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Palladium(II) compounds containing mono- and bidentate primary ferrocenylamines. a study of the cyclopalladation of: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2\}]$ (with $n=1$ or 2)

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Abstract

The reactions of palladium(II) salts with the primary ferrocenylamines: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2\}]$ [with $n=1$ (**1a**) or 2 (**1b**)] are reported. These substrates react with $Na_2[PdCl_4]$ in methanol at room temperature giving: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2]\}_2Cl_2]$ [with $n=1$ (**2a**) or 2 (**2b**)] with the ferrocenylamine acting as a monodentate N-donor ligand. However, when compounds **1** are treated with $Pd(CH_3COO)_2$ in toluene, followed by the addition of LiBr and the subsequent treatment of the solids formed with triphenylphosphine, the cyclopalladated complexes: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}(CH_2)_n\text{-}NH_2]\}Br(PPh_3)]$ [with $n=1$ (**3a**) or 2 (**3b**)] were obtained. NMR studies reveal that compounds **3** contain a five- (in **3a**) or a six- (in **3b**) membered metallacycle fused with the ferrocenyl unit. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclopalladation; Palladacycles; Ferrocenylamines; Metallation

1. Introduction

One of the areas of organometallic chemistry that has seen great advances during the last years is the area involving cyclopalladated derivatives [1–4]. A wide variety of palladacycles containing: $\sigma(Pd\text{–}C_{sp^2,aryl})$, $\sigma(Pd\text{–}C_{sp^3})$, or $\sigma(Pd\text{–}C_{sp^2,ferrocene})$ bonds have been described in the literature. Present interest in these compounds stems for their multiple applications in several fields. For instance, it is well known that palladacycles are used as precursors in the syntheses of new organic and/or organometallic compounds [5,6] and in the manufacture dyestuff materials [7]. Some cyclopalladated compounds have been also used in homogeneous catalysis [8,9]. In addition, metallomesogens [10] and antitumoral drugs [11–13] containing cyclopalladated units have also been described. Optically active palladacycles derived from amines (i.e. substituted benzyl- or naphthyl-amines (Fig. 1(A)–(C)) applied as auxiliar reagents for determining enantiomeric excesses and even for resolving of racemic mixtures of chiral phosphines arsines or amines have also been reported [14].

In spite of the range of cyclopalladated compounds containing a $\sigma(Pd\text{–}C_{sp^2,ferrocene})$ bond described so far [15–36] and the prochiral nature of ferrocene derivatives [37–39], the number of articles dealing with cyclopalladated compounds containing a $\sigma(Pd\text{–}C_{sp^2,ferrocene})$ bond and ferrocenylamines are very scarce [32–36]. As far as we know, only palladacycles derived from $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(R)H\text{-}N(CH_3)_2\}]$ (with $R=H$, CH_3 or CF_3) [Fig. 1(D)] [32–36] have been prepared and characterized. However, cyclopalladated complexes derived from primary or secondary ferrocenylamines have not been reported.

Therefore, we decided to study the reaction of the primary ferrocenylamines: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2\}]$ [with $n=1$ (**1a**) or 2 (**1b**)] [Fig. 1(E)] vs palladium(II) salts.

2. Results and discussion

2.1. The ligands

The ferrocenylamines: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2\}]$ [with $n=1$ (**1a**) or 2 (**1b**)] were prepared from *N*,*N*-dimethylaminomethylferrocene following the sequences of reactions described in the literature [40–44], which are summarized in Scheme 1. In both synthetic methods, the first step is to prepare the quaternary salt: $<(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH_2\text{-}N(CH_3)_3\}>I$ <40, 41>. In

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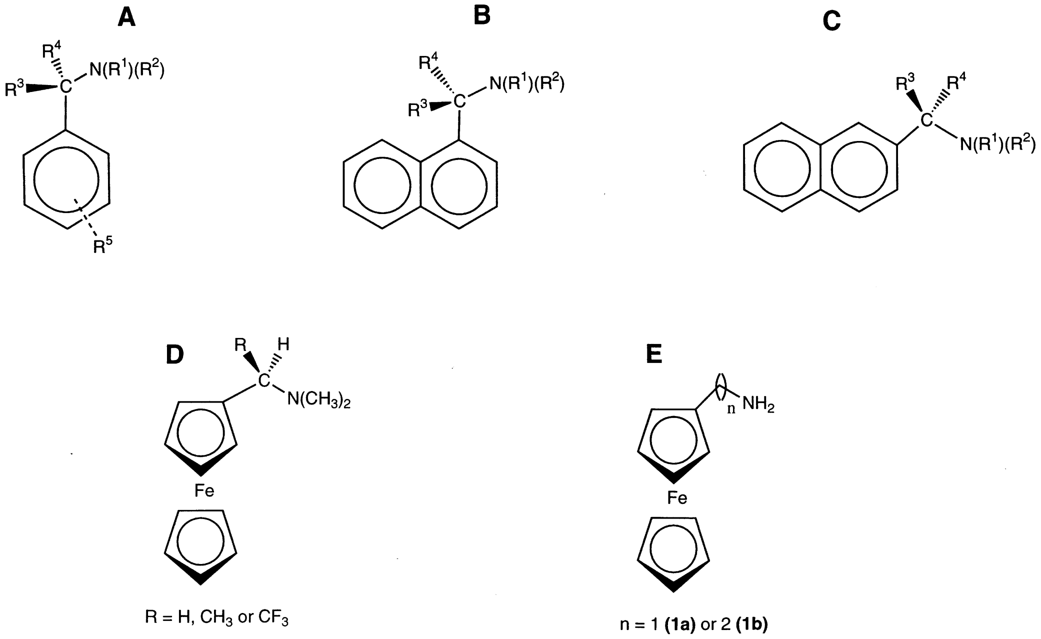
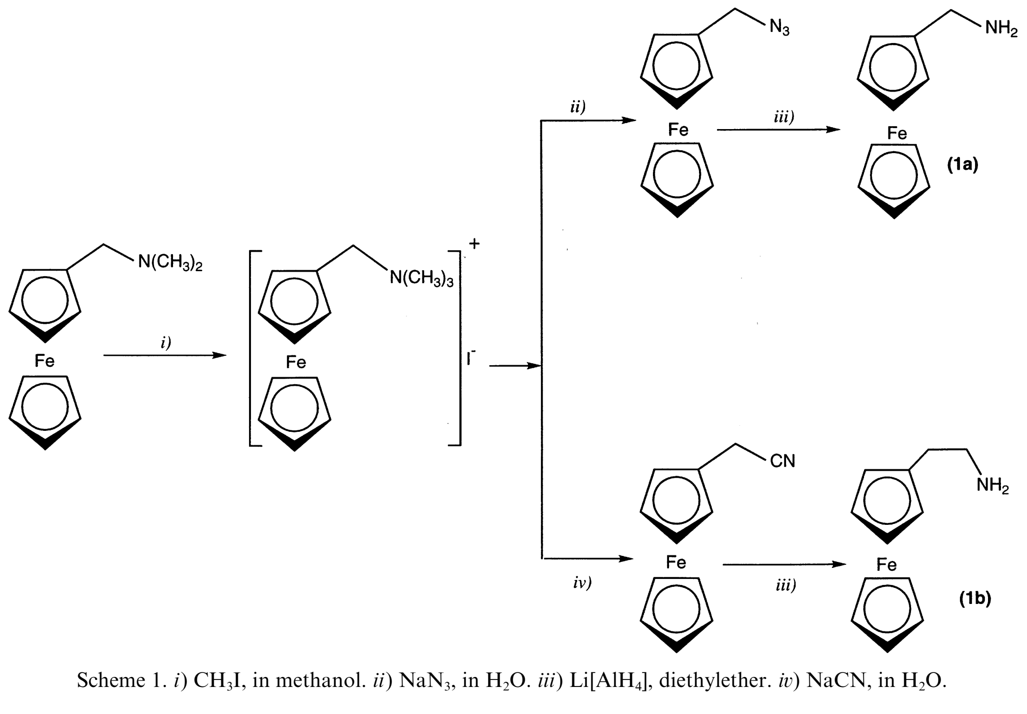


Fig. 1. Schematic view of the primary and secondary amines used in cyclopalladation reactions (A–C), derivatives of N,N-dimethylaminomethylferrocene (D) and the ferrocenylamines under study.



Scheme 1. *i)* CH_3I, in methanol. *ii)* NaN_3, in H_2O. *iii)* $Li[AlH_4]$, diethylether. *iv)* NaCN, in H_2O.

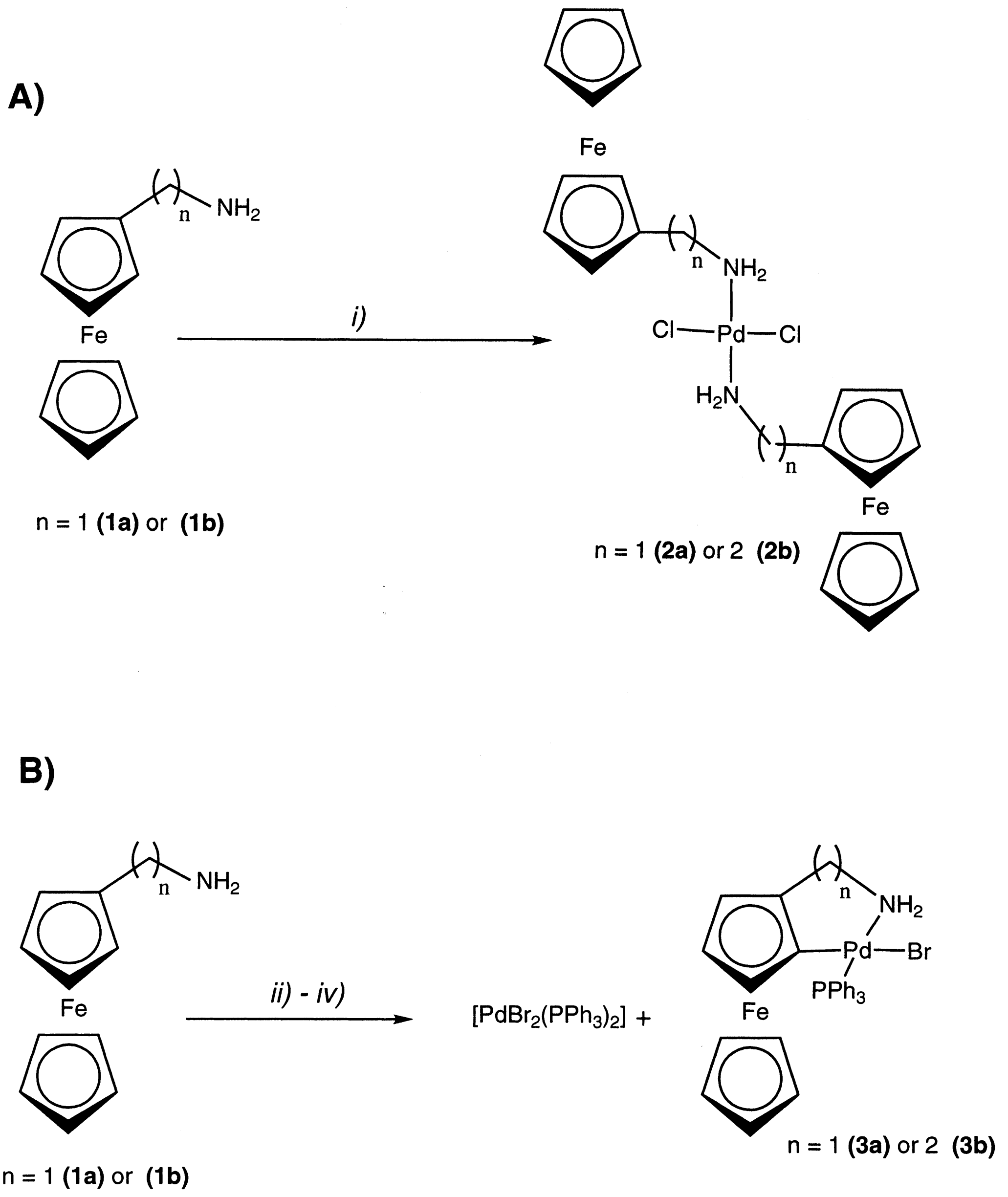
order to isolate ligand **1a**, this salt was first transformed into its azide derivative, which was later reduced to the corresponding ferrocenylamine <42>. For ligand **1b**, the quaternary salt was converted into the nitrile: $<(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH_2\text{-}CN\}>$ <41, 43> and its subsequent reduction with $Li[AlH_4]$ in anhydrous diethylether <43, 44> produced the desired ligand. The two ferrocenylamines were purified by vacuum distillation, which produced brownish oils.

2.2. *Palladium(II) compounds*

In order to study whether palladium(II) salts could induce the activation of the $\sigma(C_{sp^2,\text{ferrocene}}\text{–}H)$ bond in the ferrocenylamines **1a** and **1b**, several strategies were used. The first one involved the reaction of the ligands with $Na_2[PdCl_4]$ (in a 1:1 molar ratio) in methanol at room temperature. In both synthetic methods, pale ochre solids formed when the solution mixed. Characterization data of these solids were as expected for the coordination compounds: *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2]\}_2Cl_2]$ [with $n = 1$ (**2a**) or 2 (**2b**)] [Scheme 2, equation (A)>. Compounds **2** were obtained in higher yields (72 and 68%) when the reaction was carried out using a Pd:ligand molar ratio equal to 1:2.

Various reaction periods were used (from 1 h to 1 day), but evidence of the formation of any other palladium(II) compound was not detected by NMR. This finding differs from the results obtained in the reaction of primary and secondary benzylamines such as: $C_6H_5\text{-}C(R)(R')\text{-}NH(R'')$ (with $R = R' = Ph$ and $R'' = H$ or Me; $R = H$ and $R' = R'' = Me$ or $R = H$, $R' = Me$ and $R'' = CHMe_2$) or the naphthylamine: $C_{10}H_7\text{-}CH(Me)\text{-}NH\{CHMe_2\}$ which undergo orthopalladation of the aryl rings under identical experimental conditions (ligand:$Na_2[PdCl_4]$ in a 2:1 molar ratio in methanol at room temperature) <45–47>.

Although it is widely accepted that: (a) cyclopalladation of N-donor ligands proceeds in two steps: the coordination of the nitrogen to the palladium followed by



Scheme 2. *i*) $Na_2[PdCl_4]$, methanol, room temperature 3 h. *ii*) $Pd(AcO)_2$ in toluene, 3 h. *iii*) LiBr in ethanol at room temperature. *iv*) PPh_3 in benzene. *v*) SiO_2—column chromatography, for ligand **1b**, small amounts (<5%) of compound $[Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3)\text{-}(CH_2)_2\text{-}NH_2]\}Br(PPh_3)_2]$ (**4b**) were also isolated after the elution with a $CHCl_3 : CH_3OH$ (100 : 5) mixture.

the electrophilic attack to the σ(C–H) bond [48–51] and (b) ferrocene derivatives are more prone to undergo electrophilic attacks than benzene [23,25]; the reaction of ligands **1** with $Na_2[PdCl_4]$ does not produce the cyclopalladated compounds in contrast with the results obtained for *N*-benzylamines with bulky substituents [45–47]. Thus, the reactivity of ligands **1** is more alike to that of the less hindered benzylamines: R-C_6H_4-CH(R′)-NH_2 (with R′ = H or CH_3) [52–58] which do undergo the activation of the *ortho* σ(C–H) bond in the presence of $Na_2[PdCl_4]$.

In view of these results, we decided to test whether the general procedure described for the cyclopalladation of most N-donor ferrocenyl ligands [15–36] could also be extended to the ferrocenylamines **1**. This method, which consists of the reaction of equimolar amounts of the ligand [hereinafter referred to as (H–C–N)], $Na_2[PdCl_4]$ and $Na(CH_3COO)\cdot 3H_2O$ in methanol at room temperature, produces the di-μ-chloro-bridged cyclopalladated complexes: $[Pd(C–N)(\mu\text{-}Cl)]_2$. However, when the reaction was carried out using the ferrocenylamines (**1a** or **1b**) as starting materials and different reaction periods (from 3 to 24 h), only the coordination compounds: *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2]\}_2Cl_2]$ [with $n = 1$ (**2a**) or 2 (**2b**)] were formed in low yield (*ca.* 38%). Small amounts of starting materials were present in the filtrate but no evidence of the formation of any other palladium(II) compound was detected by NMR spectroscopy.

These findings differ from the results obtained for the tertiary amines: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH(R)\text{-}NMe_2\}]$ [where R = H (**1c**), CH_3 (**1d**) or CF_3 (**1e**)] for which cyclopalladation of the ferrocenyl fragment occurs, giving: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}CH(R)\text{-}NMe_2]\}(\mu\text{-}Cl)]_2$ in a fairly good yield (80% for **1c**, 66% for **1d** and 82% for **1e**) [32–34,36]. In addition, for amines **1c** and **1d** the formation of: *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}CH(R)\text{-}NMe_2]\}_2Cl_2]$ [with R = H (**2c**), Me (**1d**)], which are formally analogous to compounds **2a** and **2b**, could only be formed when the reaction was carried out in the absence of sodium acetate [59].

Recently, some authors have reported that the activation of the σ(C–H) bonds in benzylamines: C_6H_5-CH_2-NHR (with R = H, Me, ^{i}Pr, $CHEt_2$ or Ph), α-methylbenzylamines, 2-phenylaniline or α-methylbenzylamine can be achieved in fairly good yields (from 40 to 90%), using palladium(II) acetate as metallating agent and toluene as solvent [52–56]. On this basis, we decided to test whether this procedure could be extended to the ferrocenylamines $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2\}]$ [with $n = 1$ (**1a**) or 2 (**1b**)]. When ligands **1** were treated with $Pd(CH_3COO)_2$ in toluene at room temperature for 19 h, a deep brown solid formed. Further reaction of this material with LiBr in ethanol at room temperature produced a highly insoluble brown solid, which reacted with PPh_3 in benzene to give a red–brown solution. Concentration of the solution in a rotary evaporator followed by an SiO_2 column chromatography allowed us to isolate different sorts of palladium(II) compounds. When the reaction was carried out using $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH_2\text{-}NH_2\}]$ (**1a**), elution with $CHCl_3$ produced a yellow band which contained $[PdBr_2(PPh_3)_2]$. A second coloured fraction was eluted with mixture $CHCl_3$:CH_3OH (100:1). Concentration to dryness of the solution in a rotary evaporator enabled the isolation of the cyclopalladated compound: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}CH_2\text{-}NH_2]\}Br(PPh_3)]$ (**3a**) in a 38% yield [Scheme 2, equation (B)].

Similar results were obtained when the reaction was carried out using the ferrocenylamine **1b**. Complex: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}(CH_2)_2\text{-}NH_2]\}Br(PPh_3)]$ (**3b**) was isolated from the second band, but in this case the yield was even lower. Unlike the results obtained for ligand **1a**, an increase in the polarity of the eluant ($CHCl_3$:CH_3OH = 100:5) allowed us to collect a narrow additional band. The concentration of this solution to dryness in a rotary evaporator yielded a small amount (< 5%) of a pale orange solid. Proton and ^{31}P-NMR studies of this material were consistent with those expected for complex $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}(CH_2)_2\text{-}NH_2]\}Br(PPh_3)_2]$ (**4b**), in which the ferrocenylamine acts as a monoanionic C-donor ligand. Compound **4b** arises from **3b** by cleavage of the Pd–N bond and the incorporation of a second phosphine into the coordination sphere of the palladium.

The yields of the syntheses of compounds **3** are slightly lower than those reported for primary and secondary organic amines, particularly for substituted benzylamines (which fall in the range: 44–90%) [45–47,52–56]. In order to try to improve the yields of these reactions, different strategies were used. For instance, reaction times were increased up to two days, but no significant differences were found. In order to test whether the yield of syntheses could be increased thermically, the reaction was carried out in refluxing toluene for 1 h. However, under these conditions, the starting materials decomposed and a mirror of metallic palladium became visible. Consequently, the low yield of the reactions shown in Scheme 2[equation (B)] could be attributed to several factors, among which the instability of the ferrocenylamines and/or their highly reductive nature may be important. Electrochemical studies have demonstrated that compounds **1** are more prone to oxidize than ferrocene [the half-wave potentials (referred to ferrocene) are −0.025 and −0.031 V for **1a** and **1b**, respectively] [60]. The instability of these two ligands has been ascribed to this property since their reductive character may be responsible for the formation of metallic palladium in the course of the cyclopalladation process. A similar argument has been used to explain why cyclopalladation of the ferrocenylimines: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}(CH_2)_n\text{-}N{=}CHR]\}]$ (with $n = 1$ or 2 and R = aryl or ferrocenyl groups) also occurs at low yield [23–31], though these ferrocenylimines are a bit more resistant to oxidation than the amines (the half-wave potentials for the imines with $n=1$ and 2 range from -0.080 to -0.020 V and from -0.020 to -0.040 V, respectively [60]). As far as we know compounds **3** are the first examples of five (for **3a**) and six- (for **3b**) membered palladacycles derived from primary ferrocenylamines.

The *ortho*-$\sigma(C_{sp^2,phenyl}$–H) bonds of benzylamines C_6H_4-C(R)H-NH_2 (R = H or Me) can be activated using an alternative pathway [57, 58] which consists of (a) the reaction of the coordination compounds: *trans*-[Pd{C_6H_4-CH(R)-NH_2}X_2] (with X = Cl or I) with silver(I) salts to give: [Pd{C_6H_4-CH(R)-NH_2}(solvent)$_2$]$^{2+}$ and (b) the subsequent electrophilic attack of the coordinated palladium to the σ(C–H) bond; however, when compounds **2** were treated with $AgClO_4$ at room temperature, the formation of a metallic mirror was detected. This can also be explained by the highly reductive nature of the ferrocenylamines mentioned above.

The difference in the products obtained in the reactions of **1** with $Na_2[PdCl_4]$ or $Pd(CH_3COO)_2$ can be interpreted as due to the higher electrophilic character of the palladium(II) in the coordination complexes *trans*-[Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_4)-$(CH_2)_n$-NH_2]}$_2$(CH_3COO)$_2$] (with $n=1$ or 2) formed in the first step of the cyclopalladation reaction, which may ease the activation of the $\sigma(C_{sp^2,ferrocene}$–H) bond.

Finally, it is worth noting that compounds **2** and **3** are more stable than the free ligands, since no significant variation in their colours or their NMR spectra was detected after several weeks of storage. This finding is consistent with the results obtained for related coordination complexes such as: *trans*-[Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_4)-CH=N-$(CH_2)_2$-NMe_2]}$_2Cl_2$] or *trans*-[Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_4)-CH=N-NMe_2]}$_2Cl_2$] [61]. For these complexes, electrochemical studies, based on cyclic voltammetry, revealed that the binding of the palladium to the N-donor ligand causes an increase in the half-wave potential, so reducing the propensity of the Fe(II) to oxidize [60].

In order to check the stability of the Pd–N bond in the cyclopalladated complexes **3** an excess of PPh_3 was added to their $CDCl_3$ solutions. These experiments were performed in an NMR-tube and studied by ^{31}P-NMR spectroscopy. When the experiment was carried out using complexes **3a** and **3b**, the spectrum showed a singlet (at 29.2 and 27.5 ppm, respectively). It is worth noting that the position and multiplicity of these signals were consistent with the values expected for compounds [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)-$(CH_2)_n$-NH_2]}Br(PPh_3)$_2$] [$n=1$ (**4a**) or 2 (**4b**)] in which the amine acts as a monodentate anionic ligand bound to the palladium through the *ortho*-C atom of the ferrocenyl fragment. Compounds **4** arise from the opening of the metallacycle and the coordination of a second phosphine to the palladium(II). This finding differs from previous studies on five-membered palladacycles [Pd(C–N)Cl(PPh_3)] [where the (C–N) group represents a bidentate ferrocenylimine, oxime or azine] which do not react with large excesses of PPh_3 [15–36]. This suggests that in compounds **3** the Pd–N bond is more labile than in the palladacycles derived from ferrocenylimines, azines, oximes or hydrazones. These results are consistent with previous studies on the reactivity of cyclopalladated and cycloplatinated complexes, which showed that, depending on the nature of the metallacycle and the basicity of the nitrogen, the Pd–N bond can be cleaved [62,63]. In particular, for palladacycles derived from organic imines, an increase in the basicity enhances the reactivity of the Pd–N bond. This argument can also be used to explain the higher lability of the Pd–N bond in **3** and in their analogues: [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)-C(R)=N-R′]}Cl(PPh_3)] (with R = H, Me or Ph and R′ = phenyl or benzyl groups), since imine nitrogen is less basic than amine nitrogen.

2.2. Characterization

The compounds prepared for this study are pale-ochre (for **2**), reddish (for **3**) or orange (for **4b**) solids at room temperature. Compounds **3** are highly soluble in most common solvents and practically insoluble in alkanes or diethylether. Elemental analyses of all the complexes are consistent with the proposed formulae (see Section 3). The most relevant feature of the infrared spectra of **2** and **3** is the presence of a band in the range 3300–3150 cm^{-1} due to the stretching of the N–H bond. The IR spectra of compounds **3** showed a band at *ca.* 917 cm^{-1} which is according to Rosenblum's criteria [64], characteristic of 1,2-disubstituted ferrocene derivatives. This band was not observed in the infrared spectra of the coordination complexes **2**. Proton-NMR spectroscopic data for compounds under study are summarized in Table 1. The resonances due to the ferrocenyl fragment appeared as one singlet and two triplets of relative intensities 5:2:2 for the free ligands **1** and compounds **2** and as four singlets of relative intensities 5:1:1:1 for complexes **3** and **4**, which contain a $\sigma(Pd–C_{sp^2,ferrocene})$ bond. The highfield shift of the signal due to the H^3 proton in **3** is consistent with the results reported for palladacycles with the general formula: [Pd(C–N)Cl(PPh_3)] [where the (C–N) groups represent a metallated ferrocenylimine, oxime, hydrazone, azine or a tertiary ferrocenylamine]. It has been interpreted in terms of the ring current of the phenyl rings of the PPh_3 ligand in a *cis*-arrangement to the metallated carbon atom [23–31]. For complex **3a** the two protons of the -NH_2 group were diastereotopic and appeared as two singlets in the region: 4.5–5.3 ppm, but the ^{1}H-NMR spectra of **4**, which arose from a ring-opening process involving the cleavage of the Pd–N bond, showed broad singlets in the area 5.1–5.5 ppm.

Phosphorus-31 NMR spectra of **3** showed a singlet at 38.9 ppm (for **3a**) and at 36.5 ppm (for **3b**). The position of these signals were consistent with the values reported

Table 1
Selected ^{1}H-NMR data (in ppm) for the ferrocenylamines: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)-$(CH_2)_n$-NH_2}] and for their palladium(II) compounds **2**, **3** and **4** and ^{31}P-NMR data (in ppm) for compounds: [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)-$(CH_2)_n$-NH_2]}Br(PPh_3)] [with $n = 1$ (**3a**) and $n = 2$ (**3b**)] and [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)-$(CH_2)_n$-NH_2]}Br$(PPh_3)_2$] [with $n = 1$ (**4a**) and $n = 2$ (**4b**)]. Numbering of the atoms refers to the schemes shown below

	Proton-NMR								^{31}P-NMR	
	C_5H_5	H^2	H^3	H^4	H^5	-CH_2–N-^{a}	-CH_2-^{b}	-NH_2	others	δ^{31}P
1a	4.00	4.10	4.06	4.06	4.10	3.56	–	4.72^c	–	
1b	4.10	4.15	4.09	4.09	4.15	3.60	2.60	^{d}	–	
2a	4.14	4.20	4.01	4.01	4.20	3.60	–	^{d}	–	
2b	4.10	4.32	4.08	4.08	4.32	3.65	2.68	^{d}	–	
3a	3.92	–	3.29	4.18	4.27	3.72	–	5.20	7.30–7.80, m (Ph)	38.9
						4.00^e		4.60		
3b	4.13	–	3.38	4.06	4.40	3.88	3.10	5.28	7.25–7.75, m (Ph)	36.5
						4.10^e	2.70	4.45^f		
4a	4.06	–	4.04	4.20	4.42	3.30	–	5.26^c	7.20–7.75, m (Ph)	29.2
4b	4.17	–	4.01	4.09	4.36	3.40	2.50	5.40^c	7.29–7.85, m (Ph)	27.5

[a] The signal due to the protons of the -CH_2–N moiety appears as a singlet in compounds **1a** and **2a**, as a doublet of doublets in **3a**, as a triplet in **1b**, **2b** and **4b** and as two multiplets in **3b** (centered at the values given).

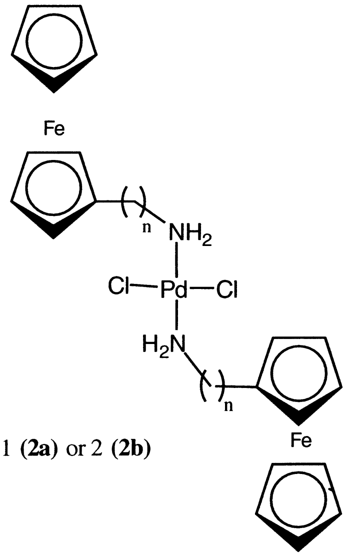
[b] The signal due to the protons of the -CH_2- group in complex **3b** appears as two multiplets.

[c] Broad signal.

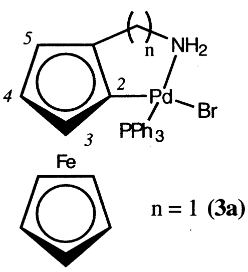
[d] Not observed.

[e] Partially overlapped by the signals due to the protons of the C_5H_5 ring and the resonance of H^4.

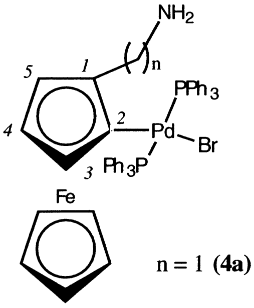
[f] Partially overlapped by the signals due to the resonance of H^5.



n = 1 (**2a**) or 2 (**2b**)



n = 1 (**3a**) or 2 (**3b**)



n = 1 (**4a**) or 2 (**4b**)

for related five- and six-membered cyclopalladated complexes containing a σ(Pd–$C_{sp^2,aryl}$) bond or a σ(Pd–$C_{sp^2,ferrocene}$) bond in which the imine nitrogen and the phosphine ligand are in a *trans*-arrangement [23–31]. For compounds **4**, the spectrum showed a singlet in the range 27–30 ppm, in good agreement with the results reported for [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)-CH_2-NMe_2]}Cl$(PPh_3)_2$] [29].

Quite recently, Albert *et al.* [56] have described the syntheses and NMR spectra of the cyclopalladated complexes: [Pd{C_6H_4-CH(Me)-NH_2}Br(PPh_3)] (**5a**) and [Pd{(C_6H_4-2-(C_6H_4)-NH_2}Br(PPh_3)] (**5b**). These two compounds contain metallated primary amines and a five- (in **5a**) or a six- (in **5b**) membered palladacycle. Since the remaining ligands bound to the palladium in compounds **3a**, **3b**, **5a** and **5b** are identical, the differences detected in the position of the signal observed in the ^{31}P-NMR spectra can be, as a first approach, indicative of the effect of the chelate ligand in compounds [Pd(C–N)Br(PPh_3)] upon the phosphine group. Such an effect can be monitored through the coordination shift $\Delta\delta$ of the phosphine ligand:

$\Delta\delta = \delta(\text{complex}) - \delta(\text{free PPh}_3)$

Since δ(free PPh_3) is a constant value (−6.02 ppm in $CDCl_3$) the lowfield shift of the signal due to the PPh_3 in the complex is directly associated with an increase in the coordination shift. Comparison of the position of this signal for compounds **3a** (38.9 ppm), **3b** (36.5 ppm), **5a** (41.7 ppm [56]) and **5b** (35.9 ppm [56]), permit the chelating ligands to be listed according to a decreasing order of the coordination shifts $\Delta\delta$:

5b < **3b** < **3a** < **5a**

This variation can be ascribed to two major effects: (a) the different basicity of the nitrogen in a *trans*-arrangement to the PPh_3 and/or (b) the electronic effects due to distinct ring-current density in the metallated rings (C_5H_3 in **3a**, **3b** or a phenyl in **5a** or **5b**). These two effects regulate the abilities of the chelated ligands to donate electrons.

2.3. Conclusions

The results reported in this paper show that the reaction of the ferrocenylamines: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH{=}N\text{-}(CH_2)_n\text{-}NH_2\}]$ (**1**) with palladium(II) salts produces (depending on the experimental conditions and on the nature of the initial palladium complex) different sorts of compounds: *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2]\}_2Cl_2]$ (**2**) or $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}(CH_2)_n\text{-}NH_2]\}Br(PPh_3)]$ (**3**), which differ in the mode of coordination of the amine [which acts as an N-donor monodentate in **2** or as a monoanionic $(C\text{–}N)^-$ bidentate group in **3**]. It is worth noting that compounds **3** are the first examples of palladacycles derived from primary ferrocenylamines containing a five [for (**3a**)] or a six-membered [for (**3b**)] ring. In addition, the reaction of compounds **3** with PPh_3 in $CDCl_3$ produces: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}(CH_2)_n\text{-}NH_2]\}Br(PPh_3)_2]$ [with $n=1$ (**4a**) or 2 (**4b**)] where the ferrocenyl amines act as a monoanionic C-donor ligand.

3. Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Cientifico-Tècnics (Universitat de Barcelona) and at the Institut de Química Bio-Orgánica (C.S.I.C.), Barcelona. Infrared spectra were recorded with a Nicolet 520-FTIR spectrophotometer using KBr pellets. Proton-NMR spectra were recorded with a Varian Gemini-200 MHz instrument using $CDCl_3$ (99.9%) as solvent and $Si(CH_3)_4$ as internal standard. Phosphorus-NMR spectra were obtained with a Bruker-250DXR instrument using $CDCl_3$ as solvent and $P(OCH_3)_3$ as internal reference (δ $^{31}P = 140.17$ ppm).

3.1. Materials and synthesis

N,*N*-Dimethylaminomethylferrocene was obtained from commercial sources and used as received. The amines: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2\}]$ [with $n=1$ (**1a**) or 2 (**1b**)] were prepared using the three-step sequences previously described [40–44]. The synthesis of **1a** requires the use and manipulation of large amounts of *highly hazardous* materials $\{NaN_3$ and $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH_2\text{-}N_3\}]\}$ which may *explode*. To prepare **1b**, KCN is needed. Consequently the two ferrocenylamines must be prepared with *maximum caution*. The ferrocenylamines were purified by vacuum distillation before their use. Due to the instability of the amines **1a** and **1b**, all the preparations described below require the use of freshly prepared and purified samples of these ligands. The preparations of compounds **3** require benzene which should be handled with *care*.

3.1.1. Preparation of trans-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2]\}_2Cl_2]$ [with n = 1 (**2a**) or 2 (**2b**)]

To a solution containing 0.500 mmol of the corresponding ferrocenylamine (freshly prepared and purified) and 30 ml of methanol, the stoichiometric amount of $Na_2[PdCl_4]$ was added. The resulting mixture was protected from the light with aluminium foil and stirred at room temperature (*ca.* 20°C) for 3 h. The pale ochre solids formed were collected by filtration, washed with methanol (3 portions of *ca.* 5 ml) and air-dried. (Yields: 72 and 68% for **2a** and **2b**, respectively.) *Characterization data* for **2a**: Anal. (%) calcd for $C_{22}H_{26}N_2Cl_2Fe_2Pd$ (found): C, 43.49 (43.5); H, 4.28 (4.3) and N, 4.26 (4.20). IR: ν(N–H) = 3236 and 3266 cm^{-1}. **2b**: Anal. (%) calcd for $C_{24}H_{30}N_2Cl_2Fe_2Pd$ (found): C, 45.35 (45.2); H, 4.76 (4.8) and N, 4.40 (4.4). IR: ν(N–H) = 3240 and 3268 cm^{-1}.

3.1.2. Preparation of $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}(CH_2)_n\text{-}NH_2]\}Br(PPh_3)]$ [with n = 1 (**3a**) or 2 (**3b**)]

A suspension containing 0.500 mmol of $Pd(CH_3COO)_2$, 0.500 mmol of the corresponding ferrocenylamine $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}NH_2\}]$ [with $n=1$ (**1a**) or 2 (**1b**)] and 50 ml of toluene was stirred at room temperature for 18 h. The resulting suspension was concentrated to dryness in a rotary evaporator. The dark brown residue was suspended in 30 ml of ethanol and treated with 0.500 mmol of LiBr. The reaction mixture was stirred at room temperature for 45 min. Then the undissolved materials were removed by filtration and discarded. The brown–red filtrate was concentrated to dryness in a rotary evaporator. The residue formed was dissolved in the minimum amount of benzene *ca.* 50 ml and treated with 0.5 mmol of triphenylphosphine. The resulting mixture was stirred at room temperature for 1 h and then concentrated to dryness on a rotary evaporator. The gummy materials formed were dissolved in the minimum amount of chloroform and passed through a SiO_2-column (250 × 10 mm). After elution with $CHCl_3$ a yellow band which containing $[PdBr_2(PPh_3)_2]$ could be collected. The cyclopalladated complexes **3a** and **3b** were isolated after elution with a $CHCl_3$:CH_3OH (100:1) mixture. Concentration to dryness of the eluted solutions in a rotary evaporator produced red solids, which were collected and air-dried. (Yields: 38 and 34%, respectively.) *Characterization data* for **3a**: Anal. (%) calcd for $C_{29}H_{27}NBrFePPd$ (found): C, 52.6 (52.8); H, 4.10 (4.15) and N, 2.11 (2.0). IR: ν(N–H) = 3215 and 3160 cm^{-1}. **3b**: Anal. (%) calcd for $C_{30}H_{29}NBrFePPd$ (found): C, 53.24 (53.4); H, 4.31 (4.35) and N, 2.07 (1.95). IR: ν(N–H) = 3197 and 3156 cm^{-1}.

3.1.3. Preparation of $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}(CH_2)_n\text{-}NH_2]\}Br(PPh_3)_2]$ *[with* $n = 1$ *(**4a**) or 2 (**4b**)]*

These compounds were prepared in an NMR tube and characterized by NMR spectroscopy. They were synthesised as follows: triphenylphosphine (4.0×10^{-2} mmol) was added to a solution containing 4.0×10^{-2} mmol of the corresponding complex **3** and 0.7 ml of $CDCl_3$. The resulting mixture was shaken vigorously for 5 min giving a pale orange solution. Complex **4b** could also be isolated as a by-product ($< 5\%$) in the preparation of **3b** and its NMR data were identical to those obtained when its preparation was carried out in an NMR tube.

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