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Journal of Organometallic Chemistry 584 (1999) 122–130

Journal of Organometallic Chemistry

# Metal complexes of biologically important ligands, CXVI. Addition of carbanions from barbituric acid derivatives to unsaturated hydrocarbons in cationic complexes for the organometallic labelling of barbituric acid☆

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Received 20 January 1999

**Abstract**

The addition of the anion of 1,3,5-trimethyl-2-thiobarbituric acid **1** to π-bonded unsaturated hydrocarbons (olefin, cyclohexadienyl, cycloheptadienyl, cycloheptatrienyl) in cationic complexes of rhenium, iron, ruthenium and chromium provides a method for the introduction of organometallic fragments into the barbituric acid moiety. Substitution of the C-5-hydrogen atom gives the complexes **4–9**. The dianions of 1,3-dimethylbarbituric acid **2** and 1,3-dimethyl-2-thiobarbituric acid **3** yield the bimetallic complexes **10–15**. The structures of **10**, **11** and **13** were determined by X-ray diffraction. Due to the protection of the N-atom there was no self-assembly via hydrogen bonds. The complexes may be useful as covalent markers for barbiturate drugs in carbonyl metalloimmunoassays. 

*Keywords:* Barbituric acid; Rhenium; Iron; Ruthenium; Chromium; Transition-metal-labelled barbituric acids

## 1. Introduction

The addition of organic nucleophiles to π-coordinated unsaturated hydrocarbons in cationic complexes is one of the most investigated reaction in organometallic chemistry [1]. Also in the stereoselective organic synthesis, e.g. of natural products, these complexes were introduced with great success [2].

We have used organometallic nucleophiles (carbonyl metallates) for the synthesis of hydrocarbon bridged complexes [3]. In many cases the cationic complexes, e.g. $[(OC)_5Re(C_2H_4)]^+$, act like the isolobal carbenium ions. Also C-nucleophiles, e.g. 2-phenyloxazolone anion [4] or $FcCOCHCOFc^-$ [5] have been added to cationic complexes to give C–C coupling. In the following we report on the addition of deprotonated barbituric acid derivatives to coordinated unsaturated hydrocarbons. The addition products may be of interest as organometallic marked drugs. The incorporation of organometallic fragments into biomolecules for the labelling of biologically important molecules was introduced by Cais [6] (metalloimmunoassay) and Jaouen [7] (carbonyl metalloimmunoassay). Phenobarbital was marked by $C_5H_4Mn(CO)_3$ [8]. It can even be detected in the presence of another organometallic labelled antiepileptic medication and permits quantitative analysis [9]. Platinum complexes with the N-coordinated anion of diethylbarbituric acid [10] and also aurated derivatives of barbituric acid with gold–carbon and gold–nitrogen bonds were synthesized by Bonati et al. [11]. Beck et al. reported carbonyl metal complexes with

☆ Part CXV: R. Urban, K. Polborn, W. Beck, Z. Naturforsch. 546b (1999) 385.

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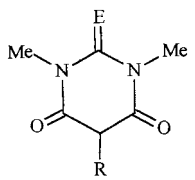
[1] Carried out X-ray structure analyses.

0022-328X/99/$ - see front matter 
PII: S0022-328X(99)00107-2

various N-bonded cyclic imidates [12] and Weigand et al. studied metal complexes with dithioylidene barbituric acid [13].

## 2. Results and discussion

Barbituric acids are well known for their strong tendency to associate through hydrogen bonds [13,14]. In order to avoid this the N-protected barbituric acid derivatives **1**–**3** were used as nucleophiles.



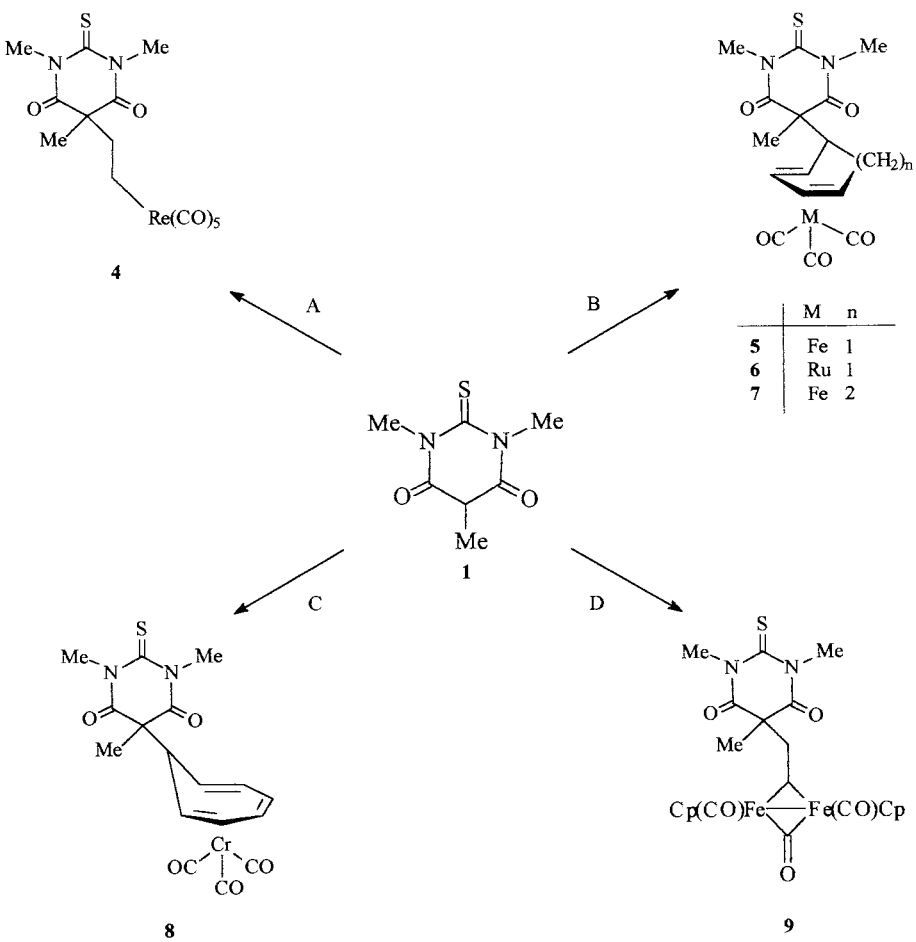
| | E | R |
|---|---|---|
| **1** | S | $CH_3$ |
| **2** | O | H |
| **3** | S | H |

### 2.1. Addition of the 1,3,5-trimethyl-2-thiobarbituric acid anion to unsaturated hydrocarbons of cationic complexes

Addition of the deprotonated 1,3,5-trimethyl-2-thiobarbituric acid **1** to cationic complexes with ethene, cyclohexadienyl and cycloheptatrienyl ligands and to $[Cp_2(OC)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)]^+$ affords the compounds **4**–**9** (Scheme 1).

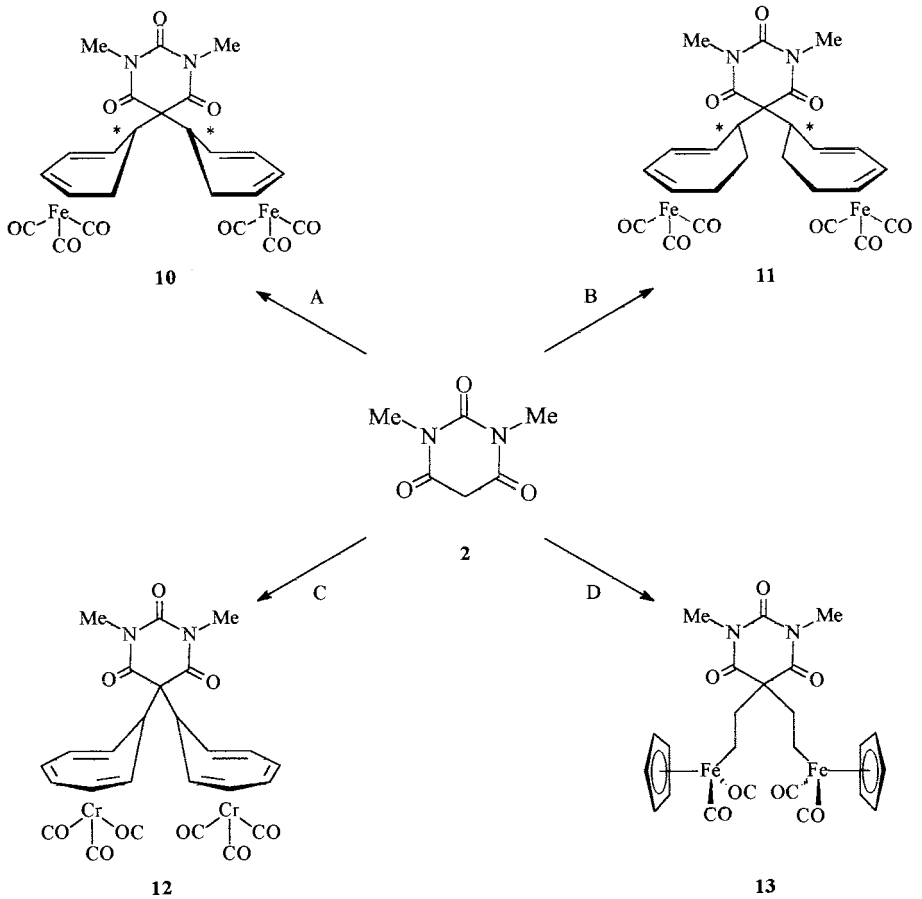
The $^1$H-NMR (400 MHz) spectrum of complex **4** shows the pattern of an AA'XX' spin system which is characteristic for compounds of the type 'Nu–$CH_2$–$CH_2$–M' (Nu = nucleophile) [15]. The coupling pattern of the signals of the ethylene hydrogen atoms indicates a staggered *trans* conformation. In compounds **5**–**7** the nucleophilic addition of the barbituric acid anion takes place at the *exo* side of the cyclohexadienyl ligand. This is proven by the $^1$H-NMR signals of the CH–$CH_2$ group.

Complex **8** is sensitive to air and decomposes in solution. After separation of the formed $Cr_2O_3$ the free ligand 5-cycloheptatrienyl-1,3,5-trimethyl-2-thiobarbituric acid **8A**, a new derivative of barbituric acid, could be isolated.

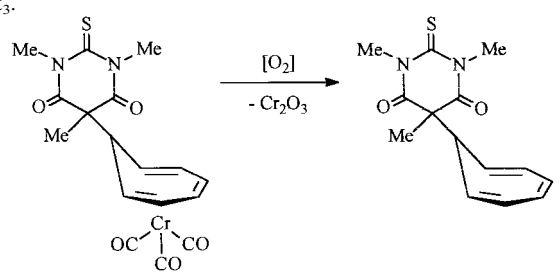


| | M | n |
|---|---|---|
| **5** | Fe | 1 |
| **6** | Ru | 1 |
| **7** | Fe | 2 |

Scheme 1. (A) $[(C_2H_4)Re(CO)_5]BF_4$, $NEt_3$; (B) $[(C_6H_7)Fe(CO)_3]BF_4$, $[(C_6H_7)Ru(CO)_3]BF_4$ or $[(C_7H_9)Fe(CO)_3]BF_4$, $NEt_3$; (C) $[(C_7H_7)Cr(CO)_3]BF_4$, $NEt_3$; (D) $[Cp_2(\mu\text{-}C_2H_3)Fe_2(CO)_3]BF_4$, $NEt_3$.




Scheme 2. (A) $2[(C_6H_7)Fe(CO)_3]BF_4$, $2NEt_3$; (B) $2[(C_7H_9)Fe(CO)_3]BF_4$, $2NEt_3$; (C) $2[(C_7H_7)Cr(CO)_3]BF_4$, $2NEt_3$; (D) 2 $[Cp(C_2H_4)Fe(CO)_2]BF_4$, $2NEt_3$.




In the $^1$H-NMR spectrum of a $CDCl_3$ solution of **8** also a signal set of the decomposition product **8A** is found. The signal of the aliphatic proton of the cycloheptatrienyl ring exhibits a high field shift of $-1.7$ ppm while the resonances of the olefinic protons shift down field up to 1.6 ppm due to the missing metal centre.

In the IR spectra of the carbonyl complexes **4–9** the intense CO absorption bands (see Section 4) are characteristic for neutral addition products.

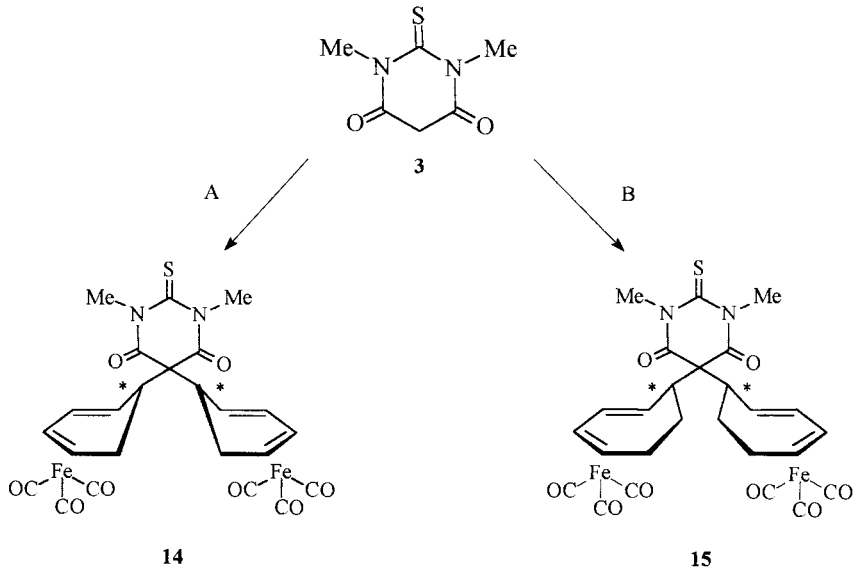
### 2.2. Addition of the 1,3-dimethylbarbituric acid and 1,3-dimethyl-2-thiobarbituric acid anion to unsaturated hydrocarbons of cationic complexes

The cationic complexes can even be added twice to the dianions of *N*,*N*′-dimethylbarbituric acid **2** and of *N*,*N*′-dimethyl-2-thiobarbituric acid **3** to give the bimetallic complexes **10–15** under C–C coupling (Schemes 2 and 3).

In compounds **10**, **11**, **14** and **15** two stereogenic centres are formed. The two diastereomers give two sets of signals in the $^1$H- and $^{13}$C-NMR spectra. For **10**, **11** and **14** the ratio is 2.2/1; 1.5/1 and 2.0/1 of the *RR*/*SS*- and the *meso*-isomers, respectively. For compound **15** formation of one diastereoisomer is preferred (3.5/1). Due to the plane of symmetry through the barbiturate moiety only one set of $^1$H-NMR signals is observed for the complexes **12** and **13**. The carbonyl IR absorptions are intensive and characteristic and indicate the good labelling properties of the synthesized barbituric acid derivatives.

### 2.3. X-ray structure determination of *10*, *11* and *13*

As might be expected, the structure of the bridging barbituric acid moiety is hardly effected by the nature of the added iron carbonyl electrophile, with the bond lengths within the six-membered ring being roughly the same in all three complexes, and only minor deviations from planarity (the '$\sigma$'-parameters [16] are 0.064, 0.039




Scheme 3. (A) $2[(C_6H_7)Fe(CO)_3]BF_4$, $2NEt_3$; (B) $2[(C_7H_9)Fe(CO)_3]BF_4$, $2NEt_3$.

and 0.040 for the three complexes). There are also no significant 'short' intermolecular contacts between the barbiturate rings, the shortest ones observed in **10**, where the shortest centroid distance measures 5.572 Å despite a small perpendicular plane distance of 3.27 Å, due to a large '$\beta$'-angle of 54.0° [16] (Table 1).

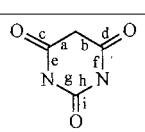
In the two cyclodiene complexes **10** and **11** the $sp^3$ carbon atoms bonded to the barbiturate methylene carbon are chiral. In the examined crystals of **10** the RR/SS diastereomer is found, while in the crystals of **11** the RS/SR isomer was measured. It seems interesting to compare the conformations of the Fe1–C–C–C–C–C–Fe2 bridges present in all three complexes. The four torsional angles along this bridge are collected in Table 2. As can be seen from these angles, *all-anti* conformations are present in **13** and **10**, with some minor deviations in the latter. If the molecules of **13** and **10** are viewed along the Fe1–Fe2 vector, it can be seen that the $Fe(CO)_3$ moieties in the latter are rotated by 180° with respect to each other (antiperiplanar conformation), while the $Fe(CO)_2Cp$ groups in **13** are rotated by ca. 123° (anticlinal conformation).

On the other hand, in **11** the angle C4–C10–C11–C17 of 49.3° makes this molecular structure the least symmetrical one. There seems to be no obvious reason for this difference, however it should be noted that the latter crystal structure provides the largest *void space* [16] in the unit cell, making up for 18.5% of the cell volume, while the voids in **10** (1.6% of the cell volume) and **13** (4.0% of cell volume) are nearly negligible. Since we could not localize any solvent within these voids, it is impossible to decide if this conformational differences are a consequence of interactions of solvent molecules with the complexes or not.

## 3. Conclusions

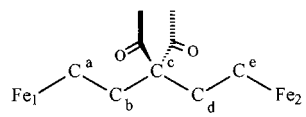
The reaction of deprotonated barbituric acid derivatives with organometallic complexes leads to new compounds which exhibit good labelling properties in their

Table 1
Bond parameters (Å) of the barbituric acid moiety



| | 10 | 11 | 13 |
|---|---|---|---|
| $(\mathbf{a},\mathbf{b})_{av}$ | 1.519(3) | 1.525(5) | 1.504(5) |
| $(\mathbf{c},\mathbf{d})_{av}$ | 1.211(3) | 1.205(5) | 1.212(4) |
| $(\mathbf{e},\mathbf{f})_{av}$ | 1.374(3) | 1.382(5) | 1.382(5) |
| $(\mathbf{g},\mathbf{h})_{av}$ | 1.386(3) | 1.375(6) | 1.383(5) |
| **i** | 1.196(4) | 1.222(7) | 1.200(7) |

Table 2
Torsional angles (°) around the Fe1–C–C–C–C–C–Fe2 bridges [a]



| | 10 | 11 | 13 |
|---|---|---|---|
| $Fe1–C^a–C^b–C^c$ | 163 | −169 | −177 |
| $C^a–C^b–C^c–C^d$ | −176 | 49 | −178 |
| $C^b–C^c–C^d–C^e$ | −176 | 172 | 178 |
| $C^c–C^d–C^e–Fe2$ | 162 | 172 | 175 |

[a] $C^a–C^b–C^c–C^d–C^e$ corresponds to C7–C8–C10–C16–C17 in **10**, C4–C10–C11–C17–C23 in **11** and C8–C9–C10–C16–C17 in **13**.

IR spectra. They may be used in the detection and identification of barbiturate drugs, e.g. in carbonyl metalloimmunoassay (CMIA). The study of such complexes may lead to a better understanding of the role of the ligand in biological systems.

## 4. Experimental

All reactions were carried out in dry solvents under argon atmosphere (Linde 4.8). NMR: Jeol GSX 270 or Jeol Ex 400, using the solvent as internal standard. IR: Nicolet 520 FT-IR. The starting materials were prepared according to literature procedures: $[(C_2H_4)Re(CO)_5]BF_4$ [17], $[(C_6H_7)Fe(CO)_3]BF_4$ [18], $[(C_6H_7)Ru(CO)_3]BF_4$ [19], $[(C_7H_9)Fe(CO)_3]BF_4$ [20], $[(C_7H_7)Cr(CO)_3]BF_4$ [21], $[Cp_2(\mu\text{-}C_2H_3)Fe_2(CO)_3]BF_4$ [22], $[Cp(C_2H_4)Fe(CO)_2]BF_4$ [23], *N*,*N*′-dimethylurea, *N*,*N*′-dimethylthiourea, malonic acid, methylmalonic acid, diethyl methylmalonate and 1,3-dimethylbarbituric acid **2** were purchased. Triethylamine was distilled prior to use.

### 4.1. General procedure for the preparation of *1–3*

The derivatives of barbituric acid were synthesized by condensation of *N*,*N*′-dimethylurea or *N*,*N*′-dimethylthiourea and malonic acid or diethyl malonate according to literature procedures for the synthesis of substituted barbituric acids [24,25].

Corresponding reactions with the 1,3,5-trimethylbarbituric acid were not successful due to its extreme instability [26]. Using similar procedure as for **1**–**3** only the oxidation product trimethyldialuric acid was obtained [27].

### 4.2. General procedure for the preparation of *4–9*

To a stirred solution of 1,3,5-trimethyl-2-thio-barbituric acid **1** in THF a slight excess of triethylamine was added. After 30 min stirring at room temperature an equimolare amount of the cationic metal complex was added and the solution was stirred for another 90 min. The solvent was evaporated under reduced pressure. The yellow residue was extracted twice with 20 ml of diethyl ether to remove the ammonium salt. After evaporation of the combined organic layers the residue was dissolved in dichloromethane and filtered through celite. The yellow solution was concentrated in vacuo to about 3 ml. The products **4–9** were precipitated with 40 ml of pentane and centrifugated off. The residues were washed twice with 3 ml of pentane and dried in vacuo at 60°C for several hours. Yield 65–75%.

(**4**): 28 mg (0.15 mmol) of 1,3,5-trimethyl-2-thio-barbituric acid **1**, 34 μl (0.25 mmol) of triethylamine and 65 mg (0.15 mmol) of $[(\eta^2\text{-}C_2H_4)Re(CO)_5]BF_4$ in 5 ml of THF were used. Yellow powder; yield 69%. IR (KBr): $\tilde{\nu} = 2130\ cm^{-1}$ vs, 2049 vs, 1999 vs, 1963 vs, 1908 s (Re–CO), 1720 s (C=S), 1685 s (C=O). $^1$H-NMR (270 MHz, $CD_2Cl_2$): $\delta = 0.62$ (m, $^3J_{AX} = 14.3$ Hz, $^3J_{A'X} = 4.1$ Hz, 2H, $ReC\underline{H}_2$), 1.47 (s, 3H, $CH_3$), 2.37 (m, 2H, $ReCH_2C\underline{H}_2$), 3.66 (s, 3H, N–$CH_3$), 3.67 (s, 3H, N–$CH_3$). $^{13}$C-NMR (67.8 MHz, $CD_2Cl_2$): $\delta = -11.2$ ($Re\underline{C}H_2$), 22.5 ($CH_3$), 35.4 (N–$CH_3$), 50.9 ($ReCH_2\underline{C}H_2$), 58.2 (C-5), 171.1 (C=O), 181.6 (Re–CO), 184.7 (C=S). $C_{14}H_{13}N_2O_7ReS{\cdot}0.75\ CH_2Cl_2$ (603.23): calc. C 29.37 H 2.42 N 4.64; Found C 29.36 H 2.77 N 4.23.

(**5**): 56 mg (0.3 mmol) of 1,3,5-trimethyl-2-thio-barbituric acid **1**, 70 μl (0.5 mmol) of triethylamine and 92 mg (0.3 mmol) of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ in 5 ml of THF were used. Yellow powder; yield 70%. IR (KBr): $\tilde{\nu} = 2049\ cm^{-1}$ vs, 1974 vs (Fe–CO), 1718 s (C=S), 1684 s (C=O), 1631 m (C=C). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta = 1.42$ (s, 3H, $CH_3$), 1.81 (ddd, 1H, $^2J_{6endo} = 16.0$ Hz, $^3J_1 = 3.0$ Hz, $^3J_5 = 3.0$ Hz, 6*exo*-$C_6H_7$), 1.95 (ddd, 1H, $^2J_{6exo} = 16.0$ Hz, $^3J_1 = 10.3$ Hz, $^3J_5 = 3.4$ Hz, 6*endo*-$C_6H_7$), 2.56 (ddd, 1H, 2-$C_6H_7$), 2.62 (ddd, 1H, $^3J_{6endo} = 11.2$ Hz, $^3J_{6exo} = 3.4$ Hz, $^3J_2 = 3.4$ Hz, 1-$C_6H_7$), 3.01 (m, 1H, 5-$C_6H_7$), 3.67 (s, 3H, N–$CH_3$), 3.68 (s, 3H, N–$CH_3$), 5.23 (m, 1H, 3–$C_6H_7$), 5.30 (m, 1H, 4-$C_6H_7$). $^{13}$C-NMR (67.8 MHz, $CDCl_3$): $\delta = 19.8$ ($CH_3$), 25.6 (6-$C_6H_7$), 35.7, 35.9 (N–$CH_3$), 49.9 (1-$C_6H_7$), 56.6, 56.8 (2,5-$C_6H_7$), 58.5 (C-5), 84.6, 86.0 (3,4-$C_6H_7$), 169.2, 170.4 (C=O), 180.9 (C=S), 210.8 (Fe–CO). m.p. 156°C. $C_{16}H_{16}FeN_2O_5S$ (404.23) calc. C 47.54 H 3.99 N 6.93; Found C 47.38 H 3.97 N 6.84.

(**6**): 53 mg (0.29 mmol) of 1,3,5-trimethyl-2-thio-barbituric acid **1**, 70 μl (0.5 mmol) of triethylamine and 100 mg (0.29 mmol) of $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]BF_4$ in 5 ml of THF were used. Orange powder; yield 70%. IR (KBr): $\tilde{\nu} = 2063\ cm^{-1}$ vs, 1988 vs (Ru–CO), 1718 s (C=S), 1683 s (C=O), 1625 m (C=C). $^1$H-NMR (270 MHz, $CD_2Cl_2$): $\delta = 1.39$ (s, 3H, $CH_3$), 1.89–1.95 (m, 2H, 6*exo*,*endo*-$C_6H_7$), 2.62 (m, 1H, 1-$C_6H_7$), 2.71 (m, 1H, 2-$C_6H_7$), 3.08 (m, 1H, 5-$C_6H_7$), 3.64 (s, 3H, N–$CH_3$), 3.65 (s, 3H, N–$CH_3$), 5.47 (m, 1H, 3-$C_6H_7$), 5.49 (m, 1H, 4-$C_6H_7$). $^{13}$C-NMR (67.8 MHz, $CDCl_3$): $\delta = 19.2$ ($CH_3$), 25.3 (6-$C_6H_7$), 35.4, 35.7 (N–$CH_3$), 50.7 (1-$C_6H_7$), 51.1, 51.4 (2,5-$C_6H_7$), 57.2 (C-5), 86.3, 88.1 (3,4-$C_6H_7$), 169.4, 170.7 (C=O), 181.3 (C=S). $C_{16}H_{16}RuN_2O_5S$ (449.45): calc. C 42.76 H 3.59 N 6.23; Found C 42.65 H 3.85 N 6.18.

(**7**): 80 mg (0.43 mmol) of 1,3,5-trimethyl-2-thio-barbituric acid **1**, 0.1 ml (0.72 mmol) of triethylamine and 138 mg (0.43 mmol) of $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]BF_4$ in 25 ml THF were used. Light brown powder; 75% yield. IR (KBr): $\tilde{\nu} = 2046\ cm^{-1}$ vs, 1974 vs (Fe–CO), 1723 s (C=S), 1686 s (C=O), 1662 m, 1634 m (C=C). $^1$H-NMR (270 MHz, $CDCl_3$): $\delta = 0.89$ (m, 1H, 7*exo*-$C_7H_9$), 1.23 (m, 1H, 7*endo*-$C_7H_9$), 1.51 (s, 3H, $CH_3$), 1.90 (m, 1H, 6*exo*-$C_7H_9$), 2.10 (m, 1H, 6*endo*-$C_7H_9$), 2.54 (m, 1H,

1-$C_7H_9$), 2.81 (m, 1H, 2-$C_7H_9$), 3.02 (m, 1H, 5-$C_7H_9$), 3.67 (s, 3H, N–$CH_3$), 3.68 (s, 3H, N–$CH_3$), 5.23 (m, 1H, 3-$C_7H_9$), 5.30 (m, 1H, 4-$C_7H_9$). $^{13}$C-NMR (67.8 MHz, $CD_2Cl_2$): $\delta = 18.6$ ($CH_3$), 25.2 (7-$C_7H_9$), 28.6 (6-$C_7H_9$), 35.5 (N–$CH_3$), 50.9 (1-$C_7H_9$), 54.7 (C-5), 58.2, 58.8 (2,5-$C_7H_9$), 87.7, 89.8 (3,4-$C_7H_9$), 169.6, 170.3 (C=O), 181.0 (C=S), 211.0 (Fe–CO). m.p. 120°C. $C_{17}H_{18}FeN_2O_5S$ (418.26): calc. C 48.83 H 4.34 N 6.70; Found C 48.82 H 4.52 N 6.70.

(**8**): 56 mg (0.3 mmol) of 1,3,5-trimethyl-2-thio-barbituric acid **1**, 70 μl (0.5 mmol) of triethylamine and 94 mg (0.3 mmol) of [($\eta^7$-$C_7H_7$)$Cr(CO)_3$]$BF_4$ in 20 ml THF were used. Filtration over celite led to decomposition. Red oily product which was dried in vacuo for a few days; yield 70%. IR (KBr): $\tilde{\nu} = 1985$ cm$^{-1}$ vs, 1915 vs, 1886 vs (Cr–CO), 1718 s (C=S), 1686 s (C=O), 1634 m, 1594 m (C=C). $^1$H-NMR (270 MHz, $CD_2Cl_2$): $\delta =$ 1.23 (s, 3H, $CH_3$), 3.42 (m, 2H, 2,7-$C_7H_7$), 3.53 (s, 6H, N–$CH_3$), 3.70 (s, 1H, 1-$C_7H_7$), 4.94 (m, 2H, 3,6-$C_7H_7$), 5.91 (m, 2H, 4,5-$C_7H_7$). $C_{17}H_{16}CrN_2O_5S \cdot 1/8CH_2Cl_2$ (423.00): calc. C 48.63 H 3.87 N 6.62; Found C 48.48 H 4.03 N 6.49.

(**8A**): The solution of 25 mg (0.06 mmol) of **8** in $CH_2Cl_2$ was stirred for 12 days in an open Erlenmeyer flask on air. Every 24 h portions of solvent were added to avoid precipitation. The clear red solution rapidly gets brown and finally green. The solution was concentrated to 3 ml and filtered over Celite to separate the green chromium species. After evaporation of the filtrate in vacuo a yellow oily product was isolated. The product could not be obtained analytically pure. IR (KBr): $\tilde{\nu} = 1710$ s (C=S), 1634 m, 1594 m (C=O and C=C). $^1$H-NMR (400 MHz, $CD_2Cl_2$): $\delta = 1.39$ (s, 3H, $CH_3$), 2.05 (m, 1H, 1-$C_7H_7$), 3.53 (s, 6H, N–$CH_3$), 5.07 (m, 2H, 2,7-$C_7H_7$), 6.21 (m, 2H, 3,6-$C_7H_7$), 6.67 (m, 2H, 4,5-$C_7H_7$).

(**9**): 38 mg (0.2 mmol) of 1,3,5-trimethyl-2-thio-barbituric acid **1**, 47 μl (0.34 mmol) of triethylamine and 90 mg (0.2 mmol) of [$Cp_2$(μ-CO)(μ-σ,π-$C_2H_3$)$Fe_2(CO)_2$]$BF_4$ in 20 ml THF were used. Red oily product which was precipitated with a small amount of $CH_2Cl_2$ and an excess of pentane; yield 64%.-IR (KBr): $\tilde{\nu} = 1985$ cm$^{-1}$ vs (Fe–CO), 1786 s (μ-CO), 1721 m (C=S), 1687 m, 1645 m (C=O), 1618 m, 1591 m (C=C). $^1$H-NMR (270 MHz, $CD_2Cl_2$): $\delta = 1.34$ ($CH_3$), 3.17, 3.22 (s, 6H, N–$CH_3$), 3.66 (m, 2H, $CH_2$), 4.85 (m, 10H, FeCp). $C_{22}H_{22}Fe_2N_2O_5S \cdot 1.9CH_2Cl_2$ (699.56): calc. C 41.03 H 3.72 N 4.01; Found C 41.04 H 4.65 N 4.81.

### 4.3. General procedure for the preparation of *10–13*

To a stirred solution of 1,3-dimethyl-barbituric acid **2** in THF two equivalents of $NEt_3$ were added. After 1 h stirring at room temperature two equivalents of the cationic metal complex, suspended in THF, were added. After stirring for another 2 h the solvent was evaporated under reduced pressure. The residue was extracted three times with 15 ml of diethyl ether to remove the ammonium salt. The combined organic layers were evaporated in vacuo, the residue was dissolved in $CH_2Cl_2$ and filtered through celite. The clear solution was concentrated in vacuo to about 3 ml. With 40 ml of pentane the products **10–13** were precipitated and centrifugated off. The residue was washed with pentane and dried in vacuo at 60°C for several hours.

(**10**): 94 mg (0.6 mmol) of 1,3-dimethylbarbituric acid **2** in 10 ml of THF, 0.22 ml (1.6 mmol) of $NEt_3$ and 367 mg (1.2 mmol) of [($\eta^5$-$C_6H_7$)$Fe(CO)_3$]$BF_4$ were used. Slow evaporation of a solution of **10** in $CH_2Cl_2$ gave crystals, suitable for X-ray analysis. Light yellow powder; yield 75%. IR (KBr): $\tilde{\nu} = 2043$ cm$^{-1}$ vs, 1971 vs (Fe–CO), 1743 m, 1679 s (CO), 1633 m (C=C). $^1$H-NMR (400 MHz resp. 270 MHz, $CDCl_3$ resp. $CD_2Cl_2$): $\delta = 1.56$, (m, 1H, 6*exo*-$C_6H_7$), 1.91 (ddd, 1H, 6′*endo*-$C_6H_7$), 2.16 (m, 1H, $^2J_{6'endo} = 12.9$ Hz, 6′*exo*-$C_6H_7$), 2.42 (ddd, $^3J_1 = 6.2$ Hz, $^3J_3 = 3.4$ Hz, $^4J_4 = 1.3$ Hz, 2-$C_6H_7$), 2.67 (m, 1H, 2′-$C_6H_7$), 2.83 (ddd, 1H, $^3J_{6endo} = 10.4$ Hz, $^3J_{6exo} = {}^3J_2 = 3.7$ Hz, 1-$C_6H_7$), 2.91 (ddd, 1H, 1′-$C_6H_7$), 3.01 (m, 1H, 5-$C_6H_7$), 3.04 (m, 1H, 5′-$C_6H_7$), 3.27, 3.29 (s, 6H, N–$CH_3$), 3.35 (s, 6H, N–$CH_3'$), 5.0 (m, 2H, 3,3′-$C_6H_7$), 5.25 (m, 2H, 4,4′-$C_6H_7$). $^{13}$C-NMR (67.8 MHz, $CD_2Cl_2$): $\delta = 24.6$, 25.6 (6,6′-$C_6H_7$), 28.3, 28.48, 28.53 (N–$CH_3$), 46.0, 47.1 (1,1′-$C_6H_7$), 58.2, 58.67, 58.68, 59.7 (2,2′,5,5′-$C_6H_7$), 62.4, 63.3 (C-5), 83.8, 85.2, 85.9, 86.2 (3,3′,4,4′-$C_6H_7$), 151.1 (C=O), 169.6, 169.8, 170.7 (C=O), 211.4, 211.5 (Fe–CO). Diastereomeric ratio 2.2/1; m.p. 190°C. $C_{24}H_{20}Fe_2N_2O_9$ (592.12): calc. C 48.68 H 3.40 N 4.73; Found C 48.53 H 3.05 N 4.70 (Fig. 1).

(**11**): 94 mg (0.6 mmol) of 1,3-dimethylbarbituric acid **2** in 5 ml of THF, 0.22 ml (1.6 mmol) of $NEt_3$ and 384 mg (1.2 mmol) of [($\eta^5$-$C_7H_9$)$Fe(CO)_3$]$BF_4$ in 20 ml of THF were used. Crystals for X-ray diffraction were obtained from a $CH_2Cl_2$/pentane mixture after 3 days.

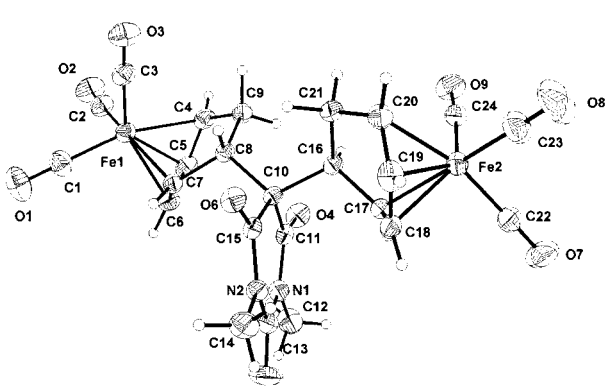



Fig. 1. Molecular structure of **10** in the crystal. Selected bond lengths (Å) and angles (°): Fe1–C1 1.781(5), Fe1–C2 1.785(4), Fe1–C3 1.768(4), Fe1–C6 2.050(4), Fe1–C7 2.109(3), C1–O1 1.136(5), C8–C10 1.571(4),C1–Fe1–C2 93.0(2), C8–C10–C16 112.7(3).

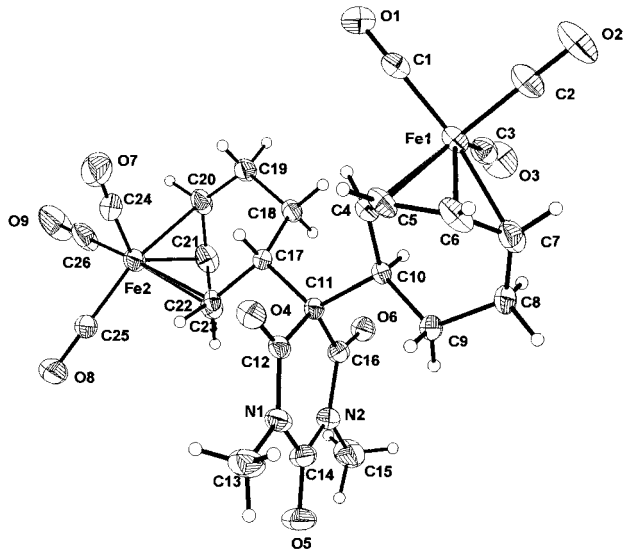



Fig. 2. Molecular structure of **11** in the crystal. Selected bond lengths (Å) and angles (°): Fe1–C1, 1.783(8), Fe1–C2 1.785(6), Fe1–C3 1.780(7), Fe1–C4 2.135(5), Fe1–C5 2.057(5), O1–C1 1.132(9), O2–C2 1.147(7), O3–C3 1.131(7), C10–C11 1.588(6), C1–Fe1–C2 91.8(3), C17–C11–C10 114.5(4).

Light yellow powder; yield 75%. IR (KBr): $\tilde{\nu} = 2047$ $cm^{-1}$ vs, 1970 vs (Fe–CO), 1744 m, 1682 s (CO), 1630 m (C=C). $^1$H-NMR (270 MHz, $CDCl_3$ resp. $CD_2Cl_2$): $\delta = 0.79–0.96$, 1.18–1.26 (m, 4H, 7,7′*exo*,*endo*-$C_7H_9$), 1.80–2.24 (m, 2H, 6,6′*exo*,*endo*-$C_7H_9$), 2.48 (m, 1H, 2-$C_7H_9$), 2.81 (m, 1H, 5-$C_7H_9$), 2.95–3.11 (m, 4H, 1,1′,2′,5′-$C_7H_9$), 3.20, 3.27, 3.28 (s, 6H, N–$CH_3$), 5.22–5.48 (m, 4H, 3,3′,4,4′-$C_7H_9$). $^{13}$C-NMR (67.8 MHz, $CD_2Cl_2$): $\delta = 25.4$, 26.4 (7,7′-$C_7H_9$), 28.8, 29.0 (6,6′-$C_7H_9$), 28.0, 28.2 (N–$CH_3$), 46.0, 46.8 (1,1′-$C_7H_9$), 55.8, 58.1, 58.8 (2,2′,5,5′-$C_7H_9$), 65.7, 65.9 (C-5), 88.0, 89.1, 89.3, 89.4 (3,3′,4,4′-$C_7H_9$), 151.1, 151.2 (C=O), 169.8, 170.1, 170.6 (C=O), 211.1 Fe–CO). Diastereomeric ratio 1.5/1; m.p. 176°C. $C_{26}H_{24}Fe_2N_2O_9$ (620.18): calc. C 50.35 H 3.90 N 4.52; Found C 50.42 H 3.93 N 4.46 (Fig. 2).

(**12**): 45 mg (0.29 mmol) of 1,3-dimethylbarbituric acid **2** in 5 ml of THF, 0.11 ml (0.76 mmol) of $NEt_3$ and 180 mg (0.57 mmol) of $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]BF_4$ in 40 ml of THF were used. Filtration over celite led to decomposition. The product was purified by dissolution in $CH_2Cl_2$ and precipitation with pentane. Red powder; yield 52%. IR (KBr): $\tilde{\nu} = 1972$ $cm^{-1}$ vs, 1906 vs, 1887 vs (Cr–CO), 1745 w, 1680 s (CO), 1632 m (C=C). $^1$H-NMR (400 MHz, $CD_2Cl_2$): $\delta = 2.03$ (br, 2H, 1,1′-$C_7H_7$), 3.21 (s, 6H, N–$CH_3$), 4.89 (m, 4H, 2,2′,7,7′-$C_7H_7$), 5.93 (m, 2H, 3,3′-$C_7H_7$), 6.18 (m, 2H, 6,6′-$C_7H_7$), 6.68 (m, 4H, 4,4′,5,5′-$C_7H_7$). $C_{26}H_{20}Cr_2N_2O_9 \cdot 1/4CH_2Cl_2$ (629.68): calc. C 50.07 H 3.28 N 4.45; Found C 50.30 H 3.61 N 3.75.

(**13**): 39 mg (0.25 mmol) of 1,3-dimethylbarbituric acid **2**, 40 μl (0.6 mmol) of $NEt_3$ and 146 mg (0.5 mmol) of $[Cp(\eta^2\text{-}C_2H_4)Fe(CO)_2]BF_4$ in 15 ml $CH_2Cl_2$ were used. Filtration through Celite gave a clear solution which was evaporated to dryness. Crystals were grown in a $CH_2Cl_2$/pentane mixture. Yellow powder; 75% yield. IR (KBr): $\tilde{\nu} = 2009$ $cm^{-1}$ vs, 1940 vs (Fe–CO), 1680 s, 1674 s (CO). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta = 0.86$ (m, 4H, FeC$\underline{H}_2$–), 2.05 (dd, $^3J_{AX} =$ 10.8 Hz, $^3J_{A'X} = 7.4$ Hz, 4H, $FeCH_2C\underline{H}_2$), 3.34 (s, 6H, N–$CH_3$), 4.70 (s, 10H, Cp). $^{13}$C-NMR (100.4 MHz, $CDCl_3$): $\delta = 8.9$ (Fe$\underline{C}H_2$–), 28.3 (N–$CH_3$), 47.5 ($FeCH_2\underline{C}H_2$–), 64.8 (C-5), 85.5 (Fe–Cp), 152.0, 172.8 (C=O), 216.9 (Fe–CO). m.p. 145°C. $C_{24}H_{24}Fe_2N_2O_7 \cdot 1/8$ $CH_2Cl_2$ (574.77): calc. C 50.41 H 4.25 N 4.87; Found C 50.57 H 4.01 N 4.76 (Fig. 3).

### 4.4. General procedure for the preparation of *14* and *15*

To a solution of 1,3,-dimethyl-2-thio-barbituric acid **3** in THF a slight excess of $NEt_3$ was slowly added. After stirring for 1 h the cationic metal complex was added and stirring for another 2 h the THF was removed in vacuo. The residue was taken up in $Et_2O$. Insoluble $HNEt_3BF_4$ was centrifugated off. The solvent was evaporated, the residue was washed once with 5 ml of pentane and dried in vacuo for several hours.

(**14**): 52 mg (0.3 mmol) of 1,3-dimethyl-2-thio-barbituric acid **3** in 20 ml of THF, 0.11 ml (0.8 mmol) of $NEt_3$ and 184 mg (0.6 mmol) of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ in 20 ml of THF were used. Yellow powder; yield 90%.-IR (KBr): $\tilde{\nu} = 2046$ $cm^{-1}$ vs, 1969 vs (Fe–CO), 1716 s (C=S), 1682 s (C=O), 1644 m (C=C). $^1$H-NMR (270 MHz, $CDCl_3$): $\delta = 1.56$, (m, 1H, 6exo-$C_6H_7$), 1.80, 1.93 (m, 2H, 6,6′*endo*-$C_6H_7$), 2.12 (m, 1H, 6′*exo*-$C_6H_7$), 2.47, 2.69 (m, 2H, 2,2′-$C_6H_7$), 2.87, 2.94 (m, 2H, 1,1′-$C_6H_7$), 3.01, 3.04 (m, 2H, 5,5′-$C_6H_7$), 3.65 (s, 6H, N–$CH_3$), 3.67, 3.72 (s, 6H, N–$CH_3'$), 5.02–5.32 (m, 4H, 3,3′,4,4′-$C_6H_7$). $^{13}$C-NMR (67.8 MHz, $CDCl_3$): $\delta =$

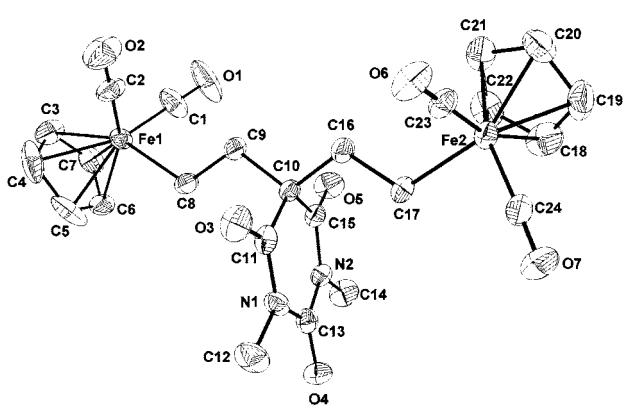



Fig. 3. Molecular structure of **13** in the crystal. Selected bond lengths (Å) and angles (°): Fe1–C1 1.724(8), Fe1–C2 1.723(8), Fe1–C3 2.079(7), Fe1–C8 2.052(5), C9–C10 1.562(6), C1–Fe1–C8 87.4(3), C9–C10–C16 109.6(4).

24.9, 25.9 (6,6′-$C_6H_7$), 35.81, 35.84 (N–$CH_3$), 46.4, 47.4 (1,1′-$C_6H_7$), 57.6, 58.1, 58.3, 59.1 (2,2′,5,5′-$C_6H_7$), 63.5, 64.4 (C-5), 83.8, 85.1, 85.7, 86.0 (3,3′,4,4′-$C_6H_7$), 168.4, 169.3 (C=O), 180.1 (C=S), 211.0, 211.1 (Fe–CO). Diastereomeric ratio: 2.0/1. $C_{24}H_{20}Fe_2N_2O_8S$ (608.19): calc. C 47.40 H 3.31 N 4.61; Found C 47.63 H 3.13 N 4.55.

(**15**): 52 mg (0.3 mmol) of 1,3-dimethyl-2-thio-barbituric acid **3** in 20 ml of THF, 0.11 ml (0.8 mmol) of $NEt_3$ and 192 mg (0.6 mmol) of $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]BF_4$ in 20 ml of THF were used. Yellow powder; yield 84%.-IR (KBr): $\tilde{\nu}$ = 2047 $cm^{-1}$ vs, 1969 vs (Fe–CO), 1715 m (C=S), 1682 s (C=O), 1632 m (C=C). $^1$H-NMR (270 MHz, $CDCl_3$): $\delta = 0.80$ (ddd, 1H, $^2J_{7endo} = 23.0$ Hz, $^3J_1 = 12.3$ Hz, $^3J_6 = 4.0$ Hz, 7*exo*-$C_7H_9$), 0.97 (m, 1H, 7*endo*-$C_7H_9$), 1.15 (m, 2H, 7′*exo*,*endo*-$C_7H_9$), 1.87 (ddd, 2H, $^2J_{6endo} = 16.9$ Hz, $^3J_{7endo} = {}^3J_5 = 3.7$ Hz, 6,6′*exo*-$C_7H_9$), 2.05 (m, 2H, 6,6′*endo*-$C_7H_9$), 2.45 (m, 1H, 2-$C_7H_9$), 2.85 (m, 1H, 2′-$C_7H_9$), 2.99-3.28 (m, 4H, 1,1′,5,5′-$C_7H_9$), 3.59 (s, 6H, N–$CH_3$), 3.66, 3.67 (s, 6H, N–$CH_3$), 5.24 (m, 2H, 3,3′-$C_7H_9$), 5.49 (m, 2H, 4,4′-$C_7H_9$). $^{13}$C-NMR (67.8 MHz, $CD_2Cl_2$): $\delta = 25.4$, 26.4 (7,7′-$C_7H_9$), 28.8, 29.0 (6,6′-$C_7H_9$), 35.1, 35.4 (N–$CH_3$), 46.9, 47.8 (1,1′-$C_7H_9$), 55.6, 55.8, 58.1, 58.8 (2,2′,5,5′-$C_7H_9$), 67.0 (C-5), 89.0, 89.4, 89.5 (3,3′,4,4′-$C_7H_9$), 168.6 (C=O), 180.5 (C=S), 211.1 Fe–CO). Diastereomeric ratio: 3.5/1; m.p. 141°C; $C_{26}H_{24}Fe_2N_2O_8S$ (636.24): calc. C 49.08 H 3.80 N 4.40; Found C 49.14 H 4.03 N 4.41.

### 4.5. X-ray diffraction analyses

Data collection: Siemens P4 Diffractometer, Mo–$K_\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator, cell constants from 25 centred reflections, $\omega$–$2\theta$-scan, intensity of three standard reflections checked every two hours. Structure solution by SHELXL-93 and refinement by SHELXL-97 (G.M. Sheldrick, University of Göttingen, Germany), nonhydrogen atoms refined anisotropically. For **10** hydrogen positions were refined freely, but with the isotopic temperature factors fixed at $U_H = kU_{eq}$ of the adjacent carbon atom, with $k = 1.2$ for the olefinic carbon atoms and $k = 1.5$ for the rest. For **11** and **13** hydrogen positions were calculated according to the riding model with the isotropic temperature factors set to $U_H = kU_{eq}$ of the adjacent carbon atom with $k = 1.2$, 1.3 or 1.5, depending on the hybridization of the carbon atom (Table 3).

Table 3
Crystal data and structure refinement for **10, 11** and **13**

| Compound number | **10** | **11** | **13** |
|---|---|---|---|
| Empirical formula | $C_{24}H_{20}O_9Fe_2N_2$ | $C_{26}H_{24}O_9Fe_2N_2$ | $C_{24}H_{24}O_7Fe_2N_2$ |
| Formula weight | 592.12 | 620.18 | 564.16 |
| Temperature (K) | 293(2) | 293(2) | 293(2) |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ |
| *Unit cell dimensions* | | | |
| $a$ (Å) | 8.684(1) | 11.320(2) | 9.103(1) |
| $b$ (Å) | 11.196(1) | 11.858(2) | 12.528(1) |
| $c$ (Å) | 14.315(1) | 12.342(2) | 22.647(2) |
| $\alpha$ (°) | 99.46(1) | 92.15(1) | 90 |
| $\beta$ (°) | 101.65(1) | 113.81(1) | 101.43(1) |
| $\chi$ (°) | 106.88(1) | 91.77(1) | 90 |
| Volume (Å$^3$) | 1266.9(2) | 1512.7(4) | 2531.5(4) |
| $Z$ | 2 | 2 | 4 |
| $D_{calc.}$ (g $cm^{-3}$) | 1.552 | 1.362 | 1.480 |
| μ (Mo–$K_\alpha$) ($mm^{-1}$) | 1.200 | 1.008 | 1.191 |
| $F$(000) | 604 | 636 | 1160 |
| Crystal size (mm) | $0.375 \times 0.25 \times 0.15$ | $0.40 \times 0.33 \times 0.05$ | $0.12 \times 0.23 \times 0.13$ |
| $2\theta$ Range (°) | 3.92–50 | 4.12–50 | 3.66–50 |
| Index ranges | $\pm h$, $\pm k$, $\pm l$ | $-h$, $\pm k$, $\pm l$ | $+h$, $+k$, $\pm l$ |
| Reflections collected | 7803 | 6165 | 5883 |
| Independent reflections | 3915 [$R_{int} = 0.0353$] | 5297 [$R_{int} = 0.0378$] | 4453 [$R_{int} = 0.0416$] |
| Absorption correction | N/A | N/A | N/A |
| Data/parameters | 3915/394 | 5297/352 | 4453/316 |
| Goodness-of-fit on $F^2$ | 1.031 | 0.985 | 0.952 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0382$, $wR_2 = 0.0861$ | $R_1 = 0.0686$, $wR_2 = 0.1660$ | $R_1 = 0.0620$, $wR_2 = 0.0935$ |
| $R$ indices (all data) | $R_1 = 0.0600$, $wR_2 = 0.0971$ | $R_1 = 0.1199$, $wR_2 = 0.1905$ | $R_1 = 0.1585$, $wR_2 = 0.1194$ |
| Largest difference peak and hole (e Å$^{-3}$) | 0.236 and −0.335 | 0.618 and −0.493 | 0.327 and −0.255 |

## 5. Supplementary material

Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the depository numbers 112437 (**10**), 112436 (**11**), 112435 (**13**).

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