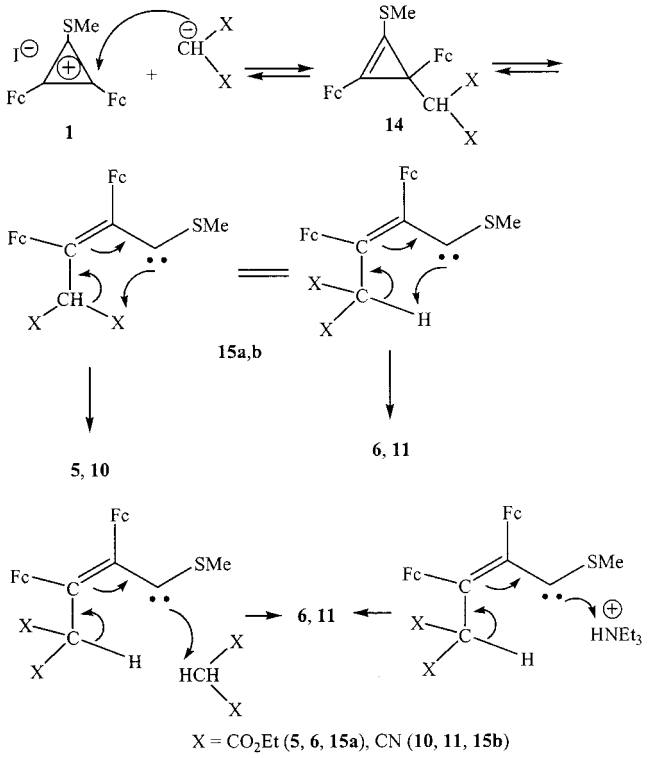
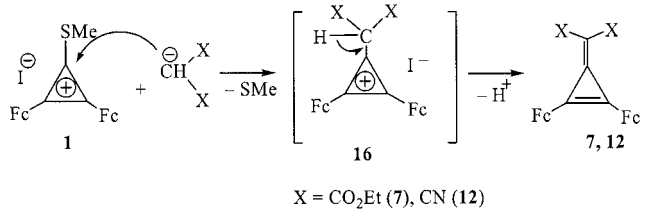


Figure 2. Molecular structure of **11** in the crystal.

The differences in the structures of compounds **10** and **11** were established from a comparative analysis of their ^{1}H NMR spectra including 1D NOE spectra. Unlike compounds **6** and **11**, no interaction of the olefinic proton with the protons of the methylthio group was observed in the spectrum of compound **10**. A putative mechanism for the formation of compounds **5**, **6**, **10** and **11** is presented in Scheme 4. Shown in Schemes 5 and 6 are putative mechanisms for the formation of compounds **7** (and **12**) and **8** (and **13**), respectively.



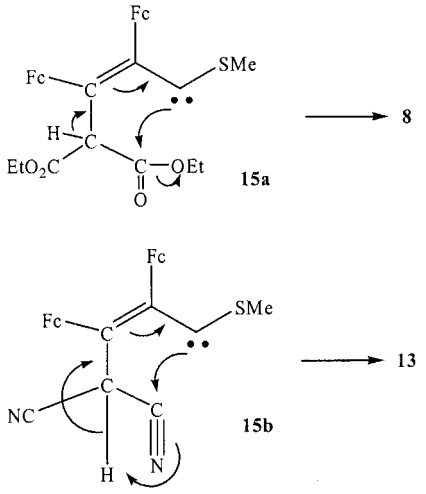
Scheme 4.



Scheme 5.

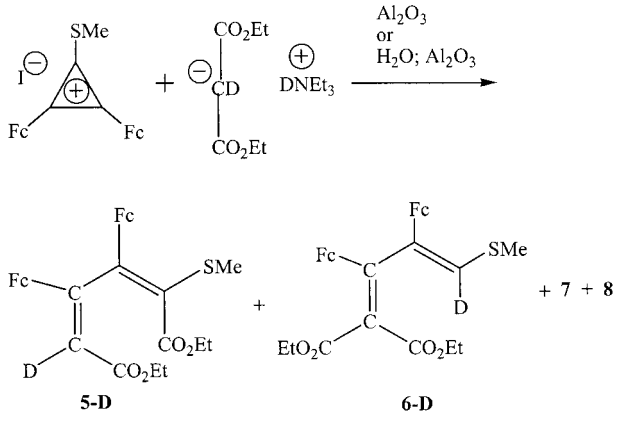
The results obtained in the present study demonstrate that the nucleophilic attack by the conjugated base is mainly directed on C-2 of the cation **1** to give intermediate 1,3-diferrocenyl-1-cyclopropene **14** (see Scheme 4).[14–16] This undergoes spontaneous opening of the three-membered ring to yield vinylcarbene **15**. The transformations of vinylcarbenes **15a**,**b** with or without migration of the functional groups seem to follow the intramolecular mechanism[4] to yield the final linear products **5** and **10** and the cyclopentadiene derivatives **8** and **13**.

The proton shift yielding compounds **6** and **11** can proceed both intra-[4] and intermolecularly[16] since the reaction mixtures contain potential proton donors such as the trieth-



Scheme 6.

ylammonium cation and the starting diethyl malonate (or malononitrile) (Scheme 4). The use of diethyl [D_2]malonate did not help solve this problem unambiguously (Scheme 7). The deuterated products **5-D** and **6-D** were isolated from the reaction mixtures with and without treatment with water prior to chromatography.



Scheme 7.

It was found that **1** reacted with NaCD(CO_2Et)$_2$ in benzene to give products **5-D** and **6-D**. This confirms the implementation of the intramolecular transformation of the ferrocenyl(vinyl)carbenes **15a**,**b**.

Conducting the reaction of cation **1** with NaCD(CO_2Et)$_2$ in the presence of MeOH under a dry inert gas resulted in compounds **5-D**, **6** and **6-D** (ca. 2:1 ratio). The results of this experiment support the involvement of proton-donating molecules (MeOH) in the intermolecular transformation of vinylcarbenes.[16] The nucleophilic attack by the conjugated base on C-1 of the three-membered ring of the cation **1** affords an intermediate **16**. This is deprotonated under the action of Et_3N to give the 1,2-diferrocenyl-1-cyclopropene derivatives **7** and **12** (Scheme 5).

Conclusion

This type of rearrangement with migration of such functional groups as CO_2Et and CN has not been documented so far. As a result, we have synthesised 3,4-diferrocenyl-2-(methylthio)hexa-2,4-dienedioic acid derivatives together with other hitherto unknown compounds of the ferrocene series. Each of them could find valuable practical applications.

Experimental Section

General: Benzene, triethylamine, methyl iodide, diethyl malonate and malononitrile were dried by standard methods and distilled prior to use.[21] Column chromatography was carried out on alumina (Brockmann activity III). The ^1H and ^{13}C NMR spectra of solutions in $CDCl_3$ with Me_4Si as the internal standard were recorded with a Unity Inova Varian spectrometer (300 and 75 MHz). The IR spectra of KBr pellets were measured with a Specord IR-75 instrument. The mass spectra were obtained with a Varian MAT CH-6 instrument (EI, 70 eV). A Vario Micro instrument (Elementar Analysensysteme GmbH) was used for elemental analyses. The following reagents were purchased from Aldrich: tetrachlorocyclopropene, 98%; ferrocene, 98%; triethyloxonium tetrafluoroborate, 1.0 M solution in dichloromethane; diethylamine, 99.5%; methyl iodide, 99.5%; sodium hydrosulfide hydrate $NaHS{\cdot}xH_2O$; triethylamine, 99+%; diethyl malonate, 99%; malononitrile, 99%; diethyl [D_2]malonate, 90 atom-% D.

1-Ethoxy-2,3-diferrocenylcyclopropenylium Tetrafluoroborate: This was obtained by treating 2,3-diferrocenyl-2-cyclopropen-1-one[22] with triethyloxonium tetrafluoroborate in dichloromethane.

1,2-Differocenyl-3-piperidinocyclopropenylium Tetrafluoroborate: This was obtained from 1-ethoxy-2,3-diferrocenylcyclopropenylium tetrafluoroborate and piperidine in dichloromethane.[4]

2,3-Diferrocenyl-2-cyclopropene-1-thione: This was obtained by treating ethanolic 1,2-differocenyl-3-piperidinocyclopropenylium tetrafluoroborate[4] with an aqueous solution of NaSH.[4] Yield: 91%, m.p. 208–209 °C.

1,2-Diferrocenyl-3-(methylthio)cyclopropenylium Iodide (1): This was obtained from 2,3-diferrocenyl-2-cyclopropene-1-thione and iodomethane.[4] It was dried in a vacuum desiccator over P_2O_5 before the reactions were carried out.

Reaction of 1 with Diethyl Malonate (4): Diethyl malonate (**4**) (0.96 g, 6 mmol) and Et_3N (10 mL) were added with stirring to a suspension of salt **1** (1.74 g, 3 mmol) in dry benzene (50 mL). After stirring at ambient temperature for 6 h, volatiles were removed in vacuo. Chromatography of the residue on Al_2O_3 (hexane/ether, 10:1) gave compounds **5**–**8**.

Diethyl (2*Z*,4*E*)-3,4-Diferrocenyl-2-(methylthio)-2,4-hexadiene-1,6-dioate (5): Yield: 0.83 g (45%), orange crystals, m.p. 181–182 °C. IR (KBr): $\tilde{\nu}$ = 776, 825, 901, 945, 1025, 1058, 1087, 1138, 1212, 1287, 1359, 1396, 1406, 1446, 1487, 1612, 1667, 1848, 2928, 2978, 3084 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.2 Hz, 3 H, CH_3), 1.28 (t, J = 7.2 Hz, 3 H, CH_3), 2.28 (s, 3 H, SCH_3),4.13 (s, 5 H, C_5H_5), 4.20 (s, 5 H, C_5H_5), 4.10 (q, J = 7.2 Hz, 2 H, CH_2), 4.22 (q, J = 7.2 Hz, 2 H, CH_2), 4.28(m, 2 H, C_5H_4), 4.32 (m, 2 H, C_5H_4), 4.48 (m, 2 H, C_5H_4), 4.72 (m, 2 H, C_5H_4), 6.22 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.07, 15.96 (2 CH_3), 59.88, 60.92 (2 CH_2), 69.76, 70.18 (2 C_5H_5), 69.02, 69.85, 70.52, 70.60 (2 C_5H_4), 80. 61, 85.02 (2 C_{ipso}Fc), 116.59 (CH=), 124.92,

139.18, 157.17 (3 C) 165.12, 179.50 (2 C=O) ppm. $C_{31}H_{32}Fe_2O_4S$ (612): calcd. C 60.81, H 5.27, Fe 18.24, S 5.23; found C 60.69, H 5.16, Fe 18.41, S 5.18. MS: *m/z* = 612 $[M]^+$.

Diethyl (3*Z*)-2,3-Diferrocenyl-4-(methylthio)buta-1,3-diene-1,1-dicarboxylate (6): Yield: 0.22 g (12%), orange crystals, m.p. 174–175 °C. IR (KBr): $\tilde{\nu}$ = 783, 805, 879, 954, 1020, 1049, 1077, 1145, 1234, 1289, 1368, 1397, 1416, 1448, 1487, 1611, 1664, 1832, 2929, 2982, 3093 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.32 (t, *J* = 6.9 Hz, 3 H, CH_3), 2.33 (s, 3 H, SCH_3), 4.08 (s, 5 H, C_5H_5), 4.13 (s, 5 H, C_5H_5), 4.15 (q, *J* = 6.9 Hz, 2 H, CH_2), 4.20 (q, *J* = 6.9 Hz, 2 H, CH_2), 4.26 (m, 2 H, C_5H_4), 4.29 (m, 2 H, C_5H_4), 4.41 (m, 2 H, C_5H_4), 4.64 (m, 2 H, C_5H_4), 6.52 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.59, 15.83 (2 CH_3), 59.65, 60.86 (2 CH_2), 70.13, 70.24 (2 C_5H_5), 69.47, 69.79, 70.64, 70.78 (2 C_5H_4), 81.80, 85.31 (2 C_{ipso}Fc), 117.05 (CH=), 125.83, 137.12, 156.19 (3 C), 169.09, 172.30 (2 C=O) ppm. $C_{31}H_{32}Fe_2O_4S$ (612): calcd. C 60.81, H 5.27, Fe 18.24, S 5.23; found C 60.92, H 5.38, Fe 18.15, S 5.33. MS: *m/z* = 612 $[M]^+$.

3-[1,1-Bis(ethoxycarbonyl)methylene]-1,2-diferrocenyl-1-cyclopropene (7): Yield: 0.15 g (9%), orange crystals, m.p. 187–188 °C. IR (KBr): $\tilde{\nu}$ = 698, 772, 824, 914, 1001, 1026, 1091, 1169, 1214, 1278, 1327, 1410, 1462, 1488, 1575, 1611, 1677, 1853, 2976, 3095 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 6.9 Hz, 6 H, 2 CH_3), 4.22 (s, 10 H, 2 C_5H_5), 4.38 (q, *J* = 6.9 Hz, 4 H, 2 CH_2), 4.66 (m, 4 H, C_5H_4), 5.20 (m, 4 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.86 (2 CH_3), 59.41 (2 CH_2), 70.09 (2 C_5H_5), 72.34, 72.62 (2 C_5H_4), 82.01 (2 C_{ipso}Fc), 138.05, 139.11, 145.37 (3 C), 167.66 (2 C=O) ppm. $C_{30}H_{28}Fe_2O_4$ (564): calcd. C 63.86, H 5.00, Fe 19.80; found C 64.01, H 4.89, Fe 19.65. MS: *m/z* = 564 $[M]^+$.

Ethyl 2,3-Diferrocenyl-4-(methylthio)-5-oxo-1,3-cyclopentadiene-1-carboxylate (8): Yield: 0.14 g (8%), orange crystals, m.p. 173–174 °C. IR (KBr): $\tilde{\nu}$ = 729, 823, 910, 1003, 1056, 1109, 1218, 1261, 1414, 1467, 1574, 1617, 1647, 1733, 2972, 3092 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 6.6 Hz, 3 H, CH_3), 2.43 (s, 3 H, SCH_3), 4.07 (q, *J* = 6.6 Hz, 2 H, CH_2), 4.13 (s, 5 H, C_5H_5), 4.27 (s, 5 H,C_5H_5), 4.19 (m, 2 H, C_5H_4), 4.32 (m, 2 H, C_5H_4), 4.39 (m, 2 H, C_5H_4), 4.50 (m, 2 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.97, 18.31 (2 CH_3), 59.73 (CH_2), 69.75, 70.26 (2 C_5H_5), 69.93, 70.84, 71.48, 72.12 (2 C_5H_4), 82.21, 83.11 (2 C_{ipso}Fc), 135.62, 136.16, 140.32, 144.34 (4 C), 167.66, 176.52 (2 C=O) ppm. $C_{29}H_{26}Fe_2O_3S$ (566): calcd. C 61.51, H 4.63, Fe 19.73, S 5.65; found C 61.39, H 4.74, Fe 19.91, S 5.43. MS: *m/z* = 566 $[M]^+$.

Reaction of 1 with Diethyl [D_2]Malonate (4-D)

a) The reaction of salt **1** (1.74 g, 3 mmol) with diethyl [D_2]malonate (**4-D**) (0.96 g, 6 mmol) and Et_3N (10 mL) in dry benzene (50 mL) was carried out under conditions described above. Subsequent chromatography afforded the following reaction products: **5-D**, **6-D**, **7** (0.13 g, 8%),and **8** (0.16 g, 9%).

Diethyl (2*Z*,4*E*)-5-Deuterio-3,4-diferrocenyl-2-(methylthio)-2,4-hexadiene-1,6-dioate (5-D): Yield: 0.86 g (47%), orange crystals, m.p. 181–183 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.29 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.27 (s, 3 H, SCH_3), 4.12 (s, 5 H, C_5H_5), 4.19 (s, 5 H, C_5H_5), 4.10 (q, *J* = 7.2 Hz, 2 H, CH_2), 4.23 (q, *J* = 7.2 Hz, 2 H, CH_2), 4.27 (m, 2 H, C_5H_4), 4.33 (m, 2 H, C_5H_4), 4.48 (m, 2 H, C_5H_4), 4.71 (m, 2 H, C_5H_4), 6.23 (s, 0.15 H, CH=) ppm. MS: *m/z* = 613 $[M]^+$.

Diethyl (3*Z*)-4-Deuterio-2,3-diferrocenyl-4-(methylthio)-1,3-butadiene-1,1-dicarboxylate (6-D): Yield: 0.20 g (11%), orange crystals, m.p. 174–175 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.30 (t, *J* = 6.9 Hz, 3 H, CH_3), 2.34 (s, 3 H, SCH_3), 4.08 (s, 5 H, C_5H_5), 4.14 (s, 5 H, C_5H_5), 4.16 (q, *J* = 6.9 Hz, 2 H, CH_2), 4.20 (q, *J* = 6.9 Hz, 2 H, CH_2), 4.27 (m, 2 H, C_5H_4), 4.29 (m, 2 H, C_5H_4), 4.40 (m, 2 H, C_5H_4), 4.65 (m, 2 H, C_5H_4), 6.53 (s, 0.14 H, CH=) ppm. MS: *m/z* 613 = $[M]^+$.

b) Diethyl [D_2]malonate (**4-D**) (0.96 g, 6 mmol) and Et_3N (10 mL) were added with stirring to a suspension of salt **1** (1.74 g, 3 mmol) in dry benzene (50 mL) and the mixture was stirred under an inert dry gas until complete dissolution of the salt **1** had occurred (ca. 6 h). The reaction mixture was then washed with water (20 mL) to remove triethylammonium iodide, the organic layer was separated, concentrated and the residue was chromatographed on alumina in hexane to yield compounds **5-D** (48%), **6-D** (11%), **7** (8.3%) and **8** (10%).

Reaction of 1 with Sodium Diethyl [D_1]Malonate (Na-4-D)

a) 1 (1.74 g, 3 mmol) was added with stirring to a suspension of sodium diethyl [D_1]malonate (1.1 g, 6 mmol) in dry benzene (70 mL). After stirring at ambient temperature for 6 h, the volatiles were removed in vacuo. According to ^1H NMR spectroscopic data, the compounds formed were **5-D** (50%), **6-D** (12%), **7** (8.0%) and **8** (10%).

b) 1 (1.74 g, 3 mmol) was added with stirring to a suspension of sodium diethyl [D_1]malonate (1.1 g, 6 mmol) in dry benzene (70 mL) and anhydrous MeOH (1.0 mL) and the mixture was stirred under an inert dry gas until complete dissolution of the salt **1** had occurred (ca. 3 h). Volatiles were then removed in vacuo. According to ^1H NMR spectroscopic data, the compounds obtained were **5-D** (35%), **6**/**6-D** (10%, ca. 2:1), **7** (6.4%), **8** (7.0%) and 1,2-diferrocenyl-1,1-dimethoxy-3-(methylthio)-1-propene (12%), orange powder, m.p. 164–165 °C.[16]

Reaction of 1 with Malononitrile (9): Analogously, the reaction of malononitrile (**9**) (0.4 g, 6 mmol) with **1** (1.74 g, 3 mmol) and Et_3N (10 mL) in dry benzene (50 mL) at 20 °C over 4 h and subsequent workup afforded compounds **10**–**13**.

(2*Z*,4*E*)-3,4-Diferrocenyl-2-(methylthio)-2,4-hexadiene-1,6-dinitrile (10): Yield: 0.53 g (34%), orange crystals, m.p. 167–168 °C. IR (KBr): $\tilde{\nu}$ = 487, 559, 622, 732, 829, 893, 948, 1033, 1046, 1107, 1218, 1290, 1329, 1391, 1414, 1447, 1521, 1569, 1647, 2210, 2932, 3092 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, SCH_3), 4.00 (s, 5 H, C_5H_5), 4.19 (s, 5 H,C_5H_5), 4.24 (m, 2 H, C_5H_4), 4.36 (m, 2 H, C_5H_4), 4.58 (m, 2 H, C_5H_4), 4.71 (m, 1 H, C_5H_4), 4.98 (m, 1 H, C_5H_4), 6.49 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.52 (CH_3), 70.56, 71.61 (2 C_5H_5), 68.76, 69.19, 69.57, 70.89, 71.21, 72.28, 72.63, 72.89 (2 C_5H_4), 80.74, 83.81 (2 C_{ipso}Fc), 133.62, 134.18, 136.32, 174.04, 174.10 (5 C) ppm. $C_{27}H_{22}Fe_2N_2S$ (518): calcd. C 62.58, H 4.28, Fe 21.56, N 5.40, S 6.18; found C 66.69, H 4.34, Fe 21.41, N 5.52,S 6.07. MS: *m/z* = 518 $[M]^+$.

(3*Z*)-2,3-Diferrocenyl-4-(methylthio)-1,3-butadiene-1,1-dicarbonitrile (11): Yield: 0.36 g (23%), orange crystals, m.p. 172–173 °C. IR (KBr): $\tilde{\nu}$ = 474, 499, 717, 822, 999, 1031, 1045, 1107, 1204, 1289, 1327, 1379, 1409, 1443, 1517, 1567, 1641, 2214, 2926, 3099 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.60 (s, 3 H, SCH_3), 4.25 (s, 5 H, C_5H_5), 4.28 (s, 5 H,C_5H_5), 3.80 (m, 1 H, C_5H_4), 4.12 (m, 1 H, C_5H_4), 4.20 (m, 1 H, C_5H_4), 4.48 (m, 1 H, C_5H_4), 4.74 (m, 1 H, C_5H_4), 4.85 (m, 1 H, C_5H_4), 4.95 (m, 1 H, C_5H_4), 5.48 (m, 1 H, C_5H_4), 6.58 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.83 (CH_3), 70.04, 71.32 (2 C_5H_5), 67.08, 68.47, 69.01, 69.44, 71.01, 73.08, 73.10, 74.16 (2 C_5H_4), 75.14, 82.25 (2 C_{ipso}Fc), 115.60 (CH=), 130.77, 132.81, 132.87, 176.12, 178.72 (5 C) ppm. $C_{27}H_{22}Fe_2N_2S$ (518): calcd. C 62.58, H 4.28, Fe 21.56, N 5.40, S 6.18; found C 62.43, H 4.19, Fe 21.63, N 5.29, S 6.23. MS: *m/z* = 518 $[M]^+$.

3-(1,1-Dicyanomethylene)-1,2-diferrocenyl-1-cyclopropene (12): Yield: 0.14 g (10%), orange crystals, m.p. 185–186 °C. IR (KBr): $\tilde{\nu}$ = 683, 770, 824, 984, 1018, 1029, 1091, 1129, 1215, 1287, 1329, 1390, 1402, 1448, 1571, 1615, 1670, 2213, 2977, 3095 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.20 (s, 10 H, 2 C_5H_5), 4.57 (m, 4 H, C_5H_4), 4.92 (m, 4 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 71.00 (2 C_5H_5), 71.49, 72.36 (2 C_5H_4), 85.34 (2 C_{ipso}Fc), 136.11, 137.08 (2 C), 140.35 (2 C), 173.63 (2 C) ppm. $C_{26}H_{18}Fe_2N_2$ (470): calcd. C 66.42, H 3.86, Fe 23.76, N 5.96; found C 66.28, H 3.77, Fe 23.64, N 6.06. MS: m/z = 470 $[M]^+$.

2,3-Diferrocenyl-5-imino-4-(methylthio)-1,3-cyclopentadiene-1-carbonitrile (13): Yield: 0.17 g (11%), orange crystals, m.p. 213–214 °C. IR (KBr): $\tilde{\nu}$ = 498, 617, 728, 824, 906, 1002, 1056, 1106, 1263, 1411, 1538, 1574, 1634, 2084, 2178, 2922, 3092, 3350, 3438 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, SCH_3), 4.09 (s, 5 H, C_5H_5), 4.36 (s, 5 H,C_5H_5), 4.16 (m, 1 H, C_5H_4), 4.31 (m, 1 H, C_5H_4), 4.40 (m, 1 H, C_5H_4), 4.44 (m, 1 H, C_5H_4), 4.48 (m, 1 H, C_5H_4), 4.55 (m, 1 H, C_5H_4), 4.46 (m, 1 H, C_5H_4), 5.05 (m, 1 H, C_5H_4), 5.56 (br. s, 1 H, NH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.22 (CH_3), 70.43, 70.58 (2 C_5H_5), 67.58, 67.75, 68.07, 68.31, 69.65, 70.96, 71.39, 72.41 (2 C_5H_4), 83.38, 84.05 (2 C_{ipso}Fc), 134.04, 136.09, 144.21, 153.11, 155.21, 172.17 (6 C) ppm. $C_{27}H_{22}Fe_2N_2S$ (518): calcd. C 62.58, H 4.28, Fe 21.56, N 5.40, S 6.18; found C 62.42, H 4.18, Fe 21.39, N 5.53, S 6.23. MS: m/z = 518 $[M]^+$.

X-ray Crystal Structure Determinations: The unit cell parameters and the X-ray diffraction intensities were recorded with a Bruker Smart Apex CCD area detector/ω diffractometer. The structures of compounds **5** and **11** were solved by direct methods (SHELXS-97) [23] and refined using full-matrix least squares on F^2. CCDC-602117 (for **5**) and -602118 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for $C_{31}H_{32}Fe_2O_4S$ (5): M_r = 612.33.18 $g\,mol^{-1}$, monoclinic $P2_1/c$, a = 19.883(1), b = 12.1987(7), c = 11.5370(6) Å, β = 101.494(1), V = 2742.1(3) $Å^3$, T = 293(2) K, Z = 4, ρ = 1.483 $Mg\,m^{-3}$, λ(Mo-K_α) = 0.71073 Å, F(000) = 1272, an analytical absorption correction was applied, index ranges $-23 \le h \le 23$, $-14 \le k \le 14$, $-13 \le l \le 13$, scan range $1.05° \le \theta \le 25.04°$, 4849 independent reflections, R_{int} = 0.0561, 21987 total reflections, 345 refinable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0595, wR_2 = 0.1443, R indices (all data) R_1 = 0.0852, wR_2 = 0.1629, goodness-of-fit on F^2 1.007, largest difference peak and hole 0.551/–0.344 $e\,Å^{-3}$.

Crystal Data for $C_{27}H_{22}Fe_2N_2S$ (11): M_r = 518.23 $g\,mol^{-1}$, monoclinic $P2_1/n$, a = 11.7906(6), b = 10.3599(5), c = 19.2415(10) Å, β = 99.537(1), V = 2317.1(2) $Å^3$, T = 291(2) K, Z = 4, ρ = 1.485 $Mg\,m^{-3}$, λ(Mo-K_α) = 0.71073 Å, F(000) = 1064, an analytical absorption correction was applied, index ranges $-14 \le h \le 13$, $-12 \le k \le 12$, $-22 \le l \le 22$, scan range $2.15° \le \theta \le 25.00°$, 4079 independent reflections, R_{int} = 0.0523, 18511 total reflections, 290 refinable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0340, wR_2 = 0.0768, R indices (all data) R_1 = 0.0430, wR_2 = 0.0793, goodness-of-fit on F^2 0.955, largest difference peak and hole 0.359/–0.254 $e\,Å^{-3}$.

Acknowledgments

This work was supported by the DGAPA – UNAM (Mexico, grant IN 207606). Thanks are due to E. A. Vázquez López, M. L. Velasco, J. Perez, H. Rios and E. R. Patiño for their technical assistance.

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Received: May 11, 2006
Published Online: August 22, 2006

