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Influences of the electronic and steric effects of the substituents in cyclopalladation of ferrocenylhydrazones

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Abstract

The syntheses and characterization of seven novel ferrocenylhydrazones of general formulae: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}CH{=}N{-}NH(R)\}]$ {with $R = C_6H_4\text{-}4\text{-}Cl$ **(1a)**, $C_6H_4\text{-}4\text{-}NO_2$ **(1b)**, C_6H_5 **(1c)**, $C_6H_3\text{-}2,4\text{-}(NO_2)_2$ **(1d)**, $C_6H_3\text{-}2,5\text{-}(Cl)_2$ **(1e)**, C_6F_5 **(1f)** or $C_6H_4\text{-}2\text{-}CH_3$ **(1g)**} are reported. We also describe the reactions of compounds **1** with $PdCl_2$ in refluxing ethanol, by which different cyclopalladated complexes containing $\sigma(C_{sp^2,\ aryl}{-}Pd)$, $\sigma(C_{sp^2,\ ferrocene}{-}Pd)$ or $\sigma(C_{sp^3}{-}Pd)$ bonds were obtained. A comparative study of the ease by which a $\sigma(C_{sp^2,\ ferrocene}{-}H)$ or a $\sigma(C_{sp^2,\ aryl}{-}H)$ bond in compounds **1** and in the ferrocenylhydrazones: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}C(CH_3){=}N{-}NH(R)\}]$ **(1′)** {derived from acetylferrocene} were to be activated is also reported. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocenylhydrazones; Palladium; Cyclopalladated

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1. Introduction

Cyclopalladated compounds derived from *N*-donor ligands have been extensively studied during the last decade [1], mainly due to their applications in a variety of areas [2]. Although the most widely studied systems described so far contain *N*-donor organic substrates, in the last few years cyclopalladation of related ligands containing ferrocenylunits {i.e. ferrocenyl amines, imines, azines and oximes and azo-derivatives} has allowed a novel type of palladacycles with a $\sigma(Pd{-}C_{sp^2,\ ferrocene})$ bond to be isolated [3–5]. However, the number of articles describing orthopalladation of ferrocenylhydrazones are scarce and to the best of our knowledge only two examples of cyclopalladation of ferrocenylhydrazones derived from 1-acetylferrocene or its 1,1′-diacetyl derivative have been reported in the literature [6,7]. On the other hand, it is well known that although *N*-benzilideneanilines exhibit a strong tendency to produce palladacycles containing the functional group $>C{=}N{-}$ (*endocyclic*) [8], for the analogous phenylhydrazones, the reaction also produces metallacycles with a $\sigma(Pd{-}C_{sp^2,\ aryl})$ bond [9], but in this case the $>C{=}N{-}$ moiety is *exocyclic*. On this basis, it seemed interesting to study the cyclopalladation of several ferrocenylhydrazones of general formula: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}CH{=}N{-}NH(R)\}]$ **(1a–1g)** (Fig. 1).

Ligands **1a–1g** might produce different types of palladocyclic compounds depending on (a) the conformation of the ligand (*E* or *Z*) (Fig. 2) and (b) the nature of the $\sigma(C{-}H)$ bond to be activated. For the *E* isomer of the ferrocenylhydrazones, the activation of a $\sigma(C_{sp^2,\ ferrocene}{-}H)$ bond would produce in all cases five-membered metallacycles {containing the functional group $>C{=}N{-}$, *endo*-type} fused with the ferrocenyl moiety. However, for substrates **1a–1d**, the formation of identically sized metallacycles with a $\sigma(Pd{-}C_{sp^2,\ phenyl})$ bond is also plausible, and in these cases the $>C{=}N{-}$ bond would be *exocyclic*.

On the other hand, two different sorts of five-membered rings with $\sigma(Pd{-}C_{sp^2,\ aryl})$ bonds could be ex-

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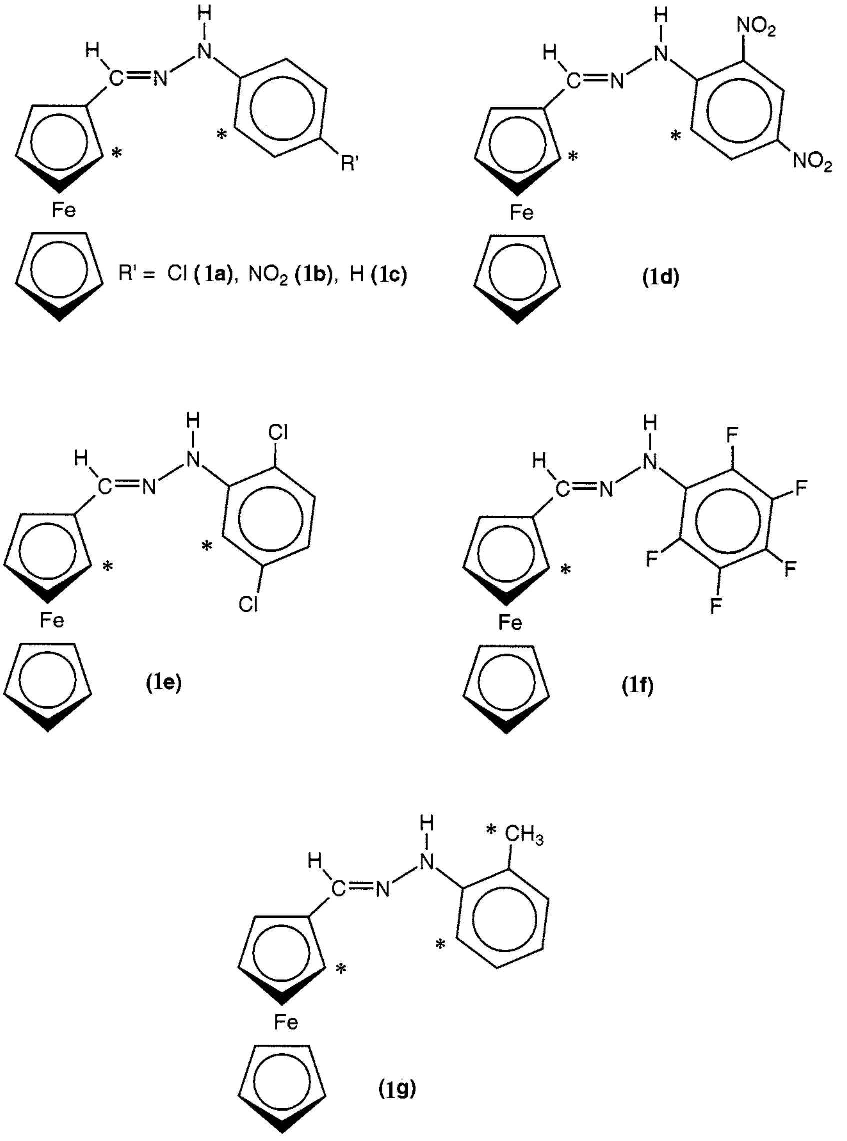


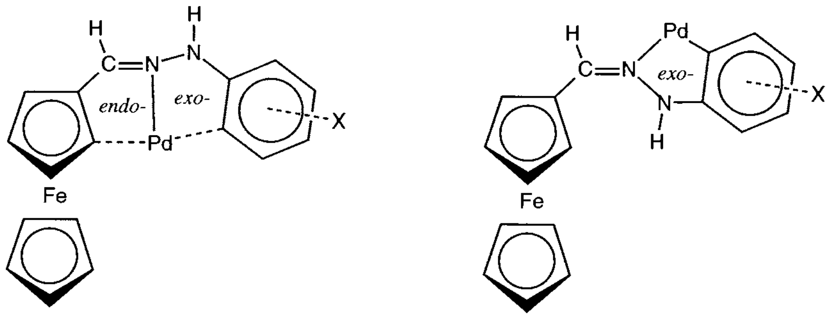
Fig. 1. Schematic view of the new ferrocenylhydrazones under study. The asterisks denote the sites susceptible to activate in these ferrocenylhydrazones. For substrate (**1g**) the rotation around the N-aryl group may allow the activation of the $\sigma(C_{sp^3}-H)$ bond.

pected a priori in the cyclopalladation of ligands **1e–1f**. One of them would arise from the activation of a σ(C–H) bond, while the other could be formed by an oxidative addition of the *ortho*-C–Cl bond (in **1e**) or C–F bond (in **1f**) of the phenyl ring to palladium(0) species which may be generated in the course of the reaction. In fact, reactions of this type have been reported in the literature for ferrocenylimines of general formula: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}(CH_2)_n\text{–}(C_6H_3\text{-}2,6\text{-}Cl_2)\}]$ or N-benzylideneanilines [10]. However, if the ligand were to have the Z conformation, the orientation of the lone pair on the imine nitrogen would only allow the ferrocenyl moiety to metallate giving *exo*- five-membered palladacycles.

2. Results and discussion

2.1. The ligands

The ferrocenylhydrazones (**1**) were prepared by condensation of equimolar amounts of ferrocenecarbaldehyde and the corresponding hydrazines in ethanol at room temperature. These compounds are orange/red solids at room temperature and exhibit high solubility in benzene, chloroform and dichloromethane, but they are poorly soluble in hexane. The new ferrocenylhydrazones have been characterized by elemental analyses, IR spectroscopy and proton-NMR. In all cases the elemental analyses are consistent with the expected



anti- (E) **isomer**

syn- (Z) **isomer**

Fig. 2. Schematic view of the two conformational isomers {*anti-(E)* or *syn-(Z)*} for the ferrocenylhydrazones. Cyclopalladated compounds containing a σ(Pd–$C_{sp2,\ ferrocene}$) bond and the funtional group >C=N– {*endocyclic*} can exclusively be formed if the ligand retains the *anti*-conformation; while the formation of *exocyclic* palladacycles {with a σ(Pd–$C_{sp2,\ aryl}$) bond} can take place for the two conformations {*syn*- or *anti*-} of the ferrocenylhydrazones **(1a–1g)**.

values (see Section 3). The most outstanding feature observed in their IR spectra was the existence of a sharp intense band in the range 1590–1620 cm^{-1}, which is due to the asymmetric stretching of the >C=N– group. In addition, the infrared spectrum of **1** showed the typical stretching band of the N–H fragment at ca. 3200–3400 cm^{-1}.

Proton-NMR spectra of **1** (Table 1) exhibited a singlet due to the imine proton in the range: 7.00–8.00 ppm. The signals due to the protons of the ferrocenyl unit appeared as a singlet and two triplets (with relative intensities 5:2:2) in the range 3.00–5.00 ppm which can be ascribed to the three types of protons of the ferrocenyl moiety: C_5H_5 and the pairs {H^2, H^5} and {H^3, H^4}. Except for ligand **1d**, the –NH– resonance appeared as a singlet in the range 7.0–8.0 ppm. The low field shift of the signal observed for substrate **1d**, can be understood as being derived from the existence of a hydrogen bond between the amine proton and the nitro-group in the *ortho* site. This result agrees with the trends found in the ^{1}H-NMR spectra of 2-nitro-substituted phenylhydrazones [9], for which structural studies have confirmed the existence of such an interaction [11].

Fluorine-19 NMR spectra of compound **1f** showed three signals, which is in good agreement with the presence of three different types of ^{19}F nuclei in the aryl ring. This result allows us to deduce that there is no hydrogen interaction between one of the *ortho*-fluorines of the aryl ring and the amine proton. Thus, indicating that the bulky C_6F_5 substituent precludes the coplanarity of the aryl ring and the N–NH fragment. The use of molecular models revealed that a coplanar orientation of these two groups would introduce strong steric repulsions between the lone pair on the amine nitrogen and the *ortho*-fluorine. This observation agrees with the conclusions obtained from the X-ray crystal structures of certain Schiff bases holding chloro or fluoro groups in the *ortho* sites such as: [4-CH_3–C_6H_4–N=CH(C_6F_5)] or [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH_2–N=CH(2,6-Cl_2–C_6H_3)}] [12] which have demonstrated that the aryl rings are nearly orthogonal to the functional group.

It is worth noting that the new ferrocenylhydrazones decompose easier than the closely related ferrocenylimines of general formula: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–R}] (with R = aryl groups). For instance, chloroform or benzene solutions of compounds **1a–g** and [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–N(CH_3)$_2$}] **(1h)** [13] turned brownish gradually, and a similar behavior was also detected for the solid samples. For instance, although ligands **1b**, **1d** and **1f** could be stored without detecting any modification in either their color or their NMR spectra, the ferrocenylhydrazones **1c** and **1h** turned brown in ca. 1 day, and after this period, their ^{1}H-NMR spectra showed broad signals which may be indicative of the presence of paramagnetic species. According to these observations, the stability of substrates **1** in solid state decreases according to the sequence: **1d ca. 1f > 1b > 1e > 1a > 1c ca. 1g > 1h**.

In order to check whether the low stability of the ligands **1** could be related to a redox process, cyclic voltammetries of these substrates were performed. In all cases, the cyclic voltammograms exhibited one anodic peak with a directly associated cathodic peak in the reverse scan. The half-wave potentials are summarized in Table 2 together with the values reported for the related compounds: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(CH_3)=N–NH(R)}] **(1′)** [13].

Comparison of the values given in Table 2 reveals that the proclivity of the Fe(II) to undergo oxidation in the ferrocenylhydrazones: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–NH(R)}] **(1)** is strongly dependent on the nature of the substituents on the amine nitrogen, in particular on the nature and position of the substituents on the aryl R-group. This finding, which is similar to that found for **(1′)** (Fig. 3), is in contrast with the

Table 1
Proton and ^{31}P-NMR data (in ppm) for the ferrocenylhydrazones of general formula: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NHR\}]$ **(1)** and their cyclopalladated complexes

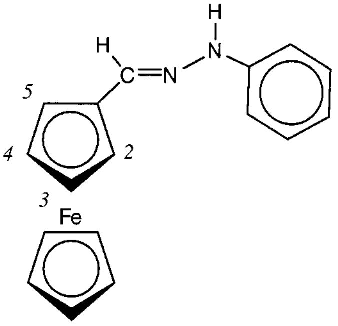
Complex	R	^{1}H-NMR				^{31}P-NMR
		Ferrocenyl	–CH=N–	–NH–	Phenyl	
1a	4-Cl	3.99, s, Cp 4.36, t, H^2, H^5	7.62, s	[a]	7.25, d 7.06, d	—
1b	4-NO_2	4.20, s, Cp 4.63, t, H^2, H^5 4.41, t, H^3, H^4	7.67, s	7.71, s	8.17, d 7.03, d	—
1c	H	4.17, s, Cp 4.58, t, H^2, H^5 4.31, t, H^3, H^4	7.33, s	7.58, s	7.04, d 7.24, d 6.82, d	—
1d	2,4-$(NO_2)_2$	4.32, s, Cp 4.79, s, H^2, H^5 4.59, t, H^3, H^4	7.90, s	11.20, br. s	9.15, d 8.32, d 7.80, d	—
1e	2,5-Cl_2	3.92, s, Cp 4.36, s, H^2, H^5 4.05, s, H^3, H^4	7.43, s	7.88, s	6.81, d 6.54, d 6.46, d	—
1f	2,3,4,5,6-C_6F_5	4.21, s, Cp 4.53, s, H^2, H^5 4.36, s, H^3, H^4	6.94, s	7.71, s	—	—
1g[b]	2-CH_3	4.20, t, Cp 4.62, t, H^2, H^5 4.33, t, H^3, H^4	[a]	7.67, s	7.48, d 7.09, d 6.79	—
2a	4-Cl	4.33, s, Cp 4.77, t, H^2, H^5 4.62, t, H^3, H^4	8.42, d	8.49, s	6.21, dd 6.78, dd 7.80, dd 7.85, d 7.2–7.8, m (PPh_3)	42.2
2b	4-NO_2	4.33, s, Cp 4.74, t, H^2, H^5 4.64, t, H^3, H^4	8.57, d	8.87, s	6.70, d, 8.27, dd 7.3–8.8, m (PPh_3)	42.0
2d	2,4-$(NO_2)_2$	4.30, s, Cp 4.95, t, H^2, H^5 4.77, t, H^3, H^4	8.78, s	11.65, br.s	8.78, d 7.3–7.8, m (PPh_3)	44.0
2g[c]	2-CH_3	4.31, s, Cp 4.78, t, H^2, H^5 4.58, t, H^3, H^4	8.57, d		6.10, dd 6.26, dd 6.72, dd 7.2–7.8, m (PPh_3)	44.7
2g′[d,e]	2-CH_3	4.24, s, Cp 4.51, t, H^2, H^5 4.60, t, H^3, H^4	7.90, d		7.1–7.8, m	41.9[f] 41.3[f]
3a[g]	4-Cl	4.28, s, Cp 4.75, t, H^2, H^5 4.63, t, H^3, H^4	8.77, s	8.60, s	6.12 dd 6.70, dd 6.85, d 7.3–7.8, m (PPh_3)	28.9
3b	4-NO_2	4.29, s, Cp 4.72, t, H^2, H^5 4.64, t, H^3, H^4	8.90, s	8.32, s	7.74, d 7.28, d 6.65, d 7.3–8.8, m (PPh_3)	24.9
3c[g]	H	4.28, s, Cp 4.63, t, H^2, H^5 4.81, t, H^3, H^4	8.30, s		6.85, d 6.70, d 6.12, d 7.3–8.8, m (PPh_3)	28.9

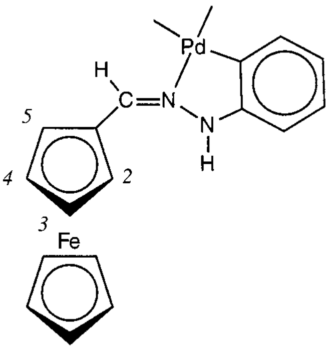
Table 1 (*Continued*)

Complex	R	^{1}H-NMR				^{31}P-NMR
		Ferrocenyl	–CH=N–	–NH–	Phenyl	
3e[g]	2,5-Cl_2	4.26, s, Cp 4.47, t, H^2, H^5 4.67, t, H^3, H^4	8.30, s	8.53	6.78, dd 7.0–7.9, m (PPh_3)	29.3
3f[g]	2,3,4,5,6-C_6F_5	4.22, s, Cp 4.59, t, H^5 4.37, t, H^4 4.31, t, H^3	7.70, br.m	7.00, br	7.1–7.8, m (PPh_3)	29.3
3g[h]	2-CH_3	4.29, s, Cp 4.79, t, H^2, H^5 4.60, t, H^3, H^4	8.52, s	7.80, br	6.76, dd 6.11, dd 7.0–7.6, m (PPh_3)	29.3

Labeling of the atoms refers to the schemes shown above.

[a] Masked by the resonances of the phenyl protons. [b] Additional signal at 2.23 ppm (CH_3). [c] Exocyclic five-membered palladocycle with a $\sigma(Pd-C_{sp2,\ aryl})$ bond. [d] Data for this complex was obtained by comparison of the ^{1}H-NMR spectrum of the (**2g**, **2g′**) mixture and that of the pure complex **2g**. [e] The resonance of the $-CH_2-$ protons appears as two singlets centered at 2.64 and 2.84 ppm due to the diastereotopicity of these two protons. [f] Two rotameric species are present in solution. [g] The ^{31}P-NMR data for this complex obtained at 240 K, (see Section 3). [h] Additional signal at 2.37 ppm (CH_3).





results reported for the Schiff bases $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-C(R')=N-R\}]$ {with R = aryl and R′ = H, CH_3 or C_6H_5} for which the degree of substitution of the aryl group only produced tiny variations of the half-wave potentials [14].

It is well known that the proclivity of ferrocene to undergo oxidation is strongly dependent on the nature of the substituents, and in particular, more anodic potentials are found for substrates holding electron withdrawing groups, while the presence of electron donor substituents involves more cathodic values [15]. On this basis, for the ferrocenylhydrazones **1** the electron withdrawing effect of the substituents upon the ferrocenyl moiety, decreased according to the sequence: **1f** > **1d** > **1b** > **1a ca. 1e** > **1h**. This trend is similar to that observed for the stability, thus suggesting that the low stability of these substrates may be related to a redox process. In addition comparison of data shown in Table 2 reveals that the ferrocenylhydrazones derived from acetylferrocene (**1′**) are more prone to oxidize than **1**, thus suggesting that the methyl group at the –C(R)=N– fragment enhances the electron donor ability of the imine fragment. This finding is similar to those reported in the electrochemical studies of the ferrocenylimines derived from formyl or acetyl ferrocene [14].

2.2. Cyclopalladation reactions

The general procedure described for the cyclopalladation of most ferrocene derivatives {i.e. ferrocenylamines, imines, oximes and azines}, which consists in 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, was unsuccessful for the ferrocenylhydrazones **1** under study, even when the reaction periods were increased up to 72 h. All the experiments revealed that for the shortest reaction times (3 h) the ferrocenylhydrazones were recovered unaltered, while for the longest periods (2–3 days) decomposition of the ligands took place. These findings differ from the results reported previously which have shown that the activation of the $\sigma(C_{sp^2,\ ferrocene}-H)$ bond in the ferrocenylhydrazones: $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-C(CH_3)=N-$

Table 2
Half-wave potentials (in V) referred to ferrocene, $E_{1/2}(Fc)$, for the ferrocenylhydrazones **1** and **1′** and for the ferrocenylimines of general formula: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(R)=N-R'\}]$

R = H	$E_{1/2}(Fc)$	R = CH_3	$E_{1/2}(Fc)^a$
(A) Ferrocenylhydrazones of general formulae: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(R)=N-NR'\}]$			
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-NH(C_6H_4\text{-}4\text{-}Cl)\}]$ **(1a)**	0.01	$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-NH(C_6H_4\text{-}4\text{-}Cl)\}]$ **(1′a)**	−0.01
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-NH(C_6H_4\text{-}4\text{-}NO_2)\}]$ **(1b)**	0.05	$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-NH(C_6H_4\text{-}4\text{-}NO_2)\}]$ **(1′b)**	0.03
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-NH(C_6H_3\text{-}2,4\text{-}(NO_2)_2\}]$ **(1d)**	0.10	$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-NH(C_6H_4\text{-}2,4\text{-}(NO_2)_2)\}]$ **(1′d)**	0.07
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-NH(C_6H_3\text{-}2,5\text{-}Cl_2)\}]$ **(1e)**	0.04	$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-NH(C_6H_3\text{-}2,5\text{-}Cl_2)\}]$ **(1′e)**	0.02
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-NH(C_6H_4\text{-}2\text{-}CH_3)\}]$ **(1g)**	−0.02	$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-NH(C_6H_4\text{-}2\text{-}CH_3)\}]$ **(1′g)**	−0.03
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-NH(C_6F_5)]$ **(1f)**	0.13		
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-N(CH_3)_2\}]$ **(1h)**	−0.03		
(B) Ferrocenylimines of general formula: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(R)=N-R'\}]^b$			
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-C_6H_5\}]$	0.15	$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-C_6H_5\}]$	0.15
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-(C_6H_4\text{-}2\text{-}CH_3)]$	0.14	$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-(C_6H_4\text{-}2\text{-}CH_3)]$	0.14
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-(CH_2-C_6H_4\text{-}2\text{-}CH_3)]$	0.13	$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-(CH_2-C_6H_4\text{-}2\text{-}CH_3)]$	0.09

[a] Data from ref. [13] and [b] ref. [14].

NH(R)}] **(1′)** and even in the 1,1′-ferrocenyldihydrazone: $[Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-NH(COCH_3)\}_2]$ can be easily achieved using the general procedure [6,7].

The varying reactivity of the ligands under study and of **1′** might be related to either the different basicity of the iminic nitrogen, the stability of the starting ferrocenyl substrate, or both simultaneously. In fact, it is well known that the methyl group is a better electron donor substituent than the hydrogen and consequently, the coordination of the palladium(II) to the iminic nitrogen in $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-NH(R)\}]$ **(1′)** or the 1,1′-derivative is expected to be more favorable than in **1**. A similar argument has also been used to justify that the cyclopalladation of ferrocenylimines of general formula: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-C(CH_3)=N-R\}]$ requires only 3 h, while for $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-R\}]$ at least 18 h were needed to detect the formation of the metallacycle [4].

On the other hand, although the activation of σ(C–H) bonds for some organic *N*-donor ligands, has been achieved using stronger reaction conditions {using $Pd(CH_3COO)_2$ as a metallating agent in refluxing acetic acid} this procedure also failed for the substrates under study. This fact can be ascribed to the high instability of ferrocene derivatives containing the functional group >C=N– in acidic media, which produces the protonation of the ferrocenecarboxaldehyde formed through hydrolyses of the >C=N– bond [16].

Based on these results we decided to study the reactions of the ferrocenylhydrazones **1** with $PdCl_2$ in ethanol, which have been very useful in the cyclopalladation of several organic hydrazones [9]. When ligand $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-NH(C_6H_4\text{-}4\text{-}Cl)\}]$ **(1a)** was treated with $PdCl_2$ {in a 1:1 or 1:2 molar ratio} in ethanol at room temperature for 3 h, the reaction produced the coordination compound: *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)-CH=N-NH(C_6H_4\text{-}4\text{-}Cl)]\}_2Cl_2]$, and no evidence of the formation of a σ(Pd–C) bond was detected by ^{1}H-NMR spectroscopy, while for longer reaction periods {up to 2 days} decomposition of either the coordination complex and/or the ligand took place. This finding is in good agreement with previous studies in this field which have shown that when the reaction between the ferrocenylhydrazone: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-N(CH_3)_2\}]$ **(1h)** and $PdCl_2$ {in a 1:2 or 1:1 molar ratio} is carried out in ethanol or methanol at room temperature the formation of the coordination complex: *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)-CH=N-N(CH_3)_2]\}Cl_2]$ takes place [13].

In contrast, for ligand **1b** (which according to the electrochemical studies previously described, is more reluctant to oxidize than **1a** or **1h**), the formation of the metallacycle can be achieved in low yield (ca. 30%) when equimolar amounts of the free ligand **(1b)** and $PdCl_2$, in ethanol are stirred at room temperature for 6 days.

However, when **1a**, **1b** and **1d** were treated with $PdCl_2$ in refluxing ethanol for 3 h, the reaction gave a brown solid. Further treatment of this material with PPh_3 in benzene at room temperature for one hour produced a brown suspension which was filtered out and the filtrate was first reduced to dryness and then passed through a SiO_2-column chromatography. The red (for **2d**) or brown (for **2a**, **b**) band eluted with chloroform was concentrated to dryness and then treated with *n*-hexane to induce the precipitation of the cyclopalladated complexes: $[Pd(C^\wedge N)Cl(PPh_3)]$ **2a**, **2b** and **2d**, respectively (Scheme 1), which contain an *exocyclic* five-membered metallacycle with a $\sigma(Pd-C_{sp^2,\ aryl})$ bond fused with the aryl ring.

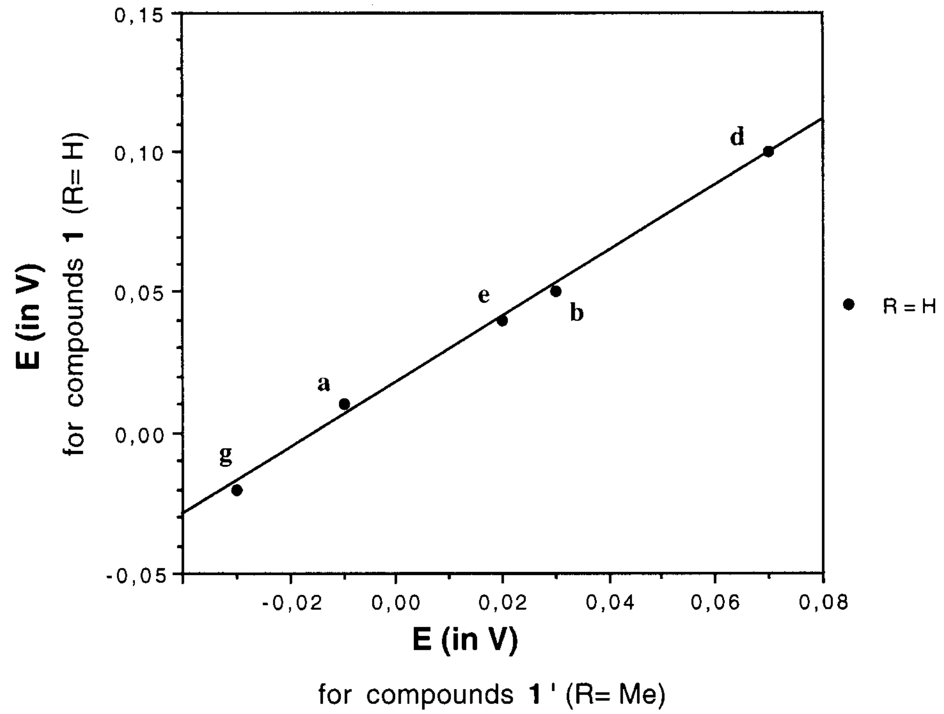
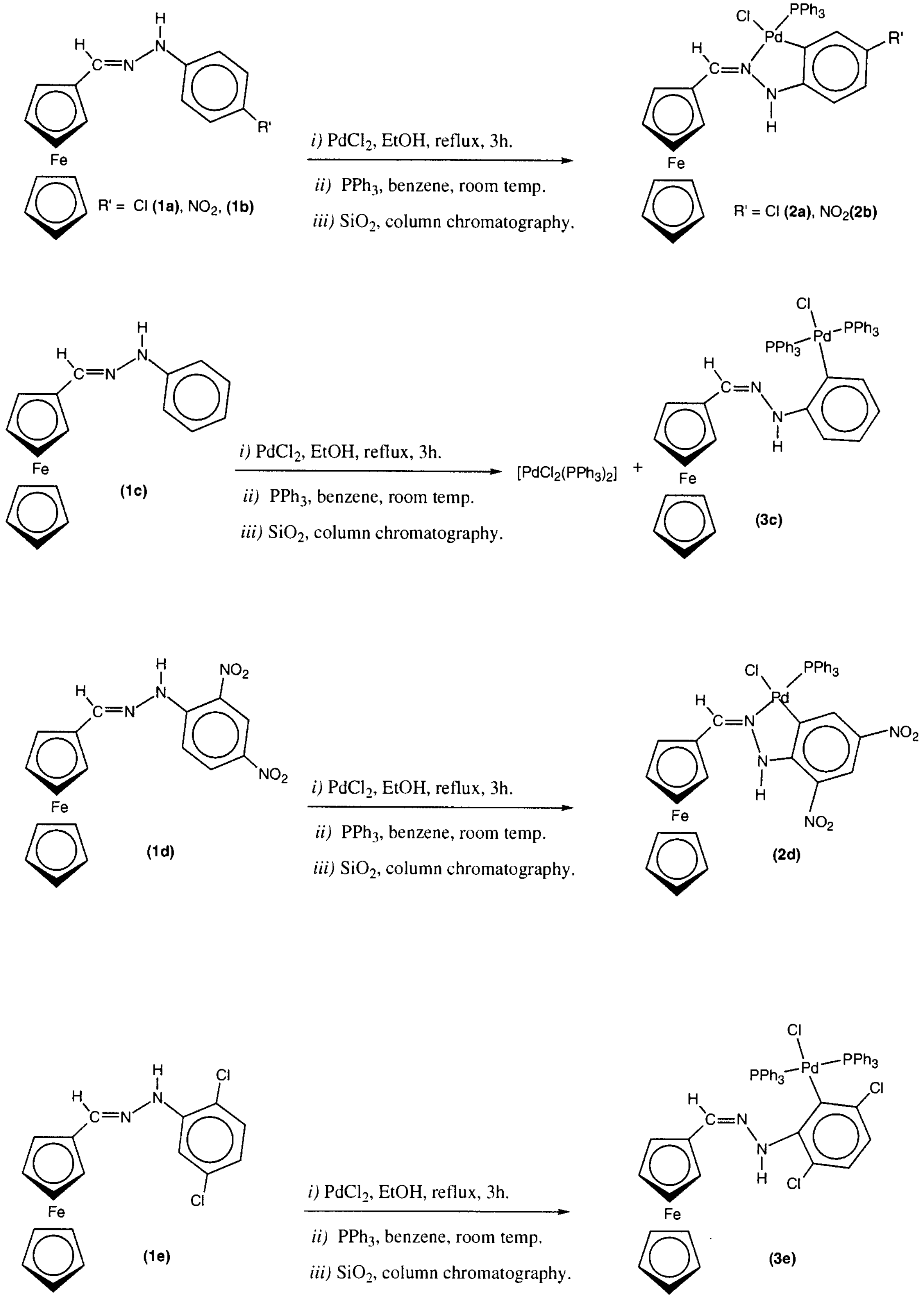


Fig. 3. Plot of the half-wave potentials referred to ferrocene, $E_{1/2}(Fc)$, {in V}, for the two families of ferrocenylhidrazones of general formulae: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}C(R'){=}N{-}NH(R)\}]$ with $R' = H$ (**1**) or CH_3 (**1′**) and $R = C_6H_4\text{-}4\text{-}Cl$ (**a**), $C_6H_4\text{-}4\text{-}NO_2$ (**b**), $C_6H_3\text{-}2,4\text{-}(NO_2)_2$ (**d**), $C_6H_3\text{-}2,5\text{-}(Cl)_2$ (**e**) or $C_6H_4\text{-}2\text{-}CH_3$ (**g**). The equation of the least-squares fit is: $E_{1/2}(Fc)$ for **1** $= 1.7(3) \times 10^{-2} + 1.17(4)$ $E_{1/2}(Fc)$ for **1′** ($r^2 = 0.996$).

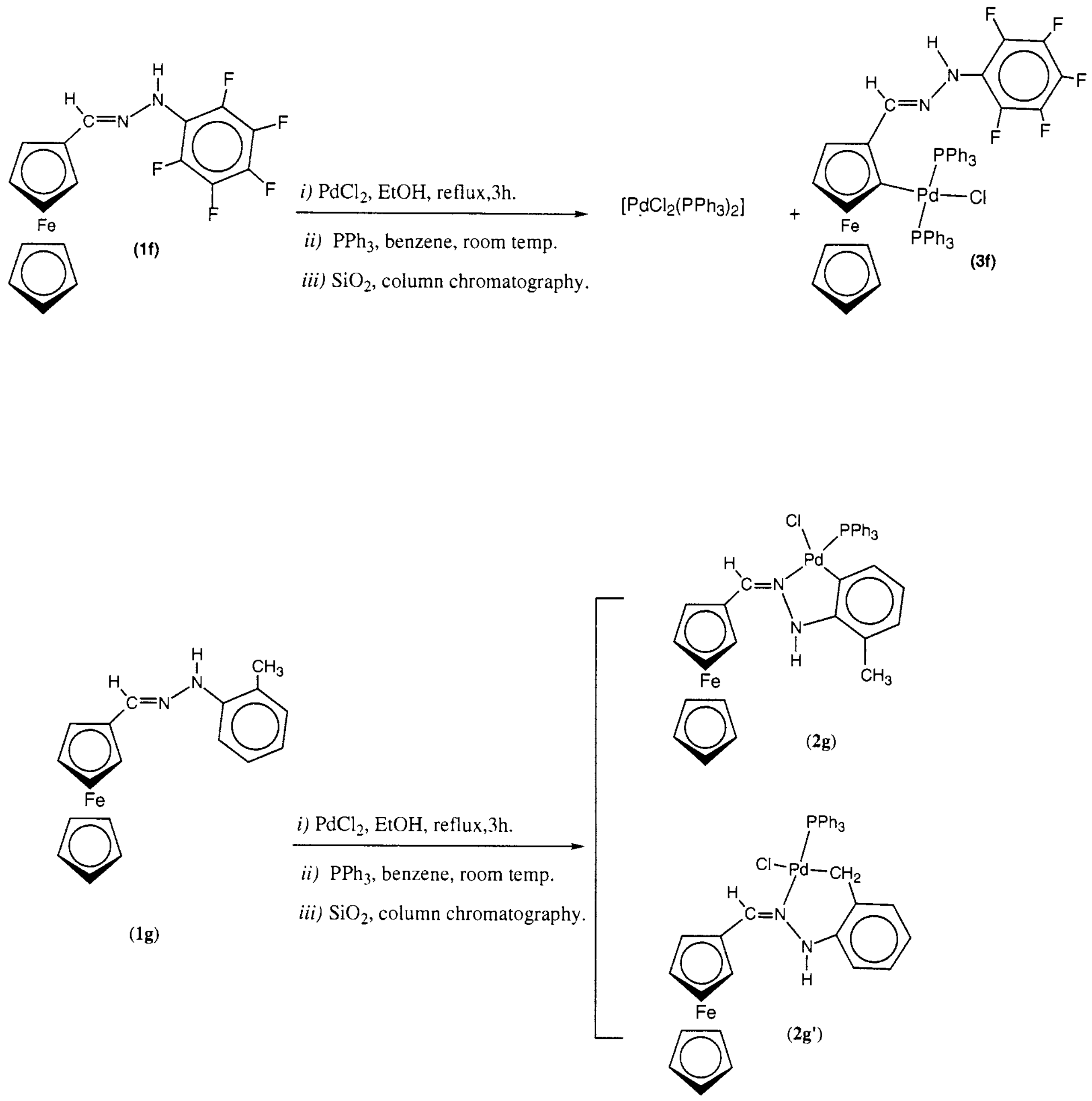
When the ferrocenylhydrazone **1e** was used as starting material, the formation of a palladium mirror in the bottom of the flask was detected, in good agreement with the stronger reductive nature of this ligand, and the reaction yielded to $[Pd\{[(3,6\text{-}Cl_2{-}C_6H_2){-}NH{=}CH{-}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2]$ (**3e**), which also contains a $\sigma(Pd{-}C_{sp^2,\ aryl})$ bond. The different structure of the final products obtained in the cyclopalladation of ligands **1a**, **b** and **d** and in this case, **1e**, may be related to steric effects. It has been reported that for cyclopalladated and cycloplatinated complexes derived from organic imines and hydrazones, the presence of bulky substituents in an adjacent position to the σ(Pd–C) bond enhances the reactivity of the Pd–N moiety. For instance, it is well known that this sort of cyclometallated compounds exhibit a higher proclivity to undergo ring opening processes through the cleavage of the Pd–N bond and the incorporation of the second phosphine in the coordination sphere of the palladium ([12]b)[17]. If a five-membered metallacycle similar to compounds **2** was to be formed in the course of the reaction with ligand **1e**, the aryl rings of the phosphine would be very close to the *ortho*-chloro group, thus increasing the instability of the molecule. While if the metallacycle opens up, the free rotation around the Pd–C bond would significantly reduce the steric effects.

Although the nature of ligand **1c** does not differ substantially from those mentioned in the previous paragraphs, the reaction produced a mixture of two complexes. The major component was the coordination compound: $[PdCl_2(PPh_3)_2]$ and traces of the palladated compound $[Pd\{[(C_6H_4){-}NH{=}CH{-}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2]$ (**3c**) were only detected by ^1H- and ^{31}P-NMR spectroscopies. No significant improvement was detected when the reaction was carried out under N_2 and using different reaction periods (from 3 to 6 h).

For compound $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}CH{=}N{-}NH(C_6F_5)\}]$ (**1f**), the reaction also produces a mixture of two compounds. The major component was the coordination compound: $[PdCl_2(PPh_3)_2]$ but small amounts ($< 10\%$) of the cyclopalladated complex: $[Pd\{[(\eta^5\text{-}C_5H_3){-}CH{=}N{-}NH(C_6F_5)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2]$ (**3f**) were also detected by ^1H- and ^{31}P-NMR spectroscopies. This result can be attributed to several effects, amongst which, the presence of electron-withdrawing groups {which are expected to modify the basicity of the nitrogen} and, the bulk of the C_6F_5 susbtituent {which may hinder the coordination of the palladium} appear to play a crucial role in the process. In addition, for ligand **1f**, the formation of the *exo-cyclic* five-membered palladacycle with a $\sigma(Pd{-}C_{sp^2,\ aryl})$ bond, would involve the activation of a σ(C–F) bond. These effects may be responsible for the formation of compound: $[Pd\{[(\eta^5\text{-}C_5H_3){-}CH{=}N{-}NH(C_6F_5)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2]$ (**3f**) in a low yield. As a first attempt to improve the yield of the process, the reaction was carried out using a longer reaction period (3 h). However, no evidence of the formation of



Scheme 1. Reaction scheme indicating the conditions necessary to produce complexes **2a**, **2b**, **3c**, **2d** and **3e**.



Scheme 2. Reaction scheme indicating the conditions necessary to produce complexes **3f** and **2g**′.

the cyclopalladated complex was detected by ^{1}H-NMR, for the longest periods, thus suggesting the low stability of complex **3f**.

More interesting though are the results obtained from the reaction with: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–NH(C_6H_4-2-CH_3)}] **(1g)** which contains a methyl group in the *ortho*-site of the aryl ring. In this case the reaction produces a mixture of two cyclopalladated compounds: **2g** and **2g**′ (Scheme 2). The major component **(2g)** which contains a five-membered palladacycle fused with aryl ring moiety could be isolated as a pure material, while, the minor component of the mixture which arises from the activation of a σ(C_{sp^3}–H) bond was only detected by ^{1}H- and ^{31}P-NMR spectroscopies. This finding is in sharp contrast with the results obtained in the cyclopalladation of [(η^5-C_5H_5)Fe{(η^5-C_5H_3)–C(CH_3)=N–NH[C_6H_4-2-CH_3)]}] **(1′g)**, which produced exclusively a five-membered palladacycle fused with the ferrocenyl fragment, and no evidence of the formation of any other type of palladacycle was detected [7].

This is particularly remarkable since, although for ligands **1g** and **1′g**, there are three different kinds of σ(C–H) bonds susceptible to activation {$C_{sp^2,\ \mathrm{ferrocene}}$–H; $C_{sp^2,\ \mathrm{phenyl}}$–H or C_{sp^3}–H, Fig. 1}, for **1g** the formation of an *endocyclic* palladacycle does not take place although it is well known that ferrocene derivatives are more prone to undergo electrophilic attacks than benzene [16]. Thus suggesting that the proclivity of the three types of σ(C–H) bonds susceptible to activation in **1g** increases according to the sequence: $C_{sp^2,\ ferrocene}$–H < C_{sp^3}–H < $C_{sp^2,\ phenyl}$–H, while for **1′g** the activation of the σ($C_{sp^2,\ ferrocene}$–H) is strongly preferred. Consequently, for ferrocenylhydrazones derived from acetylferrocene the C_{sp^3}–H and $C_{sp^2,\ phenyl}$–H bonds are more reductant to undergo metallation. On this basis, the results summarized in this work reveal that the replacement of the methyl by an hydrogen in the iminic carbon of the ferrocenylhydrazones: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(R′)=N–NH(R)}] (R′ = H, **1** or CH_3, **1′**) may be important enough as to introduce a significant variation in the geometries of the ligands and/or in the relative orientations of the C–H bonds susceptible to activation. Any of these effects may be crucial in determining the nature of σ(Pd–C) bond to be formed. In fact, structural data for ferrocenylhydrazones: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(R′)=N–NH(R)}] with R′ = H or CH_3 reveal that the larger bulk of the methyl substituent versus H involves the closing of the bond angle $C_{ipso,\ ferrocene}$–C(R′)=N– {which fall in ranges: 118.5–120.5° for R′ = H and 115.5–116.7° for R′ = Me} [11]. For the cyclopalladated complex: [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)–C(CH_3)=N–NH(R)]}Cl(PPh_3)] [7] {which contains an *endo*-type five-membered metallacycle fused with the ferrocenyl unit} the value of this angle is 112.4(14)°, thus indicating that the formation of the palladacycles with a σ(Pd–$C_{sp^2,\ ferrocene}$) bond involves a smaller variation of the angles around the iminic carbon for the ferrocenylhydrazones derived from acetylferrocene.

Although it has been previously reported that ferrocenylhydrazones derived from acetylferrocene (R = CH_3) exhibit a strong tendency to form five-membered metallacycles with a σ(Pd–$C_{sp^2,\ ferrocene}$) bond, our results indicate that those with R = H produce preferentially palladacycles with a σ(Pd–$C_{sp^2,\ phenyl}$) bond. These findings agree with the results obtained in cyclopalladation of organic hydrazones derived from ketones or aldehydes which produce *endo* and *exo*-five-membered metallacycles, respectively, thus indicating that a change in the –C(R)=N– fragment of free ligand (i.e. the replacement of a –CH_3 by a –H) is important enough as to modify the nature of the final cyclopalladated product [9].

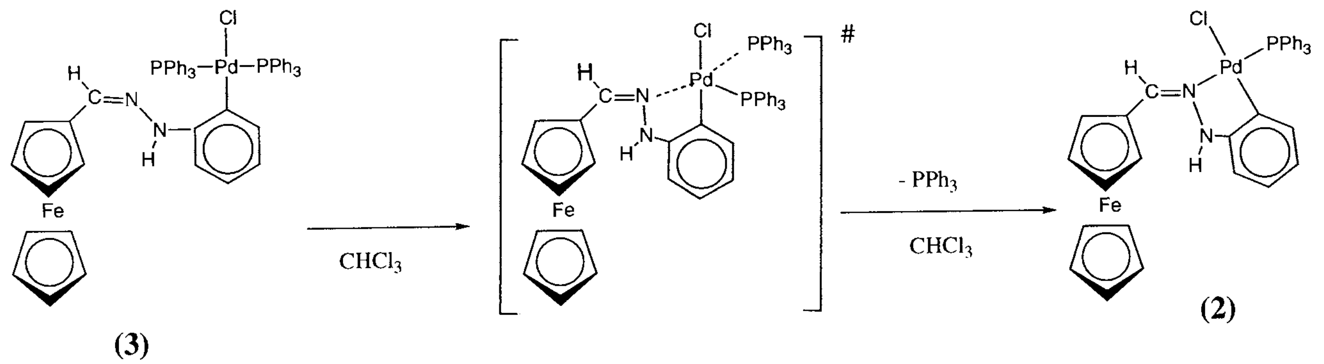
On the other hand, it is well known that the mechanism accepted for that cyclopalladation of *N*-donor ligands involves the initial coordination of the ligand and the subsequent electrophilic attack of the metal atom. It has also been postulated, that the approach of the C–H bond, which is to be activated to the coordination sphere of the metal favours the process. This is in good agreement with an electrophilic attack of the palladium using its empty $d_{x^2-y^2}$ orbital. The molecular structures of free imines: R^1CH=N–R^2 reveal that the phenyl or C_5H_4 rings of R^1 exhibit a stronger tendency to be nearly co-planar with the functional group {>C=N–} {the dihedral angles vary from 0 to 15°} [11], than the aromatic rings of the R^2 substituent. On this basis, the strong tendency of imines to form *endo*-metallacycles has been explained in terms of the better accessibility and orientation of the *ortho* C–H bond of the R^1 group to the coordination plane of the metal.

In contrast, the crystal structures of hydrazones: R^1C(R^3)=N–NHR^2, show that the phenyl rings in R^1 (or R^3) and R^2 and the functional group tend to be coplanar [11]. In addition, for these substrates, the lone pair on the nitrogen activates the hydrazine phenyl ring. All these effects could explain the great tendency of hydrazones: R^1C(H)=N–NHR^2 to produce *exocyclic* complexes, while for their analogues derived from ketones: R^1C(R^3)=N–NHR^2 {R^1, $R^3 \neq$ H} the preferential formation of the *endo*-metallacycles can be related to the steric hindrance introduced by the substituents: R^1 and/or R^3, since in the *exocyclic* palladacycles the environment of the palladium(II) is significantly more crowded due to the proximity of one of the two groups R^1 or R^3 {R^1, $R^3 \neq$ H} to the remaining ligands bound to the palladium i.e. Cl or PPh_3.

More recently, Garcia-Herbosa et al. [18] have postulated that cyclopalladation of phenylhydrazones, takes place along a different pathway than for their *N*-methyl-*N*-phenyl analogues. This consists of the coordination of the ligand to the metal and the subsequent deprotonation of the –NH– group, giving a highly conjugated ‘azobenzene-like’ species, which is highly prone to cyclometallation. The results reported in this work, can also be explained by this mechanism, since the presence of electron-withdrawing groups in the aryl ring of **1**, enhances the acidic character of the –NH– proton, facilitating the activation of the σ(C–H) bond and the formation of the metallacycle. However, the influence of other factors, such as the relative stability of the free ligands {which plays an important role in the first step of the cyclopalladation reactions} can not be discarded in principle.

2.3. Reactions of compounds **2** with PPh_3

In order to study the stability of the Pd–N bond in the cyclopalladated complexes: [Pd(C^N)Cl(PPh_3)], the reaction of compounds **2** in $CDCl_3$ {or in CH_2Cl_2} with the stoichiometric amount of PPh_3 were also studied. In all cases the addition of the phosphine ligand produced the cleavage of the Pd–N bond and the formation of the cyclopalladated compounds: [Pd(C^N)Cl(PPh_3)$_2$] **(3)**. These results are in contrast with those reported previously for related compounds, where (C^N) represents a cyclometallated ferrocenylimine, oxime or azine, or in particular a ferrocenylhydrazone derived from acetylferrocene, which do not react with excesses of PPh_3, thus indicating that the Pd–N bond in com-



Scheme 3. Exchange of PPh_3 through a fast equilibrium in **3**, suggesting a great lability of one of the Pd–P bonds in solution.

pounds **2** is more labile. The different reactivity of the two types of cyclopalladated complexes **2** and **2′** versus PPh_3, can be related to the nature of the two susbtituents ($R = H$ or CH_3) which modify the basicity of the imine nitrogen. These results are consistent with previous studies on the reactivity of cyclopalladated and cycloplatinated compounds which have shown that, depending on the nature of the metallacycle and the basicity of the nitrogen, the cleavage of the metal nitrogen bond can be achieved [17].

2.4. Characterization

The new palladium(II) compounds are solids at room temperature and exhibit higher stability than the corresponding ferrocenyl hydrazones, since they can be stored for several weeks without any appreciable change in either their colour or their NMR spectra. This finding reveals that the formation of the σ(Pd–C) bond increases the stability of the ferrocenylhydrazones. This fact is analogous to that reported for the ferrocenylimines: $[\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}N{=}CH(C_6H_4R)\}]$ **(3c)** and their cyclopalladated complexes with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2,\ \text{aryl}})$ bond, for which the increase of the stability was ascribed to more anodic half-wave potentials of the palladium (II) compounds when compared with the free ligands.

The palladated compounds **2** and **3** are soluble in chloroform, dichloromethane, slightly soluble in ethanol and practically insoluble in alkanes and acetonitrile. Their IR spectra show the typical bands of coordinated hydrazones and triphenylphosphine. Selected NMR spectral data for compounds **2** and **3** are summarized in Table 1. The assignment of the proton-NMR data affords conclusive evidence of the palladation site (*endo*- or *exo*-structures). The aromatic proton signals of the metallated ring in compounds **2** which contain a Pd–N bond are shifted to high field. This effect, which has also been observed for *endocyclic* cyclopalladated complexes derived from organic imines and hydrazones, has been interpreted in terms of the paramagnetic anisotropy of the phenyl rings of the PPh_3 ligand in a *cis*-arrangement with the metallated carbon atom. The signal due to the NH group in compound **2d** appears strongly shifted to low fields ($\delta = 11.65$ ppm), thus suggesting the existence of an intramolecular hydrogen bond between the *ortho*-NO_2 group and the amine hydrogen. This finding is in good agreement with those reported for the cyclopalladated derivatives derived from 2,4-dinitrophenylhydrazone, for which the existence of this interaction has been confirmed by X-ray difraction [11].

Phosphorus-31 NMR spectral data of compounds **2** and **3** are presented in Table 1. For compounds **2** the position of the signal {in the range of 37–45 ppm} is consistent with a *trans* orientation of the phosphine ligand and the nitrogen. ^{31}P-NMR spectra of **3** revealed the existence of dynamic processes in solution. The singlet due to the coordinated phosphines {in the range 23–25 ppm} was only detected at low temperatures {220 K}. In contrast when the spectra were recorded at higher temperatures the signal became broad and at 240 K an additional signal centered at ca. 32 ppm appeared, these findings indicate that compounds **3** exchange PPh_3 through a fast equilibrium shown in Scheme 3 {since the signal centered at ca. 32 ppm is placed between those obtained for **2** and **3**}, thus suggesting a great lability of one of the Pd–P bonds in compounds **3** in solution. In addition, this finding also agrees with the fact that when compound **3b** is passed through an SiO_2 column using $CHCl_3$ as eluant, only complex **2b** and the free phosphine could be recovered.

Dynamic processes similar to that shown in Scheme 3 have also been observed for a wide variety of cyclopalladated and cycloplatinated complexes: $[M(C^\wedge N)X(PR_3)_2]$ {with $X = Cl$, Br or I and $R =$ phenyl or alkyl} [19].

2.5. Conclusions

The results summarized in this work have allowed us not only to establish general pathways for the preparation of ferrocenylhydrazones derived from ferrocenecarboxaldehyde, but also to elucidate the influences of the substituents on the amine nitrogen on the liability of the iron(II) to undergo oxidation.

Furthermore, cyclopalladation reactions of substrates **1**, reveal that though ferrocene derivatives are more likely to undergo electrophilic attacks than aromatic ones, the formation of palladium(II) compounds with $\sigma(\text{Pd}-\text{C}_{\text{sp}^2,\ \text{aryl}})$ bonds is strongly preferred. Only for ligand $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{–CH=N–NH(C}_6\text{F}_5)]$ **1f**, for which the formation of a palladacycle with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2,\ \text{aryl}})$ bond, would require the activation of one of the *ortho* C–F bonds, the formation of small amounts of a five-membered metallacycle with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2,\ \text{ferrocene}})$ bond was detected by NMR spectroscopy. It is also interesting to point out, that for substrate **1g**, for which three different types of σ(C–H) bonds could be activated (Fig. 1), the reaction produced: $[\text{Pd}\{[(2\text{-CH}_3\text{–C}_6\text{H}_3)\text{–NH=CH–}(\eta^5\text{ - C}_5\text{H}_4)]\text{Fe}(\eta^5\text{ - C}_5\text{H}_5)\}\text{Cl(PPh}_3)]$ **(2g)**, and the formation of small amounts of the cyclopalladated complex with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^3})$ bond was also detected by NMR. However, no traces of the formation of the *endocyclic* five-membered palladocycle with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2,\ \text{ferrocene}})$ bond were detected in the course of the reaction, although it is well known that ferrocene has a greater proclivity to electrophilic attacks than benzene.

These findings are in sharp contrast with those obtained for the ferrocenyl hydrazones: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{–C(CH}_3)\text{=N–NH(R)}]$ **(1′)**, the ferrocenylimines: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{–C(R}')\text{=N–R}]$ {with R′ = H, CH_3 or C_6H_5}, and the *N*-benzylideneamines, which show a strong tendency to form *endocyclic* cyclopalladated compounds with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2,\ \text{ferrocene}})$ bond; but agree with the conclusions reached from cyclopalladation of the phenylhydrazones: $[\text{R–C}_6\text{H}_4\text{–CH=N–NH–C}_6\text{H}_{4-x}\text{R}_x]$ which produce *exocyclic* cyclopalladated compounds preferentially. Only when the aryl group bound to the amine nitrogen contained chloro groups at the *ortho* sites, was the isolation of the *endocyclic* palladacycles achieved.

In conclusion, the results described in this work show the strong tendency of hydrazones derived from ferrocenecarboxaldehyde to form *exocyclic* cyclopalladated compounds. This tendency is so strong that the metallation of an aliphatic C–H bond giving an *exo* six-membered palladacycle has been observed for the first time. These results are in sharp contrast with those reported for imines, for which the formation of *endocyclic* palladacycles is strongly preferred.

To sum up, while it is widely accepted that the formation of cyclopalladated compounds containing *N*-donor ligands involves the coordination of the ligand and the subsequent electrophilic attack of the palladium(II) on the C–H bond to be activated, the results reported in this study suggest that other factors, such as the relative orientation of the C–H bond to be activated *versus* the palladium linked to the nitrogen, the $E \rightarrow Z$ isomerization of the ligand (the Z isomer does not allow the formation of the *endocyclic* derivatives), or the presence of electron-withdrawing groups which may ease the deprotonation of the –NH– fragment, for the mechanism postulated by Garcia-Herbosa et al. [18] may also play a crucial role in these processes.

3. Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Cientifico-Tècnics (Universitat de Barcelona). Infrared spectra were obtained from KBr pellets using a NICOLET-520FTIR-spectrometer. ^{1}H- and $^{13}\text{C}\{^1\text{H}\}$-NMR spectra were recorded at ca. 20°C on a GEMINI-200MHz spectrophotometer, using CDCl_3 (99.9%) {free of acid traces} as solvent and $\text{Si(CH}_3)_4$ as internal reference. ^{31}P-NMR spectra of compounds **2** and **3** were obtained with a BRUKER-DRX-250MHz spectrophotometer using CDCl_3 as solvent and trimethylphosphite as internal reference $\{\delta(^{31}\text{P}) = 140.17\ \text{ppm}\}$. ^{1}H- and ^{31}P-NMR data for the compounds under study are presented in Table 1. ^{19}F-NMR for ligand **1f** was recorded with a Varian 300 MHz instrument using CDCl_3 as solvent and F_3CCOOH as reference.

3.1. Materials and syntheses

Ferrocenecarboxaldehyde $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{–C(O)H}\}]$ and the organic hydrazines were obtained from commercial sources and used as received. All the solvents were dried and distilled before use. Some of the preparations described below require the use of benzene which should be used with CAUTION. Compound **1h** was prepared as described previously [13].

3.1.1. Preparation of the compounds

3.1.1.1. Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{–CH=N–NH(C}_6\text{H}_4\text{-4-Cl)}\}]$ ***(1a)***. Commercial ferrocenecarbaldehyde (1.07 g, 4.98 mmol) was dissolved in the minimum amount of ethanol (ca. 5 cm^3) and the undissolved materials were filtered out and discarded. Then a solution containing 4-chlorophenylhydrazine (1.69 g, 5.00 mmol) in 5 cm^3 of ethanol was added to the filtrate. The reaction mixture was stirred at room temperature for 1.5 h and the orange/red solid formed was filtered out, washed with three (5 cm^3) portions of ethanol and air-dried. (Yield: 66%). Characterization data: Anal. (%) Calc. for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{ClFe}$ (found): C, 60.32 (60.3); H, 4.47 (4.35) and N, 8.27 (8.1). IR: $\nu_{\max}$: 1596 (>C=N–) and 3312 (N–H) cm^{-1}.

3.1.1.2. Preparation of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NH(C_6H_4\text{-}4\text{-}NO_2)\}]$ ***(1b)***. This complex was prepared following the procedure previously described for **1a**, but using the stoichiometric amount of 4-nitrophenylhydrazine as reagent. (Yield: 74%). Characterization data: Anal. (%) Calc. for $C_{17}H_{15}N_3O_2Fe$ (found): C, 58.48 (58.4); H, 4.33 (4.5) and N, 12.04 (12.1). IR: ν_{max}: 1608 (>C=N–) and 3295 (N–H) cm^{-1}.

3.1.1.3. Preparation of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NH(C_6H_5)\}]$ ***(1c)***. Ferrocenecarbaldehyde (1.00 g, 4.67mmol) was added to ethanol (ca. 10 cm^3) under N_2 and the mixture was stirred under nitrogen for an additional 5 min. The undissolved materials were removed by filtration under nitrogen. Phenylhydrazine (4.67 mmol) was poured drop-wise to the filtrate and the reaction mixture was vigorously stirred at room temperature for 1.5 h. The orange solid formed during this period was collected by filtration under nitrogen, washed with three (5 cm^3) portions of cold ethanol and air-dried. (Yield: 52%). Characterization data for **1c**: Anal. (%) Calc. for $C_{17}H_{16}N_2Fe$ (found): C, 67.13 (67.0); H, 5.30 (5.3) and N, 9.21 (9.1). IR: ν_{max}: 1597 (>C=N–) and 3308 (N–H) cm^{-1}.

3.1.1.4. Preparation of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NH\{C_6H_3\text{-}2,4\text{-}(NO_2)_2\}]$ ***(1d)***, $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NH\{C_6H_3\text{-}2,5\text{-}(Cl)_2\}]$ ***(1e)***, $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NH(C_6F_5)]$ ***(1f)*** *and* $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NH\{C_6H_4\text{-}2\text{-}(CH_3)\}]$ ***(1g)***. These complexes were prepared following the procedure previously described for **1a**, but using the stoichiometric amount of the corresponding hydrazine as reactant. (Yields: 55 **(1d)**, 57 **(1e)**, 50 **(1f)** and 62% **(1g)**). Characterization data for **1d**: Anal. (%) Calc. for $C_{17}H_{14}N_4O_4Fe$ (found): C, 51.80 (51.77); H, 3.58 (3.45) and N, 14.21 (13.92). IR: ν_{max}: 1616 (>C=N–) and 3278 (N–H) cm^{-1}. **1e**: Anal. (%) Calc. for $C_{17}H_{14}N_2Cl_2Fe$ (found): C, 54.73 (54.7); H, 3.78 (3.8) and N, 7.51 (7.5). IR: ν_{max}: 1591 (>C=N–) and 3327 (N–H) cm^{-1}. **1f**: Anal. (%) Calc. for $C_{17}H_{11}N_2F_5Fe$ (found): C, 51.77 (51.81); H, 2.81 (2.9) and N, 7.11 (7.1). IR: ν_{max}: 1541 (>C=N–) and 3261 (N–H) cm^{-1}. ^{19}F-NMR (ppm): -156.35 (d, F(2) and F(6)), -164.31 (t, F(3), F(5) and -167.86 (t, F(4)). **1g**: Anal. (%) Calc. for $C_{17}H_{18}N_2Cl_2Fe$ (found): C, 67.94 (67.85); H, 5.70 (5.65) and N, 8.80 (8.7). IR: ν_{max}: 1599 (>C=N–) and 3344 (N–H) cm^{-1}.

3.1.1.5. Preparation of trans-$[Pd\{[(4\text{-}Cl\text{-}C_6H_4)\text{–}NH\text{–}N{=}CH\text{–}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}_2Cl_2]$. A 0.50 g (1.48 mmol) sample of the ferrocenylhydrazone $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NH\text{–}(C_6H_4\text{-}4\text{-}Cl)\}]$ **(1a)** (0.74 mmol) were dissolved in 50 cm^3 of methanol and then 0.74 mmol of $PdCl_2$ were added. The reaction mixture was stirred at room temperature for 2 h. The brownish/red precipitate formed was filtered out and air-dried. (Yield: 72%). Characterization data: Anal. (%) Calc. for $C_{34}H_{30}N_4Cl_4Fe_2Pd$ (found): C, 47.77 (47.85); H, 3.51 (3.60) and N, 6.55 (6.6). IR: ν_{max}: 1582 (>C=N–) and 3264 (N–H) cm^{-1}. ^{1}H-NMR (in ppm), selected data: 4.32 {s, 5H, (C_5H_5)}, 4.29 {s, 5H, $(C_5H_5)'$}, 5.40 (t, 1H, H^2), 5.27 (t, 1H, H$^{2'}$), 4.58 (br.t 2H, H^3 and H$^{3'}$), 4.60 (t, 2H, H^4 and H$^{3'}$), 4.75 (t, 2H, H^5 an H$^{5'}$), 8.01 (s, –CH=N–) and 2.20 (s, 2H, –NH–).

3.1.1.6. Preparation of $[Pd\{[(4\text{-}Cl\text{–}C_6H_3)\text{–}NH\text{–}N{=}CH\text{–}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ ***(2a)***, $[Pd\{[(4\text{-}NO_2\text{–}C_6H_3)\text{–}NH\text{–}N{=}CH\text{–}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ ***(2b)***, $[Pd\{[\{2,4\text{-}(NO_2)_2C_6H_3)\}\text{–}NH\text{–}N{=}CH\text{–}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ ***(2d)*** *and* $[Pd\{[(2\text{-}CH_3\text{–}C_6H_3)\text{–}NH\text{–}N{=}CH\text{-}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ ***(2g)***. To a suspension containing 1.60 mmol of the corresponding ferrocenylhydrazone {**1a**, **2a** or **2g**} in 20 cm^3 of ethanol, 0.284 g (1.60 mmol) of $PdCl_2$ was added. The resulting mixture was refluxed for 3 h. During this period the formation of metallic palladium was detected. The deep brown precipitate formed was filtered out and washed with three portions of ethanol (ca. 5 cm^3) and air-dried. The solid was then suspended in 20 cm^3 of benzene and treated with 0.420 g of PPh_3 (1.60 mmol) and the mixture was stirred at room temperature for 1 h and then filtered out to remove the undissolved materials. The brownish filtrate was concentrated to dryness in a rotary evaporator and the residue was then passed through an SiO_2-column (10 × 250 mm), using $CHCl_3$ as eluant. The first colored band was collected and concentrated to dryness in a rotary evaporator giving a red solid for **2d** or a gummy material for **2a**, **2b** or **2g**. In the later cases the residual was dissolved in the minimum amount of CH_2Cl_2 and then treated with *n*-hexane to induce the precipitation. The ochre solid formed was collected by filtration and air-dried (Yields: 58 **(2a)**, 63 **(2b)** 68 **(2d)** and 45% **(2g)**). Characterization data for **2a**: Anal. (%) Calc. for $C_{35}H_{29}N_2FeCl_2PPd$ (found): C, 56.76 (56.6); H, 3.95 (3.9) and N, 3.78 (3.7). IR: ν_{max}: 1610 (>C=N–) and 3204 (N–H) cm^{-1}. **2b**: Anal. (%) Calc. for $C_{35}H_{29}N_3FeClO_2PdP$ (found): C, 55.92 (55.75); H, 3.89 (3.9) and N, 5.59 (5.5). IR (KBr pellets) ν_{max}: 1610 (>C=N–) and 3204 (N–H) cm^{-1}. **2d** Anal. (%) Calc. for $C_{35}H_{28}N_4FeClO_4PPd$ (found): C, 52.71 (52.7); H, 3.54 (3.8) and N, 7.0 (6.8). IR: ν_{max}: 1592 (>C=N–) and 3291 cm^{-1}. **2g**. Anal. (%) Calc. for $C_{36}H_{32}N_2FeClPPd$ (found): C, 59.94 (59.7); H, 4.47 (4.4) and N, 3.89 (3.7). IR: ν_{max}: 1608 (>C=N–) cm^{-1}.

3.1.1.7. Preparation of $[[Pd\{[(4\text{-}Cl\text{–}C_6H_3)\text{–}NH\text{–}N{=}CH\text{–}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2]$ ***(3a)***. A 25 mg (3.4×10^{-5} mol) sample of **2a** were dissolved in 2 cm^3 of CH_2Cl_2, then 9 mg (3.4×10^{-5} mol) of PPh_3 were added. The resulting solution was stirred at room temperature for 1 h. Slow evaporation of the solvent at room temperature produced the precipitation of ochre microcrystals. (Yield: 81.6%). Anal. (%) Calc. for $C_{53}H_{44}Cl_2N_2FePdP_2$ (found): C, 63.40 (63.2); H, 4.41(4.45) and N, 2.79 (2.8). IR (KBr pellets) ν_{max}: 3205 (N–H) and 1608 (>C=N–) cm^{-1}.

3.1.1.8. Preparation of $[Pd\{[(4\text{-}NO_2\text{–}C_6H_3)\text{–}NH\text{–}N{=}CH\text{–}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2]$ ***(3b)***. This complex was synthesized in a NMR tube by dissolving 10 mg of **2b** in 0.7 cm^3 of $CDCl_3$ and then the stoichiometric amount of PPh_3 was added. The resulting mixture was shaken at room temperature for 1 min giving a pale brown solution.

3.1.1.9. Preparation of $[Pd\{[(3,6\text{-}Cl_2\text{–}C_6H_3)\text{–}NH\text{–}N{=}CH\text{–}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2]$ ***(3e)***. This compound was prepared using the procedure previously described for **2a**, but using: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}NH\text{–}C_6H_3\text{-}2,5\text{-}(Cl)_2]$ **(1e)**, as starting material. (Yield: 37%). Characterization data: Anal. (%) Calc. for $C_{53}H_{43}Cl_3N_2FePdP_2$ (found): C, 61.30 (61.15), H, 4.17 (4.20) and N, 2.69 (2.63). IR (KBr pellets) ν_{max}: 1608 (>C=N–) cm^{-1}.

3.2. Electrochemical studies

Electrochemical data for the hydrazones under study were obtained by cyclic voltammetry under argon at 20°C using acetonitrile (HPLC-grade) as solvent and tetrabutylammonium hexafluorophosphate (0.1 mol × dm^{-3}) as supporting electrolyte. The redox half-wave potentials were referred to an Ag|$AgNO_3$ (0.1 mol × dm^{-3}, in acetonitrile) electrode separated from the solution by a medium porosity fritted disk. A platinum wire auxiliary electrode was used in conjunction with a platinum disk working electrode, TACUSSEL-EDI rotatory electrode (3.14 mm^2). Cyclic voltammograms of 10^{-3} mol × dm^{-3} solutions of the samples in acetonitrile were recorded with a VersaStat, EG&G Princenton Applied Research potentiostat.

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