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# C,H bond activation of imino substituted heterocycles: synthesis and crystal structure of $[\mu_2\text{-}\eta^3\text{-}(R)N\text{--}CH_2\text{--}\overline{C=C\text{--}C(H)=C(H)\text{--}X}]Fe_2(CO)_6$ and the isomeric clusters $[\mu_2\text{-}\eta^3\text{-}(R)N\text{--}CH_2\text{--}\overline{C=C\text{--}X\text{--}C(R')=C(R'')}]Fe_2(CO)_6$

Wolfgang Imhof *

*Max-Planck-Gesellschaft, Arbeitsgruppe "CO₂-Chemie" an der Friedrich-Schiller-Universität Jena, Lessingstr. 12, 07743 Jena, Germany*

## Abstract

The reaction of $Fe_2(CO)_9$ with heterocyclic imines derived from thiophene-2-carbaldehyde or N-methyl-pyrrole-2-carbaldehyde produces the dinuclear compounds $[\mu_2\text{-}\eta^3\text{-}(R)N\text{--}CH_2\text{--}C=C\text{--}C(H)\text{--}X(H)\text{--}X]Fe_2(CO)_6$ ($R = Ph$, $C_6H_{11}$, $p\text{-}^tBu\text{--}C_6H_4$; $X = S$, NMe). The analogous reaction with imines of thiophene-3-carbaldehyde or indole-3-carbaldehyde yields the corresponding isomeric clusters $[\mu_2\text{-}\eta^3\text{-}(R)N\text{--}CH_2\text{--}C=C\text{--}X\text{--}C(R')=C(R'')]Fe_2(CO)_6$ ($R = Ph$, $C_6H_{11}$, $R' = R'' = H$, $X = S$; $R = Ph$, $p\text{-}^tBu\text{--}C_6H_4$, $R' = R'' = -C_6H_4-$, $X = NH$). The reaction proceeds via activation of the C,H bond in β-position relative to the exocyclic C,N double bond of the imine ligands. A 1,3 hydrogen shift reaction then leads to the formation of a methylene group instead of the former imine carbon atom. So, the imine ligands are transformed into $\mu_2\text{-}\eta^3$-enyl-amido ligands being coordinated to an $Fe_2(CO)_6$ moiety, which is confirmed by X-ray structure analyses of six compounds.

*Keywords:* C,H bond activation; Imino substituted heterocycles; Iron carbonyl complexes

## 1. Introduction

A promising pathway in the development of organometallic catalysts capable of C,C bond formation is to look for metal ligand systems in which a C,H bond activation of the ligand is observed. In this context the activation of aromatic C,H bonds is one of the most attractive goals, and only a few reactions have been described in the literature, which include the activation of benzene in the presence of CO to give benzaldehyde [1], or in the presence of CO and ethylene leading to propiophenone [2], as well as the reaction of pyridine with CO and olefins respectively [3]. Very recently, Murai and coworkers [4] reported the coupling of an imidazole with CO and a wide variety of olefins. We are interested in the reactivity of 1-azadiene ligands towards Group 8 organometallic compounds, in particular against the metal carbonyls $Fe_2(CO)_9$,

$Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. The reactivity of 1-azadienes against $Ru_3(CO)_{12}$ is well documented, with the activation of the C,H bond in β-position with respect to the C,N imine double bond being the starting point of a reaction sequence leading to a large number of di-, tri- and tetranuclear ruthenium–azadiene cluster compounds [5].

The reaction of $Fe_2(CO)_9$ with 1-azadienes is reported to yield complexes (azadiene)$Fe(CO)_3$ [6]. Their reactivity against organic substrates is not investigated in detail, in contrast to that of their analogues (1,3-butadiene)$Fe(CO)_3$ [7] and (1,4-diazadiene)$Fe(CO)_3$ [8].

We report herein the reaction of 1-azadiene ligands, in which the C,C double bond is part of a heterocyclic system, with $Fe_2(CO)_9$ giving the dinuclear cluster compounds $[\mu_2\text{-}\eta^3\text{-}(R)N\text{--}CH_2\text{--}C=C\text{--}C(H)=C(H)\text{--}X]\text{--}Fe_2(CO)_6$ ($R = Ph$, $C_6H_{11}$, $p\text{-}^tBu\text{--}C_6H_4$; $X = S$, NMe) when starting from ligands with the imino group in 2-position of the heterocyclic ring. The isomers being substituted in 3-position of the heterocyclic systems therefore give the isomeric clusters $[\mu_2\text{-}\eta^3\text{-}(R)N\text{--}CH_2\text{--}C=C\text{--}X\text{--}C(R')=C(R'')]Fe_2(CO)_6$ ($R = Ph$, $C_6H_{11}$, $R'$

* Corresponding author.

= R″ = H, X = S; R = Ph, *p*-'Bu–C$_6$H$_4$, R′ = R″ = –C$_6$H$_4$–, X = NH). The reaction proceeds via activation of the C,H bond in β-position to the exocyclic imine bond, followed by a 1,3-hydrogen transfer to the carbon atom of the imine group.

## 2. Results and discussion

Imines with the C,C double bond being part of a heterocyclic ring are easily prepared by condensation of thiophene-2-carbaldehyde (**1–3**), N-methyl-pyrrole-2-carbaldehyde (**4–6**), thiophene-3-carbaldehyde (**13, 14**) or indole-3-carbaldehyde (**17, 18**) with the corresponding amines. Reaction of these imine ligands with Fe$_2$(CO)$_9$ in n-heptane at 50 °C results in the formation of the dinuclear compounds [μ$_2$-η$^3$-(R)N–CH$_2$–$\overline{\text{C=C–C(H)=C(H)–X}}$]Fe$_2$(CO)$_6$ (**7–12**) or [μ$_2$-η$^3$-(R)N–CH$_2$–$\overline{\text{C=C–X–C(R′)=C(R″)}}$]Fe$_2$(CO)$_6$ (**15, 16, 19** and **20**, Scheme 1) in moderate to good yield. The complexes are formed by an intramolecular 1,3-hydrogen shift from the carbon atom in β-position to the C,N double bond to the carbon atom of the imine moiety producing a CH$_2$ group instead. The dinuclear product clusters thus show a μ$_2$-η$^3$-enyl-amido ligand bridging an Fe$_2$(CO)$_6$ moiety. Complexes with the same structural principles have been observed as by-products from the reaction of Ru$_3$(CO)$_{12}$ with α,β-unsaturated imines [5,9] by reacting [CpCo(C$_2$H$_4$)$_2$] with N-phenyl-benzylideneamine [10] or from the reaction of Fe$_3$(CO)$_{12}$ with benzalazine [11]. Related iron compounds of formula [(R)N–C(H)–C(H)–Fe–C(O)]Fe(CO)$_3$ have been prepared from the reaction of the carbene cluster (μ$_2$-CH$_2$)Fe$_2$(CO)$_8$ with phosphine imides in the presence of CO [12]. Thermally induced rearrangement of those binuclear cluster compounds yields the isomeric clusters [C(H)–C(H)–N(R)–Fe–C(O)]Fe(CO)$_3$ [12].
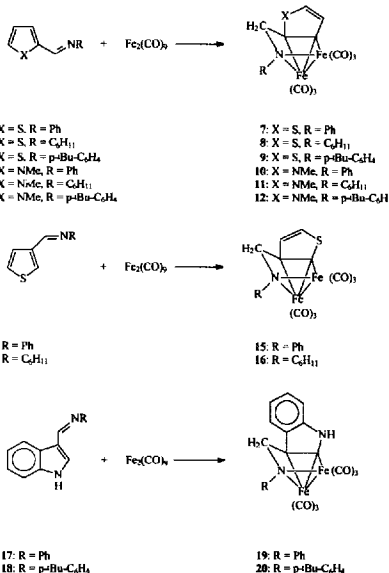
1,3-Hydrogen shift reactions are quite common in isomerisation reactions of olefins, not only using Group 8 organometallic catalysts like Fe(CO)$_5$, Fe$_3$(CO)$_{12}$ or Ru(H$_2$O)$_6$(tos)$_2$ (tos = *p*-toluene sulphonate) [13], but also using Group 9 organometallic compounds like HCo(CO)$_4$, Co$_2$(CO)$_8$ or CpRh(diene) [14]. There are
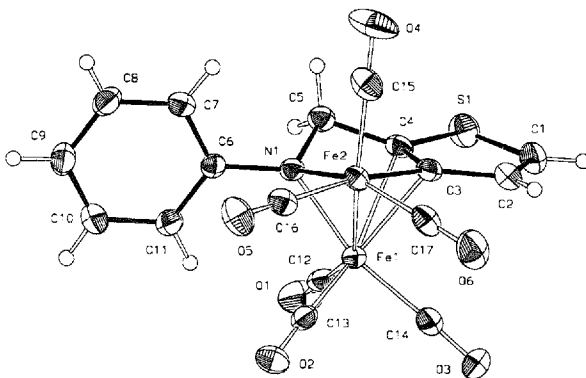


1: X = S, R = Ph
2: X = S, R = C$_6$H$_{11}$
3: X = S, R = *p*-'Bu-C$_6$H$_4$
4: X = NMe, R = Ph
5: X = NMe, R = C$_6$H$_{11}$
6: X = NMe, R = *p*-'Bu-C$_6$H$_4$

7: X = S, R = Ph
8: X = S, R = C$_6$H$_{11}$
9: X = S, R = *p*-'Bu-C$_6$H$_4$
10: X = NMe, R = Ph
11: X = NMe, R = C$_6$H$_{11}$
12: X = NMe, R = *p*-'Bu-C$_6$H$_4$

13: R = Ph
14: R = C$_6$H$_{11}$

15: R = Ph
16: R = C$_6$H$_{11}$

17: R = Ph
18: R = *p*-'Bu-C$_6$H$_4$

19: R = Ph
20: R = *p*-'Bu-C$_6$H$_4$

Scheme 1.



Fig. 1. Molecular structure of [μ$_2$-η$^3$-(Ph)N–CH$_2$–$\overline{\text{C=C–C(H)=C(H)–S}}$]Fe$_2$(CO)$_6$ **7**.
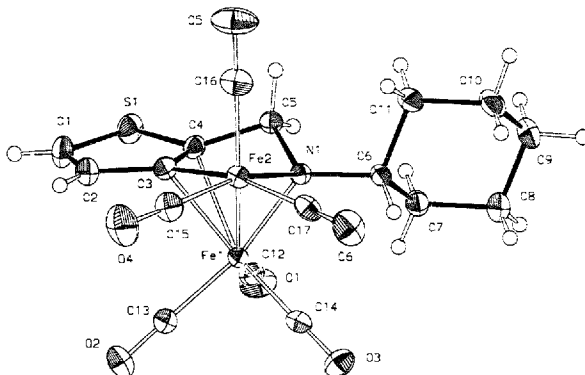
Fig. 2. Molecular structure of $[\mu_2\text{-}\eta^3\text{-}(C_6H_{11})N\text{-}CH_2\text{-}\overline{C=C\text{-}C(H)=C(H)\text{-}S}]Fe_2(CO)_6$ **8**.

also isomerisation reactions of olefins reported using $M(CO)_6$ (M = Cr, Mo, W) or $(MeCN)_3Cr(CO)_3$ as the catalyst [15]. $Fe(CO)_5$ is also known to catalyse the isomerisation of allylalcohol to propionaldehyde [16].

In the imines 1–6, 17 and 18 producing the clusters 7–12, 19 and 20 respectively, only one H atom is available, so the $\mu_2\text{-}\eta^3$-enyl-amido ligands are the only products to be obtained from a 1,3 hydrogen shift reaction of the H atom to the imine carbon atom. In contrast, the imines 13 and 14 should have two possibilities of realizing a 1,3 hydrogen shift reaction due to the presence of two β-H atoms, namely at $C_2$ and $C_3$ of the

thiophene ring. The formation of 15 and 16 as the only isolable products of the reaction proves the formation of $[\mu_2\text{-}\eta^3\text{-enyl-amido}]Fe_2(CO)_6$ systems to be the most favoured reaction pathway.

## 2.1. Structure determinations

By means of recrystallization of the clusters 7, 8, 10, 11, 16 and 19 from mixtures of light petroleum (b.p. 40–60 °C) and $CH_2Cl_2$ it was possible to grow crystals suitable for X-ray analysis. The molecular structures of the compounds are shown in Figs. 1–6, selected bond
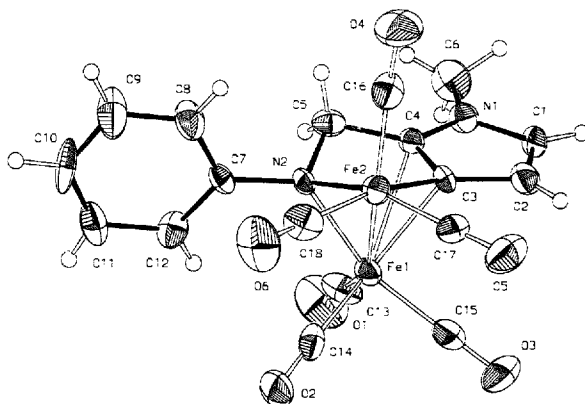


Fig. 3. Molecular structure of $[\mu_2\text{-}\eta^3\text{-}(Ph)N\text{-}CH_2\text{-}\overline{C=C\text{-}C(H)=C(H)\text{-}NMe}]Fe_2(CO)_6$ **10**.
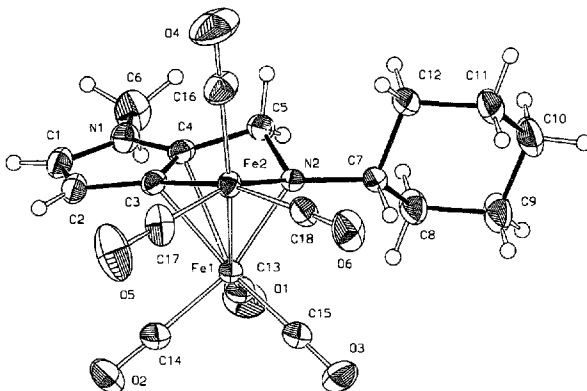
Fig. 4. Molecular structure of [μ₂-η³-(C₆H₁₁)N–CH₂–$\overline{C=C–C(H)=C(H)}$–NMe]Fe₂(CO)₆ **11**.

lengths and angles are collected in Tables 1–6 (**7**: Fig. 1, Table 1; **8**: Fig. 2, Table 2; **10**: Fig. 3, Table 3; **11**: Fig. 4, Table 4; **16**: Fig. 5, Table 5; **19**: Fig. 6, Table 6).

All structures have some details in common. They all consist of an Fe₂(CO)₆ moiety, which adopts a nearly ecliptic conformation, and a formal 6e-donating enyl-amido ligand. So another way to describe these molecules would be as aza-ferra-cyclopentadiene ligands which are coordinated to an apical Fe(CO)₃ fragment. This view is consistent with the fact that the atoms which are connected to the apical Fe(CO)₃ unit and the atoms building up the thiophene, pyrrole or indole heterocyclic system show a planar arrangement (Tables 1–6). The methylene group at C5 is shifted 34.8 pm

(**10**) to 55.7 pm (**19**) out of this plane. This corresponds very well with the values being observed for other structurally characterized η⁴-metalla-azacyclo-pentadiene complexes [10,11] and for η⁴-cyclo-pentadiene complexes in general [17]. In the X-ray structure determinations of **7**, **8** and **10**, all hydrogen atoms were determined by Fourier difference calcula-tions. In the case of **11** the hydrogen atoms of the methylene group (C5) and the olefinic hydrogen atoms at C1 and C2 have also been determined by Fourier difference calculations, whereas the hydrogen atoms of the methyl group and of the cyclohexyl ligand were calculated into idealized positions. For **16** only the olefinic hydrogen atoms at C1 and C2 have been deter-
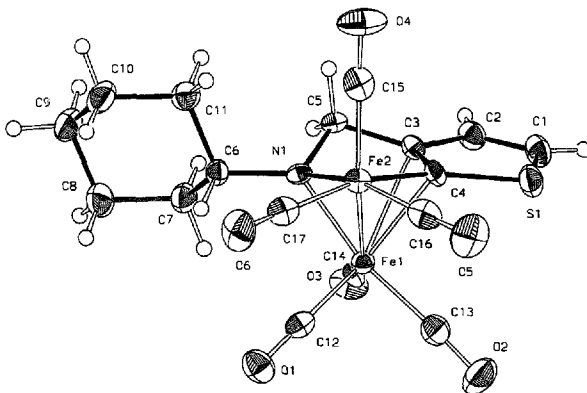


Fig. 5. Molecular structure of [μ₂-η³-(C₆H₁₁)N–CH₂–$\overline{C=C–S–C(H)=C(H)}$]Fe₂(CO)₆ **16**.
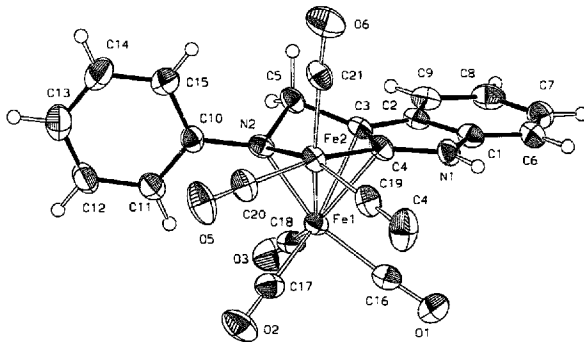
Fig. 6. Molecular structure of [μ₂-η³-(Ph)N–CH₂–C̄=C–N(H)–C(H)=C̄(H)–(CH)₄]Fe₂(CO)₆ 19.

mined by Fourier difference calculations. The other hydrogen atoms in **16** were calculated into idealized positions. In the structural analysis of **19**, the hydrogen atoms at C5 have been determined by Fourier difference calculations again, while the aromatic hydrogen atoms have been calculated into idealized positions. In all structure determinations the enyl-amido ligands show a slightly elongated double bond between C3 and C4 in the range 138.2 pm (**10**) to 140.5 pm (**11**, **19**) due to the interaction of this double bond with the apical Fe(CO)₃ group (Fe1). The C,C and C,N single bonds of the methylene group (**7**, **8**: C4–C5, C5–N1; **10**, **11**: C4–C5, C5–N2; **16**: C3–C5, C5–N1; **19**: C3–C5, C5–N2) are of expected values for all structurally characterized compounds (Tables 1–6). The Fe,C bond lengths are very different. For all structures the Fe,C bond inside the aza-ferracyclopentadiene ring systems (**7**, **8**, **10**, **11**,

**16**: Fe2–C4; **19**: Fe2–C3), which can be considered as representing a σ bond, is the shortest Fe–C bond of the Fe₂(CO)₆ moiety to the ligand. They vary from 193.8 pm (**19**) to 197.7 pm (**10**) with the Fe,C bond in **16** and **19**, where the corresponding carbon atom is also bound to the sulphur atom of the thiophene ring or the indole nitrogen atom respectively, being slightly shorter than the Fe,C bonds of the other compounds in which this carbon atom is bound to another sp² hybridized carbon atom (**16**: Fe2–C4 194.8 pm; **19**: Fe2–C3 193.8 pm). The Fe,C bond lengths of the double bond between C3 and C4 to the apical Fe1 depend a lot on the constitution of the enyl-amido ligand as well as on the heteroatom involved. **7**, **8**, **10** and **11** were derived from heterocyclic ligands bearing the imino substituent in 2-position. So C3 is connected to C2, C4 and both iron atoms, while C4 is bound to C3, C5, Fe1 and the

Table 1
Selected bond lengths [pm] and angles [°] for 7

| Fe1–Fe2 | 243.43(6) | Fe1–N1 | 197.1(2) |
|---|---|---|---|
| Fe1–C3 | 216.6(3) | Fe1–C4 | 227.9(3) |
| S1–C1 | 173.7(3) | S1–C4 | 173.4(3) |
| C1–C2 | 133.3(5) | C2–C3 | 145.3(4) |
| C3–C4 | 140.2(4) | C4–C5 | 149.3(4) |
| C5–N1 | 149.2(4) | Fe2–C3 | 196.2(3) |
| Fe2–N1 | 199.3(2) | N1–C6 | 144.3(3) |
|  |  |  |  |
| N1–Fe2–C3 | 78.6(1) | Fe2–C3–C4 | 113.6(2) |
| C3–C4–C5 | 117.2(2) | C4–C5–N1 | 98.6(2) |
| C5–N1–Fe2 | 113.2(2) | S1–C1–C2 | 113.4(3) |
| C1–C2–C3 | 113.9(3) | C2–C3–C4 | 109.3(3) |
| C3–C4–S1 | 113.2(2) | C4–S1–C1 | 90.2(2) |
| S1–C4–C5 | 127.3(2) | Fe2–C3–C2 | 136.9(2) |
| N1–Fe1–Fe2 | 52.53(6) | N1–Fe1–C3 | 74.3(1) |
| N1–Fe1–C4 | 63.84(9) | Fe2–Fe1–C3 | 50.06(7) |
| Fe2–Fe1–C4 | 73.77(7) | C3–Fe1–C4 | 36.7(1) |

Deviations [pm] from plane [S1–C1–C2–C3–C4–Fe2–N1]: S1 −8.7, C1 4.9, C2 9.0, C3 0.6, C4 −6.9, Fe2 −14.9, N1 16.3, C5 48.8.

Table 2
Selected bond lengths [pm] and angles [°] for 8

| Fe1–Fe2 | 244.99(7) | Fe1–N1 | 196.3(2) |
|---|---|---|---|
| Fe1–C3 | 218.3(2) | Fe1–C4 | 228.0(2) |
| S1–C1 | 173.1(3) | S1–C4 | 173.0(2) |
| C1–C2 | 135.0(4) | C2–C3 | 145.5(3) |
| C3–C4 | 140.1(3) | C4–C5 | 149.8(3) |
| C5–N1 | 148.4(2) | Fe2–C3 | 195.9(2) |
| Fe2–N1 | 198.9(2) | N1–C6 | 148.3(2) |
|  |  |  |  |
| N1–Fe2–C3 | 79.30(8) | Fe2–C3–C4 | 112.7(2) |
| C3–C4–C5 | 116.9(2) | C4–C5–N1 | 98.9(2) |
| C5–N1–Fe2 | 111.5(1) | S1–C1–C2 | 113.6(2) |
| C1–C2–C3 | 113.2(2) | C2–C3–C4 | 109.2(2) |
| C3–C4–S1 | 113.7(2) | C4–S1–C1 | 90.2(1) |
| S1–C4–C5 | 126.8(2) | Fe2–C3–C2 | 137.9(2) |
| N1–Fe1–Fe2 | 52.18(5) | N1–Fe1–C3 | 74.63(7) |
| N1–Fe1–C4 | 64.04(7) | Fe2–Fe1–C3 | 49.61(6) |
| Fe2–Fe1–C4 | 72.89(6) | C3–Fe1–C4 | 36.51(8) |

Deviations [pm] from plane [S1–C1–C2–C3–C4–Fe2–N1]: S1 −9.8, C1 4.3, C2 10.1, C3 1.5, C4 −6.4, Fe2 −16.6, N1 16.9, C5 49.9.

Table 3
Selected bond lengths [pm] and angles [°] for 10

| | | | |
|---|---|---|---|
| Fe1–Fe2 | 242.1(1) | Fe1–N2 | 197.5(5) |
| Fe1–C3 | 212.7(6) | Fe1–C4 | 247.5(6) |
| N1–C1 | 138.8(8) | N1–C4 | 134.3(7) |
| C1–C2 | 135.0(9) | C2–C3 | 144.1(9) |
| C3–C4 | 138.3(8) | C4–C5 | 147.7(9) |
| C5–N2 | 148.8(8) | Fe2–C3 | 197.7(6) |
| Fe2–N2 | 199.0(5) | N2–C7 | 144.1(7) |
| N2–Fe2–C3 | 76.6(2) | Fe2–C3–C4 | 113.6(5) |
| C3–C4–C5 | 117.7(6) | C4–C5–N2 | 100.6(5) |
| C5–N2–Fe2 | 112.9(4) | N1–C1–C2 | 109.7(7) |
| C1–C2–C3 | 107.5(7) | C2–C3–C4 | 104.4(6) |
| C3–C4–N1 | 111.6(5) | C4–N1–C1 | 106.7(5) |
| N1–C4–C5 | 130.1(6) | Fe2–C3–C2 | 139.4(6) |
| N2–Fe1–Fe2 | 52.7(1) | N2–Fe1–C3 | 73.6(2) |
| N2–Fe1–C4 | 60.4(2) | Fe2–Fe1–C3 | 51.0(2) |
| Fe2–Fe1–C4 | 70.6(2) | C3–Fe1–C4 | 33.9(2) |

Deviations [pm] from plane [N1–C1–C2–C3–C4–Fe2–N2]: N1 15.0, C1 −0.5, C2 −16.1, C3 −10.2, C4 8.3, Fe2 25.8, N2 −22.3, C5 34.8.

Table 5
Selected bond lengths [pm] and angles [°] for 16

| | | | |
|---|---|---|---|
| Fe1–Fe2 | 245.9(1) | Fe1–N1 | 196.5(3) |
| Fe1–C3 | 234.2(4) | Fe1–C4 | 217.1(4) |
| S1–C1 | 173.1(5) | S1–C4 | 174.6(4) |
| C1–C2 | 134.9(7) | C2–C3 | 142.1(6) |
| C3–C4 | 140.4(7) | C3–C5 | 149.9(6) |
| C5–N1 | 148.6(5) | Fe2–C4 | 194.8(4) |
| Fe2–N1 | 199.8(4) | N1–C6 | 148.2(6) |
| N1–Fe2–C4 | 78.3(2) | Fe2–C4–C3 | 115.9(3) |
| C4–C3–C5 | 113.7(4) | C3–C5–N1 | 101.4(3) |
| C5–N1–Fe2 | 111.1(3) | S1–C1–C2 | 112.6(4) |
| C1–C2–C3 | 111.9(5) | C2–C3–C4 | 114.6(4) |
| C3–C4–S1 | 108.3(3) | C4–S1–C1 | 92.4(2) |
| C2–C3–C5 | 130.1(4) | Fe2–C4–S1 | 135.3(3) |
| N1–Fe1–C4 | 52.2(1) | N1–Fe1–C3 | 64.2(2) |
| N1–Fe1–C4 | 73.9(2) | Fe2–Fe1–C3 | 73.0(1) |
| Fe2–Fe1–C4 | 49.3(1) | C3–Fe1–C4 | 36.0(2) |

Deviations [pm] from plane [S1–C1–C2–C3–C4–Fe2–N1]: S1 −11.6, C1 −1.8, C2 8.7, C3 8.3, C4 −2.4, Fe2 16.9, N1 −18.2, C5 47.5.

Table 4
Selected bond lengths [pm] and angles [°] for 11

| | | | |
|---|---|---|---|
| Fe1–Fe2 | 242.13(6) | Fe1–N2 | 196.6(2) |
| Fe1–C3 | 213.7(2) | Fe1–C4 | 241.4(4) |
| N1–C1 | 138.5(4) | N1–C4 | 136.1(3) |
| C1–C2 | 134.9(4) | C2–C3 | 144.9(3) |
| C3–C4 | 140.5(4) | C4–C5 | 148.1(3) |
| C5–N2 | 149.1(3) | Fe2–C3 | 197.0(2) |
| Fe2–N2 | 200.3(2) | N2–C7 | 148.5(3) |
| N2–Fe2–C3 | 77.69(9) | Fe2–C3–C4 | 112.2(2) |
| C3–C4–C5 | 118.9(2) | C4–C5–N2 | 99.2(2) |
| C5–N2–Fe2 | 112.2(2) | N1–C1–C2 | 110.0(2) |
| C1–C2–C3 | 108.0(3) | C2–C3–C4 | 104.3(2) |
| C3–C4–N1 | 110.4(2) | C4–N1–C1 | 107.4(2) |
| N1–C4–C5 | 130.0(2) | Fe2–C3–C2 | 142.3(2) |
| N2–Fe1–Fe2 | 53.09(6) | N2–Fe1–C3 | 74.68(9) |
| N2–Fe1–C4 | 61.20(8) | Fe2–Fe1–C3 | 50.76(7) |
| Fe2–Fe1–C4 | 71.33(6) | C3–Fe1–C4 | 35.29(9) |

Deviations [pm] from plane [N1–C1–C2–C3–C4–Fe2–N2]: N1 14.1, C1 −3.7, C2 −14.8, C3 −5.7, C4 10.7, Fe2 22.5, N2 −23.0, C5 40.8.

Table 6
Selected bond lengths [pm] and angles [°] for 19

| | | | |
|---|---|---|---|
| Fe1–Fe2 | 245.9(1) | Fe1–N2 | 196.9(5) |
| Fe1–C3 | 222.6(5) | Fe1–C4 | 219.9(6) |
| N1–C1 | 140.8(8) | N1–C4 | 138.6(8) |
| C1–C2 | 140.8(9) | C2–C3 | 140.5(8) |
| C3–C4 | 140.5(8) | C3–C5 | 149.1(8) |
| C5–N2 | 148.7(7) | Fe2–C4 | 193.8(6) |
| Fe2–N2 | 200.3(5) | N2–C10 | 143.5(8) |
| N2–Fe2–C4 | 78.7(2) | Fe2–C4–C3 | 115.2(4) |
| C4–C3–C5 | 114.8(5) | C3–C5–N2 | 99.1(5) |
| C5–N2–Fe2 | 112.5(3) | N1–C1–C2 | 107.9(5) |
| C1–C2–C3 | 106.6(5) | C2–C3–C4 | 108.0(5) |
| C3–C4–N1 | 107.8(5) | C4–N1–C1 | 109.6(5) |
| C2–C3–C5 | 133.2(5) | Fe2–C4–N1 | 136.9(4) |
| N2–Fe1–Fe2 | 52.4(1) | N2–Fe1–C3 | 65.1(2) |
| N2–Fe1–C4 | 73.4(2) | Fe2–Fe1–C3 | 74.4(2) |
| Fe2–Fe1–C4 | 48.8(2) | C3–Fe1–C4 | 37.0(2) |

Deviations [pm] from plane [N1–C1–C2–C3–C4–Fe2–N2]: N1 −6.1, C1 −4.4, C2 6.2, C3 6.2, C4 0.3, Fe2 9.0, N2 −11.1, C5 55.7.

heteroatom (Figs. 1–4). In all cases Fe1–C3 is shorter than Fe1–C4. In 7 and 8 with sulphur as the heteroatom the Fe1–C3 bonds (7: 216.6 pm; 8: 218.3 pm) are slightly longer than the corresponding bonds in 10 (212.7 pm) and 11 (213.7 pm) with nitrogen being the heteroatom. In contrast the Fe1–C4 bonds in 7 (227.9 pm) and 8 (228.0 pm) are nearly 20 pm shorter compared with the corresponding bond lengths in 10 (245.5 pm) and 11 (241.4 pm). The same structural features are observed for the isomeric cluster 16, although it is derived from a ligand with the imino substituent in 3-position of the heterocycle. The bond lengths of C3 and C4 to Fe1 are again different from the bond of C3, which is also bound to Fe2 via a σ bond, and is 17 pm longer than the bond of C4 to Fe1. The bond length of C3–Fe1 (217.1 pm) corresponds very well with those of the other sulphur containing compounds 7 and 8. The value of C4–Fe1 (234.2 pm) is between the values observed for 7, 8 and 10, 11 respectively. 19 is also derived from a ligand with the imino substituent in 3-position of the heterocycle. But in this case, in contrast to all of the other structures, the bond lengths Fe1–C3 (19: 222.6 pm) and Fe1–C4 (19: 219.9 pm) are of similar value, presumably due to a more effective delocalization of π electrons in the ligand.

The compounds [(R)N–C(H)–C(H)–Fe(CO)₃–C(O)]Fe(CO)₃ and [C(H)–C(H)–N(R)–Fe(CO)₃–C(O)]Fe(CO)₃ described by Geoffroy and coworkers [12] show a ferrapyrrolinone ligand, which is η⁴-coordinated to a second iron atom. Their crystal structure

analyses reveal the two carbon atoms, the nitrogen and the iron atom showing a planar arrangement, and the carbonyl group being bent out of this plane. But due to the different constitution of the ring system compared with the compounds reported herein, and because of the presence of a carbonyl group instead of a $CH_2$ group, the bond distances are quite different for those compounds reported in Ref. [12] compared with 7, 8, 10, 11, 16 and 19. The clusters reported by Geoffroy and coworkers always show a longer iron bond as well as a

Table 7
Spectroscopic data for compounds 7–12, 15, 16, 19 and 20

| Compound | IR [a] | ^{1}H NMR [b] | ^{13}C{^{1}H} NMR [b] |
|---|---|---|---|
| 7 | 2068s, 2033vs, 1988vs | 4.26 (s, 2H)<br>7.00–7.28 (m, 5H)<br>7.40 (d, 1H, $J_{HH}$ = 5.1 Hz)<br>7.49 (d, 1H, $J_{HH}$ = 5.1 Hz) | 72.8, 113.0, 123.4<br>125.8, 129.2, 131.3<br>139.6, 158.2, 158.2<br>209.9 |
| 8 | 2063m, 2026vs, 1983vs | 0.95–1.76 (m, 10H)<br>2.16 (m, 1H)<br>3.84 (s, 2H)<br>7.36 (s, 2H) | 26.0, 26.3, 35.7, 61.6<br>74.2, 116.3, 130.5<br>139.8, 154.8, 210.4 |
| 9 | 2068m, 2030vs, 1991vs | 1.27 (s, 9H)<br>4.23 (s, 2H)<br>6.92 [c] (m, 2H)<br>7.20 [c] (m, 2H)<br>7.39 (d, 1H, $J_{HH}$ = 5.1 Hz)<br>7.48 (d, 1H, $J_{HH}$ = 5.1 Hz) | 31.3, 34.4, 72.8<br>112.8, 122.8, 125.7<br>131.2, 139.6, 148.8<br>155.7, 158.3, 210.0 |
| 10 | 2060m, 2014vs, 1981vs<br>1967s | 3.64 (s, 3H)<br>4.13 (s, 2H)<br>6.59 (s, 1H)<br>6.94 (s, 1H)<br>7.13–7.23 (m, 5H) | 35.4, 69.6, 118.8<br>125.7, 125.8, 126.2<br>128.8, 131.5, 137.0<br>159.2, 211.2 |
| 11 | 2054m, 2013vs, 1973s<br>1962s | 0.86–1.76 (m, 10H)<br>2.18 (m, 1H)<br>3.61 (s, 3H)<br>3.78 (s, 2H)<br>6.51 (s, 1H)<br>6.84 (s, 1H) | 26.2, 29.3, 35.1, 35.9<br>56.2, 74.8, 114.7<br>126.5, 130.9, 141.0<br>211.7 |
| 12 | 2059m, 2018vs, 1981s<br>1967s | 1.29 (s, 9H)<br>3.62 (s, 3H)<br>4.12 (s, 2H)<br>6.59 (d, 1H, $J_{HH}$ = 2.8 Hz)<br>6.93 (d, 1H, $J_{HH}$ = 2.8 Hz)<br>7.03c (m, 2H)<br>7.22c (m, 2H) | 31.3, 34.4, 35.3<br>69.7, 119.1, 125.0<br>125.5, 126.1, 131.4<br>136.7, 148.7, 156.7<br>211.3 |
| 15 | 2067m, 2027vs, 1991s | 4.12 (s, 2H)<br>7.00–7.27 (m, 6H)<br>7.87 (d, 1H, $J_{HH}$ = 5.2 Hz) | 72.5, 123.3, 123.8<br>124.5, 125.8, 129.0<br>142.6, 157.4, 158.3<br>209.7 |
| 16 | 2064m, 2027vs, 1983s | 0.86–1.75 (m, 10H)<br>2.23 (m, 1H)<br>3.74 (s, 2H)<br>7.13 (d, 1H, $J_{HH}$ = 5.1 Hz)<br>7.84 (d, 1H, $J_{HH}$ = 5.1 Hz) | 26.2, 29.7, 35.8, 60.6<br>74.2, 110.7, 124.0<br>127.7, 143.4, 210.2 |
| 19 | 2066m, 2029vs, 1990s<br>1958sh | 4.16 (s, 2H)<br>7.09–7.29 (m, 8H)<br>7.66 (m, 1H)<br>8.19 (s, 1H) | 70.2, 89.2, 110.1<br>120.6, 121.3, 123.8<br>125.7, 125.8, 128.0<br>128.9, 146.7, 158.4<br>170.7, 210.2 |
| 20 | 2061m, 2028vs, 1988s<br>1969sh | 1.34 (s, 9H)<br>4.20 (s, 2H)<br>7.05–7.33 (m, 7H)<br>7.69 (m, 1H)<br>8.24 (s, 1H) | 31.3, 34.4, 70.2, 89.1<br>110.1, 120.5, 121.2<br>123.2, 125.6, 125.7<br>128.0, 146.6, 148.7<br>155.9, 170.7, 210.2 |

[a] In $CH_2Cl_2$, 293 K, vs = very strong, s = strong, m = middle, sh = shoulder.
[b] In $CDCl_3$, 293 K, s = singlet, d = doublet, m = multiplet.
[c] The signals are part of the AA'BB' system of the p-substituted phenyl ring.

longer bond of the nitrogen atom to the apical iron atom. The bond lengths of the apical iron atom to the ring carbon atoms are much shorter than for **7**, **8**, **10**, **11**, **16** and **19**, and those bond lengths are of nearly equal value in contrast to all structural determinations reported herein, except that for **19**.

## 2.2. Spectroscopy

The IR and NMR data for compounds **7–12**, **15**, **16**, **19** and **20** are given in Table 7. The IR spectra of all compounds show a very similar pattern of bands. It is remarkable that, for the compounds derived from thiophene derivatives (**7–9**, **15** and **16**, X = S), only three IR bands are observed, with the one at the lowest frequency being rather broad, whereas **19** and **20** (X = NH) show a shoulder for the corresponding band and for **10–12** (X = NMe) this band is split into two distinct bands.

The most characteristic fact of all $^1$H NMR spectra is the resonance of the methylene group formed from the former imine group of the ligand by 1,3 hydrogen shift. This resonance is observed in the range 4.12–4.26 ppm for all compounds bearing aromatic substituents at the former imine nitrogen atom (**7**, **9**, **10**, **12**, **15**, **19** and **20**) and in the range 3.74–3.84 ppm for cyclohexyl substituted enyl-amido ligands (**8**, **11**, **16**). The resonances of the olefinic hydrogen atoms of the heterocyclic ring systems in **7–12**, **15** and **16** are shifted about 0.1–0.4 ppm downfield compared with the free ligands (see Table 9, experimental part). All other substituents as well as the methyl group of the N-methyl-pyrrole system in **10–12** and the proton resonance of the NH function of **19** and **20** show the expected chemical shifts.

In the $^{13}$C NMR spectra of **7–12** the resonance of the methylene group is again most characteristic of this class of compounds. In general the resonances show a nearly identical chemical shift, if aromatic substituents are present at the former imine nitrogen atom (**7**: R = Ph, X = S, 72.8 ppm; **9**: R = p-$^t$Bu–C$_6$H$_4$, X = S, 72.8 ppm; **10**: R = Ph, X = NMe, 69.6 ppm; **12**: R = p-$^t$Bu–C$_6$H$_4$, X = NMe, 69.7 ppm) with an approximately 3 ppm highfield shift by exchanging sulphur for nitrogen as the heteroatom of the ligand. The resonances of the methylene group in **8** and **11** with a cyclohexyl substituent are shifted 11 ppm (**8**: X = S, 61.6 ppm) or 13 ppm (**11**: X = NMe, 56.2 ppm) highfield compared with their analogues with aromatic substituents.

The $^{13}$C NMR spectrum of **15** shows a resonance for the methylene group at 72.5 ppm, which is about the same chemical shift as for its isomer **7**. Again the corresponding resonance in the cyclohexyl substituted derivative **16** is shifted 12 ppm to higher field, which is about the same value as for **10–12**.

The $^{13}$C NMR spectra of **19** and **20** both show a signal at 70.2 ppm for the methylene group of the ligand, which is about the same value as for the other derivatives with aromatic substituents at the nitrogen atom (**7**, **9**, **10**, **12**, **15**).

The resonances of all other carbon atoms in **7–12**, **15**, **16**, **19** and **20** are of expected values (Table 7).

The $^{13}$C NMR spectra of all compounds show only one resonance for the CO ligands at room temperature, indicating a dynamic behaviour in solution as has been reported for compounds of general formula [$\mu_2$-$\eta^3$-(R)N–CH$_2$–C(H)–C(R')]Ru$_2$(CO)$_6$ [5].

## 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 two days before use. Fe$_2$(CO)$_9$ was prepared from Fe(CO)$_5$ (Lancaster) by irradiation in acetic acid [18].

### 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 ($^1$H: 200 MHz with SiMe$_4$ as internal standard; $^{13}$C: 50.32 MHz with CDCl$_3$ as internal standard); HMQC, HMBC, NOESY and TOCSY spectra of **19** on a Bruker DRX 400 spectrometer; 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 **7**, **8**, **10**, **11** and **19** were carried out on an Enraf–Nonius CAD4 diffractometer, the crystal structure determination of **16** was carried out on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation. The crystals were mounted in a stream of cold nitrogen. Data were corrected for Lorentz and polarization effects, **7**, **8**, **10** and **11** also for absorption. The structures were solved by direct methods and refined by full-matrix least-squares techniques against $F^2$ using the programs SHELXS-86 and SHELXL-93 [19]. Computations of the structures were done with the program XPMA and the molecular illustrations were drawn using the program ZORTEP [20]. The crystal and intensity data are given in Table 8. Additional material on the structure analyses is available from the Fachinformationszentrum Chemie, Physik, Mathematik GmbH, 76344 Eggenstein-Leopoldshafen 2, Germany by mentioning

Table 8
Crystal and intensity data for compounds 7, 8, 10, 11, 16 and 19

| compound | 7 | 8 | 10 | 11 | 16 | 19 |
|---|---|---|---|---|---|---|
| formula | $C_{17}H_9NO_6SFe_2$ | $C_{17}H_{15}NO_6SFe_2$ | $C_{18}H_{12}N_2O_6Fe_2$ | $C_{18}H_{18}N_2O_6Fe_2$ | $C_{17}H_{15}NO_6SFe_2$ | $C_{21}H_{12}N_2O_6Fe_2$ |
| mol. weight [g mol$^{-1}$] | 467.01 | 473.06 | 464.00 | 470.04 | 473.06 | 500.03 |
| radiation | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ |
| monochromator | graphite | graphite | graphite | graphite | graphite | graphite |
| temperature [K] | 173 | 173 | 173 | 173 | 183 | 173 |
| crystal colour | red | red | red | orange | orange | orange |
| crystal size [mm$^3$] | $0.3 \times 0.3 \times 0.2$ | $0.4 \times 0.2 \times 0.05$ | $0.5 \times 0.1 \times 0.02$ | $0.6 \times 0.4 \times 0.1$ | $0.5 \times 0.4 \times 0.02$ | $0.6 \times 0.2 \times 0.1$ |
| $a$ [Å] | 8.621(2) | 18.0598(7) | 9.816(2) | 12.347(3) | 17.760(2) | 15.714(7) |
| $b$ [Å] | 8.774(2) | 8.564(5) | 13.120(4) | 16.105(2) | 8.721(3) | 8.137(2) |
| $c$ [Å] | 12.135(1) | 12.285(2) | 15.449(3) | 20.072(4) | 12.258(3) | 16.749(2) |
| $\alpha$ [°] | 78.85(1) | 90 | 90 | 90 | 90 | 90 |
| $\beta$ [°] | 85.36(1) | 98.949(5) | 106.02(2) | 90 | 98.38(2) | 108.99(2) |
| $\gamma$ [°] | 81.18(2) | 90 | 90 | 90 | 90 | 90 |
| $V$ [Å$^3$] | 888.7(3) | 1877(1) | 1912.3(8) | 3991(1) | 1878(1) | 2025(1) |
| $Z$ | 2 | 4 | 4 | 8 | 4 | 4 |
| $F(000)$ | 468 | 960 | 936 | 1920 | 960 | 1008 |
| $\rho_{calc}$ [g cm$^{-3}$] | 1.745 | 1.674 | 1.612 | 1.564 | 1.673 | 1.640 |
| crystal system | triclinic | monoclinic | monoclinic | orthorhombic | monoclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ | $Pbca$ | $P2_1/c$ | $P2_1/c$ |
| abs. coeff. [mm$^{-1}$] | 1.789 | 1.695 | 1.558 | 1.494 | 1.693 | 1.478 |
| abs. correction | psi-scan | psi-scan | psi-scan | psi-scan | — | — |
| min.–max. transmisson | 94.15%–99.91% | 90.31%–99.89% | 89.16%–99.86% | 87.74%–99.95% | — | — |
| $\theta$ limit [°] | 1–22 | 1–27 | 1–27 | 1–28 | 1–23 | 1–25 |
| scan mode | $\omega$–2$\theta$ | $\omega$–2$\theta$ | $\omega$–2$\theta$ | $\omega$–2$\theta$ | $\omega$–2$\theta$ | $\omega$–2$\theta$ |
| scan speed [° min$^{-1}$] | 1–10 | 1–10 | 1–10 | 1–10 | 7–60 | 1–10 |
| refl. measured | 2288 | 4380 | 3815 | 4714 | 3309 | 3685 |
| independent refl. | 2162 | 4248 | 3604 | 4714 | 2462 | 3547 |
| obs. refl. $F_o^2 > 2\sigma(F_o^2)$ | 2016 | 3616 | 2310 | 3584 | 1926 | 2610 |
| no. of parameters | 280 | 305 | 301 | 273 | 255 | 287 |
| GOOF | 1.062 | 1.077 | 1.117 | 1.128 | 1.025 | 0.938 |
| $R_1$ | 0.0246 | 0.0274 | 0.0370 | 0.0331 | 0.0401 | 0.0538 |
| $wR_2$ | 0.0639 | 0.0709 | 0.0778 | 0.0763 | 0.0980 | 0.1336 |
| final diff. map electron density [e Å$^{-3}$] | 0.503 | 0.435 | 0.463 | 0.479 | 0.676 | 0.948 |

the deposition numbers CSD-405223 (7), CSD-405224 (8), CSD-405225 (10), CSD-405226 (11), CSD-405438 (16), CSD-405227 (19), the name of the author and the journal citation.

### 3.3. Preparation of the compounds

#### 3.3.1. Preparation of the imines 1–6
5 ml of the aldehyde (thiophene-2-carbaldehyde 0.055 mol, N-methylpyrrole-2-carbaldehyde 0.047 mol) were stirred at 60 °C overnight together with an equimolar amount of the corresponding amine (1: 5 ml aniline, 2: 6.3 ml cyclohexylamine, 3: 8.8 ml 4-tert-butyl-aniline, 4: 4.3 ml aniline, 5: 5.4 ml cyclohexylamine, 6: 7.5 ml 4-tert-butyl-aniline). During the reaction a small layer of water was formed. The reaction mixture was distilled under vacuum to give the imines as yellow (1, 3, 4–6) or colourless (2) oils in yields of 85–90%. The imines 1–3 crystallized upon standing in the refrigerator

overnight (m.p. 1: 16 °C, 2: 37 °C, 3: 56 °C; b.p. 4: 68 °C (1.8 × 10$^{-3}$ mbar), 5: 98 °C (1.5 × 10$^{-3}$ mbar), 6: 124 °C (1 × 10$^{-3}$ mbar)).

#### 3.3.2. Preparation of 13 and 14
3 ml thiophene-3-carbaldehyde (0.034 mol) was stirred at 60 °C overnight together with an equimolar amount of the corresponding amine (13: 3.1 ml aniline, 14: 3.9 ml cyclohexylamine). Again the formation of a small water layer was observed. Vacuum distillation of the reaction mixtures gave 5.47 g (86%) of 13 as a light green oil and 4.92 g (75%) of 14 as a pale yellow oil. Both oils crystallized upon standing in the refrigerator overnight (m.p. 13: 13 °C, 14: 42 °C).

#### 3.3.3. Preparation of 17 and 18
3 g of indole-3-carbaldehyde (0.021 mol) was dissolved in 60 ml cyclohexane and an equimolar amount of the corresponding amine (17: 1.9 ml aniline, 18:

Table 9
Spectroscopic data for compounds 1–6, 13, 14, 17 and 18

| Compound | IR [a] | $^1$H NMR [b] | $^{13}$C{$^1$H} NMR [b] |
|---|---|---|---|
| 1 | 1676vs | 7.08 (dd, 1H, $J_{HH}$ = 3.6 Hz, $J_{HH}$ ≈ 4.9 Hz) | 120.9, 125.9, 127.6 |
| | | 7.15–7.22 (m, 3H) | 129.0, 130.2, 132.1 |
| | | | 142.8, 151.3, 152.9 |
| | | 7.30–7.47 (m, 4H) | |
| | | 8.52 (s, 1H) | |
| 2 | 1632vs | 1.1–1.86 (m, 10H) | 24.7, 25.5, 34.2, 69.4 |
| | | 3.14 (m, 1H) | 127.1, 128.2, 129.7 |
| | | 7.03 (dd, 1H, $J_{HH}$ = 3.6 Hz, $J_{HH}$ ≈ 4.8 Hz) | 142.9, 151.6 |
| | | 7.26 (dd, 1H, $J_{HH}$ = 0.8 Hz, $J_{HH}$ ≈ 3.6 Hz) | |
| | | 7.34 (dd, 1H, $J_{HH}$ = 0.8 Hz, $J_{HH}$ ≈ 4.8 Hz) | |
| | | 8.38 (s, 1H) | |
| 3 | 1616vs | 1.34 (s, 9H) | 31.4, 34.5, 120.6 |
| | | 7.11 (dd, 1H, $J_{HH}$ = 3.7 Hz, $J_{HH}$ ≈ 5.0 Hz) | 126.0, 127.6, 129.9 |
| | | 7.15–7.20 (m, 2H) | 131.7, 143.1, 148.7 |
| | | | 149.1, 152.2 |
| | | 7.36–7.49 (m, 4H) | |
| | | 8.58 (s, 1H) | |
| 4 | 1685vs | 4.08 (s, 3H) | 36.8, 108.7, 115.0 |
| | | 6.26 (dd, 1H, $J_{HH}$ = 2.5 Hz, $J_{HH}$ = 3.8 Hz) | 118.6, 120.7, 124.9 |
| | | 6.74 (dd, 1H, $J_{HH}$ = 1.7 Hz, $J_{HH}$ = 3.8 Hz) | 129.1, 130.3, 150.9 |
| | | | 152.9 |
| | | 6.82 (dd, 1H, $J_{HH}$ = 1.7 Hz, $J_{HH}$ = 2.5 Hz) | |
| | | 7.17–7.26 (m, 3H) | |
| | | 7.37–7.46 (m, 2H) | |
| | | 8.34 (s, 1H) | |
| 5 | 1712vs | 1.22–1.89 (m, 10H) | 24.5, 25.8, 34.7, 36.3 |
| | | 3.06 (m, 1H) | 69.9, 107.7, 115.2 |
| | | 3.95 (s, 3H) | 127.1, 130.2, 149.5 |
| | | 6.16 (dd, 1H, $J_{HH}$ = 2.6 Hz, $J_{HH}$ = 3.7 Hz) | |
| | | 6.49 (dd, 1H, $J_{HH}$ = 1.8 Hz, $J_{HH}$ = 3.7 Hz) | |
| | | 6.69 (dd, 1H, $J_{HH}$ = 1.8 Hz, $J_{HH}$ = 2.6 Hz) | |
| | | 8.21 (s, 1H) | |
| 6 | 1712vs | 1.39 (s, 9H) | 31.4,34.4,36.8 |
| | | 4.09 (s, 3H) | 108.6, 118.2, 120.3 |
| | | 6.25 (dd, 1H, $J_{HH}$ = 2.6 Hz, $J_{HH}$ = 3.8 Hz) | 125.9, 128.8, 130.5 |
| | | 6.71 (dd, 1H, $J_{HH}$ = 1.7 Hz, $J_{HH}$ = 3.8 Hz) | 148.0, 150.2, 150.3 |
| | | 6.81 (dd, 1H, $J_{HH}$ = 1.7 Hz, $J_{HH}$ = 2.6 Hz) | |
| | | 7.12–7.25 (m, 2H) | |
| | | 7.41–7.48 (m, 2H) | |
| | | 8.36 (s, 1H) | |
| 13 | 1692vs | 7.19–7.29 (m, 3H) | 120.7, 125.8, 125.9 |
| | | 7.36–7.46 (m, 3H) | 126.6, 128.6, 129.2 |
| | | 7.72 (dd, 1H, $J_{HH}$ = 1.2 Hz, $J_{HH}$ = 5.1 Hz) | 130.1, 140.8, 152.0 |
| | | 7.80 (dd, 1H, $J_{HH}$ = 1.2 Hz, $J_{HH}$ = 2.9 Hz) | 154.3 |
| | | 8.46 (s, 1H) | |
| 14 | 1639vs | 1.17–1.85 (m, 10H) | 24.8, 25.6, 34.3, 69.9 |
| | | 3.02–3.16 (m, 1H) | 125.9, 126.1, 127.6 |
| | | 7.26 (dd, 1H, $J_{HH}$ = 2.9 Hz, $J_{HH}$ = 5.0 Hz) | 140.9, 152.8 |
| | | 7.49 (d, 1H, $J_{HH}$ = 5.0 Hz) | |
| | | 7.53 (dd, 1H, $J_{HH}$ = 0.9 Hz, $J_{HH}$ = 2.9 Hz) | |
| 17 | 1631vs | 7.15–7.42 (m, 8H) | 111.5, 116.5, 120.9 |
| | | 7.52 (s, 1H) | 121.8, 121.9, 123.7 |
| | | 8.48 (m, 1H) | 125.0, 125.3, 129.2 |
| | | 8.63 (s, 1H) | 130.2, 136.8, 153.3 |
| | | 8.88 (br, 1H) | 154.8 |
| 18 | 1624vs | 1.33 (s, 9H) | 31.5, 34.5, 111.4 |
| | | 7.16–7.41 (m, 9H) | 116.5, 120.5, 121.8 |
| | | 7.61 (s, 1H) | 122.0, 123.6, 125.4 |
| | | 8.43–8.50 (m, 1H) | 126.0, 129.8, 136.9 |
| | | 8.55 (br, 1H) | 148.1, 150.7, 154.1 |
| | | 8.67 (s, 1H) | |

[a] In CH$_2$Cl$_2$, 293 K, C=N bond vibration, vs = very strong.
[b] In CDCl$_3$, 293 K. s = singlet. dd = doublet of doublets, m = multiplet, br = broad.

3.3 ml 4-*tert*-butyl-aniline) was added. The mixture was refluxed in a water separator until no more formation of water was observed. Upon cooling the product precipitated as a light brown microcrystalline powder. After filtration the imines were purified by recrystallization from a cyclohexane/ethanol mixture to yield 3.51 g **17** (76%, m.p. 132 °C) and 4.93 g **18** (85%, m.p. 178 °C) respectively.

The IR and NMR data of the compounds **1–6, 13, 14, 17** and **18** are given in Table 9.

### 3.3.4. Preparation of 7–12, 14, 15, 19 and 20

In a typical experiment 0.5 g of $Fe_2(CO)_9$ (1.37 mmol) was suspended in 30 ml n-heptane together with 2.05 mmol of the corresponding imine (**7**: 383 mg **1**, **8**: 498 mg **2**, **9**: 396 mg **3**, **10**: 377 mg **4**, **11**: 492 mg **5**, **12**: 390 mg **6**, **15**: 383 mg **13**, **16**: 396 mg **14**, **19**: 451 mg **17**, **20**: 566 mg **18**). The mixture was stirred at 50 °C until all of the material had dissolved. The colour of the solution changed from yellow to deep red. Afterwards the solvent was removed under vacuum. The red oily residue was dissolved in 10 ml $CH_2Cl_2$ and 1 g silanized silica gel was added. After removal of the solvent the mixture of products was chromatographed. Using light petroleum (b.p. 40–60 °C) as eluent, an orange band of **7–12, 15, 16, 19** or **20** respectively was obtained (yields **7**: 409 mg, 64%, **8**: 337 mg, 52%, **9**: 150 mg, 21%, **10**: 369 mg, 58%, **11**: 290 mg, 45%, **12**: 93 mg, 13%, **15**: 441 mg, 68%, **16**: 650 mg, 67%, **19**: 411 mg, 60%, **20**: 137 mg, 18%). With light petroleum/$CH_2Cl_2$ (3:1) a green band of $Fe_3(CO)_{12}$ was eluted in the chromatography of **9, 12** and **20**. This band increased if the temperature during the reaction was raised above 50 °C. In all cases with $CH_2Cl_2$/EtOH (20:1) a small deep red band was eluted, which could not be identified due to the very low yields ( < 10 mg) and the instability of the product. Anal. Found: C, 44.11; H, 2.21; N, 3.02. **7** $C_{17}H_9NO_6SFe_2$ Calc.: C, 43.72; H, 1.94; N, 3.00%. Anal. Found: C, 43.46; H, 3.91; N, 2.73. **8** $C_{17}H_{15}NO_6SFe_2$ Calc.: C, 43.16; H, 3.20; N, 2.96%. Anal. Found: C, 46.90; H, 3.41; N, 2.68. **9** $C_{21}H_{17}NO_6SFe_2$ Calc.: C, 48.22; H, 3.28; N, 2.68%. Anal. Found: C, 46.63; H, 2.86; N, 5.93. **10** $C_{18}H_{12}N_2O_6Fe_2$ Calc.: C, 46.59; H, 2.61; N, 6.04%. Anal. Found: C, 45.97; H, 3.90; N, 5.90. **11** $C_{18}H_{18}N_2O_6Fe_2$ Calc.: C, 46.00; H, 3.86; N, 5.96%. Anal. Found: C, 50.72; H, 4.38; N, 5.07. **12** $C_{22}H_{20}N_2O_6Fe_2$ Calc.: C, 50.81; H, 3.88; N, 5.39%. Anal. Found: C, 43.75; H, 2.08; N, 3.01. **15** $C_{17}H_9NO_6SFe_2$ Calc.: C, 43.72; H, 1.94; N, 3.00%. Anal. Found: C, 43.01; H, 3.48; N, 2.84. **16** $C_{17}H_{15}NO_6SFe_2$ Calc.: C, 43.16; H, 3.20; N, 2.96%. Anal. Found: C, 50.44; H, 2.58; N, 5.48. **19** $C_{21}H_{12}N_2O_6Fe_2$ Calc.: C, 50.44; H, 2.42; N, 5.60%. Anal. Found: C, 54.05; H, 4.30; N, 4.88. **20** $C_{25}H_{20}N_2O_6Fe_2$ Calc.: C, 53.99; H, 3.62; N, 5.04%.

### 3.4. Mass spectrometry

**1**. Electron impact (EI): $m/z$ (%) 187 (94, $M^+$), 186 (100, $M^+ - R$), 154 (4, $C_{11}H_8N^+$), 153 (4, $C_{11}H_7N^+$), 115 (7, $C_8H_5N^+$), 104 (6, $C_7H_6N^+$), 93 (5, $C_6H_7N^+$), 77 (46, $C_6H_5^+$), 51 (19, $C_4H_3^+$), 45 (5, CHS$^+$), 39 (8, $C_3H_3^+$).

**2**. EI: $m/z$ (%) 193 (100, $M^+$), 150 (6, $C_7H_{14}NS^+$), 137 (5, $C_7H_{11}NS^+$), 123 (3, $C_6H_7NS^+$), 110 (18, $C_5H_4NS^+$), 97 (8, $C_5H_5S^+$), 83 (10, $C_4H_3S^+$), 70 (3, $C_2H_2NS^+$), 55 (7, $C_4H_7^+$), 41 (8, $C_2H_3N^+$), 39 (7, $C_3H_3^+$).

**3**. EI: $m/z$ (%) 243 (62, $M^+$), 228 (100, $C_{14}H_{14}NS^+$), 212 (7, $C_{13}H_{10}NS^+$), 200 (11, $C_{12}H_{10}NS^+$), 186 (6, $C_{11}H_8NS^+$), 144 (22, $C_{10}H_{10}N^+$), 115 (24, $C_5H_9NS^+$), 100 (33, $C_5H_8S^+$), 91 (18, $C_7H_7^+$), 77 (22, $C_6H_5^+$), 65 (5, $C_5H_5^+$), 51 (6, $C_4H_3^+$), 41 (9, $C_2H_3N^+$), 39 (10, $C_3H_3^+$).

**4**. EI: $m/z$ (%) 184 (100, $M^+$), 168 (11, $C_{11}H_8N_2^+$), 156 (27, $C_{10}H_8N_2^+$), 107 (24, $C_6H_7N_2^+$), 91 (17, $C_7H_7^+$), 80 (20, $C_5H_6N^+$), 77 (34, $C_6H_5^+$), 65 (6, $C_5H_5^+$), 51 (17, $C_4H_3^+$), 39 (9, $C_3H_3^+$).

**5**. EI: $m/z$ (%) 190 (100, $M^+$), 175 (3, $C_{11}H_{15}N_2^+$), 160 (18, $C_{10}H_{12}N_2^+$), 147 (45, $C_9H_{11}N_2^+$), 133 (18, $C_8H_9N_2^+$), 120 (14, $C_7H_8N_2^+$), 107 (81, $C_6H_7N_2^+$), 94 (80, $C_5H_6N_2^+$), 82 (16, $C_5H_6N^+$), 66 (10, $C_4H_4N^+$), 55 (10, $C_4H_7^+$), 41 (14, $C_2H_3N^+$), 39 (11, $C_3H_3^+$).

**6**. EI: $m/z$ (%) 240 (79, $M^+$), 225 (100, $C_{15}H_{17}N_2^+$), 212 (10, $C_{14}H_{16}N_2^+$), 197 (5, $C_{13}H_{13}N_2^+$), 183 (18, $C_{12}H_{11}N_2^+$), 168 (3, $C_{11}H_8N^+$), 144 (15, $C_9H_8N_2^+$), 115 (16, $C_8H_5N^+$), 98 (26, $C_5H_{10}N_2^+$), 91 (20, $C_7H_7^+$), 82 (21, $C_5H_8N^+$), 77 (8, $C_6H_5^+$), 43 (17, $C_2H_5N^+$), 39 (5, $C_3H_3^+$).

**7**. EI: $m/z$ (%) 467 (21, $M^+$), 439 (12, $M^+ - CO$), 411 (32, $M^+ - 2CO$), 383 (10, $M^+ - 3CO$), 355 (20, $M^+ - 4CO$), 327 (62, $M^+ - 5CO$), 299 (100, $M^+ - 6CO$), 273 (12, $C_5H_7FeNS^+$), 246 (19, $C_7H_4Fe_2NS^+$), 149 (41, $C_8H_7NS^+$), 144 (97, $C_3H_6FeNS^+$), 112 (13, $Fe_2^+$), 77 (16, $C_6H_5^+$), 56 (37, $C_3H_6N^+$, $Fe^+$).

**8**. EI: $m/z$ (%) 473 (3, $M^+$), 445 (2, $M^+ - CO$), 417 (11, $M^+ - 2CO$), 389 (3, $M^+ - 3CO$), 361 (24, $M^+ - 4CO$), 333 (60, $M^+ - 5CO$), 305 (100, $M^+ - 6CO$), 248 (4, $C_{10}H_{14}FeNS^+$), 236 (7, $C_9H_{12}FeNS^+$), 222 (7, $C_8H_{10}FeNS^+$), 209 (9, $C_7H_8FeNS^+$), 196 (9, $C_6H_8FeNS^+$), 182 (12, $C_5H_6FeNS^+$), 169 (20, $C_4H_5FeNS^+$), 152 (27, $C_4H_2FeNS^+$), 144 (42, $C_3H_6FeNS^+$), 112 (16, $Fe_2^+$), 97 (20, $C_5H_5S^+$), 56 (20, $C_3H_6N^+$, $Fe^+$), 41 (10, $C_3H_5^+$).

**9** EI: $m/z$ (%) 523 (29, $M^+$), 495 (15, $M^+ - CO$), 467 (21, $M^+ - 2CO$), 439 (25, $M^+ - 3CO$), 411 (16, $M^+ - 4CO$), 383 (63, $M^+ - 5CO$), 355 (100, $M^+ - 6CO$), 144 (67, $C_3H_6FeNS^+$), 106 (89, $C_7H_8N^+$), 91 (80, $C_7H_7^+$), 77 (19, $C_6H_5^+$), 56 ($C_4H_8^+$).

**10** EI: $m/z$ (%) 464 (4, $M^+$), 436 (3, $M^+ - CO$), 408 (9, $M^+ - 2CO$), 380 (4, $M^+ - 3CO$), 352 (7, $M^+ - 4CO$), 324 (44, $M^+ - 5CO$), 296 (100, $M^+ - 6CO$), 281

(2, $C_{11}H_9Fe_2N_2^+$), 240 (13, $C_8H_4Fe_2N_2^+$), 225 (21, $C_{11}H_9FeN_2^+$), 204 (4, $C_5H_4Fe_2N_2^+$), 176 (7, $C_7H_8FeN_2^+$), 162 (11, $C_6H_6FeN_2^+$), 148 (50, $C_5H_4FeN_2^+$), 112 (10, $Fe_2^+$), 94 (8, $C_2FeN^+$), 56 (20, $C_3H_6N^+$, $Fe^+$).

**11.** EI: $m/z$ (%) 470 (14, $M^+$), 442 (6, $M^+ - CO$), 414 (14, $M^+ - 2CO$), 386 (13, $M^+ - 3CO$), 358 (35, $M^+ - 4CO$), 330 (37, $M^+ - 5CO$), 302 (100, $M^+ - 6CO$), 207 (17, $C_9H_{15}FeN_2^+$), 193 (8, $C_8H_{13}FeN_2^+$), 179 (14, $C_7H_{11}FeN_2^+$), 165 (21, $C_6H_9FeN_2^+$), 151 (92, $C_5H_7FeN_2^+$), 137 (13, $C_4H_5FeN_2^+$), 124 (7, $C_3H_4FeN_2^+$), 112 ($Fe_2^+$), 94 (33, $C_2FeN^+$), 56 ($C_3H_6N^+$, $Fe^+$).

**12.** EI: $m/z$ (%) 520 (35, $M^+$), 492 (17, $M^+ - CO$), 464 (10, $M^+ - 2CO$), 436 (16, $M^+ - 3CO$), 408 (9, $M^+ - 4CO$), 380 (33, $M^+ - 5CO$), 352 (63, $M^+ - 6CO$), 296 (9, $C_{16}H_{20}FeN_2^+$), 281 (19, $C_{15}H_{17}FeN_2^+$), 176 (29, $C_7H_8FeN_2^+$), 112 (13, $Fe_2^+$), 106 (80, $C_7H_8N^+$), 91 (100, $C_7H_7^+$), 78 (33, $C_6H_6^+$), 56 (30, $C_3H_6N^+$, $Fe^+$), 52 (22, $C_4H_4^+$), 44 (21, $C_2H_6N^+$).

**13.** EI: $m/z$ (%) 187 (91, $M^+$), 186 (100, $M^+ - H$), 154 (4, $C_{11}H_8N^+$), 115 (9, $C_8H_5N^+$), 104 (8, $C_7H_6N^+$), 93 (7, $C_6H_7N^+$), 77 (71, $C_6H_5^+$), 51 (29, $C_4H_3^+$), 45 (7, $CHS^+$), 39 (11, $C_3H_3^+$).

**14.** EI: $m/z$ (%) 193 (48, $M^+$), 176 (9, $C_{10}H_{10}NS^+$), 164 (44, $C_9H_{10}NS^+$, 150 (74, $C_8H_8NS^+$), 138 (53, $C_7H_8NS^+$), 136 (48, $C_7H_6NS^+$), 123 (16, $C_6H_5NS^+$), 110 (100, $C_5H_4NS^+$), 96 (69, $C_5H_4S^+$), 83 (20, $C_4H_3S^+$), 70 (18, $C_3H_2S^+$), 55 (21, $C_4H_7^+$), 45 (22, $CHS^+$), 41 (51, $C_3H_5^+$), 32 (44, $S^+$).

**15.** EI: $m/z$ (%) 466 (33, $M^+$), 438 (12, $M^+ - CO$), 411 (80, $M^+ - 2CO$), 383 (13, $M^+ - 3CO$), 355 (50, $M^+ - 4CO$), 327 (91, $M^+ - 5CO$), 299 (100, $M^+ - 6CO$), 273 (10, $C_9H_7Fe_2NS^+$), 150 (36, $C_8H_8NS^+$), 144 (43, $C_5H_6NS^+$), 112 (8, $Fe_2^+$), 77 (11, $C_6H_5^+$), 56 (28, $C_3H_6N^+$, $Fe^+$).

**16.** EI: $m/z$ (%) 473 (11, $M^+$), 445 (7, $M^+ - CO$), 417 (24, $M^+ - 2CO$), 389 (13, $M^+ - 3CO$), 361 (34, $M^+ - 4CO$), 333 (39, $M^+ - 5CO$), 305 (99, $M^+ - 6CO$), 279 (13, $C_9H_{13}NSFe^+$), 249 (6, $C_{11}H_{15}NSFe^+$), 222 (10, $C_5H_4NSFe_2^+$), 209 (8, $C_4H_3NSFe_2^+$), 197 (11, $C_3H_3NSFe_2^+$), 181 (29, $C_3HSFe_2^+$), 169 (67, $C_2HSFe_2^+$), 153 (100, $C_4H_3NSFe^+$), 112 (53, $Fe_2^+$), 97 (66, $C_5H_5S^+$), 84 (18, $C_4H_4S^+$), 56 (87, $Fe^+$), 41 (29, $C_3H_5^+$).

**17.** Chemical impact CI: $m/z$ (%) 249 (10, $M^+ + C_2H_5$), 221 (100, $M^+ + H$).

**18.** EI: $m/z$ (%) 276 (43, $M^+$), 261 (100, $C_{18}H_{17}N_2^+$), 245 (7, $C_{17}H_{13}N_2^+$), 233 (4, $C_{16}H_{13}N_2^+$), 219 (13, $C_{15}H_{10}N_2^+$), 145 (25, $C_9H_9N_2^+$), 131 (15, $C_9H_9N^+$), 116 (63, $C_8H_6N^+$), 102 (12, $C_7H_4N^+$), 91 (22, $C_7H_7^+$), 77 (19, $C_6H_5^+$), 65 (5, $C_5H_5^+$), 57 (13, $C_4H_7^+$), 41 (12, $C_2H_3N^+$), 39 (8, $C_3H_3^+$).

**19.** EI: $m/z$ (%) 500 (15, $M^+$), 472 (12, $M^+ - CO$), 444 (30, $M^+ - 2CO$), 416 (6, $M^+ - 3CO$), 388 (25, $M^+ - 4CO$), 360 (62, $M^+ - 5CO$), 332 (100, $M^+ - $

6CO), 276 (20, $C_{15}H_{12}FeN_2^+$), 259 (7, $C_8H_9Fe_2N_2^+$), 219 (9, $C_6H_5Fe_2N_2^+$), 166 ($C_3H_4Fe_2N^+$), 112 (3, $Fe_2^+$), 77 (4, $C_6H_5^+$), 56 (15, $C_3H_6N^+$, $Fe^+$).

**20.** EI: $m/z$ (%) 556 (20, $M^+$), 528 (8, $M^+ - CO$), 500 (10, $M^+ - 2CO$), 472 (15, $M^+ - 3CO$), 444 (24, $M^+ - 4CO$), 416 (51, $M^+ - 5CO$), 388 (100, $M^+ - 6CO$), 332 (13, $C_{19}H_{20}FeN_2^+$), 317 (6, $C_{18}H_{17}FeN_2^+$), 275 (5, $C_{15}H_{11}FeN_2^+$), 194 (50, $C_4H_6Fe_2N_2^+$), 187 (32, $C_8H_7FeN_2^+$), 112 (5, $Fe_2^+$), 77 (6, $C_6H_5^+$), 57 (18, $C_4H_9^+$), 56 (28, $C_3H_6N_7^+$, $Fe^+$), 43 (34, $C_3H_7^+$).

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