Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 263–268
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Reaction of ferrocenecarbothioamide and *N*-(ethoxycarbonyl)ferrocenecarbothioamide with alkyl halides

Anna Wrona [a], Marcin Palusiak [b], Janusz Zakrzewski [a,*]

[a] *Department of Organic Chemistry, University of Łódź, 90-136 Łódź, Narutowicza 68, Poland*
[b] *Department of Crystallography and Crystal Chemistry, University of Łódź, 90-236 Łódź, Pomorska 149/153, Poland*

Received 15 March 2007; received in revised form 29 October 2007; accepted 31 October 2007
Available online 4 November 2007

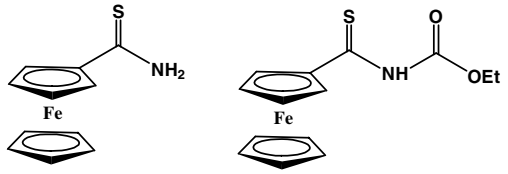
Abstract

Reaction of ferrocenecarbothioamide and *N*-(ethoxycarbonyl)ferrocenecarbothioamide with alkyl (mainly benzyl) halides in the presence of K_2CO_3 has been studied. The former compound yielded cyanoferrocene in high yield whereas the latter was transformed into the corresponding thioimidates as a result of *S*-alkylation and deprotonation. The molecular structure of *S*-*p*-nitrobenzyl-*N*-(ethoxycarbonyl)-ferrocenethioimidate was determined by single-crystal X-ray analysis and revealed the *E* configuration. The plausible reaction mechanism is discussed.

Keywords: Ferrocene; Thioamide; Nitrile; Thioimidate; Alkylation; X-ray analysis

1. Introduction

We have recently reported the direct synthesis of ferrocenecarbothioamide (**1**) and *N*-(ethoxycarbonyl)ferrocenecarbothioamide (**2**) from ferrocene [1].



1 **2**

Since thioamides are versatile starting materials in organic synthesis [2] we decided to study the reactivity of these new compounds and their application in syntheses of new ferrocenyl sulfur-containing compounds. Although a few ferrocenyl (tertiary) thioamides have been synthesized [3–5] the reactivity of the thioamido group directly bound to the ferrocenyl moiety has not been systematically studied. Only in a very recent paper [6] the use of a 1,1′-ferrocene bisthioamide, activated by *S*-alkylation with a Meerwein salt, in the synthesis of a ferrocenyl-bisimidazoline is described. Herein, we report the reactivity of **1**–**2** towards alkylating agent such as alkyl (mostly benzyl) halides.

2. Results and discussion

It is known that thioamides undergo *S*-alkylation by reactive alkyl halides leading to thioiminium salts or thioimidates [7]. However, we have found that **1** reacts with benzyl chlorides in the presence of potassium carbonate in DMF to give cyanoferrocene **3** as the sole isolable organometallic product (78–96% yield, Table 1). In the course of the reaction, two molecules of benzyl halide are transformed into the corresponding benzyl sulfide (formally **3** is the product of the elimination of H_2S from **1**). The sulfide is easily separable from **3** by column chromatography.

* Corresponding author. Tel.: +48 42 678 4731; fax: +48 42 678 6583.
E-mail address: janzak@uni.lodz.pl (J. Zakrzewski).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.10.049

Table 1
Reaction of **1** with benzyl halides and K_2CO_3

Entry	R	X	Yield of **3** (%)
1	C_6H_5	Cl	78
2	*p*-NO_2-C_6H_4	Br	96
3	*p*-CN-C_6H_4	Br	92

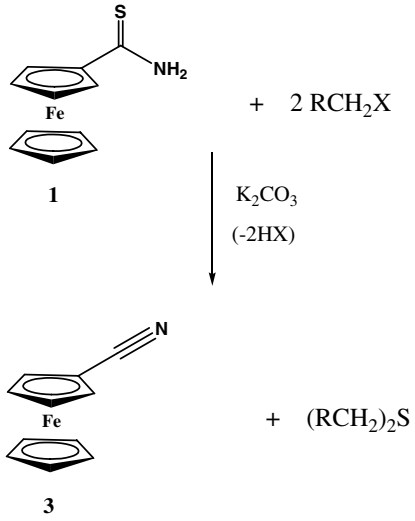
In the case of the reaction of **1** with *p*-$NO_2C_6H_4CH_2Br$ the sulfide (*p*-$NO_2C_6H_4CH_2)_2S$ was completely characterized.

The earlier reported synthesis of compound **3** from ferrocene [8] involves three steps: the Vilsmeyer formylation, transformation of the aldehyde into the corresponding oxime (α- or β-form) and dehydration of the oxime. As **1** can be prepared in one step from ferrocene (55% optimized yield [9]), its reaction with *p*-nitrobenzyl bromide constitutes a simple and efficient (53% overall yield) alternative way of preparation of **3** from ferrocene (Scheme 1).

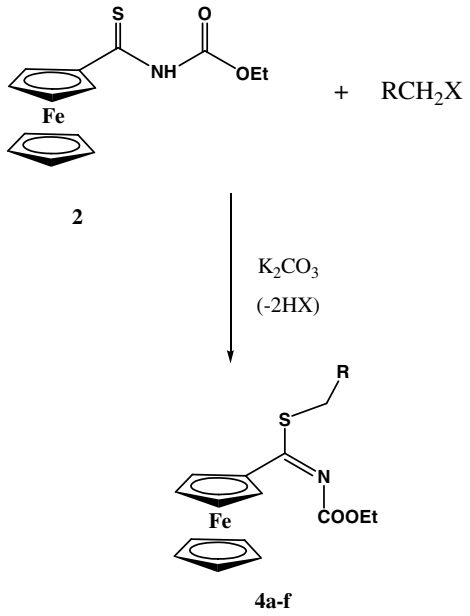
In contrast to **1**, its *N*-ethoxycarbonyl derivative **2** reacts with alkyl halides to afford *N*-ethoxycarbonyl thioimidates **4a**–**e** in 67–93% yield (Scheme 2, Table 2). Although benzyl halides were mostly used, the Entry 6 shows that reaction also occurs with a simple alkyl halide. Reactive chloromethylferrocene [10], prepared *in situ* from ferrocenylmethanol and oxalyl chloride in DMF, was treated with **2** and K_2CO_3 to afford **4f** in a one-pot procedure in 53% yield (Table 2, Entry 7).

Complexes **4a**–**f** were fully characterized by spectral and elemental analysis data.

Additionally, the molecular structure of **4b** was determined by single-crystal X-ray diffraction (*vide infra*). The structure revealed the *E* configuration of this compound. We assume that all synthesized compound **4a**–**f** have the same configuration. In any case we have not observed formation of the second (*Z*) stereoisomer. This means that *S*-alkylation of **2** is totally stereoselective.



Scheme 1. Reaction of **1** with benzyl halides in the presence of K_2CO_3.



Scheme 2. Reaction of **2** with alkyl halides in the presence of K_2CO_3. (a) R = Ph, (b) R = *p*-NO_2-Ph, (c) R = *p*-NC-Ph, (d) R = *p*- MeOOC-Ph, (e) R = Pr, (f) R = Fc.

Table 2
Reaction of **2** with alkyl halides and K_2CO_3

Entry	R	X	Product (%Yield)
1	C_6H_5	Cl	**4a** (92)
2	*p*-NO_2-C_6H_4	Cl	**4b** (86)
3	*p*-NO_2-C_6H_4	Br	**4b** (93)
4	*p*-NC-C_6H_4	Br	**4c** (89)
5	*p*-MeOOC-C_6H_4	Br	**4d** (85)
6	$CH_3(CH_2)_2$	Br	**4e** (67)
7	Fc[a]	Cl[a]	**4f** (53)

[a] Ferrocenylmethyl chloride prepared *in situ* from ferrocenylmethanol and oxalyl chloride.

3. Crystal structure of 4b

Crystals of this compounds suitable for X-ray analysis were grown from layered dichloromethane-pentane. The crystallographic data and selected geometrical parameters are collected in Tables 3 and 4, respectively. The molecular structure of **4b** is shown in Fig. 1.

Compound **4b** crystallizes in monoclinic *P*2/*c* space group with one molecule in the asymmetric unit. The ferrocenyl moiety has nearly eclipsed conformation. The CnA–CgA–CgB–CnB (*n* = 1–5, atoms CnA and CnB form substituted CpA and unsubstituted CpB rings, respectively) dihedral angle describing this conformation adopts value 5.6(4)°. The best planes of both Cp rings are almost coplanar, forming angle of 0.6(2)°. The distances CgA–Fe and CgB–Fe are 1.640(2) Å and 1.654(2) Å, respectively, while the angle CgA–Fe–CgB adopts value 178.70(7)°. Atoms C21, N1, C6, S2 are practically coplanar and the best plane calculated on the basis of their positions forms the dihedral angle of 3.4(2)° with the CpA best plane. This suggests con-

Table 3
Crystallographic data and structure refinement for **4b**

Formula	$C_{21}H_{20}FeN_2O_4S$
M	452.3
Crystal system	Monoclinic
Space group	*C2/c*
a (Å)	15.413(3)
b (Å)	7.883(5)
c (Å)	33.740(3)
β	92.678(12)
V (Å^3)	4095(3)
Z	8
D_x (g cm^{-3})	1.467
μ (mm^{-1})	0.868
T (K)	293(1)
λ (Å)	0.71073
Index ranges	$0 \leqslant h \leqslant 18$, $0 \leqslant k \leqslant 9$, $-41 \leqslant l \leqslant 41$
Number of data collected	4181
Number of unique data	4030
R_{int}	0.0139
Number of $I > 2\sigma(I)$ data	2706
Number of parameters	263
R_1 (all data)	0.0619
wR_2 (all data)	0.1110
R_1 [$I > 2\sigma(I)$]	0.0374
wR_2 [$I > 2\sigma(I)$]	0.1059
$\Delta\rho_{min}$ (e Å^{-3})	−0.563
$\Delta\rho_{max}$ (e Å^{-3})	0.330

Table 4
Selected geometrical parameters (Å, °) for **4b**

S2–C6	1.771(2)
S2–C7	1.818(2)
O2–N2	1.195(3)
O3–N2	1.210(3)
O22–C21	1.338(3)
O22–C22	1.462(3)
O21–C21	1.207(3)
N1–C6	1.273(3)
N1–C21	1.388(3)
N2–C11	1.475(3)
C6–S2–C7	101.77(11)
C21–O22–C22	115.3(2)
C6–N1–C21	124.3(2)
O2–N2–O3	122.7(2)
O2–N2–C11	119.2(2)
O3–N2–C11	118.1(2)
N1–C6–S2	119.09(17)
C8–C7–S2	111.72(16)
O21–C21–O22	124.1(2)
O21–C21–N1	125.4(2)
O22–C21–N1	110.1(2)
C5A–C1A–C6–S2	3.1(3)
C5A–C1A–C6–N1	−176.9(2)
C21–N1–C6–S2	173.19(18)
O2–N2–C11–C10	−3.2(4)
C6–N1–C21–O21	−84.9(3)
C6–N1–C21–O22	102.0(3)
C22–O22–C21–O21	1.7(4)
C21–O22–C22–C23	173.1(3)
C6–S2–C7–C8	88.02(18)

jugation of the S–C=N group with the ferrocenyl moiety. However, the spatial orientation of the C21/O21/O22 ester

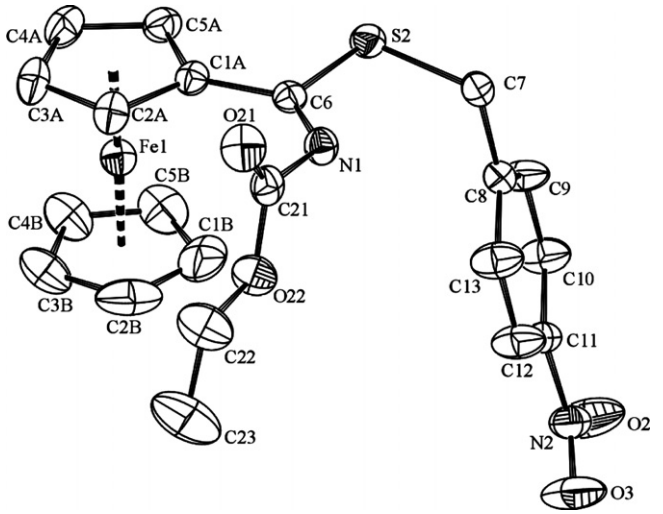


Fig. 1. Scheme of atoms labelling in crystal structure of **4b**. Thermal ellipsoids are drawn with 30% probability. H atoms have been omitted for clarity.

group clearly indicates, that this group does not undergo conjugation with the π-system of the imine moiety. The (C21/O21/O22/N1) and (C1A/C6/S2/N1) best planes are almost perpendicular, forming an angle of 84.8(2)°. It should be pointed out, that there is no intramolecular steric hindrance which could force such a conformation in the free molecule. There is also a lack of intramolecular interactions which could additionally stabilize this geometry, thus the most probable reason of the molecule twisting along N1–C21 bond is connected with the packing of molecules in the crystal state. However, it should be noticed that the perpendicular orientation of the above mentioned planes may be stabilized by conjugation of the CO group with the lone pair located at nitrogen. The inspection of Crystal Structure Database (CSD) [11] using the ConQuest Interface [12] revealed that among 70 reported structures containing unconstrained C=N–C=O motif a considerable number (13) has nearly perpendicular orientation of C=N and C=O planes (the corresponding dihedral angle 80–120°) presumably due to CO–nitrogen long pair conjugation. The plane of the phenyl ring forms an angle of 71.7(3)° with the best plane estimated for C1A/C6/S2/C7 sequence of atoms. As one could expect, the nitro group attached in position 4 of the phenyl ring is almost coplanar with this ring. The dihedral angle describing this arrangement adopts value of 4.6(4)°.

The molecule of **4b** does not have typical proton donating group. Therefore, there is a lack of the classic hydrogen bonds which could stabilize the crystal structure of **4b**. However, the detailed analysis of the molecular packing allows to suppose, that crystal structure is partially stabilized by stacking interactions. As it is shown in Fig. 2, the arrangement of phenyl rings belonging to neighbouring molecules symmetrically equivalent by inversion suggests the existence of such interaction. The distance between potentially interacting adjacent rings is 3.724(2) Å, while

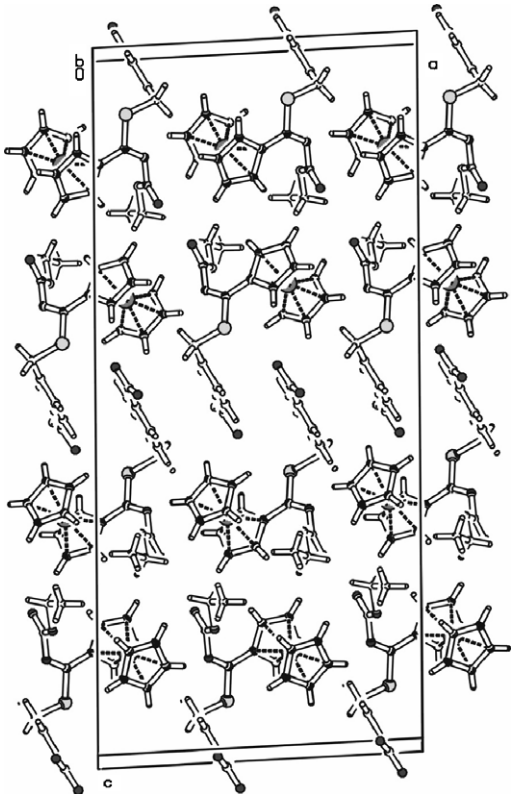
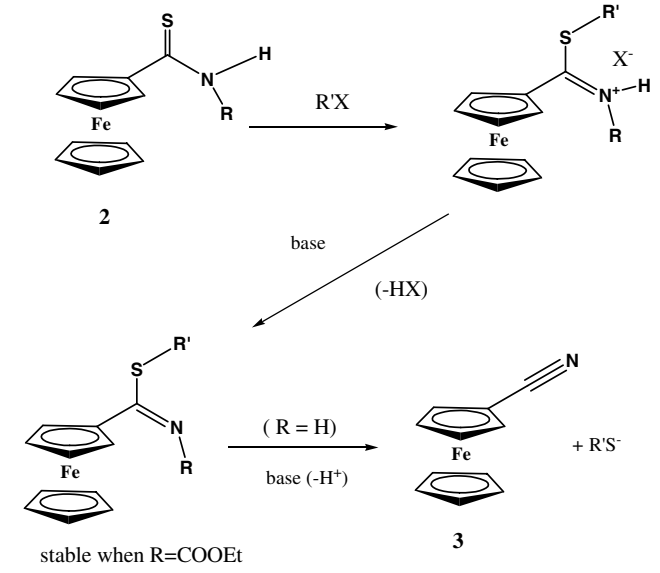


Fig. 2. Packing of molecules of **4b** in crystal.

the distance between the corresponding *Cg*'s of these rings is 3.823(2) Å.

We suggest the following mechanism for the transformation of **1** into **3** and **2** into **4a–e** (Scheme 3).

The reaction starts with the *S*-alkylation which is followed by deprotonation leading to the thioimidate, which is stable if R = COOEt. If R = H the imidate undergoes deprotonation and elimination the thiolate anion $R'S^-$ to form **3**. Finally, the strongly nucleophilic thiolate anion reacts with the halide to afford sulfide R′SR′. A analogous mechanism has been proposed by Takido et al. who observed transformation of primary thioamides into nitriles in reaction with benzyl chloride under phase transfer conditions [13]. The reaction takes place in the benzene −30% aq. NaOH system. To compare, the reaction of **1** with benzyl halides described here occurs under milder (less basic) conditions but its scope seems to be limited to this compound (attempts to transform *p*-methoxybenzenecarbothioamide into the corresponding nitrile under these conditions failed).



Scheme 3. The suggested mechanism of the reaction of **1** and **2** with alkyl halides in the presence of K_2CO_3.

4. Conclusion

It has been found that ferrocenyl thioamides **1** and **2** react with alkyl halides in the presence of potassium carbonate in a different manner: compound **1** undergoes elimination of hydrogen sulfide to afford cyanoferrocene **3**, whereas compound **2** is *S*-alkylated and yields *N*-(ethoxycarbonyl)thioimidates **4a–f**. We think that these compounds as well as compound **2** itself can be interesting redox active ligands, e.g. for ferrocene-based biosensors.

5. Experimental

All reactions were carried out under argon. All reagents used in this work are commercially available (Aldrich) and were used without further purifications. Solvents were dried over appropriate drying agents and distilled before use. Compounds **1–2** were prepared according to the literature procedure [1]. Chromatographic separations were carried out using Silica gel 60 (Merck, 230-400 mesh ASTM). The NMR spectra were run on a Varian Gemini 200 BB (200 MHz for ^{1}H) and IR spectra on a FT-IR Nexus spectrometer. Mass spectra and high resolution mass spectra (HRMS) were measured on a Finnigan MAT 95 spectrometer. Melting points were determined on a Boetius apparatus and were uncorrected. Elemental analyses were performed by Analytical Services of the Center of Molecular and Macromolecular Studies of the Polish Academy of the Sciences (Łódź).

5.1. Synthesis of 3

Ferrocenecarbothioamide **1** (60 mg, 0.25 mmol) was dissolved in DMF (3 ml) and treated with K_2CO_3 (345 mg, 2.5 mmol) and a halide (0.50 mmol). The reaction mixture was heated to 50 °C for 1 h, cooled to room temperature, filtrated and evaporated to dryness. Flash chromatography ($CHCl_3$ as eluent) afforded two fractions. The first fraction contained the sulfide by-product and the second (more polar) fraction contained nitrile **3**. Yields of **3** are shown in Table 1.

Compound **3**: Yellow plates. M.p. 106–106.5 °C (Lit. [8]. M.p. 107–108 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.20 (s,

5H, Cp′), 4.38 (t, $J = 1.9$ Hz, 2H, Cp), 4.65 (t, $J = 1.9$ Hz, 2H, Cp). IR ($CHCl_3$, cm^{-1}): 2225 (CN). Anal. Calc. for $C_{11}H_9FeN$: C, 62.60, H, 4.30, N, 6.64, Found: C, 62.57, H, 4.31, N, 6.50%.

Bis(p-nitrobenzyl)sulfide M.p. 156–157 °C (Lit. [14]. M.p. 158–159 °C). ^1H NMR (200 MHz, $CDCl_3$): 7.58 (d, $J = 8.2$ Hz, 4H, Ar), 7.38 (d, $J = 8.2$ Hz, 4H, Ar), 3.61 (s, 4H, CH_2). HRMS: Found: 304.05178, Calc. for $C_{14}H_{12}N_2O_4S$: 304.05178.

5.2. Synthesis of *4a–e*

To a solution of *N*-(ethoxycarbonyl)ferrocenecarbothioamide (**2**) (80 mg, 0.25 mmol) in DMF (3 ml) K_2CO_3 (345 mg, 2.5 mmol) and chloride or bromide (0.25 mmol) were added and the mixture was heated to 50 °C for 10 min. After cooling to room temperature, filtration and evaporation to dryness the residue was subjected to flash chromatography (CH_2Cl_2 as eluent). Yields are shown in Table 2.

*Compound **4a***: Red oil. ^1H NMR (200 MHz, $CDCl_3$): δ 1.33 (t, $J = 7.1$ Hz, 3H, CH_2CH_3), 4.23 (s, 5H, Cp′), 4.26 (s, 2H, CH_2Ph), 4.27 (q, $J = 7.2$ Hz, 2H, CH_2CH_3), 4.41 (t, $J = 2.1$ Hz, 2H, Cp), 4.65 (t, $J = 2.1$ Hz, 2H, Cp), 7.28–7.37 (m, 5H, Ph). ^{13}C NMR (200 MHz, $CDCl_3$): δ 172.6 (C=N), 161.8 (CO), 136.6 (Ph), 129.3 (Ph), 128.6 (Ph), 127.4 (Ph), 70.9 (Cp), 70.8 (Cp′), 68.9 (Cp), 62.4 (CH_2), 35.7 (CH_2), 14.2 (CH_3). IR ($CHCl_3$, cm^{-1}):1701 (CO), 1608 (CN), MS (EI): 407 (M^+), HRMS: Found: 407.064250, Calc. for $C_{21}H_{21}SFeNO_2$: 407.064240.

*Compound **4b***: Red plates. ^1H NMR (200 MHz, $CDCl_3$): δ 1.30 (t, $J = 7.1$ Hz, 3H, CH_2CH_3), 4.21 (s, 5H, Cp′), 4.22 (q, $J = 7.2$ Hz, 2H, CH_2CH_3), 4.29 (s, 2H, CH_2Ar), 4.43 (t, $J = 1.9$ Hz, 2H, Cp), 4.62 (t, $J = 1.9$ Hz, 2H, Cp), 7.57 (d, $J = 8.7$ Hz, 2H, Ar), 8.15 (d, $J = 8.7$ Hz, 2H, Ar). ^{13}C NMR (200 MHz, $CDCl_3$): δ 171.3(C=N), 161.4 (CO), 147.1 (Ar), 145.2 (Ar), 129.9 (Ar), 123.7 (Ar), 71.3 (Cp), 70.8 (Cp′), 68.9 (Cp), 62.5 (CH_2), 34.6 (CH_2), 14.3 (CH_3). IR ($CHCl_3$, cm^{-1}): 1698 (CO), 1608 (CN), 1520, 1344 (NO_2), MS (EI): 452 (M^+), HRMS: Found: 452.049314, Calc. for $C_{21}H_{20}SFeN_2O_4$: 452.049318. Anal. Calc. for $C_{21}H_{20}SFeN_2O_4$: C, 55.75, H, 4.46, N, 6.20, S, 7.07, Found: C, 55.94, H, 4.55, N, 6.70, S, 7.08%.

*Compound **4c***: Red oil. ^1H NMR (200 MHz, $CDCl_3$): δ 1.31 (t, $J = 7.1$ Hz, 3H, CH_2CH_3), 4.20 (s, 5H, Cp′), 4.22 (q, $J = 7.0$ Hz, 2H, CH_2CH_3), 4.26 (s, 2H, CH_2Ar), 4.42 (t, $J = 1.9$ Hz, 2H, Cp), 4.62 (t, $J = 1.9$ Hz, 2H, Cp), 7.50 (d, $J = 8.5$ Hz, 2H, Ar), 7.58 (d, $J = 8.5$ Hz, 2H, Ar). ^{13}C NMR (200 MHz, $CDCl_3$): δ 171.4(C=N), 161.4 (CO), 142.9 (Ar), 132.3 (Ar), 129.9 (Ar), 129.6 (Ar), 118.7 (CN), 71.3 (Cp), 70.8 (Cp′), 68.9 (Cp), 62.5 (CH_2), 34.9 (CH_2), 14.3 (CH_3). IR ($CHCl_3$, cm^{-1}): 2231 (CN), 1703 (CO), 1608 (CN), Anal. Calc. for $C_{22}H_{20}FeN_2O_2S$: C, 60.30, H, 4.34, N, 6.70, S, 7.66, Found: C, 60.33, H, 4.42, N, 6.59, S, 7.43%.

*Compound **4d***: Red oil. ^1H NMR (200 MHz, $CDCl_3$): δ 1.31 (t, $J = 7.1$ Hz, 3H, CH_2CH_3), 3.90 (s, 3H, OCH_3), 4.21 (s, 5H, Cp′), 4.23 (q, $J = 7.1$ Hz, 2H, CH_2CH_3), 4.28 (s, 2H, CH_2Ar), 4.41 (t, $J = 1.9$ Hz, 2H, Cp), 4.64 (t, $J = 1.9$ Hz, 2H, Cp), 7.48 (d, $J = 8.1$ Hz, 2H, Ar), 7.98 (d, $J = 8.2$ Hz, 2H, Ar). ^{13}C NMR (200 MHz, $CDCl_3$): δ 171.8(C=N), 166.7 (CO), 161.5 (CO), 142.4 (Ar), 129.8 (Ar), 129.1 (Ar), 128.9 (Ar), 77.2 (Cp), 71.1 (Cp), 70.8 (Cp′), 68.9 (Cp), 62.4 (CH_2), 52.0 (CH_3), 35.2 (CH_2), 14.3 (CH_3). IR ($CHCl_3$, cm^{-1}): 1716 (CO), 1612 (CN), Anal. Calc. for $C_{23}H_{23}FeNO_4S$: C, 59.36, H, 4.98, N, 3.01, S, 6.89, Found: C, 59.31, H, 5.07, N, 3.12, S, 6.67%.

*Compound **4e***: Orange oil. ^1H NMR (200 MHz, $CDCl_3$): δ 0.94 (t, $J = 7.3$ Hz, 3H, $(CH_2)_3CH_3$), 1.30 (t, $J = 7.1$ Hz, 3H, CH_2CH_3), 1.37–1.54 (m, 2H $(CH_2)_2CH_2CH_3$), 1.59–1.73 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.99 (t, $J = 7.1$ Hz, 2H, $CH_2(CH_2)_2CH_3$), 4.20 (q, $J = 7.1$ Hz, 2H, CH_2CH_3), 4.24 (s, 5H, Cp′), 4.39 (t, $J = 1.9$ Hz, 2H, Cp), 4.64 (t, $J = 1.9$ Hz, 2H, Cp). ^{13}C NMR (200 MHz, $CDCl_3$): δ 172.9 (C=N), 161.8 (CO), 78.3 (Cp), 70.8 (Cp′), 68.9 (Cp), 62.3 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 22.1 (CH_2), 14.3 (CH_3), 13.7 (CH_3). IR ($CHCl_3$, cm^{-1}): 1697 (CO), 1608 (CN). MS (EI): 373 (M^+), HRMS: Found: 373.079890, Calc. for $C_{21}H_{21}SFeNO_2$: 373.079903.

5.3. Synthesis of *4f*

Oxalyl chloride (64 mg, 0.5 mmol) was added rapidly to a solution of ferrocenylmethanol (108 mg, 0.5 mmol) in DMF (5 ml). When the HCl evolution stopped, K_2CO_3 (690 mg, 5 mmol) and *N*-(ethoxycarbonyl)ferrocenecarbotioamide (**2**) (159 mg, 0.5 mmol) were added. The reaction mixture was stirred for 15 min. at r.t., filtrated and concentrated *in vacuo*. The product was isolated by flash chromatography on silica gel (chloroform). Recrystallization from dichloromethane–pentane yielded **4f** (137 mg, 53%). ^1H NMR (200 MHz, $CDCl_3$): δ 1.33 (t, $J = 7.1$ Hz, 3H, CH_2CH_3), 4.05 (s, 2H, CH_2Cp), 4.12–4.17 (m, 2H, CH_2CH_3), 4.14 (t, $J = 1.9$ Hz, 2H, Cp), 4.19 (s, 5H, Cp′), 4.24 (s, 5H, Cp′), 4.27 (t, $J = 1.9$ Hz, 2H, Cp), 4.40 (t, $J = 1.9$ Hz, 2H, Cp), 4.64 (t, $J = 1.9$ Hz, 2H, Cp). ^{13}C NMR (200 MHz, $CDCl_3$): δ 172.8 (CS), 161.8 (CO), 82.9 (Cp), 70.9 (Cp), 70.8 (Cp), 69.4 (Cp), 69.3 (Cp), 68.9 (Cp), 68.8 (Cp), 68.3 (Cp), 62.3 (CH_2), 31.6 (CH_2), 14.3 (CH_3). Anal. Calc. for $C_{25}H_{25}SFe_2NO_2$: C, 58.25, H, 4.89, N, 2.72, S, 6.21, Found: C, 58.09, H, 4.96, N, 2.97, S, 6.04%.

5.4. X-ray measurements

Orange, needle shaped crystal of compound **4b**, mounted on glass fiber, has been used for X-ray diffraction measurement. The data were collected on a Rigaku AFC5S single crystal diffractometer, using Mo Kα source and a graphite monochromator. The Lorentz and polarization corrections were applied.

The structure was solved by direct methods using SHELXS97 [15] and refined by full-matrix least-squares methods on F^2 using SHELXL97 [16]. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters.

Hydrogen atoms were located geometrically using AFIX in SHELXL97. Molecular geometries were calculated by PLATON [17]. Molecular graph with thermal ellipsoids was performed using PLATON.

Appendix A. Supplementary material

CCDC 639644 contains 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.10.049.

References

[1] D. Plażuk, J. Zakrzewski, A. Rybarczyk-Pirek, S. Domagała, J. Organomet. Chem. 690 (2005) 4302.
[2] S. Jagodziński, Chem. Rev. 103 (2003) 197.
[3] M. Nonoyama, K. Hamura, J. Organomet. Chem. 407 (1991) 271.
[4] K. Hamamura, M. Kita, M. Nonoyama, J. Fujita, J. Organomet. Chem. 463 (1993) 169.
[5] P.D. Beer, A.G. Graydon, A.O.M. Johnson, D.K. Smith, Inorg. Chem. 36 (1997) 2112.
[6] S. Jautze, P. Seiler, R. Peters, Angew. Chem., Int. Ed. 46 (2007) 1260.
[7] B.G. Shearer, J.A. Oplinger, S. Lee, Tetrahedron Lett. 38 (1997) 179.
[8] G.D. Broadhead, J.M. Osgerby, J.M. Pauson, J. Chem. Soc. (1958) 650.
[9] A.Wrona, J. Zakrzewski, unpublished data.
[10] See for example T.T. Tidwell, T.G. Taylor, J. Am. Chem. Soc. 84 (1966) 3422.
[11] F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380, CSD version 5.28 (November 2006.
[12] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macray, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr., Sect. B 58 (2002) 389.
[13] Y. Funakoshi, T. Takido, K. Itabashi, Synth. Commun. 15 (1985) 1299.
[14] W.J. Horn, J. Am. Chem. Soc. 43 (1921) 2610.
[15] G.M. Sheldrick, SHELXS97. Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
[16] G.M. Sheldrick, SHELXL97 Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[17] A.L. Spek, PLATON – Molecular Geometry Program, University of Utrecht, The Netherlands, 1998.