

Ferrocenecarbothioamide and *N*-ethoxycarbonylferrocenecarbothioamide: Synthesis, structure and application in synthesis of 2,4-diferrocenylthiazole

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Abstract

Ferrocenecarbothioamide (**1**) and its *N*-ethoxycarbonyl derivative (**2**) were synthesised by a Friedel–Crafts type reaction of ferrocene with potassium thiocyanate and ethoxycarbonyl isothiocyanate, respectively, in a strongly acidic medium. The X-ray structure of **1** was determined and shows conjugation between the ferrocene moiety and the thioamido group. Compound **1** reacts with chloroacetylferrocene affording 2,4-diferrocenylthiazole, whose structure was determined by X-ray diffraction and electronic properties studied by cyclic voltammetry.

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1. Introduction

During recent years, there has been a growing interest in heterocycles containing ferrocenyl groups due to their applications as redox active markers of natural products [1,2], biological activity [3–5] and interesting electronic [6], non-linear optical [7] and ligating properties [8]. Since thioamides have an established utility in synthesis of heterocycles (especially primary thioamides and thioamides containing *N*-carbonyl groups [9]), we thought that it would be of interest to synthesize ferrocenecarbothioamide (**1**) and its *N*-ethoxycarbonyl derivative (**2**) (Scheme 1).

Here, we report on direct synthesis of **1** and **2** from ferrocene by a Friedel–Crafts type reaction with potas-

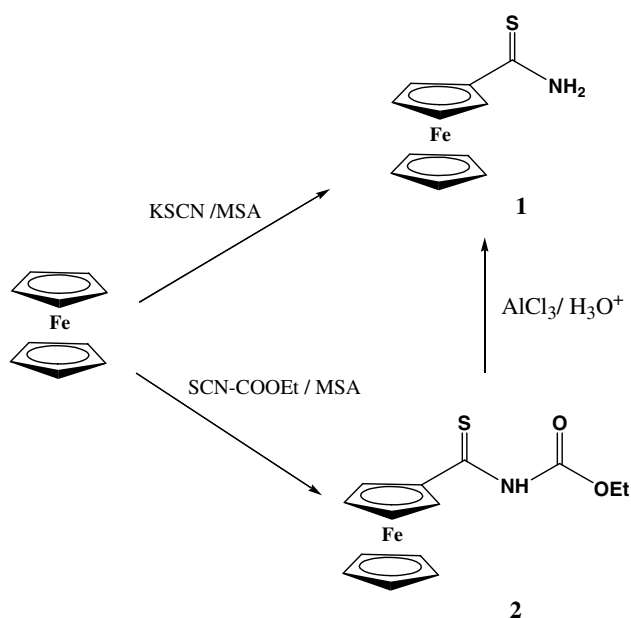
sium thiocyanate and ethoxycarbonyl isothiocyanate, respectively, in a strongly acidic medium. The synthetic potential of **1** was exemplified by its use in the synthesis of 2,4-diferrocenylthiazole (**4**), compound for which interesting electronic properties can be expected (the 2,5- isomer of **4** was synthesized earlier and shows electronic communication between metal centres and redox-switchable proton affinity [6]).

2. Results and discussion

2.1. Synthesis of **1** and **2**

It has been recently reported that electron-rich arenes (e.g., anisole) react with potassium thiocyanate in methanesulfonic acid (MSA) to afford the corresponding primary thioamides [10]. We applied this reaction

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Scheme 1. MSA – methanesulfonic acid.

for synthesis of **1**. Ferrocene, dissolved in a MSA–dichloromethane mixture, was treated with potassium thiocyanate (3 moles per mol of ferrocene) at r.t. A partial oxidation of ferrocene to the ferrocenium ion took place, observed as appearance of an intense blue coloration of the reaction mixture. Quenching with water, extraction and flash chromatography afforded **1** along with unchanged ferrocene (18%). The isolated yield of **1** was 36% (44% based on the consumed ferrocene). All attempts to carry out this reaction to completion, as well as to improve yield of **1** failed. The structure of **1** was confirmed by spectral data, elemental analysis and by X-ray diffraction analysis (vide infra).

So far ferrocenyl thioamides have not attracted much attention, although some superiority of the thioamido function over its oxygen counterpart in ferrocenyl anion sensors has been demonstrated [11]. Scarce syntheses of these compounds (*N*-substituted and *N,N*-disubstituted) are based on the reaction of the lithiated ferrocene with thiocarbonyl chlorides [12,13] and thionation of amides [11]. Compound **1** is mentioned in a patent contribution [14], but no information concerning its synthesis was given.

We expected that reaction of ferrocene with ethoxycarbonyl isothiocyanate would afford **2** (such a reaction is known for electron-rich arenes [15]). In fact, this reaction gave **2** as a purple solid in 49% isolated yield. Treatment of **2** with AlCl₃ in refluxing benzene gave **1** in 70% yield.

2.2. Synthesis of 2,4-diferrocenylthiazole (**4**)

Taking into account numerous applications of thioamides in syntheses of heterocycles [9] compound **1** is a potential starting material in such syntheses. To exem-

plify its synthetic utility, we performed reaction of **1** with chloroacetylferrocene (**3**) (Scheme 2). The latter compound can be obtained by the Friedel–Crafts acylation of ferrocene with chloroacetyl chloride in reaction promoted by AlCl₃ [16] or EtAlCl₂–Me₃Al [17]. We found that it is also formed in 42% yield in reaction of ferrocene with chloroacetic acid, trifluoroacetic anhydride and trifluoromethanesulfonic acid in dichloromethane at r.t. (we applied earlier this method for synthesis of other acylferrocenes [18]).

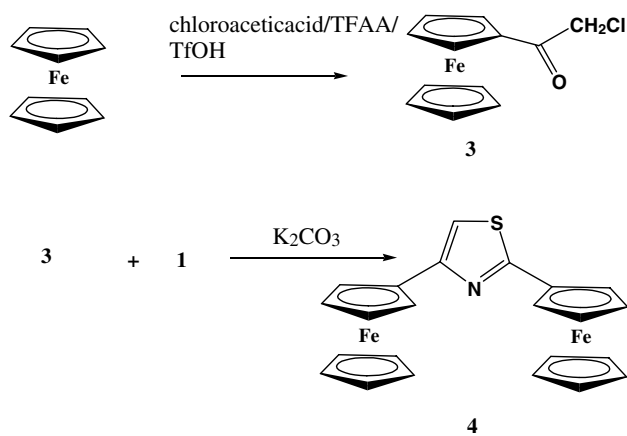
Refluxing of **3** with **1** in toluene in the presence of K₂CO₃ afforded **4** in 74% isolated yield. The structure of this compound was confirmed by spectral data, elemental analysis and X-ray diffraction study (vide infra). The ¹H NMR spectrum of **4** in CDCl₃ shows a significant difference in chemical shifts of ferrocenyl groups in this compound. A separate set of signals was observed for each ferrocenyl group indicating that their electronic surroundings are substantially different (a similar phenomenon was reported for 2,5-diferrocenylthiazole [6]).

2.3. X-ray diffraction analysis for **1** and **4**

Crystals of **1** and **4** suitable for the X-ray diffraction study were grown from layered dichloromethane–pentane. The crystal and structure refinement data are gathered in Table 1.

The molecular structure of **1** is shown in Fig. 1. Table 2 shows selected geometric parameters for **1** and **3**.

The structure of **1** shows that the thioamido group is practically planar and the C=S bond coplanar with the substituted Cp ring plane which may be interpreted in terms of the conjugation between this group and the ferrocene π-system. The lengths of the C11=S (1.680(2) Å), C11–N1, (1.324(3) Å) and C11–C1 (1.463(3) Å) bonds are close to the lengths of analogous bonds in *N,N,N',N'*-tetramethylferrocene-1,1'-dicarbothioamide (1.684(3), 1.338(4) and 1.479(5) Å, respectively)



Scheme 2. TFAA – trifluoroacetic anhydride; TfOH – trifluoromethanesulfonic acid.

Table 1
Crystal data and structure refinement details for **1** and **4**

	1	4
Empirical formula	C ₁₁ H ₁₁ FeNS	C ₂₃ H ₁₉ Fe ₂ NS
Formula weight	245.12	453.15
Crystal system, space group	Monoclinic, <i>C2/c</i>	Orthorhombic, <i>Pbca</i>
Unit cell dimensions		
<i>a</i> (Å)	12.186(1)	15.636(3)
<i>b</i> (Å)	18.709(2)	23.400(3)
<i>c</i> (Å)	10.726(1)	10.434(2)
β (°)	123.252(6)	
Volume (Å ³)	2045.0(3)	3817.6(11)
Z, Calculated density (g cm ⁻³)	8, 1.592	8, 1.577
Absorption coefficient (mm ⁻¹)	1.633	1.636
<i>F</i> (0 0 0)	1008	1856
Crystal size (mm)	0.6 × 0.4 × 0.2	0.60 × 0.60 × 0.05
θ Range for data collection (°)	2.18–25.49	1.74–24.99
Limiting indices	0 ≤ <i>h</i> ≤ 14; 0 ≤ <i>k</i> ≤ 22; -12 ≤ <i>l</i> ≤ 10	0 ≤ <i>h</i> ≤ 18; 0 ≤ <i>k</i> ≤ 27; 0 ≤ <i>l</i> ≤ 12
Reflections collected/unique	2007/1916 [<i>R</i> _{int} = 0.016]	3365/3365 [<i>R</i> _{int} = 0.000]
Completeness (%)	100.0	100.0
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1916/0/138	3365/165/264
Goodness-of-fit on <i>F</i> ²	1.107	0.971
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0227, <i>wR</i> = 0.0825	<i>R</i> = 0.0558, <i>wR</i> = 0.1659
<i>R</i> indices (all data)	<i>R</i> = 0.0331, <i>wR</i> = 0.0834	<i>R</i> = 0.1018, <i>wR</i> = 0.1814
Largest difference peak and hole (e Å ⁻³)	0.194 and -0.276	0.650 and -0.572

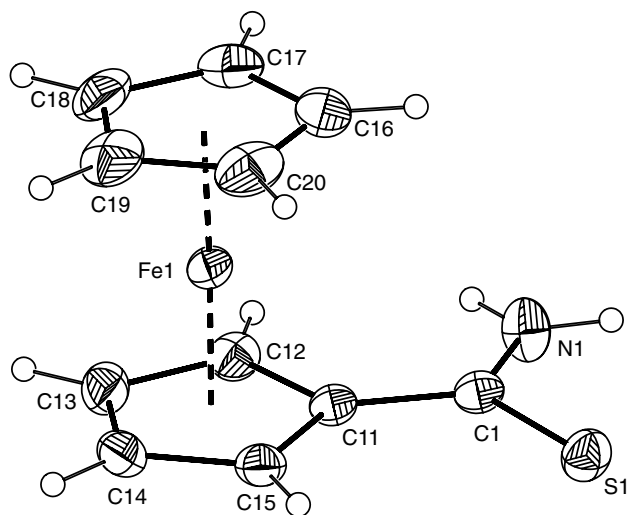


Fig. 1. View of **1** molecule with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at 30% probability level. Hydrogen atoms are shown as small spheres of arbitrary radii.

[13]. In crystals, the molecules of **1** forms hydrogen-bonded chains parallel to the *c*-axis of the unit cell (Fig. 2, Table 3).

In the molecule of **4** (Fig. 3) both ferrocene moieties are arranged on the same side of the thiazole ring plane. Since an analysis of intramolecular interactions showed no steric hindrance between the ferrocenyl substituents, this conformation could be regarded as a stable one. The dihedral angles between the thiazole ring and the adjacent cyclopentadienyl rings are 7.6(2)° for the ferrocenyl

Table 2
Selected geometric parameters (Å, °) for **1** and **4**

	1	4
Fe1–C mean	2.046(6)	
Fe2–C mean		
C1–C11	1.463(3)	1.481(8)
C3–C21		1.443(8)
S1–C1	1.680(2)	1.717(6)
S1–C2		1.781(9)
N1–C1	1.324(3)	1.317(6)
N1–C3		1.365(7)
C2–C3		1.350(11)
N1–C1–C11	116.9(2)	122.4(5)
N1–C1–S1	119.5(2)	115.1(4)
C11–C1–S1	123.6(2)	122.5(4)
C1–S1–C2		88.7(6)
S1–C2–C3		108.5(9)
C2–C3–N1		116.6(8)
C2–C3–C21		122.1(9)
N1–C3–C21		121.2(5)
C1–N1–C3		111.1(5)
C15–C11–C1–N1	178.1(2)	177.1(5)
C12–C11–C1–N1	0.2(4)	-6.9(8)
C15–C11–C1–S1	-3.7(3)	-5.5(8)
C12–C11–C1–S1	178.3(2)	170.5(5)
C25–C21–C3–N1		164.5(5)
C22–C21–C3–N1		-9.8(9)
C25–C21–C3–C2		-12.3(10)
C22–C21–C3–C2		173.5(10)

group at C-2 and 12.5(2)° for the ferrocenyl group at C-4. The bigger twisting of the latter Cp-ring is presumably due to steric interactions between C2–H2 and C25–H25,

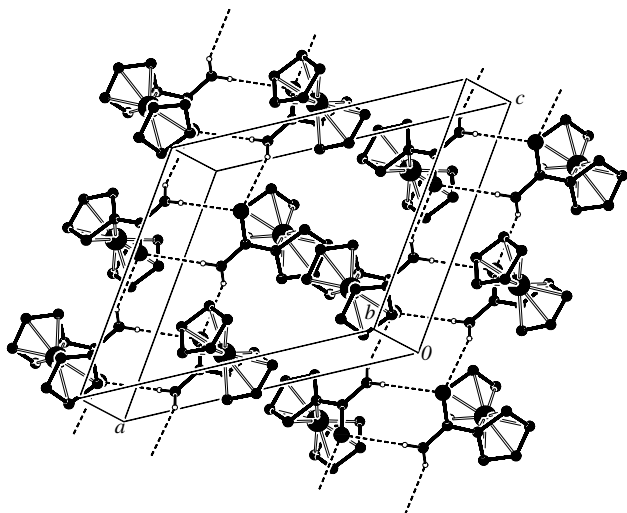


Fig. 2. The scheme of intermolecular hydrogen bonding net in the crystal of **1**. The N–H...S hydrogen bonds linking molecules into infinite chains of molecules parallel to *c*-direction are shown with dotted lines. All hydrogen atoms except for those of amide group are omitted for clarity.

destabilizing planar conformation. The above-mentioned angles indicate extensive π -conjugation of both ferrocenyl groups with the thiazole ring. Interestingly, the lengths of the bonds between ferrocenyl units and the thiazole ring are different (compare C1–C11, 1.481(8) Å with C3–C21, 1.443(8) Å). The ferrocenyl

Table 3
Hydrogen bonding geometry for **1** [Å, °]

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	\angle DHA
N1–H1A...S1 ⁱ	0.860	2.540	3.294(3)	147(2)
N1–H1B...S1 ⁱⁱ	0.860	2.602	3.413(3)	158(2)

Symmetry codes: ⁱ*x*, *−y*, 0.5 + *z*; ⁱⁱ*−x*, *y*, 1.5 − *z*.

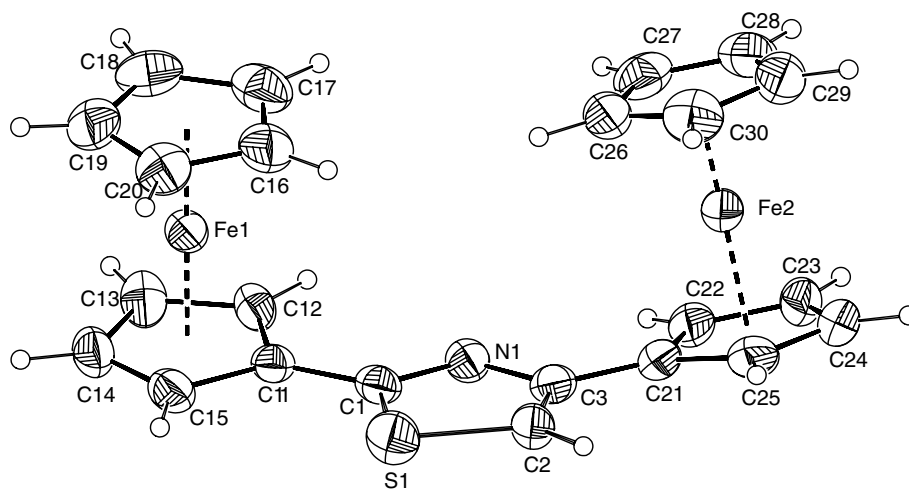


Fig. 3. View of **3** molecule with atom numbering scheme. Only the atoms of major disorder component are shown. Displacement ellipsoids for non-H atoms are drawn at 30% probability level. Hydrogen atoms are shown as small spheres of arbitrary radii.

group at C-4 is more efficiently conjugated with the thiazole ring than its counterpart at C-2, despite the bigger deviation from coplanarity with this ring. The different coupling of the ferrocenyl groups at C-2 and C-4 with the central thiazole ring brings about observed significant difference in chemical shifts of the respective ferrocenyl protons.

3. Electrochemistry

The electrochemical behaviour of **4** has been studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The voltammograms are shown in Fig. 4. Compound **4** exhibits three redox processes. Processes with $E_{1/2} = 51$ mV (vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$) and ($E_{1/2} = 206$ mV show separation between cathodic and anodic pics typical for one-electron redox processes (60 mV) and can be assigned to the reversible Fe(II)/Fe(III) oxidation/reduction of the ferrocenyl groups. The third redox process occurs at $E_{1/2} = 372$ mV ($\Delta E = 40$ mV). We tentatively assigned it to an oxidation/reduction of the thiazole ring. Interestingly, the isomeric compound, 2,5-diferrocenylthiazole, shows only two reversible one-electron redox processes localized at the ferrocenyl substituents [6]. Both CV and DPV data reveal that two ferrocenyl groups present in **4** are significantly non-equivalent. Presumably, the group at C-2 position is less readily oxidizable than its counterpart at C-4 [6]. The difference of the formal redox potentials of the ferrocenyl group in **4** (155 mV) is close to that reported for 2,5-diferrocenylthiazole (140 mV) [6], where significant electronic interaction between the iron centres was postulated. Since the π -electron density in the thiazole ring is lower at C-4 than at C-5 [19], one should expect that the redox potential of 4-ferrocenylthiazole

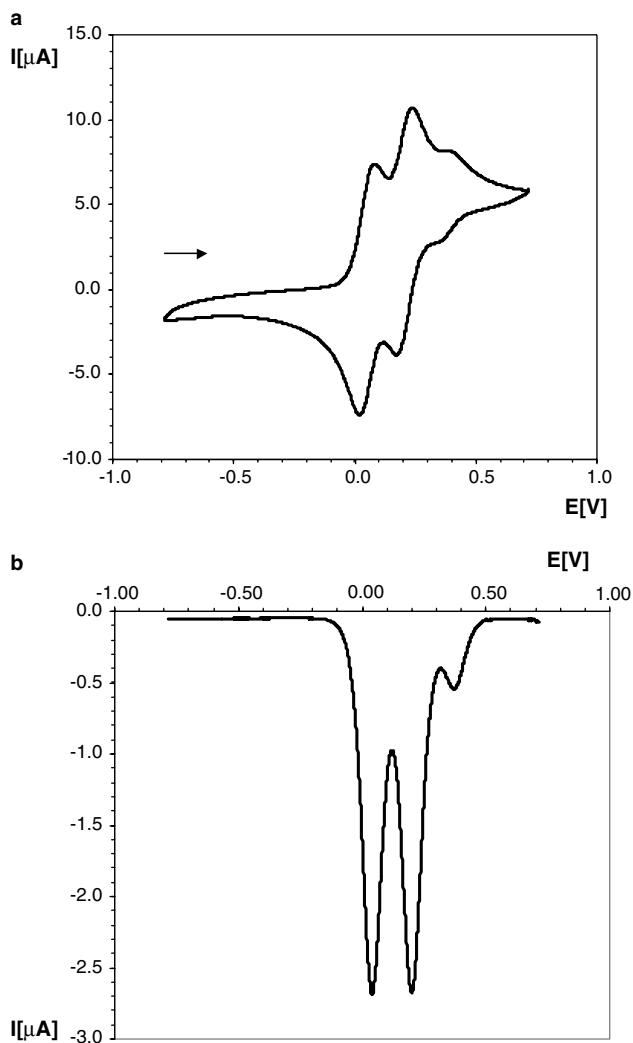


Fig. 4. (a) Cyclic voltammogram of **4** in CH_3CN with 0.1 M Bu_4NClO_4 at Pt-disk electrode, $\phi = 1.5$ mm, scan rate: 0.1 V s^{-1} . (b) Differential pulse voltammogram of **4** in CH_3CN with 0.1 M Bu_4NClO_4 at Pt-disk electrode, $\phi = 1.5$ mm, scan rate: 0.01 V s^{-1} , pulse amplitude: 10 mV, pulse width: 50 ms; amplitude: 10 mV.

will be higher than that of its 2,5-isomer. This means that electronic communication between the iron centres in **4** is comparable or stronger than that in 2,5-diferrocenylthiazole.

4. Conclusion

We have elaborated simple and efficient syntheses of ferrocenecarbothioamide (**1**) and its *N*-ethoxycarbonyl derivative (**2**) directly from ferrocene. Both compounds are of interest as starting materials in syntheses of heterocyclic compounds containing ferrocenyl groups. As an example of such applications 2,4-diferrocenylthiazole (**4**) has been synthesized by condensation of (**1**) with chloroacetylferrocene (**3**) in a basic medium.

5. Experimental

All reagents used in this work are commercially available (Aldrich). All syntheses were carried out under an argon atmosphere. Chromatographic separations were performed using Silica gel 60 (Merck, 230–400 mesh ASTM). The NMR spectra were run on a Varian Gemini 200 BB s (200 MHz for ^1H), IR spectra on a FT-IR Nexus and mass spectra on a Finnigan MAT 95 spectrometer.

5.1. Synthesis of ferrocenecarbothioamide (**1**)

Ferrocene (186 mg, 1.0 mmol) was dissolved in MSA (5 ml) and CH_2Cl_2 (2.5 ml) at r.t. To this solution potassium thiocyanate (290 mg, 3 mmol) was added, the mixture was stirred for 2 h and then poured onto ice–water (30 ml). Extraction with CH_2Cl_2 , washing with aq. NaHCO_3 and chromatography (CH_2Cl_2 as eluent) afforded unreacted ferrocene (34 mg, 18%) and **1** (88 mg, 36%); m.p.: decomposition at 160°C . ^1H NMR (CDCl_3 , δ): 4.85 (t, $J = 1.9$ Hz, 2H, Cp), 4.51 (t, $J = 1.9$ Hz, 2H, Cp), 4.22 (s, 5H, Cp). ^{13}C NMR (acetone- d_6 , δ): 203.79 (C=S), 83.10 (Cp), 72.11 (Cp), 71.47 (Cp), 70.48 (Cp). IR (CHCl_3 , cm^{-1}): 3502, 3386 (NH_2), 1597, 1228 (thioamide). MS (EI): 245 (M^+), 211 ($\text{M} - \text{H}_2\text{S}^+$). HRMS: Found: 244.99672; Calc. for $\text{C}_{11}\text{H}_{11}\text{FeNS}$: 244.99616. Anal. Calc. for $\text{C}_{11}\text{H}_{11}\text{FeNS}$: C, 53.90; H, 4.52; Found: C, 54.12 H, 4.32.

5.2. Synthesis of **2**

To a solution of ferrocene (93 mg, 0.5 mmol) in MSA (5 ml) ethoxycarbonyl isothiocyanate (131 mg, 1 mmol) was added at r.t. After 2 h stirring, the reaction mixture was poured onto ice–water (30 ml) and extracted with CH_2Cl_2 . Flash chromatography (CH_2Cl_2 as eluent) afforded **2** as a red band. Yield 78 mg (49%); m.p. $89\text{--}91^\circ\text{C}$. ^1H NMR (CDCl_3 , δ): 8.65 (bs, 1H, NH), 4.92 (s, 2H, Cp), 4.59 (s, 2H, Cp), 4.32 (q, $J = 7.2$ Hz, 2H, CH_2), 4.23 (s, 5H, Cp'), 1.37 (t, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , δ): 201.45 (CS), 150.76 (CO), 84.25 (Cp), 72.72 (Cp), 71.31 (Cp), 69.42 (Cp), 62.40 (CH_2), 14.31 (CH_3). MS (EI) 317 (M^+), 271 ($\text{M} - \text{EtOH}^+$), 211 ($\text{M} - \text{HS-COOEt}^+$). HRMS: Found: 317.01709; Calc. for $\text{C}_{14}\text{H}_{15}\text{FeNO}_2\text{S}$: 317.01729. Anal. Calc. for $\text{C}_{14}\text{H}_{15}\text{FeNO}_2\text{S}$: C, 53.01; H, 4.77; N, 4.42; Found: C, 52.85; H, 4.52; N, 4.16.

5.3. Transformation of **2** into **1**

AlCl_3 (100 mg, 0.75 mmol) was added to a solution of **2** (36 mg, 0.113 mmol) in benzene (5 ml) and the mixture was refluxed for 10 min. The deep red coloration of the mixture turned dark blue. The mixture was then poured onto 15% aq. HCl (15 ml) and extracted with CH_2Cl_2 .

Flash chromatography (CH_2Cl_2 as eluent) afforded **1**, identified by comparison with the sample obtained in the reaction of ferrocene with potassium thiocyanate. Yield: 19 mg (70%).

5.4. Synthesis of chloroacetylferrocene (**3**)

A solution of chloroacetic acid (106 mg, 1.1 mmol) and trifluoroacetic anhydride (236 mg, 156 μl , 1.1 mmol) in dichloromethane (10 ml) was stirred at r.t. for 30 min. Ferrocene (208 mg, 1.1 mmol) and trifluoromethanesulfonic acid (600 mg, 4 mmol) were added and the stirring continued 2 h. The reaction mixture was poured onto water and extracted with dichloromethane. Flash chromatography (chloroform as eluent) afforded **4** as orange crystals. Yield 125 mg (42%). ^1H NMR (CDCl_3 , δ): 4.84 (t, $J = 1.8$ Hz, 2H, Cp), 4.60 (t, $J = 1.8$ Hz, 2H, Cp), 4.42 (s, 2H, CH_2Cl), 4.25 (s, 5H, Cp). IR (KBr): 1678 cm^{-1} (CO). These spectra are in full accord with those reported in the literature [17].

5.5. Synthesis of **4**

A mixture of **1** (93 mg, 0.38 mmol), **5** (100 mg, 0.38 mmol) and K_2CO_3 in toluene (5 ml) was refluxed for 2 h. The solid was filtered off, the solvent evaporated and the residue subjected to a flash chromatography (chloroform as eluent) to afford **3** as dark yellow crystals. Yield: 127 mg (74%); m.p. 89–91 °C. ^1H NMR (CDCl_3 , δ): 6.96 (s, 1H, thiazolyl H-5), 4.93 (t, $J = 1.8$ Hz, Cp), 4.80 (t, $J = 1.8$ Hz, 2H, Cp), 4.80 (t, $J = 1.8$ Hz, 2H, Cp), 4.40 (t, $J = 1.9$ Hz, 2H Cp), 4.30 (t, $J = 1.8$ Hz, 2H, Cp), 4.13 (s, 5H, Cp), 4.09 (s, 5H, Cp). ^{13}C NMR (CDCl_3 , δ): 201.45 (CS), 150.76 (CO), 84.25 (Cp), 72.72 (Cp), 71.31 (Cp), 69.42 (Cp), 62.40 (CH_2), 14.31 (CH_3). Anal. Calc. for $\text{C}_{23}\text{H}_{19}\text{Fe}_2\text{NS}$: C, 60.96; H, 4.23; N, 3.09; Found: C, 60.83; H, 4.32; N, 3.06.

5.5.1. X-ray structure determination

The procedure of crystal structure determination for both **1** and **4** was the same. X-ray data were collected at 293(2) K on a Rigaku AFC5S diffractometer [20] using Mo $\text{K}\alpha$ X-ray (0.71069 Å) source and a graphite monochromator. The unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections. Psi scan absorption corrections were applied [21].

The structures were solved by direct methods using CRYSTAL STRUCTURE [22] and refined by full-matrix least square method using SHELXL97 [23]. In the final step of refinement procedure, all non-hydrogen atoms were refined with anisotropic displacement parameters. Two hydrogen atoms of the amide group in **1** were found on the difference Fourier map. The other hydrogen atoms were introduced in calculated positions with idealized geometry and refined using a rigid body model.

The crystal structure of **3** was refined as a disordered one with the occupancy factors equal 0.75 for the major component of disorder and 0.25 for the minor one. The disorder concerns two non-hydrogen atoms of the thiazole ring, S1 and C2. The position of the sulfur S1A atom of one component is overlapping with the position of the carbon C2B atom of the second component. The same situation is observed for S1B and C1A atoms. By using SIMU, DELU and ISOR instructions, some restraints were applied to the refinement of disordered heterocyclic ring.

The molecular geometry was calculated by PARST [24] and WINGX [25]. For **3**, the major disorder component geometry is given. The drawings were made by PLATON [26]. A summary of crystallographic relevant data is given in Table 1.

6. Electrochemistry

The cyclic voltammetry and differential pulse voltammetry measurements of 10^{-3} M solutions of **4** in CH_3CN with 0.1 M Bu_4NClO_4 were done under an argon atmosphere on AUTOLAB (Eco Chemie BV) apparatus in three electrode system, where the working electrode was Pt-disk ($\phi = 1.5$ mm), the reference was ferrocene electrode ($\text{FeCp}_2/\text{FeCp}_2^+$), and the counter electrode was cylindrical platinum gauze.

7. Supplementary Material

Atoms' coordinates and displacement parameters are deposited with CCDC (deposition numbers 238309 for **1** and 265059 for **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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