

# Synthesis and crystal structure of N-ferrocenyl substituted heterocyclic imine ligands and their reactivity towards $\text{Fe}_2(\text{CO})_9$ ; crystal structure of $[\mu_2-\eta^3-(\text{Fc})\text{N}-\text{CH}_2-\overline{\text{C}=\text{C}-\text{C}(\text{H})=\text{C}(\text{H})-\text{NMe}}]\text{Fe}_2(\text{CO})_6$ ( $\text{Fc} = (\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\eta^5-\text{C}_5\text{H}_4)$ )<sup>1</sup>

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## Abstract

The condensation of thiophene-2-carbaldehyde or N-methyl-pyrrole-2-carbaldehyde with ferrocenylamine ( $(\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{NH}_2)$ ) leads to the formation of heterocyclic imine ligands with a ferrocenyl group as the substituent at the imino nitrogen atom. These ligands react with  $\text{Fe}_2(\text{CO})_9$  to produce dinuclear cluster compounds of the type  $[\mu_2-\eta^3-(\text{Fc})\text{N}-\text{CH}_2-\overline{\text{C}=\text{C}-\text{C}(\text{H})=\text{C}(\text{H})-\text{X}}]\text{Fe}_2(\text{CO})_6$  ( $\text{Fc} = (\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\eta^5-\text{C}_5\text{H}_4)$ ;  $\text{X} = \text{S}, \text{NMe}$ ) by activation of a heteroaromatic C–H bond in  $\beta$ -position relative to the exocyclic C–N double bond of the imine ligands followed by a 1,3-hydrogen shift reaction. The molecular structure of the heterocyclic imine ligands as well as of one of the dinuclear cluster compounds have been determined by X-ray structure analyses. © 1997 Elsevier Science S.A.

**Keywords:** Iron; Ferrocene; Imine; C–H activation; Cluster; X-ray structure

## 1. Introduction

The activation of aromatic C–H bonds by organometallic compounds can be used to develop catalytic C–C bond formation reactions. Only a few efficient catalytic reactions of this type have been reported in the literature so far, including the activation of benzene in the presence of CO giving benzaldehyde [1] or in the presence of CO and ethylene leading to the formation of propiophenone [2] as well as the reaction of pyridine with CO and olefins respectively [3]. Very recently Murai and coworkers reported the coupling of an imidazole C–H bond with CO and a wide variety of olefins to give heterocyclic ketones [4]. Recently we reported the synthesis of cluster compounds of the type  $[\mu_2-\eta^3-(\text{R})\text{N}-\text{CH}_2-\overline{\text{C}=\text{C}-\text{C}(\text{H})=\text{C}(\text{H})-\text{X}}]\text{Fe}_2(\text{CO})_6$  ( $\text{R} = \text{aromatic or aliphatic group}$ ;  $\text{X} = \text{S}, \text{NMe}$ ), which are formed by the reaction of  $\text{Fe}_2(\text{CO})_9$  with imine ligands derived from thiophene-2-carbaldehyde or N-methyl-pyrrole-2-carbaldehyde respectively [5]. This reaction proceeds via the activation of a heteroaromatic

C–H bond in  $\beta$ -position with respect to the exocyclic C–N double bond of the imine ligand followed by a 1,3-hydrogen shift reaction to the carbon atom of the imine producing the methylene group of the product clusters. The synthesis and complexation of ligands containing ferrocenyl moieties have found increasing interest in the last years [6]. We decided to introduce ferrocenyl groups into the imine ligands because of their potential as an electron reservoir system [7] and their possible application as electrocatalysts [8].

We report herein the synthesis of ferrocenyl substituted imine ligands derived from thiophene- and N-methyl-pyrrole-carbaldehydes and their reactivity towards  $\text{Fe}_2(\text{CO})_9$ .

## 2. Results and discussion

Condensation of ferrocenylamine with thiophene-2-carbaldehyde or N-methyl-pyrrole-2-carbaldehyde respectively gives the corresponding ferrocenyl substituted imine ligands **1** and **2** in quite good yields. The reaction of these ligands with  $\text{Fe}_2(\text{CO})_9$  results in the

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formation of dinuclear cluster compounds of the type  $[\mu_2-\eta^3-(\text{Fc})\text{N}-\text{CH}_2-\overset{\ominus}{\text{C}}=\text{C}-\text{C}(\text{H})=\overset{\ominus}{\text{C}}(\text{H})-\text{X}]\text{Fe}_2(\text{CO})_6$  ( $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$ ;  $\text{X} = \text{S}, \text{NMe}$ ) **3** and **4** (Scheme 1). The formation of these products occurs by subsequent activation of a heteroaromatic C–H bond in  $\beta$ -position to the exocyclic imino moiety of the ligands and a 1,3-hydrogen shift reaction to transfer this hydrogen atom to the carbon atom of the imino substituent producing a methylene group. We recently reported the analogous formation of derivatives of **3** and **4** from the reaction of  $\text{Fe}_2(\text{CO})_9$  with imino ligands bearing organic substituents at the nitrogen atom of the imino group [5]. The formal substitution of an organic substituent against a ferrocenyl moiety, which acts as an ‘electron source’, induces a higher basicity of the nitrogen atom. This improves the rate of a first substitution of a CO ligand in  $\text{Fe}_2(\text{CO})_9$  by the imine, which may explain the higher yields that are observed in the reaction of **1** and **2** with  $\text{Fe}_2(\text{CO})_9$ , compared to those in reactions with purely organic imine ligands. The reaction of 1-azadiene ligands with  $\text{Fe}_2(\text{CO})_9$  normally leads to mononuclear  $[\eta^4\text{-azadiene}]\text{Fe}(\text{CO})_3$  complexes [9] whereas the activation of the C–H bond in  $\beta$ -position relative to the C–N double bond of the azadiene ligand is known to be the starting point of reactions of  $\text{Ru}_3(\text{CO})_{12}$  with 1-azadienes [10].

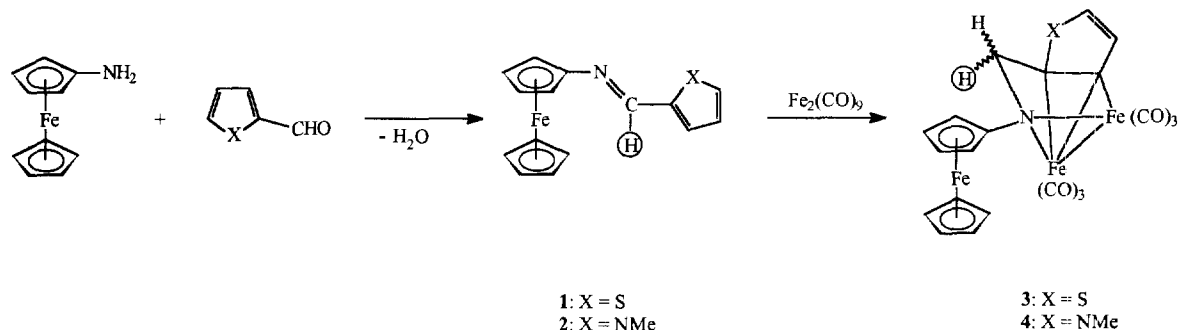
The dinuclear cluster compounds **3** and **4** show a  $\mu_2-\eta^3$ -enyl-amido ligand bridging an  $\text{Fe}_2(\text{CO})_6$  moiety. Similar complexes have been observed from the reaction of  $\alpha,\beta$ -unsaturated imines with  $\text{Ru}_3(\text{CO})_{12}$  [10,11] as well as by reacting  $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$  with N-phenylbenzylideneamine [12] or from the reaction of  $\text{Fe}_3(\text{CO})_{12}$  with benzalazine [13]. Iron compounds with a keto group instead of the methylene moiety in **3** and **4** have been prepared by the reaction of the carbene cluster  $[(\mu_2\text{-CH}_2)\text{Fe}_2(\text{CO})_8]$  with phosphine imides in the presence of CO [14]. 1,3-Hydrogen shift reactions often occur in isomerisation reactions of olefins in which not only catalysts containing Group 8 metals are used [15], but also organometallic compounds of Group 9 [16] and Group 6 transition metals [17].

## 2.1. Spectroscopy

All IR and NMR data as well as the mass spectroscopic data are summarized in the Experimental part. The dinuclear iron carbonyl cluster compounds show the expected band pattern for  $\text{Fe}_2(\text{CO})_6$  moieties in the IR spectra. As was observed for derivatives of **3** and **4** with organic substituents at the nitrogen atom [5], the thiophene derivative **3** shows three absorptions for the carbonyl ligands with the one at lowest frequency being very broad. In the IR spectrum of **4** this broad band is split into two distinct bands.

The  $^1\text{H}$  NMR spectra of **1–4** show the expected signals for the protons of the cyclopentadienyl groups. One singlet resonance for the  $(\eta^5\text{-C}_5\text{H}_5)$  ligand indicating a free rotation of this group and an AA'BB' coupling pattern for the cyclopentadienyl ring bearing the imino substituent. The imine ligands **1** and **2** also show three distinct doublets of doublets for the aromatic protons at the thiophene or pyrrole ring respectively and a singlet resonance for the hydrogen atom of the imino group. In **3** and **4** there are only two doublets for the remaining aromatic protons at the heterocyclic ring systems, which are shifted downfield by about 0.1–0.3 ppm compared to the free ligands **1** and **2**. The methylene groups, which were formed during the reaction by a 1,3-hydrogen shift reaction, give rise to a signal at 4.46 ppm (**3**) or 4.37 ppm (**4**) respectively. This is about the range that was observed for derivatives of **3** and **4** bearing aromatic substituents at the nitrogen atom, whereas derivatives with aliphatic groups connected to the former imino nitrogen atom showed  $^1\text{H}$  signals at about 3.8 ppm [5]. The methyl groups connected to the ring nitrogen atoms of the pyrrole ring in **2** and **4** show expected chemical shifts.

In the  $^{13}\text{C}$  NMR spectrum of **1** and **2** the cyclopentadienyl groups as well as the N-methyl group in **2** show resonances at the expected values. The carbon atoms of the thiophene ring in **3** show signals at 128–143 ppm, the corresponding resonances for the pyrrole system in **4** are observed at 108–130 ppm. The signal representing



Scheme 1.

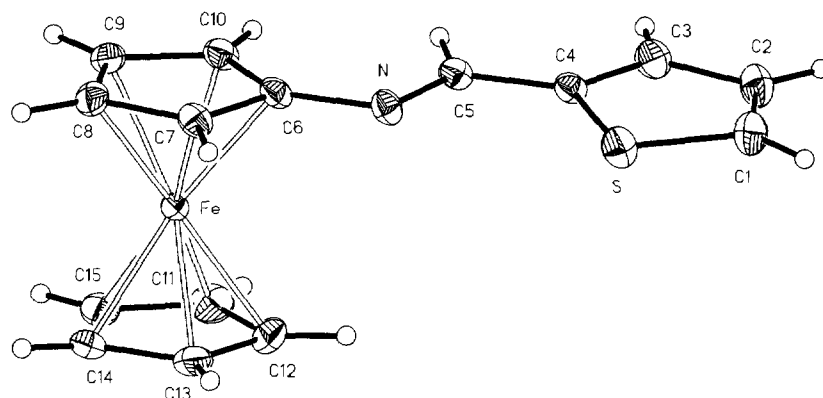


Fig. 1. Molecular structure of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-N}=\text{C}(\text{H})\text{-C}_4\text{H}_3\text{S}$  1.

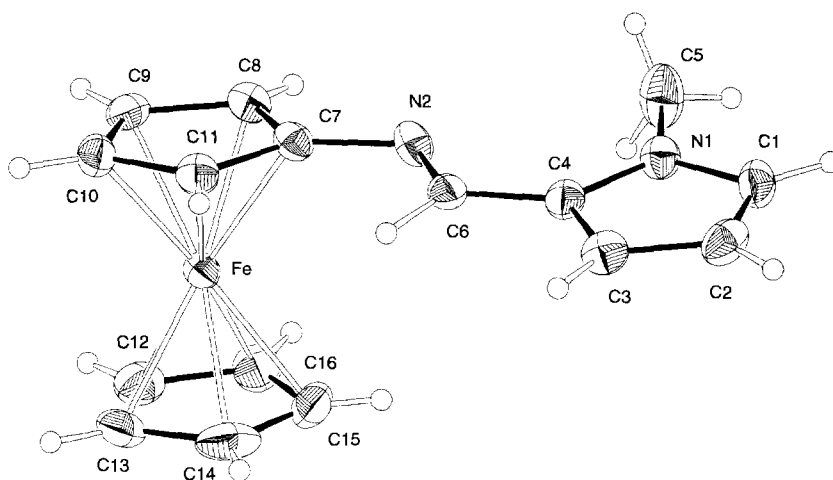


Fig. 2. Molecular structure of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-N}=\text{C}(\text{H})\text{-C}_4\text{H}_3\text{NMe}$  2.

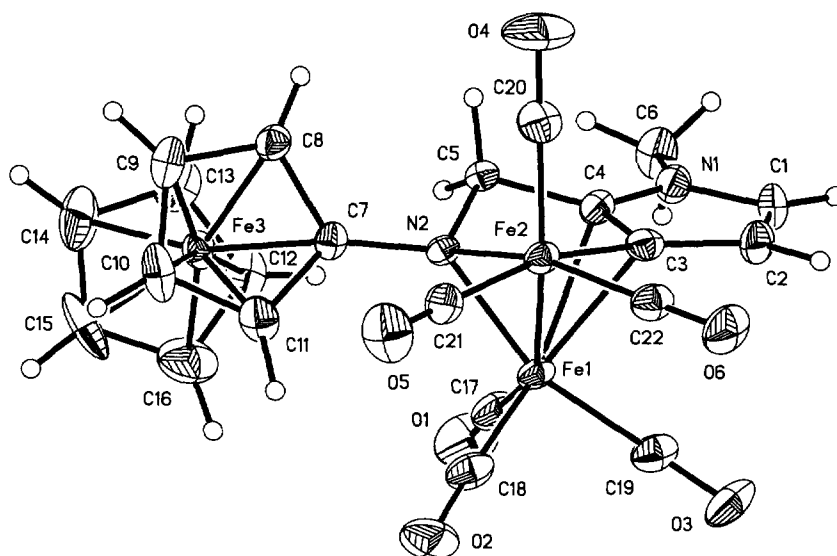


Fig. 3. Molecular structure of  $[\mu_2\text{-}\eta^3\text{-(Fc)N-CH}_2\text{-C}\equiv\text{C-C(H)=C(H)-N Me}] \text{Fe}_2(\text{CO})_6$  4.

the carbon atom of the exocyclic imino substituent in both cases is observed at about 150 ppm.

The  $^{13}\text{C}$  NMR spectra of **3** and **4** show the signal for the methylene group that has been produced during the reaction as the most characteristic one. It is observed at 71.6 ppm (**3**) or 66.2 ppm (**4**), which again is about the value that has been observed for analogues of **3** and **4** with aromatic substituents present at the nitrogen atoms, whereas the derivatives with aliphatic groups in the same position showed chemical shifts about 12 ppm to higher field [5]. Resonances representing the cyclopentadienyl carbon atoms in **3** and **4** and the N-methyl group in **4** again show expected chemical shifts. The signals for the carbon atoms of the thiophene ring in **3** are observed in a range from 122–157 ppm with the tertiary carbon atom, which is now connected to both iron atoms, showing the signal at lowest field. The corresponding carbon atoms of the pyrrole ring in **4** give resonances at 122–135 ppm. The carbonyl ligands in both cases show one sharp singlet at 210.1 ppm (**3**) or 211.5 ppm (**4**) indicating a dynamic behaviour of **3** and **4** in solution at room temperature as has been reported for compounds of the general formula  $[\mu_2-\eta^3(\text{R})\text{N}-\text{CH}_2-\text{C}(\text{H})=\text{CR}')] \text{Ru}_2(\text{CO})_6$  [10].

## 2.2. Structure determinations

By means of recrystallization of **1**, **2** and **4** from mixtures of light petroleum (b.p. 40–60°C) and  $\text{CH}_2\text{Cl}_2$  it is possible to grow crystals suitable for X-ray structure determinations. The molecular structures of the compounds are shown in Figs. 1–3, selected bond lengths and angles are collected in Tables 1–3, the crystal and intensity data are given in Table 4.

The ferrocenylimine compounds **1** and **2** show nearly identical solid state structures. The cyclopentadienyl ligands in both cases have a perfectly eclipsed arrangement and the heterocyclic ring system, the imino group as well as the cyclopentadienyl ring to which the imino group is attached are situated in one plane (Tables 1 and

Table 1  
Selected bond lengths [pm] and angles [°] of **1**

Fe–C <sub>Cp</sub>	204.3(2)	S–C1	171.7(2)
S–C4	172.2(2)	C1–C2	135.2(3)
C2–C3	142.1(3)	C3–C4	137.8(3)
C4–C5	144.7(3)	C5–N	127.5(2)
C6–N	140.8(2)		
C5–N–C6	119.3(2)	C4–C5–N	121.5(2)
C4–S–C1	91.6(1)	S–C1–C2	112.0(2)
C1–C2–C3	113.0(2)	C2–C3–C4	112.0(2)
C3–C4–S	111.3(2)	C3–C4–C5	127.5(2)

Deviations [pm] from plane [Cp–N=CH–C<sub>4</sub>H<sub>3</sub>S]: S 4.0, C1 4.7, C2 0.5, C3 4.3, C4 2.4, C5 5.5, N 1.2, C6 0.3, C7 5.2, C8 2.5, C9 4.3, C10 6.5.

Table 2  
Selected bond lengths [pm] and angles [°] of **2**

Fe–C <sub>Cp</sub>	203.8(4)	N1–C1	137.0(4)
N1–C4	137.6(4)	N1–C5	145.1(4)
C1–C2	135.1(5)	C2–C3	139.4(5)
C3–C4	138.5(5)	C4–C6	143.9(4)
C6–N2	127.5(4)	N2–C7	140.8(4)
C6–N2–C7	118.8(3)	C4–C6–N2	124.9(3)
C4–N1–C1	108.2(3)	N1–C1–C2	109.1(3)
C1–C2–C3	107.9(3)	C2–C3–C4	107.5(3)
C3–C4–N1	107.4(3)	C3–C4–C6	126.3(3)
C1–N1–C5	123.4(3)	C4–N1–C5	128.4(3)

Deviations [pm] from plane [Cp–N=CH–C<sub>4</sub>H<sub>3</sub>NMe]: N1 7.6, C1 4.6, C2 5.4, C3 8.1, C4 0.6, C6 2.0, N2 4.0, C7 2.2, C8 8.5, C9 7.3, C10 4.0, C11 9.5.

2). The bond length of the C–N double bond in **1** and **2** is of exactly the same value. Only bond lengths and angles inside the thiophene and pyrrole ring differ slightly due to the presence of the bigger sulphur atom in **1** compared to the nitrogen in **2**.

The molecular structure of **4** consists of an  $\text{Fe}_2(\text{CO})_6$  moiety with a nearly eclipsed arrangement, which is bridged by a formal six-electron donating enyl-amido ligand. Another way to describe the molecule would be as an aza-ferro-cyclopentadienyl ligand which is  $\eta^4$ -coordinated to an apical  $\text{Fe}(\text{CO})_3$  fragment. This is consistent with the fact that the atoms of the pyrrole ring, Fe2 and N2, show a planar arrangement whereas the methylene group C5 is shifted 45.8 pm out of this plane (Table 3). This observation corresponds with the values that have been observed for derivatives of **4** bearing

Table 3  
Selected bond lengths [pm] and angles [°] of **3**

Fe1–Fe2	244.0(1)	Fe1–C3	217.9(6)
Fe1–C4	236.4(6)	Fe1–N2	198.6(4)
Fe2–C3	195.9(6)	Fe2–N2	200.9(4)
C3–C4	141.8(7)	C4–C5	149.0(7)
C5–N2	149.9(7)	C3–C2	143.2(8)
C2–C1	136.3(9)	C1–N1	140.0(7)
N1–C4	134.8(7)	N1–C6	147.2(7)
N2–C7	142.1(7)	Fe3–C <sub>Cp</sub>	204.2(6)
Fe2–Fe1–C3	49.8(2)	Fe2–Fe1–C4	72.2(1)
Fe2–Fe1–N2	52.8(1)	N2–Fe1–C3	74.2(2)
N2–Fe1–C4	62.4(2)	C3–Fe1–C4	36.1(2)
Fe2–N2–C5	112.9(3)	N2–C5–C4	99.1(4)
C5–C4–C3	118.4(5)	C4–C3–Fe2	113.0(4)
C3–Fe2–N2	78.7(2)	Fe2–C3–C2	141.6(4)
C5–C4–N1	129.4(5)	C3–C2–C1	108.8(5)
C2–C1–N1	108.6(5)	C1–N1–C4	107.9(5)
N1–C4–C3	110.4(5)	C1–N1–C6	124.5(5)
C4–N1–C6	127.3(5)	Fe2–N2–C7	119.1(3)
C5–N2–C7	112.0(4)		

Deviations [pm] from plane [N1,C1,C2,C3,C4,N2,Fe2]: N1 10.4, C1 1.4, C2 11.0, C3 6.3, C4 6.9, C5 45.8, N2 16.0, Fe2 17.4.  
Angle [°] between planes [N1,C1,C2,C3,C4,N2,Fe2]–[C7–C11]: 114.7.

aromatic or aliphatic substituents at the former imine nitrogen atom [5], for other structurally characterized  $\eta^4$ -metalla-aza-cyclopentadiene complexes [12,13] and for  $\eta^4$ -cyclopentadiene complexes in general [18]. The C–C double bond between C3 and C4 in **4** is slightly elongated compared to the same bond in **2** due to the coordination of this double bond to the apical  $\text{Fe}(\text{CO})_3$  moiety (Tables 2 and 3). The bond lengths of the methylene group C5 with C4 (149.0(7)) and N2 (149.9(7)) are clearly single bonds. The Fe–Fe bond length of 244.0(1) pm is in the same range as the corresponding bond lengths observed for the derivatives of **4**, that we reported in Ref. [5]. Analogously to those compounds the Fe–C bond length inside the aza-ferracyclopentadienyl ligand (Fe2–C3, Fig. 3), which is considered to be a  $\sigma$ -bond, is by far the shortest Fe–C bond of the  $\text{Fe}_2(\text{CO})_6$  fragment to the ligand present in the molecule. The Fe–C bond lengths of the apical  $\text{Fe}(\text{CO})_3$  moiety to the C–C double bond of the pyrrole system are quite different. The bond between Fe1 and C3, which is also connected to Fe2, is nearly 20 pm shorter compared to the bond between Fe1 and C4

(Table 3). The ferrocenyl moiety in **4** shows a nearly perpendicular arrangement with respect to the plane of the aza-ferracyclopentadienyl ligand (Table 3). Both cyclopentadienyl rings still adopt a nearly eclipsed conformation. The bond lengths and angles inside the ferrocenyl fragment as well as for the terminal CO ligands are of expected values.

### 3. Experimental

#### 3.1. Reagents and solvents

All procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents. Chromatography was done using silica gel 60 and silanized silica gel 60, 70–230 mesh ASTM (Merck), which were dried at  $10^{-2}$  bar ( $10^3$  Pa) for 2 days before use.  $\text{Fe}_2(\text{CO})_9$  was prepared from  $\text{Fe}(\text{CO})_5$  (Lancaster) by irradiation in acetic acid [19].  $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{NH}_2)\text{Fe}$  was prepared from O-benzyl-hydroxylamine and ferrocene following the procedure published by Knox et al. [20].

Table 4  
Crystal and intensity data for the compounds **1**, **2** and **4**

compound	<b>1</b>	<b>2</b>	<b>4</b>
formula	$\text{C}_{15}\text{H}_{13}\text{NSFe}$	$\text{C}_{16}\text{H}_{16}\text{N}_2\text{Fe}$	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_6\text{Fe}_2$
mol. weight [ $\text{g mol}^{-1}$ ]	295.17	292.16	571.92
radiation	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
monochromator	graphite	graphite	graphite
temperature [K]	183	183	213
crystal colour	red	red	red
crystal size [ $\text{mm}^3$ ]	$0.3 \times 0.3 \times 0.2$	$0.5 \times 0.4 \times 0.1$	$0.4 \times 0.2 \times 0.02$
$a$ [Å]	9.825(2)	17.439(2)	8.538(3)
$b$ [Å]	14.912(2)	7.4016(7)	16.730(5)
$c$ [Å]	17.219(1)	20.983(3)	15.412(4)
$\alpha$ [°]	90	90	90
$\beta$ [°]	90	90	96.69(2)
$\gamma$ [°]	90	90	90
$V$ [Å <sup>3</sup> ]	2522.8(5)	2708.4(6)	2186(1)
$Z$	8	8	4
$F(000)$	1216	1216	1152
$\rho_{\text{calc}}$ [ $\text{g cm}^{-3}$ ]	1.554	1.433	1.737
crystal system	orthorhombic	orthorhombic	monoclinic
space group	<i>Pbca</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>
abs. coeff. [ $\text{mm}^{-1}$ ]	1.342	1.103	2.012
abs. correction	psi-scan	psi-scan	psi-scan
min.–max. transmission	83.66%–99.83%	92.49%–99.98%	83.14%–99.52%
$\theta$ limit [°]	1–30	1–26	1–24
scan mode	$\omega$ – $2\theta$	$\omega$ – $2\theta$	$\omega$ – $2\theta$
scan speed [° min <sup>-1</sup> ]	1–10	1–10	4–60
refl. measured	3822	2708	4482
independent refl.	3822	2708	3426
obs. refl. $F_o^2 > 2\sigma(F_o^2)$	2874	1837	2508
No. of parameters	215	226	318
GOOF	1.083	1.108	1.026
$R_1$	0.0294	0.0342	0.0492
$wR_2$	0.0684	0.0631	0.1156
final diff. map electron density [ $\text{e} \text{Å}^{-3}$ ]	0.369	0.382	0.479

### 3.2. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes; NMR spectra on a Bruker AC 200 spectrometer ( $^1\text{H}$ : 200 MHz with  $\text{SiMe}_4$  as internal standard,  $^{13}\text{C}$ : 50.32 MHz with  $\text{CDCl}_3$  as internal standard); mass spectra on a Finnigan MAT SSQ 710 instrument. Elemental analyses were carried out at the laboratory of the Institute of Organic and Macromolecular Chemistry of the Friedrich-Schiller University Jena. Crystal structure determinations of **1** and **2** were carried out on an Enraf–Nonius CAD4 diffractometer, the crystal structure determination of **4** was carried out on a Siemens P4 diffractometer using graphite monochromated  $\text{Mo K}\alpha$  radiation. The crystals were mounted in a stream of cold nitrogen. Data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares techniques against  $F^2$  using the programs SHELXS86 and SHELXL93 [21]. Computations of the structures were done with the program XPTMA and the molecular illustrations were drawn using the program ZORTEP [22]. The crystal and intensity data are given in Table 4. Additional material on the structure analyses is available from the Fachinformationszentrum Chemie, Physik, Mathematik GmbH, 76344 Eggenstein-Leopoldshafen 2, Germany by mentioning the deposition numbers CSD-406596 (**1**), CSD-406597 (**2**), CSD-406598 (**4**), the author and the journal citation.

### 3.3. Preparation of **1** and **2**

1 g (5 mmol) of ferrocenylamine is dissolved in 20 ml of toluene together with the corresponding amount of thiophene-2-carbaldehyde (560 mg, 0.52 ml) or N-methyl-pyrrole-2-carbaldehyde (545 mg, 0.54 ml) respectively. The solution is stirred at 70 °C for 1 day and the reaction is monitored by thin layer chromatography. Afterwards the solvent is removed under vacuum. The red oily residue is dissolved in 10 ml  $\text{CH}_2\text{Cl}_2$  and 1 g silanized silica gel is added. After removal of the solvent the mixture of products is chromatographed. Using a mixture of light petroleum (b.p. 40–60 °C) and  $\text{CH}_2\text{Cl}_2$  (4:1) as the eluent in both cases a small yellow band of ferrocene is obtained. A deep red band of **1** is eluted with  $\text{CH}_2\text{Cl}_2$  whereas **2** is obtained by using a mixture of light petroleum/ $\text{CH}_2\text{Cl}_2$  (2:1) (yields: 790 mg **1**, 54%; 850 mg **2**, 58%). The compounds are recrystallized from light petroleum/ $\text{CH}_2\text{Cl}_2$  (3:1) at –20 °C (m.p. **1** 127 °C, **2** 138 °C). Anal. Found: C, 61.05; H, 4.69; N, 4.68. **1**  $\text{C}_{15}\text{H}_{13}\text{NSFe}$  Calc.: C, 61.04; H, 4.44; N, 4.75%. Anal. Found: C, 65.57; H, 5.74; N, 9.49. **2**  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{Fe}$  Calc.: C, 65.78; H, 5.52; N, 9.59%.

#### 3.3.1. MS and spectroscopic data for **1**

MS (EI):  $m/z$  (%) 295 ( $\text{M}^+$ , 100), 230 ( $\text{M}^+ - \text{Cp}$ , 10), 204 ( $\text{C}_8\text{H}_6\text{NSFe}^+$ , 6), 186 ( $\text{C}_9\text{H}_8\text{NFe}^+$ , 18), 174 ( $\text{M}^+ - \text{Cp} - \text{Fe}$ , 16), 147 ( $\text{C}_8\text{H}_5\text{NS}^+$ , 15), 121 ( $\text{FeCp}^+$ , 48), 94 ( $\text{C}_6\text{H}_8\text{N}^+$ , 7), 63 ( $\text{C}_5\text{H}_3^+$ , 6), 56 ( $\text{Fe}^+$ , 24), 39 ( $\text{C}_3\text{H}_3^+$ , 8). IR (in  $\text{CH}_2\text{Cl}_2$ , 273 K) [ $\text{cm}^{-1}$ ]: 1602 (C=N).  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ , 273 K) [ppm]: 4.21 (s, 5H, Cp), 4.22–4.25 (m, 2H, Cp), 4.56–4.58 (m, 2H, Cp), 7.09 (dd,  $^3J_{\text{HH}} = 3.5$  Hz,  $^3J_{\text{HH}} = 4.8$  Hz, 1H, =CH), 7.36 (dd,  $^3J_{\text{HH}} = 1.1$  Hz,  $^3J_{\text{HH}} = 3.5$  Hz, 1H, =CH), 7.44 (dd,  $^3J_{\text{HH}} = 1.1$  Hz,  $^3J_{\text{HH}} = 4.8$  Hz, 1H, =CH), 8.71 (s, 1H, N=CH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 273 K) [ppm]: 62.9 (Cp), 67.2 (Cp), 69.6 (Cp), 104.9 (Cp), 127.7 (=CH), 128.9 (=CH), 130.1 (=CH), 143.6 (=C), 150.7 (N=CH).

#### 3.3.2. MS and spectroscopic data for **2**

MS (EI):  $m/z$  (%) 292 ( $\text{M}^+$ , 100), 227 ( $\text{M}^+ - \text{Cp}$ , 20), 171 ( $\text{M}^+ - \text{Cp} - \text{Fe}$ , 18), 121 ( $\text{FeCp}^+$ , 40), 94 ( $\text{C}_6\text{H}_8\text{N}^+$ , 6), 65 ( $\text{Cp}^+$ , 6), 56 ( $\text{Fe}^+$ , 22), 39 ( $\text{C}_3\text{H}_3^+$ , 6). IR (in  $\text{CH}_2\text{Cl}_2$ , 273 K) [ $\text{cm}^{-1}$ ]: 1611 (C=N).  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ , 273 K) [ppm]: 3.89 (s, 3H, Me), 4.07 (s, 5H, Cp), 4.07–4.09 (m, 2H, Cp), 4.37–4.39 (m, 2H, Cp), 6.08 (dd,  $^3J_{\text{HH}} = 2.5$  Hz,  $^3J_{\text{HH}} = 3.9$  Hz, 1H, =CH), 6.50 (dd,  $^3J_{\text{HH}} = 1.7$  Hz,  $^3J_{\text{HH}} = 3.9$  Hz, 1H, =CH), 6.65 (dd,  $^3J_{\text{HH}} = 1.7$  Hz,  $^3J_{\text{HH}} = 2.5$  Hz, 1H, =CH), 8.37 (s, 1H, N=CH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 273 K) [ppm]: 35.6 (Me), 61.2 (Cp), 65.5 (Cp), 68.3 (Cp), 106.2 (Cp), 107.5 (=CH), 115.6 (=CH), 127.2 (=CH), 129.9 (=C), 148.3 (N=CH).

### 3.4. Preparation of **3** and **4**

500 mg (1.4 mmol)  $\text{Fe}_2(\text{CO})_9$  are stirred together with 1.2 equiv. of the corresponding imine (495 mg **1**, 490 mg **2**) in 30 ml n-heptane at 50 °C. During the reaction the colour of the solution darkens from light red to deep red and the  $\text{Fe}_2(\text{CO})_9$  slowly disappears. After 1 h all of the starting material is dissolved and the solvent is evaporated in vacuo. The resulting oily residue is dissolved in 10 ml  $\text{CH}_2\text{Cl}_2$  and 1 g silanized silica gel is added. Chromatography in both cases yields a green fraction of  $\text{Fe}_3(\text{CO})_{12}$  first using a mixture of light petroleum (b.p. 40–60 °C)/ $\text{CH}_2\text{Cl}_2$  10:1 and a second red coloured band of **3** or **4** respectively using a mixture of light petroleum/ $\text{CH}_2\text{Cl}_2$  4:1 as the eluent (yields: 660 mg **3**, 82%; 590 mg **4**, 74%). Both compounds are recrystallized from a mixture of light petroleum/ $\text{CH}_2\text{Cl}_2$  at –20 °C (m.p. **3** 146 °C, **4** 193 °C (decomp.)). Anal. Found: C, 44.27; H, 2.38; N, 2.63. **3**  $\text{C}_{21}\text{H}_{13}\text{NO}_6\text{SFe}_3$  Calc.: C, 43.87; H, 2.28; N, 2.44%. Anal. Found: C, 45.77; H, 2.80; N, 4.77. **4**  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_6\text{Fe}_3$  Calc.: C, 46.20; H, 2.82; N, 4.90%.

#### 3.4.1. MS and spectroscopic data for **3**

MS (EI):  $m/z$  (%) 575 ( $\text{M}^+$ , 25), 519 ( $\text{M}^+ - 2\text{CO}$ , 9), 491 ( $\text{M}^+ - 3\text{CO}$ , 22), 463 ( $\text{M}^+ - 4\text{CO}$ , 11), 435

( $M^+ - 5CO$ , 55), 407 ( $M^+ - 6CO$ , 100), 381 ( $C_{13}H_{11}NSFe_3^+$ , 26), 352 ( $C_{12}H_8SF_3^+$ , 8), 342 ( $C_{10}H_8NSFe_3^+$ , 7), 328 ( $C_8H_6NSFe_3^+$ , 33), 286 ( $C_{10}H_8NSFe_2^+$ , 12), 217 ( $C_9H_7NSFe^+$ , 26), 204 ( $C_8H_6NSFe^+$ , 98), 144 ( $C_6H_2NFe^+$ , 28), 121 ( $CpFe^+$ , 20), 112 ( $Fe_2^+$ , 9), 56 ( $Fe^+$ , 24). IR (in  $CH_2Cl_2$ , 273 K) [ $cm^{-1}$ ]: 2065 (m), 2028 (vs), 1988 (br).  $^1H$  NMR (in  $CDCl_3$ , 273 K) [ppm]: 3.96–3.98 (m, 2H, Cp), 4.01–4.03 (m, 2H, Cp), 4.30 (s, 5H, Cp), 4.46 (s, 2H,  $CH_2$ ), 7.25 (d,  $^3J_{HH} = 5.1$  Hz, 1H, =CH), 7.44 (d,  $^3J_{HH} = 5.1$  Hz, 1H, =CH).  $^{13}C$  NMR ( $CDCl_3$ , 273 K) [ppm]: 61.3 (Cp), 64.9 (Cp), 69.3 (Cp), 71.6 ( $CH_2$ ), 113.4 (Cp), 121.6 (=C), 130.9 (=CH), 139.6 (=CH), 157.1 (=C), 210.1 (CO).

### 3.4.2. MS and spectroscopic data for 4

MS (EI):  $m/z$  (%) 572 ( $M^+$ , 40), 516 ( $M^+ - 2CO$ , 7), 488 ( $M^+ - 3CO$ , 21), 460 ( $M^+ - 4CO$ , 9), 432 ( $M^+ - 5CO$ , 43), 404 ( $M^+ - 6CO$ , 100), 375 ( $C_{15}H_{13}NFe_3^+$ , 8), 348 ( $C_{13}H_{10}NFe_3^+$ , 13), 290 ( $C_{13}H_8NFe_2^+$ , 15), 253 ( $C_{10}H_7NFe_2^+$ , 14), 216 ( $C_7H_6NFe_2^+$ , 16), 202 ( $C_6H_4NFe_2^+$ , 76), 186 ( $C_5H_2NFe_2^+$ , 24), 144 ( $C_6H_2NFe^+$ , 11), 121 ( $CpFe^+$ , 31), 112 ( $Fe_2^+$ , 11), 56 ( $Fe^+$ , 16). IR (in  $CH_2Cl_2$ , 273 K) [ $cm^{-1}$ ]: 2057 (m), 2017 (vs), 1976 (s), 1969 (s).  $^1H$  NMR (in  $CDCl_3$ , 273 K) [ppm]: 3.77 (s, 3H, N–Me), 3.99–4.01 (m, 2H, Cp), 4.05–4.08 (m, 2H, Cp), 4.28 (s, 5H, Cp), 4.37 (s, 2H,  $CH_2$ ), 6.51 (d,  $^3J_{HH} = 2.8$  Hz, 1H, =CH), 6.93 (d,  $^3J_{HH} = 2.8$  Hz, 1H, =CH).  $^{13}C$  NMR ( $CDCl_3$ , 273 K) [ppm]: 35.4 (N–Me), 61.6 (Cp), 64.8 (Cp), 66.2 ( $CH_2$ ), 69.2 (Cp), 118.9 (Cp), 122.4 (=C), 126.0 (=CH), 131.7 (=CH), 135.4 (=C), 211.5 (CO).

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