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Journal of Organometallic Chemistry 672 (2003) 34–42

Journal  
of Organo  
metallic  
Chemistry

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# Activation of $\sigma(\text{C-H})$ bonds of $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N-N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-2,6-R})\}_2]$ (with $\text{R} = \text{Cl}$ or $\text{H}$ ) promoted by palladium(II)

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Received 17 December 2002; received in revised form 12 February 2003; accepted 12 February 2003

## Abstract

The synthesis, characterisation and the study of the reactivity of the novel and bifunctional ferrocenyl Schiff bases  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N-N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-2,6-R}_2)\}_2]$  (with  $\text{R} = \text{Cl}$  or  $\text{H}$ ) with palladium(II) salts under different experimental conditions are reported. The treatment of  $\text{Na}_2[\text{PdCl}_4]$ ,  $\text{Na}(\text{CH}_3\text{COO})\cdot 3\text{H}_2\text{O}$  and the corresponding ligand  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N-N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-2,6-R}_2)\}_2]$  (with  $\text{R} = \text{Cl}$  or  $\text{H}$ ) (in a 2:2:1 molar ratio) in methanol for 6 days followed by the addition of triphenylphosphine ( $\text{PPh}_3$ ), and a  $\text{SiO}_2$  column chromatography, allowed the isolation of the two isomers (*meso*- and *D,L*- forms) of the heterotrimetallic complexes of general formula  $[\text{Pd}_2\{\text{Fe}\{(\eta^5\text{-C}_5\text{H}_3)\text{-C}(\text{Me})=\text{N-N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-2,6-R}_2)\}_2\text{Cl}_2(\text{PPh}_3)_2]$ , (with  $\text{R} = \text{Cl}$  or  $\text{H}$ ).

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**Keywords:** Activation of C–H; Iron; Schiff base; Palladium

## 1. Introduction

Palladium(II) compounds containing  $(\text{C,N})^-$  bidentate ligands have attracted great interest in recent years [1] due to their potential applications in a wide variety of areas [2,3] including their use as precursors for organic or organometallic synthesis [3]. Among all cyclopalladated derivatives reported so far, the most widely studied systems are those containing  $[\text{C}(\text{sp}^2, \text{aryl}), \text{N}]^-$ ,  $[\text{C}(\text{sp}^3), \text{N}]^-$  or  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$  chelate ligands. Some examples of bis(cyclopalladated) derivatives arising from the activation of  $\sigma[\text{C}(\text{sp}^2, \text{aryl})\text{-H}]$  bonds have also been reported in the literature [4]. However, examples involving the cyclopalladation of the two rings of a ferrocenyl ligand are scarce [5,6]. To our knowledge only three articles have been published on this field [5,6], one of them involved the double

cyclopalladation of the 1,1'-ferrocenylhydrazone:  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N-NH}-(\text{CO}_2\text{Me})\}_2]$  (**1**) [5], while the others were focussed on the cyclopalladation of 1,1'-ferrocenyldiimines of general formula:  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{R})=\text{N-R}'\}_2]$  {with  $\text{R} = \text{H}$ ,  $\text{R}' = \text{CH}_2\text{C}_6\text{H}_5$  (**2a**),  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{C}_6\text{H}_5$  (**3a**) or  $\text{C}_6\text{H}_4\text{-4-Me}$  (**3b**)} [Fig. 1] [6]. All of these ligands (**1–3**) had only one type of  $\sigma(\text{C-H})$  bond susceptible to undergo palladation, and their reactions with  $\text{Na}_2[\text{PdCl}_4]$  in the presence of sodium acetate lead to the heterotrimetallic complexes containing two five-membered palladacycles with a  $\sigma[\text{Pd-C}(\text{sp}^2, \text{ferrocene})]$  bond fused with the pentagonal rings of the ferrocenyl fragment [6]. In the view of these results and as a part of a project directed towards the synthesis and study of the potential applications of cyclopalladated compounds containing  $\sigma[\text{Pd-C}(\text{sp}^2, \text{ferrocene})]$  bonds we decided to elucidate whether the replacement of the  $\text{R}'$  group in  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{R})=\text{N-R}'\}_2]$  (**2–3**) by an additional  $-\text{N}=\text{CH}(\text{R}'')$  containing an  $\text{R}''$  group susceptible to metalate (i.e. a phenyl ring) could be important to determine: (a) the nature of the  $\sigma(\text{C-H})$  bond to be activated; (b)

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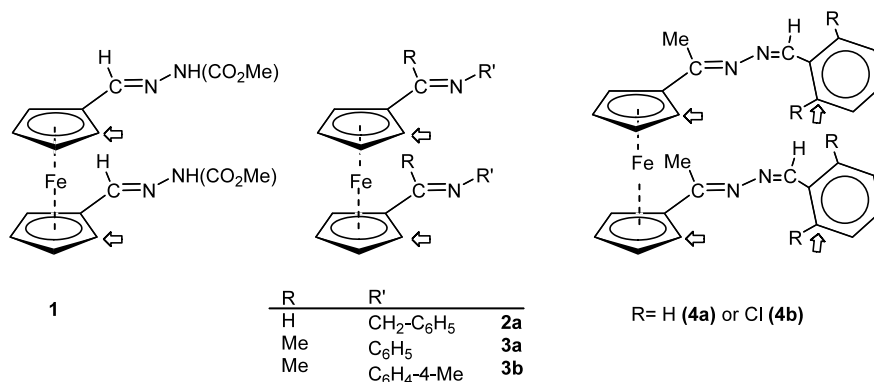


Fig. 1. Schematic view of the bifunctional ferrocenyl Schiff bases used in bis(cyclopalladation) reactions (**1–3**), together with that of the two ligands under study (**4a** and **4b**).

the number of palladacycles contained in the final products; or (c) their sizes. With this aim in this paper we report the synthesis of  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-2,6-R}_2)\}_2]$  {with R = Cl (**4a**) or H (**4b**)} and the results obtained from their reactions with palladium(II) salts.

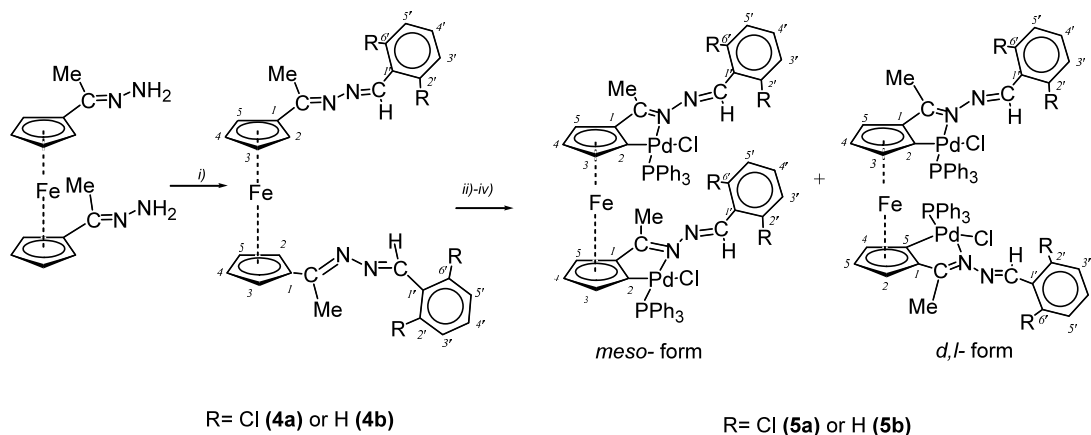
## 2. Results and discussion

### 2.1. The ligands

Compounds  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-2,6-R}_2)\}_2]$  with R = Cl (**4a**) or H (**4b**) were prepared by condensation of the corresponding aldehyde and  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{Me})=\text{N}-\text{NH}_2\}_2]$  [7] in a 2:1 molar ratio in refluxing ethanol for 2 h (Scheme 1), using the procedure described before for the mono-functional ferrocenyl Schiff bases of general formula:  $[\eta^5\text{-C}_5\text{H}_4\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-(CH}_2\text{)}_n\text{-C}(\text{R}^2\text{)}\text{R}^3\}]$  where  $n = 1$  or 2; R<sup>2</sup> is H or Me and R<sup>3</sup> represents a phenyl

or a ferrocenyl group [8], which consists on the condensation of the ferrocenylamine  $[\eta^5\text{-C}_5\text{H}_4\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-(CH}_2\text{)}_n\text{-NH}_2\}]$  ( $n = 1$  or 2) and equimolar amounts of the corresponding aldehyde or ketone in refluxing ethanol. When  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{Me})=\text{N}-\text{NH}_2\}_2]$  [7] was treated with  $(2,6\text{-R}_2\text{-C}_6\text{H}_3)\text{C}(\text{H})\text{O}$  (R = Cl or H) in a 1:2 molar ratio in ethanol under reflux for 2 h (Scheme 1) followed by the slow evaporation of the solvent, compounds  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-2,6-R}_2)\}_2]$  {R = Cl (**4a**) or H (**4b**)} were obtained as deep red microcrystalline products in a fairly good yield (65%).

Compounds **4** are highly soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>, practically insoluble in *n*-hexane and they hydrolyse slowly in water. These new ligands have been characterised by elemental analyses, infrared and mono- and two-dimensional NMR spectroscopies. The elemental analyses (see Section 3) were consistent with those expected for  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-2,6-R}_2)\}_2]$  {R = Cl (**4a**) or H (**4b**)}. The most relevant feature observed in the infrared spectra is



Scheme 1. (i) 2,6-Dichlorobenzaldehyde (for **4a**) or benzaldehyde (for **4b**) in a 1:2 molar ratio in refluxing ethanol for 2 h. (ii) Na<sub>2</sub>[PdCl<sub>4</sub>], Na(CH<sub>3</sub>COO)·3H<sub>2</sub>O, in methanol, at room temperature for 6 days. (iii) Filtration and treatment of the solid with PPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>. (iv) SiO<sub>2</sub>-column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluant, in this process small amounts of *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] were also isolated as a by-product in the two cases (see text).

the presence of a intense band in the range 1600–1700  $\text{cm}^{-1}$  which is ascribed to the stretching of the two  $>\text{C}=\text{N}-$  functional groups.

Proton NMR spectra of **4** showed a singlet in the range 8.30–8.70 ppm, which is ascribed, according to the literature, to the imine proton. For compound **4a** this resonance appeared at lower fields ( $\delta = 8.60$  ppm) than for **4b** ( $\delta = 8.38$  ppm). This finding is similar to that reported for the monofunctional ferrocenylienes:  $[\{(\eta^5\text{-C}_5\text{H}_5)\text{-Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-}(\text{CH}_2)_2\text{-N}=\text{C}(\text{H})(\text{R}')\}]$  with  $\text{R} = 2,6\text{-C}_6\text{H}_3\text{Cl}_2$  ( $\delta = 8.38$  ppm) or  $\text{C}_6\text{H}_5$  ( $\delta = 8.04$  ppm) [8] which has been attributed to the existence of a weak hydrogen interaction between one of the chloro groups on the aryl ring and the imine proton.

Ligand **4a** has also been characterised by X-ray diffraction. The molecular structure of **4a** together with the atom labelling scheme is depicted in Fig. 2, and a selection of bond lengths and angles is presented in Table 1.

The structure consists on discrete molecules of  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-}2,6\text{-Cl}_2)\}_2]$  separated by van der Waals contacts. In each molecule the two ' $\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-}2,6\text{-Cl}_2)\}$ ' fragments are related by a symmetry element.

The values of the  $\text{C}(7)\text{-C}(6)\text{-N}(1)\text{-N}(2)$  [ $1.76^\circ$ ] and  $\text{N}(1)\text{-N}(2)\text{-C}(8)\text{-C}(9)$  [ $173.56^\circ$ ] indicate that the methyl group and the aryl ring are on the same side of the plane defined by the atoms  $\text{C}(6)$ ,  $\text{N}(1)$ ,  $\text{N}(2)$  and  $\text{C}(8)$ . The  $\text{C}(7)$  atom deviates by ca.  $0.01\text{\AA}$  from the plane defined by the  $\text{C}(5)$ ,  $\text{C}(6)$  and  $\text{N}(1)$  atoms. A similar type of distortion has also been reported for the monofunctional ferrocenylienes of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N}=\text{R}''\}]$  with  $\text{R}'' = \text{phenyl}$  or  $\text{benzyl}$  groups [9]. The cyclopentadienyl ring is planar [10] and forms an angle of ca.  $8.28^\circ$  with the  $\text{C}(5)\text{-C}(6)\text{-}$

Table 1

Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(2,6\text{-Cl}_2\text{-C}_6\text{H}_3)\}_2]$  (**4a**) (standard deviation parameters are given in parenthesis)

Bond lengths			
$\text{N}(1)\text{-C}(6)$	1.282(3)	$\text{N}(2)\text{-C}(8)$	1.237(3)
$\text{Cl}(1)\text{-C}(10)$	1.739(2)	$\text{Cl}(2)\text{-C}(14)$	1.727(3)
$\text{C}(9)\text{-C}(10)$	1.396(3)	$\text{C}(9)\text{-C}(14)$	1.402(3)
$\text{C}(10)\text{-C}(11)$	1.380(3)	$\text{C}(11)\text{-C}(12)$	1.386(4)
$\text{C}(12)\text{-C}(13)$	1.373(4)	$\text{C}(13)\text{-C}(14)$	1.383(4)
$\text{Fe}\text{-C}^a$	2.045(9)	$\text{C}\text{-C}^a$	1.416(11)
Bond angles			
$\text{C}(6)\text{-N}(1)\text{-N}(2)$	113.7(2)	$\text{C}(8)\text{-N}(2)\text{-N}(1)$	112.7(2)
$\text{N}(1)\text{-C}(6)\text{-C}(5)$	116.0(2)	$\text{N}(1)\text{-C}(6)\text{-C}(7)$	125.0(2)
$\text{C}(5)\text{-C}(6)\text{-C}(7)$	119.0(2)	$\text{N}(2)\text{-C}(8)\text{-C}(9)$	125.5(2)
$\text{C}(9)\text{-C}(10)\text{-Cl}(1)$	120.03(18)	$\text{C}(11)\text{-C}(10)\text{-Cl}(1)$	116.3(2)
$\text{C}(9)\text{-C}(14)\text{-Cl}(2)$	121.65(19)	$\text{C}(13)\text{-C}(14)\text{-Cl}(2)$	116.2(2)

<sup>a</sup> Average value for the ' $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-})_2$ ' moiety.

$\text{N}(1)$  unit. All the atoms belonging to the  $\text{C}_5\text{H}_4$  ring, the functional groups and the phenyl ring are nearly coplanar [11]

The  $\text{Cl}(1)\text{-C}(10)$  bond length is slightly larger [ $1.739(2)$   $\text{\AA}$ ], if significant, than the  $\text{Cl}(2)\text{-C}(14)$  bond distance [ $1.727(3)$   $\text{\AA}$ ] while the  $\text{Cl}(1)\cdots\text{H}(8)$  distance [ $2.48(6)$   $\text{\AA}$ ] is clearly smaller than the sum of the van der Waals radii of these atoms ( $\text{Cl}$ ,  $1.75$   $\text{\AA}$  and  $\text{H}$ ,  $1.20$   $\text{\AA}$ ) [12], thus suggesting a weak  $\text{C}(8)\text{-H}(8)\cdots\text{Cl}(1)$  intramolecular interaction. A similar type of interaction has been found in the closely related monofunctional Schiff bases holding ferrocenyl units such as  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-}2,6\text{-Cl}_2)\}]$  [8c]. Bond lengths and angles of the ' $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-})_2$ ' fragment are consistent with those reported for most of ferrocene derivatives [13].

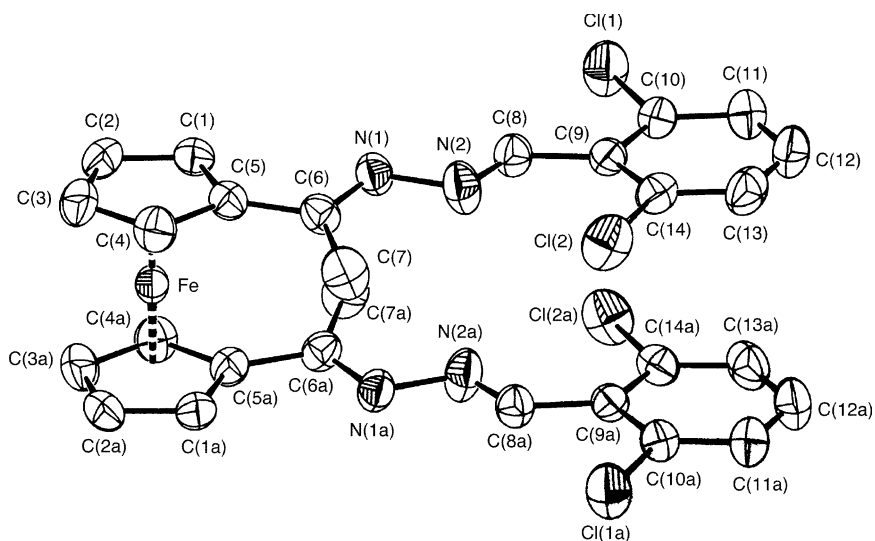


Fig. 2. Molecular structure and atom labelling scheme for ligand  $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(2,6\text{-Cl}_2\text{-C}_6\text{H}_3)\}_2]$  (**4a**).

## 2.2. Activation of $\sigma(C-H)$ bonds of compounds

$[Fe\{(\eta^5-C_5H_4)-C(Me)=N-N=C(H)(C_6H_3-2,6-R_2)\}_2]$  with  $R = Cl$  (**4a**) or  $H$  (**4b**)

In a first attempt to achieve the cyclopalladation of ligands **4**, we decided to use the procedure described before for the metallation of the monofunctional ferrocenyl Schiff bases of general formula:  $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-C(R)=N-R'\}]$  with  $R = H, Me$  or  $Ph$  and  $R' =$  phenyl or a benzyl group. This method, which is based on the treatment of equimolar amounts of the free ligand,  $Na_2[PdCl_4]$  and  $Na(CH_3COO) \cdot 3H_2O$  in methanol at room temperature [9,14,15], produces the di- $\mu$ -chloro-bridged cyclopalladated derivatives:  $[Pd\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_3)-C(R)=N-R']\}(\mu-Cl)]_2$ . Due to the low solubility of these dimers in most common solvents, they are difficult to characterise and they are usually treated with phosphine ligands to produce the monomeric derivatives:  $[Pd\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_3)-C(R)=N-R']\}Cl(PPh_3)]$  which are more soluble.

The reaction of ligand **4a** with  $Na_2[PdCl_4]$  and  $Na(CH_3COO) \cdot 3H_2O$  in a 1:2:2 molar ratio in methanol at room temperature for 6 days produced a nearly black solid and its subsequent treatment with triphenylphosphine in  $CH_2Cl_2$  at room temperature for 1 h followed by concentration of the solution gave a deep purple solid. Its  $^{31}P\{^1H\}$ -NMR spectrum showed three singlets at  $\delta = 38.7, 37.6$  and  $23.2$  ppm. The chemical shift of the signal at lower higher fields suggested the presence of the coordination complex  $trans-[PdCl_2(PPh_3)_2]$  [16]. Due to the low solubility of  $trans-[PdCl_2(PPh_3)_2]$  in  $CH_2Cl_2$  it was easily removed from the mixture by dissolving the crude of the reaction in the minimum amount of  $CH_2Cl_2$ . The elemental analyses of the solid obtained by concentration of the resulting filtrate were consistent with those expected for  $[Pd_2\{Fe[(\eta^5-C_5H_3)-C(Me)=N-N=C(H)(C_6H_3-2,6-Cl_2)]_2\}Cl_2(PPh_3)_2]$  (**5a**), but its  $^1H$ -,  $^{13}C\{^1H\}$ - and  $^{31}P\{^1H\}$ -NMR were more complex than expected. In the  $^{31}P\{^1H\}$ -NMR spectrum, two singlets of identical intensity at  $\delta = 38.7$  and  $37.6$  ppm were observed, and the position of these signals was consistent with those reported for cyclopalladated complexes of general formula:  $[Pd\{[(\eta^5-C_5H_3)-C(R)=N-R']Fe(\eta^5-C_5H_5)\}Cl(PPh_3)]$  (with  $R = H, Me$  or  $C_6H_5$  and  $R' =$  phenyl benzyl or naphthyl) in which the  $PPh_3$  and the metallated carbon are in a *cis*-arrangement [12]. This is the typical result of the reaction of palladacycles derived from  $(C,N)^-$  bidentate ligands and  $PPh_3$ , due to the so-called *transphobia* effect [17]. The proton NMR spectrum showed two superimposed sets of signals (Fig. 3A) and in particular the most relevant feature observed in the spectrum was the presence of six singlets in the range 3.0–5.0 ppm, two resonances due to the imine protons and two singlets in the higher fields area assigned to the protons of the

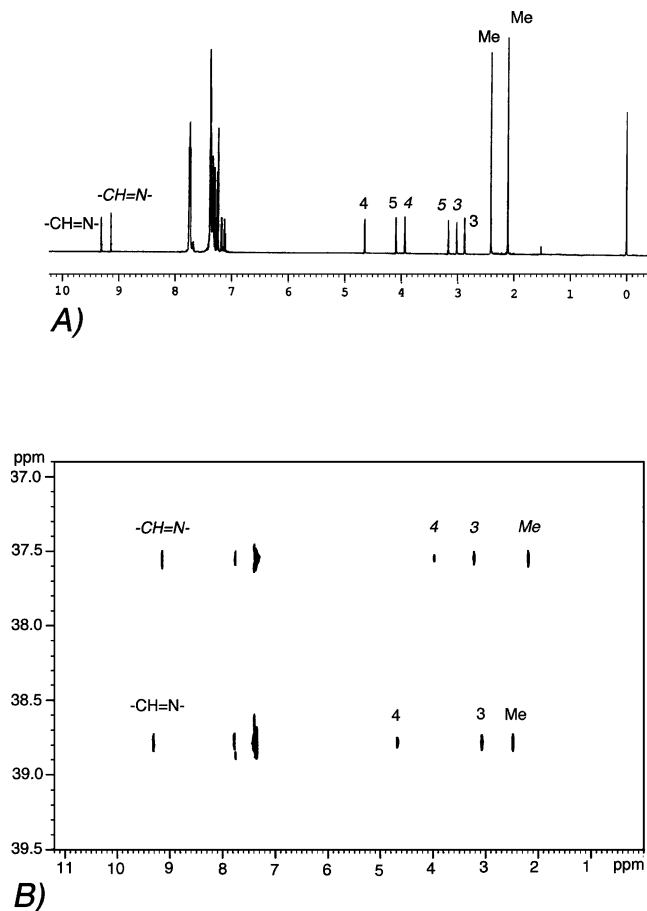
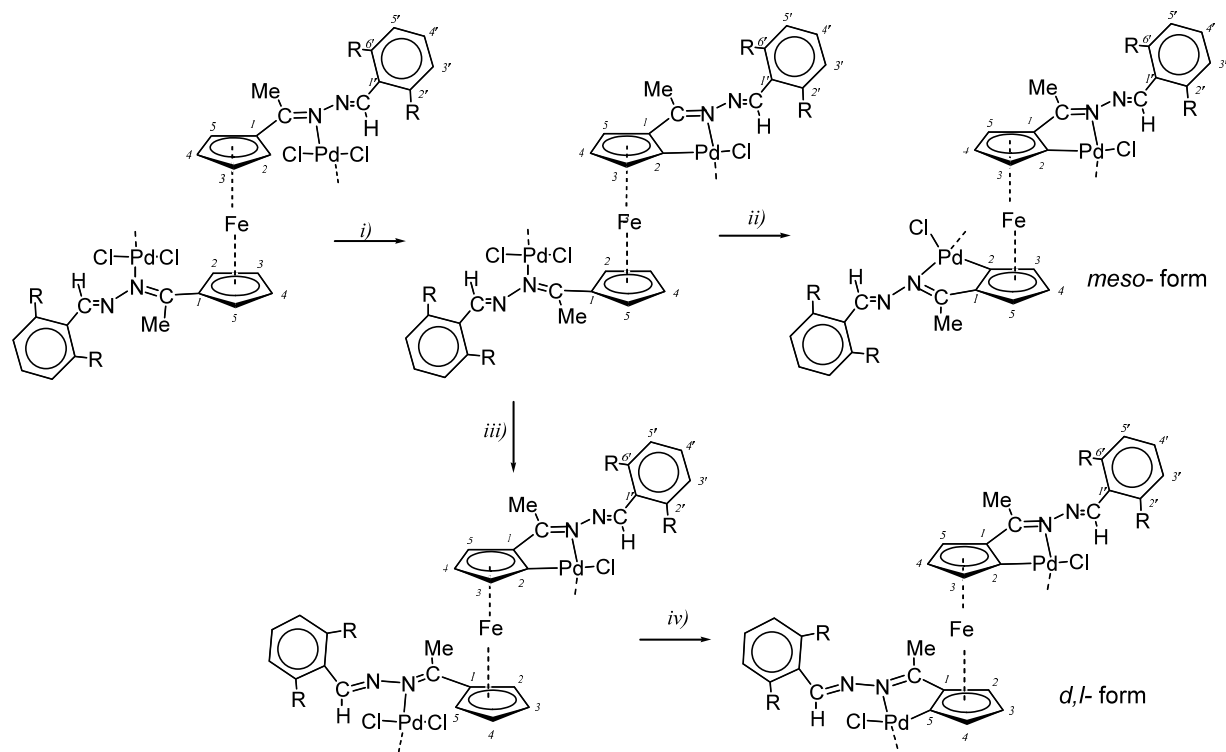


Fig. 3. Partial views of the  $^1H$ -NMR spectra of **5a** (A) and of the two-dimensional  $\{^{31}P-^1H\}$ -NMR spectrum of **5a** (B). (The signals marked in italics correspond to the *meso*- form of **5a**.)

methyl groups. The two dimensional  $^{31}P-^1H$ -NMR spectrum is presented in Fig. 3B, and shows that one of the signals due to the phosphorous has cross peaks with one of the singlets due to the proton of the imine group and with two of the six singlets detected in the range 3.00–5.00 ppm and with one of the resonances due to the methyl groups and a similar result is obtained for the signal due to the other  $^{31}P$  nucleus.

The doubling of the signals observed in the NMR spectra could be indicative of the presence of two species in solution. However, no evidences for any interchange between them was obtained from the  $^1H-^1H$ -NOESY experiment at room temperature. On the other hand, it is well known that the activation of a  $\sigma(Csp^2, ferrocene-H)$  bonds in the *N*-donor ferrocenyl ligands introduces planar chirality, and consequently for ligands **4**, the cyclopalladation of the two rings may produce two stereoisomers {*meso*- and *D,L*- forms} (Scheme 2). In order to confirm these findings we decided to try to separate the two isomers and to characterise them separately.

In a first attempt to achieve the separation of the two isomers compound **5a** was passed through a short  $SiO_2$



Scheme 2. R = Cl or H. (i) Cyclopalladation of one of the rings. (ii) Cyclopalladation of the other ring. (iii) Rotation around the C–C<sup>1</sup> bond of the non-metallated ring. (iv) Palladation of the other ring.

column chromatography using a CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (100:0.05) mixture as eluant. This produced the release of a band which lead after concentration to a deep red solid. Its proton NMR spectrum showed only four signals of relative intensities 3:1:1:1 in the region 2.0–5.0. The former was assigned to the methyl protons while the remaining signals correspond to the protons of the C<sub>5</sub>H<sub>3</sub> rings. The position of these signals as well as the magnitude of their shifts compared with that of the free ligand were very similar to those observed for the *meso*- forms of the bis(metallated) complexes derived from ligands **2**: [Pd{Fe{(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)–C(H)=N–R'}<sub>2</sub>}]<sub>2</sub>. The <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum showed only one signal at δ = 37.6 ppm. These findings suggested that the first eluted band contained the *meso*- form of **5a**. The second component was isolated after the elution with a CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (100:0.1) mixture and the work up. This deep-purple solid was identified according to its NMR data as the D,L- form of **5a**.

More complex were the results obtained when the reaction was performed under identical experimental conditions but using ligand **4b** as starting material. In this case, the <sup>1</sup>H- and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra of the crude of the reaction were more complex and suggested that it contained a mixture of several compounds. In particular, the <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum showed three singlets at δ = 37.6, 36.0 and 23.2 ppm. The later signal at (δ = 23.2 ppm) was indicative of the presence of *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], which was also formed as a by-

product in the reaction described above. The position of the two signals at δ = 36.0 and 37.6 ppm were very similar to those of **5a** and could be indicative of the presence of the two isomers of the bis(cyclopalladated) complex [Pd<sub>2</sub>{Fe{(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)–C(Me)=N–N=C(H)-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}]<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**5b**). In addition, the <sup>1</sup>H-NMR spectrum of the crude material indicated also the presence of the free ligand. The use of an SiO<sub>2</sub>-column chromatography allowed the isolation of **4b**, *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and complex **5b**. The subsequent separation of the two isomeric forms of **5b** was achieved using the same procedure as described for **5a**, and *meso*- and D,L- forms were isolated in a molar ratio of 1.10. Also in this case the *meso*- form- exhibited higher R<sub>f</sub> value than the D,L- form.

It is worth to mention that although ligand **4b** contains two different types of σ(C–H) bonds susceptible to activate {a σ[C(sp<sup>2</sup>, ferrocene)–H] and a σ[C(sp<sup>2</sup>, phenyl)–H] bond} the cyclopalladation at the ferrocenyl unit occurs and no evidences of the formation of any other palladacycle with one or two σ[C(sp<sup>2</sup>, phenyl)–H] bonds was detected by <sup>1</sup>H- and <sup>31</sup>P-NMR spectroscopy. This finding is consistent with the higher proclivity of the ferrocene derivatives to undergo electrophilic attacks [17].

In a first attempt for the synthesis of the monometallated derivatives the reactions between the equimolar amounts of corresponding ligand **1**, Na<sub>2</sub>[PdCl<sub>4</sub>] and Na(CH<sub>3</sub>COO)·3H<sub>2</sub>O in methanol at room temperature

were also studied. However, in the two cases, no evidences of the formation of the complexes arising from the activation of only one  $\sigma[\text{Csp}^2, \text{ferrocene}]\text{-H}$  bond were detected by NMR.

### 2.3. Conclusions

The results reported in this work have allowed the isolation and characterisation of the two isomeric forms (*meso*- and *D,L*-) of the bis(cyclopalladated) compounds:  $[\text{Pd}_2\{\text{Fe}\{\eta^5\text{-C}_5\text{H}_3\}\text{-C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{H})\text{-}(\text{C}_6\text{H}_5\text{-}2,6\text{-R}_2)\}_2]\text{Cl}_2(\text{PPh}_3)_2$ , {with  $\text{R} = \text{Cl}$  (**5a**) or  $\text{H}$  (**5b**)} in a nearly equimolar ratio formed by the activation of two  $\sigma[\text{C}(\text{sp}^2, \text{ferrocene})\text{-H}]$  bonds belonging to two different ' $\text{C}_5\text{H}_4$ ' rings of the ligands bases  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\}\text{-C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-}2,6\text{-R}_2)\}_2]$  with  $\text{R} = \text{Cl}$  (**4a**) or  $\text{H}$  (**4b**). The yield of **5b** was significantly smaller than that of **5a** and unreacted ligand **4b** was also recovered from the crude of the reaction. Thus, the comparison of these findings suggests that tiny changes in the nature of the aryl ring bound to the nitrogen are important to determine the ease with which these substrates undergo the double cyclopalladation. Although ligand **4a** contains a bulkier aryl group than **4b** [18], it is more prone to undergo the bis(metallation) process.

On the other side, since the formation of the bis(cyclopalladated) complexes **5** requires longer reaction periods (6 days) than those derived from the bis(ferrocenylimines) of the type:  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\}\text{-C}(\text{R})=\text{N}-\text{R}'\}_2]$  {with  $\text{R} = \text{H}$ ,  $\text{R}' = \text{CH}_2\text{C}_6\text{H}_5$  (**2**),  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{C}_6\text{H}_5$  (**3a**) or  $\text{C}_6\text{H}_4\text{-}4\text{-Me}$  (**3b**) (Fig. 1) (2 days) [6] we can conclude that in this type of processes ligands **4** are less reactive than compounds **2** and **3**.

The relative abundance of the *meso*- and *D,L* forms of **5a** and **5b** [*meso*- and *D,L* molar ratios = 1.02 (for **5a**) and 1.10 (for **5b**)] was very similar and the interconversion of the two stereoisomers *meso*- form  $\leftrightarrow$  *D,L*- would require the cleavage of the  $\sigma(\text{Pd}-\text{C})$  bond. Since it is well known that the reaction of the di- $\mu$ -chloro-bridged-cyclopalladated complexes with Lewis bases, such as  $\text{PPh}_3$ , does not involve the cleavage of the  $\sigma(\text{Pd}-\text{C})$  or  $\sigma(\text{Pd}-\text{N})$  bond, the relative ratio of the two stereoisomers of **5** should be predetermined in the cyclometallation process which takes place before the addition of the triphenylphosphine.

It is widely accepted that the cyclopalladation of *N*-donor ligands proceeds in two steps: the binding of the palladium and the subsequent electrophilic attack [19]. On this basis, the formation of nearly equimolar amounts of the two isomeric forms [*meso*-/*D,L*- form molar ratio = 1.02 (for **5a**) and 1.10 (for **5b**)], can be rationalised using a similar argument as reported for the double cycloplatination of the 1,1'-bis(ferrocenylamine)  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\}\text{-CH}_2\text{-NMe}_2\}_2]$  [20]. Once the first metallacycle is formed, the remaining  $\text{C}_5\text{H}_5$  moiety may

undergo the cyclopalladation to produce the *meso*- form (Scheme 2). However, if this ring rotates around the  $\text{C}^1\text{-C}_{\text{ipso}}$  bond prior to the metallation, this would lead to the *D,L*- form (Scheme 2). Thus, the presence of bulky groups in the vicinity of the non-metallated ring should hinder the free rotation around the  $\text{C}^1\text{-C}_{\text{ipso}}$  bond, and consequently a decrease of molar ratio *meso*-/*D,L*- form should be expected. The similarity between the *meso*-/*D,L*- form molar ratios [1.02 (for **5a**) and 1.10 (for **5b**)] for compounds **5**, suggests that once the metallation of one of the rings occurs, the rotation around the  $\text{C}^1\text{-C}_{\text{ipso}}$  bond of the other half of the molecule is not hindered.

Finally, since it is well known that some cyclopalladated derivatives are useful precursors for the synthesis of organic or organometallic derivatives [3], the two isomeric forms of compounds **5** presented in this work have an additional interest since they appear to be excellent candidates to undertake further studies focused on the reactivity of the  $\sigma(\text{Pd}-\text{C})$  bonds versus small molecules such as alkynes, alkenes or CO, which may allow the preparation of novel tetrasubstituted ferrocenyl derivatives with planar chirality.

## 3. Experimental

### 3.1. Materials and synthesis

All the reagents used for the preparations described in this work were obtained from Aldrich, except for compound:  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\}\text{-C}(\text{Me})=\text{N}-\text{NH}_2\}_2]$  which was prepared as described previously [7], and the solvents were distilled and dried according to the standard procedures [21] before their use.

Elemental analyses (C, H and N) were carried out at the Serveis Científico-Tècnics (Universitat de Barcelona) or at the Institut de Química Bio-Orgànica (C.S.I.C., Barcelona). Infrared spectra were recorded with a Nicolet-Impact 400 instrument using KBr pellets. Routine  $^1\text{H}$ - and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were obtained with a Gemini-200 MHz instrument using  $\text{CDCl}_3$  as solvent and  $\text{SiMe}_4$  as internal reference. High resolution  $^1\text{H}$ -NMR spectra and the two dimensional  $\{^1\text{H}-^{13}\text{C}\}$ -NMR experiments {heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond coherence (HMBC)} were carried using either a Varian 500 or a Bruker 500 instrument, and the same solvents as mentioned above for the monodimensional experiments.  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **5** were recorded with a Bruker-250 DXR instrument using  $\text{CDCl}_3$  as solvent and  $\text{P}(\text{OMe})_3$  as reference [ $\delta$   $^{31}\text{P}\{\text{P}(\text{OMe})_3\} = 140.17$  ppm] and the two-dimensional  $\{^1\text{H}-^{31}\text{P}\}$ -NMR spectra were recorded with a Bruker Avance 600 MHz instrument. In all cases the chemical shifts ( $\delta$ ) are given in ppm, the coupling constants ( $J$ ) in Hz and the labelling

scheme used for the assignment of the signals corresponds to that shown in Scheme 1.

### 3.1.1. Preparation of $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\}\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(2,6\text{-Cl}_2\text{-C}_6\text{H}_3)\}_2]$ (**4a**)

A suspension formed by  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\}\text{-C}(\text{Me})=\text{N}=\text{NH}_2\}_2]$  (250 g,  $1.03 \times 10^{-3}$  mol), 2,6-dichlorobenzaldehyde (300 mg,  $2.05 \times 10^{-3}$  mol) and 30 ml of ethanol was refluxed for 3 h. After this period the hot and red solution was filtered out. The filtrate was allowed to cool down to room temperature (r.t.) on an open vessel. The red crystals formed were collected, air-dried and then dried in vacuum for 1 day (yield: 0.413 g, 65.5%). Characterisation data for **4a**: Anal. Calc. for:  $\text{C}_{28}\text{H}_{22}\text{Cl}_4\text{N}_4\text{Fe}$  (Found): C, 54.94 (54.87); H, 3.62 (3.65) and N, 9.15 (9.12)%. IR:  $1613\text{ cm}^{-1}$ ,  $\nu(>\text{C}=\text{N}-)$ .  $^1\text{H-NMR}$  data: 2.39 [s, 6H, Me], 4.83 [t, 4H,  $\text{H}^2$  and  $\text{H}^5$ ], 4.47 [t, 4H,  $\text{H}^3$  and  $\text{H}^4$ ], 8.60 [s, 2H,  $-\text{CH}=\text{N}-$ ], 7.31 [d, 2H,  $\text{H}^3$ ], 7.15 [t, 2H,  $\text{H}^4$ ] and 7.31 [d, 2H,  $\text{H}^5$ ].  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  data: 16.69 (Me), 152.4 ( $>\text{C}=\text{N}-$ ), 82.5 ( $\text{C}^1$ ), 71.86 ( $\text{C}^2$  and  $\text{C}^5$ ), 69.28 ( $\text{C}^3$  and  $\text{C}^5$ ), 167.2 ( $-\text{CH}=\text{N}-$ ), 135.33 ( $\text{C}^2$  and  $\text{C}^6$ ), 128.80 ( $\text{C}^3$  and  $\text{C}^5$ ) and 130.0 ( $\text{C}^4$ ).

### 3.1.2. Preparation of $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\}\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_5)\}_2]$ (**4b**)

This compound was prepared using the same procedure as described above for **4a**, but using  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\}\text{-C}(\text{Me})=\text{N}=\text{NH}_2\}_2]$  (800 mg,  $2.7 \times 10^{-3}$  mol) and benzaldehyde (600 mg,  $5.7 \times 10^{-3}$  mol). (Yield: 850 mg, 66.8%). Characterisation data for **4b**: Anal. Calc. for  $\text{C}_{28}\text{H}_{26}\text{FeN}_4$  (Found): C, 70.89 (70.6); H, 5.52 (5.6) and N, 11.81 (11.7)%. IR:  $\nu(>\text{C}=\text{N}-) = 1611\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  data: 2.39 [s, 6H, Me], 4.80 [t, 4H,  $\text{H}^2$  and  $\text{H}^5$ ], 4.45 [t, 4H,  $\text{H}^3$  and  $\text{H}^4$ ], 8.38 [s, 2H,  $-\text{CH}=\text{N}-$ ], 7.64 [d, 4H,  $\text{H}^2$ ,  $\text{H}^6$ ] and 7.28 [m, 6H,  $\text{H}^3$ ,  $\text{H}^4$  and  $\text{H}^5$ ].  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  data: 16.1 (Me), 158.4 ( $>\text{C}=\text{N}-$ ), 83.9 ( $\text{C}^1$ ), 71.7 ( $\text{C}^2$  and  $\text{C}^5$ ), 68.9 ( $\text{C}^3$  and  $\text{C}^5$ ), 166.5 ( $-\text{CH}=\text{N}-$ ), 128.5 ( $\text{C}^2$ ), 130.3 ( $\text{C}^3$  and  $\text{C}^5$ ), 134.2 ( $\text{C}^4$ ) and 130.3 ( $\text{C}^6$ ).

### 3.1.3. Preparation of $[\text{Pd}_2\{\text{Fe}\{\eta^5\text{-C}_5\text{H}_3\}\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-}2,6\text{-Cl}_2\text{-})\}_2\}\text{Cl}_2(\text{PPh}_3)_2]$ (**5a**)

A mixture containing ligand **4a** (200 mg,  $3.26 \times 10^{-4}$  mol),  $\text{Na}_2[\text{PdCl}_4]$  (191 mg,  $6.5 \times 10^{-4}$  mol) and  $\text{Na}(\text{CH}_3\text{COO})\cdot 3\text{H}_2\text{O}$  (88 mg,  $6.5 \times 10^{-4}$  mol) and 60 ml of methanol was protected from the light with aluminium foil and stirred at r.t. for 6 days. After this period the solid formed was collected by filtration and washed with three (5 ml) portion of methanol. The deep purple solid was then dissolved in 50 ml of  $\text{CH}_2\text{Cl}_2$  and treated with 170 mg ( $6.5 \times 10^{-4}$  mol) of  $\text{PPh}_3$  and stirred at r.t. for 2 h. The undissolved material were removed by filtration and concentrated to ca. 10 ml then *n*-hexane was added. The solid formed was collected by filtration and then dissolved in the minimum amount of

$\text{CH}_2\text{Cl}_2$ . The yellow needles of *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$  formed were removed from the solution by filtration and the evaporation of the filtrate produced **5a** (yield: 245 mg, 53%). The separation of the two isomers was carried out as follows: **5a** (200 mg,  $1.4 \times 10^{-4}$  mol) were dissolved in 5 ml of  $\text{CH}_2\text{Cl}_2$  and the resulting solution was passed by a short (6 cm  $\times$  2 cm)  $\text{SiO}_2$ -column chromatography. The elution with a  $\text{CH}_2\text{Cl}_2$ -MeOH (100/0.1) solution produced the release of a deep-red band which gave after concentration to dryness to the *meso*- form of **5a** (98 mg). Once this band was collected a mixture of  $\text{CH}_2\text{Cl}_2$ -MeOH (100/0.1) was used as eluant and a deep purple band was collected. The *D,L*- form of **5a** was isolated from this solution by concentration to dryness on a rotary evaporator (81 mg). Characterisation data for **5a**: Anal. Calc. for  $\text{C}_{64}\text{H}_{50}\text{N}_4\text{Cl}_6\text{FeP}_2\text{Pd}_2$  (Found): C, 54.19 (54.1); H, 3.55 (3.6) and N, 3.95 (3.90)%. IR:  $\nu(>\text{C}=\text{N}-) = 1610$  and  $1596\text{ cm}^{-1}$ . *Meso*- form:  $^1\text{H-NMR}$  data (in ppm): 2.18 [s, 6H, Me], 3.20 [t, 2H,  $\text{H}^3$ ], 4.10 [t, 2H,  $\text{H}^4$ ], 4.60 [t, 2H,  $\text{H}^5$ ], 9.20 [d, 2H,  $-\text{CH}=\text{N}-$ ] and 7.3–7.90 [m, 36H,  $\text{H}^3$ ,  $\text{H}^4$ ,  $\text{H}^5$  and aromatic protons of  $\text{PPh}_3$ ];  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  data (in ppm): 37.6. *D,L*- form:  $^1\text{H-NMR}$  data (in ppm): 2.41 [s, 6H, Me], 2.98 [t, 2H,  $\text{H}^3$ ], 3.05 [t, 2H,  $\text{H}^4$ ], 4.79 [t, 2H,  $\text{H}^5$ ], 9.60 [d, 2H,  $-\text{CH}=\text{N}-$ ], 7.18 [t, 2H,  $\text{H}^4$ ] and 7.30–7.80 [m, 34H,  $\text{H}^3$ ,  $\text{H}^5$  and aromatic protons of  $\text{PPh}_3$ ];  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  data (in ppm): 38.7.

### 3.1.4. Preparation of $[\text{Pd}_2\{\text{Fe}\{\eta^5\text{-C}_5\text{H}_3\}\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_5)\}_2\}\text{Cl}_2(\text{PPh}_3)_2]$ (**5b**)

This compound was prepared using the procedure described above for  $[\text{Pd}_2\{\text{Fe}\{\eta^5\text{-C}_5\text{H}_3\}\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-}2,6\text{-Cl}_2\text{-})\}_2\}\text{Cl}_2(\text{PPh}_3)_2]$ , but using ligand **4a** (400 mg,  $8 \times 10^{-4}$  mol),  $\text{Na}_2[\text{PdCl}_4]$  (470 mg,  $1.6 \times 10^{-4}$  mol) and  $\text{Na}(\text{CH}_3\text{COO})\cdot 3\text{H}_2\text{O}$  (217 mg,  $1.6 \times 10^{-4}$  mol) as starting material. Since the crude of the reaction was a mixture of several compounds, it was dissolved in  $\text{CH}_2\text{Cl}_2$  and passed through a short  $\text{SiO}_2$ -column chromatography (20 cm  $\times$  2 cm). Elution with  $\text{CH}_2\text{Cl}_2$  produced the release of two bands. The pale yellow band lead by concentration *cis*- $[\text{PdCl}_2(\text{PPh}_3)_2]$  and the second and red band gave unreacted ligand **4b**. Once these bands were collected, the use of a  $\text{CH}_2\text{Cl}_2$ :MeOH (100:0.1) mixture as eluant produced the release of a deep-red band which gave, after concentration, **5b**. Characterisation data for **5b**: Anal. Calc. for  $\text{C}_{64}\text{H}_{54}\text{N}_4\text{Cl}_3\text{FeP}_2\text{Pd}_2$  (Found): C, 60.02 (59.8); H, 4.25 (4.2) and N, 4.37 (4.3)%. IR:  $\nu(>\text{C}=\text{N}-) = 1610$  and  $1592\text{ cm}^{-1}$ . The *meso*- and the *D,L*- forms were separated from the crude **5b** (0.382 mg) using the same procedure as described in the previous section. (*meso*- form: 90 mg; *D,L*- form: 81 mg). *Meso*- form:  $^1\text{H-NMR}$  data (in ppm): 1.98 [s, 6H, Me], 3.18 [t, 2H,  $\text{H}^3$ ], 3.92 [t, 2H,  $\text{H}^4$ ], 4.18 [t, 2H,  $\text{H}^5$ ], 8.42 [d, 2H,  $-\text{CH}=\text{N}-$ ], and 7.29–7.90 [m, 40 H, aromatic protons of the  $\text{C}_6\text{H}_5$  rings of the ligand and of the  $\text{PPh}_3$  groups];  $^{31}\text{P}\{^1\text{H}\}\text{-$

NMR data (in ppm): 36.03. D,L- form:  $^1\text{H}$ -NMR data (in ppm): 2.42 [s, 6H, Me], 2.95 [t, 2H,  $\text{H}^3$ ], 3.06 [t, 2H,  $\text{H}^4$ ], 4.40 [t, 2H,  $\text{H}^5$ ], 9.02 [d, 2H,  $-\text{CH}=\text{N}-$ ] and 7.30–7.80 [m, 40H, aromatic protons of the  $\text{C}_6\text{H}_5$  rings of the ligand; of the  $\text{PPh}_3$  groups] and  $^{31}\text{P}\{^1\text{H}\}$ -NMR data (in ppm): 37.63.

### 3.2. Crystal structure determination

A prismatic crystal of **4a** (0.1 mm  $\times$  0.1 mm  $\times$  0.2 mm) was selected and mounted on a MAR345 diffractometer with a image plate detector. Unit cell parameters (Table 2) were determined from automatic centring of 7548 reflections in the range  $3 \leq \theta \leq 31^\circ$  and refined by least-squares method. Intensities were collected with graphite monochromatized Mo- $\text{K}_\alpha$  radiation. The number of reflections measured in the range  $2.08 \leq \theta \leq 28.84^\circ$  was 10308, of which 3452 were non-equivalent by symmetry  $R_{\text{int}}$  (on  $I$ ) = 0.030; 2943 reflections were assumed as observed applying the condition  $I > 2\sigma(I)$ . Lorentz-polarisation corrections were made but absorption corrections were not.

The structure was solved by Direct methods using SHELXS computer program [22] and refined by the least-squares method with the SHELX-97 computer program [23] using 3452 reflections (very negative intensities were not assumed). The function minimized was  $\sum w||F_o|^2 - |F_c|^2|^2$  where  $w = [\sigma^2(I) + (0.0433P)^2 + 4.4914P]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .  $f$ ,  $f'$  and  $f''$  were taken from International tables of X-ray crystallography [24]. All

Table 2  
Crystal data and details of the refinement of the crystal structure of compound  $[\text{Fe}\{\eta^3\text{-C}_5\text{H}_4\}\text{-C}(\text{Me})=\text{N}=\text{N}=\text{C}(\text{H})(2,6\text{-Cl}_2\text{-C}_6\text{H}_3)\}_2]$  (**4a**)

Empirical formula	$\text{C}_{28}\text{H}_{22}\text{Cl}_4\text{FeN}_4$
$M_w$	612.15
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
$a$ (Å)	16.680(1)
$b$ (Å)	14.690(1)
$c$ (Å)	13.5738(7)
$\alpha$ (°)	90
$\beta$ (°)	127.844(5)
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	2626.5(3)
$Z$	4
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.548
Absorption coefficient (mm <sup>-1</sup> )	1.008
$\theta$ Range for data collection (°)	2.08–28.84
No. of reflections collected	10308
No. of unique reflections [ $R_{\text{int}}$ ]	0.0302
No. of data	3452
No. of parameters	212
Goodness-of-fit on $F^2$	1.121
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0440$ , $wR_2 = 0.1030$
$R$ indices (all data)	$R_1 = 0.0531$ , $wR_2 = 0.1162$

hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. The final  $R$  (on  $F$ ) factor was 0.044,  $wR$  (on  $F$ ) = 0.103. Further details concerning the resolution and refinement of the crystal structure of **4a** are presented in Table 2.

### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 199101 for **4a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

### Acknowledgements

We are grateful to the Ministerio de Ciencia y Tecnología of Spain and to the Generalitat de Catalunya (grants: BQU2000-0654 and 2001SGC-00054, respectively) for financial support.

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