Diferrocenyl(methylthio)cyclopropenylium Iodide in the Synthesis of 2,3-Diferrocenyl-1-methylthio-1,3-dienes and -1,3,5-trienes

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Diferrocenyl(methylthio)cyclopropenylium iodide reacts with organometallic compounds (methyllithium, benzyl- and ethylmagnesium chlorides, and allylmagnesium bromide) to yield 2,3-diferrocenyl-1-methylthio-1,3-dienes or -1,3,5-triene together with 3,3-dialkyl-1,2-diferrocenylcyclopropenes. We present data from X-ray diffraction analyses of (*E*)-2,3-diferrocenyl-1-methylthio- and (*E*,*Z*)-2,3-diferrocenyl-1-methylthio-4-phenyl-1,3-butadienes.

Introduction

Previously, we reported the synthesis of 2,3-diferrocenylcyclopropenone (**1**) through the alkylation of ferrocene with tetrachlorocyclopropene in the presence of $AlCl_3$[1] and its subsequent transformation into the diferrocenyl(ethoxy)cyclopropenylium cation (**2**) under the action of triethyloxonium tetrafluoroborate[2,3] (Scheme 1).

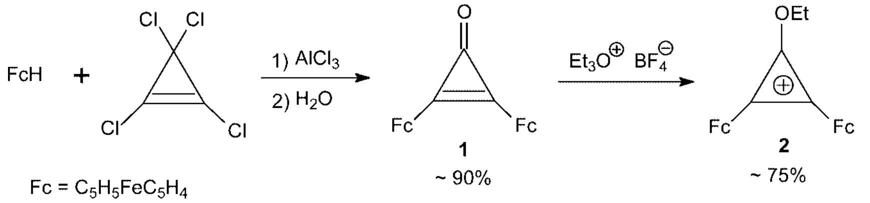
In the reactions of cyclopropenone **1** with RLi, diferrocenylallylic alcohols **3** were the main three-carbon ring-opened products,[1] whereas diferrocenyl ketones **4** together with small amounts of 3,3-dialkyl-1,2-diferrocenylcyclopropenes **5** were obtained from reactions with RMgX[4,5] (Scheme 2).

Unlike cyclopropenone **1**, cation **2** reacts with methyl- and butyllithium regioselectively to give compounds of the type **5** (R = Me, *n*Bu), that is, with the preservation of the three-membered ring[2] (Scheme 3).

Replacement of the ethoxy group in compound **2** for a more electron-donating alkylthio group would, in our opinion, affect the regioselectivity of the reactions of the cyclopropenyl cation with organometallic compounds and result in other types of products.

2,3-Diferrocenylcyclopropenethione (**6**), a sulfur analog of the cyclopropenone **1**, had to be employed as the starting material in the preparation of alkylthio(diferrocenyl)cyclopropenyl cations. Note that the chemistry of sulfur-containing derivatives of the ferrocene series has not been widely studied[6] and that 2,3-diferrocenylcyclopropenethione is a hitherto unknown compound.

In this report we describe the synthesis of 2,3-diferrocenylcyclopropenethione (**6**) and its derivative, diferrocenyl(methylthio)cyclopropenylium iodide (**7**), as well as some chemical properties of the latter.



Scheme 1.

Results and Discussion

Three main methods for the preparation of cyclopropenethiones are known, viz., nucleophilic substitution of a heterosubstituent (Cl, NR_2) in cyclopropenylium salts with Na_2S, NaHS, or H_2S as nucleophiles,[7] conversion of the carbonyl group in cyclopropenones into a thiocarbonyl

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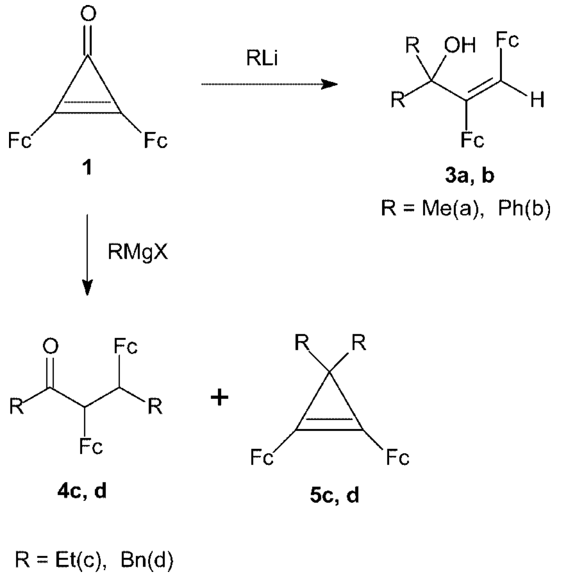
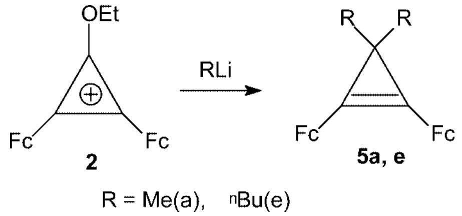


Scheme 2.



Scheme 3.

group,[8] and construction of the three-membered ring by [2+1] cycloaddition.[9]

In this work, we used the first of the above-mentioned methods to synthesize 2,3-diferrocenylcyclopropenethione (**6**), as shown in Scheme 4

The ethoxy group in cation **2** is easily replaced by an NR_2 group when treated with secondary amines. The aminocyclopropenyl salt **8**,[10,11] unlike the tetrafluoroborate salt **2**, is moderately soluble in ethanol and gives stable solutions. This has allowed us to use sodium sulfide or sodium hydrogensulfide as sulfur nucleophiles in the preparation of the thione **6**.

Cyclopropenethione **6** is a fine-crystalline dark-red compound that is storage-stable under ordinary conditions. Its structure was confirmed by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. Treatment of a solution of cyclopropenethione **6** in benzene with methyl iodide resulted in diferrocenyl(methylthio)cyclopropenylium iodide (**7**) as a red-violet precipitate (Scheme 4). This salt is stable when stored in a dry inert atmosphere.

We also found that diferrocenyl(methylthio)cyclopropenylium iodide (**7**) reacts with methyllithium to afford three products, viz., 1,2-diferrocenyl-3,3-dimethylcyclopropene (**5a**) and 2,3-diferrocenyl-1-methylthiobuta-1,3-dienes (**9**) and (**10**) in an approximately 1:1 ratio (Scheme 5).

Their structures were confirmed by ^1H (with a one-dimensional NOE experiment, Figure 1) and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

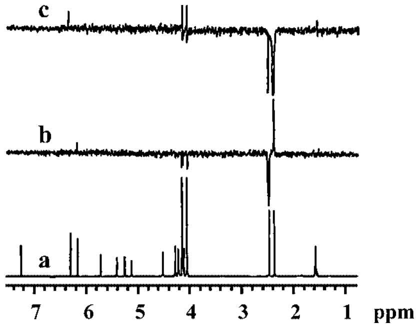
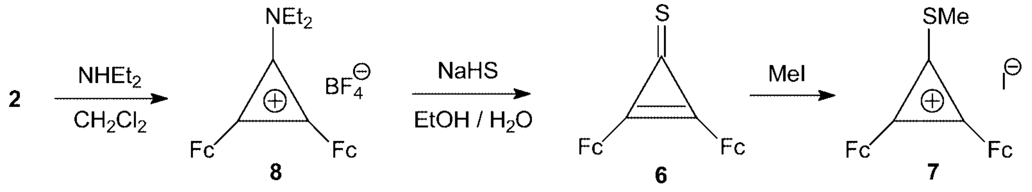
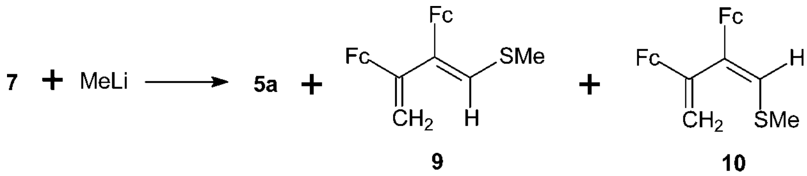


Figure 1. NOE difference spectra of **9** and **10** in $CDCl_3$ at 293 K generated by irradiation of the methyl protons (300 MHz). (a) ^1H NMR spectrum of the mixture of **9** and **10** (≈ 1:1); (b) irradiation of the CH_3 group of **9**; (c) irradiation of the CH_3 group of **10**.

The isomers were separated by TLC on silica gel. The spatial structures of compounds **9** and **10** were established by X-ray diffraction analysis of a single crystal of compound **9** prepared by crystallization from diethyl ether. The general view of molecule **9** is shown in Figure 2, and the main geometric parameters of compound **9** are given in the caption to Figure 2. The lengths of the C–Fe and C–C



Scheme 4.



Scheme 5.

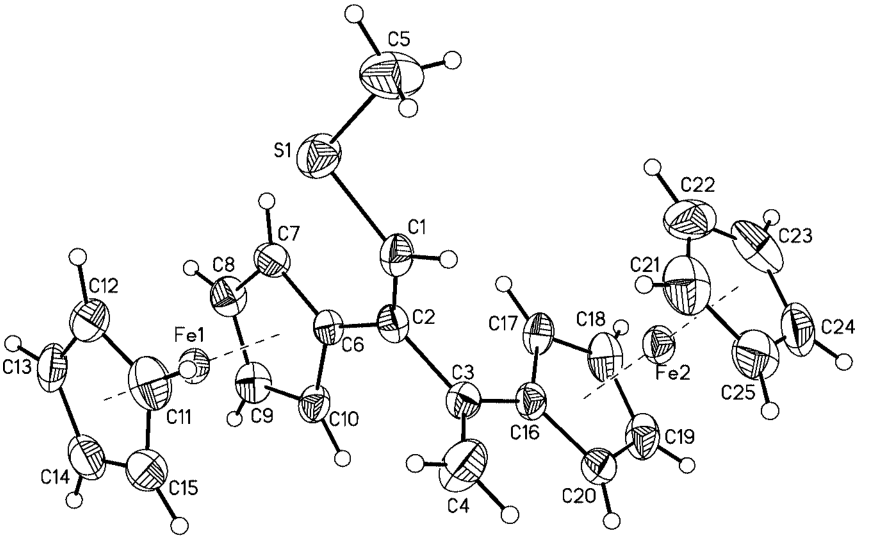
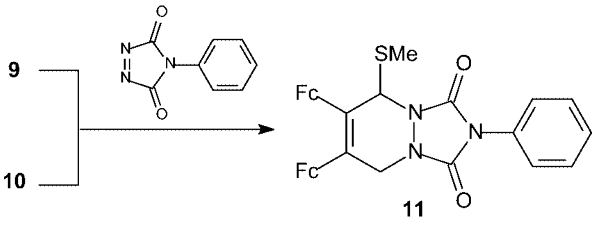


Figure 2. Crystal structure of **9**. Selected bond lengths [Å]: C(3)–C(4) = 1.319(3), C(2)–C(3) = 1.488(3), C(2)–C(1) = 1.399(3), C(6)–C(2) = 1.470(3), C(1)–S(1) = 1.743(2), C(5)–S(1) = 1.787(3). Selected bond angles [°]: C(4)–C(3)–C(2) = 120.5(2), C(3)–C(2)–C(1) = 117.3(2), C(2)–C(1)–S(1) = 128.4(2), C(1)–S(1)–C(5) = 99.97(13), C(16)–C(3)–C(2) = 116.4(2), C(3)–C(2)–C(6) = 116.5(2).

bonds in the ferrocenyl substituents, as well as the geometric parameters of the ferrocene sandwiches are close to standard values.[12] The X-ray results indicate that the diene **9** has an (*E*) configuration.

We also established that (*E*)- and (*Z*)-2,3-diferrocenyl-1-methylthio-1,3-butadienes (**9** and **10b**) react with *N*-phenylazodicarboximide to form the adduct **11** by [4+2] cycloaddition reactions (Scheme 6).



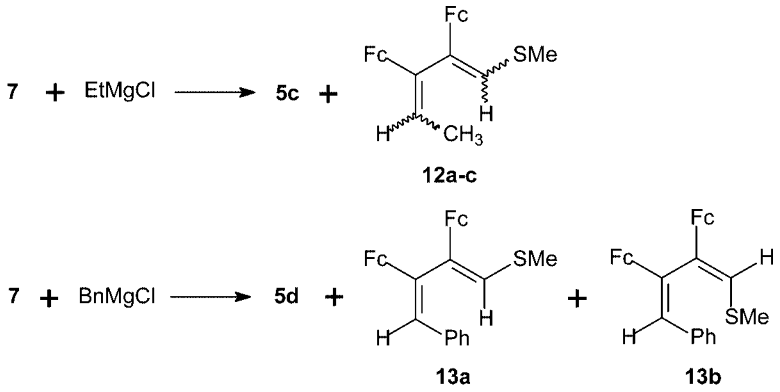
Scheme 6.

Diferrocenyl(methylthio)cyclopropenylium iodide (**7**) reacts with ethyl- and benzylmagnesium chlorides in the same fashion as with MeLi (Scheme 7).

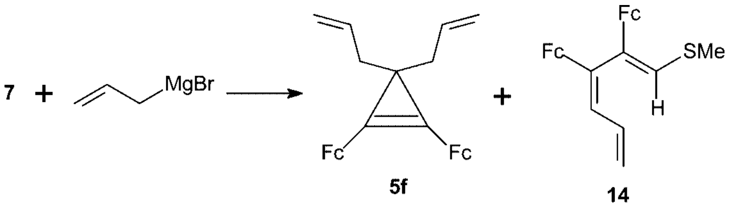
The ^{1}H and ^{13}C NMR spectroscopic data of the dienes **12** and **13** suggest that they were formed in three and two isomeric forms, respectively: **12a**, **12b**, and **12c** in a 3:2:1 ratio and **13a** and **13b** in a 1:1 ratio. This isomerism seems to be related to the different configurations of the FcC^2=C^{1}H(SMe) fragments of the dienic systems and the different or same configurations of the C^{3}Fc=C^{4}HR fragments.

Our attempts to separate the isomeric dienes **12a**, **12b**, and **12c** by chromatography failed, however they were easily identified by spectroscopy because the positions of all the signals in their ^{1}H and ^{13}C NMR spectra, their multiplicities, and integral intensities are distinctly different (see Exp. Sect.).

The isomers **13a** and **13b** were separated by TLC on silica gel. The spatial structures of compounds **13a** and **13b** were established by X-ray diffraction analysis of a single crystal of compound **13a** prepared by crystallization from dichloromethane. The general view of molecule **13a** is shown in Figure 3 and no special comments are needed.



Scheme 7.



Scheme 8.

The X-ray results indicate that diene **13a** has an (*E*,*Z*) configuration.

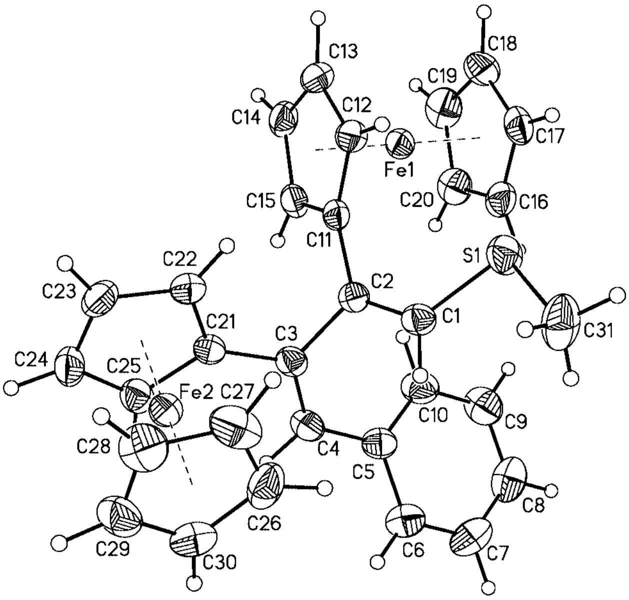


Figure 3. Crystal structure of **13a**. Selected bond lengths [Å]: C(1)–C(2) = 1.333(3), C(2)–C(3) = 1.502(3), C(3)–C(4) = 1.334(3), C(4)–C(5) = 1.469(4), C(1)–S(1) = 1.751(3), C(31)–S(1) = 1.794(3). Selected bond angles [°]: C(4)–C(3)–C(2) = 123.8(2), C(3)–C(2)–C(1) = 117.4(2), C(2)–C(1)–S(1) = 127.0(2), C(1)–S(1)–C(31) = 100.89(14), C(3)–C(4)–C(5) = 128.7(2), C(1)–C(2)–C(11) = 126.1(2).

Presumably, diene **12a** has an (*E*,*Z*) configuration analogous to those of **13a**, dienes **12b** and **13b** have an (*Z*,*Z*) configuration analogous to that of **10**, and diene **12c**, possibly, has an (*E*,*E*) configuration.

Unlike ethyl- and benzylmagnesium chlorides, allylmagnesium bromide reacts with diferrocenyl(methylthio)cyclopropenylium iodide (**7**) to give 2,3-diferrocenyl-1-methylthiohexa-1,3,5-triene (**14**) as a single [presumably, (*E*,*Z*)] isomer (Scheme 8).

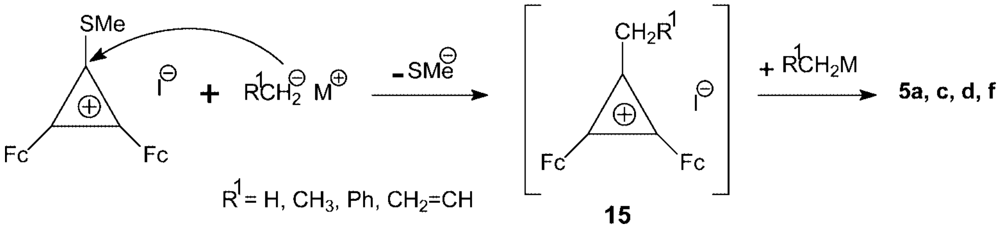
In addition, 3,3-diallyl-1,2-diferrocenylcyclopropene (**5f**) was isolated from the reaction mixture in approximately 25% yield. The structures of the reaction products **5f** and **14** were confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

Tentative mechanisms for the reactions of the cation **7** with organometallic compounds are represented in Scheme 9 and Scheme 10.

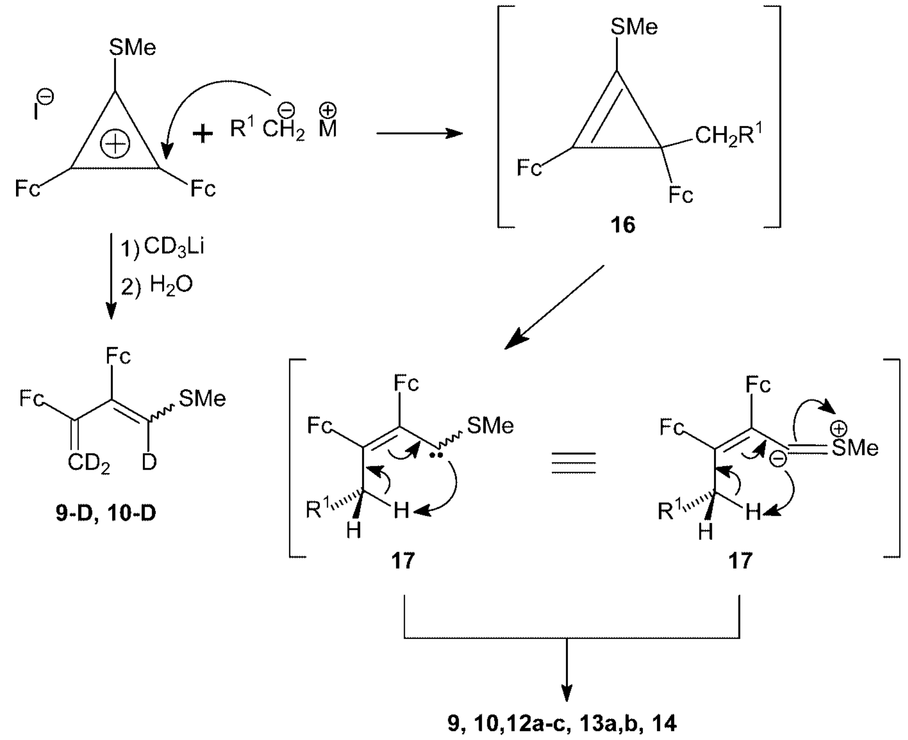
The results presented in this paper allow us to conclude that, depending on whether the nucleophile attacks at the C-1 (Scheme 9) or C-2 (Scheme 10) positions of **7**, the initially formed intermediates **15** and **16** usually form products that retain the original three-membered ring or undergo C–C bond cleavage to give ring-opened products. Note that small ring-opened products that retain the methylthio substituent dominate in all the reaction products. This behavior of diferrocenyl(methylthio)cyclopropenylium (**7**) is substantially different to that of its ethoxy analog **2**.

We believe, that the data we have collected show that the intramolecular transformation of the intermediate **17** into the final product is favored. Thus, the strained ring of diferrocenyl(methylthio)cyclopropenylium iodide is also readily opened when treated with [D$_3$]methyllithium. Quenching of the reaction mixture with H$_2$O resulted in compounds **9-D** and **10-D** (≈1:1) with about 92% deuterium, as judged by ^{1}H NMR data (Scheme 10).

The reactions described in this study will be, in our opinion, of interest to synthetic organic chemists looking to access functionalized ferrocenylpolyenes.



Scheme 9.



Scheme 10.

Experimental Section

All the solvents were dried according to standard procedures[13] and freshly distilled prior to use. Column chromatography was carried out on alumina (Brockmann activity III). The ^{1}H and ^{13}C NMR spectra were recorded with a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$, with Me_4Si as the internal standard. The ^{1}H NMR spectra of the tetrafluoroborates **2** and **8**, and diferrocenyl(methylthio)cyclopropenylium iodide (**7**) were recorded in CD_2Cl_2. The IR spectra were measured with a Specord IR-75 instrument in KBr pellets. UV spectra were recorded with a Specord UV/Vis spectrophotometer. The mass spectra were obtained with a Varian MAT CH-6 instrument (EI-MS, 70 eV). 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%; piperidine, 99%; morpholine, 99+%; methyllithium, 1.6 M solution in diethyl ether; [D$_3$]methyllithium, as a complex with lithium iodide, 0.5 M solution in diethyl ether; ethylmagnesium chloride, 2.0 M solution in diethyl ether; benzylmagnesium chloride, 1.0 M solution in diethyl ether; allylmagnesium bromide, 1.0 M solution in diethyl ether; iodomethane, 99.5%; sodium hydrosulfide hydrate $NaHS\cdot xH_2O$.

2,3-Diferrocenylcyclopropenone (1): Compound **1** was obtained from ferrocene and tetrachlorocyclopropene in the presence of $AlCl_3$ according to the standard procedure.[1,3]

Ethoxy(diferrocenyl)cyclopropenylium Tetrafluoroborate (2): Triethyloxonium tetrafluoroborate (1.0 M solution in dichloromethane, 5 mmol) was added with stirring to a solution of diferrocenylcyclopropenone (**1**) (0.85 g, 2 mmol) in dichloromethane (50 mL) in a dry inert atmosphere. Stirring was continued for 2 h and dry diethyl ether (100 mL) was then added. The violet precipitate was filtered off, washed with dry ether, and dried in vacuo. The yield of the title compound was 0.88 g (82%), m.p. 209–211 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 1.62$ (t, $J = 7.2$ Hz, 3 H, CH_3), 4.34 (s, 10 H, 2 C_5H_5), 4.77 (q, $J = 7.2$ Hz, 2 H, CH_2), 4.85 (m, 4 H, C_5H_4), 5.06 (m, 4 H, C_5H_4) ppm. $C_{25}H_{23}BF_4Fe_2O$ (538): calcd. C 55.81, H 4.31, F 14.13, Fe, 20.77; found C 55.73, H 4.50, F 14.09, Fe 20.93.

***N,N*-Diethylamino(diferrocenyl)cyclopropenylium Tetrafluoroborate (8):** Diethylamine (3.0 mL) was added dropwise to a solution of salt **2** (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, m.p. 182–184 °C. IR (KBr): $\tilde{\nu}$ = 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 °C): λ_{max} = 249, 284, 308, 349, 361, 419, 499 nm. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 1.50$ (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, 10 H, 2 C_5H_5), 4.83 (m, 4 H, C_5H_4), 4.90 (m, 4 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 14.62$ (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) ppm. $C_{27}H_{28}BF_4Fe_2N$ (565): calcd. 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 (6): A solution of NaHS (1.0 g) in water (10 mL) was added to a stirred suspension of salt **8** (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 approximately 2.0 g (91%), dark-red fine crystals, m.p. 208–209 °C. Following purification by chromatography on alumina (hexane/dichloromethane, 5:1), thione **6** had a m.p. of 209–210 °C. IR (KBr): $\tilde{\nu}$ = 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 °C): λ_{max} = 248, 280, 298, 416, 475 nm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.27 (s, 10 H, 2 C$_5$H$_5$), 4.69 (m, 4 H, C$_5$H$_4$), 4.98 (m, 4 H, C$_5$H$_4$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 63.25 (2 C$_{ipso}$Fc), 70.14 (2 C$_5$H$_5$), 71.29, 72.95 (2 C$_5$H$_4$), 152.66 (2 C), 171.15 (C=S) ppm. C$_{23}$H$_{18}$Fe$_2$S (438): calcd. 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 (7): Methyl iodide (0.5 mL) was added dropwise to a solution of cyclopropenethione **6** (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 **7** was filtered off, washed with benzene, and dried in a vacuum desiccator. The yield of the iodide **7** was 0.93 g (80%), m.p. 248–250 °C. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 3.25 (s, 3 H, CH$_3$), 4.49 (s, 10 H, 2 C$_5$H$_5$), 5.09 (m, 8 H, 2 C$_5$H$_4$) ppm. ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ = 21.26 (CH$_3$), 58.79 (2 C$_{ipso}$Fc), 72.26 (2 C$_5$H$_5$), 74.32, 77.50 (2 C$_5$H$_4$), 151.27 (2 C), 152.30 (C–S) ppm. C$_{24}$H$_{21}$Fe$_2$IS (580): calcd. 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 (7) with Organometallic Compounds (General Procedure): Organometallic compounds (1.0–2.0 M solutions in diethyl ether, 5.0–7.0 mL) were added to a suspension of salt **7** (2.0 mmol) in dry benzene (100 mL) and the mixture was stirred in an inert dry atmosphere until complete dissolution of the salt **7** occurred (≈6 h). The excess of the organometallic compound was quenched with water (20 mL), the organic layer was separated, concentrated, and the residue was purified by chromatography on alumina in hexane to yield 3,3-dialkyl-1,2-diferrocenylcyclopropenes **5a**,**c**,**d**,**f** and 2,3-diferrocenyl-1-methylthiopolyenes **9**, **10**, **12a**,**b**,**c**, **13a**,**b**, and **14**.

Reactions of Salt 7 with Methyllithium: Following the procedure above, the reaction of salt **7** (1.18 g, 2 mmol) with MeLi (5.0 mL of 1.6 M solution in diethyl ether) in dry benzene and subsequent work up afforded the following reaction products: 1,2-diferrocenyl-3,3-dimethylcyclopropene (**5a**) [0.087 g (10%), orange crystals, m.p. 132–133 °C (ref.[2] m.p 132–133 °C)] and 2,3-diferrocenyl-1-methylthio-1,3-butadiene as a mixture of two isomers **9** and **10** in an approximate 1:1 ratio (by ^{1}H NMR spectroscopy) [0.78 g (82%), orange powder, m.p. 165–167 °C].

1,2-Diferrocenyl-3,3-dimethylcyclopropene (5a): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.38 (s, 6 H, 2 CH$_3$), 4.14 (s, 10 H, 2 C$_5$H$_5$), 4.35 (m, 4 H, C$_5$H$_4$), 4.48 (m, 4 H, C$_5$H$_4$) ppm. C$_{25}$H$_{24}$Fe$_2$ (436): calcd. C 68.84, H 5.55, Fe 25.61; found C 68.73, H 5.46, Fe 25.81. MS: m/z = 436 [M]$^+$.

(*E*)-2,3-Diferrocenyl-1-methylthio-1,3-butadiene (9): Yield: 0.34 g (35%), orange crystals, m.p. 176–177 °C. IR (KBr): $\tilde{\nu}$ = 821, 873, 1000, 1026, 1054, 1108, 1232, 1287, 1371, 1435, 1605, 1640, 1752, 2927, 2948, 2971, 3059 cm^{-1}. UV (CHCl$_3$, 20 °C): λ_{max} = 246, 392, 450 nm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.47 (s, 3 H, CH$_3$), 4.04 (s, 5 H, C$_5$H$_5$), 4.13 (s, 5 H, C$_5$H$_5$), 4.12 (m, 2 H, C$_5$H$_4$), 4.15 (m, 2 H, C$_5$H$_4$), 4.23 (m, 2 H, C$_5$H$_4$), 4.52 (m, 2 H, C$_5$H$_4$), 5.13 (d, J = 2.4 Hz, 1 H, CH$_2$=), 5.41 (d, J = 2.4 Hz, 1 H, CH$_2$=), 6.17 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 18.74 (CH$_3$), 68.31, 69.57 (2 C$_5$H$_5$), 67.61, 68.11, 68.32, 68.87 (2 C$_5$H$_4$), 83.17, 85.27 (2 C$_{ipso}$Fc), 110.72 (CH$_2$=), 124.31 (CH=), 136.0, 149.24 (2 C) ppm. C$_{25}$H$_{24}$Fe$_2$S (468): calcd. C 64.12, H 5.16, Fe 23.90, S 6.82; found C 64.23, H 5.06, Fe 24.01, S 6.98. MS: m/z = 468 [M]$^+$.

(*Z*)-1,3-Diferrocenyl-1-methylthio-1,3-butadiene (10): Yield: 0.31 g (32%), red-brown powder, m.p. 172–173 °C. IR (KBr): $\tilde{\nu}$ = 818, 864, 1001, 1027, 1051, 1100, 1229, 1292, 1363, 1447, 1605, 1644, 1768, 2934, 2952, 2969, 3090 cm^{-1}. UV (CHCl$_3$, 20 °C): λ_{max} = 247, 394, 452 nm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.37 (s, 3 H, CH$_3$), 4.06 (s, 5 H, C$_5$H$_5$), 4.15 (s, 5 H, C$_5$H$_5$), 4.10 (m, 2 H, C$_5$H$_4$), 4.14 (m, 2 H, C$_5$H$_4$), 4.21 (m, 2 H, C$_5$H$_4$), 4.28 (m, 2 H, C$_5$H$_4$), 5.26 (d, J = 1.8 Hz, 1 H, CH$_2$=), 5.73 (d, J = 1.8 Hz, 1 H, CH$_2$=), 6.30 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 17.62 (CH$_3$), 69.39, 69.81 (2 C$_5$H$_5$), 66.22, 67.78, 67.90, 68.05 (2 C$_5$H$_4$), 84.68, 86.17 (2 C$_{ipso}$Fc), 113.74 (CH$_2$=), 122.67 (CH=), 137.05, 144.74 (2 C) ppm. C$_{25}$H$_{24}$Fe$_2$S (468): calcd. C 64.12, H 5.16, Fe 23.90, S 6.82; found C 64.06, H 5.25, Fe 23.71, S 6.67. MS: m/z = 468 [M]$^+$.

Reactions of Salt 7 with Ethylmagnesium Chloride: Following the general procedure, the reaction of salt **7** (1.18 g, 2 mmol) with EtMgCl (4.0 mL of a 2 M solution in diethyl ether) in dry benzene afforded the following reaction products: 1,2-diferrocenyl-3,3-diethylcyclopropene (**5c**) [0.19 g (20%), orange crystals, m.p. 169–169 °C (ref.[3] m.p. 168–169 °C)] and 2,3-diferrocenyl-1-methylthio-1,3-pentadiene as a mixture of three isomers **12a**, **12b**, and **12c** in an approximate 3:2:1 ratio (by ^{1}H NMR spectroscopy). Yield of isomers **12**, 0.52 g (55%), orange powder, m.p. 148–151 °C. IR (KBr): $\tilde{\nu}$ = 468, 489, 694, 755, 813, 857, 1000, 1030, 1103, 1183, 1254, 1325, 1384, 1409, 1490, 1593, 1637, 1682, 2919, 3024, 3090 cm^{-1}. UV (CHCl$_3$, 20 °C): λ_{max} = 252, 280, 304, 414, 457 nm. C$_{26}$H$_{26}$Fe$_2$S (482): calcd. C 64.75, H 5.44, Fe 23.16, S 6.65; found C 64.93, H 5.28, Fe 23.24, S 6.58. MS: m/z = 482 [M]$^+$.

(*E*,*Z*)-2,3-Diferrocenyl-1-methylthio-1,3-pentadiene (12a): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.82 (d, J = 6.9 Hz, 3 H, CH$_3$), 2.47 (s, 3 H, CH$_3$), 4.03 (s, 5 H, C$_5$H$_5$), 4.20 (s, 5 H, C$_5$H$_5$), 4.11 (m, 2 H, C$_5$H$_4$), 4.24 (m, 2 H, C$_5$H$_4$), 4.36 (m, 2 H, C$_5$H$_4$), 4.81 (m, 2 H, C$_5$H$_4$), 5.95 (q, J = 6.9 Hz, 1 H, CH=), 6.01 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 15.44, 18.64 (2 CH$_3$), 69.12, 69.16 (2 C$_5$H$_5$), 67.67, 67.83, 67.98, 68.86, 69.09, 69.21, 69.56, 69.68 (2 C$_5$H$_4$), 84.10, 87.98 (2 C$_{ipso}$Fc), 120.39, 125.48 (2 CH=), 131.97, 140.67 (2 C) ppm.

(*Z*,*Z*)-2,3-Diferrocenyl-1-methylthio-1,3-pentadiene (12b): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.05 (d, J = 7.2 Hz, 3 H, CH$_3$), 2.45 (s, 3 H, CH$_3$), 4.07 (s, 5 H, C$_5$H$_5$), 4.13 (s, 5 H, C$_5$H$_5$), 4.15 (m, 2 H, C$_5$H$_4$), 4.22 (m, 2 H, C$_5$H$_4$), 4.32 (m, 2 H, C$_5$H$_4$), 4.44 (m, 2 H, C$_5$H$_4$), 5.73 (q, J = 7.2 Hz, 1 H, CH=), 6.03 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 15.49, 18.66 (2 CH$_3$), 69.07, 69.20 (2 C$_5$H$_5$), 68.20, 68.28, 68.92, 69.56 (2 C$_5$H$_4$), 84.08, 84.25 (2 C$_{ipso}$Fc), 123.32, 123.66 (2 CH=), 135.62, 142.00 (2 C) ppm.

(*E*,*E*)-2,3-Diferrocenyl-1-methylthio-1,3-pentadiene (12c): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.79 (d, J = 7.2 Hz, 3 H, CH$_3$), 2.38 (s, 3 H, CH$_3$), 4.02 (s, 5 H, C$_5$H$_5$), 4.08 (s, 5 H, C$_5$H$_5$), 3.98 (m, 2 H, C$_5$H$_4$), 4.10 (m, 2 H, C$_5$H$_4$), 4.19 (m, 2 H, C$_5$H$_4$), 4.31 (m, 2 H, C$_5$H$_4$), 6.07 (q, J = 7.2 Hz, 1 H, CH=), 6.38 (s, 1 H, CH=) ppm.

Reactions of Salt 7 with Benzylmagnesium Chloride: Following the general procedure, the reaction of salt **7** (1.18 g, 2 mmol) with BnMgCl (7.0 mL of a 1 M solution in diethyl ether) in dry benzene afforded the following reaction products: 1,2-diferrocenyl-3,3-dibenzylcyclopropene (**5d**) [0.23 g (20%), orange crystals, m.p. 112–114 °C (ref.[4] m.p. 112–113 °C)] and 2,3-diferrocenyl-1-methylthio-4-phenyl-1,3-butadiene **13** as a mixture of two isomers **13a** and **13b** in an approximate 1:1 ratio (by ^{1}H NMR spectroscopy) [0.70 g (68%), orange powder, m.p. 139–141 °C].

(*E*,*Z*)-2,3-Diferrocenyl-1-methylthio-4-phenyl-1,3-butadiene (13a): Yield: 0.34 g (32%), orange crystals, m.p. 149–150 °C. IR (KBr): $\tilde{\nu}$ = 472, 698, 753, 814, 855, 1001, 1030, 1105, 1182, 1253, 1326, 1384, 1410, 1451, 1493, 1599, 1625, 1652, 2839, 2889, 2931, 3026, 3058, 3088 cm^{-1}. UV (CHCl$_3$, 20 °C): λ_{max} = 251, 279, 305, 415, 457 nm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.37 (s, 3 H, CH$_3$), 4.07 (s, 5 H, C$_5$H$_5$), 4.22 (s, 5 H, C$_5$H$_5$), 4.16 (m, 2 H, C$_5$H$_4$), 4.20 (m, 2 H,

C_5H_4), 4.32 (m, 2 H, C_5H_4), 4.64 (m, 2 H, C_5H_4), 6.18 (s, 1 H, CH=), 6.79 (s, 1 H, CH=), 7.16–7.66 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.42 (CH_3), 70.50, 70.62 (2 C_5H_5), 68.86, 69.11, 69.33, 69.57 (2 C_5H_4), 87.24, 90.51 (2 C_{ipso}Fc), 125.19, 127.90 (2 CH=), 126.60, 127.91, 129.09 (C_6H_5), 131.33, 137.04, 141.75 (3 C) ppm. $C_{31}H_{28}Fe_2S$ (544): calcd. C 68.40, H 5.20, Fe 20.52, S 5.88; found C 68.51, H 5.08, Fe 20.67, S 6.08. MS: m/z = 544 $[M]^+$.

(*Z*,*Z*)-2,3-Diferrocenyl-1-methylthio-4-phenyl-1,3-butadiene (13b): Yield: 0.32 g (31%), red-brown powder, m.p. 146–147 °C. IR (KBr): $\tilde{\nu}$ = 474, 696, 757, 813, 858, 1002, 1029, 1103, 1180, 1254, 1324, 1386, 1412, 1453, 1491, 1600, 1626, 1648, 2840, 2890, 2930, 3027, 3056, 3082 cm^{-1}. UV ($CHCl_3$, 20 °C): λ_{max} = 250, 281, 303, 414, 456 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.375 (s, 3 H, CH_3), 4.08 (s, 5 H, C_5H_5), 4.23 (s, 5 H, C_5H_5), 4.13 (m, 2 H, C_5H_4), 4.21 (m, 2 H, C_5H_4), 4.35 (m, 2 H, C_5H_4), 4.53 (m, 2 H, C_5H_4), 6.20 (s, 1 H, CH=), 6.80 (s, 1 H, CH=), 7.19–7.70 (m, 5 H, C_6H_5) ppm. $C_{31}H_{28}Fe_2S$ (544): calcd. C 68.40, H 5.20, Fe 20.52, S 5.88; found C 68.29, H 5.31, Fe 20.37, S 5.72. MS: m/z = 544 $[M]^+$.

Reactions of Salt 7 with Allylmagnesium Bromide: Following the general procedure, the reaction of salt **7** (1.18 g, 2 mmol) with allylMgBr (7.0 mL of a 1 M solution in diethyl ether) in dry benzene afforded **5f** and **14**.

3,3-Diallyl-1,2-diferrocenylcyclopropene (5f): Yield: 0.24 g (25%), orange crystals, m.p. 89–90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (dt, J = 1.2, 7.5 Hz, 4 H, 2 CH_2), 4.14 (s, 10 H, 2 C_5H_5), 4.33 (m, 4 H, C_5H_4), 4.47 (m, 4 H, C_5H_4), 5.03 (m, 1 H, CH_2=), 5.05 (m, 1 H, CH_2=), 5.07 (m, 1 H, CH_2=), 5.11 (m, 1 H, CH_2=), 6.00 (m, 2 H, 2 CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.11 (C), 42.14 (2 CH_2), 69.32, (2 C_5H_5), 68.77, 69.16 (2 C_5H_4), 74.32 (2 C_{ipso}Fc), 115.63 (2 CH_2=), 117.0 (2 C), 138.19 (2 CH=) ppm. $C_{29}H_{28}Fe_2$ (488): calcd. C 71.34, H 5.78, Fe 22.88; found C 71.45, H 5.61, Fe 23.03. MS: m/z = 488 $[M]^+$.

(*E*,*Z*)-2,3-Diferrocenyl-1-methylthio-1,3,5-hexatriene (14): Yield: 0.63 g (63%), orange crystals, m.p. 59–60 °C. IR (KBr): $\tilde{\nu}$ = 666, 757, 817, 898, 999, 1030, 1050, 1106, 1218, 1254, 1291, 1385, 1413, 1430, 1577, 1617, 1658, 1762, 2834, 2920, 3006, 3092 cm^{-1}. UV ($CHCl_3$, 20 °C): λ_{max} = 251, 277, 300, 409, 451 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 4.04 (s, 5 H, C_5H_5), 4.19 (s, 5 H, C_5H_5), 4.03 (m, 1 H, C_5H_4), 4.09 (m, 2 H, C_5H_4), 4.31 (m, 1 H, C_5H_4), 4.23 (m, 2 H, C_5H_4), 4.47 (m, 1 H, C_5H_4), 4.86 (m, 1 H, C_5H_4), 5.15 (dd, J = 1.2, 11.1 Hz, 1 H, CH_2=), 5.35 (dd, J = 1.5, 16.8 Hz, 1 H, CH_2=), 6.07 (s, 1 H, CH=), 6.50 (d, J = 11.1 Hz, 1 H, CH=), 6.79 (td, J = 11.1, 16.8 Hz, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.64 (CH_3), 69.12, 69.39 (2 C_5H_5), 67.47, 67.60, 68.44, 68.54, 68.88, 69.0, 69.25, 69.57 (2 C_5H_4), 84.19, 86.16 (2 C_{ipso}Fc), 115.14 (CH_2=), 125.52, 126.29, 135.50 (3 CH=), 126.60, 131.57, 143.28 (2 C) ppm. $C_{27}H_{26}Fe_2S$ (494): calcd. C 65.61, H 5.30, Fe 22.60, S 6.49; found C 65.47, H 5.19, Fe 22.76, S 6.68. MS: m/z = 494 $[M]^+$.

Reaction of Diene 9 (or 10) with *N*-Phenylazodicarboximide: A solution of *N*-phenylazodicarboximide (0.18 g, 1 mmol) and diene **9** (or **10**) (0.47 g, 1 mmol) in toluene (50 mL) was refluxed for 3 h. Then the solvent was evaporated and the residue was purified by chromatography on alumina (hexane/dichloromethane, 3:1) to give 0.42 g (65%) of *N*-phenyl-4,5-diferrocenyl-3-methylthio-1,2,3,6-tetrahydropyridazine-1,2-dicarboximide (**11**) as orange crystals, m.p. 238–239 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, CH_3), 4.15 (s, 5 H, C_5H_5), 4.17 (s, 5 H, C_5H_5), 3.94 (m, 1 H, C_5H_4), 3.97 (m, 1 H, C_5H_4), 4.12 (m, 1 H, C_5H_4), 4.16 (m, 1 H, C_5H_4), 4.33 (m, 3 H, C_5H_4), 4.74 (m, 1 H, C_5H_4), 4.61 (d, J = 16.5 Hz, 1 H, CH_2), 4.85 (d, J = 16.5 Hz, 1 H, CH_2), 6.39 (s, 1 H, CH), 7.37–7.65 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.32 (CH_3), 46.02 (CH_2), 63.78 (CH), 69.25, 69.44 (2 C_5H_5), 67.49, 67.77, 68.26, 68.37, 68.32, 68.82, 69.77, 70.19 (2 C_5H_4), 81.81, 84.56 (2 C_{ipso}Fc), 125.36, 128.11, 129.16 (C_6H_5), 125.45, 126.76, 131.43, 150.28, 150.52 (5 C) ppm. $C_{33}H_{29}Fe_2N_3O_2S$ (643): calcd. C 61.61, H 4.54, Fe 17.36, N 6.53, S 4.98; found C 61.46, H 4.71, Fe 17.41, N 6.63, S 4.69. MS: m/z = 644 $[M]^+$.

Crystal Structure Determination: 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 **9** and **13a** were solved by the direct method (SHELXS-97[14]) and refined using full-matrix least-squares on F^2.

Crystal Data for $C_{25}H_{24}Fe_2S$ (9): M_r = 468.20 g mol^{-1}, monoclinic, $P2_1/c$, a = 11.1342(7), b = 12.8526(8), c = 15.0620(9) Å, α = 90, β = 107.636(1), γ = 90°, V = 2054.1(2) Å^3, T = 291(2) K, Z = 4, ρ = 1.514 Mg m^{-3}, λ (Mo-K_α) = 0.71073 Å, F(000) = 968, analytical absorption correction, index ranges: $-13 \le h \le 13$, $-15 \le k \le 15$, $-17 \le l \le 17$, scan range: $1.92 \le \theta \le 24.99°$, 3619 independent reflections, R_{int} = 0.0423, 16503 total reflections, 254 refinable parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0314, wR_2 = 0.0576, R indices (all data): R_1 = 0.0442, wR_2 = 0.0598, goodness-of-fit on F^2 = 0.867, max. and min. transmission = 0.9179 and 0.6565, largest difference peak and hole = 0.463/–0.192 e Å^{-3}.

Crystal Data for $C_{31}H_{28}Fe_2S$ (13a): M_r = 544.29 g mol^{-1}, triclinic, $P\bar{1}$, a = 8.9484(5), b = 12.4854(7), c = 12.5132(7) Å, α = 110.01(1), β = 104.341(1), γ = 97.800(1)°, V = 1234.74(12) Å^3, T = 291(2) K, Z = 2, ρ = 1.464 Mg m^{-3}, λ (Mo-K_α) = 0.71073 Å, F(000) = 564, analytical absorption correction, index ranges: $-10 \le h \le 10$, $-14 \le k \le 14$, $-14 \le l \le 14$, scan range: $1.83 \le \theta \le 25.00°$, 4344 independent reflections, R_{int} = 0.0350, 10200 total reflections, 308 refinable parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0368, wR_2 = 0.0742, R indices (all data): R_1 = 0.0487, wR_2 = 0.0779, goodness-of-fit on F^2 = 0.972, max. and min. transmission = 0.8462 and 0.6895, largest difference peak and hole = 0.289/–0.287 e Å^{-3}.

CCDC-280308 (for **9**) and -280309 (for **13a**) 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.

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