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A convenient access to 1,2-diferrocenyl-substituted ethylenes via [3 + 2]-cycloelimination of 2-silylated 4,4,5,5-tetrasubstituted 1,3-dithiolanes

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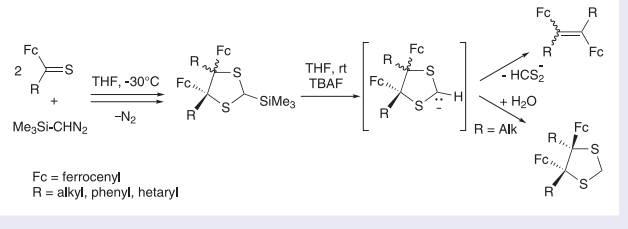
ABSTRACT

Ferrocenyl thioketones bearing a hetaryl, phenyl or alkyl group as the second substituent react with (trimethylsilyl)diazomethane at ca. −30°C in THF solution without formation of a stable [3 + 2]-cycloadduct. After the spontaneous evolution of N_2, the corresponding sterically crowded 4,4,5,5-tetrasubstituted 2-silylated 1,3-dithiolanes are formed as products of the second [3 + 2]-cycloaddition of the intermediate thiocarbonyl *S*-methanide with the starting thioketone. After desilylation by treatment with TBAF, they are converted into the corresponding carbanions, which display different stability depending on the type of substituent. The presence of hetaryl and phenyl groups results in the exclusive formation of 1,2-diferrocenyl ethylenes. In contrast, the presence of methyl groups significantly enhances the stability of the carbanion, which by protonation yields *trans*-4,5-diferrocenyl-4,5-dimethyl-1,3-dithiolane.



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1. Introduction

In a series of recent publications, reactions of aryl/hetaryl thioketones **1** with diazomethane and its derivatives, such as diazoethane, 2-diazopropane and (trimethylsilyl)diazomethane, were reported [1–4]. The non-concerted pathway of the formal [3 + 2]-cycloaddition with participation of a diradical intermediate was demonstrated by the formation of a

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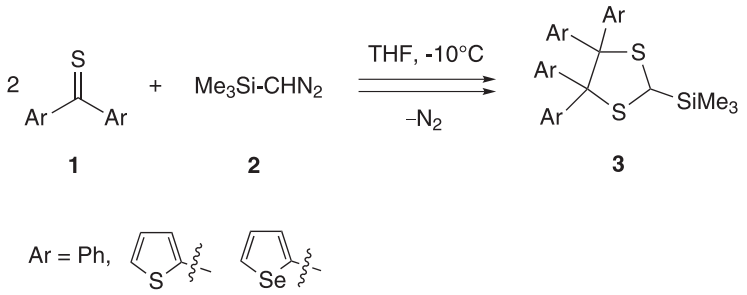


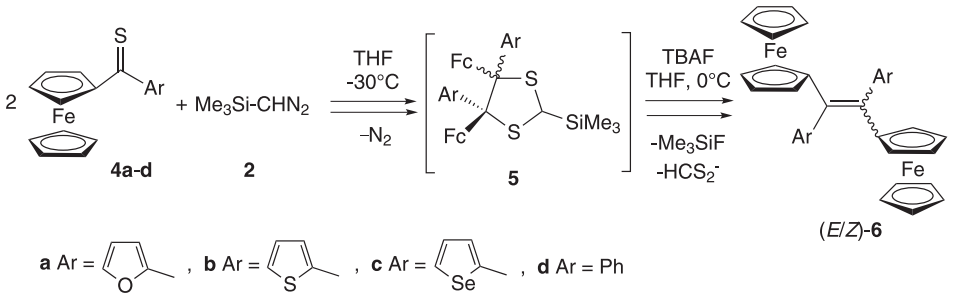
Scheme 1. A multi-step reaction of aryl/hetaryl thioketones **1** with TMS-diazomethane (**2**) yielding sterically crowded 4,4,5,5-tetraaryl-1,3-dithiolanes **3**.

macrocyclic dimer of the intermediate thiocarbonyl *S*-methanide [1,5] as well as sterically crowded 4,4,5,5-tetrasubstituted 1,3-dithiolanes [2]. The latter products were formed via trapping of the intermediate diradical species by the starting thioketones in a regioselective manner. In the case of (trimethylsilyl)diazomethane **2**, 2-silylated sterically crowded 1,3-dithiolanes **3** were formed as single products (Scheme 1).

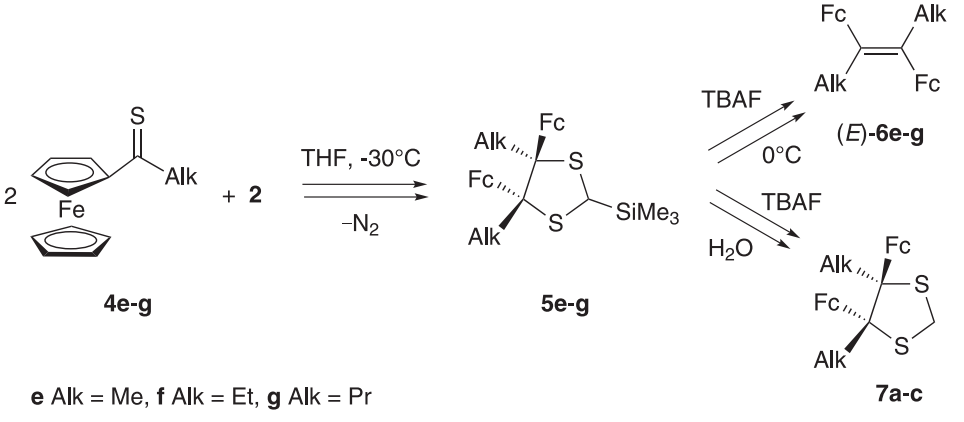
Ferrocenyl thioketones with an alkyl, aryl or hetaryl substituent are attractive building blocks for the preparation of ferrocenyl-functionalized molecules, *e.g.* sulfur heterocycles [6–8] and tetrasubstituted ethylenes [4,9]. The goal of present study was the reaction of ferrocenyl thioketones with (trimethylsilyl)diazomethane and subsequent desilylation of the expected 2-silylated 1,3-dithiolanes, and the observation of differences in the behavior of ferrocenyl hetaryl and alkyl ferrocenyl thioketones was of special interest.

2. Results and discussion

In the first part of the study, ferrocenyl hetaryl thioketones **4a**–**c** as well as ferrocenyl phenyl thioketone (**4d**) were tested in the reaction with TMS-diazomethane (**2**) in THF solution. The reaction mixture of equimolar amounts of both reagents was prepared at –75°C, but in contrast to aryl and hetaryl thioketones, no decoloration of the solution was observed, and for that reason, the mixture was slowly warmed to room temperature. Around −30°C, a vigorous evolution of N_2 and change of the color of the solution (blue → red) were observed. The crude mixture was treated with TBAF solution at 0°C, and after 30 min, the TLC control indicated the disappearance of the initially formed 1,3-dithiolane **5** (Scheme 2). The chromatographic separation delivered pure products, which were identified as (*E*/*Z*)-mixtures of tetrasubstituted 1,2-differocenyl ethylenes **6**. For example, in the case of the product prepared from ferrocenyl furan-2-yl thioketone (**4a**), a 10:1 mixture of isomers (^{1}H NMR) was isolated, and after crystallization from hexane/CH_2Cl_2, the pure major product was obtained in 54% yield. The ^{1}H NMR spectrum showed a set of signals for the ferrocenyl and furan-2-yl groups only. On the other hand, ^{13}C NMR spectra revealed a signal for the ethylene C=C unit at 129.1 ppm in addition to the characteristic signals for ferrocenyl and furan-2-yl moieties. Finally, the structure of (*E*)-**6a** was unambiguously established by X-ray crystallography [10].



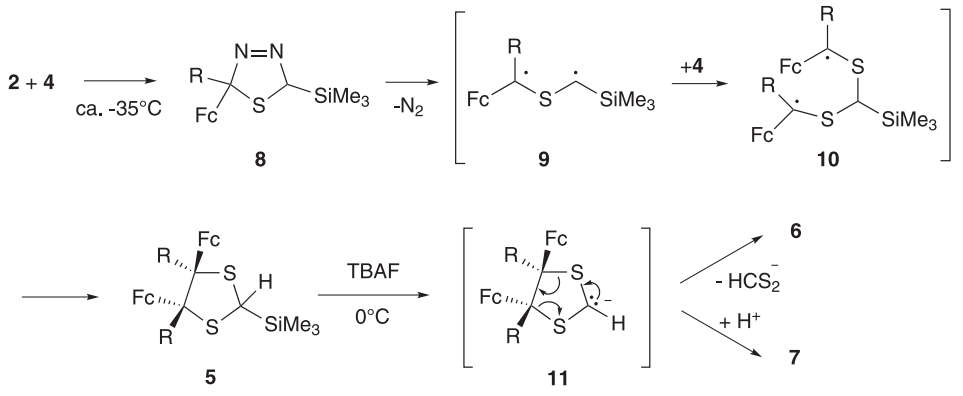
Scheme 2. Reaction of ferrocenyl hetaryl/phenyl thioketones **4a**–**d** with TMS-diazomethane (**2**).



Scheme 3. Reaction of alkyl ferrocenyl thioketones **4e**–**g** with TMS-diazomethane (**2**).

Analogous reaction courses were observed using thioketones **4b**–**d**. In all cases, products **6** were isolated in good yields. Whereas, **6b** and **6c** were also obtained as mixtures of (*E*)-and (*Z*)-isomers (ca. 17:1), product **6d** was isolated as a single isomer (most likely with (*E*)-configuration).

In an extension of the study, TMS-diazomethane (**2**) was reacted with alkyl ferrocenyl thioketones **4e**–**g** under conditions presented in Scheme 3. In all experiments, the crude products obtained after desilylation were separated chromatographically, yielding two fractions. Thus, in the case of **4e**, the expected olefin **6e** formed the less polar fraction and was isolated in ca. 4% yield. Based on the ^{1}H NMR spectra, only one isomer was present, and tentatively the (*E*)-configuration can be attributed to this product. The more polar fraction contained the major product, isolated in 32% yield. The ^{1}H NMR spectrum showed the presence of the typical set of ferrocene signals along with a singlet of an Me group at 1.76 ppm and a signal of a CH_2 unit at 3.97 ppm. The latter is characteristic for the $H_2C(2)$ group of 4,4,5,5-tetrasubstituted 1,3-dithiolanes [11]. This hypothesis was confirmed by ^{13}C NMR spectra, where this group was located at 27.5 ppm. Based on these data, the structure of the major product was postulated as 4,5-differocenyl-4,5-dimethyl-1,3-dithiolane (**7a**). Both products, **6e** and **7a**, were isolated as single isomers. In analogy to **6e**, the *trans*-configuration can be tentatively attributed to **7a**. The diastereoselective course of this reaction was additionally supported by the ^{1}H NMR spectrum of the crude



Scheme 4. Mechanistic interpretation of the reactions of ferrocenyl thioketones **4** with TMS-diazomethane (**2**) and subsequent desilylation.

reaction mixture containing the 2-silylated product **5e**, which indicated the presence of only one diastereoisomer.

Unexpectedly, the analogous experiment performed with **4 g** afforded also a mixture of products **6 g** and **7c**, but in that case, the less polar alkene **6 g** was the major product (37% yield) and **7c** was isolated in only ca. 5% yield. Finally, the reaction with **4f** yielded **6f** and **7b** in a ratio of 1:10.

The mechanistic interpretation of the presented results is depicted in Scheme 4. In agreement with an earlier postulated reaction sequence, the first step is the [3 + 2]-cycloaddition of TMS-diazomethane (**2**) with ferrocenyl thioketone **4** leading to 1,3,4-thiadiazoline **8**, which spontaneously eliminates N_2 generating the 1,3-diradical **9**, a mesomeric form of the thiocarbonyl *S*-methanide, acting as a reactive intermediate. This species is trapped by a second molecule of the starting thioketone **4** in a regioselective manner to give a new 1,5-diradical **10**. The subsequent 1,5-cyclization leads to 1,3-dithiolane **5** in a diastereoselective. Complete diastereoselectivity was observed in systems with R = phenyl or alkyl. The final step comprises desilylation of **5** affording the carbanion **11**. Apparently, its stability depends on the type of substituents R. Whereas hetaryl groups accelerate the [3 + 2]-cycloelimination to give ethylenes **6**, alkyl groups enhance the stability of **11** and protonation during chromatographic workup converts this intermediate into 2-CH_2-1,3-dithiolane **7**. The obtained results with derivatives bearing methyl or propyl groups suggest that the stabilizing effect of the methyl group is bigger.

3. Conclusions

Ferrocenyl-substituted ethylenes attract attention as compounds of practical importance for materials and medicinal chemistry [12]. Some of them display interesting photo-optical properties and in the case of so-called ferrocifens, their antitumor activity has extensively been studied [13]. The generally applied method for their synthesis is the McMurry coupling of a ferrocenyl ketone with a corresponding benzophenone derivative [14,15]. The method presented in this study offers a new approach to 1,2-diferrocenyl ethylenes based on the application of ferrocenyl hetaryl thioketones. The obtained results show that,

in comparison with diaryl and dihetaryl thioketones, ferrocenyl-containing representatives are less reactive towards (trimethylsilyl)diazomethane and react at ca. –35°C with immediate evolution of N_2 to generate the corresponding thiocarbonyl *S*-methanides as reactive intermediates. The latter react with a second molecule of the starting thioketone yielding sterically crowded 4,4,5,5-tetrasubstituted 2-silylated 1,3-dithiolanes in a diastereoselective manner. These products can be easily desilylated by treatment with tetrabutylammonium fluoride to give the respective carbanion. The stability of the latter is determined by the type of the substituent of the starting ferrocenyl thioketone. In contrast to aryl and hetaryl substituents, which accelerate the [3 + 2]-cycloelimination leading to 1,2-diferrocenylethylenes, simple alkyl groups enhance the stability of the intermediate carbanion resulting in the subsequent protonation to give 2-CH_2-1,3-dithiolane derivatives and, therefore, they behave similar to 4,5-unsubstituted 2-silylated 1,3-dithiolanes, which are applied as masked carbanions used for C,C-bond formation [16,17].

4. Experimental design

4.1. General

All solvents were dried over appropriate drying agents and distilled before use. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III instrument (600 and 150 MHz, respectively), using the solvent ($CDCl_3$/residual $CHCl_3$) signal as reference. The IR spectra (KBr pellets) were recorded on a Nexus FT-IR spectrophotometer. The elemental analyses were determined on a Vario Micro Cube. Flash column chromatography (FCC) was carried out using Silica gel 60 (Sigma-Aldrich, 230–400 mesh). Melting points were measured in a capillary using a Stewart® SMP30. The notation Fc in this study represents ferrocenyl. Ferrocenyl thioketones **4** applied in the study were obtained by a known method according to the recently published literature protocols [3,6]. Other reagents used were commercially available chemicals.

4.2. Reactions of thioketones 4a–d with (trimethylsilyl)diazomethane (2) – a general procedure

A solution of a thioketone **4** (1 mmol) in THF (3 mL) was cooled to –75°C (acetone/dry ice). Then, an equimolar amount of TMS-CHN_2 was added and the mixture was allowed to warm slowly to rt. Next, the solvent was evaporated, and the crude products were purified by FCC (silica gel, CH_2Cl_2/hexane 3:7).

4.3. Reactions of thioketones 4e–g with (trimethylsilyl)diazomethane (2) – a general procedure

A solution of a thioketone **4** (1 mmol) in dry THF (2 mL) was cooled to 0°C and the commercial solution of TMS-CHN_2 (2M in THF) was added in portions. The mixtures were allowed to warm to rt. The solvent was evaporated and the crude mixtures were dissolved in 1 mL of THF and treated with an excess of a 1M solution of TBAF in THF. After completion of the reactions, the solvent was evaporated and the crude mixtures were purified by FCC (SiO_2, CH_2Cl_2/hexane 1:1). The main fractions were separated on preparative plates

(SiO_2, CH_2Cl_2/hexane 3:7) to give alkenes **6e**–**g** (less polar fractions) and 1,3-dithiolanes **7a**–**c** (more polar).

4.4. Desilylation of crude 1,3-dithiolane derivatives 5 – a general procedure

To the solution of crude 1,3-dithiolanes (1 mmol) in THF (4 mL), TBAF (1M, 1 mL) was added at 0°C. The mixture was stirred for 20 min. Then, the solvent was evaporated and the crude product was purified by FCC (silica gel, CH_2Cl_2/hexane 3:7).

4.4.1. 1,2-Diferrocenyl-1,2-di(furan-2-yl)ethenes (6a)

The product isolated after chromatography was a mixture of (*E*)/(*Z*)-isomers in a ratio of ca. 10:1. Fractional crystallization yielded the pure major component identified as the (*E*)-isomer.

(E)-**6a** [10]: Orange-yellow crystals; m.p. 212.0–214.0°C (from pentane/CH_2Cl_2); yield: 406 mg (77%). ^{1}H NMR [600 MHz, $CDCl_3$, δ (ppm), J (Hz)]: 3.63–3.65 (m, 4CH(Fc)), 4.13–4.15 (m, 4CH(Fc)), 4.16 (s, 10CH(Fc)), 6.40 (d, $^3J_{H,H} = 3.0$, 2CH(Fur)), 6.54 (dd, $^4J_{H,H} = 1.8$, $^3J_{H,H} = 3.0$, 2CH(Fur)), 7.58 (brs, 2CH(Fur)). ^{13}C NMR [150 MHz, $CDCl_3$, δ (ppm)]: 68.5, 68.9 (2 signals for 8CH(Fc)), 69.6 (10CH(Fc)), 85.4 (2C(Fc)), 109.1, 111.1, 140.8 (3 signals for 6CH(Fur)), 129.1, 153.3 (C=C, 2C(Fur)). IR (KBr): υ 3146*w*, 3109*w*, 3077*w*, 1560*m*, 1540*m*, 1495*s*, 1458 *m*, 1405*m*, 1258*s*, 1236*m*, 1189*m*, 1144*s*, 1103*s*, 1049*m*, 1033*m*, 1011s, 939*m*, 923*m*, 813*vs*, 780*m*, 743*vs*, 596*m*, 527*m*, 476*vs* cm^{-1}. ESI-MS (mixture of isomers): 528 (100, $[M]^+$), 529 (50, $[M+1]^+$). Anal. calcd. for $C_{30}H_{24}Fe_2O_2$ (528.20): C 68.22, H 4.58%; found: C 68.38, H 4.61%.

(*Z*)-**6a** (minor product) was identified based on the spectra of the isolated mixture of isomers: ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.99 (s, 10CH(Fc)), 4.12–4.13 (m, 4CH(Fc)), 4.17–4.18 (m, 4CH(Fc)), 6.11 (d, $^3J_{H,H} = 3.0$ Hz, 2CH(Fur)), 6.36 (dd, $^4J_{H,H} = 1.8$ Hz, $^3J_{H,H} = 3.0$ Hz, 2CH(Fur)), 7.41 (brs, 2CH(Fur)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 67.7, 70.7 (2 signals for 8CH(Fc)), 69.3 (10CH(Fc)), 108.1, 110.6, 140.3 (3 signals for 6CH(Fur)), 129.7 (2C(Fur)) ppm.

4.4.2. 1,2-Diferrocenyl-1,2-di(thiophen-2-yl)ethenes (6b)

The product isolated after chromatography was a mixture of (E)/(*Z*)-isomers in a ratio of ca. 17:1. Fractional crystallization yielded the pure major component identified as the (*E*)-isomer.

(*E*)-**6b**: Yellow-orange crystals; m.p. > 158°C (decomp., from pentane/CH_2Cl_2); yield: 420 mg (75%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.45 (brs, 4CH(Fc)), 4.09 (brs, 4CH(Fc)), 4.14 (s, 10CH(Fc)), 6.99 (d, $^3J_{H,H} = 3.0$ Hz, 2CH(Thi)), 7.17 (dd, $^3J_{H,H} = 3.0$ Hz, $^3J_{H,H} = 4.8$ Hz, 2CH(Thi)), 7.48 (d, $^3J_{H,H} = 4.8$ Hz, 2CH(Thi)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 68.9, 69.6 (2 signals for 8CH(Fc)), 69.7 (10CH(Fc)), 86.7 (2C(Fc)), 125.3, 126.8, 127.4 (3 signals for 6CH(Thi)), 131.0, 143.3 (C=C, 2C(Thi)) ppm. IR (KBr): υ 3086*w*, 2924*w*, 1645*w*, 1385*w*, 1250*m*, 1227*m*, 1103*m*, 1065*m*, 1039*w*, 999*m*, 925*w*, 837*m*, 814*s*, 723*m*, 695*vs* cm^{-1}. ESI-MS: 560 (100, $[M]^+$), 561 (49, $[M+1]^+$). Anal. calcd. for $C_{30}H_{24}Fe_2S_2$ (560.33): C 64.30, H 4.32, S 11.45, found: C 64.32, H 4.42, S 11.37.

(*Z*)-**6b** (minor product) was identified based on the spectra of a mixture of isomers: ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.91 (s, 10CH(Fc)), 4.17 (brs, 8CH(Fc)), 6.84–6.88 (m, 2CH(Thi)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 67.7, 70.5 (2 signals for 8CH(Fc)), 69.3

(10CH(Fc)), 87.7 (2C(Fc)), 124.0, 125.5, 126.7 (3 signals for 6CH(Thi)), 133.4, 145.6 (C = C, 2C(Thi)) ppm.

4.4.3. 1,2-Diferrocenyl-1,2-di(selenophen-2-yl)ethenes (6c)

The product isolated after chromatography was a mixture of (*E*)/(*Z*)-isomers in a ratio of ca. 18:1. Fractional crystallization yielded the pure major component described as the (*E*)-isomer.

(*E*)-**6c**: Yellow-orange crystals; m.p. > 160°C (decomp., from pentane/CH_2Cl_2); yield: 523 mg (80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.66 (t, $J_{H,H}$ = 1.8 Hz, 4CH(Fc)), 4.11 (t, $J_{H,H}$ = 1.8 Hz, 4CH(Fc)), 4.14 (s, 10CH(Fc)), 7.13 (dd, $^4J_{H,H}$ = 0.6 Hz, $^3J_{H,H}$ = 3.6 Hz, 2CH(Sel)), 7.39 (dd, $^3J_{H,H}$ = 3.6 Hz, $^3J_{H,H}$ = 5.4 Hz, 2CH(Sel)), 8.16 (d, $^3J_{H,H}$ = 5.4 Hz, 2CH(Sel)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 68.9, 70.2 (2 signals for 8CH(Fc)), 69.6 (10CH(Fc)), 86.6 (2C(Fc)), 129.2, 129.6, 131.2 (3 signals for 6CH(Sel)), 132.3, 150.4 (C = C, 2C(Sel)) ppm. IR (KBr): υ 3089*m*, 3044*w*, 2925*w*, 2848*w*, 1630*w*, 1446*m*, 1409*w*, 1385*w*, 1238*m*, 1213*m*, 1099*s*, 1066*s*, 1037*m*, 997*m*, 923 *m*, 813*vs*, 765*m*, 723*m*, 686*vs*, 502*vs* cm^{-1}. ESI-MS: 654 (72, $[M]^+$), 656 (100). Anal. calcd. for $C_{30}H_{24}Fe_2Se_2$ (654.12): C 55.08, H 3.70, found: C 55.03, H 3.79.

(*Z*)-**6c**: (minor product) was identified based on the spectra of a mixture of isomers: ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.92 (s, 10CH(Fc)), 4.07–4.08 (m, 4CH(Fc)), 4.17–4.18 (m, 4CH(Fc)), 7.08 (d, $^3J_{H,H}$ = 3.6 Hz, 2CH(Sel)), 7.91 (d, $^3J_{H,H}$ = 5.4 Hz, CH(Sel)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 67.7, 70.6 (2 signals for 8CH(Fc)), 69.4 (10CH(Fc)), 87.8 (2C(Fc)), 128.1, 129.0, 130.3 (3 signals for 6CH(Sel)), 134.7, 152.4 (C = C, 2C(Sel)) ppm.

4.4.4. 1,2-Diferrocenyl-1,2-diphenylethene (6d)

The product was isolated after chromatography as a single compound described as the (*E*)-isomer.

(*E*)-**6d**: Yellow-orange crystals, m.p. > 170°C (decomp.); yield: 307 mg (56%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.77 (s, 10CH(Fc)), 4.00 (brs, 4CH(Fc)), 4.14 (brs, 4CH(Fc)), 7.03–7.06 (m, $2CH_{arom.}$), 7.08–7.11 (m, $4CH_{arom.}$), 7.13–7.16 (m, $4CH_{arom.}$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 67.6, 70.0 (2 signals for 8CH(Fc)), 69.0 (10CH(Fc)), 88.2 (2C(Fc)), 125.4, 126.9, 129.5 (3 signals for $10CH_{arom.}$), 137.4, 144.3 (C = C, $2C_{arom.}$) ppm. IR (KBr): υ 3092*m*, 3057*m*, 3023*m*, 2950*m*, 2872*m*, 1593*m*, 1577 *m*, 1491*m*, 1438*m*, 1405*m*, 1381*m*, 1307*m*, 1225*m*, 1180*m*, 1107*s*, 1078 *m*, 1025*s*, 1005*s*, 890*m*, 829*s*, 817*s*, 768*m*, 715*vs*, 694*s*, 641*m*, 547*m*, 490*vs* cm^{-1}. Anal. calcd. for $C_{34}H_{28}Fe_2$ (548.28): C 74.48, H 5.15, found: C 74.43, H 5.28.

4.4.5. (E)-2,3-Diferrocenylbut-2-ene (6e)

The product was isolated in trace amounts (5–10 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.20 ($2CH_3$); 4.19 (s, 10CH(Fc)); 4.25–4.26 (m, 4CH(Fc)); 4.35–4.36 (m, 4CH(Fc)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 22.6 ($2CH_3$); 67.4, 68.9, 69.1 (3 signals for 18CH(Fc)), 90.6 (2C(Fc)), 127.8 (C = C) ppm.

4.4.6. 3,4-Diferrocenylhex-3-enes (6f)

The product was isolated in trace amounts (5–10 mg) as a ca. 1:1 mixture of (*E*)- and (*Z*)-isomer. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.16 (*t*, $J_{H,H}$ = 7.38 Hz, $4CH_2CH_3$), 2.64–2.69 (m, $4CH_2CH_3$), 4.01–4.02 (m, 4CH(Fc)), 4.06 (s, 10CH(Fc)), 4.08–4.09 (m, 4CH(Fc)), 4.16 (s,

10CH(Fc)), 4.25–4.26 (m, 4CH(Fc)), 4.34–4.35 (m, 4CH(Fc)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 15.2, 15.9 ($2CH_2\mathit{C}H_3$), 28.8, 28.9 ($2\mathit{C}H_2CH_3$), 66.9, 67.4, 68.8, 69.0, 69.1, 69.5 (5 signals for 36CH(Fc)), 90.2, 90.8 (2 signals for 4C(Fc)), 128.9, 130.9 (2C = C) ppm.

4.4.7. (E)-4,5-Diferrocenyloct-4-ene (6g)

Reddish crystals; m.p. = 111–113°C (petroleum ether); yield: 180 mg (37%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.96 (t, $J_{H,H}$ = 7.32 Hz, $2CH_2CH_2C\mathit{H}_3$), 1.51–1.58, 2.61–2.68 (2 m, $2C\mathit{H}_2C\mathit{H}_2CH_3$), 4.17 (s, 10CH(Fc)), 4.25–4.27 (m, 4CH(Fc)), 4.28–4.30 (m, 4CH(Fc)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.2 ($2CH_2CH_2\mathit{C}H_3$), 23.4, 38.4 ($2\mathit{C}H_2\mathit{C}H_2CH_3$), 67.4, 69.0, 69.1 (3 signals for 18CH(Fc)), 90.8 (2C(Fc)), 133.6 (C = C). IR (KBr): υ 3094*m*, 2953*vs*, 2923*m*, 2867*s*, 1467*m*, 1467*m*, 1452*m*, 1258*m*, 1105*vs*, 1064*m*, 1041*m*, 1000*s*, 923*m*, 874*m*, 816*vs*, 500*s*, 484*vs* cm^{-1}. Anal. calcd. for $C_{28}H_{32}Fe_2$ (480.12): C 70.03, H 6.72; found: C 70.02, H 6.84.

4.4.8. Trans-4,5-Diferrocenyl-4,5-dimethyl-1,3-dithiolane (7a)

Pale yellow crystals; m.p. = 150–151°C (petroleum ether); yield: 160 mg (32%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.76 (s, $2CH_3$), 3.54–3.56 (m, 2CH(Fc)), 3.96 (s, CH_2S), 4.04–4.05 (m, 2CH(Fc)), 4.14 (s, 10CH(Fc)), 4.14–4.16 (m, 2CH(Fc)), 4.57–4.58 (m, 2CH(Fc)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 27.5 ($2CH_3$), 29.2 (CH_2S), 66.1 ($2C_q$-S), 66.9, 67.6, 68.8, 68.9, 69.1 (5 signals for 18CH(Fc)), 87.5 (2C(Fc)) ppm. IR (KBr): υ 3091*m*, 2973*m*, 2931*m*, 1451*m*, 1410*m*, 1388*m*, 1359*s*, 1237*m*, 1105*vs*, 1058 *m*, 1025*s*, 1000*s*, 908*m*, 828*s*, 815*vs*, 490*vs* cm^{-1}. Anal. calcd. for $C_{25}H_{26}Fe_2S_3$ (502.29): C 59.78, H 5.22, S 12.77; found: C 59.52, H 5.50, S 12.68.

4.4.9. Trans-4,5-Diethyl-4,5-diferrocenyl-1,3-dithiolane (7b)

Yellow crystals; m.p. = 147–149°C (petroleum ether); yield: 230 mg (43%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.50 (t, $J_{H,H}$ = 7.38 Hz, $2CH_2C\mathit{H}_3$), 1.86–1.93, 2.07–2.12 (2 m, $2C\mathit{H}_2CH_3$), 3.45–3.46 (m, 2CH(Fc)), 3.79 (s, CH_2S), 4.04–4.05 (m, 2CH(Fc)), 4.08 (s, 10CH(Fc)), 4.10–4.11 (m, 2CH(Fc)), 4.59–4.60 (m, 2CH(Fc)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 12.1 ($2CH_2\mathit{C}H_3$), 29.5 (CH_2S), 33.8 ($2\mathit{C}H_2CH_3$), 66.1, 67.4, 68.2, 69.3, 69.4 (5 signals for 18CH(Fc)), 71.5 ($2C_q$-S), 88.9 (2C(Fc)) ppm. IR (KBr): υ 3095*m*, 2962*m*, 2918*m*, 2871*m*, 1447*m*, 1411*m*, 1388*m*, 1369*m*, 1262*m*, 1105*vs*, 1038*m*, 1029*s*, 998*s*, 934*m*, 816*vs*, 483*vs* cm^{-1}. Anal. calcd. for $C_{27}H_{30}Fe_2S_2$ (530.35): C 61.15, H 5.70, S 12.09; found: C 61.19, H 5.78, S 12.04.

4.4.10. Trans-4,5-Diferrocenyl-4,5-dipropyl-1,3-dithiolane (7c)

The product was isolated in trace amounts (5–10 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.95 (t, $J_{H,H}$ = 7.32 Hz, $2CH_2CH_2C\mathit{H}_3$), 1.88–1.93 (m, $2CH_2\mathit{C}H_2CH_3$), 2.04–2.12, 2.13–2.21 (2 m, $2C\mathit{H}_2CH_2CH_3$), 4.52–3.53 (m, 2CH(Fc)), 4.07–4.09 (m, 2CH(Fc)), 4.11 (s, 10CH(Fc)), 4.14–4.15 (m, 2CH(Fc)), 4.61–4.62 (m, 2CH(Fc)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.9 ($2CH_2CH_2\mathit{C}H_3$), 20.2 ($2CH_2\mathit{C}H_2CH_3$), 29.8 (CH_2S), 44.1 ($2\mathit{C}H_2CH_2CH_3$), 66.1, 67.5, 68.3, 69.1, 69.3 (5 signals for 18CH(Fc)), 70.9 ($2C_q$-S), 89.9 (2C(Fc)) ppm.

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