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Palladium(II) compounds with planar chirality. X-Ray crystal structures of (+)-(*R*)-[{(η^5-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$}Fe(η^5-C_5H_5)] and (+)-(R_p,*R*)-[Pd{[(Et–C=C–Et)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl]

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Abstract

A wide variety of planar chiral cyclopalladated compounds of general formulae [Pd{[(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl(L)] (with L=py-d_5 or PPh_3), [Pd{[(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}(acac)] or [Pd{[(R^1–C=C–R^2)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (with R^1=R^2=Et; R^1=Me, R^2=Ph; R^1=H, R^2=Ph; R^1=R^2=Ph; R^1=R^2=CO_2Me or R^1=CO_2Et, R^2=Ph) are reported. The diastereomers {(R_p,*R*) and (S_p,*R*)} of these compounds have been isolated by either column chromatography or fractional crystallization. The free ligand (*R*)-(+)-[{(η^5-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$}Fe(η^5–C_5H_5)] (**1**) and compound (+)-(R_p,*R*)-[Pd{[(Et–C=C–Et)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (**7a**) have also been characterized by X-ray diffraction. Electrochemical studies based on cyclic voltammetries of all the compounds are also reported.

1. Introduction

The study of palladium(II) complexes containing N-donor ligands and a σ(Pd–$C_{sp^2,aryl}$) or even a σ(Pd–C_{sp^3}) bond has increased considerably during the last decade[1–4] due to a wide variety of interesting and novel applications in different areas.[5–15] In particular, the study of chiral cyclopalladated derivatives has attracted great interest since these compounds have been found to be interesting substrates for the determination of the enantiomeric excesses of chiral reagents, or for their resolution, and as chiral discriminators or in asymmetric syntheses.[15–22]

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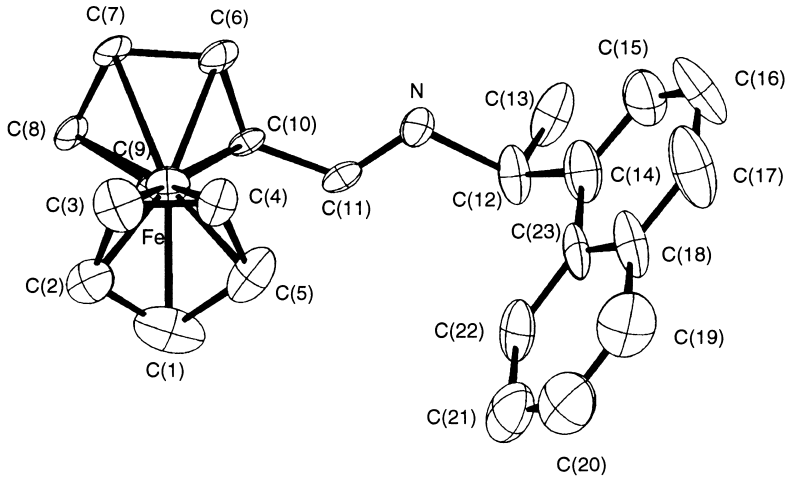


Figure 1. Molecular structure and atom numbering scheme for (*R*)-(+)-[{(η^5-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$}Fe(η^5-C_5H_5)] (**1**). Selected bond lengths (Å): C(10)–C(11): 1.408(10), C(11)–N: 1.238(9), N–C(12): 1.518(11), C(12)–C(13): 1.547(14); C(12)–C(14): 1.55(2), C(14)–C(15): 1.34(2). Selected bond angles (°): C(10)–C(11)–N: 123.1(9), C(11)–N–C(12): 116.7(8), N–C(12)–C(14): 107.6(9), N–C(12)–C(13): 104.6(10), C(13)–C(12)–C(14): 114.7(11) and C(12)–C(14)–C(15): 125(2)

Some applications in organic synthesis have also been described.[23]

Although *ortho*-metallation of N-donor ferrocenyl ligands produces 1,2-disubstituted ferrocene derivatives, cyclopalladation of most N-donor ferrocenyl substrates (i.e. amines, imines, oximes, hydrazones, azines and azo-derivatives) reported so far has yielded racemates,[24–38] and examples of diastereomerically pure cyclopalladated complexes containing ferrocenyl units are scarce.[39–46]

In this paper we report the synthesis and characterization of (*R*)-(+)-[{(η^5-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$}Fe(η^5-C_5H_5)] (**1**), its cyclopalladation reaction and a wide variety of palladium(II) compounds containing planar chirality and [5,5] or [5,9] bicyclic systems.

2. Results and discussion

2.1. The ligand

The ferrocenylimine (*R*)-(+)-[{(η^5-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$}Fe(η^5-C_5H_5)] (**1**) was prepared by condensation between equimolar amounts of ferrocene carboxaldehyde and (*R*)-(+)-1-naphthylethylamine following the general procedure described in the literature for [{(η^5-C_5H_4)–CH=N–R}Fe(η^5-C_5H_5)] (with R=phenyl, benzyl or naphthyl).[34,36]

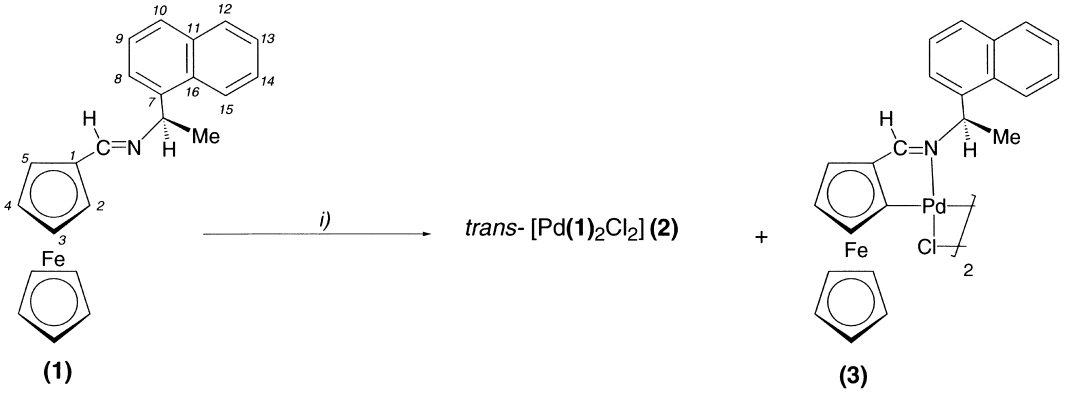
Compound **1** is an orange-yellow solid at room temperature, and it has been characterized by elemental analysis, infrared spectroscopy, and ^{1}H and ^{13}C NMR. ^{1}H and ^{13}C NMR spectra of **1** were consistent with those reported for related ferrocenyl Schiff bases[34,36,37,47] and indicated that only the *E*-isomer was present in solution. Compound **1** has also been characterized by X-ray diffraction (Fig. 1). The structure consists of discrete molecules of (*R*)-(+)-[{(η^5-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$}Fe(η^5-C_5H_5)] separated by van der Waals contacts. It should be noted that the absolute configuration of this ferrocenylimine is identical to that of the (*R*)-(+)-1-naphthylethylamine, which was used in the preparation of **1**.

The >C=N– bond length [1.238(9) Å] in **1** is similar to that reported for other ferrocenyl Schiff bases.[47] The value of the bond angle C(10)–C(11)–N–C(12) [−178.9 (4)°] is close to the ideal value expected for the *E*-isomer. Bond distances and angles of the '[(η^5-C_5H_4)Fe(η^5-C_5H_5)]' moiety are consistent with

those reported for most ferrocene derivatives.[48] The two pentagonal rings are planar and nearly parallel as reflected in the value of the *tilt angle* (1.3°), and their conformation is close to the ideal eclipsed (*twist angle*: 5.6°).

2.2. Reactivity of **1** with palladium(II) salts

When **1** was treated with $Na_2[PdCl_4]$ (in a 2:1 molar ratio) in methanol at room temperature (ca. 20°C) for 2 h a red solid was formed. Its characterization data were consistent with those expected for the coordination complex *trans*- [Pd{[(η^5-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}$_2$$Cl_2$] (**2**). An identical result was obtained when the molar ratio Pd:**1** was reduced to 1:1 though in this case complex **2** was obtained in a lower yield (ca. 40%). However, when the reaction was carried out in the presence of $Na(CH_3COO)\cdot 3H_2O$, complex **2** or [Pd{[(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ (**3**) (or mixtures of both) (Scheme 1) were isolated depending on the experimental conditions. For instance, for short reaction periods of ca. 2–4 h only **2** was obtained, but when the reaction time was increased to 24 h a mixture of **2** and **3**. For longer reaction periods (ca. 60 h), **3** was isolated in a higher yield and in this case no evidence of the presence of **2** was detected by NMR spectroscopy.



i) $Na_2[PdCl_4]$, $Na(CH_3COO)\cdot 3H_2O$ in methanol at room temperature (see text).

Scheme 1.

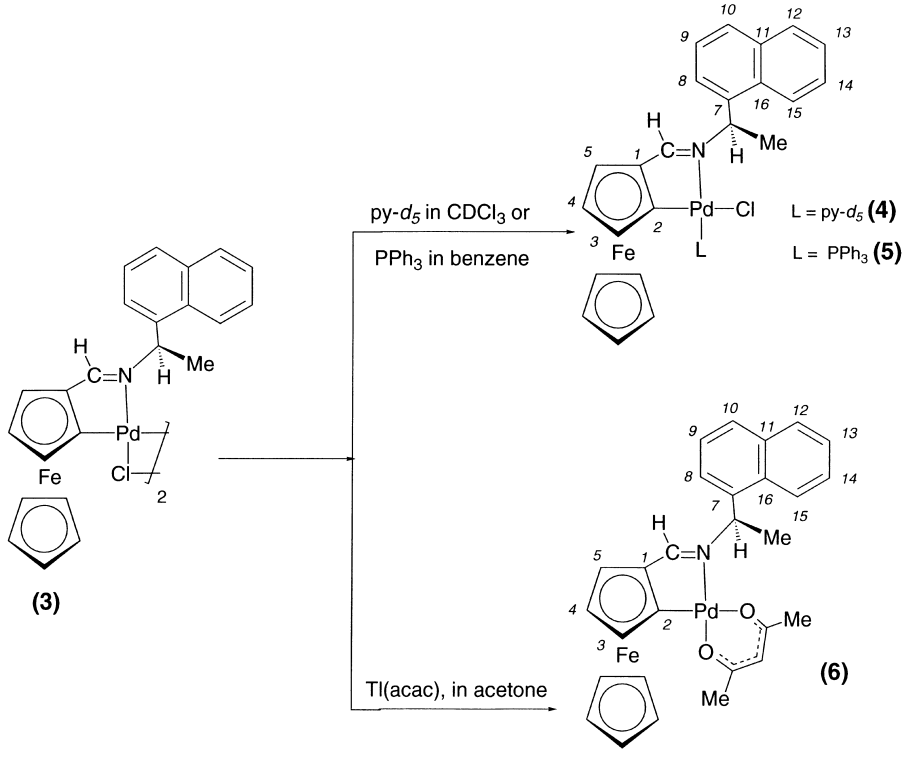
These observations suggest that the coordination complex **2** is formed before the activation of the σ(C_{sp^2},ferrocene–H) bond to give **3**. These findings are consistent with the results reported by Ryabov et al.[49] for the cyclopalladation of *N*,*N*-dimethylbenzylamines. It should be pointed out that the activation of the σ(C_{sp^2},ferrocene–H) bond introduces planar chirality, and consequently, several isomers of **3** could be formed in the cyclopalladation of **1**. These isomers may differ in their absolute configuration {(R_p,*R*,*R*,R_p), (S_p,*R*,*R*,S_p) or (R_p,*R*,*R*,S_p)} and/or in the relative arrangement of the two imine nitrogens (*syn*- or *anti*-). However, in most of the di-μ-chloro-bridged cyclopalladated compounds containing imine ligands a *syn*-arrangement of the two nitrogen atoms has been found.[41,42] ^{1}H NMR spectra of **3** showed two superimposed sets of signals due to the ferrocenyl fragments, of relative intensities 3:1, thus suggesting that a maximum of two isomers (hereinafter referred to **3a** and **3b**) could be present in **3**.

Attempts to separate the components of **3** by column chromatography or slow evaporation of their benzene solutions were unsuccessful. The failure of all these procedures could be related to the low solubility of the di-μ-chloro-bridged cyclopalladated compounds. Therefore, we decided to prepare some monomeric derivatives of these isomers, which were expected to be more soluble in the most common

solvents. With this aim, we studied the reactivity of the 'Pd(μ-Cl)$_2$Pd' units and of the σ(Pd–C$_{sp^2,ferrocene}$) bond in **3**. These types of reactions have an additional interest since the formation of the monomeric derivatives would produce a maximum of two isomers: {(R_p,*R*) or (S_p,*R*)}.

2.3. *Reactivity of the 'Pd(μ-Cl)$_2$Pd' moiety*

The addition of deuterated pyridine (py-d_5) (in $CDCl_3$) or PPh_3 (in benzene) to suspensions of **3** produced the cleavage of the 'Pd(μ-Cl)$_2$Pd' units and the formation of the mononuclear derivatives [Pd{[(η^5-C$_5$H$_3$)–CH=N–CH(Me)–C$_{10}$H$_7$]Fe(η^5-C$_5$H$_5$)}Cl(L)] (with L=py-d_5 **4** or PPh_3 **5**; Scheme 2). It is well known that these bridge splitting reactions do not affect the planar chirality of the metallacycle,[41] and consequently the formation of two diastereomers {(R_p,*R*) or (S_p,*R*)} could be expected in principle. NMR spectra of **4** and **5** showed two superimposed sets of signals of relative intensities of ca. 2.8:1. This suggests that these compounds consisted of a mixture of the two diastereomers **4a**, **4b** or **5a**, **5b**.



Scheme 2.

The separation of the two diastereomers of complex **5** was achieved succesfully by SiO_2 column chromatography using $CHCl_3$ as eluant. The major component **5a** was obtained from the first eluted band, while the second **5b**, which showed a higher R_f value, was isolated from the second reddish-orange band. In both cases, the solutions collected were concentrated to dryness on a rotary evaporator, and addition of *n*-hexane produced the precipitation of the desired diastereomers **5a** and **5b**.

Addition of thallium(I) acetylacetonate to acetone suspensions of **3** at room temperature produced the precipitation of TlCl, which was collected by filtration and discarded. Concentration to dryness of the filtrate on a rotary evaporator produced a dark red solid. Elemental analyses of this material were consistent with those expected for [Pd{[(η^5-C$_5$H$_3$)–CH=N–CH(Me)–C$_{10}$H$_7$]Fe(η^5-C$_5$H$_5$)}(acac)] (**6**).

Table 1
Electronic and steric parameters of the substituents R^1 and R^2 on the alkynes R^1–C≡C–R^2[a]

R^1 or R^2	σ_I	σ_R	ES-CH
H	0.0	0.0	0.0
Me	-0.08	-0.15	1.0
Et	-0.01	-0.14	2.0
Ph	0.12	0.10	3.0
CO_2Me	0.21	0.16	4.0
CO_2Et	0.21	0.16	4.0

[a] σ_I and σ_R are inductive (*para*) and mesomeric (*para*) values for the R^1 or R^2 groups. Positive s values indicate an electron-withdrawing effect of the substituents, while negative s values correspond to electron-donnor substituents. The ES-CH values are Charton's steric parameters calculated according to the structural data. All the values reported in this table were obtained from reference 50.

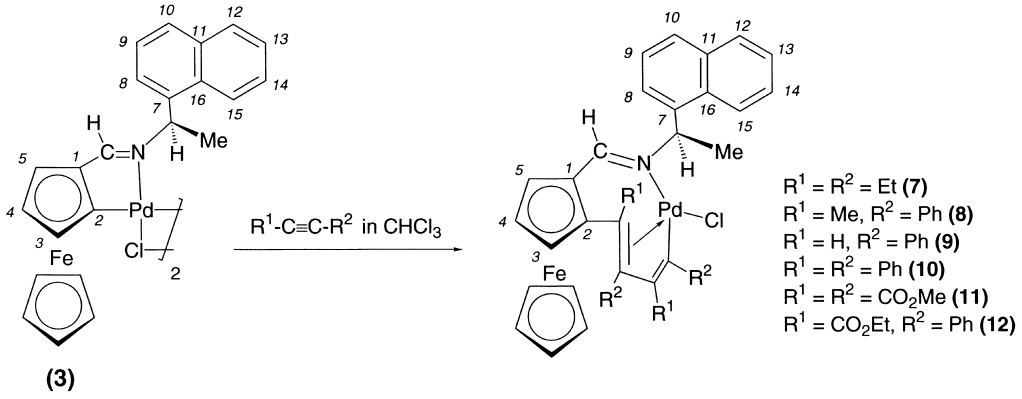
NMR spectra (^{1}H and ^{13}C) suggested that the two diastereomers **6a** and **6b** coexisted in a 3.1:1 molar ratio. Complex **6a** was isolated by slow evaporation (at ca. 4°C) of a solution of **6** in a mixture of acetone: methanol (1:1). The solution obtained after the separation of **6a** was enriched by ca. 80% in **6b**. When the fractional crystallization was repeated complex **6b** was isolated from the filtrate with higher purity {ca. 95%, based on its ^{1}H NMR spectrum (500 MHz)}. Attempts to obtain good quality crystals of **4**–**6a**,**b** for X-ray diffraction studies failed. However, the NMR studies and the crystal structure of one of the isomers of [Pd{[(Et–C=C–Et)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (vide infra) allowed us to deduce the absolute configuration of the major **4a**–**6a** and minor components **4a**–**6a** of **4**–**6**.

2.4. Reactivity of the σ(Pd–C$_{sp^2}$,$_{ferrocene}$) bond versus alkynes

One of the main interests in cyclopalladated complexes lies in the high reactivity of the σ(Pd–C) bond, which has provided new methods for the syntheses of organic and organometallic compounds.[9–11] Most of these reactions are based on the insertion of small molecules (mainly alkynes, and to a lesser extent alkenes, CO or isonitriles) into the σ(Pd–C) bond and the subsequent depalladation process. On this basis, **3** appeared to be a good candidate to study the reactivity of the σ(Pd–C_{sp^2},$_{ferrocene}$) bond versus alkynes since these studies could allow isolation of diastereomerically pure 1,2-disubstituted ferrocenes containing two different functional groups (>C=N– and one or more >C=C< groups). With this aim we decided to study the reactivity of **3** versus a wide variety of alkynes of general formula R^1–C≡C–R^2 (with R^1=R^2=Et; R^1=Me, R^2=Ph; R^1=H, R^2=Ph; R^1=R^2=Ph; R^1=R^2=CO_2Me or R^1=CO_2Et, R^2=Ph), which differ in the electronic and steric nature of the substituents R^1 and R^2 (Table 1).[50]

These reactions were undertaken using an R^1–C≡C–R^2:**3** molar ratio of 4:1 and different experimental conditions. Attempts to insert these alkynes in mild conditions (room temperature, ca. 20°C, CH_2Cl_2 as solvent and reaction periods from 3 h to 24 h) were unsuccessful, and in all cases the starting materials were recovered from the reaction medium. However, when more dras-

tic experimental conditions were used (refluxing chloroform for 1.5 h), mixtures of the diastereomers of the bis(insertion) products [Pd{[(R^1–C=C–R^2)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (with R^1=R^2=Et **7**; R^1=Me, R^2=Ph **8**; R^1=H, R^2=Ph **9**; R^1=R^2=Ph **10**; R^1=R^2=CO_2Me **11** or R^1=CO_2Et, R^2=Ph **12**) (shown in Scheme 3) were obtained. According to the literature, the bis(insertion) of alkynes into the σ(Pd–$C_{sp^2,ferrocene}$) bond does not affect the chirality of the 1,2-disubstituted ferrocenyl fragment,[41] and consequently two diastereomers {(R_p,R) or (S_p,R)} of compounds [Pd{[(R^1–C=C–R^2)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (**7**–**12**) could be expected. NMR spectra of **7**–**12** showed two overlapped sets of signals (of relative intensities varying from 3.3 for **7** to 2.5 for **12**). This indicated that **7**–**12** consisted of a mixture of diastereomers.



Scheme 3.

Except for compound **12**, in the remaining cases the isomers of **7**–**11** were separated by SiO_2 column chromatography. Elution with a $CHCl_3$:methanol (100:1) mixture produced a band, which gave after concentration to dryness on a rotary evaporator, an orange (for **7a**–**10a** and **12a**) or red (for **11a**) oil. Addition of *n*-hexane at ca. 20°C produced the precipitation of the solids. The minor diastereomers **7b**–**11b** were isolated similarly after elution with a $CHCl_3$:CH_3OH (100:3) mixture. It should be pointed out that the two diastereomers of each complex were isolated in molar ratios **a**:**b** which ranged from 3.2:1 to 2.7:1, which are very similar to the composition of **3** (**3a**:**3b**=3.0:1.0), thus suggesting that σ(Pd–$C_{sp^2,ferrocene}$) bond shows similar reactivity versus the alkynes in isomers of **3**. Unfortunately, attempts to separate the two isomers of **12** failed but the analyses of the relative intensities of the signals observed in the ^{1}H NMR revealed that the two isomers **12a**:**12b** coexisted in a molar ratio of ca. 2.5:1.

The results summarized here indicate that the reaction of **3** with the alkynes under study produces the bis(insertion) products in all cases. It is widely accepted that the nature of the final product formed in the reaction of alkynes and cyclopalladated complexes containing σ(Pd–$C_{sp^2,aryl}$) bonds is dependent on a wide variety of factors including: (a) the nature of the substituents R^1 and R^2 on the alkyne R^1–C≡C–R^2; (b) the structure and nature of the metallated ligand; (c) the stoichiometry; (d) the lability of the Pd–N bond; and (e) the remaining ligands bound to the palladium.[9] In the reactions under study, the nature of the substituent on the alkyne was the only variable introduced in all the reactions. It has been postulated that for the insertion of alkynes into the σ(Pd–$C_{sp^2,aryl}$) bonds of cyclopalladated complexes containing *N*,*N*-dimethylbenzylamines the electron-donating or electron-withdrawing nature of the two groups R^1 and R^2 appears to play a crucial role in determining the nature of the final product {a mono(insertion) or a bis(insertion) derivative}.[51] However, the results presented here reveal that, for complex **3**, the formation of the bis(insertion) products [Pd{[(R^1–C=C–R^2)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (**7**–**12**) is strongly favoured.

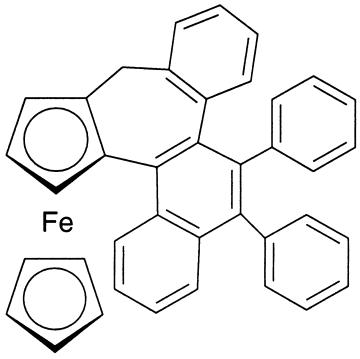


Figure 2. Schematic view of the compounds obtained by depalladation of: [Pd{[(Ph–C=C–Ph)$_2$(η^5-C_5H_3)–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl] (**10c**)

On the other hand, it is well known that complex [Pd{[(Ph–C=C–Ph)$_2$(η^5-C_5H_3)–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl] (**10c**) {which arises from the bis(insertion) of diphenylacetylene into the σ(Pd–$C_{sp^2,ferrocene}$) bond of [Pd{[(η^5-C_5H_3)–CH_2–NMe_2]Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ (**3c**)} undergoes depalladation under refluxing chlorobenzene to give complex **13c** (Fig. 2),[52] so consequently it seemed interesting to study a 'parallel' reaction using compounds [Pd{[(Ph–C=C–Ph)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (**10a** and **10b**).

Complexes **10a** or **10b** were refluxed separately in chlorobenzene for different reaction periods (from 1 h to 12 h). However, according to the NMR spectra of the residues obtained after the evaporation of the solutions to dryness no evidence of any chemical reaction was detected. This finding suggests that compounds **10a** and **10b** are more stable in chlorobenzene than their analogue [Pd{[(Ph–C=C–Ph)$_2$(η^5-C_5H_3)–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl] (**10c**). This can be attributed to several factors, among which the different basicity of the nitrogen donor atom, the higher flexibility of the nine-membered metallacycle in **10c** or the steric effects arising from the different bulk of the substituents on the nitrogen {Me in (**10c**) or CHMe–Ph in (**10a**) or (**10b**)} appear to be especially important.

2.5. Characterization of the palladium(II) compounds

The new palladium(II) complexes prepared here (**2**, **3**, **4a**,**b**–**11a**,**b** and **12**) have been characterized by elemental analyses, and infrared and NMR spectroscopies {^{1}H, ^{13}C and ^{31}P NMR (for **5**)}. In all cases the elemental analyses are consistent with the proposed formulae. A selection of the most relevant features observed in the infrared, ^{1}H and ^{13}C NMR spectra of the palladium(II) compounds are summarized in the Experimental section. ^{31}P NMR spectra of compounds **5a** and **5b** showed a singlet in the range 37.0–38.0 ppm. The position of this signal agrees with a *trans*-arrangement between the imine nitrogen and the phosphine ligand.[34–37,41,43] The specific rotations of the two diastereomers of compounds **5**–**11** were also determined in CH_2Cl_2 at 20°C; the corresponding values are summarized in the Experimental section. The low solubility of **2** precluded determination of the specific rotation, and no such measurement was carried out for complexes **3** and **12**, since it was impossible to isolate diastereomerically pure **3a** and **3b** or **12a** and **12b**.

The major component of **7** (complex **7a**) has also been characterized by X-ray diffraction. The molecular structure and the atom numbering scheme for complex **7a** are presented in Fig. 3.

The structure consists of discrete molecules of [Pd{[(EtC=CEt)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]-Fe(η^5-C_5H_5)}Cl] separated by van der Waals contacts. The palladium is tetracoordinate bound to a chlorine, Cl, the imine nitrogen, N, the terminal carbon atom of the η^3-butadienyl fragment, C(21), and

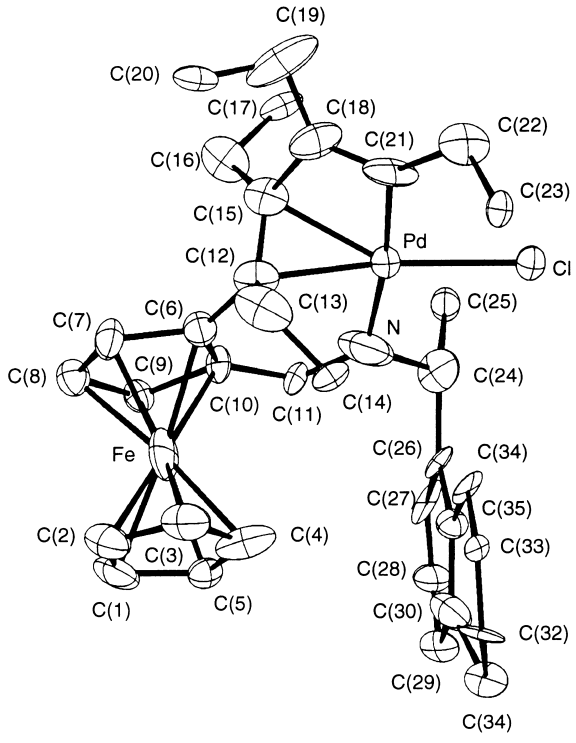


Figure 3. Molecular structure and atom numbering scheme for compound (R_p,*R*)-(+)-[Pd{[(Et–C=C–Et)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (**7a**). Selected bond lengths (Å) Pd–N: 2.209(10), Pd–Cl: 2.346(4), Pd–C(21): 2.000(12), Pd–C(15): 2.221(10), Pd–C(12): 2.225(9), Pd–X[a]: 2.133(11) {where X represents the middle point of the segment defined by the carbon atoms C(12) and C(15)}, C(10)–N: 1.42(2), N–C(11): 1.291(13), N–C(24): 1.489(13) and C(24)–C(25): 1.55(2). Selected bond angles (°): C(21)–Pd–Cl: 92.0(4), N–Pd–Cl: 93.2(2), C(21)–Pd–N: 170.9(4), C(21)–Pd–C(12): 83.6(5), C(21)–Pd–C(15): 65.0(5), N–Pd–C(15): 107.7(4), C(11)–N–Pd: 125.9(7), C(10)–C(11)–N: 124.9(11), N–C(24)–C(26): 113.0(9) and N–C(24)–C(25): 108.0(9)

the middle point of the segment defined by the atoms C(12) and C(15) (hereinafter referred to as X), in a slightly distorted square-planar environment. The deviations from the main plane are as follows: Cl, 0.045; N, −0.042; C(21), −0.062 and X, 0.057 Å.

The complex contains a [5,9] bicyclic system, which is formed by the fusion of the substituted pentagonal ring of the ferrocenyl moiety and a nine-membered metallacycle formed by the following atoms: Pd, N, C(6), C(11), C(10), C(12), C(15), C(18) and C(21). The >C=N– functional group is contained in the metallacycle (*endocyclic*) and the >C=N– bond length [1.292(13) Å] is similar to those reported for five-membered palladacycles of general formula [Pd{[(η^5-C_5H_3)–C(R)=N–R′]Fe(η^5-C_5H_5)}Cl(PPh_3)] (with R=H or Me; R′=CH_2Ph), and clearly larger than in the ferrocenylimines [{(η^5-C_5H_4)–C(R)=N–R′}Fe(η^5-C_5H_5)] with R=H, Me or Ph and R′=phenyl or benzyl groups (ca. 1.24–1.26 Å).[47] The imine ligand has an *E* conformation as reflected in the torsion angle: C(10)–C(11)–N–C(24): 178.8(4)°.

The Pd–C(12) and Pd–C(15) bond distances [2.224(10) and 2.222(10) Å, respectively] are practically identical and the angle C(12)–Pd–C(15) is 36.1(4)°. The C(12)–C(15) double bond forms a dihedral angle of 54.5(4)° with the coordination plane of the palladium. The tiny differences (if significant) observed for the C(12)–C(15) [1.31(2) Å] and C(18)–C(21) [1.38(2) Å] are similar to those reported for related nine-membered rings and can be attributed to the different type of coordination of the two >C=C< groups to the palladium {η^2- and η^1-, respectively}.The ethyl substituents on the double bond C(12)–C(15) are

trans to each other, and those of C(18)–C(21) are *cis*. This arrangement is consistent with the results published by Ryabov et al.[51] who showed that, during the insertion of the second molecule of the alkyne, the *cis*→*trans* isomerization of the fragment –C(R^1)=C(R^2)– (formed in the first insertion process) takes place.

The X-ray crystal structure of **7a** shows that the C(12)–C(21) bond of the butadienyl unit is located above the plane defined by the atoms N, C(11) and C(6) (on the opposite side of the iron centre and the C_5H_5 ring), and the ethyl group formed by the carbons C(12) and C(21) is oriented towards the unsusbstituted pentagonal ring [C(1)–C(5)]. This orientation is similar to that reported for [Pd{[(R^1–C=C–R^2)$_2$(η^5-C_5H_3)–C(R)=N–CH_2–Ph]Fe(η^5-C_5H_5)}Cl] (with R^1=R^2=Et or Ph; R=H or Me).[53] The Fe–C(ring) and C–C(ring) bond distances of the ferrocenyl group are similar to those found in the literature for related complexes.[48] The two pentagonal rings are parallel {*tilt angle* 6.0(4)°} and nearly staggered as reflected in the *twist angle* (32.6°).

2.6. Absolute configurations of compounds 4–12a,b

The assignment of the absolute configuration of these compounds has been carried out on the basis of: (a) the X-ray crystal structure of **7a** and (b) the NMR studies. The molecular structure of complex **7a** indicates that it is the (R_p,*R*) isomer, and in this complex (Fig. 3) the naphthyl ring is below the plane defined by the atoms C(10)–C(11)–N.

For this arrangement of groups, the C_5H_5 and the $C_{10}H_7$ are very close (Figs. 3 and 4), and the protons of the pentagonal ring might be strongly influenced by the ring current induced by the naphthyl group. This could be the cause of the high field shift of the signal due to the C_5H_5 protons in **7a** (3.52 ppm) with respect to that observed in **7b** (4.28 ppm). In the (S_p,*R*) isomer the naphthyl group is further away from the C_5H_5 ring (Fig. 4). The methyl groups in the two isomers are in different environments, and consequently, the comparison of the chemical shifts of the C_5H_5 and CH_3 protons in **4**–**6a**,**b** and **8**–**12a**,**b** with those of **7a**, **7b** can be a useful tool to elucidate the absolute configuration of these complexes. In compounds **4**–**6a**, **8**–**12a**, the resonance of the C_5H_5 protons appears at higher fields than in their diastereomers **4**–**6b** and **8**–**12b**, thus suggesting that the naphthyl and C_5H_5 substituents are proximal. In addition the doublets due to the methyl protons in compounds **4b**–**7b** are shifted to lower fields than in **4**–**12a**. Some regular trends were also observed in the ^{13}C NMR spectra of the compounds under study, for instance in **5b**–**11b** the signals due to the carbons of the C_5H_5, –CH_3 and >CH– groups appear at lower fields than in **6a**–**11a** and the opposite trend is found for the resonance of the imine carbon. These findings suggest that the absolute configuration of **4**–**6a**, **8**–**12a** is the same as in the **7a** (R_p,*R*) isomer. Since only two diastereomers of the monomeric derivatives can be expected, the absolute configuration of compounds **4**–**12b** should be (S_p,*R*).

2.7. Electrochemical studies

In order to elucidate the effects induced by the formation of the σ(Pd–$C_{sp^2,ferrocene}$) bond and by the incorporation of an η^3-butadienyl fragment into this bond, upon the electronic environment of the iron(II), electrochemical studies based on cyclic voltammetry for **1**, **3**, **5**, **7**–**11** were undertaken. In all cases, the experiments were performed at 20°C using 10^{-3} M solutions of the complexes in acetonitrile (HPLC-grade) and using different scan rates (from 0.1 to 100 V s^{-1}). Electrochemical studies for compound **2** could not be carried out due to its low solubility in acetonitrile.

The cyclic voltammogram of ligand **1** showed one anodic peak with a directly associated reduction peak on the reverse scan, which is attributed to the one-electron oxidation–reduction process (Table 2).

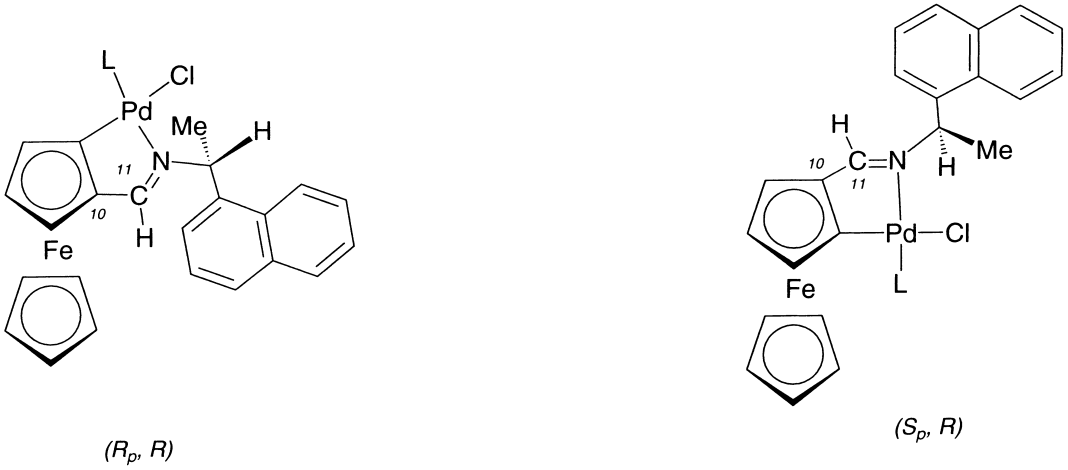


Figure 4. Schematic view of the arrangement of the naphthyl and C_5H_5 groups in the two diastereomers [(R_p,R) and (S_p,R)] of the palladium complexes containing 1,2-disubstituted ferrocenyl groups of general formula [Pd{[(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}(L)Cl] (**4a**–**5a**). In compounds **6** the Cl and L ligands have been replaced by an (O,O')-acetylacetonato (-1) ligand, while in **7**–**12** there is an η^3-butadienyl fragment in position 2 with respect to the imine group

The positions of the peaks for **1** are consistent with the values reported for related ferrocenyl Schiff bases of general formula [{(η^5-C_5H_4)–CH=N–R′}Fe(η^5-C_5H_5)] (with R′=phenyl or benzyl groups).[54]

Electrochemical data for **3**, **5** and **7**–**12** are summarized in Table 2. Comparison of data shows that in compounds **3** and **5**, which contain a five-membered palladacycle with a σ(Pd–$C_{sp^2,ferrocene}$) bond, the 'ferrocene-centred' redox transition shifts cathodically. Similar variations were reported for ferrocene palladacycles[54–57] and platinacycles.[58,59] In contrast, for complexes **7**–**12**, which arise from **3** by a bis(insertion) of the corresponding alkyne R^1–C≡C–R^2 into the σ(Pd–$C_{sp^2,ferrocene}$) bond, the oxidation occurs at higher potentials, thus indicating that the nine-membered cyclopalladated derivatives are less prone to oxidation than the free ligand **1**.

Comparison of the anodic potentials of compounds [Pd{[(R^1–C=C–R^2)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (R^2=Ph and R^1=Me **8**, H **9**, Ph **10** or CO_2Me **11**) suggests that the higher values of the anodic potentials ($E_1^{Ox.}$) are found for compounds that have electron-withdrawing R^1 substituents (Table 1). However, since the oxidation involves the highest occupied molecular orbital (HOMO) in the nine-membered palladacycles it may not be solely iron based; consequently, changes on the substituents R^1 at a distance of two bond lengths from the C_5H_3 ring could modify the energy of the HOMO.

The main difference detected in the cyclic voltammograms of the two diastereomers of compounds **7**–**12** is the position of the wave, as can easily be seen in Fig. 5, which shows the cyclic voltammograms of the two diastereomers of compound [Pd{[(Ph–C=C–Ph)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (**10**) (**10a** and **10b**). The anodic potential of compound **10a** is higher (ca. 70 mV) than that obtained for its diastereomer **10b**.

3. Conclusions

The results reported in this work reveal that although cyclopalladation of ligand **1** could produce different sorts of metallacycle {depending on the nature of the σ(C–H) bond to be activated}, the

Table 2
Electrochemical data for compounds under study: anodic potential: $E_1^{Ox.}$, cathodic potential: $E_1^{Red.}$ and the peak to peak separation: $\Delta E=\{E_1^{Ox.}-E_1^{Red.}\}$. All the potentials (in mV) quoted in this table are referred to the ferrocene/ferricinium couple

Compound	$E_1^{Ox.}$	$E_1^{Red.}$	ΔE
1a	105	29	76
3[a]	29	-46	75
5a	64	-19	83
7a	330	204	126
8a	346	235	111
9a	373	251	122
10a	379	262	117
10b	449	324	125
11a	464	[b]	-----
12[c]	417	293	126

[a] These data correspond to the 3:1 mixture of the two diastereoisomers of complex **3** (see text). [b] Irreversible process. [c] These data correspond to the 2.5:1 mixture of the two diastereoisomers of **12** (see text).

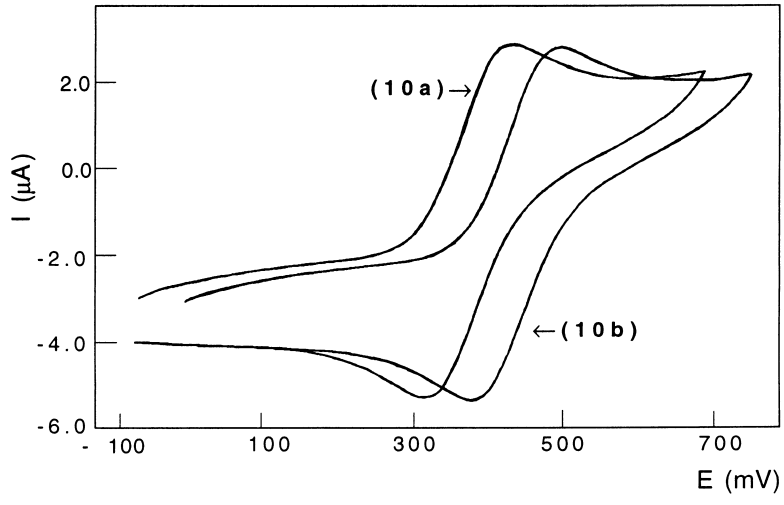


Figure 5. Cyclic voltammograms of the two diastereomers [(R_p,R) (**10a**) and (S_p,R) (**10b**)] of [Pd{[(Ph–C=C–Ph)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (**10**)

formation of metallacycles with a σ(Pd–$C_{sp^2,ferrocene}$) bond is strongly preferred. Besides that, this work shows that the presence of a stereogenic centre {a –CH(Me)–$C_{10}H_7$ group in **1**} in the vicinity of the coordinative nitrogen is an important factor in determining the diastereoselectivity of the process.

However, the study of the reactivity of the 'Pd(μ-Cl)$_2$Pd' moiety and of the σ(Pd–$C_{sp^2,ferrocene}$) bond in **3** has allowed us to isolate the two diastereomers of the five-membered metallacycles [Pd{[(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl(PPh$_3$)] (**5**), [Pd{[(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}(acac)] (**6**), and of the nine-membered palladacycles [Pd{[(R^1–C=C–R^2)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (**7**–**11**) (with R^1=R^2=Et **7**; R^1=Me, R^2=Ph **8**; R^1=H, R^2=Ph **9**; R^1=R^2=Ph **10** or R^1=R^2=CO_2Me **11**). It is well known that depalladation reactions of bis(insertion) products lead to a wide variety of materials, the nature of which depends on several factors,[9,51] especially on the substituents of the butadienyl fragment R^1 and R^2. Consequently, compounds **7a**–**11a** and **7b**–**11b** appear to be good candidates not only for elucidating the influence of the R^1 and R^2 groups upon the nature of the final product, but also for the synthesis of other diastereomerically pure 1,2-disubstituted ferrocenes either by depalladation reactions, or on the basis of futher reactivity studies on the >C=N– or the >C=C< (η^3-butadienyl group) fragments. Further work in this area is now under study.

And finally, the electrochemical studies indicate that the proclivity of the palladium(II) compounds to oxidation is strongly dependent not only on the substituents attached to the ferrocenyl fragment, a 'Pd(ligands)' unit (in **3** or **5**) or a 'η^3-butadienyl group bound to the palladium' (in **7**–**11**), but also on the substituents on the butadienyl fragment.

4. Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Científico-Tècnics de la Universitat de Barcelona. Infrared spectra were obtained with a NICOLET-520 FTIR instrument using KBr pellets. Routine ^{1}H NMR spectra were recorded at 20°C on a Gemini-200 MHz instrument using $CDCl_3$ (99.9%) as solvent and $SiMe_4$ as internal reference. High resolution ^{1}H NMR spectra were obtained with a Varian-500 MHz. ^{13}C{^{1}H} and ^{31}P NMR spectra were recorded with a Bruker-250DXR instrument using $CDCl_3$ as solvent and $SiMe_4$ or P(OMe)$_3$ as internal references, respectively {δ ^{31}P[P(OMe)$_3$]=140.17 ppm}. Optical rotations of the complexes (in CH_2Cl_2) were determined at 20°C using a Perkin–Elmer 241MC polarimeter.

4.1. Materials and synthesis

Ferrocenecarboxaldehyde, (*R*)-(+)-1-naphthylethylamine, thallium(I) acetylacetonate {Tl(acac)}, PPh_3 and the alkynes R^1–C≡C–R^2 (with R^1=R^2=Et; R^1=Me, R^2=Ph; R^1=H, R^2=Ph; R^1=R^2=Ph; R^1=R^2=CO_2Me or R^1=CO_2Et, R^2=Ph) were obtained from Aldrich and used as received. All the solvents except benzene were dried and distilled before use. Some of the preparations described below require the use of highly HAZARDOUS materials {such as Tl(acac) or benzene} which should be handled with CAUTION.

*4.1.1. (*R*)-(+)-[{(η^5-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$}Fe(η^5-C_5H_5)] (**1**)*

Ferrocenecarboxaldehyde (2.0 g, 9.14×10^{-3} mol) was suspended in 25 mL of benzene and stirred at room temperature for 10 min. The undissolved material was removed by filtration and discarded. The amine (*R*)-(+)-H_2N–CH(Me)–$C_{10}H_7$ (9.14×10^{-3} mol) was added to the filtrate and the reaction flask

was connected afterwards to a condenser equipped with a Dean–Stark apparatus (ca. 20 ml). The wine-red solution was refluxed on an ethyleneglycol bath until ca. 15 ml of the azeotrope (benzene:water) had condensed in the Dean–Stark apparatus. The hot solution was carefully filtered out and the filtrate was concentrated to dryness on a rotary evaporator. Addition of *n*-hexane (ca. 10 ml) to the filtrate, followed by vigorous stirring at room temperature for ca. 15 min, produced a pale orange solid, which was collected by filtration and air-dried (yield: 76%). Anal. (%) calcd for $C_{23}H_{21}FeN$ (found): C, 75.24 (75.6); H, 3.81 (3.8); N, 5.73 (5.9). IR: ν(>C=N–): 1620 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety protons: 4.01 [s, 5 H, C_5H_5]; 4.62 [s, 1 H, H^2]; 4.34 [s, 2 H, H^3 and H^4]; 4.69 [s, 1 H, H^5]; 1.72 [d, 3 H, *Me*]; 5.27 [q, 1 H, >*CH*–]; 8.19 [s, 1 H, –*CH*=*N*–] and 7.40–7.90 [m, 7 H, H^9–H^{15}]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 69.40 [C_5H_5]; 81.22 [C^1]; 69.25 [C^2]; 70.89 [C^3 and C^4]; 68.20 [C^5]; 24.25 [*Me*]; 65.20 [>*CH*–] and 160.33 [–*CH*=*N*–]. $[\alpha]_D^{20}$=+64.9 (*c*=0.1 g/100ml).

4.1.2. trans-*[Pd{[(η⁵-C_5H_4)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η⁵-C_5H_5)}$_2Cl_2$] (**2**)*

A 200 mg amount of **1** (5.4×10^{-4} mol) was dissolved in 15 ml of methanol and then $Na_2[PdCl_4]$ (80 mg, 2.7×10^{-4} mol) was added. The reaction mixture was stirred at room temperature (ca. 20°C) for 2 h. The reddish solid formed was collected by filtration and washed with two (10 ml) portions of methanol and air-dried (yield: 82%). Anal. (%) calcd for: $C_{46}H_{42}Cl_2N_2Fe_2Pd$ (found): C, 60.59 (60.4); H, 4.64 (4.7); N, 3.07 (2.95). IR: ν(>C=N–)=1571 cm^{-1}.

*4.1.3. [Pd{[(η⁵-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η⁵-C_5H_5)}(μ-Cl)]$_2$ (**3**)*

The imine **1** (1.016 g, 2.77×10^{-3} mol), $Na_2[PdCl_4]$ (0.813 g, 2.77×10^{-3} mol) and $Na(CH_3COO)\cdot3H_2O$ (0.37 g, 2.77×10^{-3} mol) were suspended in 50 ml of methanol and stirred at room temperature (ca. 20°C) for two days. The deep-red solid formed was filtered, washed in methanol until colourless filtrates were obtained, and then air-dried. The red solid was then dissolved in the minimum amount of $CHCl_3$ and passed through an SiO_2 column (20×250 mm) using $CHCl_3$ as eluant. The red band was collected and concentrated to dryness on a rotary evaporator giving a bright red solid which was collected and dried in a vacuum (yield: 58%). Anal. (%) calcd for: $C_{46}H_{40}N_2Fe_2Pd_2Cl_2$ (found): C, 54.37 (54.25); H, 3.94 (4.0); N, 2.75 (2.7). IR: ν(>C=N–)=1577 cm^{-1}. **3a**: ^1H NMR (in ppm)†: ferrocenyl moiety: 3.76 [s, 5 H, C_5H_5]; 4.11 [s, 1 H, H^3]; 4.15 [s, 1 H, H^4]; 4.19 [s, 1 H, H^5]; 1.83 [d, 3 H, *Me*]; 6.45 [q, 1 H, >*CH*–]; 7.87 [s, 1H, –*CH*=*N*–]. **3b**: ^1H NMR (in ppm)†: ferrocenyl moiety: 4.21 [s, 5 H, C_5H_5]; 4.13 [s, 1 H, H^3]; 4.17 [s, 1 H, H^4]; 4.20 [s, 1 H, H^5]; 2.01 [d, 3 H, *Me*]; 6.38 [q, 1 H, >*CH*–]; 7.95 [s, 1H, –*CH*=*N*–].

*4.1.4. [Pd{[(η⁵-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η⁵-C_5H_5)}Cl(*py*-d_5)] (**4**)*

This compound was prepared in situ in an NMR tube and characterized by ^1H and ^{13}C NMR spectroscopy. For the synthesis of complex **4** the following procedure was used. A 50 mg (4.93×10^{-5} mol) amount of **3** was suspended in $CDCl_3$ (0.7 ml) and then deuterated pyridine (8 ml, 9.85×10^{-5} mol) was added. The reaction mixture was shaken vigorously for 5 min. During this time, **3** dissolved to an orange solution, which contained a 3.1:1 mixture of the two diastereomers: **4a** [major isomer: (R_p,*R*)] and **4b** [minor isomer: (S_p,*R*)]. **4a**: ^1H NMR (in ppm)†: ferrocenyl moiety: 3.88 [s, 5 H, C_5H_5]; 4.13 [s, 1 H, H^3]; 4.16 [s, 1 H, H^4]; 4.15 [s, 1 H, H^5]; 1.83 [d, 3 H, *Me*]; 6.47 [q, 1 H, >*CH*–]; 8.66 [d, 1 H, H^{15}] and 7.40–8.00 [br. m, 6 H, *aromatic*]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 69.20 [C_5H_5]; 87.24 [C^1]; 66.38 [C^3]; 72.39 [C^4]; 67.97 [C^5]; 19.82 [*Me*]; 59.09 [>*CH*–] and 171.87 [–*CH*=*N*–]. **4b**:

† Labelling of the atoms refers to those shown in Schemes 1–3.

^{1}H NMR (in ppm)[14]: ferrocenyl moiety: 4.18 [s, 5 H, C_5H_5]; 4.14 [s, 1 H, H^3]; 4.17 [s, 1 H, H^4]; 4.19 [s, 1 H, H^5]; 2.09 [d, 3 H, *Me*]; 6.40 [q, 1 H, >*CH*–]; 8.34 [d, 1 H, H^{15}] and 7.40–8.00 [br. m, 6 H, H^9–H^{14}]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 69.66 [C_5H_5]; 86.65 [C^1]; 66.45 [C^3]; 69.96 [C^4]; 68.29 [C^5]; 20.86 [*Me*]; 58.95 [>*CH*–] and 171.02 [–*CH*=*N*–].

4.1.5. [Pd{[(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl(PPh_3)] (**5**)

To a benzene (20 ml) suspension of **3** (0.300 g, 2.96×10^{-3} mol), triphenylphosphine (0.155 g, 5.92×10^{-3} mol) was added. The reaction mixture was stirred at room temperature (ca. 20°C) for 1 h. The resulting wine-red solution was then filtered out and the filtrate was concentrated to dryness on a rotary evaporator. The residue was treated with 15 ml of *n*-hexane and stirred at room temperature for 20 min. The solid formed was collected and air-dried (yield: 80%). This material contains a mixture of the two diastereosomers: **5a** (R_p,*R*) and **5b** (S_p,*R*), in a 3.1:1.0 molar ratio. The isomers were separated by SiO_2 column chromatography as follows: 200 mg of the solid was dissolved in the minimum amount of chloroform (ca. 15 ml) and passed through an SiO_2 column (10×250 mm) using $CHCl_3$ as eluant. The three bands formed were collected separately and concentrated to dryness on a rotary evaporator. The gummy residues formed were dissolved in the minimum amount of CH_2Cl_2 and addition of *n*-hexane at room temperature (ca. 20°C) produced the precipitation of the solids. NMR studies of the three solids revealed that the major component **5a** (R_p,*R*) of the mixture was isolated in the first band eluted (120 mg). The third band contained the other diastereomer: **5b** (S_p,*R*) (30 mg) while the intermediate band consisted of a mixture of the two isomers. **5a** (R_p,*R*): Anal. (%) calcd for: $C_{41}H_{35}ClNFePPd$ (found): C, 63.91 (64.0); H, 4.58 (4.6); N, 1.82 (1.9). IR: ν(>C=N–)=1594 cm^{-1}. ^{1}H NMR (in ppm)†: ferrocenyl moiety: 3.34 [s, 5 H, C_5H_5]; 3.24 [s, 1 H, H^3]; 4.08 [s, 1 H, H^4]; 4.09 [s, 1 H, H^5]; 1.80 [d, 3 H, *Me*]; 6.74 [q, 1 H, >*CH*–]; 8.70 [d, 1 H, H^{15}] and 7.40–7.90 [br. m, 22 H, H^9–H^{14}; –*CH*=*N* and C_6H_5 (PPh_3)]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 69.68 [C_5H_5]; 87.90 [C^1]; 102.00 [C^2]; 69.53 [C^3]; 69.22 [C^4]; 67.66 [C^5]; 20.30 [*Me*]; 56.51 [>*CH*–] and 170.92 [–*CH*=*N*–]. ^{31}P NMR data (in ppm): 37.60. Optical rotation: $[\alpha]_D^{20}$=+98 (*c*=0.02 g/100ml). **5b** (S_p,*R*): Anal. (%) calcd for: $C_{41}H_{35}ClNFePPd$ (found): C, 63.91 (63.8); H, 4.58 (4.6); N, 1.82 (1.9). IR: ν(>C=N–)=1594 cm^{-1}. ^{1}H NMR (in ppm)†: ferrocenyl moiety: 3.92 [s, 5 H, C_5H_5]; 3.20 [s, 1 H, H^3]; 4.40 [s, 1 H, H^4]; 4.80 [s, 1 H, H^5]; 1.91 [d, 3 H, *Me*]; 6.61 [q, 1 H, >*CH*–]; 8.45 [d, 1 H, H^{15}] and 7.40–7.90 [br. m, 22 H, H^9–H^{14}; –*CH*=*N* and C_6H_5 (PPh_3)]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 70.23 [C_5H_5]; 69.97 [C^3]; 67.10 [C^4]; 67.20 [C^5]; 20.97 [*Me*]; 56.93 [>*CH*–] and 169.98 [–*CH*=*N*–]. ^{31}P NMR data (in ppm): 37.82. Optical rotation: $[\alpha]_D^{20}$=−24 (*c*=0.02 g/100 ml).

4.1.6. [Pd{[(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}(acac)] (**6**)

The preparation of this complex requires the use of thallium(I) acetylacetonate which is a HIGHLY HAZARDOUS MATERIAL. Only a small amount of this product should be used and this should be done with EXTREME CAUTION. Thallium(I) acetylacetonate (0.060 g, 1.97×10^{-4} mol) was added carefully to a suspension containing 0.100 g (9.85×10^{-5} mol) of **3** in acetone (20 ml). The reaction mixture was vigorously stirred at room temperature for 1.5 h. The solution was then filtered twice with Whatman paper to remove the thallium(I) chloride formed in the course of the reaction. The wine-red solution was concentrated to dryness on a rotary evaporator, and the solid formed was collected and air-dried (yield: 84%). The solid material was dissolved in the minimum amount of acetone. The resulting solution was then layered with methanol. Slow evaporation of the solution at ca. 20°C gave the diastereomer (R_p,*R*), **6a**, as the most insoluble product (yield: 65%) and the filtrate was enriched in the other isomer, **6b** (in a **6b**:**6a** molar ratio=80:20). When this recrystallization process was repeated, **6b** was isolated from the filtrate with a purity higher than 95%. **6a** (R_p,*R*): Anal. (%) calcd for: $C_{28}H_{27}NFePdO_2$ (found): C, 58.80

(58.6); H, 4.76 (4.9); N, 2.45 (2.5). IR: ν(>C=N–)=1577 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 3.93 [s, 5 H, C_5H_5]; 4.13 [s, 1 H, H^3]; 4.20 [s, 1 H, H^4]; 4.47 [s, 1 H, H^5]; 1.74 [d, 3 H, *Me*]; 5.95 [q, 1 H, >*CH*–]; 1.97 [s, 3 H, *Me*(acac)]; 2.07 [s, 3 H, *Me*(acac)]; 5.18 [s, 1 H, >*CH*– (acac)]; 8.44 [d, 1 H, H^{15}] and 7.40–8.00 [br. m, 7 H, H^9–H^{14} and –*CH*=*N*–]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 69.36 [C_5H_5]; 87.08 [C^1]; 100.12 [C^2]; 65.98 [C^3]; 68.07 [C^4]; 72.66 [C^5]; 171.94 [–*CH*=*N*–]; 19.99 [*Me*]; 56.83 [>*CH*–]; 28.19 and 27.64 [*Me*(acac)]; 187.93 and 187.47 [>*CO*(acac)]. Specific rotation: $[\alpha]_D^{20}$=−460.8 (*c*=0.05 g/100 ml). **6b** (S_p,*R*): Anal. (%) calcd for: $C_{28}H_{27}NFePdO_2$ (found): C, 58.80 (58.95); H, 4.76 (4.6); N, 2.45 (2.4). IR: ν(>C=N–)=1576 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 4.26 [s, 5 H, C_5H_5]; 4.14 [s, 1 H, H^3]; 4.20 [s, 1 H, H^4]; 4.75 [s, 1 H, H^5]; 1.90 [d, 3 H, *Me*]; 5.90 [q, 1 H, >*CH*–]; 1.82 [s, 3 H, *Me*(acac)]; 2.03 [s, 3 H, *Me*(acac)]; 5.05 [s, 1 H, >*CH*– (acac)]; 8.16 [d, 1 H, H^{15}] and 7.40–8.00 [br. m, 7 H, H^9–H^{14} and –*CH*=*N*–]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 69.80 [C_5H_5]; 66.03 [C^3]; 68.53 [C^4]; 72.83 [C^5]; 20.77 [*Me*]; 57.03 [>*CH*–]; 171.31 [>C=N–]; 28.19 and 27.64 [*Me*(acac)] and 187.93 and 187.47 [>*CO*(acac)].

*4.1.7. [Pd{[(R^1–C=C–R^2)$_2$(η^5-C_5H_3)–CH=N–CH(Me)–$C_{10}H_7$]Fe(η^5-C_5H_5)}Cl] (with R^1=R^2=Et **7**, R^1=Me, R^2=Ph **8**, R^1=H, R^2=Ph **9**, R^1=R^2=Ph **10**, R^1=R^2=CO_2Me **11** or R^1=CO_2Et and R^2=Ph **12**)*

To a suspension containing 0.400 g (3.94×10^{-4} mol) of **3** in 25 ml of chloroform, the stoichiometric amount (1.57×10^{-3} mol) of the corresponding alkyne: R^1–C≡C–R^2 (with R^1=R^2=Et; R^1=Me, R^2=Ph; R^1=H, R^2=Ph; R^1=R^2=Ph; R^1=R^2=CO_2Me or R^1=CO_2Et and R^2=Ph) was added slowly. Once the addition had finished, the reaction flask was connected to a condenser and the mixture was refluxed for 1.5 h. The undissolved material was removed by filtration and discarded. The dark red filtrate was concentrated to dryness in a rotary evaporator, and the resulting residues were dissolved in the minimum amount of $CHCl_3$ and passed through an SiO_2 column (10×250 mm). Elution with a chloroform:methanol (100:1) mixture gave an orange (for **7**–**10**) or red (for **11** and **12**) band, which was concentrated to dryness on a rotary evaporator. Further treatment of the residue with CH_2Cl_2 followed by the addition of *n*-hexane produced the precipitation of the major diastereomer (R_p,*R*): compounds **7a**–**11a**, which were collected by filtration, air-dried and finally dried in a vacuum. The yields of these reactions fall in the range 65% (for **7a**) to 57% (for **11a**). The minor component of the mixtures: (S_p,*R*) isomers (**7b**–**11b**) were obtained similarly after the elution with a $CHCl_3$:CH_3OH (100:3) mixture (yields from 30 to 35%). When the alkyne used in the reaction was EtO_2C–C≡C–Ph a 3.0:1.0 mixture of the two diastereomers of **12** was obtained in 79% yield. In this case the use of column chromatography did not allow us to isolate the two components of the mixture in their diastereomerically pure forms. **7a** (R_p,*R*): Anal. (%) calcd for: $C_{35}H_{40}NFePdCl$ (found): C, 62.52 (62.7); H, 6.00 (5.95); N, 2.08 (2.1). IR: ν(>C=N–)=1629 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 3.52 [s, 5 H, C_5H_5]; 3.75 [s, 1 H, H^3]; 4.16 [s, 1 H, H^4]; 4.51 [s, 1 H, H^5]; 1.66 [d, 3 H, *Me*]; 7.13 [q, 1 H, >*CH*–]; 8.50 [d, 1 H, H^{15}]; 7.40–8.0 [br. m, 7 H, H^9–H^{14} and –*CH*=*N*–]; butadienyl fragment: 1.52 [t, 3 H, *Me*]; 1.29 [t, 3 H, *Me*]; 1.03 [t, 3 H, *Me*]; 0.95 [t, 3 H, *Me*] and 2.00–2.60 [m, 8 H, –CH_2–]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 69.92 [C_5H_5]; 99.63 [C^2]; 70.22 [C^3]; 72.93 [C^4]; 71.57 [C^5]; 20.56 [*Me*]; 58.16 [>*CH*–]; 163.57 [–*CH*=*N*–]; butadienyl fragment: 12.74, 14.30, 15.08 and 18.14 [*Me*]; 21.80, 24.67, 24.97 and 35.17 [–CH_2–]. Specific rotation: $[\alpha]_D^{20}$=+194.3 (*c*=0.02 g/100 ml). **7b** (S_p,*R*): Anal. (%) calcd $C_{35}H_{40}NFePdCl$ (found): C, 62.52 (62.5); H, 6.00 (6.1); N, 2.08 (1.95). IR: ν(>C=N–)=1629 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 4.28 [s, 5 H, C_5H_5]; 4.37 [s, 1 H, H^3]; 4.43 [s, 1 H, H^4]; 4.51 [s, 1 H, H^5]; 1.71 [d, 3 H, *Me*]; 7.06 [q, 1 H, >*CH*–]; 8.32 [d, 1 H, H^{15}]; 7.40–7.90 [br. m, 7 H, H^9–H^{14} and –*CH*=*N*–]; butadienyl fragment: 1.67 [t, 3 H, *Me*]; 1.31 [t, 3 H, *Me*]; 1.10 [t, 3 H, *Me*]; 0.93 [t, 3 H, *Me*] and 2.00–2.50 [m, 8 H, –CH_2–]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 70.64 [C_5H_5]; 70.42 [C^3]; 73.04 [C^4]; 71.69 [C^5]; 21.61 [*Me*]; 50.07 [>*CH*–]; 162.64 [–*CH*=*N*–]; butadienyl fragment: 12.81, 14.14, 15.08 and

17.98 [*Me*]; 21.98, 24.71, 25.00 and 35.08 [–CH_2–]. Optical rotation: $[\alpha]_D^{20}$=+773 (*c*=0.02 g/ 100 ml). **8a** (R_p,*R*): Anal. (%) calcd for: $C_{41}H_{36}NFePdCl\cdot 1/4CHCl_3$ (found): C, 64.26 (64.1); H, 4.71 (4.8); N, 1.81 (1.7). IR: ν(>C=N–)=1629 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 3.81 [s, 5 H, C_5H_5]; 3.90 [s, 1 H, H^3]; 4.88 [s, 1 H, H^4]; 4.43 [s, 1 H, H^5]; 1.50 [d, 3 H, *Me*]; 8.50 [d, 1 H, H^{15}] and 6.80–7.90 [br. m, 17 H, H^9–H^{14}; –*CH*=*N*– and *Ph* (R^2)]; butadienyl fragment: 2.76 [s, 3 H, *Me*]; 2.60 [s, 3 H, *Me*]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 70.55 [C_5H_5]; 88.06 [C^1]; 88.79 [C^2]; 71.08 [C^3]; 73.75 [C^4]; 72.82 [C^5]; 21.89 [*Me*]; 58.92 [>*CH*–]; 164.48 [–*CH*=*N*–]; butadienyl fragment: 19.94 and 31.48 [*Me*]. Optical rotation: $[\alpha]_D^{20}$=−325.5 (*c*=0.05 g/ 100 ml). **8b** (S_p,*R*): Anal. (%) calcd for: $C_{41}H_{36}NFePdCl$ (found): C, 66.51 (66.4); H, 4.90 (4.7); N, 1.89 (1.8). IR: ν(>C=N–)=1629 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 4.37 [s, 5 H, C_5H_5]; 4.10 [s, 1 H, H^3]; 4.99 [s, 1 H, H^4]; 4.50 [s, 1 H, H^5]; 1.74 [d, 3 H, *Me*]; 8.30 [d, 1 H, H^{15}] and 6.80–7.90 [br. m, 17 H, H^9–H^{14}; –*CH*=*N*– and C_6H_5 (R^2)]; butadienyl fragment: 2.56 [s, 3 H, *Me*]; 2.60 [s, 3 H, *Me*]. ^{13}C NMR data {selected data (in ppm)†}: ferrocenyl moiety: 71.08 [C_5H_5]; 89.93 [C^1]; 94.95 [C^2]; 71.33 [C^3]; 73.20 [C^4]; 72.63 [C^5]; 22.38 [*Me*]; 58.88 [>*CH*–]; 163.46 [–*CH*=*N*–]; butadienyl fragment: 17.07 and 31.10 [*Me*]. Specific rotation: $[\alpha]_D^{20}$=+635 (*c*=0.02 g/100 ml). **9a** (R_p,*R*): Anal. (%) calcd for: $C_{39}H_{32}NFePdCl$ (found): C, 65.69 (65.5); H, 4.49 (4.5); N, 1.97 (2.0). IR: ν(>C=N–)=1612 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 3.03 [s, 5 H, C_5H_5]; 2.97 [s, 1 H, H^3]; 4.58 [s, 1 H, H^4]; 3.67 [s, 1 H, H^5]; 1.68 [d, 3 H, *Me*]; 6.40–8.0 [br. m, 17 H, H^9–H^{14}; –*CH*=*N*– and *Ph* (R^2)]; butadienyl fragment: 4.72 [s, 1 H, >*CH*–]; 4.51 [s, 1 H, >*CH*–]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 69.63 [C_5H_5]; 82.09 [C^1]; 97.22 [C^2]; 70.72 [C^3]; 71.31 [C^5]; 19.26 [*Me*]; 59.03 [>*CH*–]; 162.90 [–*CH*=*N*–]. Optical rotation: $[\alpha]_D^{20}$=−212 (*c*=0.05 g/100 ml). **9b** (S_p,*R*): Anal. (%) calcd for: $C_{39}H_{32}NFePdCl$ (found): C, 65.69 (65.7); H, 4.49 (4.6); N, 1.97 (2.1). IR: ν(>C=N–)=1612 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 3.97 [s, 5 H, C_5H_5]; 3.60 [s, 1 H, H^3]; 4.39 [s, 1 H, H^4]; 3.95 [s, 1 H, H^5]; 1.93 [d, 3 H, *Me*]; 6.40–8.00 [br. m, 17 H, H^9–H^{14}; –*CH*=*N*– and *Ph* (R^2)]; butadienyl fragment: 4.40 [s, 1 H, >*CH*–]; 4.20 [s, 1 H, >*CH*–]. **10a** (R_p,*R*): Anal. (%) calcd for: $C_{51}H_{40}NFePdCl\cdot 1/2CH_2Cl_2$ (found): C, 68.10 (67.8); H, 4.41(4.5); N, 1.54 (1.6). IR: ν(>C=N–)=1628 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 3.56 [s, 5 H, C_5H_5]; 3.97 [s, 1 H, H^3]; 4.44 [s, 1 H, H^4]; 4.60 [s, 1 H, H^5]; 1.59 [d, 3 H, *Me*]; 8.62 [d, 1 H, H^{15}] and 6.60–7.80 [br. m, 27 H, H^9–H^{14}; –*CH*=*N*– and *Ph* (R^1, R^2)]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 71.17 [C_5H_5]; 88.31 [C^1]; 112.20 [C^2]; 71.48 [C^3]; 74.92 [C^4]; 73.15 [C^5]; 21.43 [*Me*]; 59.45 [>*CH*–] and 164.01 [–*CH*=*N*–]. Specific rotation: $[\alpha]_D^{20}$=−238 (*c*=0.05 g/100 ml). **10b** (S_p,*R*): Anal. (%) calcd for: $C_{51}H_{40}NFePdCl$ (found): C, 71.69 (71.5); H, 3.54 (3.4); N, 1.64 (1.5). IR: ν(>C=N–)=1628 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 4.14 [s, 1 H, C_5H_5]; 4.25 [s, 1 H, H^3]; 4.56 [s, 1 H, H^4]; 4.71 [s, 1 H, H^5]; 1.78 [d, 3 H, *Me*]; 8.65 [d, 1 H, H^{15}] and 6.50–7.90 [br. m, 27 H, H^9–H^{14}; –*CH*=*N*– and *Ph* (R^1, R^2)]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 71.71 [C_5H_5]; 88.73 [C^1]; 91.00 [C^2]; 73.21 [C^3]; 74.84 [C^4]; 73.72 [C^5]; 22.44 [*Me*]; 58.81 [>*CH*–] and 163.45 [–*CH*=*N*–]. **11a** (R_p,*R*): Anal. (%) calcd for: $C_{35}H_{32}NO_8FePdCl\cdot 1/2CH_2Cl_2$ (found): C, 51.03 (51.0); H, 3.95 (4.05); N, 1.70 (1.8). IR: ν(>C=N–)=1591 cm^{-1} and ν(>CO)=1710 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 3.91 [s, 5 H, C_5H_5]; 4.20 [s, 1 H, H^3]; 4.61 [s, 1 H, H^4]; 4.38 [s, 1 H, H^5]; 1.79 [d, 3 H, *Me*]; 7.00 [q, 1 H, >*CH*–]; 8.45 [d, 1 H, H^{15}]; 7.40–8.00 [br. m, 7 H, H^9–H^{14} and –*CH*=*N*–]; butadienyl fragment: 3.67 [s, 3 H, *Me*]; 3.74 [s, 3 H, *Me*]; 3.96 [s, 3 H, Me] and 4.03 [s, 3 H, *Me*]. ^{13}C NMR {selected data (in ppm)†}: ferrocenyl moiety: 71.74 [C_5H_5]; 98.61 [C^1]; 111.52 [C^3]; 75.49 [C^4]; 73.76 [C^5]; 20.78 [Me]; 60.45 [>*CH*–]; 165.02 [–*CH*=*N*–]; butadienyl fragment: 52.25, 52.36, 52.87 and 53.68. Specific rotation: $[\alpha]_D^{20}$=+395 (*c*=0.02 g/100 ml). **11b** (S_p,*R*): Anal. (%) calcd for: $C_{35}H_{32}NO_8FePdCl$ (found): C, 53.06 (52.8); H, 4.07 (3.9); N, 1.77 (1.7). IR: ν(>C=N–)=1591 cm^{-1} and ν(>CO)=1710 cm^{-1}. ^1H NMR (in ppm)†: ferrocenyl moiety: 4.37 [s, 5 H, C_5H_5]; 4.40 [s, 1 H, H^3]; 5.11 [s, 1 H, H^4]; 4.69 [s, 1 H, H^5]; 1.82 [d, 3 H, *Me*]; 6.80 [q, 1 H, >*CH*–]; 8.40 [d, 1 H, H^{15}]; 7.40–8.00 [br. m, 7 H, H^9–H^{14} and –*CH*=*N*–];

butadienyl fragment: 3.11 [s, 3 H, *Me*]; 3.72 [s, 3 H, *Me*]; 3.90 [s, 3 H, *Me*] and 4.03 [s, 3 H, *Me*]. **12**: Anal. (%) calcd for: $C_{45}H_{40}NFePdClO_4 \cdot 1/2H_2O$ (found): C, 62.39 (62.4); H, 4.74 (4.7); N, 1.61 (1.5). IR: ν(>C=N–)=1621 cm^{-1} and ν(>CO)=1708 cm^{-1}. **12a**‡ (R_p,*R*) ^{1}H NMR (in ppm)†: ferrocenyl moiety protons: 3.90 [s, 5 H, C_5H_5]; 3.87 [s, 1 H, H^3]; 4.50 [s, 1 H, H^4]; 5.00 [s, 1 H, H^5]; 1.37 [d, 3 H, *Me*]; 8.42 [d, 1 H, H^{15}]; 6.80–7.90 [br. m, 17 H, H^9–H^{14}; –*CH*=*N*–and *Ph* (R^2)]; butadienyl fragment: 1.29 [t, 3 H, *Me*]; 0.87 [t, 3 H, *Me*] and 3.90–4.20 [m, 4 H, –CH_2–]. ^{13}C NMR {selected data (in ppm)†}: 71.62 [C_5H_5]; 87.83 [C^1]; 100.51 [C^2]; 71.44 [C^3]; 73.46 [C^4]; 73.40 [C^5]; 21.19 [*Me*]; 62.41 [>*CH*–]; 163.85 [–*CH*=*N*–]; butadienyl fragment: 59.85 and 59.61 [–CH_2–]; 14.14 and 13.72 [*Me*]; 168.40 and 166.92 [–*COO*]. **12b**‡: ^{1}H NMR data (in ppm)†: ferrocenyl moiety protons: 4.40 [s, 5 H, C_5H_5]; 3.84 [s, 1 H, H^3]; 4.57 [s, 1 H, H^4]; 5.10 [s, 1 H, H^5]; 1.72 [d, 3 H, *Me*]; 7.89 [d, 1 H, H^{15}]; 6.80–7.90 [br. m, 17 H, H^9–H^{14}; –*CH*=*N*–and *Ph* (R^2)]; butadienyl fragment: 1.29 [t, 3 H, *Me*]; 0.85 [t, 3 H, *Me*]; 3.90–4.18 [m, 4 H, –CH_2–]. ^{13}C NMR {selected data (in ppm)†}: 73.24 [C_5H_5]; 90.86 [C^1]; 98.95 [C^2]; 72.23 [C^3]; 73.23 [C^4]; 74.49 [C^5]; 20.36 [*Me*]; 62.41 [>*CH*–]; 163.63 [–*CH*=*N*–]; butadienyl fragment: 59.51 and 59.80 [–CH_2–]; 14.14 and 13.72 [*Me*]; 168.10 and 165.58 [–*COO*].

4.2. Electrochemical studies

Electrochemical data for the compounds under study were obtained by cyclic voltammetry under argon at 20°C using acetonitrile (HPLC grade) as solvent and tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The measured potentials were referred to an Ag–$AgNO_3$ (0.1 M in acetonitrile) electrode separated by a medium-porosity fritted disc. A platinum wire auxiliary electrode was used in conjunction with a platinum disc working electrode TACUSSEL-EDI rotatory electrode (3.14 mm^2). Cyclic voltammograms of 10^{-3} M solutions of the samples in acetonitrile were run and the measured potentials were then referred to ferrocene which was used as an internal standard to facilitate the interpretation of the results. In all cases, the experiments were carried out at different scan rates, υ (from 0.05 to 1.0 V/s).

4.3. Crystallography

A prismatic crystal of **1** or **7a** (sizes in Table 3) was selected and mounted on an ENRAF-CAD-4 four-circle diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections in the range $12<\theta<21°$ (for **1** and for **7a**) and refined by the least-squares method. Intensities were collected with graphite monochromated Mo-K_α radiation using the $\omega-2\theta$ scan technique. Three reflections were measured every two hours as orientation and intensity control and no significant intensity decay was observed. A total of 1285 reflections (for **1**) and 3209 reflections (for **7a**) were collected in the ranges $2.23<\theta<29.91°$ (for **1**) and $2.10<\theta<29.94°$ (for **7a**). 1221 reflections (for **1**) and 3049 reflections (for **7a**) were non-equivalent by symmetry {R_{int} (on *I*)=0.014 for **1** and R_{int} (on *I*)=0.027 for **7a**}. 648 reflections for **1** and 2368 reflections for **7a** were assumed as observed applying the condition $I>2\sigma(I)$. In both cases three reflections were measured every two hours as orientation and intensity control but no significant intensity decay was observed. Lorentz polarization, but not absorption, corrections were made.

The structures were solved by direct methods using the SHELXS computer program[60] and refined by full matrix least-squares method using the SHELX93 computer program[61] using 1171 reflections

‡ Although it was not possible to separate the two diastereomers of compound **12**, the NMR data reported for these compounds were assigned according to the relative intensities of the two sets of signals due to **12a** and **12b**, and the comparison of the positions of the resonances of the ferrocenyl moiety with those of compounds **7a**–**11a** and **7b**–**11b**.

Table 3
Summary of the crystallographic data for compounds **1** and **7a**

	1	**7a**
Crystal size (mm × mm × mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.1
Empirical formula	$C_{23}H_{21}FeN$	$C_{35}H_{35}ClFeNPd$
Formula weight	367.26	631.31
Crystal system	Monoclinic	Monoclinic
Unit cell dimensions	a = 10.932(6)Å, α = 90 °	a = 9.702(2) Å, α = 90 °
	b = 7.546(6) Å, β = 108.98(5) °	b = 14.635(9) Å, β = 93.68(2) °
	c = 11.506(6) Å, γ = 90 °	c = 10.993(2) Å, γ = 90 °
Space group:	$P2_1$	$P2_1$
Volume (Å^3)	897.6(10)	1557.7(10)
Z	2	2
D_{calcd} (Mg × m^{-3})	1.359	1.346
Absorption coefficient (mm^{-1})	0.844	1.148
F(000)	384	646
Θ range for data collection	2.23° ≤ Θ ≤ 29.91°	2.10° ≤ Θ ≤ 29.94 °
Index ranges	-15 ≤ *h* ≤ 14,	-13 ≤ *h* ≤ 13,
	0 ≤ *k* ≤ 10	0 ≤ *k* ≤ 20
	0 ≤ *l* ≤ 15	-1 ≤ *l* ≤ 15
N. of reflections collected	1285	3209
N. of independent reflections	1221 [R_{int} = 0.014]	3049 [R_{int} = 0.0271]
Refinement method	<----------Full matrix least-squares on F^2 ---------->	
Data / restrains / parameters	1221 / 47 / 227	2999 / 13 / 425
Goodness of fit on F^2	0.905	1.037
Final R indices [I>2σ(I)]	R1 = 0.0327; wR2 = 0.0416	R1 = 0.0645; wR2 = 0.1224
R indices [all data]	R1 = 0.0930; wR2 = 0.2742	R1 = 0.0874; wR2 = 0.1512
Absolute configuration parameter:	0.01(4)	0.01(6)
Largest difference peak and	0.141 and	0.892 and
hole (eÅ^{-3})	-0.133	-0.409

(for **1**) and 2999 (for **7a**) (very negative intensities were not considered). The function minimized was: $\sum w \mid |F_o|^2 - |F_c|^2 \mid^2$, where $w=[\sigma(I)+0.0706P^2]^{-1}$ and $P=(|F_o|^2+2|F_c|^2)/3\}$ for **1a** and $w=[\sigma(I)]^{-1}$ and $P=(|F_o|^2+2|F_c|^2)/3\}$ for **7a**. *f*, *f′* and *f″* were taken from the literature.[62] In complex **7a** the naphthyl moiety was disordered and an occupancy factor of 0.5 was assigned to each position according to the height of the Fourier synthesis. The chirality of the structures was defined from the Flack coefficient,[63]

which was equal to 0.01(4) (for **1**) and 0.04(6) (for **7a**), for the given results. Further details concerning the crystal structures of compounds **1** and **7a** are also given in Table 3.

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