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Five- and six-membered palladacycles derived from $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)\}]$

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Abstract

The reaction of the novel ferrocenyl Schiff base: $[(\eta^5-C_5H_5)Fe{(\eta^5-C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)}]$ (1) with Na₂[PdCl₄] and Na(CH₃COO)·3H₂O in a 1:1:1 molar ratio in methanol is reported. In this reaction two different di- μ -chloro-bridged cyclopalladated complexes: $[Pd{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_5)}(\mu-Cl)]_2$ (2a) and $[Pd{[(C_6H_4-2-C_6H_4)-N=CH-(\eta^5-C_5H_4)]Fe(\eta^5-C_5H_5)}(\mu-Cl)]_2$ (2b) can be formed depending on the experimental conditions. Compounds 2a and 2b, which differ in the nature of the metallated carbon atom ($C_{sp^2,ferrocene}$ or $C_{sp^2,biphenyl}$, respectively), undergo cleavage of the 'Pd(μ -Cl)₂Pd' bridges in the presence of thallium (I) acetylacetonate, deuterated pyridine or triphenylphosphine giving the monomeric derivatives: $[Pd(C^{^N})(acac)]$ (3a, 3b) and $[Pd(C^{^N})Cl(L)]$ (with L=py- d_5 (4a, 4b), PPh₃(5a, 5b)}. The reactions of 2 with 1,2-bis(diphenylphosphino)ethane (dppe) reveal that the two isomers (2a and 2b) exhibit different reactivity versus dppe. These results have been interpreted on the basis of steric effects. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

During the last decade the interest in cyclopalladated compounds derived from N-donor ligands has increased exponentially [1-3] mainly due to their novel and outstanding applications [4-13]. To date most of these systems contain organic amines, imines, oximes and, to a lesser extent, hydrazones or azo-derivatives, bound to the palladium atoms through a $C_{sp^2,phenyl}$ or a C_{sp^3} , carbon atom. More recently, the study of cyclopalladation of N-donor ferrocenyl ligands (such as: ferrocenylamines, imines, oximes, hydrazones, azines and azoderivatives) has allowed the isolation and characterization of a novel type of palladacycle with a $\sigma(Pd-C_{sp^2,ferrocene})$ bond [14–43]. Furthermore, these studies have shown that although the cyclopalladation of the ferrocenyl Schiff bases: $[(\eta^{3} C_5H_5$)Fe{ $(\eta^5-C_5H_4)-C(R)=N-R'$ } {R=H, CH₃ or C₆H₅ and R'=susbtituted phenyl, benzyl rings} (Fig. 1A) produced five-membered rings with a $\sigma(Pd-C_{sp^2,ferrocene})$ bond [28,29], the results obtained for: $[(\eta^2-C_5H_5)Fe\{(\eta^2-C_5H_4) (CH_2)_n$ -N=CH(R)] {n=1 or 2 and R=substituted phenyl groups} (Fig. 1B) revealed that minor changes in (a) the

*Corresponding author. Tel.: +34-93-402-1274; fax: +34-93-490-7725. length of the $-(CH_2)_n$ -chain, or (*b*) the R group bound to the imine carbon atom are enough to modify the structure of the metallacycle [28,29] (Fig. 1).

In order to elucidate whether the incorporation of a bulky substituent on the imine nitrogen in: $[(\eta^5 - C_5H_5)Fe\{(\eta^5 - C_5H_4) - C(H) = N - R'\}]$ could also be important in determining the type of $\sigma(C-H)$ bond to be activated, we studied the cyclopalladation of the ferrocenylimine: $[(\eta^5 - C_5H_5)Fe\{(\eta^5 - C_5H_4) - C(R) = N - (C_6H_4 - 2 - C_6H_5)\}]$ (1) (Fig. 1C). This substrate could produce two types of palladacycle: (a) a six-membered ring with a $\sigma(Pd - C_{sp^2, biphenyl})$ bond or (b) a five-membered palladacycle containing the >C = N- bond, which would require the activation of the *ortho*- $\sigma(C_{sp^2, ferrocene} - H)$ bond.

In this paper we describe the synthesis of compound **1** and the activation of two different *ortho* σ (C-H) bonds: σ (C_{sp²,ferrocene}-H) or σ (C_{sp²,biphenyl}-H). This study has allowed us to isolate and characterize two types of metallacycle, containing a σ (Pd-C_{sp²,biphenyl}) or a σ (Pd-C_{sp²,ferrocene}) bond.

2. Experimental

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Elemental analyses (C, H and N) were carried out at the



Fig. 1. Schematic view of some of the ferrocenylimines used in the cyclopalladation reactions (A-B) and of the novel ferrocenyl Schiff base under study (C). All these ligands could produce two different types of palladacycles depending on the relative position of the functional group >C=N- versus the metallacycle (endo- and exo-derivatives).

Serveis Cientifico-Tècnics de la Universitat de Barcelona. Infrared spectra were obtained with a Nicolet-500-FTIR instrument using KBr pellets for the solid samples or NaCl discs for the imine **1**. Routine ¹H-NMR spectra were recorded at 20°C on a Gemini-200 MHz instrument using benzene $-d_6$ or CDCl₃ (99.9%) as solvents. Si(CH₃)₄ was used as internal standard in the later cases. ¹³C{¹H} and ³¹P-NMR spectra were recorded with a Bruker-250DXR instrument using CDCl₃ (99.9%) as solvent. Trimethylphosphite was used as internal reference for ³¹P-NMR spectra [δ^{31} P for P(OCH₃)₃: 141.17 ppm].

2.1. Materials and synthesis

Ferrocenecarboxaldehyde, 2-phenylaniline, triphenylphosphine, thallium acetylacetonate and 1,2-bis-(diphenylphosphino)ethane were obtained from commercial sources and used as received. The solvents, except benzene, were dried and distilled before use. Some of the procedures described below require the use of hazardous materials, such as thallium(I) salts or benzene, which should be handled with caution.

2.1.1. Preparation of the ferrocenylimine (1)

Ferrocenecarboxaldehyde (2.00 g, 9.34×10^{-3} mol) and 2-phenylaniline (1.58 g, 9.34×10^{-3} mol) were dissolved in 25 ml of benzene. The reaction flask was connected to a Dean–Stark apparatus and to a condenser. The reaction mixture was then refluxed on an ethyleneglycol bath until ca. 20 ml of the azeotrope benzene–water had condensed in the Dean–Stark. The resulting solution was concentrated to dryness on a rotary evaporator. The ¹H-NMR spectrum of the residue (in CDCl₃) was recorded to check the progress of the reaction, and revealed that the residue contained a 1:2 mixture of unreacted ferrocenecarboxaldehyde and the ferrocenyl Schiff base (1). In order to achieve the total conversion of the aldehyde, the residue

was dissolved in benzene (ca. 20 ml) and 0.615 g (3.6×10^{-3} mol) of the amine was added. The flask was again connected to the Dean–Stark apparatus and the procedure was repeated. Finally, the solution obtained after the reflux was filtered out. The undissolved materials were discarded and the filtrate was concentrated to dryness on a rotary evaporator, producing a red–brownish oily residue, which contained ligand **1**. The addition of *n*-hexane to the residue followed by vigorous stirring for ca. 10 min at room temperature, produced **1** (yield: 72%). Characterization data for **1**: IR: ν (>C=N-)=1625 cm⁻¹.

2.1.2. Preparation of compounds 2

The imine **1** (1.81 g, 4.96×10^{-3} mol), Na₂[PdCl₄] (1.46 g, 5.07×10^{-3} mol) and Na(CH₃COO)·3H₂O (0.68 g, 5.00×10^{-3} mol) were suspended in 25 ml of methanol. The reaction flask was protected from the light with aluminium foil and the reaction mixture was stirred at room temperature for 3 h (for 2b) or 7 days (for 2a). The isolation of complex 2a was achieved as follows: the red precipitate formed was dissolved in the minimum amount of CHCl₃ and purified by SiO₂-column chromatography using CHCl₃ as eluant. The red band eluted was collected and concentrated in vacuum on a rotary evaporator. The resulting residue was then treated with *n*-hexane (ca. 20) ml) and stirred at room temperature for 20 min. The solid formed was filtered out and dried in vacuum (yield: 65%). When the reaction was carried out for 3 h the solid formed consisted of a 1.3:1.0 mixture of 2a and 2b, which were separated by SiO₂-column chromatography using a CHCl₃: n- hexane (100:10) mixture as eluant. During the elution, two red bands were collected. The former contained complex 2b. The solution of 2b was concentrated to dryness on a rotary evaporator, and the residue was dissolved in the minimum amount of CH₂Cl₂ and the addition of *n*-hexane followed by vigorous stirring at room temperature for 5 min produced the precipitation of 2b (yield: 32%). When this treatment was repeated with the

second eluted band it yielded complex 2a (yield: 20%) which was collected by filtration and air-dried. Compound 2a can also be obtained using the following procedure: palladium(II) acetate (0.500 g, 2.23×10^{-3} mol) and the imine **1** (0.815 g, 2.23×10^{-3} mol) were refluxed in glacial acetic acid (30 ml) for 2 h. Then the resulting suspension was concentrated to dryness on a rotary evaporator and the residue was treated with LiCl (106 mg, 2.5×10^{-3} mol) in ethanol (40 ml). The resulting reaction mixture was refluxed for 30 min. The orange-red solid formed was filtered out, washed with three portions (5 ml) of ethanol and air-dried. Finally the solid was purified by SiO₂ column chromatography using CHCl₃ as eluant (yield: 49%). Characterization data for 2a: Anal. (%) Calcd. for C₄₆H₃₆N₂Cl₂Fe₂Pd₂ (found): C, 54.5 (54.6); H, 3.6 (3.59) and N, 3.1 (2.77). IR: $\nu(>C=N-)=1586 \text{ cm}^{-1}$. For **2b**: Anal. (%) Calcd. for C46H36N2Cl2Fe2Pd2 (found): C, 54.4 (54.6); H, 3.6 (3.59) and N, 2.9 (2.77). IR: ν (>C=N-)= 1603 cm^{-1} .

2.1.3. Preparation of compounds 3

A 0.100-g $(9.9 \times 10^{-5} \text{ mol})$ amount of the corresponding di-µ-chloro-bridged cyclopalladated derivative (2a or 2b) was suspended in 20 ml of acetone, then the stoichiometric amount of thallium(I) acetylacetonate was added. The resulting mixture was stirred at room temperature for 1.5 h and then filtered out with Whatman paper, to remove the thallium(I) chloride formed during the process. The resulting solution was concentrated to dryness on a rotary evaporator. The red solid formed was washed with nhexane and air-dried (yield: 74 and 68% for 3a and 3b, respectively). Characterization data for 3a: Anal. (%) Calcd. for C₂₇H₃₅NClFeO₂Pd (found): C, 58.9 (59.00); H, 4.6 (4.40) and N, 2.5 (2.52). IR: ν (>C=N-)=1590 cm⁻¹. For **3b**: Anal.(%) Calcd. for C₂₇H₃₅NClFeO₂Pd (found): C, 58.9 (59.00); H, 4.69 (4.40) and N, 2.5 (2.52). IR: ν (>C=N-)=1598 cm⁻¹.

2.1.4. Preparation of compounds 4

These compounds were prepared in situ and characterized by NMR spectroscopy. The method used for these preparations was the following: the corresponding complex 2 (30 mg, 2.97×10^{-5} mol) was suspended in 0.7 ml of CDCl₃. An excess of deuterated pyridine (5 µl, 6.2×10^{-5} mol) was then added and the reaction mixture was shaken vigorously for 2 min to aid the dissolution of the di-µchloro-bridged cyclopalladated complex, which produced a dark orange solution.

2.1.5. Preparation of compounds 5

Triphenylphosphine (178 mg, 6.9×10^{-4} mol) was added to a suspension containing 340 mg (3.4×10^{-4} mol) of the corresponding di- μ -chloro-bridged cyclopalladated complex (**2a** or **2b**) and 10 ml of benzene. The reaction mixture was then stirred at room temperature for 1 h. The

undissolved materials were removed by filtration and discarded. The filtrate was then concentrated to dryness on a rotary evaporator, giving an orange–red solid which was collected and air-dried. (yield: 87 and 72% for **5a** and **5b** respectively). Characterization data for **5a**: Anal. (%) Calcd. for C₄₁H₃₃NCIFePPd (found): C, 63.9 (64.0); H, 4.3 (4.29) and N, 1.8 (1.87). IR: ν (>C=N-)=1590 cm⁻¹. For **5b**: Anal. (%) Calcd. for C₄₁H₃₃NCIFePPd (found): C, 64.1 (64.1); H, 4.3 (4.5) and N, 1.8 (2.0). IR: ν (>C=N-)=1617 cm⁻¹.

2.1.6. Preparation of compound 6b

A 100 mg $(9.9 \times 10^{-5} \text{ mol})$ amount of the di- μ -chlorobridged cyclopalladated derivative **2b** was suspended in 20 ml of CH₂Cl₂, and the stoichiometric amount of dppe (40 mg, 4.9×10^{-5} mol) was then added. The resulting mixture was stirred at room temperature for 20 min and filtered out. The orange–red filtrate was concentrated to dryness on a rotary evaporator. Addition of *n*-hexane produced the precipitation of the compound, which was filtered out and air-dried. (yield: 65%). Characterization data for **6b**: Anal. (%) Calcd. for C₄₉H₄₂NCIFeP₂Pd (found): C, 65.1 (65.15); H, 4.7 (4.6) and N, 1.6 (1.45). IR: ν (>C=N-)= 1611 cm⁻¹.

2.2. Computational details

The calculations were performed with the SPARTAN 4.1 suite of programs [58] using silicon graphics (model: INDIGO-2 power ZX). The pm3 method was used with the default parameters provided by the program. Geometrical restrictions were not imposed in any case. The calculations were undertaken with the option SCF=converge and the number of cycles required for the optimization of the geometry of the ligand and of the model complex: $[Pd{(\eta^5-C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)]}Cl_3]^-$ was greater than the default value (200 cycles). A minimum of 10^3 cycles was necessary in both cases.

3. Results and discussion

3.1. The ligand

The new ferrocenylimine $[(\eta^5 - C_5 H_5)Fe\{(\eta^5 - C_5 H_4) - CH = N - (C_6 H_4 - 2 - C_6 H_5)\}]$ (1) was prepared following the general procedure described for the synthesis of related ferrocenyl Schiff bases of general formula: $[(\eta^5 - C_5 H_5)Fe\{(\eta^5 - C_5 H_4) - CH = N - R\}]$ {with R=phenyl or benzyl groups} [26–28], which consists of the reaction of stoichiometric amounts of ferrocenecarboxaldehyde and the corresponding amine under reflux using a Dean–Stark apparatus (to remove the benzene–water azeotrope formed in the course of the reaction). When this reaction was performed in identical experimental conditions, but using

2-phenylaniline as reagent, a mixture of the imine: $[(\eta^5 - C_5H_5)Fe\{(\eta^5 - C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)\}]$ (1) and ferrocenecarboxaldehyde (in a 5:1 molar ratio) was obtained. However, the complete conversion of the aldehyde was easily achieved using a large excess of the amine. The use of excesses of amines were also required in the preparation of ferrocenyl Schiff bases derived from acetyl or benzoyl ferrocene and it has been postulated that an increase in the bulk of the reagents hinders the condensation process [26–28].

3.2. Activation of $\sigma(C-H)$ bonds in $[(\eta^5 - C_5H_5)Fe\{(\eta^5 - C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)\}]$ (1)

When compound **1** was reacted with Na₂[PdCl₄] and Na(CH₃COO)·3H₂O (in a 1:1:1 molar ratio) in methanol at room temperature for 3 h a reddish precipitate formed (Scheme 1). Elemental analyses of this solid were consistent with those expected for a di- μ -chloro-bridged cyclopalladated complex: [Pd(C^N)(μ -Cl)]₂. However, its ¹H-NMR spectra showed two superimposed sets of signals. For instance, two singlets due to the imine proton appeared at 8.64 and 8.06 ppm. The relative intensities of these signals was 1.3:1.0. In addition, thin layer chromatography revealed that the solid consisted of a mixture of at least two compounds.

Ligand 1 has two different $\sigma(C-H)$ bonds susceptible to metallation { $\sigma(C_{sp^2,ferrocene}-H)$ and $\sigma(C_{sp^2,biphenyl}-H)$ }. Thus, the reaction could produce different types of isomer depending on (i) the relative arrangement of the two imine nitrogens (*syn-* or *anti-*) in the dimers and (ii) the nature of the metallated carbon atom ($C_{sp^2,ferrocene}$ or $C_{sp^2,biphenyl}$). In addition, the activation of the $\sigma(C_{sp^2,ferrocene}-H)$ bond introduces planar chirality (R_p or S_p), and the formation of several diastereomers of $[Pd\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_5)\}(\mu-Cl)]_2$ cannot be ruled out. Consequently, the cyclopalladation of **1** may produce a wide variety of isomeric species.

In order to try and elucidate the nature of the components of the mixture, SiO₂ column chromatography was used. Elution with a CHCl₃: n-hexane (100:10) mixture allowed us to isolate two different compounds 2a and 2b (in a ratio: 2b/2a=1.3). Elemental analyses of these solids were consistent with those expected for a di-µ-chlorobridged cyclopalladated complex: $[Pd(C^N)(\mu-Cl)]_2$, thus suggesting that two different isomers formed during the reaction. The proton NMR spectrum of the minor component, 2a, was coincident with one of the sets of signals observed in the NMR spectrum of the crude material, showing one singlet at 8.06 ppm (Table 1). The signals due to the ferrocenyl fragment appeared as four singlets of relative intensities 1:1:1:5 in the range: 3.50-5.20 ppm (Fig. 2A), thus suggesting the formation of $[Pd{[(\eta^5 C_5H_3$)-CH=N-(C_6H_4 -2- C_6H_5)]Fe(η^5 - C_5H_5)}(μ -Cl)]₂ (2a) which contains a five-membered palladacycle with a σ (Pd- $C_{sp^2, ferrocene}$) bond.

In contrast with these results, the ¹H-NMR spectra of the major component (**2b**) showed a group of five singlets (with a relative intensity of 1:1:1:1:5) which suggested that the ferrocenyl fragment contained a non-metallated C_5H_4 ring (Fig. 2B). In addition, the resonance of the H¹¹ proton¹ appeared at higher fields than in the free ligand (**1**) and in complex **2a**. Previous ¹H-NMR studies on cyclopal-

¹For the identification of this atom see scheme shown at the bottom of Scheme 1.



Scheme 1. (i) $Na_2[PdCl_4]$, $Na((CH_3COO) \cdot 3H_2O)$, room temperature (see Section 3.2). (ii) SiO_2 -column chromatography using a mixture: $CHCl_3$: *n*-hexane (100:10), as eluant. (iii) $Pd(CH_3COO)_2$, glacial CH_3COOH , reflux, 2 h. (iv) LiCl in ethanol, 30 min. (v) SiO_2 -column chromatography using CHCl₃ as eluant.

Compound	Proton-NM	³¹ P-NMR data					
	C ₅ H ₅	H^2	H^3	H^4	H^5	-CH=N	$\delta(^{31}\text{P})$
1 ^a	4.10	4.70	4.42	4.42	4.70	8.26	_
2 a ^b	3.75	_	3.40	4.29	4.45	8.05	_
2 b ^b	3.81	4.32	4.26	4.38	4.60	8.64	-
3a	3.91	_	4.42	4.34	4.75	8.12	-
3b	3.81	3.55	4.57	4.45	4.72	8.51	-
4a	3.83	_	4.31	4.25	4.70	8.07	-
4b	3.75	3.45	4.59	4.54	4.84	8.61	_
5a	3.81	_	4.34	4.72	4.76	8.20°	34.8
5b	3.70	3.55	4.58	4.77	4.80	8.56°	34.3
6a ^d	4.16	_	4.20	4.40	4.65	e	$43.41^{f,g}$ and $56.89^{f,h}$
6b	3.68	4.59	4.59	4.49	5.52	8.19 ^c	$39.81^{f,g}$ and $55.36^{f,h}$

Selected ¹H-NMR data (in ppm) for compounds under study and chemical shifts of ³¹P (in ppm) for compounds **4a,b** and **6a,b**. Numbering of the atoms refers to the schemes shown below

^a In the free ligand the protons H^2 and H^5 are equivalent and the same happens with H^3 and H^4 .

^b Low solubility.

^c Doublet due to phosphorus coupling.

^d In this case the spectrum was recorded at 240 K (see Section 3.5).

^e Masked by the multiplet due to the aromatic protons of the 1,2-bis(diphenylphosphino)ethane.

f Doublet.

^g Phosphorus *trans*- to the nitrogen.

^h Phosphorus *cis*- to the nitrogen.



ladated compounds of general formulae: $[Pd\{(C_6H_4)-CH=$ $N-R'{(\mu-Cl)}_2$, (with R=phenyl or benzyl groups) which contain an ortopalladated imine ligand, have shown that the formation of the $\sigma(Pd-C_{sp^2, aryl})$ bond produces a high field shift of the proton on the adjacent position to the metallated carbon [44-47]. These results suggested that complex 2b contained a six-membered palladacycle fused with the biphenyl ring, which would arise from the activation of a $\sigma(Pd-C_{sp^2, biphenyl})$ bond. The formulae proposed for the two isomeric complexes: $[Pd\{[(\eta^5-C_5H_3)-$ CH=N-(C₆H₄-2-C₆H₅)]Fe(η^5 -C₅H₅)}(μ -Cl)]₂ (**2a**) and $[Pd\{[(C_6H_4 - 2 - C_6H_4)N = CH - (\eta^3 - C_5H_3)]Fe(\eta^3 - C_5H_5)\} (\mu$ -Cl)]₂ (**2b**), which differ in the nature of the metallated carbon atom is also supported by the results obtained in the study of the reactions of these complexes with neutral ligands such as deuterated pyridine, PPh₂ (see below) and with alkynes [48,49]. The X-ray crystal structure of the complex: $[Pd{[{Et-C=C-Et}_2(C_6H_4-2-C_6H_4)}]N=CH-(\eta^5-M_4)]N=CH-(\eta^5-M_4)$

 C_5H_3]Fe(η^5 - C_5H_5)}(μ -Cl)]₂ which arises from the *bis*(insertion) of hex-3-yne into the σ (Pd-C) bond of complex **2b** confirm that in **2b** metallation occurred on the biphenyl group [48,49].

In order to elucidate whether the preferential formation of **2a** and **2b** could be controlled experimentally, several strategies were used. First, the cyclopalladation process was studied at room temperature using different reaction periods (from 3 h to 7 days). In all cases, the elemental analyses of the solids obtained in each one of the experiments were consistent with those expected for di- μ -chlorobridged cyclopalladated compounds: [Pd(C^N)(μ -Cl)]₂. The compositions of these materials were studied by ¹H-NMR spectroscopy immediately after the addition of the solvent. When the reaction was carried out for short times (3 h), the ¹H-NMR spectrum (in CDCl₃) showed two singlets (at ca. 8.06 and 8.64 ppm in a relative ratio 1.0:1.3) due to the imine protons were detected and their



Fig. 2. Partial views of the proton spectrum of (**A**) $[Pd\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_3)(\mu-CI)]_2(2a)$ and (**B**) $[Pd\{[(C_6H_4-2-C_6H_4)-N=CH-(\eta^5-C_5H_4)]Fe(\eta^5-C_5H_5)(\mu-CI)]_2$ (2b).

positions and multiplicities were identical to those of 2a and 2b. For intermediate reaction periods (from 1 day to 6 days) the intensities of the signals due to the '*endocyclic*' palladacycle (2a) increased progressively in respect to those of (2b).

In contrast, when the reaction was performed for 7 days, the ¹H-NMR spectrum showed one signal and the ¹H-NMR spectrum was identical to that of complex: $[Pd\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_5)\}(\mu-Cl)]_2$ (2a), in which the palladium is bound to the ferrocenyl unit. The comparison of the results obtained in these experiments suggests that when the reaction time of the cyclopalladation process increases, a greater proportion of the '*endocyclic*' complex **2a** is formed. This suggests that **2a** might be formed under thermodynamic control.

Furthermore, for shorter reaction times (i.e. 1.5 h), the isolated solid consisted of a mixture of the two di- μ -chloro-bridged cyclopalladated compounds **2** and the coordination complex: [Pd{(η^5 -C₅H₅)Fe[(η^5 -C₅H₄)-CH= N-(C₆H₄-2-C₆H₅)]₂Cl₂] (**2'**). According to the general mechanism accepted for the cyclopalladation of N-donor ligands, the reaction takes place in two steps: (*a*) the coordination of the ligand and (*b*) the subsequent electrophilic attack of the coordinated palladium to the carbon [50,51]. On this basis, the formation of **2'** could be expected to take place before the activation of the σ (C-H) bond.

Despite the large variety of cyclopalladated complexes

described so far, the number of published articles involving the formation of isomeric palladacycles with different σ (Pd-C) bond is scarce [52–54]. As far as we know only three examples of this sort of reaction have been described so far. In one of them, the cyclopalladated complex at the peri-position of the di(naphthalene-1-yl)diazene (compound Ia in Scheme 2) [52] evolves under heating in toluene to the five-membered metallacycle Ib, in which the palladium is bound to the ortho site. A few years ago, Rvabov [53] reported that when the cyclopalladated complex derived from 1-(3,4-dimethyloxyphenyl)-2-(4-nitrophenyl)-2-azopropene (compound IIa in Scheme 2), was refluxed in a benzene: acetic acid (1:1) mixture for 4 h, the reaction produced the palladated complex (IIb) (Scheme 2) in which the palladium is bound to the nitrosubstituted phenyl ring. In these two cases the isomerization involves the cleavage of a $\sigma(Pd-C_{sp^2, aryl ring})$ bond in the starting material and the formation of a different $\sigma(Pd C_{sp^2, aryl ring}$) bond. Albert et al. [54] have also reported that exocyclic five-membered palladacycles of general $[Pd{2-[CH_2-N=CH-2',4',6'-(CH_3)_3-C_6H_2]-3$ fomula (C_6H_3-R) {(μ -CH₃COO)]₂ {with R=H or CH₃} {(IIIa) in Scheme 2} isomerized in acetic acid to give the sixmembered cyclopalladated complexes (IIIb) with a σ (Pd- C_{sp^3}) bond. Besides that, recent mechanistic studies have



Scheme 2. (i) In boiling toluene at 136°C. (ii) In benzene: CH_3COOH (1:1), 4 h at 70°C. (iii) In refluxing CH_3COOH during 45 min. (For further information about these reactions see Refs. [52–54].)

shown that the five-membered *exocyclic* cyclopalladated complexes: $[Pd\{(3-R-C_6H_3)-2-CH_2-N=CH-C_6H_4-R'\}(\mu-CH_3COO)]_2$ {with R=H and R'=3-NO₂ or 2,4,6-Me₃ and R=Me, R'=2,4,6-Me_3\} {(**IIIa**) in Scheme 2} in acetic acid produce a deep red solution which rapidly evolves to give the corresponding *endocyclic* metallacycles (**IIIb**) in quantitative yield [55,56].

In view of these facts, we decided to perform the cyclopalladation reaction in acidic media. When equimolar amounts of 1 and palladium(II) acetate were refluxed in acetic acid for 2 h a dark red suspension was obtained. The removal of the solvent, followed by the subsequent treatment with LiCl in ethanol at room temperature produced a red solid (Scheme 1). The proton-NMR spectrum of the crude material showed one singlet at ca. 8.05 ppm and a group of four signals of relative intensities 1:5:1:1 in the range 3.5–4.5 ppm. The position and multiplicities of these signals were identical to those observed for $Pd\{[(\eta^2 - \eta^2)]$ C_5H_3)-CH=N-(C_6H_4 -2- C_6H_5)]Fe(η^5 - C_5H_5)}(μ -Cl)]₂ (**2a**) and no evidence of the formation of any other cyclopalladated complex was detected by ¹H-NMR spectroscopy. These findings suggests that the formation of the metallacycle with a $\sigma(Pd-C_{sp^2,ferrocene})$ bond is strongly preferred in acidic media.

On the other hand, it should also be mentioned that the 'exocyclic' complex 2b degradates slowly in CDCl₃ at room temperature. For instance, after 3 days of storage at room temperature (ca. 20°C) the ¹H-NMR spectrum also revealed the presence of small amounts (ca. 8%) of the 'endocyclic' 2a. For longer periods an increase of the relative proportion of 2a:2b was observed. The coexistence of a nearly equimolar ratio of the two isomers (2a) and 2b) was detected after 10 days. However, when these experiments were repeated using benzene-d₆ instead of CDCl₃, no evidence of any isomerization change was detected after 15 days. These findings suggest that the $2b \rightarrow 2a$ interconversion takes place in protic solvents, and that it could be promoted by the traces of acids, in good agreement with the results obtained when the cyclopalladation reaction was carried out in acetic acid, which yielded the 'endocyclic' derivative 2a, exclusively.

To sum up, the results described in this section are in sharp contrast with our previous results on cyclopalladation of ferrocenylimines of general formula: $[(\eta^{5} - \eta^{5})]$ C_5H_5)Fe{ $(\eta^5-C_5H_4)-C(R)=N-R'$ }] (with R=H, Me or Ph and R'=phenyl or benzyl groups) [26-38] for which the formation of five membered metallacycles with $\sigma(Pd C_{sp^2,ferrocene}$) bonds was detected exclusively. It should be noted that despite for ligands with R'=benzyl groups the formation of five- or six-membered palladacycles with a $\sigma(Pd-C_{sp^2,arvl})$ could also take place no evidences of the formation of the metallacycles was detected by NMR [26–38]. These differences suggest that the activation of the $\sigma(C_{sp^2,biphenyl}-H)$ bond in 1 could be attributable to the higher bulk of the R' substituent (biphenyl versus benzyl [57]) in the substrate under study, which could induce steric effects.

3.3. Approaches to rationalize the activation of σ (C-H) bonds in **1**

In an attempt to explain how it is possible to activate the two types of $\sigma(C-H)$ bonds in $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)\}]$ (1), molecular models were used. Their manipulation showed that in 1 the bulk of the biphenyl group precludes the free rotation around the N-C_{ipso} bond in the free ligand. In order to confirm this finding, semiempirical calculations were performed using the SPARTAN 4.0 program [58] and the pm3(tm) method. For this substrate, the formation enthalpy of the molecule, ΔH_{form} was calculated for a wide variety of orientations of the three unsaturated rings: C_5H_4 and the two aryl rings of the biphenyl group. Such arrangements were generated by modifying the torsion angles: [C(2)-C(1)-C(6)-N], [C(6)-N-C(1')-C(2')] and [C(1')-C(6')-C(7')-C(12')], (hereinafter referred to as Φ_1 , Φ_2 and Φ_3 , Fig. 3).

Though the calculations were carried out for different Φ_1 values (from 0° to 90°), the results showed that a co-planar orientation of the C_5H_4 ring and the imine fragment ($\Phi_1 \sim 0^\circ$) is strongly preferred. This is consistent with earlier results on the ferrocenyl Schiff bases: $[(\eta^5 - C_5H_5)Fe\{(\eta^5 - C_5H_4)-C(R)=N-R'\}]$, [59] (with R=H, Me or Ph and R'=phenyl or benzyl groups). The minimum values of the formation enthalphy (ΔH_{form}) correspond to Φ_2 and Φ_3 larger than zero. Consequently, the arrangement of these groups precludes the π -conjugation between (a) the two phenyl rings of the (C_6H_4 -2- C_6H_5) group or (b) the imine group and the phenyl ring (of the bipenyl group) bound to the nitrogen.

The Φ_2 and Φ_3 angles obtained for the optimized geometry (Fig. 3A) of this molecule were 121.6° and 74.6°, respectively. For this arrangement of substituents the two C-H bonds susceptible to activation {C(2)-H} and {C(12')-H} are on the same side as the lone pair of the imine nitrogen, thus suggesting that when the palladium(II) binds to the nitrogen, the two carbon atoms are expected to be very close to the palladium.

Further, it is widely accepted that cyclopalladation of N-donor ligands proceeds in two steps, which consist of the coordination of the nitrogen to the palladium and subsequent electrophilic attack [50,51]. On this basis, we attempted to assess whether, once the Pd-N bond is formed, the orientation of the two σ (C-H) bonds susceptible to metallation ($C_{sp^2,ferrocene}$ -H or $C_{sp^2,biphenyl}$ -H) could be suitable for the electrophilic attack. The optimization of the geometry of the model complex: $[Pd{(\eta^{2}-C_{5}H_{5})Fe[(\eta^{2}-C_{5}H_{5})Fe]}$ $C_{5}H_{4}$)-CH=N-($C_{6}H_{4}$ -2- $C_{6}H_{5}$)] Cl_{3}]⁻, (where the palladium is bound to the imine through the nitrogen exclusively), was undertaken using the pm3(tm) model [58]. The results revealed that the 'PdCl₃' fragment is nearly orthogonal to the imine group (Fig. 3B). This arrangement is similar to that found for: trans-[Pd{(η^{2} -C₅H₅)Fe[(η^{2} - C_5H_4)-CH=N-N(CH₃)₂]₂Cl₂] [60] whose crystal structure shows that the two ferrocenyl ligands are practically orthogonal to the 'PdCl₃' unit. In addition, for the opti-



Fig. 3. Optimized geometries of: (**A**) the ferrocenylimine $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)]$ and (**B**) the coordination complex: $[Pd\{(\eta^5-C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)]C_1]^-$. The values of the Φ_2 and Φ_3 torsion angles for the optimized geometries are: 121.6° and 74.6° (for the ligand, **1**) and 124.4° and 56.7° for the coordination complex.

mized geometry, the distances between the palladium and the carbon atoms potentially involved in the metallation process are C(2) and C(12'), 2.77 Å and 2.83 Å, respectively. These values are quite similar and consequently, according to this approach, the orientation of the two C-H bonds appears to be suitable for activation. Besides that, since the activation of the $\sigma(C_{sp^2,ferrocene}-H)$ or $\sigma(C_{sp^2,biphenyl}-H)$ requires the electrophilic attack of the coordinated palladium(II) to the carbon atom [50,51], the viability of the formation of compounds 2a or 2b from $[Pd\{(\eta^{5}-C_{5}H_{5})Fe[(\eta^{5}-C_{5}H_{4})-CH=N-(C_{6}H_{4}-2-C_{6}H_{5})]\} Cl_3$ is expected to depend also on the net charges on the two carbon atoms susceptible to palladation C(2) and C(12'). For the complex under study the differences in the values of the net charges on C(2) (-0.27) and C(12')(-0.33) are very small. Consequently, the results obtained from this approach suggest that the arrangement of ligands around the palladium(II) atom and the tiny differences of the net charges on the carbons C(2) and C(12') in the model complex $[Pd{(\eta^{5}-C_{5}H_{5})Fe[(\eta^{5}-C_{5}H_{4})-CH=N (C_6H_4-2-C_6H_5)$]Cl₃ may be responsible for the formation of the two types of palladacycle 2a and 2b, which arise respectively from the activation of a $\sigma(C_{sp^2,ferrocene})$ -H) or a $\sigma(C_{sp^2,biphenyl}-H)$ bond.

3.4. Reactivity of the 'Pd(μ -Cl)₂Pd' units in compounds 2

The action of thallium(I) acetylacetonate, deuterated pyridine and triphenylphosphine on the di- μ -chlorobridged cyclopalladated compounds **2**, was also studied. Addition of the stoichiometric amount of thallium(I) acetylacetonate to a suspension of **2a** in acetone at room temperature produced the precipitation of TlCl, which was removed by filtration. The subsequent concentration of the bright-red filtrate to dryness produced $[Pd\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_5)\}(acac)]$ (**3a**) in a fairly good yield (74%).

The reaction of **2a** with deuterated pyridine or triphenylphosphine produced: $[Pd\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_5)\}Cl(L)]$ {L=py-d₅ (**4a**) or PPh₃ (**5a**)}, (Scheme 3), which contain a five-membered metallacycle with a σ (Pd-C_{sp²,ferrocene}) bond.

Similarly, when these reactions were carried out using complex **2b** as starting material, compounds: $[Pd{[(C_{e}H_{4} 2-C_6H_4$)-N=CH-($\eta^5-C_5H_4$)]Fe($\eta^5-C_5H_5$)}(acac)] (**3b**) and $[Pd\{[(C_6H_4 - 2 - C_6H_4) - N = CH - (\eta^5 - C_5H_4)]Fe(\eta^5 - C_5H_5)\}-$ Cl(L)] {L=py-d₅ (4b) or PPh₃ (5b)} (Scheme 4) were obtained. According to the NMR spectra (vide infra) these compounds contain a six-membered palladacycle with a $\sigma(Pd-C_{sp^2,biphenyl})$ bond. It should be noted that previous studies on cyclopalladation of N-donor ferrocenyl substrates have shown that except when (a) the N-donor ligand has a stereogenic centre or (b) chiral aminoacids were present in the cyclopalladation process [21-25,48,49], in remaining cases, the monomeric derivatives: the $[Pd(C^N)Cl(L)]$ {with L=py or PR₃}, containing $\sigma(Pd-$ C_{sp²,ferrocene}) bonds are racemates [14-20,26-38]. On this basis, we assume that compounds 3a-5a consist on a 1:1 mixture of the two enantiomers $\{R_{p} \text{ and } S_{p}\}$.

The reactions of the di- μ -chlorobridged cyclopalladated complexes with PPh₃ have also been very useful in



Scheme 3. (i) Tl(acac), acetone. (ii) py-d₅ in CDCl₃ for (4a), or PPh₃ in benzene (5a). (iii) dppe in CH₂Cl₂ (see Section 3.4).

confirming the nature of the complexes formed in the cyclopalladation reaction using different reaction times (see above). A small amount of the crude materials obtained in each case (reaction periods equal to 12 h, 2 days and 6 days) was suspended in $CDCl_3$ and treated with the stoichiometric amount of PPh₃ to produce the bridge splitting reaction and the coordination of the phosphine ligand, giving compound **5**. The comparison of the ¹H and ³¹P NMR of the solutions obtained immediately after the mixing (Fig. 4A–C), revealed that the amount of the '*exocyclic*' complex **2b** decreased for the experiments

performed with the material obtained after longer reaction periods. This finding also indicates that an increase of the reaction period favours the formation of the '*endocyclic*' derivative.

More interesting are the reactions of compound **2** with 1,2-bis(diphenylphosphino)ethane (dppe). The addition of the stoichiometric amount of the diphosphine to a CH_2Cl_2 suspension of **2b** produced a dark red solution, which yielded (after concentration to dryness) [Pd{[(C_6H_4 -2- C_6H_4)-N=CH-(η^5 - C_5H_4)]Fe(η^5 - C_5H_5)}(dppe)]Cl (**6b**). In this complex the dppe acts as a neutral (P, P') bidentate



Scheme 4. (i) Tl(acac), acetone. (ii) py-d₅ in **4b**, or PPh₃ in benzene **5b**. (iii) dppe in CH₂Cl₂.



Fig. 4. Partial views of the proton and ³¹P-NMR spectra of the solutions obtained by treatment of the solids obtained in the cyclopalladation reaction using reaction periods equal to 12 h (A), 2 days (B) and 6 days (C), with triphenylphosphine in $CDCl_3$.

ligand. No evidence of the formation of any other complex containing dppe as ligand was detected by ³¹P-NMR spectrocopy. In contrast, the reaction of complex 2a with dppe is more complex. For instance, when the reaction was carried out at room temperature, only one singlet at ca. 64.10 ppm was detected in the ³¹P-NMR spectrum. The position of this signal was similar to that reported for the coordination complex [PdCl₂(dppe)] (7) { δ^{31} P=64.20 ppm [59]}. However, when the ³¹P-NMR spectrum was recorded at low temperature (240 K, immediately after mixing} two doublets centered at: 43.41 and 56.89 ppm (Fig. 5) were detected. In addition, the proton NMR spectrum showed the typical pattern of 1,2-disubstituted ferrocenes (Table 1). These results suggested the formation of $[Pd\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_5)\}$ -(dppe)]Cl (6a).

However, ¹H and ³¹P-NMR changed with time (Fig. 5). For instance, after 2 h of storage, an additional singlet at ca. 64.10 ppm appeared in the ³¹P-NMR spectrum (Fig. 5B). For longer times, the singlet was more intense than the two initial doublets (Fig. 5C). These observations suggested that a reaction involving complex **6a** was taking place. The position of the singlet was identical to that reported for [PdCl₂(dppe)] (**7**) [59]. Several changes were

also detected in the ¹H-NMR spectra of these samples, i.e. two singlets (at ca. 9.95 ppm and 4.28 ppm) and two triplets (at ca. 4.82 ppm and 4.26 ppm) appeared and their intensity increased with time. The position and multiplicities of these signals were coincident with those of ferrocenecarboxaldehyde [60]. These observations suggested that complex **6a** deteriorated in solution.

The results obtained in this reaction are in sharp contrast with those reported previously for the cyclopalladated $[Pd\{[(\eta^5-C_5H_3)-CH=N-(CH_2)_n-C_6H_5)]$ complexes $Fe(\eta^{5}-C_{5}H_{5})(\mu-Cl)]_{2}$ {with n=1 (2c) or 2 (2d)}, which C_6H_5]Fe(η^3 - C_5H_5){(dppe)]Cl and no evidence of the decomposition of these materials was detected either in solution or in the solid state [14]. The comparison of the results obtained in the reaction of complexes 2a, 2c and 2d with dppe suggested that the different reactivity could be ascribed to the presence of the bulky biphenyl group [57]. The use of molecular models for compound 6a indicated a strong steric hindrance between one of the phenyl groups bound to the phosphorus in a trans- arrangement to the metallated carbon and the biphenyl ring, which could be responsible for the low stability of complex 6a. Quite recently, it has been postulated that the decomposition



Fig. 5. Variation of the ³¹P- NMR spectrum of the solution obtained by treatment of complex **2a** with the stoichiometric amount of dppe: **(A)** immediately after the mixing (at 240 K); **(B)** after 2 h and **(C)** after 1 day. The signal at ca. 64.10 ppm corresponds to compound **7** [PdCl₂(dppe)] [59], (see Section 3.4).

of complex: $[Pd\{[(\eta^5-C_5H_3)-CH(CH_3)-N(CH_3)_2]Fe(\eta^5-C_5H_5)\}[(-)-binap]]Cl {(-) binaph=bis(diphenylphosphino)-1,1'-naphthyl}, which also contains a five-membered metallacycle with a <math>\sigma(Pd-C_{sp^2,ferrocene})$ bond, was induced by steric effects [43].

3.5. Characterization of the compounds

All the compounds used in this study are orange or dark-red solids at room temperature, except ligand **1** which is an oil. The mononuclear complexes show high solubility in the most common solvents: $CHCl_3$, CH_2Cl_2 , benzene, toluene, but they are practically insoluble in alkanes and methanol. However, the di- μ -chloro-bridged compounds **2a** and **2b** are less soluble in most common solvents. Elemental analyses of the complexes are consistent with the proposed formulae (see Section 2). Infrared spectra of all the compounds show a sharp intense band in the range

1650–1500 cm⁻¹, which is ascribed to the stretching of the >C=N bond.

NMR spectra [¹H, ¹³C and ³¹P- (for **5a,b** and **6a,b**)] of compounds under study were also recorded. The proton-NMR spectrum of **1** (Table 1) showed a group of three signals in the range: 3.0–5.0 ppm due to the three types of proton of the ferrocenyl moiety (the pairs: (H³, H⁴) and (H², H⁵) and those of the C₅H₅ ring). The signal due to the methinic proton appears as a singlet at ca. 8.17 ppm. Only one isomer of **1** was detected in solution, and the position of the signals due to the ferrocenyl fragment and the methinic proton were consistent with those of related ferrocenylimines: $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-C(H)=N-R'\}]$ {with R'=phenyl or benzyl groups} for which an anticonformation has been reported [61,62].

Comparison of the chemical shifts of the ligand and those of compounds 2a-6a in the range 3.00-6.00 ppm (Table 1) shows that the two doublets due to the pairs $\{H^2, H^2\}$ H^{5} and $\{H^{3}, H^{4}\}$ of the imine split into three signals (of relative intensities 1:1:1) upon metallation, thus confirming the formation of the $\sigma(Pd-C_{sp^2,ferrocene})$ bond. In contrast, for 2b-6b a group of five signals (of relative intensities: 1:1:1:1:5) was detected in the same region, and in these cases the resonance due to the proton $(H^{11'})$ on the adjacent position to the metallated carbon $(C^{12'})$ was strongly shifted to high fields. These findings are consistent with the formation of the six-membered palladacycles with a $\sigma(Pd-C_{sp^2,biphenyl})$ bond. Furthermore, in 2b-6b, the signal due to the imine proton is clearly low-field shifted in respect to that of 1, thus suggesting that the ligand adopts the Z-conformation in these compounds. In contrast, for 2a-6a, the signal appeared at higher fields, indicating an E-conformation of the imine. It should be mentioned that since only the anti-isomer of the imine 1 was detected in solution, the formation of the 'exocyclic' derivatives **2b–6b** requires the *anti–\rightarrowsyn-*isomerization of the free ligand and/or the coordination complex $[Pd{(\eta^{5} C_5H_5)Fe[(\eta^5-C_5H_4)-CH=N-(C_6H_4-2-C_6H_5)]_2Cl_2]$ (2') which forms before the activation of the σ (C-H) bond. However, recent studies have demonstrated that the enthalpy required for the anti- \rightarrow syn-isomerization of the related coordination complex $[Pd{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4) CH=N-CH_2-CH_2-N(CH_3)_2]_2Cl_2$ is very small (4.32) kcal/mol) [63,64].

Except for **2a,b** (which have low solubility) and **6a** (which decomposes in solution), the remaining compounds were also characterized by ¹³C-NMR. A summary of the most relevant data is presented in Table 2. In all cases the number and position of the signals observed are compatible with the proposed formulae.

Phosphorous-31 NMR spectra for **5a** and **5b**, which contain a five- and a six-membered palladacycle, respectively, showed a singlet [at 34.3 (for **5a**) and at 33.9 (for **5b**) ppm]. The position and multiplicity of this signal are consistent with the values obtained for related cyclopalla-

Selected - C Twirk data (in ppin) for compounds under study. Eabening of the atoms corresponds to the schemes shown in the lower part of Table T											
Compound	C ₅ H ₅	C^1	C^2	C ³	C^4	C^5	-CH=N				
1 ^a	69.13	84.41	68.93	71.49	71.49	68.93	161.06				
3a	69.68	101.10	97.77	72.65	74.68	73.63	166.91				
3b	70.22	80.55	75.62	73.74	74.40	72.65	169.46				
4a	70.29	b	b	69.39	73.93	73.52	167.61				
4b	69.93	b	72.75	74.75	74.84	73.09	168.61				
5a	69.92	b	b	72.69	73.90	73.40	165.75				
5b	70.16	b	69.22	73.95	74.95	72.49	166.47				
6b	70.07	81.05	75.36	74.03	73.96	74.34	167.91				

Table 2 Selected ¹³C-NMR data (in ppm) for compounds under study. Labelling of the atoms corresponds to the schemes shown in the lower part of Table 1

 a In the free ligand the carbons C^{2} and C^{5} are equivalent and the same happens with C^{3} and $C^{4}.$

^b Not observed.

dated complexes containing ferrocenyl units [26-31], for which structural studies have revealed a *trans*-arrangement between the phosphine ligand and the imine nitrogen [26-31]. The phosphorus-31 NMR spectra of **6a** and **6b** showed two doublets centered at: 43.41 and 56.89 ppm for **6a** (in this case the spectrum was recorded at 240 K), and at 44.30 and 60.10 ppm for **6b**. The position and multiplicities of these signals are in good agreement with the results obtained for related cyclopalladated derivatives containing five- or six-membered palladacycles and dppe as a bidentate group.

3.6. Conclusions

Cyclopalladation of ferrocenyl Schiff bases of general formula: $[(\eta^{5}-C_{5}H_{5})Fe\{(\eta^{5}-C_{5}H_{4})-C(R')=N-R\}]$ (with R= phenyl or benzyl groups and with R'=H, Me or Ph) produces the corresponding five-membered palladacycles fused with the ferrocenyl fragment. However, for ligand 1 which contains a biphenyl ring bound to the nitrogen, two types of palladacycle can be formed. One of which (2a) arises from the activation of the $\sigma(C_{sp^2, ferrocene}-H)$ bond, while the other (2b), which contains a six-membered cycle fused with the biphenyl ring, forms through the activation of the $\sigma(C_{sp^2,biphenyl}-H)$ bond. Complex **2a** is formed preferentially for longer reaction periods or when the reaction is carried out in acidic media (glacial acetic acid), thus suggesting that it might be formed under thermodynamic control. The semiempirical calculations, based on the pm3(tm) method [58], reported in this work, have allowed us to explain the formation of the two types of metallacycle, since once the palladium binds to the imine nitrogen the distances between the palladium and the two carbon atoms susceptible to metallation (C_{sp²,ferrocene}, $C_{sp^2,biphenyl}$) as well as the net charges on these carbons are similar. The reactions of compounds 2a and 2b with Tl(acac), $py-d_5$ or PPh₃ have allowed us to isolate and characterize two isomers of the monomeric cyclopalladated complexes 3-5a,b. Compounds 3a-5a contain a five membered palladacycle with a $\sigma(Pd-C_{sp^2,ferrocene})$ bond, while in 3b-5b, the palladium is linked to the biphenyl group forming a six-membered ring that does not contain the functional >C=N- group ('*exocyclic*').

Besides that, the different reactivity of **2** with dppe indicates that the presence of the bulky biphenyl group bound to the imine nitrogen in **2a** introduces strong steric hindrance, which reduces the stability of compound: $[Pd\{[(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_3)-CH=N-(C_6H_4-2-C_6H_5)]Fe(\eta^5-C_5H_$

 C_5H_5 }(dppe)]Cl (6a), which degradates to the coordination compound [PdCl₂(dppe)] (7).

Finally, it is well known that one of the interests of cyclopalladated complexes is their usefulness as precursors for the organic and organometallic syntheses by insertion of small molecules into the σ (Pd-C) bond [4,5,65–70]. In these reactions the nature of the final product is strongly dependent on several factors of which the nature of (*a*) the inserted molecule, (*b*) the metallated ligand and (*c*) the remaining ligands bound to the palladium are specially important [4,5]. Compounds **2a** and **2b** differ exclusively in the nature of the metallated ligand, thus they appear to be candidates to undertake a comparative study of the reactivity of the σ (Pd-C_{sp²,ferrocene}) and σ (Pd-C_{sp²,biphenyl}) bonds. Further work on this field is now in progress.

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