

Chiral diazadiene and β -ketoimine ligands from the reaction of N,N' -bis-aryl-oxalimidoylchlorides with (*S*)-prolinol and their reactivity towards iron carbonyls

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Abstract

N,N' -Bis-aryl-oxalimidoylchlorides react with (*S*)-prolinol to give chiral N,N' -bis-aryl-tetrahydropyrrolo-[2,1-c][1,4]oxazine-3,4-diylienediamines. These compounds exhibit a 1,3-diazadiene subunit which may be reacted either with $\text{Fe}(\text{CO})_5$ under photochemical or with $\text{Fe}_2(\text{CO})_9$ under thermal reaction conditions to yield dinuclear complexes of the general formula (ligand) $\text{Fe}_2(\text{CO})_6$. In these complexes an unsymmetrical binding mode of the $\text{Fe}_2(\text{CO})_6$ moiety is realized. One of the iron atoms is coordinating both imine nitrogen atoms, whereas the second iron atom is connected to one of the C–N double bonds in a side-on fashion. If the aromatic substituent of the oxalimidoylchloride is $p\text{-OCH}_3\text{-C}_6\text{H}_4$ the reaction with $\text{Fe}(\text{CO})_5$ or $\text{Fe}_2(\text{CO})_9$ produces a mixture of diastereomers. In all other cases the (*S*)-configuration of the starting material is retained. If the aromatic substituent is $p\text{-Br-C}_6\text{H}_4$ the corresponding tetrahydropyrrolo-[2,1-c][1,4]oxazine derivative undergoes a quantitative rearrangement reaction to produce the isomeric 2-(4-bromophenyl)-3-(4-bromophenylimino)-tetrahydropyrrolo[1,2-a]pyrazine-4-one. The reaction of this ligand with $\text{Fe}(\text{CO})_5$ or $\text{Fe}_2(\text{CO})_9$ ends up in the formation of a complex of the general formula [(ligand) $_3\text{Fe}][(\mu_2\text{-H})\text{Fe}_3(\text{CO})_{11}]_2$ consisting of an octahedrally coordinated Fe^{2+} and two triangular $[(\mu_2\text{-H})\text{Fe}_3(\text{CO})_{11}]$ anions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Diazadiene; β -Ketoimine; Bis-aryl-oxalimidoylchloride; (*S*)-Prolinol; Iron carbonyls

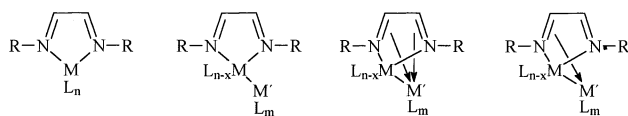
1. Introduction

(Butadiene) $\text{Fe}(\text{CO})_3$ complexes are widely used as starting materials in organic synthesis [1]. In these compounds the organometallic moiety may act as an activating as well as a stereodirecting group, since it efficiently shields one side of the conjugated system. So if a prochiral diene is used, stereoselective reactions at the coordinated substrate may be achieved. In contrast, not much information is available on the chemistry of the nitrogen analogs of (butadiene) $\text{Fe}(\text{CO})_3$ complexes. Although a lot of (1-azadiene) $\text{Fe}(\text{CO})_3$ compounds are described in the literature, up to now only their reactivity towards organolithium reagents has been investigated.

These reactions always proceed via the attack of the organolithium reagent at one of the CO ligands. Depending on the organic residue of the organolithium reagent either pyrrole derivatives [2] or the intramolecular formation of Fischer type carbene complexes is observed [3]. Complexes of the form (1-azadiene) $\text{Fe}(\text{CO})_3$ have also been used as reagents that allow the transfer of $\text{Fe}(\text{CO})_3$ groups to butadiene ligands in a very effective way under mild reaction conditions [4]. In addition, only a few compounds have been structurally characterized [5]. Very recently it was shown that 1-azadienes may be catalytically activated by $\text{Ru}_3(\text{CO})_{12}$ to insert CO into the C–H bond in the β -position with respect to the imine bond which after a subsequent nucleophilic attack of the imine nitrogen at the carbonyl carbon produces 1,5-dihydropyrrol-2-one derivatives [6]. If at the same time ethylene is also present in the reaction mixture the thermodynamically less stable 1,3-dihydropyrrol-2-one derivatives may be obtained [7].

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Scheme 1. Binding modes of 1,4-diazadiene ligands in mono- and dinuclear transition metal complexes (M = Group 8 metal).

Since the preparation of the first (1,4-diazadiene)Fe(CO)₃ complex in 1967, a number of derivatives have been synthesized and structurally characterized [8]. In contrast to the above-mentioned butadiene and 1-azadiene complexes in which the iron atom coordinates the conjugated π -system of the ligand and thus is situated beneath the plane of the ligand, in (diazadiene)Fe(CO)₃ compounds the iron atom interacts with the imine nitrogen lone pairs thus building up a planar five-membered FeC₂N₂ ring. In transition metal complexes of higher nuclearity containing diazadiene ligands, three different binding modes have been observed. In all compounds one of the metal atoms is again coordinated by the two imine nitrogen lone pairs in analogy to the mononuclear complexes. The second metal atom is either not coordinated to the ligand at all [9] or it interacts with both the C–N double bonds in terms of an η^4 -coordination [10] or it just interacts with one of the imine subunits thus producing an unsymmetrical binding mode of the dinuclear transition metal fragment [9a,b,10k,11] (Scheme 1).

Both mono- and dinuclear diazadiene iron carbonyl complexes may be reacted with alkynes to produce various nitrogen containing heterocycles by cycloaddition reactions [12].

To our knowledge there are no reactions of iron carbonyls with chiral diazadiene ligands published up to now. Some of us recently showed that starting from (*S*)-prolinol chiral ligands with diazadiene substructures may be obtained in only a few synthetic steps [13].

In this paper we wish to report the synthesis and spectroscopical as well as the structural characterization of a number of new chiral diazadiene and β -ketoimine ligands derived from (*S*)-prolinol and various *N,N'*-bis-aryl-oxalimidoylchlorides and their reactivity towards iron carbonyls. The molecular structures of the new

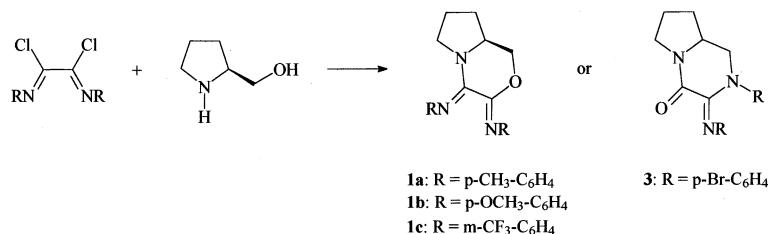
complexes are also determined by spectroscopic methods as well as by X-ray structure analysis.

2. Results and discussion

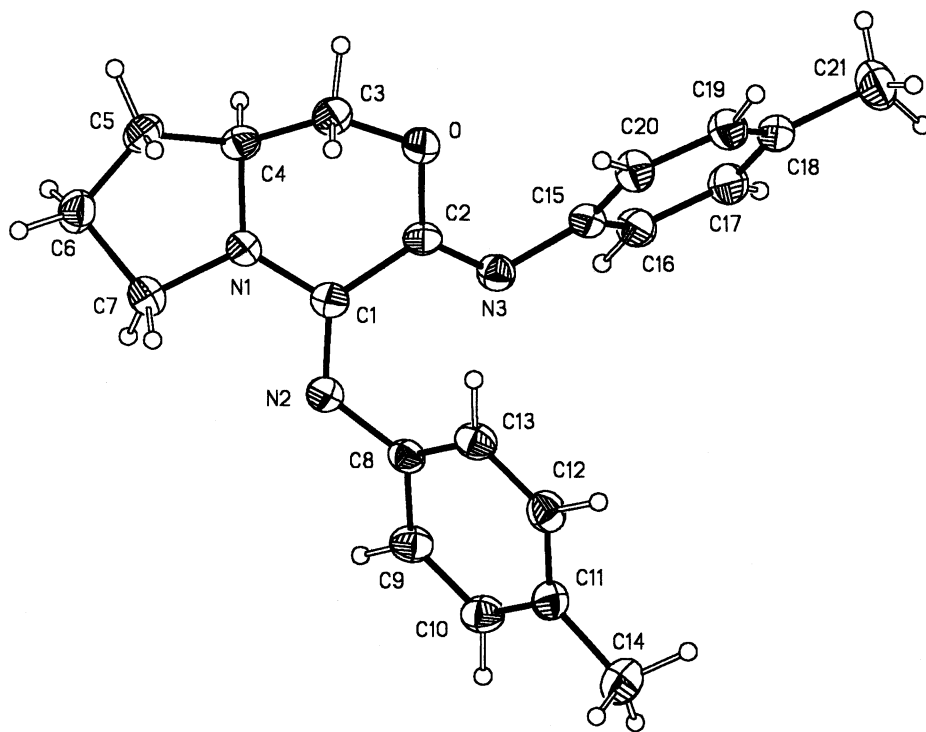
2.1. Synthesis and characterization of the ligands

Scheme 2 shows the synthesis of the ligands **1a–c** and **3**. The reaction of *N,N'*-bis-aryl-oxalimidoylchlorides with (*S*)-prolinol leads to the formation of chiral *N,N'*-bis-aryl-tetrahydropyrrolo-[2,1-c][1,4]oxazine-3,4-diylidenediamines **1a–c** in acceptable yields. The synthesis of **1a** has already been published [13]. Surprisingly variation of the aryl group to *p*-Br-C₆H₄ changes the reaction pathway dramatically. The formation of the ligands **1a–c** required 2 days of stirring in toluene at room temperature, whereas the reaction of the corresponding *p*-Br-C₆H₄ derivative with prolinol made it necessary to keep the reaction mixture at reflux temperature for 4 days to obtain **3** in quite moderate yield. Compound **3** is an isomer of the expected tetrahydropyrrolo-[2,1-c][1,4]oxazine derivative and is best described as a 2-(4-bromophenyl)-3-(4-bromophenylimino)-tetrahydropyrrolo[1,2-a]pyrazine-4-one. The formation of this product may be explained by the assumption that first the expected product of type **1** is formed. A subsequent Chapman-like rearrangement then may lead to the pyrazine system which finally undergoes a transacylation reaction leading to **3**. So in general the reaction of the *p*-Br-C₆H₄ derivative with prolinol yields a 1-oxa-4-azadiene in contrast to the other oxalimidoylchlorides which produce 1,4-diazadiene systems.

The tetrahydropyrrolo-[2,1-c][1,4]oxazine core of **1a–c** shows characteristic signals in the ¹³C-NMR spectra which are nearly not affected by the nature of the aromatic groups attached to the imine nitrogen atoms. So for the methylene groups resonances at about δ = 24, 28, 47 and 71 are observed with the signals at lower field representing the methylene groups *ortho* to the pyrrole nitrogen and the oxazine oxygen atom, respectively. The tertiary carbon atom of the pyrrole ring gives rise to a signal at δ = 56 and the two quaternary



Scheme 2. Synthesis of the ligands **1a–c** and **3**.

Fig. 1. Molecular structure of **1a**.

imine carbon atoms show two signals at about $\delta = 142$ – 145 . The ^{13}C -NMR spectrum of **3** is quite similar concerning the carbon atoms which form the tetrahydropyrrolo[1,2-*a*]pyrazine-4-one ring system. The only difference being the signal representing the methylene moiety ortho to the pyrazine nitrogen atom at $\delta = 54.6$ and of course the quaternary carbonyl carbon atom at $\delta = 154.4$.

By recrystallization from diethylether (**1a–c**) or toluene- CHCl_3 (**3**) it was possible to obtain crystals suitable for X-ray structure determination. The molecular structure of **1a** is shown in Fig. 1; the numbering scheme has been adopted for the molecular structures of **1b** and **1c**. Selected bond lengths and angles of **1a–c** are depicted in Table 1. As expected, the variation of aromatic substituents at the imine nitrogen atoms does not affect the bond lengths and angles inside the tetrahydropyrrolo-[2,1-*c*][1,4]oxazine core. The single bond between the pyrrole nitrogen atom N1 and the imine carbon atom C1 is quite short corresponding to the sp^2 hybridization of C1 and the electronic effect of the imine moiety itself. Both nitrogen carbon bonds of the imine groups clearly are double bonds with that of C1 to N2 being about 3 pm longer than C2–N3 for all compounds **1a–c**.

The molecular structure of (*S*)-**3** is shown in Fig. 2; selected bond lengths and angles are summarized in Table 2. The bond lengths and angles are all of expected values again with the carbon nitrogen bonds of the pyrrole as well as of the pyrazine nitrogen atoms to

the imine carbon atoms being quite short due to the same facts that were already mentioned above. The most interesting fact in the structural analysis of **3** is that the intensity data clearly show that the crystal was a racemic twin. So obviously during one of the rear-

Table 1
Selected bond lengths (pm) and angles ($^\circ$) of **1a–c**

	1a	1b	1c
<i>Bond lengths</i>			
N1–C1	136.2(3)	133.6(9)	134.1(5)
C1–C2	151.2(3)	150(1)	152.8(5)
C2–O1	136.6(2)	135.9(7)	135.3(5)
O1–C3	145.7(3)	144.1(8)	145.1(5)
C3–C4	150.3(3)	151(1)	149.5(6)
C4–N1	147.4(3)	147.5(8)	146.2(5)
C1–N2	129.9(2)	129.8(8)	128.5(5)
C2–N3	126.7(3)	126.4(8)	125.9(5)
<i>Bond angles</i>			
N1–C1–C2	114.6(2)	113.0(6)	115.2(3)
C1–C2–O1	118.0(2)	118.6(6)	118.4(3)
C2–O1–C3	117.1(2)	115.8(6)	117.3(3)
O1–C3–C4	110.4(2)	111.2(5)	109.9(4)
C3–C4–N1	109.0(2)	107.6(6)	108.7(3)
C4–N1–C1	122.2(2)	122.4(6)	122.4(3)
N1–C1–N2	118.7(2)	119.0(7)	120.3(3)
C2–C1–N2	126.6(2)	127.8(7)	124.5(3)
C1–N2–C8	124.6(2)	121.3(6)	123.1(3)
C1–C2–N3	119.1(2)	119.7(6)	117.3(3)
O1–C2–N3	122.8(2)	121.7(7)	124.3(3)
C2–N3–C15	123.1(2)	123.2(5)	126.8(3)

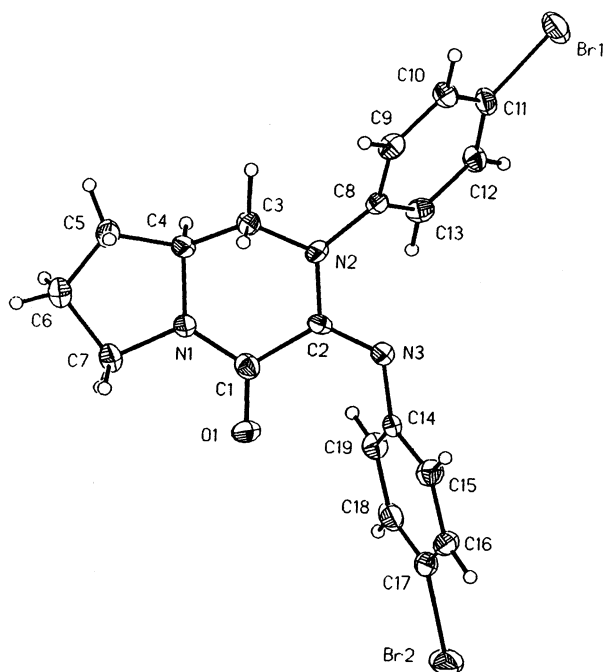


Fig. 2. Molecular structure of (S)-3.

rangement processes in the formation of **3** racemisation of the prolinol substructure must have taken place.

2.2. Synthesis and characterization of the iron carbonyl complexes

Scheme 3 shows the reactions of **1a–c** and **3** with iron carbonyls. Both $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}(\text{CO})_5$ may be used in these complexation reactions. Thermal activation of $\text{Fe}_2(\text{CO})_9$ and photochemical activation of $\text{Fe}(\text{CO})_5$ give the same products with the yields being much better in the latter case.

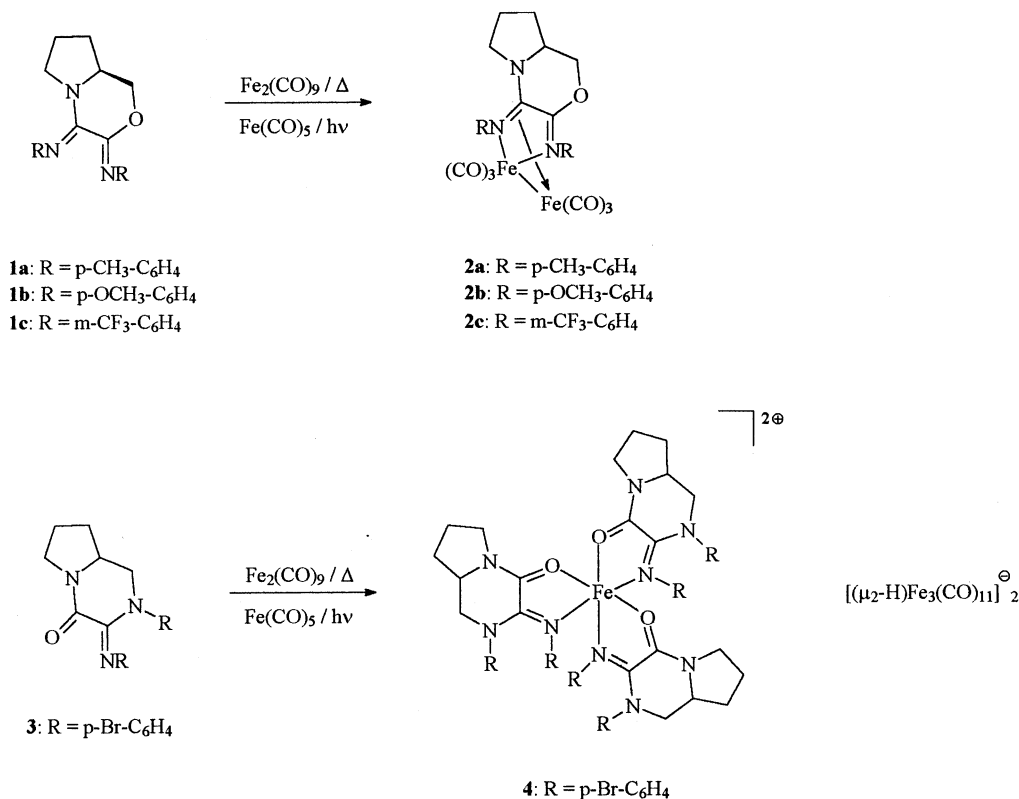
The reaction of the chiral diazadiene ligands **1a–c** with iron carbonyls produces the dinuclear complexes **2a–c**. The ^{13}C -NMR spectra of **2a–c** clearly indicate that only one of the C–N double bonds of the diazadi-

ene ligand is coordinated by metal atoms, since one of the imine carbon atoms shows a signal at about $\delta = 93$ whereas the other quaternary imine carbon atom still gives a resonance at very low field at $\delta = 161$. The chemical shift of the carbon atoms of the tetrahydropyrrolo-[2,1-c][1,4]oxazine core does not change significantly upon coordination of the ligand. The CO ligands of **2a–c** show more than one signal, meaning that the structure is not flexible enough to exchange all iron and CO positions fast enough to make them equivalent on the NMR time-scale. In contrast to the ^{13}C -NMR spectra of **2a** and **2c**, the spectrum of **2b** shows the presence of two diastereomers in solution. Together with the result of the X-ray structure analysis (see below) this proves that racemisation at the asymmetric carbon atom of the pyrrole ring has occurred. Since ^1H -NMR measurements of the ligand **1b** together with various shift reagents gave no evidence for racemisation during the synthesis of the ligand, this process must have taken place during the formation of the complex. Although there are quite a lot of reactions reported in the literature where $\text{Fe}_2(\text{CO})_9$ might induce C–H activation reactions at imine ligands, these reactions normally take place at aromatic carbon atoms [14]. So it is reasonable that in the case of **1b** the effect of the neighboring pyrrole nitrogen atom as well as the electronic effect of the *p*-OMe groups may increase the acidity of the hydrogen at the asymmetric carbon atom to the extent that an iron carbonyl fragment may activate this bond and thus induce racemisation.

By recrystallization of **2a** and **2b** from mixtures of light petroleum– CH_2Cl_2 it was possible to obtain crystals suitable for X-ray structure determination. Fig. 3 shows the result of the structural analysis of **2a**; the numbering scheme has also been adopted for **2b**. The most important bond lengths and angles are summarized in Table 3, which clearly shows that the variation of the aromatic groups does not have a drastic effect on the bonding parameters. The iron–iron bond lengths are in the range typical for single bonds. One of the iron tricarbonyl fragments (Fe1) is coordinated by the two lone pairs of the imine nitrogen atoms. The other $\text{Fe}(\text{CO})_3$ group (Fe2) interacts with one of the imine C=N double bonds in a side-on binding mode. This is one of the three types of binding modes in dinuclear transition metal complexes of diazadiene ligands, other examples were reported in [9a,9b,10k,11]. The iron nitrogen bond of Fe1 to the nitrogen atom of the imine group being noncoordinated (N2) is about 6 pm longer than the other one (Fe1–N3). The bond lengths inside the ligand do not differ very much compared to those of the free ligand, with the exception of the imine double bond $\text{C2}=\text{N3}$, which is elongated due to the side-on coordination of one of the $\text{Fe}(\text{CO})_3$ moieties for about 13 pm. The structure analysis of **2b** in accordance with the observations made in the ^{13}C -NMR spectrum

Table 2
Selected bond lengths (pm) and angles ($^\circ$) of **3**

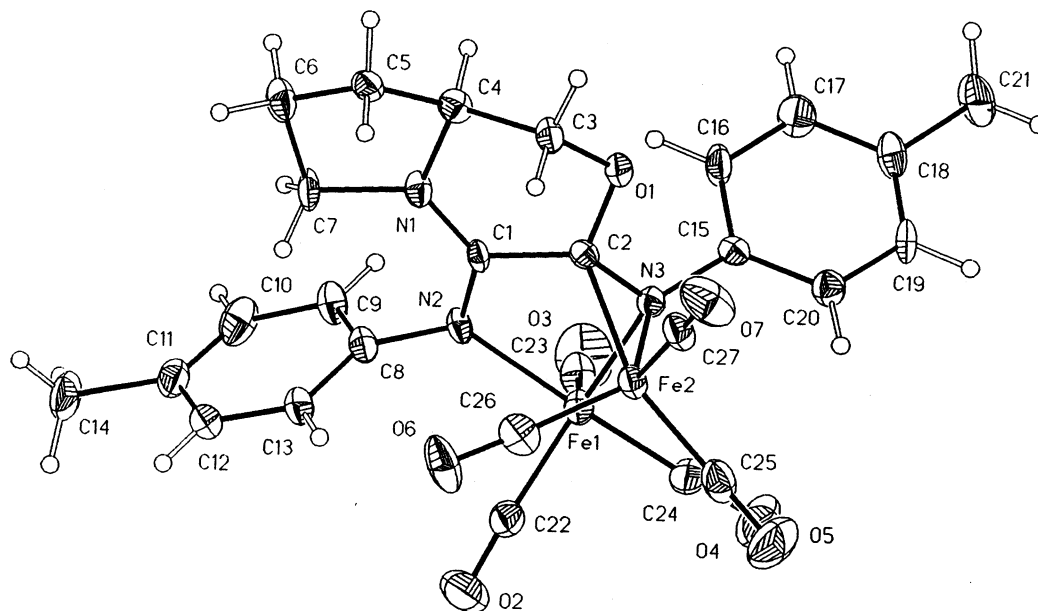
Bond lengths			
N1–C1	136.2(7)	C1–C2	152.7(8)
C2–N2	137.9(7)	N2–C3	149.3(6)
C3–C4	149.6(7)	C4–N1	148.1(7)
C1–O1	121.1(7)	C2–N3	128.7(7)
N3–C14	140.9(7)	N2–C8	142.4(7)
Bond angles			
N1–C1–C2	115.6(5)	C1–C2–N2	117.3(4)
C2–N2–C3	117.6(5)	N2–C3–C4	108.6(4)
C3–C4–N1	108.9(4)	C4–N1–C1	124.2(4)
C1–C2–N3	123.2(5)	N3–C2–N2	119.5(5)
C2–N3–C14	125.2(5)	C2–N2–C8	123.7(4)
C3–N2–C8	118.6(4)		

Scheme 3. Synthesis of the complexes **2a–c** and **4**.

shows the presence of two diastereomers that are statistically disordered in the packing of the crystal. The bond lengths and angles given in Table 3 correspond to the diastereomer with (*S*)-configuration at the asymmetric carbon atom of the pyrrole ring in order to allow a comparison with **2a** which is exclusively (*S*)-

configured since no racemisation processes occurred in the formation of this derivative.

In contrast to **1a–c**, which show a diazadiene substructure, in **3** a β-ketoimine substructure is present. In principle this α, β-unsaturated ligand should be able to interact with iron carbonyl fragments the same way

Fig. 3. Molecular structure of (*S*)-**2a**.

1a–c do. In Scheme 3 the reaction of **3** with $\text{Fe}(\text{CO})_5$ under photochemical and with $\text{Fe}_2(\text{CO})_9$ under thermal reaction conditions is shown. Again the photochemical reaction gives an improved yield compared with the thermal reaction. The only product that may be obtained by column chromatography of the crude reaction mixture is the ionic compound **4**. This compound consists of a cation of the general formula $[\text{Fe}(\text{ligand})_3]^{2+}$ with an iron atom octahedrally surrounded by three ligand molecules in a meridional arrangement. To our knowledge there is no structurally characterized transition metal complex of a β -ketoimine reported in the literature. The anions are two $[(\mu_2\text{-H})\text{Fe}_3(\text{CO})_{11}]^-$ moieties of triangular shape. The hydride signal in the ^1H -NMR spectrum of **4** is in the typical range at $\delta = -13.9$. Carbonylate anions of this type are well known from the reaction of the metal carbonyls with sodium or potassium hydroxide [15]. Fig. 4 shows the molecular structure of the cation in **4**. Since the anions are highly disordered in the crystal the *R*-values are not satisfactory and thus no discussion of bond lengths and angles is possible and Fig. 4 only gives the motif of the cation.

3. Experimental

3.1. General

All procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents. Chromatography was carried out 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 $\text{Fe}(\text{CO})_5$ (Aldrich) by irradiation in acetic acid [16]. *N,N'*-Bis-aryl-oxalimidoylchlorides were prepared from the corresponding aromatic amines and oxalylchloride to give the *N,N'*-bis-aryl-oxamides, which were then treated with PCl_5 according to Ref. [13]. IR spectra were recorded on a Perkin–Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes. NMR spectra were recorded on a Bruker AC 200 spectrometer (^1H , 200 MHz with SiMe_4 as internal standard; ^{13}C , 50.32 MHz with CDCl_3 as internal standard). Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. Elemental analyses were carried out at the laboratory of the Institute of Organic and Macromolecular Chemistry, Friedrich Schiller University Jena.

3.2. X-ray crystallographic studies

The structure determinations of **1c** and **2a** were carried out on an Enraf–Nonius CAD4 diffractometer,

those of **1a**, **1b**, **2b**, **3** and **4** were carried out on an Enraf–Nonius Kappa CCD diffractometer, crystal detector distance 25 mm, 180 frames. Both diffractometers used 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 but not 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 [17]. Computations of the structures were carried out with the XPLA program [18] and the molecular illustrations were drawn using the XP program [19]. The crystal and intensity data are given in Table 4.

3.3. Preparation of the ligands **1a–c**

The synthesis of **1a** has been reported in Ref. [13]. The identity and purity of the ligand used in this work was ensured by comparison of the melting point as well as the spectroscopic data with those reported in the literature. In analogy, **1b** and **1c** were prepared by adding a total of 40 mmol triethylamine (3.99 g, 5.50 ml) and 20 mmol (*S*)-prolinol (2.02 g) to a solution of 20 mmol of the corresponding *N,N'*-bis-aryl-oxalimidoylchloride (**1b**: aryl = *p*- $\text{OCH}_3\text{-C}_6\text{H}_4$, 6.77 g; **1c**: aryl = *m*- $\text{CF}_3\text{-C}_6\text{H}_4$, 8.26 g) in 150 ml of toluene. After stirring at room temperature (r.t.) for 2 days the solution was filtered, the solvent evaporated in vacuo and the residue was recrystallized from diethylether. This procedure gave **1b** and **1c** as yellow crystalline solids. Yields: 3.00 g (41.0%) **1b**, 6.01 g (68.1%) **1c**. Melting points: **1b** 141–144°C; **1c** 100–102°C. Analyses Found (Calc.): **1b** $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_3$ C 68.17 (69.02), H 6.62 (6.34), N 11.55 (11.50); **1c** $\text{C}_{21}\text{H}_{17}\text{F}_6\text{N}_3\text{O}$ C 57.14 (57.15), H 4.09 (3.88), N 9.55 (9.52).

3.4. MS and spectroscopic data for **1b**

MS (CI, H_2O) (m/z): 366 [M^+]. IR (CH_2Cl_2 , 298 K) (cm^{-1}): 1674 (vs, C=N), 1615 (vs, br, C=N). ^1H -NMR (CDCl_3 , 298 K) (ppm): 1.36–1.62 (m, 1H, CH_2), 1.84–2.24 (m, 3H, CH_2), 3.49–3.83 (m, 2H, CH_2), 3.70 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 3.83–4.16 (m, 2H, CH, CH_2), 4.22–4.48 (m, 1H, CH_2), 6.40–7.30 (m, 8H, CH). ^{13}C -NMR (CDCl_3 , 298 K) (ppm): 24.0 (CH_2), 28.4 (CH_2), 47.0 (CH_2), 55.3 (CH_3), 55.5 (CH_3), 56.3 (CH), 71.3 (CH_2), 113.5 (CH), 113.6 (CH), 122.3 (CH), 124.6 (CH), 137.6 (C), 142.3 (C), 144.4 (C), 144.9 (C), 154.7 (C), 157.7 (C).

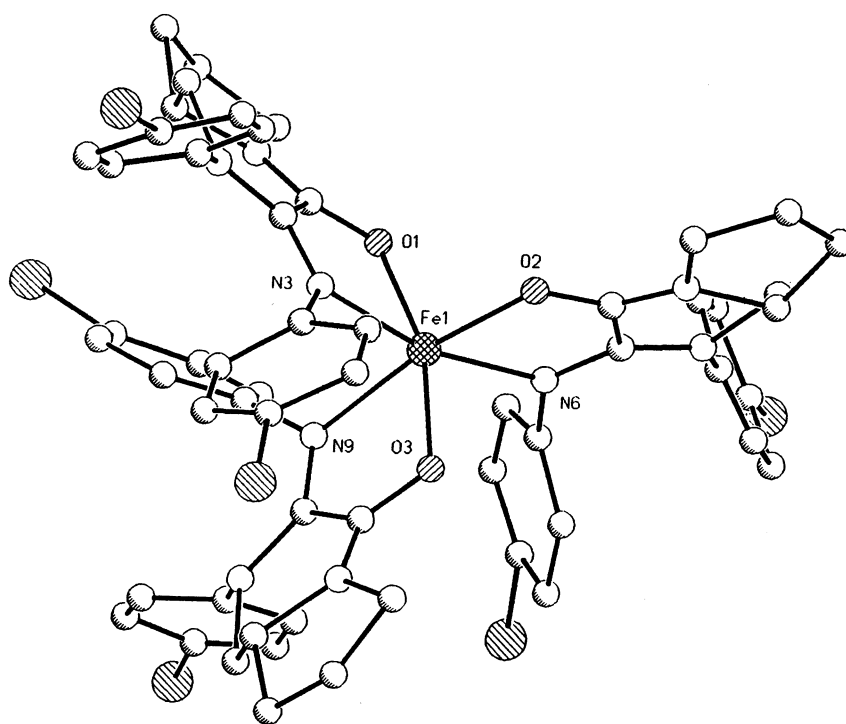
3.5. MS and spectroscopic data for **1c**

MS (CI, H_2O) (m/z): 442 [MH^+], 422 [$\text{M}^+ - \text{F}$]. IR (CH_2Cl_2 , 298 K) (cm^{-1}): 1679 (vs, C=N), 1631 (vs, br, C=N). ^1H -NMR (CDCl_3 , 298 K) (ppm): 1.40–1.82 (m,

Table 3

Selected bond lengths (pm) and angles (°) of **2a** and **2b**

	2a	2b		2a	2b		2a	2b
<i>Bond angles</i>								
Fe1–Fe2	256.5(1)	259.2(9)	N1–C1	132.9(8)	133.6(6)	C4–N1	148.6(8)	148.6(6)
Fe1–N2	201.5(6)	201.5(4)	C1–C2	149.7(9)	149.5(6)	C1–N2	130.4(8)	131.3(6)
Fe1–N3	195.9(6)	196.8(4)	C2–O1	138.4(8)	140.0(5)	C2–N3	139.4(8)	139.7(6)
Fe2–N3	192.6(6)	192.9(4)	O1–C3	143.0(7)	143(1)			
Fe2–C2	202.1(6)	204.5(5)	C3–C4	149.8(9)	146(1)			
<i>Bond lengths</i>								
N2–Fe1–N3	83.3(2)	83.7(2)	Fe1–Fe2–N3	49.3(2)	49.0(1)	C4–N1–C1	122.4(5)	120.2(4)
Fe1–N2–C1	113.7(4)	113.4(3)	Fe2–N3–Fe1	82.6(2)	83.3(2)	N1–C1–N2	129.9(6)	128.9(4)
Fe1–N3–C2	107.3(4)	107.6(3)	N1–C1–C2	117.8(6)	118.2(4)	C2–C1–N2	112.3(6)	112.9(4)
N2–Fe1–Fe2	87.2(2)	86.5(1)	C1–C2–O1	116.9(5)	118.1(4)	C1–N2–C8	123.1(6)	123.8(4)
C2–N3–Fe2	73.0(4)	73.9(3)	C2–O1–C3	110.4(5)	116.2(5)	C1–C2–N3	116.0(6)	116.4(4)
C2–Fe2–Fe1	71.7(2)	71.2(1)	O1–C3–C4	109.9(5)	112.4(8)	O1–C2–N3	115.8(6)	115.5(4)
N3–Fe1–Fe2	48.1(2)	47.7(1)	C3–C4–N1	109.1(6)	110.8(5)	C2–N3–C15	121.0(5)	121.6(4)

Fig. 4. Molecular structure of the cation of complex **4**.

¹H, CH₂), 1.82–2.51 (m, 3H, CH₂), 3.39–3.87 (m, 2H, CH₂), 3.87–4.26 (m, 2H, CH₂, CH), 4.26–4.67 (m, 1H, CH₂), 6.54–7.79 (m, 8H, CH). ¹³C-NMR (CDCl₃, 298 K) (ppm): 23.9 (CH₂), 28.5 (CH₂), 47.2 (CH₂), 56.1 (CH), 71.4 (CH₂), 118.1 (CH, ³J_{CF} = 3 Hz), 118.9 (CH, ³J_{CF} = 4 Hz), 120.9 (CH, ³J_{CF} = 4 Hz), 123.9 (CF₃, ¹J_{CF} = 273 Hz), 124.4 (CF₃, ¹J_{CF} = 272 Hz), 125.1 (CH), 125.4 (CH), 128.7 (CH), 128.8 (CH), 130.5 (C, ²J_{CF} = 32 Hz), 130.7 (C, ²J_{CF} = 32 Hz), 143.4 (C=N), 145.1 (C=N), 151.9 (C).

3.6. Preparation of the complexes **2a–c**

3.6.1. Synthesis via thermal activation

A 1.37 mmol (0.5 g) sample of Fe₂(CO)₉ was stirred together with 1.65 mmol of the corresponding ligand (**1a** 0.55 g; **1b** 0.60 g; **1c** 0.73 g) in 40 ml of *n*-heptane at 50°C for 1.5 h. The yellow suspension turned deep red and a small amount of a red precipitate was formed. After the solvent was evaporated in vacuo the oily residue was dissolved in 10 ml of CH₂Cl₂, 1 g

silanized silica gel was added and the solvent was again evaporated. Chromatography using a mixture of light petroleum (b.p. 40–60°C) and CH₂Cl₂ (**2a** 5:1; **2b** 4:1; **2c** 6:1) as the eluent yielded **2a–c** as deep red solutions. After the solvents were evaporated the crude products were recrystallized from mixture of light petroleum (b.p. 40–60°C) and CH₂Cl₂ at –20°C. Yields: 200 mg (23.7%) **2a**, 180 mg (20.0%) **2b**, 170 mg (17.5%) **2c**.

3.6.2. Synthesis via photochemical activation

In a typical experiment a total of 1 mmol Fe(CO)₅ (196 mg) was irradiated together with an equimolar amount of the corresponding ligand (**1a** 333 mg; **1b** 365 mg; **1c** 441 mg) in 85 ml of THF for 20 min at 0°C. The color of the solution immediately turned deep blue and then changed to deep red. After the solvent was evaporated the residue was dissolved in CH₂Cl₂, 1 g silanized silica gel was added and the solvent was again evaporated. Chromatography with the eluents mentioned above again yielded the compounds **2a–c**. Yields: 410 mg (67.0%) **2a**, 500 mg (77.5%) **2b**, 687 mg (95.3%) **2c**.

2a–c decomposed before their melting points could be determined. Analyses Found (Calc.): **2a** C₂₇H₂₃N₃O₇Fe₂ C 53.06 (52.89), H 3.92 (3.78), N 6.92 (6.85); **2b** C₂₇H₂₃N₃O₉Fe₂ C 49.85 (50.26), H 4.17 (3.59), N 5.84 (6.51); **2c** C₂₇H₁₇F₆N₃O₇Fe₂ C 45.34 (44.97), H 2.85 (2.38), N 5.01 (5.83).

3.7. MS and spectroscopic data for **2a**

MS (FAB) (*m/z*): 614 [MH⁺], 598 [M⁺ – Me], 585 [M⁺ – CO], 557 [M⁺ – 2CO], 529 [M⁺ – 3CO], 501 [M⁺ – 4CO], 473 [M⁺ – 5CO], 445 [M⁺ – 6CO], 417 [C₁₉H₁₉N₃OFe₂⁺], 406 [C₁₈H₂₀N₃OFe₂⁺], 389 [M⁺ – 6CO – Fe], 334 [MH⁺ – 6CO – 2Fe], 307 [C₁₉H₂₁N₃O⁺], 289 [C₁₉H₁₉N₃⁺]. IR (CH₂Cl₂, 298 K) (cm^{–1}): 2049 (vs, CO), 1937 (vs, br, CO). ¹H-NMR (CDCl₃, 298 K) (ppm): 1.20–1.46 (m, 1H, CH₂), 1.46–1.65 (m, 1H, CH₂), 1.65–1.94 (m, 2H, CH₂), 2.19–2.50 (m, 7H, CH₂, CH₃), 2.56–2.79 (m, 1H, CH₂), 3.50–3.74 (m, 2H, CH, CH₂), 4.08–4.25 (m, 1H, CH₂), 6.60–7.46 (m, 8H, CH). ¹³C-NMR (CDCl₃, 298 K) (ppm): 20.8

Table 4
Crystal and intensity data for the compounds **1a–c**, **2a**, **2b** and **3**

	1a	1b	1c	2a	2b	3
Formula	C ₂₁ H ₂₃ N ₃ O	C ₂₁ H ₂₃ N ₃ O ₃	C ₂₁ H ₁₇ F ₆ N ₃ O	C ₂₇ H ₂₃ N ₃ O ₇ Fe ₂	C ₂₇ H ₂₃ N ₃ O ₉ Fe ₂	C ₁₉ H ₁₇ N ₃ OBr ₂
Molecular weight (g mol ^{–1})	333.42	365.42	441.38	613.18	645.18	463.18
Radiation	Mo–K _α	Mo–K _α	Mo–K _α	Mo–K _α	Mo–K _α	Mo–K _α
Monochromator	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite
Temperature (K)	183	183	213	213	183	183
Crystal color	Yellow	Yellow	Yellow	Red	Red	Yellow
Crystal size	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.1	0.6 × 0.3 × 0.2	0.6 × 0.2 × 0.2	0.4 × 0.2 × 0.1	0.4 × 0.1 × 0.1
<i>a</i> (Å)	6.0051(3)	8.225(2)	8.124(2)	8.707(2)	8.4501(3)	11.5415(3)
<i>b</i> (Å)	11.9454(6)	9.515(2)	9.889(2)	13.233(3)	12.4030(5)	12.5793(3)
<i>c</i> (Å)	25.816(2)	23.717(4)	24.720(6)	23.813(5)	14.1358(4)	12.7361(3)
<i>α</i> (°)	90	90	90	90	73.511(2)	90
<i>β</i> (°)	90	90	90	90	83.830(2)	90
<i>γ</i> (°)	90	90	90	90	81.529(2)	90
Volume (Å ³)	1851.9(2)	1856.1(7)	1986.0(8)	2744(1)	1401.73(9)	1849.08(8)
<i>Z</i>	4	4	4	4	2	4
<i>F</i> (000)	712	776	904	1256	660	920
<i>ρ</i> _{calc} (g cm ^{–3})	1.196	1.308	1.476	1.484	1.529	1.664
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Absorption coefficient (mm ^{–1})	0.075	0.089	0.131	1.110	1.095	4.396
<i>θ</i> limit	3.41–23.25	2.31–23.30	1.65–30.00	1.71–29.99	2.44–23.28	4.89–23.27
Scan mode	<i>φ</i>	<i>φ</i>	<i>θ</i> – 2 <i>θ</i>	<i>θ</i> – 2 <i>θ</i>	<i>φ</i>	<i>φ</i>
Scan speed (° min ^{–1})			3–60	3–60		
Reflections measured	4932	4750	3450	3144	3819	4922
Independent reflections	2644	2623	3437	3132	3819	2619
<i>R</i> _{int}	0.0326	0.1294	0.0170	0.0201	0.0000	0.0668
Reflections observed <i>F</i> _o ² > 2σ(<i>F</i> _o ²)	2339	1429	2388	2321	3539	2544
No. of parameters	319	238	301	358	405	229
Goodness-of-fit	0.854	0.851	1.026	0.978	1.262	1.057
<i>R</i> ₁	0.0352	0.0752	0.0672	0.0474	0.0453	0.0451
<i>wR</i> ₂	0.0842	0.1731	0.1641	0.1062	0.1224	0.1159
Final diffraction map electron density (e Å ^{–3})	0.171	0.208	0.501	0.744	0.387	0.428

(CH₃), 20.9 (CH₃), 23.9 (CH₂), 27.0 (CH₂), 49.6 (CH₂), 57.2 (CH), 68.6 (CH₂), 93.9 (C=N), 124.2 (C), 125.5 (C), 125.9 (CH), 129.4 (CH), 135.4 (CH), 135.6 (CH), 146.9 (C), 150.6 (C), 161.5 (C=N), 202.2 (CO), 210.0 (CO), 214.3 (CO), 217.6 (CO).

3.8. MS and spectroscopic data for **2b**

MS (FAB) (m/z): 664 [MH₃O⁺], 646 [MH⁺], 630 [M⁺ – Me], 617 [M⁺ – CO], 589 [M⁺ – 2CO], 561 [M⁺ – 3CO], 533 [M⁺ – 4CO], 505 [M⁺ – 5CO], 477 [M⁺ – 6CO], 438 [C₁₈H₂₀N₃O₃Fe₂⁺], 421 [M⁺ – 6CO – Fe], 391 [C₂₀H₂₁N₃O₂Fe⁺], 366 [MH⁺ – 6 CO – 2Fe], 307 [C₁₈H₁₇N₃O₂⁺], 289 [C₁₈H₁₅N₃O⁺]. IR (CH₂Cl₂, 298 K) (cm^{–1}): 2054 (vs, CO), 1999 (vs, CO), 1979 (vs, br, CO), 1928 (vs, CO). ¹H-NMR (CDCl₃, 298 K) (ppm): 1.07–1.45 (m, 1H, CH₂), 1.45–2.19 (m, 3H, CH₂), 2.32–2.61 (m, 1H, CH₂), 2.61–2.85 (m, 1H, CH₂), 3.41–3.96 (m, 8H, CH, CH₂, CH₃), 3.96–4.40 (m, 1H, CH₂), 6.54–7.64 (m, 8H, CH). ¹³C-NMR (CDCl₃, 298 K) (ppm): 23.9 (CH₂), 26.5 (CH₂), 26.9 (CH₂), 49.5 (CH₂), 55.3 (CH₃), 57.1 (CH), 57.6 (CH), 68.5 (CH₂), 69.5 (CH₂), 92.2 (C=N), 94.0 (C=N), 113.2 (CH), 113.7 (CH), 125.2 (CH), 125.9 (CH), 126.5 (CH), 126.9 (CH), 127.0 (CH), 142.2 (C), 142.5 (C), 146.0/146.7 (C), 157.0 (C), 157.1 (C), 157.4 (C), 157.5 (C), 161.2 (C=N), 161.4 (C=N), 210.2 (CO), 214.2 (CO), 217.4 (CO).

3.9. MS and spectroscopic data for **2c**

MS (FAB) (m/z): 722 [MH⁺], 693 [M⁺ – CO], 665 [M⁺ – 2CO], 637 [M⁺ – 3CO], 609 [M⁺ – 4CO], 581 [M⁺ – 5CO], 553 [M⁺ – 6CO], 514 [C₁₈H₁₄F₆N₃OFe₂⁺], 497 [M⁺ – 6CO – Fe], 459 [C₁₈H₁₅F₆N₃OFe⁺], 442 [MH⁺ – 6CO – 2Fe], 422 [C₂₁H₁₇F₅N₃OFe⁺], 391 [C₂₀–H₁₇F₄N₃O⁺]. IR (CH₂Cl₂, 298 K) (cm^{–1}): 2059 (vs, CO), 2010 (vs, br, CO), 1937 (vs, br, CO). ¹H-NMR (CDCl₃, 298 K) (ppm): 1.03–1.52 (m, 2H, CH₂), 1.72–2.07 (m, 2H, CH₂), 2.30–2.56 (m, 1H, CH₂), 2.56–2.78 (m, 1H, CH₂), 3.52–3.88 (m, 2H, CH, CH₂), 3.88–4.31 (m, 1H, CH₂), 6.84–7.77 (m, 8H, CH). ¹³C-NMR (CDCl₃, 298 K) (ppm): 23.9 (CH₂), 26.8 (CH₂), 50.0 (CH₂), 57.5 (CH), 68.4 (CH₂), 93.3 (C=N), 121.4 (CH), 122.5 (CH, ³J_{CF} = 4 Hz), 123.3 (CF₃, ¹J_{CF} = 273 Hz), 123.6 (CF₃, ¹J_{CF} = 271 Hz), 127.9 (CH), 128.0 (CH), 129.1 (CH), 129.2 (CH), 129.4 (CH), 129.6 (CH), 131.2 (C, ²J_{CF} = 34 Hz), 131.4 (C, ²J_{CF} = 33 Hz), 149.6 (C), 153.6 (C), 161.5 (C=N), 209.3 (CO), 213.4 (CO).

3.10. Preparation of the ligand **3**

In analogy to the synthesis of **1a–c**, a total of 20 mmol (8.70 g) *N,N'*-bis-(4-bromophenyl)-oxalimidoylchloride together with 40 mmol (3.99 g, 5.5 ml) triethylamine and 20 mmol (2.02 g) (*S*)-prolinol in 150 ml of toluene was stirred at r.t. overnight. Thin-layer chromatography

showed that no reaction had taken place up to then, so the solution was refluxed for 4 days. After being cooled down the solution was filtered and the solvent removed stepwise. By this procedure yellow crystals which still contain triethylammoniumhydrochloride precipitated. The crude product was purified by recrystallisation from toluene/chloroform. Yield: 1.81 g (19.6%) **3**. M.p.: 275–278°C. Analysis Found (Calc.): C₁₉H₁₇N₃OBr₂ C 49.17 (49.27), H 3.88 (3.70), N 8.84 (9.07).

3.11. MS and spectroscopic data of **3**

MS (CI, H₂O) (m/z): 466 [MH⁺], 401 [C₁₄H₁₄N₃OBr₂⁺], 102 [C₇H₄N⁺], 93 [C₆H₇N⁺]. IR (CH₂Cl₂, 298 K) (cm^{–1}): 1675 (vs, CO), 1635 (vs, br, C=N). ¹H-NMR (CDCl₃, 298 K) (ppm): 1.46–1.70 (m, 1H, CH₂), 1.76–2.28 (m, 3H, CH₂), 3.37–3.93 (m, 3H, CH, CH₂), 3.98–4.22 (m, 2H, CH₂), 6.43–6.72 (m, 2H, CH), 7.05–7.19 (m, 4H, CH), 7.35–7.69 (m, 2H, CH). ¹³C-NMR (CDCl₃, 298 K) (ppm): 23.2 (CH₂), 30.2 (CH₂), 45.6 (CH₂), 54.6 (CH), 56.0 (CH₂), 114.3 (C), 119.3 (C), 121.2 (CH), 127.1 (CH), 131.1 (CH), 132.1 (CH), 142.9 (C), 143.8 (C), 149.8 (C=N), 154.4 (C=O).

3.12. Preparation of the complex **4**

3.12.1. Synthesis via thermal activation

A 0.5 g sample of Fe₂(CO)₉ (1.37 mmol) together with 0.76 g **3** (1.65 mmol) was stirred in 40 ml of *n*-heptane at 50°C for 3 h. The color of the solution turned reddish brown with a small amount of a light brown solid precipitating. After evaporation of the solvent the residue was dissolved in 10 ml of CH₂Cl₂ and 1 g silanized silica gel was added. Chromatography using a mixture of light petroleum (b.p. 40–60°C) and THF (5:2) yielded 240 mg of **3**. Using a mixture of THF and ethanol (2:1) **4** could be eluted as a deep red solution. Yield: 90 mg (14.2%) **4**.

3.12.2. Synthesis via photochemical activation

A total of 0.59 mmol of Fe(CO)₅ (0.12 g) together with 0.59 mmol **3** (0.27 g) was irradiated in 85 ml of THF at 0°C for 20 min. The color of the solution changed from yellow to deep red. After evaporation of the solvent the product mixture was chromatographed. Using a mixture of light petroleum (b.p. 40–60°C) and THF (5:2) yielded 30 mg of **3**. Again using a mixture of THF and ethanol (2:1) **4** could be eluted as a deep red solution. Yield: 130 mg (80.1%) **4**. Complex **4** decomposes before melting. Analysis Found (Calc.): C₇₉H₅₃N₉O₂₅Br₆Fe₇ C 39.46 (39.56), H 2.46 (2.23), N 4.39 (5.26).

3.13. MS and spectroscopic data for **4**

IR (KBr, 298 K) (cm^{–1}): 2065 (w, CO), 2040 (m, CO), 1997 (vs, CO), 1971 (vs, CO), 1722 (m, br, μ₂-CO), 1658

(s, C=O), 1608 (s, br, C=N). ¹H-NMR (CDCl₃, 298 K) (ppm): –13.9 (s, 3H, μ_2 -H), 1.00–1.27 (m, 6H, CH₂), 1.33–2.09 (m, 6H, CH₂), 2.35–2.65 (m, 9H, CH₂, CH), 3.84–4.52 (m, 6H, CH₂), 6.38–6.56 (m, 6H, CH), 6.80–6.97 (m, 6H, CH), 7.09–7.57 (m, 12H, CH).

4. Supplementary material

Additional material on the structure analysis is available from the Cambridge Crystallographic Data Centre by mentioning the deposition numbers 127809 (**1a**), 127810 (**1b**), 127811 (**1c**), 127812 (**2a**), 127813 (**2b**), 127814 (**3**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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