

# Knoevenagel condensation of $[\text{NC-CH}_2\text{C(O)-NH-CH(CO}_2\text{Et)-S}]_2$ with ferrocenecarbaldehyde and the activation of the $\sigma(\text{C-S})$ bond of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=C(CN)-C(O)-NH-CH(CO}_2\text{Et)-CH}_2\text{-S-}\}]_2$ induced by palladium(II)

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## Abstract

The results obtained from the Knoevenagel condensation between the aldehydes  $\text{R-CHO}$  {with  $\text{R} = 4\text{-MeO-C}_6\text{H}_4$ ,  $4\text{-NO}_2\text{-C}_6\text{H}_4$ ,  $4\text{-Cl-C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ,  $2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$  or  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$ } and  $[\text{NC-CH}_2\text{C(O)-NH-CH(CO}_2\text{Et)-S}]_2$  under different experimental conditions are reported. These studies have allowed the isolation and characterisation of three optically pure polyamides of general formula  $[\text{R-CH=C(CN)-C(O)-NH-CH(CO}_2\text{Et)-CH}_2\text{-S-}]_2$  with  $\text{R} = 4\text{-MeO-C}_6\text{H}_4$  (**3a**),  $4\text{-NO}_2\text{-C}_6\text{H}_4$  (**3b**) or  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$  (**3f**). The reactions of **3f** with  $\text{Na}_2[\text{PdCl}_4]$  or  $\text{Pd}(\text{AcO})_2$  are also studied. The treatment of  $\text{Pd}(\text{AcO})_2$  with **3f** in a 2:1 molar ratio in refluxing toluene leads to the formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=C(CN)-C(O)-NH-C(CO}_2\text{Et)=CH}_2\}]$  (**5f**). Electrochemical studies based on cyclic voltammetry of compounds **3f** and **5f** are also reported.

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**Keywords:** Activation of  $\sigma(\text{C-S})$  bonds; Palladium(II); Ferrocene

## 1. Introduction

The search for new chiral ligands, which can be efficiently applied in asymmetric catalysis, is a field of great interest in modern chemistry [1].  $\text{C}_2$ -symmetric ligands are among the leading classes of compounds used in catalytic asymmetric carbon-carbon bond-formation reactions and usually contain nitrogen, oxygen or phosphorus coordination functionalities [2]. In particular, bisoxazolines have found broad use due to their versatility and easy preparation [3]. Less attention has been addressed to the development of sulphur-containing ligands [4]. Moreover, ferrocene derivatives have found numerous applications in asymmetric catalysis, biological and new materials sciences [5] and to the best of our knowledge, there have been a few reported

examples dealing with the synthesis of chiral sulphur-containing ferrocenyl ligands [6].

The search of new materials of relevance to the field of molecular sensors has led in recent years to considerable interest in the synthesis of redox-active molecules that contain a redox centre in close proximity to a cation or anion binding site. Bearing in mind that the binding process in these systems may lead to a shift of the oxidation potential of the redox-active groups, they may be considered as potentially new electrochemical cation- or anion-sensing receptors [7].

We have recently become interested in the development of simple procedures to build polyamides from L-cysteine that have good coordination properties in front of some transition metals. We have found that L-cysteine reacts with malononitrile in the presence of ammonium chloride to give in a straightforward manner the 22-membered macrocycle **1** [8], shown in Fig. 1.

Herein, we propose a simple method allowing the synthesis of enantiopure  $[\text{NC-CH}_2\text{-C(O)-NH-CH-}$

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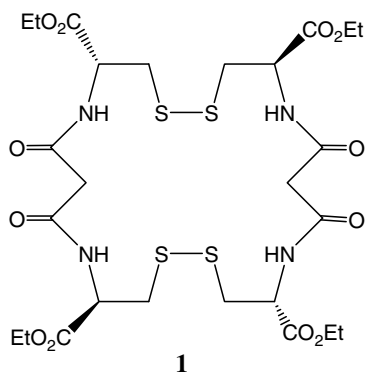


Fig. 1. Schematic view of the 22-membered macrocycle **1**.

(CO<sub>2</sub>Et)-S]<sub>2</sub>- (**2**) based on a minor modification of the previous reported condensation between L-cysteine and malononitrile. Starting from L-cysteine ethyl ester hydrochloride we have obtained in a one-pot two-steps protocol ligand **2**, which is formally one-half of macrocycle **1**.

In this paper, we report the Knoevenagel condensation of **2** with the aromatic aldehydes R-CHO {with R = 4-MeO-C<sub>6</sub>H<sub>4</sub>, 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 4-Cl-C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, or 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>} or ferrocenecarbaldehyde [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe{(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-CHO}] and the reactivity of the bisferrocenyl derivative [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe{(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-CH=C(CN)-C(O)-NH-CH(COOEt)-CH<sub>2</sub>-S-}]<sub>2</sub> (**3f**) with several palladium(II) compounds.

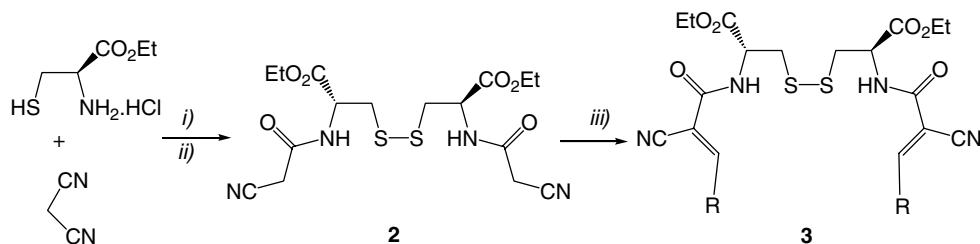
## 2. Results and discussion

### 2.1. Synthesis of ligands

In a previous work, we have reported the synthesis of the 22-membered macrocycle **1** by condensation of L-cysteine and malononitrile in water solution (85 °C, 24 h) to give the free carboxylic acid, which was later esterified. Moreover, this compound can also be pre-

pared by initial condensation of malonic acid dichloride with L-cysteine ethyl ester in organic solvent, followed by oxidation of the isolable dithiol [9]. On the other hand, the condensation of L-cysteine ethyl ester hydrochloride with malononitrile (room temperature or 85 °C, 24 h) gave an intermediate thiol as the only isolable product in 46% yield as a white crystalline solid. This result agreed with a literature report on the condensation of L-cysteine derivatives with *aliphatic* nitriles to give the corresponding amides instead of the expected thiazolines that were obtained only with *aromatic* nitriles [10]. Oxidation of the thiol with sodium perborate [11] in aqueous solution yielded the protected L-cysteine ethyl ester derivative, [NC-CH<sub>2</sub>-C(O)-NH-CH(CO<sub>2</sub>Et)-S]<sub>2</sub>- (**2**) (Scheme 1).

Herein we report the results of the study on the Knoevenagel condensation of **2** with aldehydes. In order to establish the scope of the reaction, the condensation of **2** with *p*-methoxybenzaldehyde under classical conditions (EtOH, piperidine, reflux) was studied [12]. Surprisingly, the reaction proceeded very slowly and the desired double condensation product [(4-MeO-C<sub>6</sub>H<sub>4</sub>)-CH=C(CN)-C(O)-NH-CH(CO<sub>2</sub>Et)-CH<sub>2</sub>-S-}]<sub>2</sub> (**3a**) was detected together with the monocondensed one in rather low yields. Initially, the viability of extending the classical methodology for the Knoevenagel reaction (Dean-Stark, toluene, catalytic piperidine, catalytic acetic acid) was explored. The use of R-CHO {with R = 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 4-Cl-C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub> or (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe{(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-} in front of **2** did not produce any of the expected products [R-CH=C(CN)-C(O)-NH-CH(CO<sub>2</sub>Et)-CH<sub>2</sub>-S-}]<sub>2</sub> (**3**) {with R = 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, **3b**; 4-Cl-C<sub>6</sub>H<sub>4</sub>, **3c**; C<sub>6</sub>H<sub>5</sub>, **3d**; 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub> **3e** or (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe{(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-}, **3f**}. In the view of this, we were prompted to use inorganic catalysts (Al<sub>2</sub>O<sub>3</sub> [13] or MgO [14]), which are known to promote the condensation. The best results were obtained using basic Al<sub>2</sub>O<sub>3</sub> in CHCl<sub>3</sub>. After a long incubation period (4 days) of *p*-methoxybenzaldehyde and **2**, we were able to isolate, after work up, **3a** (18%), a minor



R = 4-MeO-C<sub>6</sub>H<sub>5</sub> (**3a**), 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> (**3b**), 4-Cl-C<sub>6</sub>H<sub>4</sub> (**3c**), C<sub>6</sub>H<sub>5</sub> (**3d**), 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub> (**3e**) or [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-] (**3f**).

Scheme 1. (i) H<sub>2</sub>O, room temperature, (ii) NaBO<sub>3</sub>, (iii) Al<sub>2</sub>O<sub>3</sub>, CHCl<sub>3</sub>, R-CHO.

amount of the monocondensation derivative and unreacted **2** (80%). The same experimental procedure was used for the aromatic aldehydes with similar disappointing results (Scheme 1), and only the reaction of *p*-nitrobenzaldehyde with **2** allowed us to isolate **3b** in very low yield (16%). Fortunately, when we changed to ferrocenecarbaldehyde, **3f** was isolated in a 62% yield.

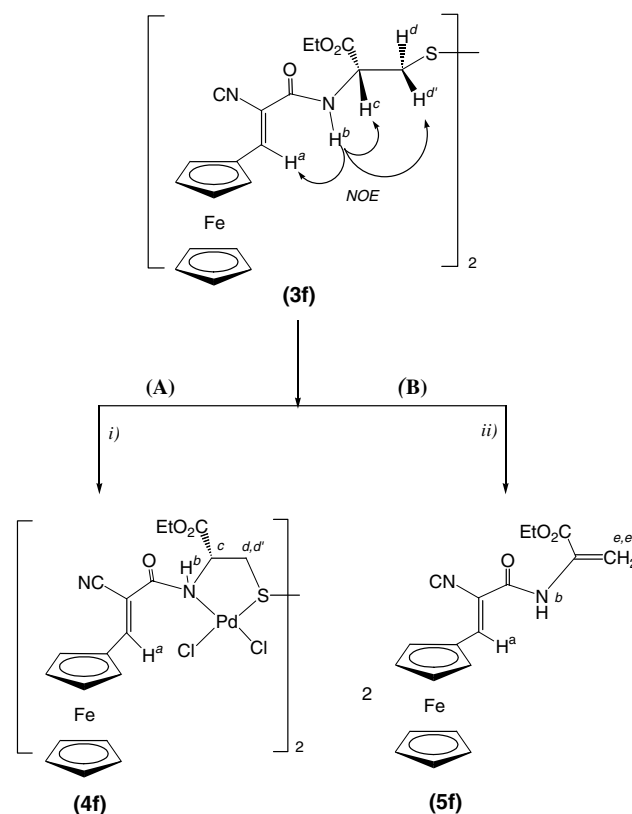
## 2.2. NMR study of ligand **3f**

Proton and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopic data for **3f** under study (in  $\text{CDCl}_3$ ) are presented in Section 3. The most relevant features observed in the  $^1\text{H}$  NMR spectra are the presence of: a singlet at  $\delta = 8.23$  ppm which is assigned to the proton bound to the alkene ( $\text{H}^a$ ) and a doublet at  $\delta = 7.02$  ppm due to the  $-\text{NH}$  proton (herein after referred to as  $\text{H}^b$ ) which is coupled with the proton of the stereogenic centre ( $\text{H}^c$ ). The resonance due to the  $\text{H}^c$  proton appeared as a complex multiplet at  $\delta = 4.98$  ppm. The signals due to the protons of the  $-\text{CO}_2\text{Et}$  moieties were also observed in the spectra, and a complex multiplet in the range  $\delta = 3.20$ – $3.30$  ppm (partially masked by the signal due to the water of the  $\text{DMSO}-d_6$ ) was attributed to the protons ( $\text{H}^d$  and  $\text{H}^{d'}$ ) of the  $-\text{SCH}_2-$  moiety.

The most outstanding difference in its  $^1\text{H}$  NMR spectrum in acetone- $d_6$  is the presence of two separated doublets of doublets in the range 3.4–3.5 ppm due to the  $-\text{CH}_2-$  protons ( $\text{H}^d$  and  $\text{H}^{d'}$  in Scheme 2). In the [ $^1\text{H}-^1\text{H}$ ]-NOESY spectra of **3f** in acetone- $d_6$  at 20 °C (Fig. 2), the signal due to the NH proton showed NOE's with three protons, one of them being  $\text{H}^a$ . This is only possible if the two substituents on the  $>\text{C}=\text{C}<$  group (the  $-\text{CN}$  and the ferrocenyl group) are in a *cis*-arrangement. This finding established the absolute configuration of the substituents at the double bond as *E*. The remaining two cross peaks involved one of the protons of the  $-\text{SCH}_2-$  moiety ( $\text{H}^d$ ) and the  $\text{H}^c$ .

## 2.3. Metal coordination studies

It is well known that ferrocene derivatives containing substituents having (a) heteroatoms with good electron-donating abilities (i.e. N, O, S, P, etc.), (b) unsaturated groups, or both (a) and (b) have attracted great interest in late years since they may allow the coordination of one or more metal ions to produce heteropolymetallic organometallic compounds [15], which are particularly interesting due to their applications in several fields [16], including homogeneous catalysis [17]. Since the substituent on the ferrocenyl unit in **3f** has simultaneously an unsaturated group and several heteroatoms with donor properties, as a first approach to elucidate the potential co-ordinating abilities of this substrate we were prompted to study its reactivity versus  $\text{Na}_2[\text{PdCl}_4]$ . Due to the formal similarity of the moieties holding the



Scheme 2. (i)  $\text{Na}_2[\text{PdCl}_4]$  in acetone at room temperature in a Pd:3f molar ratio = 2. (ii)  $\text{Pd}(\text{AcO})_2$  (in a Pd:3f molar ratio = 2) in refluxing toluene (see text), followed by  $\text{SiO}_2$  column chromatography using  $\text{CH}_2\text{Cl}_2$  as eluant.

“ $-\text{NH}-\text{CH}(\text{COOEt})-\text{CH}_2-\text{S}-$ ” fragments in **1** and **3f**, we decided to use the same procedure as described previously for the preparation of the palladium(II) derivative of **1** [7]. Treatment of an acetone solution of **3f** with  $\text{Na}_2[\text{PdCl}_4]$  in a 1:2 molar ratio at room temperature lead to a brown-red solution which produced after slow evaporation of the solvent a micro-crystalline product. Its elemental analyses were consistent with those expected for:  $[\text{Pd}_2(3f)\text{Cl}_4] \cdot 2\text{H}_2\text{O}$  (**4f**) (Scheme 2). In the infrared spectrum of **4f** the position of the bands due to the stretchings of the  $-\text{CN}$ , the  $-\text{COO}$  and  $>\text{CO}$  groups were very similar to those of **3f**, thus suggesting that the palladium(II) was not directly bound to any of the heteroatoms of these groups. Besides that, the presence of a broad band in the range  $3400$ – $3200$   $\text{cm}^{-1}$  adscribed to the water did not allow us to detect the absorption due to the stretching of the  $-\text{NH}$  group. Compound **4f** is practically insoluble in the most common solvents, this precluded its characterisation by NMR spectroscopy.

More interesting are the results obtained in the reaction of **3f** with  $\text{Pd}(\text{AcO})_2$  [Pd:3f molar ratio = 2] in refluxing toluene for different reaction periods (from 3 h to 3 days). In all the studied cases, the formation of a metallic mirror on the walls of the reaction flask was

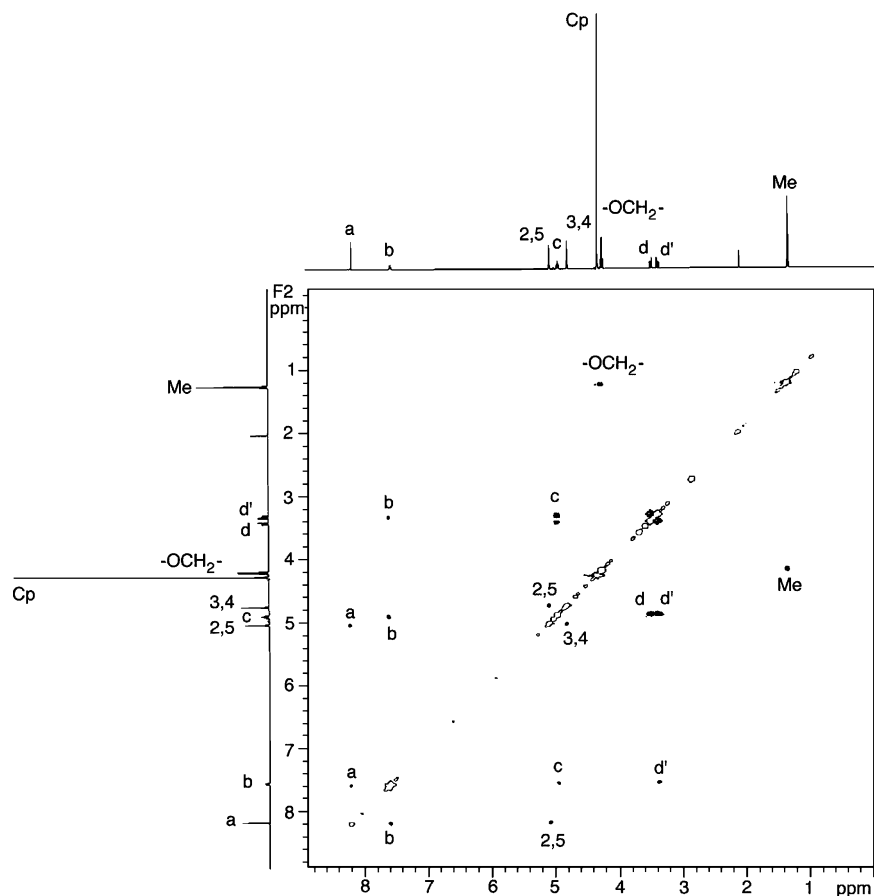


Fig. 2. [ $^1\text{H}$ - $^1\text{H}$ ]-NOESY spectrum of **3f** in acetone- $d_6$ .

detected and the use of a  $\text{SiO}_2$  column chromatography allowed us to isolate unreacted **3f** and an additional deep purple compound (hereinafter referred to as **5f**). The relative proportion **5f**:**3f** increased with longer reaction periods<sup>1</sup> thus suggesting that the formation of **5f** was time dependent. However, no significant improvement was detected when the refluxing period was increased from 2 to 3 days.

The infrared spectrum of **5f** showed the typical band due to the stretching of the  $-\text{NH}$  group thus indicating that deprotonation of the amine groups had not taken place. The position of the band due to the  $-\text{CN}$  group was also observed at  $2002\text{ cm}^{-1}$  and the two absorptions of the  $-\text{COO}$  and  $-\text{CO}$  groups shifted to the lower energy region when compared with those of **3f**.

The most relevant features observed in the  $^1\text{H}$  NMR spectrum of **5f** are: (a) the existence of two singlets at 8.26 ppm due to the  $\text{H}^a$  proton, (b) the presence of a broad singlet at ca. 8.62 ppm (due to  $\text{H}^b$  proton) which

did not show any cross peak in the two-dimensional HSQC NMR spectrum. Thus confirming that the deprotonation of the  $\text{NH}$  group did not take place in the course of the reaction; (c) the signals due to the  $\text{H}^c$ ,  $\text{H}^d$  and  $\text{H}^{d'}$  protons were not detected in the  $^1\text{H}$  NMR spectrum and (d) two additional narrow doublets (of relative intensities 1:1) appeared in the range 6.0–6.7 ppm. The later two findings suggested that the palladium(II) acetate modified significantly the environment of the “ $-\text{CH}(\text{CO}_2\text{Et})-\text{CH}_2-\text{S}-$ ” moieties of **3f**.

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **5f** showed also some interesting features such as the absence of the signal due to the carbon nuclei of the  $-\text{CH}_2-\text{S}-$  moiety and the presence of an additional resonance at  $\delta = 109$  ppm, which correlated in the HSQC spectra with the signals at  $\delta = 6.02$  and 6.67 ppm observed in the  $^1\text{H}$  NMR spectrum. These findings could be indicative of the presence of a terminal “ $=\text{CH}_2$ ” group.

Elemental analyses and mass spectrum of **5f** (see Section 3) agreed with those expected for:  $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}\{(\eta^5-\text{C}_5\text{H}_4)-\text{C}(\text{H})=\text{C}(\text{CN})-\text{C}(\text{O})-\text{NH}-\text{C}(\text{CO}_2\text{Et})=\text{CH}_2\}]$ .

Since it is well known that the proton bound to the stereogenic centres of **3f** ( $\text{H}^c$ ) is acidic, the formation of **5f** (which involves not only the cleavage of the  $\text{C}-\text{S}$  and

<sup>1</sup> For illustrative purposes the amounts (in mg) of **5f** and **3f** isolated after different refluxing periods ( $t$ ) are as follows:  $t = 3$  h: 46 mg (**3f**) and traces (ca. 6 mg) of **5f**;  $t = 12$  h: 30 mg of **3f** and 18 mg of **5f**;  $t = 24$  h: 12 mg of **3f** and 30 mg of **5f**;  $t = 48$  h: 8 mg of **3f** and 41 mg of **5f** and  $t = 72$  h, traces of **3f** (<5 mg) and 43 mg of **5f**.

C–H<sup>c</sup> bonds, but also the formation of a C–C double bond) may be visualised as a consequence of a  $\beta$ -SR elimination reaction. This type of process has also been reported for palladacycles containing [Csp<sup>3</sup>,S]<sup>-</sup> bidentate ligands [18], such as [Pd{C(CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>5</sub>)-(CH<sub>2</sub>)<sub>2</sub>-SR}( $\mu$ -Br)}<sub>2</sub> (with R = Ph or Bu) [18b].

#### 2.4. Electrochemical studies of **3f** and **5f**

Electrochemical data for **3f** and **5f** were obtained from cyclic voltammetry of freshly prepared solutions (10<sup>-3</sup> M) in acetonitrile (HPLC-grade) using (But<sub>4</sub>N)-[PF<sub>6</sub>] as supporting electrolyte. The most relevant electrochemical data are presented in Table 1. The cyclic voltammogram of **3f** (Fig. 3) exhibits an anodic peak with a directly associate reduction in the reverse scan. The experiments were carried out at different scan rates,  $\nu$  {from 10 to 100 mV s<sup>-1</sup>}. In all cases, the  $I_{pa}/I_{pc}$  ratio was close to one, with a linear relationship between the  $I_{pa}$  and  $\nu^{1/2}$ , suggesting an electrochemically reversible oxidation–reduction process [19].

However the peak-to-peak separation ( $\Delta E$ ) increased progressively from 91 to 187 mV. It is well known that the trend of  $\Delta E$  with scan rate can give information on the extent of the structure reorganisation accompanying the redox change [20].

The half-wave potential ( $E_{1/2}$ ) obtained for **3f** is higher than that of ferrocene, thus indicating that the replacement of the hydrogen by the substituted alkene clearly inhibits the oxidation of the iron(II) centre. From electrochemical studies on ferrocene derivatives it is widely accepted that the  $E_{1/2}$  values are clearly dependent on the nature of the substituents [21]. In general higher values are found for derivatives containing electron-withdrawing groups, while electron-donor substituents facilitate the oxidation of the iron centre (as reflected in their  $E_{1/2}$  values which are more cathodic than that of ferrocene). Consequently, in **3f** the substituent in the ferrocenyl fragment has stronger electron-withdrawing ability than the aldehyde or ketone groups in ferrocenecarbaldehyde ( $E_{1/2}$  = 240 mV) or in the acetylferrocene ( $E_{1/2}$  = 220 mV) [22].

Except for the intensities of the cathodic and anodic peaks, the cyclic voltammogram of **5f** is very similar to that of **3f** and the position of the anodic peak and cathodic peak do not differ significantly from those

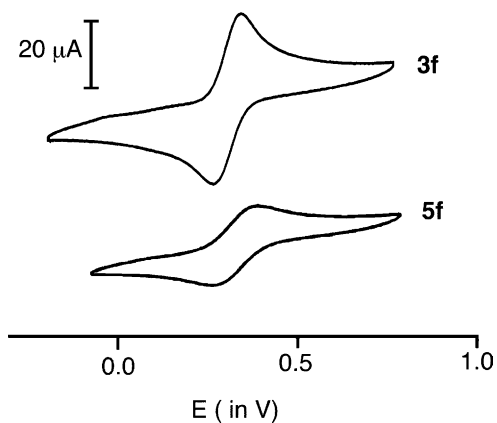


Fig. 3. Cyclic voltammogram of a 10<sup>-3</sup> M solutions of **3f** and **5f** in CH<sub>3</sub>CN registered at 20 °C and at a scan speed  $\nu$  = 100 mV s<sup>-1</sup>.

obtained for **3f**. These results are not surprisingly since the differences in the chemical formulae of these two compounds are far away from the iron(II) centre.

### 3. Experimental

#### 3.1. General information

All chemicals were of commercial grade and used as received and Na<sub>2</sub>[PdCl<sub>4</sub>] was prepared as described previously [23]. The basic Al<sub>2</sub>O<sub>3</sub> used in this work was previously treated using the procedure described before [24]. Elemental analyses (C, H and N) were carried out at the *Servei de Recursos Científics i Tècnics* (Universitat Rovira i Virgili, Tarragona). Infrared spectra were recorded with a Nicolet-Impact 400-FTIR instrument using KBr pellets. <sup>1</sup>H NMR spectra were run using a Varian Gemini 200 or 300 instrument. High resolution NMR spectra and the two-dimensional {<sup>1</sup>H–<sup>13</sup>C} heteronuclear correlation experiments of **3f** were recorded with a Varian VRX-500 instrument. In all cases the chemical shifts ( $\delta$ ) are given in ppm. The optical rotations were determined with a Perkin–Elmer 241 MC polarimeter [ $\lambda$  (Na) = 589.5 nm and 70 mA]. Mass spectra were obtained with a VG-Quattro Fission Instrument using 3-nitrobenzylalcohol (NBA) as matrix. MALDI-TOF mass spectra for **3f** and **5f** were obtained with a Voyager DE RP Applied Biosystems instrument

Table 1

Summary of electrochemical data for compounds **3f** and **5f**: measured anodic ( $E_{pa}$ ) and cathodic ( $E_{pc}$ ) potentials, separation of peaks  $\Delta E$  [ $\Delta E = E_{pa} - E_{pc}$ ] and half-wave potentials  $E_{1/2}$  [ $E_{1/2} = 1/2\{(E_{pa}) + (E_{pc})\}$ ] (in mV)

| Compound  | $E_{pa}$ | $E_{pc}$ | $\Delta E$ | $E_{1/2}$ | $E_{pa}(\text{Fc})$ | $E_{pc}(\text{Fc})$ | $E_{1/2}(\text{Fc})$ |
|-----------|----------|----------|------------|-----------|---------------------|---------------------|----------------------|
| <b>3f</b> | 373      | 282      | 91         | 327       | 316                 | 225                 | 279                  |
| <b>5f</b> | 376      | 275      | 101        | 325       | 319                 | 218                 | 269                  |

$E_{pa}(\text{Fc})$ ,  $E_{pc}(\text{Fc})$ ,  $\Delta E(\text{Fc})$  and  $E_{1/2}(\text{Fc})$  are the corresponding values referred to ferrocene which was used as internal standard [ $E_{1/2}$  for ferrocene = 0.0 mV]. All the values quoted were obtained at a scan speed  $\nu$  = 100 mV.

and the matrix used was 2,5-dihydroxybenzoic acid (DBA). The UV–visible spectra of  $10^{-4}$  M solutions of **3f** or **5f** in  $\text{CH}_2\text{Cl}_2$  were recorded at 20 °C with a Hewlett-Packard 845 spectrophotometer.

### 3.2. Preparation of the compounds

#### 3.2.1. *N,N'*-bis[cyanoacetyl]-L-cysteine ethyl ester (**2**)

A solution of L-cysteine ethyl ester hydrochloride (8.9 g, 0.048 mol), malononitrile (3.16 g, 0.048 mol) in  $\text{H}_2\text{O}$  (80 ml) was stirred at room temperature for 72 h under inert atmosphere. The resulting suspension was diluted with  $\text{H}_2\text{O}$  (175 ml) followed by slow addition of sodium perborate tetrahydrate (14.6 g, 0.095 mol) and stirring was continued for 48 h. The solution was filtered and the remaining product was washed with water and dried under vacuum to afford the disulfide **2** as a white solid 7.4 g (72%). This precipitate (1.04 g) was further purified by column chromatography (silica gel, ethyl acetate) to afford crystalline **2** (0.97 g, 93%). *Characterisation data*: Anal. (%) Calc. for  $\text{C}_{16}\text{H}_{22}\text{N}_4\text{O}_6\text{S}_2 \cdot 1/4\text{CH}_3\text{CO}_2\text{Et}$  (found): C, 45.12(45.6); H, 5.35(5.25) and N, 12.38 (12.71%); m.p. 159–60 °C;  $[\alpha]_{\text{D}}^{20} = -102$  ( $c = 0.135$ , DMSO). IR (KBr): 3301, 2983, 2926, 2230(CN), 1736 ( $\text{C}=\text{O}_{\text{ester}}$ ), 1660, 1548, 1405, 1237, 1038  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 8.94$  (d, 2H,  $J = 7.4$  Hz), 4.54(q, 2H,  $J = 8$  Hz,  $J = 13$  Hz), 4.11(q, 4H,  $J = 7$  Hz), 3.73(s, 4H), 3.14(q, 2H,  $J = 5.6$  Hz,  $J = 13$  Hz), 2.95(q, 2H,  $J = 5.6$  Hz,  $J = 8$  Hz), 1.19(t, 6H,  $J = 7$  Hz).  $^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 170.3(\text{COO})$ , 163.1(>CO), 116.4(CN), 61.9 ( $\text{CH}_2\text{O}$ ), 52.4 (CH), 39.5 ( $\text{CH}_2\text{S}$ ), 25.8 ( $\text{CH}_2$ ), 14.6( $\text{CH}_3$ ).

#### 3.2.2. General procedure for the Knoevenagel condensation

To a  $\text{CHCl}_3$  (14 ml) solution of **2** (0.43 g, 1 mmol) and the aldehyde (2 mmol), basic alumina (1.2 g) was added and the suspension was stirred for 48 h at room temperature. Then, basic alumina (1.2 g) was added and stirring was continued for 48 h. The suspension was filtered and the solid washed with  $\text{CHCl}_3$  ( $3 \times 35$  ml). The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography to give the desired esters **3**.

#### 3.2.2.1. *N,N'*-bis[(2E)-2-cyano-3-(4-methoxyphenyl)-2-propenoyl]-L-cysteine ethyl ester (**3a**)

The above procedure was followed using **2** and *p*-methoxybenzaldehyde (0.27 g, 2 mmol). After silica gel column chromatography (ether:ethyl acetate 9:1) it gave 120 mg (18%) of **3a** as a white solid; *Characterisation data*: Anal. (%) Calc. for  $\text{C}_{32}\text{H}_{34}\text{N}_4\text{O}_8\text{S}_2$  (found): C, 57.64(57.58); H, 5.13(4.89) and N, 8.40(8.08%); m.p. 143 °C;  $[\alpha]_{\text{D}}^{20} = -257$  ( $c = 0.06$  g/100 ml, DMSO). IR (KBr): 3366, 2970, 2932, 2214 (CN), 1736 ( $\text{C}=\text{O}_{\text{ester}}$ ), 1657, 1584, 1518, 1313, 1205, 1179, 1023  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200

MHz,  $\text{DMSO-d}_6$ ):  $\delta = 8.2$ (s, 2H), 7.90(d, 4H,  $J = 8$  Hz), 7.15(d, 2H,  $J = 7$  Hz), 6.96(d, 4H,  $J = 8$  Hz), 4.98(q, 2H,  $J = 5.8$  Hz,  $J = 11.6$  Hz), 4.27(q, 4H,  $J = 7.4$  Hz), 3.88(s, 6H), 3.52–3.20 (m, 4H), 1.32(t, 6H,  $J = 7.4$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 169.5(\text{COO})$ , 163.3, 160.9, 152.8( $\text{CH}_{\text{alq}}$ ), 133.2, 124.4, 117.0(CN), 114.5, 99.7( $\text{C}_{\text{alq}}$ ), 62.2( $\text{CH}_2\text{O}$ ), 55.5( $\text{CH}_3\text{O}$ ), 52.9(CH), 40.1( $\text{CH}_2\text{S}$ ), 14.1( $\text{CH}_3$ ).

#### 3.2.2.2. *N,N'*-bis[(2E)-2-cyano-3-(4-nitrophenyl)-2-propenoyl]-L-cysteine ethyl ester (**3b**)

The above procedure was followed using **2** and *p*-nitrobenzaldehyde (0.30 g, 2 mmol). After silica gel column chromatography (ether:ethyl acetate 9:1) it gave 111 mg (16%) of **3b** as a yellow solid. *Characterisation data*: Anal. (%) Calc. for  $\text{C}_{30}\text{H}_{28}\text{N}_6\text{O}_{10}\text{S}_2 \cdot 1/2\text{H}_2\text{O}$  (found): C, 51.06(51.05); H, 4.14(3.99) and N, 11.90(11.67); m.p. 130 °C;  $[\alpha]_{\text{D}}^{20} = -199$  ( $c = 0.085$  g/100 ml, DMSO). IR (KBr): 3345, 2983, 2933, 2220 (CN), 1731 ( $\text{C}=\text{O}_{\text{ester}}$ ), 1682, 1608, 1593, 1520, 1344, 1203, 1022  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200MHz,  $\text{DMSO-d}_6$ ):  $\delta = 8.39$ (s, 2H), 8.34(d, 4H,  $J = 8.8$ Hz), 8.10(d, 4H,  $J = 8.8$ Hz), 7.36(d, 2H,  $J = 7.4$  Hz), 5.0 (q, 2H,  $J = 6$  Hz,  $J = 11.4$ Hz), 4.29 (q, 4H,  $J = 7$ Hz), 3.60–3.20(m, 4H), 1.33(t, 6H,  $J = 7$ Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 169.1$  (COO), 159.2, 150.4( $\text{CH}_{\text{alq}}$ ), 149.4, 137.1, 131.2, 124.2, 115.4(CN), 107.7( $\text{C}_{\text{alq}}$ ), 62.5( $\text{CH}_2\text{O}$ ), 53.1 (CH), 39.9( $\text{CH}_2\text{S}$ ), 14.1( $\text{CH}_3$ ).

#### 3.2.2.3. *N,N'*-bis[(2E)-2-cyano-3-ferrocenyl-2-propenoyl]-L-cysteine ethyl ester (**3f**)

The above procedure was followed using **2** and ferrocenecarbaldehyde (0.43 g, 2 mmol). After silica gel column chromatography (ether) it gave 0.51 g (62%) of **3f** as red crystals; m.p. 140 °C; *Characterisation data*: Anal. Calc. for  $\text{C}_{38}\text{H}_{38}\text{Fe}_2\text{N}_4\text{O}_6\text{S}_2$ : C, 55.49(55.62); H, 4.66(4.67); N, 6.81(6.75). MS (MALDI-TOF)  $m/z = 822$  [ $\text{M}^+$ ].  $[\alpha]_{\text{D}}^{20} = -648$  ( $c = 0.01$  g/100 ml,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr): 3301, 2978, 2935, 2206 (CN), 1737 ( $\text{C}=\text{O}_{\text{ester}}$ ), 1658, 1590, 1529, 1246, 1195, 1080  $\text{cm}^{-1}$ . UV–Vis:  $\lambda_{\text{max}}$ , ( $\epsilon$ ,  $\text{mol}^{-1}\text{dm}^2$ ): 262 (7908), 322(4623), 382(1950) and 518(2278) nm.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.23$ (s, 2H,  $\text{H}^{\text{a}}$ ), 7.02(d, 4H,  $\text{H}^{\text{b}}$ ,  $J = 8$ Hz), 4.98(m, 6H,  $\text{H}^{\text{c}}$  and the  $\text{H}^2$ ,  $\text{H}^5$  protons of the ferrocenyl unit); 3.18–3.30(m, 4H,  $\text{H}^{\text{d}}$  and  $\text{H}^{\text{d}'}$ ), 4.70(m, 4H,  $\text{H}^3$  and  $\text{H}^4$  of the ferrocenyl unit); 4.25(m, 14H,  $\text{C}_5\text{H}_5$  and  $-\text{OCH}_2-$ ) and 1.32(t, 6H, Me,  $J = 7.0$  Hz);  $^1\text{H}$  NMR (500 MHz, in acetone- $d_6$ ):  $\delta = 8.20$ (s, 2H,  $\text{H}^{\text{a}}$ ); 7.59(d, 4H,  $\text{H}^{\text{b}}$ ,  $J = 7.5$  Hz); 4.93(m, 2H,  $\text{H}^{\text{c}}$ ); 3.45(dd, 2H,  $\text{H}^{\text{d}}$ ,  $J = 14$  and 8Hz) and 3.35(dd, 2H,  $\text{H}^{\text{d}}$ ,  $J = 4$  and 5Hz); 4.23(q, 4H,  $-\text{OCH}_2$ ,  $J = 7.2$ Hz); 1.32(t, 6H, Me,  $J = 7.2$ Hz) and two additional triplets 5.05 [m, 4H,  $\text{H}^2$  and  $\text{H}^5$  (ferrocenyl unit)] and 4.77 [m, 4H,  $\text{H}^3$  and  $\text{H}^4$  (ferrocenyl unit)].  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 169.5(\text{COO})$ , 161.0, 156.8( $\text{CH}_{\text{alq}}$ ), 117.6(CN), 97.8( $\text{C}_{\text{alq}}$ ), 74.4( $\text{C}_5\text{H}_4$ ), 73.7( $\text{C}_5\text{H}_4$ ), 71.7( $\text{C}_5\text{H}_4$ ), 71.3( $\text{C}_5\text{H}_4$ ), 70.5( $\text{C}_5\text{H}_5$ ), 62.2( $\text{CH}_2\text{O}$ ), 52.8(CH), 40.2( $\text{CH}_2\text{S}$ ) and 14.2( $\text{CH}_3$ ).

### 3.2.3. Preparation of $[Pd_2(3f)Cl_4] \cdot 2H_2O$ (**4f**)

A 100 mg ( $1.27 \times 10^{-4}$  mol) amount of **3f** was dissolved in 20 ml of acetone, then a solution formed by 74 mg ( $2.54 \times 10^{-4}$  mol) of  $Na_2[PdCl_4]$  and 5 ml of acetone was added. The resulting reaction mixture was stirred at room temperature for 4 h. and then filtered out. The deep-brown filtrate was allowed to evaporate overnight at ca. 4 °C. The brown micro-crystals formed were then collected, washed with small portions (ca. 1 ml) of  $CHCl_3$ , air-dried and then dried in vacuum for 3 days. Yield 118 mg (80 %). *Characterisation data*: Anal. (%) Calc. for  $C_{38}H_{38}Cl_4Fe_2N_4O_6S_2Pd_2 \cdot 2H_2O$  (found): C, 37.62(37.50); H, 3.49(3.61); N, 4.62(4.47) and S, 5.29(5.03%). IR: 2007(–CN), 1727(>COO), 1653(>CO) and 1617(>C=C<)  $cm^{-1}$ .

### 3.2.4. Preparation of $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-C(H)=C(CN)-C(O)-NH-C(CO_2Et)=CH_2\}]$ (**5f**)

Compound **3f** (59 mg,  $7.17 \times 10^{-5}$  mol) was dissolved in the minimum amount of distilled toluene (ca. 15 ml). Then a solution containing 16 mg of  $Pd(AcO)_2$  ( $7.1 \times 10^{-5}$  mol) and 20 ml of toluene was added dropwise at room temperature under continuous stirring. Once the addition had finished the reaction mixture was refluxed for 2 days. After this period the deep-brownish reaction mixture was filtered out, and the filtrate was concentrated to dryness on a rotary evaporator. The crude of the reaction was dissolved in the minimum amount of  $CH_2Cl_2$  and passed through a short  $SiO_2$  column chromatography (2.5 cm  $\times$  3.0 cm). Elution with  $CH_2Cl_2$  produced the release of a deep purple band which gave **5f**, after concentration to dryness on a rotary evaporator. Compound **5f** was collected and dried in vacuum for 6 days. (yield: 41 mg, 75%). The subsequent elution with a  $CH_2Cl_2/MeOH$  (100/0.1) lead, after work up, small amounts (ca. 8 mg) of unreacted **3f**. *Characterisation data*: Anal. (%) Calc. for  $C_{19}H_{18}N_2O_3Fe$  (found): C, 60.34(60.52); H, 4.80(4.93); N, 7.41(7.35%). MS(FAB<sup>+</sup>):  $m/z = 378$  [M<sup>+</sup>]. IR: 3371 [ $\nu(NH)$ ], 2202 [ $\nu(-CN)$ ], 1709 [COO], 1680 [ $\nu(C=O)$ ], 1580 and 1515 [ $\nu(>C=C<)$ ]. UV–Vis ( $CH_2Cl_2$ ):  $\lambda_{max}(\epsilon)$  329(36900); 390(sh) and 520(6200). <sup>1</sup>H NMR data (200 MHz,  $CDCl_3$ )  $\delta = 8.26$  (s, 1H, H<sup>a</sup>), 8.62(br s, 1H, H<sup>b</sup>), 6.67 and 6.02(d, 2H, <sup>2</sup>J = 1Hz, H<sup>e</sup> and H<sup>e'</sup>), 4.35(q, 2H, <sup>2</sup>J = 7Hz, –OCH<sub>2</sub>–), 1.38(t, 3H, <sup>2</sup>J = 7Hz, CH<sub>3</sub>), 4.73(t, 2H, H<sup>3</sup> and H<sup>4</sup>), 5.01(t, 2H, H<sup>2</sup> and H<sup>5</sup>) and 4.27[s, 5H, (C<sub>5</sub>H<sub>5</sub>)]. <sup>13</sup>C{<sup>1</sup>H} NMR data (in  $CDCl_3$ ):  $\delta = 159.5$  [ $>C(O)$ ], 156.9(=CH–), 117.5(–CN), 109.4 (=CH<sub>2</sub>), 98.5(–CCN), 62.4(–OCH<sub>2</sub>), 70.5(C<sub>5</sub>H<sub>5</sub>), 71.5 (C<sup>2</sup> and C<sup>5</sup>), 73.9(C<sup>3</sup> and C<sup>4</sup>), 74.4 (C<sup>1</sup>) and 14.0 (–CH<sub>3</sub>).

### 3.3. Electrochemical studies

Electrochemical data for **3f** and **5f** were obtained by cyclic voltammetry under nitrogen at ca. 20 °C using acetonitrile HPLC-grade as solvent, tetrabu-

thylammonium hexafluorophosphate,  $\{(Bu_4N)[PF_6]\}$ , (0.1 M) as supporting electrolyte and a M263A potentiostat from EG&G instruments. The measured potentials were referred to an Ag–AgNO<sub>3</sub> (0.1 M in acetonitrile) electrode separated by the solution by a medium porosity fritted disk. A platinum wire auxiliary electrode was used in conjunction with a platinum disk working rotatory electrode TACUSSEL-EDI rotatory electrode (3.14 mm<sup>2</sup>). Cyclic voltammograms of ferrocene were recorded before and after each sample to ensure the repeatability of the results, in particular to test and monitor the stability of the Ag–AgNO<sub>3</sub> electrode. Cyclic voltammograms of a freshly prepared solution ( $10^{-3}$  M) of **3f** and **5f** in  $CH_3CN$  were run and average values of the  $E_{pa}$ ,  $E_{pc}$  and  $E_{1/2}$  values measured were then referred to ferrocene, which was used as internal reference. In these experimental conditions the standard error of the measured potentials is  $\pm 5$  mV. The cyclic voltammograms of **3f** and **5f** were registered using scan speeds varying from 10 to 100 mV s<sup>–1</sup>.

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### References

- [1] (a) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, 1994; (b) R.E. Gawley, J. Aube, *Principles of Asymmetric Synthesis*, Pergamon Press, Oxford, 1996.
- [2] (a) C. Bolm, M. Martin, O. Simic, M. Verrucci, *Organic Lett.* 5 (2003) 427–429; (b) M. Yus, D.J. Ramon, O. Prieto, *Tetrahedron* 14 (2003) 1103–1114; (c) C. Mailet, T. Praveen, P. Janvier, S. Minguet, M. Evain, C. Saluzzo, M.L. Tommasino, B. Bujoli, *J. Org. Chem.* 67 (2002) 8191–8196; (d) G. Chelucci, G. Loriga, G. Murineddu, G.A. Pinna, *Tetrahedron Lett.* 43 (2002) 8599–8602; (e) W. Li, J.P. Waldkirch, X. Zhang, *J. Org. Chem.* 67 (2002) 7618–7623.
- [3] (a) S. Iwasa, S. Tsushima, K. Nishiyama, Y. Tsuchiya, F. Takezawa, H. Nishiyama, *Tetrahedron* 14 (2003) 855–865; (b) M. Gerish, J.R. Krumper, R.G. Bergman, T.D. Tilley, *Organometallics* 22 (2003) 47–58; (c) D.M. Du, Z.Y. Wang, D.C. Xu, W.T. Hua, *Synthesis* (2002) 2347–2352; (d) J. Clariana, J. Comelles, M. Moreno-Mañas, A. Vallribera, *Tetrahedron* 13 (2002) 1551–1554; (e) Y.Z. Zhu, Z.P. Li, J.A. Ma, F.Y. Tang, L. Kang, Q.L. Zhou, A.S.C. Chan, *Tetrahedron* 13 (2002) 161–165; (f) I.M. Pastor, H. Adolfsson, *Tetrahedron Lett.* 43 (2002) 1743–1746;

- (g) M.I. Burguete, J.M. Fraile, J.I. Garcia, E. Garcia-Verdugo, C.I. Herrerias, S.V. Luis, J.A. Mayoral, *J. Org. Chem.* 66 (2001) 8893–8901.
- [4] (a) A.L. Braga, H.R. Appelt, P.H. Schneider, O.E.D. Rodrigues, C.C. Silveira, L.A. Wessjohann, *Tetrahedron* 57 (2001) 3291–3295;  
(b) J. Christoffers, A. Mann, J. Pickard, *Tetrahedron* 55 (1999) 5377–5388;  
(c) M. Kossenjans, J. Martens, *Tetrahedron* 9 (1998) 1409–1417;  
(d) Y. Sun, A.E. Martell, R.J. Motekaitis, M.J. Welch, *Tetrahedron* 54 (1998) 4203–4210.
- [5] A. Togni, T. Hayashi (Eds.), *Ferrocenes, Homogeneous Catalysis, Organic Synthesis and Material Science*, VCH, Weinheim, 1993.
- [6] (a) H. Huang, L. Mu, J. He, J.-P. Cheng, *J. Org. Chem.* 68 (2003) 7605–7611;  
(b) A. Tárraga, P. Molina, D. Curiel, D. Bautista, *Tetrahedron* 13 (2002) 1621–1628;  
(c) P. Molina, A. Tárraga, D. Curiel, *Synlett* 3 (2002) 435–438;  
(d) S.L. You, X.L. Hou, L.X. Dai, Y.H. Yu, W. Xia, *J. Org. Chem.* 67 (2002) 4684–4695;  
(e) W.P. Deng, S.L. You, X.L. Hou, L.X. Dai, Y.H. Yu, W. Xia, *J. Am. Chem. Soc.* 123 (2001) 6508–6519;  
(f) A. Gonzalez, J.R. Granell, C. López, *J. Organomet. Chem.* 637–639 (2001) 418–425;  
(g) V.C. Gibson, N.J. Long, A.J.P. White, C.K. Williams, D.J. Williams, *Chem. Commun.* (2000) 2359–2360;  
(h) C.J. Richards, A.J. Locke, *Tetrahedron* 9 (1998) 2377–2407;  
(i) K. Bushell, C. Gialou, C.H. Goh, N.J. Long, J. Martin, A.J.P. White, C.K. Williams, D.J. Williams, M. Fontani, P. Zanello, *J. Organomet. Chem.* 637–639 (2001) 116–125.
- [7] (a) O.B. Sutcliffe, A. Chesney, M.R. Bryce, *J. Organomet. Chem.* 637–639 (2001) 134–138;  
(b) A. Tárraga, P. Molina, D. Curiel, M.D. Velasco, *Tetrahedron* 57 (2001) 6765–6774;  
(c) J.M. Lloris, R. Martínez-Mañez, J. Soto, T. Pardo, *J. Organomet. Chem.* 637–639 (2001) 151–158;  
(d) L.F. Tang, W.L. Jia, Z.H. Wang, J.F. Chai, J.T. Wang, *J. Organomet. Chem.* 637–639 (2001) 209–215;  
(e) A. Chesney, M.R. Bryce, A.S. Batsanov, J.A.K. Howard, L.M. Goldenberg, *Chem. Commun.* (1998) 677–678.
- [8] L. Gilbert, A. González, J. Granell, C. López, *Tetrahedron* 13 (2002) 983–988.
- [9] H. Kudo, F. Sanda, T. Endo, *Tetrahedron Lett.* 42 (2001) 7847–7850.
- [10] H.P. Krimmer, K. Drauz, A. Kleemann, *Chem. Zeitung* 111 (1987) 357–361.
- [11] A. McKillop, D. Koyuncu, A. Krief, W. Dumont, P. Renier, M. Trabelsi, *Tetrahedron Lett.* 31 (1990) 5007–5010.
- [12] (a) S. Siegel, H.G. Schmalz, *Angew. Chem., Int. Ed. Engl.* 36 (1997) 2456–2458;  
(b) J. Pigulla, E. Röder, *Arch. Pharm.* 311 (1978) 822–827;  
(c) C.N. O'Callaghan, T.B.H. McMurry, *J. Chem. Res. (S)* (1989) 169;  
(d) F.D. Popp, *J. Org. Chem.* 25 (1960) 646–647;  
(e) F.D. Popp, A. Catala, *J. Org. Chem.* 26 (1961) 2738–2740.
- [13] (a) G. Cooke, H.M. Palmer, O. Schulz, *Synthesis* (1995) 1415–1418;  
(b) E. Stankovic, S. Toma, R.V. Boxel, I. Asselberghs, A. Persoons, *J. Organomet. Chem.* 637–639 (2001) 426–434.
- [14] H. Moison, F. Texier-Boullet, A. Foucaud, *Tetrahedron* 43 (1987) 537–542.
- [15] (a) A. Togni, R.L. Haltermann, *Metalloenes*, Wiley-VCH, Weinheim, 1998;  
(b) N.L. Long, *Metalloenes: An Introduction to Sandwich Complexes*, Blackwell, Oxford, 1998;  
(c) K. Severin, R. Bergs, W. Beck, *Angew. Chem., Int. Ed.* 37 (1998) 1635–1654;
- (d) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* 43 (1998) 349–401;  
(e) M.A. Zhuravel, D.S. Glueck, L.M. Liable-Sands, A.L. Reinhold, *Organometallics* 17 (1998) 574–578;  
(f) W.M. Xue, T.E. Khün, C. Herdtweg, Q. Li, *Eur. J. Inorg. Chem.* (2001) 213–221;  
(g) W.M. Xue, E. Fritz, *Eur. J. Inorg. Chem.* (2001) 2041–2047;  
(h) F. Chen-Jie, D. Chun-Ying, H. Cheung, M. Qing-jin, *Chem. Commun.* (2000) 1187–1188;  
(i) V.C. Ginson, N.L. Long, A.J.P. White, C.K. Williams, D.J. Williams, *Chem. Commun.* (2000) 2359–2360;  
(j) R.H. Fish, G. Jaouen, *Organometallics* 22 (2003) 2166–2177.
- [16] (a) D. Astruc, *Electron Transfer and Radical processes in Transition Metal Chemistry*, VCH, New York, 1995 (Chapter 2);  
(b) P.D. Beer, D.K. Smith, *Prog. Inorg. Chem.* 46 (1997) 1–96;  
(c) D.P. Kingsborough, T.M. Swager, *Prog. Inorg. Chem.* 48 (1999) 123–231;  
(d) W.R. Cullen, J.D. Woolins, *Coord. Chem. Rev.* 39 (1981) 1–30, and references therein;  
(e) N.J. Long, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 21–31, and references therein;  
(f) O. Briel, K. Sünkel, I. Krossing, H. Nölth, E. Schmäzlin, K. Meerholz, C. Bräuchle, W. Beck, *Eur. J. Inorg. Chem.* 3 (1999) 483–490;  
(g) I.R. Whittall, A.M. McDonald, M.G. Humphrey, M. Samoc, in: F.G.A. Stone, R. West (Eds.), *Advances in Organometallic Chemistry*, vol. 42, Academic Press, San Diego, 1998, pp. 291–362;  
(h) P. Köpf-Maier, H. Köpf, *Chem. Rev.* 87 (1987) 1137–1152;  
(i) I. Omae, *Applications of Organometallic Compounds*, Wiley, Chichester, 1988;  
(j) A.V. Sokolov, *Chirality and Optical Activity in Organometallic Compounds*, Gordon and Breach, London, 1993;  
(k) K. Tamaka, S. Quiao, M. Tobisu, M.C. Lo, G.C. Fu, *J. Am. Chem. Soc.* 122 (2000) 9870–9871;  
(l) J.A. Mata, E. Falomir, R. Llusar, E. Peris, *J. Organomet. Chem.* 616 (2000) 80–88;  
(m) T.R. Fethouse, E.L. Laskowski, D.N. Hendrickson, *Inorg. Chem.* 16 (1977) 1077–1089.
- [17] (a) For recent articles focused on the utility of some ferrocene derivatives holding heteroatoms on homogeneous catalysis, see for instance: S. Mourgues, D. Serra, F. Lamy, S. Vincendeau, J.C. Daran, E. Mournoury, M. Gouygou, *Eur. J. Inorg. Chem.* (2003) 2820–2826;  
(b) T.T. Co, S.W. Paek, S.C. Shim, C.S. Cho, T.J. Kim, D.W. Choi, S.D. Kamp, J.H. Jeong, *Organometallics* 22 (2003) 1475–1482;  
(c) O.B. Sutcliffe, M.R. Bryce, *Tetrahedron* 14 (2003) 2297–2325;  
(d) J.H. Lee, S.U. Son, Y.K. Chung, *Tetrahedron* 14 (2003) 2109–2113;  
(e) X. Hu, H. Chen, H. Dai, X. Hu, Z. Zheng, *Tetrahedron* 14 (2003) 2073–2080;  
(f) S. Bastin, M. Ginj, J. Brocards, L. Péliniski, G. Novogrocki, *Tetrahedron* 14 (2003) 1701–1708.
- [18] (a) A.C. Albeniz, P. Espinet, Y.S. Lin, *Organometallics* 15 (1996) 5010–5017;  
(b) A.C. Albeniz, P. Espinet, Y.S. Lin, A.G. Orpen, A. Martin, *Organometallics* 15 (1996) 5003–5009.
- [19] E.R. Brown, J.R. Sandifer, in: B.W. Rossiter, J.H. Hamilton (Eds.), *Physical Methods in Chemistry. Electrochemical Methods*, vol. 4, Wiley, New York, 1986 (Chapter 4).
- [20] P. Zanello, in: J. Bernal (Ed.), *Stereochemistry of Organometallic and Inorganic Compounds*, vol. 4, Elsevier, Amsterdam, 1990.
- [21] (a) P. Zanello, A. Cinquantini, S. Mangani, G. Opromolla, L. Pardi, C. Janiak, M.D. Rausch, *J. Organomet. Chem.* 471 (1994) 171–177;



- (b) G.L. Hoh, W.W. Mc Ewen, J.J. Kleinberg, *J. Am. Chem. Soc.* 83 (1961) 3949–3953;
- (c) W.F. Little, C.N. Reilly, J.D. Johnson, A.P. Saunders, *J. Am. Chem. Soc.* 86 (1964) 1376–1381;
- (d) M.L. Good, J. Buttone, D. Foyt, *Ann. N. Y. Acad. Sci.* 239 (1974) 193–198;
- (e) N.F. Blom, E.W. Neuse, H.G. Thomas, *Transition Met. Chem.* 12 (1987) 301–310;
- (f) A. Benito, J. Cano, R. Martínez, J. Soto, J. Payá, F. Lloret, M. Julve, J. Faus, M.D. Cano, *Inorg. Chem.* 32 (1993) 1197–1203;
- (g) M. Bracci, E. Ercolani, B. Floris, M. Bassetti, A. Chiesi-Vila, C. Guastini, *J. Chem. Soc., Dalton Trans.* (1990) 1357–1363;
- (h) A. Louati, M. Gross, L. Duce, D. Mat, *J. Organomet. Chem.* 463 (1993) 169–177.
- [22] *Gmelins Handbuch der Organische Chemie, Eisen Organische Verbindungen, Ferrocen 1, Teil A1*, 1976, Springer, Heidelberg, p. 19.
- [23] G. Brauer, in: *Handbook of Preparative Inorganic Chemistry*, vol. 2, Academic Press, New York, 1965, pp. 1586–1587.
- [24] (a) J. Castells, G.A. Fletcher, *J. Chem. Soc.* (1956) 3245–3246;
- (b) A. González, C. Gálvez, *Synthesis* (1982) 946.