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Synthesis of Ortho-, Meta- and Paracyclo(1,1′)ferrocenophanes Containing Sulfide Bonds

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The title dithiaferrocenophanes (**1**–**5**) have been synthesized in reactions of 1,1′-di(hydroxymethyl)ferrocene with o-, m- and p-dithiophenols, applying high dilution technique and small amount of trifluoracetic acid as catalyst. As by-products insoluble ferrocene polysulphides formed in competitive intermolecular condensations were isolated in all cases. In reactions of isomeric dithiophenols with ferrocenylmethanol acyclic model compounds (**6**–**10**) were prepared for spectral comparisons. The complexing ability of the synthesized ortho- and meta(1,1′)ferrocenophanes **1** and **3** with metal cations was measured by a solvent-extraction method, and was found to be poor with alkali cations but significantly better with Ag^+ cations.

Key words: iron, ferrocenes, ferrocenophanes, complexing ability

Ferrocenophanes containing one or more aromatic ring have been described [1–5]. An interesting electronic structure, nontypical stereochemistry, transannular interactions and complexing ability of the ortho-, meta- and paracyclo(1,1′)ferrocenophanes stimulated an interest in such compounds.

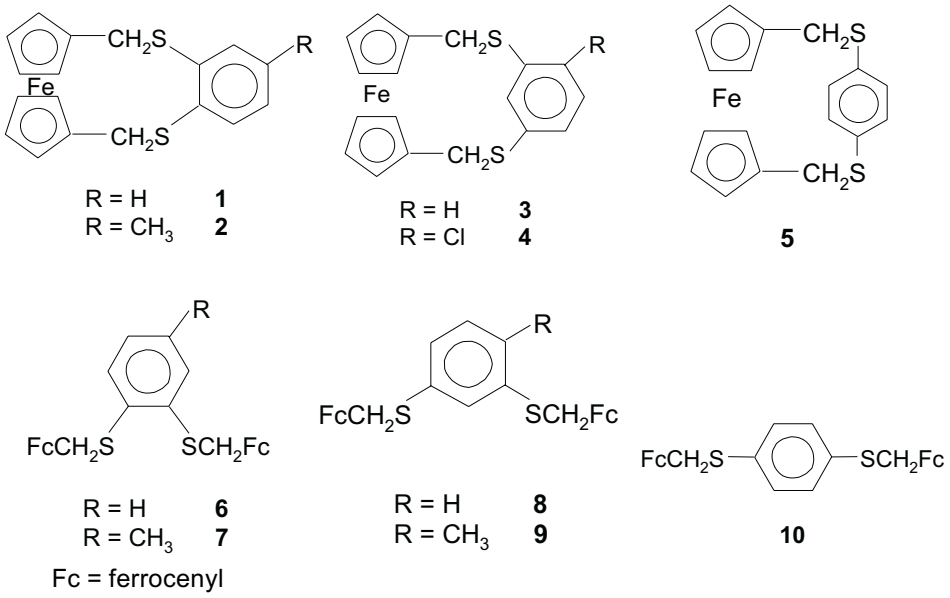

Figure 1.

This work discusses the synthesis of a few new analogs of dithiaortho-, dithiameta- and dithiaparacyclo(1,1′)ferrocenophanes. A novel method developed in our laboratory was applied. It consists in a cyclization of 1,1′-di(hydroxymethyl)ferrocene with the respective dithiol under high dilution (conc. 4 mmole, N_2, 40°C, *ca* 15 h) and in the presence of the catalytic amount of trifluoracetic acid [6]. The spectroscopic data: ^{1}H NMR, IR and UV of the ferrocenophanes **1–5** and model acyclic compounds **6–10** (Fig. 1), obtained by a similar method, allow the analysis of the potential intermolecular interactions of the ferrocenophanes discussed. It can be speculated that in some cases these compounds have the structure of ferrocene ring-tilt distortion. We also present the results of the complexing ability of dithia(1,1′)ferrocenophanes **1** and **3**.

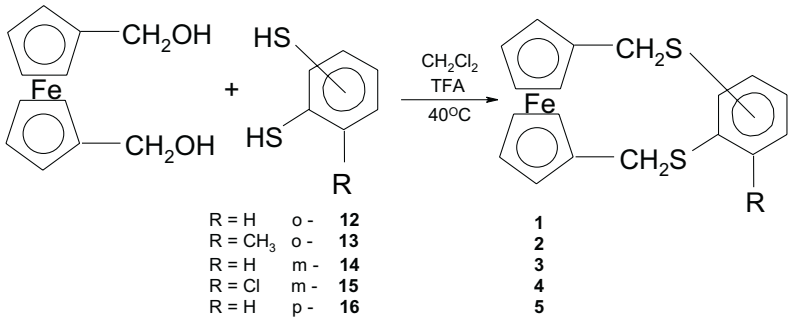

Figure 2.

RESULTS AND DISCUSSION

Dithia(1,1′)ferrocenophanes **1–5** (Fig. 1) were obtained in the reaction of 1,1′-di(hydroxymethyl)ferrocene **11** and respective dithiophenols **12–16** (Fig. 2). 1,1′-Di(hydroxymethyl)ferrocene **11** was synthesized according to the method described in [7]. Dithiophenols **12**, **14** and **16** were synthesized in the reaction of cuprous phenylmercaptide with o-, m- or p-dichlorobenzene, followed by the reduction (with natrium in liquid ammonia) of the respective 1,2-, 1,3- and 1,4-bis(phenylthia)benzene [8,9]. Dithiophenols **13** and **15** were of the highest commercially available purity. The reactions were performed using a high dilution technique under nitrogen in the presence of the catalytic amounts of TFA at 40°C. Methylene chloride or a mixture of CH_2Cl_2 and benzene 1:1 were used as solvents. The obtained ferrocenophanes were separated from the reaction mixture by crystallization or by column chromatography. The yields of the reactions, given in Table 1, vary from 32% (5) to 81% (compound **1**).

The structure of the ferrocenophanes was proved by spectroscopic analysis (MS, IR, ^{1}H NMR, UV) and elemental analysis. The molecular mass was measured also by the osmometric and the isothermal distillation methods. The analysis proved that the molecules of the compounds obtained involve a single ferrocene moiety.

Table 1. Reaction of 1,1′-di(hydroxymethyl)ferrocene **11** with dithiophenols **12–16**.

Dithiophenol	Product	Yield [%]	Mp [°C]
12	**1**	82	56–57
13	**2**	44	165
14	**3**	71	137–139
15	**4**	41	178–179
16	**5**	32	160 (decomp.)

The ^{1}H NMR spectra of the ferrocenophanes **1** and **2** are almost the same as those of the acyclic analogs **6** and **7**. Therefore, it can be speculated that orthocyclo-(1,1′)ferrocenophanes **1** and **2** have a strainless structure without distortions within the ferrocene unit. Because the chemical shifts of benzene protons in ferrocenophanes **1** and **2** are the same as those for acyclic model compounds **6** and **7**, it can be speculated that the benzene ring takes a position perpendicular to the cyclopentadiene ligands. In such a structure the benzene hydrogens are located outside the ferrocene deshielding field [10]. This is proved by the comparison of the UV spectra **1** and **2**, and **6** and **7**, respectively. The absorption band, corresponding to the d-d transition, can be found at $\lambda = 440$ nm for all ferrocenophanes and reference acyclic compounds. This indicates clearly no structural distortion of the ferrocene unit, that would otherwise be manifested by a shifting of this sensitive band, even within few nanometers [11]. Also Dreidings models of these molecules seem to indicate such a structure. Moreover, the comparison of the ^{1}H NMR spectra of **3** and **4** and those for acyclic analogs suggests a planar position of the benzene ring in relation to the cyclopentadiene ligands. Such a location explains the deshielding effect, observed for the benzene proton located near two sulfur atoms. For compound **3** this signal appears at $\delta = 7.48$ ppm and for compound **4** at $\delta = 7.62$ ppm. Ferrocene absorption band at $\lambda = 445$ nm decreases slightly, that suggests a little deviation of the cyclopentadiene rings from their planar position.

For the compound **5** ferrocene band occurs near $\lambda = 470$ nm, while the same band for the acyclic model **10** is shifted to $\lambda = 435$ nm. The substantial bathochrome shift clearly indicates the deformation within the ferrocene unit. A signal of the benzene ring protons in ^{1}H NMR spectrum of the paracyclo(1,1′)ferrocenophane **5** occurs as quartet at $\delta = 7.30$ ppm, and at multiplet $\delta = 7.23$ ppm for the model compound **10**. This suggests that rotation of the benzene ring at ambient temperature is hindered.

The ^{1}H NMR spectra of **1** and **3** registered at 28°C, 50°C, 70°C, 90°C and 120°C (DMSO-d_6) do not show any substantial changes, if compared with standard ones.

The spectroscopic investigations indicate that dithiaorthocyclo(1,1′)ferrocenophanes **1** and **2** as well as dithiametacyclo(1,1′)ferrocenophanes **3** and **4** have a strainless structure with none significant deformations within the ferrocene unit. The benzene ring in ferrocenophanes **1**, **2** and **5** takes approximately a location perpendicular to the cyclopentadienyl ligands, while in dithiametacyclo(1,1′)ferrocenophanes **3** and **4** this arrangement is parallel to each other. Moreover, the ^{1}H NMR spectra sug-

gest a restricted rotation of the benzene ring in metacycloferrocenophanes **3** and **4**, while in paracycloferrocenophane **5** such a rotation is significantly hindered. Ferrocenophane **5** has a strain structure, that is significantly deformed within the ferrocene unit. Ortho- and metacyclo(1,1′)ferrocenophanes **1**, **2**, **3** and **4** are formed much easier with higher yields and they are much more stable, while storing in comparison to paracyclo(1,1′)ferrocenophane **5**.

The extraction ability of ferrocenophanes **1** and **3** was tested using the Pedersen extraction technique [12]. Dithiaorthocyclo(1,1′)ferrocenophane **1** shows the lowest complexing ability of all cations tested, excluded the Ag^+ one (Table 2). The complexing ability of Ag^+ can be explained by the role that the soft atom of S plays in the complexing compound, decreasing the affinity to the hard cations (the alkali metals and alkali earth metals), while increasing the affinity to the soft cations of the transition metals. The increased complexing ability of ferrocenophane **3** comparing to **1** can be observed, which can be explained by the fact that meta ferrocenophane can acquire a conformation that is more suitable for complexing the respective cation. Since the cavity size is the same in both molecules, it cannot explain this difference. It has been observed previously that polyoxa-, polyoxathia- and dioxathiaferrocenophanes almost immediately decompose if oxidized with the complexed Ag^+ ion [13,14]. For dithia(1,1′)ferrocenophanes **1** and **3** investigated, a slow decomposition was observed only after few days, which was manifested by the "silver mirror". The extractions with Hg^{2+} failed, because just during the experiments ferrocenophanes **1** and **3** decomposed, which was proved by the TLC method. We did not test the extraction ability for the compound **5**, because of its quick decomposition in the aqueous picrate solutions.

Table 2. Extraction data (water-dichloromethane)[a], extracted %.

Compound	Na^+	Rb^+	Mg^{2+}	Cd^{2+}	Ca^{2+}	Ba^{2+}	La^{3+}	Ni^{2+}	Cu^{2+}	Ag^+	Zn^{2+}
1	7.2	2.2	0	2.4	6.8	6.4	8.2	0	2.2	23.2	3.5
3	9.1	0	13.0	4.3	9.8	4.3	7.1	8.0	12.8	25.0	0

[a]Equal volumes of water and dichloromethane and picric acid at 7.0×10^{-5} M. Concentration of ferrocenophane: 7.0×10^{-4} M. Concentration of metal nitrate: 0.1 M.

EXPERIMENTAL

Melting points were determined on a Boetius hot-stage apparatus with microscope VEB Analytic and were given as uncorrected values. ^{1}H NMR spectra were obtained with a JEOL FX -90, Bruker HX 90 and Tesla – 100 spectrometers for solution in CH_2Cl_2 with tetramethylsilane as internal standard. IR spectra were recorded with a Pye Unicam SP-200 and Specord 71 IR spectrometers. Mass spectra were determined with a LKB 2091 spectrometer. UV-visible spectra were measured on a Specord UV-VIS Carl Zeiss Jena spectrometer ($c = 2\times10^{-3}$ M; solvent – CH_2Cl_2). The molecular weights were measured on a vapour-gas osmometer Hewlett Packard 302 B and on an apparatus Micromol OX-103 Labor MIM Budapest. Column chromatography was performed on Merck Aluminiumoxid 90 neutral (0.063–0.200 nm) and on Merck Kieselgel 40 (0.063–0.200 nm). All solvents were dried and purified by standard techniques. Dithiophenols **13** and **15** were of the highest purity commercially available (Fluka).

General description for preparation of dithiaferrocenophanes 1–5: Dithiaferrocenophanes were obtained by using a high-dilution method in a nitrogen atmosphere. Solutions: 2–4 mmole of 1,1′--di(hydroxymethyl)ferrocene in 50 mL of methylene chloride or in 50 mL of methylene chloride and benzene mixture (1:1) and 2–4 mmole of appropriate aromatic dithiol in 50 mL of methylene chloride or in 50 mL of methylene chloride and benzene mixture (1:1) were added dropwise simultaneously and slowly from separate dropping funnels (about 1 hour), during intensive stirring and boiling of the solvent into 2 L three-neck flask, containing 500 mL of freshly distilled methylene chloride and 10 drops of trifluoroacetic acid. The reaction mixture was refluxed in a nitrogen atmosphere for 15 hrs. After cooling to room temperature, the reaction mixture was washed with 5% sodium hydroxide solution, and then several times with water. After drying of the solution over anhydrous sodium sulphate, the solvent was evaporated under reduced pressure. The product was purified by column chromatography or by crystallization. Details concerning the preparation and purification of individual compounds are given below. As by-products insoluble ferrocene polysulphides (*ca* 10%) were isolated in all cases.

2,9-Dithia[2]orthocyclo[2](1,1′)ferrocenophane **1**: 1,1′-Di(hydroxymethyl)ferrocene – 0.984 g (4 mmole) and 0.568 g (4 mmole) of 1,2-benzenedithiol were dissolved in 50 mL of methylene chloride. The product was purified by column chromatography (neutral, deactivated aluminium oxide; eluent – benzene-hexane mixture 1:1). Yield 1.15 g (82%), orange crystals, m.p. 56–57°C. IR (KBr) : 3030, 2900, 1590, 1495, 1440, 1270, 1250, 1220, 1100, 740, 700 cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.90 (s, 4H, CH2), 4.10 (br-s, 8H, Fc-H), 7.20–7.35 (m 4H, Ph-H). MS (15 eV) m/e : 352 [M^+]. Found: C, 60.93; H, 5.02; S, 18.62%. Calcd. for $C_{18}H_{16}S_2Fe$: C, 61.34; H, 4.58; S, 18.20%. Side products of the reaction are polymeric compounds (about 0.2 g), which were washed out of the column with chloroform.

5-Methyl-2,9-dithia[2]orthocyclo[2](1,1′)ferrocenophane **2**: 1,1′-Di(hydroxymethyl)ferrocene – 0.984 g (4 mmole) and 0.624 g (4 mmole) of 3,4-tolyldithiol in 50 mL portions of methylene chloride and benzene mixture (1:1) were used. The product was purified by crystallization from benzene. Yield 0.650 g (44%), yellow crystals, m.p. 165°C. IR (KBr): 3060, 2910, 1580, 1500, 1465, 1260, 1250, 1100, 820, 705 cm^{-1}. ^1H NMR (CD_2Cl_2): δ =2.26 (s, 3H, CH_3), 4.01 (m, 4H, CH_2), 4.20 (m, 8H, Fc-H), 7.09 (m, 3H, Ph-H). MS (15 eV) m/e: 366 [M^+]. Found: C, 62.01; H, 5.26%. Calcd. for $C_{19}H_{18}S_2Fe$: C, 62.27; H, 4.95%.

2,9-Dithia[2]metacyclo[2](1,1′)ferrocenophane **3**: 1,1′-Di(hydroxymethyl)ferrocene – 0.984 g (4 mmole) and 0.568 g (4 mmole) of 1,3-benzenedithiol dissolved in 50 mL of methylene chloride were used. The product was purified by column chromatography (neutral, deactivated aluminium oxide; eluent – benzene). Yield 1.0 g (71%), orange crystals, m.p. 137–179°C. IR (CCl_4): 3050, 2910, 2840, 1580, 1480, 1420, 1390, 1260, 1240, 1220, 1095, 1025, 815, 790, 690 cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.98 (s, 4H, CH_2), 4.15 (br-s, 8H, Fc-H), 7.12 (m, 3H, Ph-H), 7.48 (s, 1H, Ph-H). MS (15 eV) m/e: 352 [M^+]. Found: C, 61.05; H, 4.89%. Calcd. for $C_{18}H_{16}S_2Fe$: C, 61.34; H, 4.58%.

4-Chloro-2,9-dithia[2]metacyclo[2](1,1′)ferrocenophane **4**: 1,1′-Di(hydroxymethyl)ferrocene – 0.492 g (2 mmole) and 0.354 g (2 mmole) of 4-chloro-1,3-benzenedithiol dissolved in 50 mL of methylene chloride were used. The product was purified by crystallization from benzene. Yield 0.320 g (41%), yellow needles, m.p. 178–179°C. IR (KBr): 3045, 2920, 2850, 1580, 1485, 1430, 1375, 1260, 1240, 1100, 810, 780, 710, 680 cm^{-1}. ^1H NMR (CD_2Cl_2): δ =3.85 (m, 2H, CH_2), 3.95 (s, 2H, CH_2), 4.12 (m, 8H, Fc-H), 7.45 (s, 1H, Ph-H), 7.52 (s, 1H, Ph-H), 7.62 (s, 1H, Ph-H). MS (15 eV) m/e: 386 [M^+]. Found: C, 55.78; H, 3.91%. Calcd for $C_{18}H_{15}ClS_2Fe$: C, 55.88; H, 3.87%.

2,9-Dithia[2]paracyclo[2](1,1′)ferrocenophane **5**: 1,1′-Di(hydroxymethyl)ferrocene – 0.984 g (4 mmole) and 0.568 g (4 mmole) of 1,4-benzenedithiol dissolved in 50 mL of benzene-hexane mixture (1:1) were used. The product was purified on a column chromatography (neutral, deactivated aluminium oxide; eluent – benzene). Yield 0.450 g (32%), yellow crystals, m.p. 160°C (decomp.). IR (KBr): 3060, 2920, 2840, 580, 1500, 1440, 1390, 1260, 1240, 1220, 1100, 1050, 1020, 810, 680 cm^{-1}. ^1H NMR (CD_2Cl_2): δ =3.90 (m, 4H, CH_2), 4.12 (m, 8H, Fc-H), 7.30 (q, 4H, Ph-H). MS (15 eV) m/e: 352 [M^+]. Found: C, 62.01; H, 4.92%. Calcd. for $C_{18}H_{16}S_2Fe$: C, 61.34; H, 4.58%. Also polymeric products (about 0.3 g) insoluble in benzene were obtained.

General description for the preparation of compounds 6–10: Hydroxymethylferrocene – 4 mmole and 2 mmole of appropriate aromatic dithiol were dissolved in 500 mL of freshly distilled methylene chloride, after the addition of 10 drops of trifluoroacetic acid. The reaction mixture was refluxed in a nitrogen atmosphere and with vigorous stirring for 10 hours. After cooling to room temperature the reaction mixture was washed with a 5% sodium hydroxide solution, and then several times with water. After

drying of the solution over anhydrous sodium sulphate, the solvent was evaporated under reduced pressure. The product was purified by column chromatography or by crystallization. Details concerning preparations and purification of these compounds are given below.

1,2-Di(ferrocenylmethylthia)benzene **6**: Hydroxymethylferrocene – 0.846 g (4 mmole) and 0.284 g (2 mmole) of 1,2-benzenedithiol were used in the reaction. The product was purified by column chromatography (neutral, deactivated aluminium oxide; eluent – benzene and hexane mixture 1:1). Yield 0.950 g (88%), yellow crystals, m.p. 57–58°C. IR (CCl_4): 3030, 2900, 1590, 1495, 1445, 1420, 1260, 1245, 1100, 1000, 810 cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.91 (s, 4H, CH_2), 4.10 (m, 8H, Fc-H), 4.14 (s, 10H, Fc-H), 7.28 (m, 4H, Ph-H). MS (15 eV) m/e: 538 [M^+]. Found: C, 62.85; H, 5.26%. Calcd for $C_{28}H_{26}S_2Fe_2$: C, 62.43; H, 4.87%.

3,4-Di(ferrocenylmethylthia)tolyl **7**: Hydroxymethylferrocene – 0.864 g (4 mmole) and 0.312 g (2 mmole) of 3,4-tolyldithiol were used. The product was purified first by column chromatography (basic, deactivated aluminium oxide; eluent – benzene and hexane mixture 2:1) and then by crystallization from benzene. Yield 0.820 g (74%), yellow crystals, m.p. 159–161°C. IR (KBr): 2920, 1500, 1375, 1260, 1100, 1020, 815,740 cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 2.29 (s, 3H, CH_3), 3.86 (d, 4H, CH_2), 4.16 (m, 18H, Fc-H), 7.10 (m, 3H, Ph-H). MS (15 eV) m/e: 552 [M^+]. Found: C, 63.31; H, 5.27%. Calcd for $C_{29}H_{28}S_2Fe_2$: C, 63.02; H, 5.11%.

1,3-Di(ferrocenylmethylthia)benzene **8**: Hydroxymethylferrocene – 0.864 g (4 mmole) and 0.284 g (2 mmole) of 1,3-benzenedithiol were used. The product was purified by crystallization from benzene. Yield 0.875 g (81%), yellow crystals, m.p. 183–184°C. IR (KBr): 3055, 2920, 2840, 1495, 1440, 1260, 1245, 1110, 1000, 810, 790, 700 cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.92 (s, 4H, CH_2), 4.16 (br-s, 18H, Fc-H), 7.20 (m, 4H, Ph-H). MS (15 eV) m/e : 538 [M^+]. Found: C, 62.28; H, 5.03%. Calcd for $C_{28}H_{26}S_2Fe_2$: C, 62.43; H, 4.87%.

2,4-Di(ferrocenylmethylthia)chlorobenzene **9**: Hydroxymethylferrocene – 0.864 g (4 mmole) and 0.354 g (2 mmole) of 4-chloro-1,3-benzenedithiol were used. The product was purified by column chromatography (neutral, deactivated aluminium oxide; eluent – benzene). Yield 1.040 g (91%), yellow-orange viscous oil. IR (KBr): 2920, 2840, 1585, 1500, 1440, 1380, 1265, 1240, 1100, 1015, 805 cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.88 (s, 2H, CH_2), 3.95 (s, 2H, CH_2), 4.10 (m, 18H, Fc-H), 7.23–7.29 (m, 3H, Ph-H). MS (15 eV) m/e: 572 [M^+]. Found: C, 58.64; H, 4.67%. Calcd for $C_{28}H_{25}ClS_2Fe_2$: C, 58.68; H, 4.40%.

1,4-Di(ferrocenylmethylthia)benzene **10**: Hydroxymethylferrocene – 0.864 g (4 mmole) and 0.284 g (2 mmole) of 1,4-benzenedithiol were used. A crude product was purified by column chromatography (neutral, deactivated aluminium oxide; eluent – benzene). Yield 0.690 g (64%), orange crystals, m.p. 113.5°C. IR (CCl_4): 3080, 2920, 1440, 1265, 1240, 1100, 1045, 1030, 1020, 1005, 820 cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.82 (s, 4H, CH_2), 4.12 (m, 18H, Fc-H), 7.23 (m, 4H, Ph-H). MS (15 eV) m/e : 538 [M^+]. Found: C, 62.90; H, 5.20%. Calcd for $C_{28}H_{26}S_2Fe_2$: C, 62.43; H, 4.87%.

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