

# Palladium(II) compounds containing $\sigma[\text{Pd}-\text{C}_{\text{sp}^2}(\text{ferrocene})]$ bonds and ferrocenyloximes as bidentate $\{\text{C N}\}$ -ligands

## X-ray crystal structure of [Pd{[( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)-C(CH<sub>3</sub>)=N(OH)]Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}Cl(PPh<sub>3</sub>)]

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### Abstract

Ferrocenyloximes of general formula  $\{[(\eta^5\text{-C}_5\text{H}_4)\text{-C(R)=N(OH)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}$  with R = H (**1a**) or CH<sub>3</sub> (**1b**) react at room temperature in methanol with Na<sub>2</sub>[PdCl<sub>4</sub>] and Na(CH<sub>3</sub>COO) · 3H<sub>2</sub>O in a 1:1:1 molar ratio producing the di- $\mu$ -chloro-bridged derivatives [Pd{[( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)-C(R)=N(OH)]Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}( $\mu$ -Cl)]<sub>2</sub> (with R = H (**2a**) or CH<sub>3</sub> (**2b**)) which undergo cleavage of the 'Pd( $\mu$ -Cl)<sub>2</sub>Pd' units in the presence of PPh<sub>3</sub> to give the mononuclear cyclopalladated complexes [Pd{[( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)-C(R)=N(OH)]Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}Cl(PPh<sub>3</sub>)] (with R = H (**3a**) or CH<sub>3</sub> (**3b**)). The molecular structure of compound **3b** has been determined by X-ray crystallography: monoclinic, space group C2/c with  $a = 27.485(5)$  Å;  $b = 9.964(2)$  Å;  $c = 24.778(4)$  Å and  $\beta = 131.07(3)^\circ$ . These studies confirm the presence of a five-membered palladacycle fused with the C<sub>5</sub>H<sub>3</sub> ring of the ferrocenyl moiety, and a trans arrangement of the phosphine and the nitrogen. © 1997 Elsevier Science S.A.

**Keywords:** Palladium(II) compounds; Ferrocenyloximes; Molecular structure

### 1. Introduction

One of the areas of organometallic chemistry that has shown a fast development in recent years is that involving the synthesis, characterization and study of cyclometallated compounds [1]. For instance, a wide variety of cyclopalladated complexes containing Pd–C(aryl) or Pd–C(aliphatic) bonds and different types of N-donor ligands have been reported. Most of these studies involve amines, imines, azines and hydrazones, but derivatives containing oximes are not so common [2,3]. In fact, some authors have mentioned that the preparation and isolation of palladacycles containing oximes is problematic due to the formation of by-products [2,4,5].

Recently, ortho-palladation of ferrocenylamines,

imines and azo-derivatives has allowed the preparation of a novel kind of palladacyclic complex, containing  $\sigma[\text{Pd}-\text{C}_{\text{sp}^2}(\text{ferrocene})]$  bonds (Fig. 1) [6–9], which have been found to be a useful intermediate for the synthesis of other ferrocene derivatives through alkyne insertions into the  $\sigma(\text{Pd}-\text{C})$  bond [10].

According to the general rules of cyclopalladation of N-donor ligands, the formation of the  $\sigma(\text{Pd}-\text{C})$  bond takes place in two steps: (i) coordination of the nitrogen to the palladium(II) and (ii) the electrophilic attack of the Pd(II) species. Previous work in this area has shown that for imines, the activation of  $\sigma[\text{C}_{\text{sp}^2}(\text{ferrocene})-\text{H}]$  bonds is achieved more easily than the  $\sigma[\text{C}_{\text{sp}^2}(\text{aryl})-\text{H}]$  [8,9], in good agreement with the higher proclivity of ferrocene derivatives to undergo electrophilic attacks [11]. On this basis we decided to study the reactivity of ferrocenyloximes of general formula  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-C(R)=N(OH)}]$  (**1**) (Fig. 1) vs. palladium(II), since if metallation were to occur the reaction would

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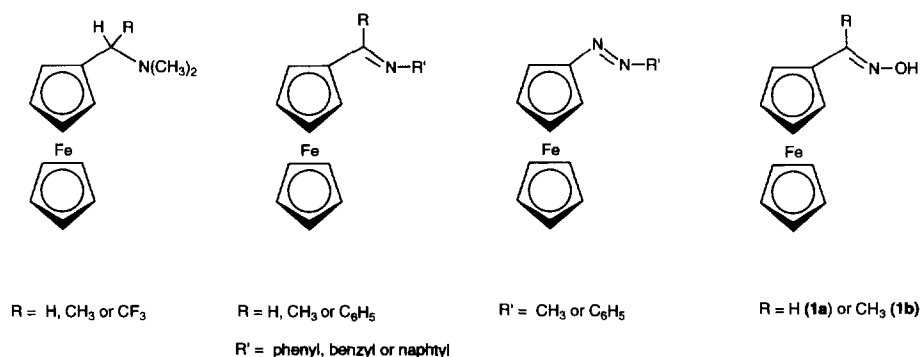


Fig. 1. Schematic view of ferrocenylamines, imines and azo-derivatives which have allowed the preparation of cyclopalladated complexes with  $\sigma[\text{Pd}-\text{C}_{\text{sp}^2}(\text{ferrocene})]$  bond and the ferrocenyloximes **1** under study.

yield palladacyclic complexes containing a  $\sigma[\text{Pd}-\text{C}_{\text{sp}^2}(\text{ferrocene})]$  bond and the oxime group simultaneously.

In this paper we report the syntheses and characterization of a series of compounds which constitute the first example of the activation of a  $\sigma[\text{C}_{\text{sp}^2}(\text{ferrocene})-\text{H}]$  bond in ferrocenyloximes derived from formyl (**1a**) and acetylferrocene (**1b**) (Fig. 1), promoted by palladium(II).

## 2. Results and discussion

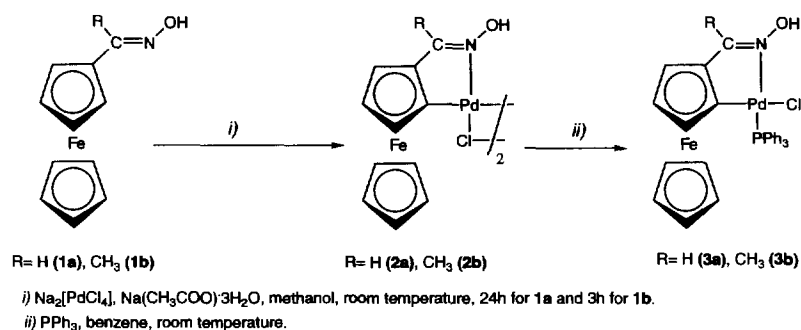
### 2.1. Syntheses

The ferrocenyloximes  $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\eta^5-\text{C}_5\text{H}_4)-\text{C}(\text{R})=\text{N}(\text{OH})]$  with R = H (**1a**) or CH<sub>3</sub> (**1b**) were prepared as described in the literature [12–14]. Spectroscopic analyses of the two reagents were identical to those reported previously for the anti isomer [13]. Addition of equimolar amounts of these oximes to suspensions containing Na<sub>2</sub>[PdCl<sub>4</sub>] and Na(CH<sub>3</sub>COO) · 3H<sub>2</sub>O in a 1:1 molar ratio and methanol as solvent produces the formation of red solids (Scheme 1). Further treatment of these materials with chloroform followed by

SiO<sub>2</sub> column chromatography using CHCl<sub>3</sub> allowed isolation of the di- $\mu$ -chloro-bridged cyclopalladated complexes  $[\text{Pd}\{[(\eta^5-\text{C}_5\text{H}_5)-\text{C}(\text{R})=\text{N}(\text{OH})]\text{Fe}(\eta^5-\text{C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$  (**2**).

For ligand **1b** the formation of the palladacycle **2b** required shorter reaction periods (ca. 3 h) than for **1a**, for which the partial activation of the  $\sigma[\text{C}_{\text{sp}^2}(\text{ferrocene})-\text{H}]$  bond became evident only after a minimum of 18 h. This result is consistent with the conclusions reached following the cyclopalladation of related ferrocenyl Schiff bases of general formula  $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\eta^5-\text{C}_5\text{H}_4)-\text{C}(\text{R})=\text{N}-\text{R}']$  (with R = H or CH<sub>3</sub> and R' = phenyl or benzyl) [9], which has been explained in terms of the higher basicity of the nitrogen in complexes with R = CH<sub>3</sub>. However, the yields of the two reactions under study (Scheme 1) were smaller than those reported for the corresponding ferrocenyloximes,  $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\eta^5-\text{C}_5\text{H}_4)-\text{C}(\text{R})=\text{N}-\text{R}']$  (50–80%).

This result can be attributed to several factors, among which the conformation of the ligand and the proclivity of the two atoms involved in the oxime group (N and O) to coordinate may play an important role. It is well known that ferrocenyloximes and oximes can take two conformations (anti or syn) (Fig. 2) depending on the



Scheme 1.

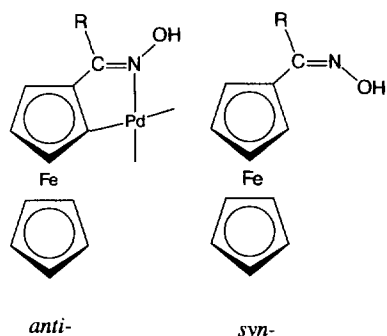


Fig. 2. Schematic view of the two isomers (syn and anti) of ferrocenyloximes, showing that cyclopalladated complexes can be formed exclusively if the ligand has the anti conformation.

relative orientation of the ferrocenyl group and the substituent bound to the nitrogen.

In the anti isomers the relative orientation of the  $\sigma[C_{sp^2}(\text{ferrocene})-H]$  bond vs. the lone pair of the nitrogen is suitable for the formation of the five-membered palladacycles, while for the syn isomers, once the palladium binds to the nitrogen, the activation of one of the ortho  $\sigma(C-H)$  bonds is precluded. Although recent studies on ferrocenyloximes derived from formyl- and acetylferrocene have shown that these substrates are present in solution and in solid state, in the anti form [9], ferrocenyloximes show both conformations. Although some articles dealing with the preparation and separation of the two isomers of several ferrocenyloximes (including compounds (1)) have been reported [12–14], structural studies undertaken by Glidewell and coworkers [15] on the low-melting form of **1a** have demonstrated not only that the two isomers coexist in the crystal, but also that two molecules of the oximes with identical conformation interact with weak hydrogen bonding. Consequently, for the oximes **1** the effective amount of the active species in cyclopalladation reaction (anti isomer) is apparently smaller. A similar argument has been used to explain the low yields of the

cyclopalladation of some ketimines derived from benzoylferrocene [8]. However, the formation of the metalacycle could also induce, at least partially, the displacement of the anti  $\leftrightarrow$  syn isomerization equilibrium.

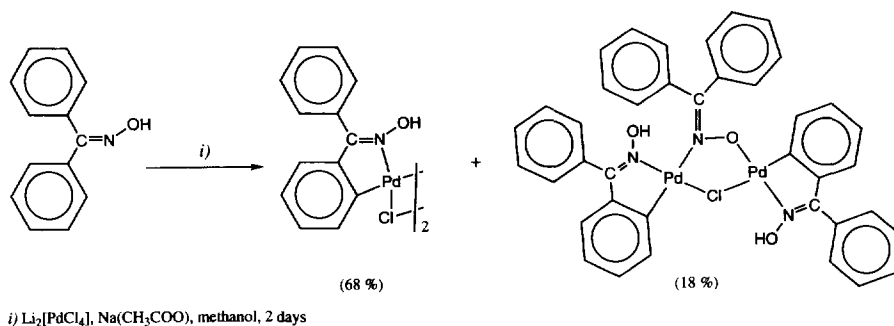
The second factor which may be responsible for the low yield of the reactions, is the presence of an additional atom with good donor ability. Previous studies on cyclopalladation of aromatic aldoximes and ketoximes using  $[PdCl_4]^{2-}$  as reagent have shown that in most cases the reaction is not neat and several by-products are formed, such as  $[PdCl_2(\text{oxime})_2]$ , or even more complex species, such as that reported by Onoue et al. [2], which contains an oximate group acting as a bridging ligand (Scheme 2) bound through the nitrogen and the deprotonated oxygen of the oxime group.

Quite recently, Ryabov et al. [3] have reported the advantages of using ligand exchange reactions such as those shown in Scheme 3 in the preparation of cyclopalladated complexes containing  $[CN]^-$  chelated oximes.

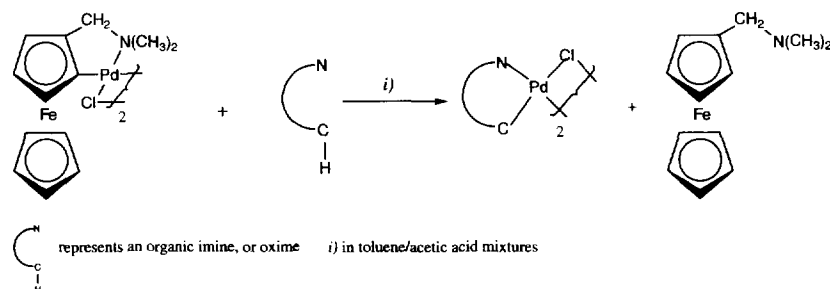
In order to test whether this method would improve the yield of the cyclopalladation of ligands **1**, we decided to study the reactions between  $[Pd\{(\eta^5-C_5H_3)-CH_2-N(CH_3)_2\}Fe(\eta^5-C_5H_5)](\mu-Cl)_2$  (**4**) and the oximes in a 1:2 molar ratio and chloroform–glacial acetic acid mixtures of different compositions from (90:10 to 70:30). In all cases the initial colour of the mixtures changed instantaneously to deep-purple, but no evidence of the formation of cyclopalladated complexes (**2**) was detected by NMR spectroscopy. This can be interpreted in terms of the great instability of the ferrocenyloximes in acidic media, which rapidly undergo hydrolysis and protonation of the formed formylferrocene or acetylferrocene [11].

Addition of triphenylphosphine to the benzene suspensions of complexes **2** produced the cleavage of the  $\mu-Cl$  bridges giving  $[Pd\{(\eta^5-C_5H_3)-C(R)=N(OH)Fe(\eta^5-C_5H_5)\}Cl(PPh_3)]$  (**3**). Evidence of the cleavage of the Pd–N bond was not observed in any case, even in the presence of larger excesses of  $PPh_3$  (Pd: $PPh_3$  molar ratios up to 1:3).

Furthermore, when complexes **3** were treated under



Scheme 2.



Scheme 3.

reflux in benzene with  $\text{PPh}_3$  (in a 1:2 molar ratio) for 48 h, the formation of the monomeric compounds  $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-C}(\text{R})=\text{N}(\text{OH})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)_2]$  (**5**), which arise from the opening of the five-membered metallacycle, did not take place. This finding suggests that the Pd–N bond is remarkably stable in compounds **2** and **3**.

## 2.2. Characterization

The new cyclopalladated complexes are air-stable orange-red solids at room temperature. The monomeric compounds **3** are very soluble in chloroform and dichloromethane, slightly soluble in methanol, ethanol and diethyl ether, and insoluble in water and alkanes; **2** exhibits low solubility in the most common solvents. Elemental analyses for all the compounds are consistent with the proposed formulae (see Section 3).

Comparison of the IR-spectra of compounds **2** and **3**

reveal that the band due to the absorption of the  $\text{>C=N-}$  bond is shifted to lower energies than those of the free ligands, thus indicating that nitrogen is coordinated to palladium(II) through its lone pair of electrons [8,9].

Proton-NMR data are summarized in Table 1. The doublets due to the pairs (H(3), H(4)) and (H(2), H(5)) of the free ligands (in the range 3.0–5.0 ppm) split into three signals for the cyclopalladated complexes, thus confirming the metallation of the ferrocenyl unit. The assignment of the signals is consistent with previous work in this area, where the high field shielding of the H(4) resonance has been interpreted in terms of the anisotropy due to the aryl ring of the neutral ligand [9].

Compounds **3** have also been characterized by  $^{31}\text{P}$  NMR spectroscopy. In all cases the spectrum showed a singlet in the range 37.0–39.0 ppm, the position of which is in good agreement with a trans arrangement of the nitrogen and the phosphorus ligand [9,16].

Table 1  
Most relevant proton-NMR data (in ppm) for the ferrocenylloximes **1** and their cyclopalladated compounds **2,3**<sup>a</sup>

	$\text{C}_5\text{H}_5$	H <sup>3</sup>	H <sup>4</sup>	H <sup>5</sup>	–C(H)=N–	CH <sub>3</sub>	–OH
<b>1a</b>	4.22	4.54 <sup>b</sup>	4.35 <sup>b</sup>	4.35	7.99	—	— <sup>c</sup>
<b>1b</b>	4.19	4.52	4.32	4.32	—	2.18	— <sup>c</sup>
<b>2a</b> <sup>d</sup>	4.13	4.42	4.06	3.72	7.90	—	9.74
<b>2b</b> <sup>d</sup>	4.03	4.38	4.11	3.61	—	2.12	9.66
<b>3a</b>	4.20	4.43	3.81	3.92	7.91 <sup>e</sup>	—	9.96 <sup>c</sup>
<b>3b</b>	3.88	4.30	3.97	3.81	—	2.19	9.94 <sup>c</sup>

<sup>a</sup> Labelling refers to the schemes shown below.

<sup>b</sup> The two protons H<sup>3</sup> and H<sup>4</sup> are equivalent in the free ligand.

<sup>c</sup> Not observed due to fast interchange process.

<sup>d</sup> The spectrum was recorded in  $\text{CDCl}_3$  and in the presence of deuterated pyridine ( $\text{py-}d_5$ ).

<sup>e</sup> Doublets due to phosphorus coupling.

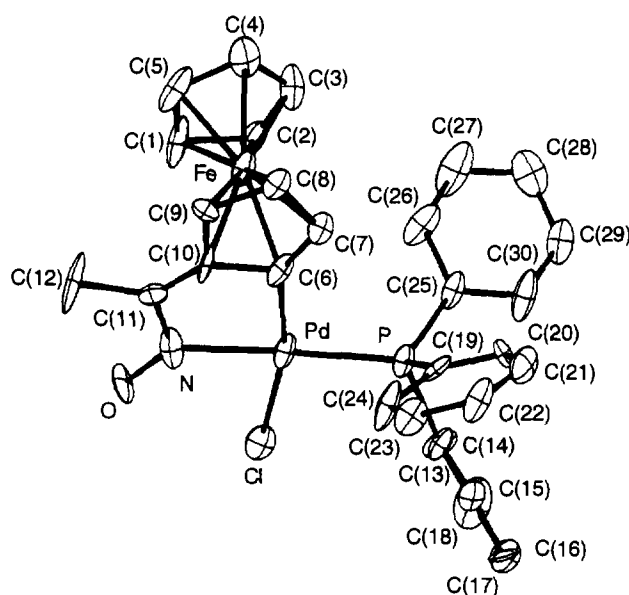
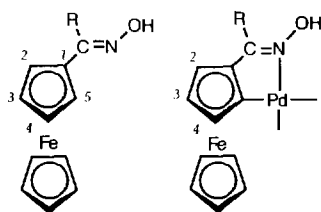


Fig. 3. Molecular structure and atom labelling scheme for compound  $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{-C}(\text{CH}_3)=\text{N}(\text{OH})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$  (**3b**). The thermal ellipsoids have been drawn with the 50% of probability.

### 2.3. Crystal structure of $[Pd\{[(\eta^5-C_5H_5)-C(CH_3)=N(OH)]Fe(\eta^5-C_5H_5)\}Cl(PPh_3)]$ (**3b**)

A perspective drawing of the molecular structure of compound **3b** and the atom labelling scheme are presented in Fig. 3. Final atomic coordinates for non-hydrogen atoms and a selection of bond lengths and angles are given in Tables 2 and 3 respectively.

The structure consists of discrete molecules of  $[Pd\{[(\eta^5-C_5H_5)-C(CH_3)=N(OH)]Fe(\eta^5-C_5H_5)\}Cl(PPh_3)]$  separated by van der Waals contacts. The palladium atom is in a slightly distorted square-planar environment, linked to Cl, P, N and the C(6) atom of the ferrocenyl moiety. The deviations from the plane are: Pd  $-0.052$  Å; Cl,  $0.079$  Å; N,  $0.100$  Å; P,  $-0.053$  Å; C(6),  $-0.074$  Å. This confirms the formation of a bicyclic system arising from the fusion of the substituted pentagonal ring of the ferrocenyl ligand and the metallacycle defined by the atoms Pd, N, C(6), C(10) and C(11).

Table 2

Final atomic coordinates ( $\times 10^4$ ) for non-hydrogen atoms in  $[Pd\{[(\eta^5-C_5H_5)-C(CH_3)=N(OH)]Fe(\eta^5-C_5H_5)\}Cl(PPh_3)]$  (**3b**). The e.s.d. values are given in parentheses

	x	y	z
Pd	1664(1)	299(1)	478(1)
Fe	764(1)	3430(2)	-198(1)
P	2651(1)	834(4)	1514(1)
Cl	1925(2)	-1680(5)	179(1)
O	491(3)	-1276(10)	-850(4)
N	682(4)	-147(12)	-398(5)
C(1)	424(4)	3293(17)	-1219(4)
C(2)	1106(4)	3681(14)	-708(4)
C(3)	1191(5)	4935(14)	-387(4)
C(4)	575(5)	5358(15)	-656(4)
C(5)	115(5)	4367(20)	-1160(4)
C(6)	1229(4)	1867(11)	510(4)
C(7)	1355(4)	3077(14)	880(4)
C(8)	752(4)	3684(14)	613(4)
C(9)	251(4)	2797(13)	68(4)
C(10)	535(4)	1667(12)	-6(4)
C(11)	262(4)	655(13)	-503(4)
C(12)	-454(3)	416(14)	-1103(4)
C(13)	3272(3)	-476(14)	1880(4)
C(14)	3486(4)	-727(16)	1535(5)
C(15)	3985(5)	-1600(18)	1846(6)
C(16)	4253(5)	-2346(15)	2469(5)
C(17)	4013(4)	-2125(12)	2788(5)
C(18)	3520(4)	-1145(12)	2492(4)
C(19)	2645(4)	1167(13)	2244(4)
C(20)	3108(4)	1923(13)	2847(4)
C(21)	3086(5)	2025(18)	3377(5)
C(22)	2627(4)	1364(16)	3340(4)
C(23)	2165(4)	573(17)	2753(4)
C(24)	2163(4)	391(16)	2193(4)
C(25)	3046(4)	2243(15)	1483(4)
C(26)	2698(5)	3178(17)	940(4)
C(27)	2951(5)	4287(18)	868(5)
C(28)	3628(5)	4502(17)	1423(5)
C(29)	3987(5)	3549(17)	1963(5)
C(30)	3712(4)	2492(18)	2011(4)

Table 3

Selected bond lengths (Å) and angles (deg) for compound  $[Pd\{[(\eta^5-C_5H_5)-C(CH_3)=N(OH)]Fe(\eta^5-C_5H_5)\}Cl(PPh_3)]$  (**3b**). The e.s.d. values are given in parentheses

Bond lengths			
Pd(1)–C(6)	2.000(11)	Pd(1)–N	2.121(7)
Pd(1)–P	2.249(3)	Pd(1)–Cl	2.378(3)
C(10)–C(11)	1.372(14)	C(11)–C(12)	1.516(10)
C(11)–N	1.282(13)	N–O	1.422(12)
P–C(13)	1.829(11)	P–C(19)	1.857(8)
P–C(25)	1.823(13)		
Bond angles			
C(6)–Pd(1)–N	79.2(4)	C(6)–Pd(1)–P	94.7(3)
N–Pd(1)–P	94.7(3)	N–Pd(1)–Cl	87.1(3)
P–Pd(1)–Cl	99.12(11)	C(11)–N–Pd(1)	116.6(7)
O–N–Pd(1)	122.3(7)	O–N–C(11)	121.1(8)
C(11)–C(10)–C(9)	121.9(13)	C(10)–C(11)–C(12)	126.0(10)
C(12)–C(11)–N	121.1(10)	N–C(11)–C(10)	112.8(8)
Pd(1)–P–C(13)	116.1(4)	Pd(1)–P–C(19)	112.2(3)
Pd(1)–P–C(25)	116.8(3)		

Bond angles between adjacent atoms in the coordination sphere lie in the range from 79.2(4) to 94.7(3) $^\circ$  (Table 3). The phosphine ligand and the imine nitrogen are in a trans arrangement (bond angle P–Pd–N = 170.4(2) $^\circ$ ) as suggested by the  $^{31}\text{P}$  NMR spectra. The palladium atom deviates from the plane defined by the four atoms linked to it by  $-0.065$  Å towards the  $C_5H_5$  ring.

The metallacycle is practically planar<sup>1</sup> and contains the  $>\text{C}=\text{N}-$  functional group. The dihedral angle formed by the two fused rings is 3.1(3) $^\circ$ .

The  $>\text{C}=\text{N}-$  bond length (1.282(13) Å) is similar to those found in related five-membered endocyclic palladacycles with a  $\sigma[\text{Pd}-\text{C}_{\text{sp}^2}(\text{ferrocene})]$  bond, which fall in the range 1.26–1.31 Å [9], and the imine group forms an angle of 7.7 $^\circ$  with the  $C_5H_5$  ring of the ferrocenyl unit.

In complex **3b**, the ferrocenyl fragment and the  $-\text{OH}$  group are in a trans arrangement (torsion angle C(10)–C(11)–N–O = 178.7(10) $^\circ$ ) thus confirming the anti conformation of the ligand.

Bond lengths and angles of the ferrocenyl fragment are consistent with those reported for most other ferrocene derivatives [17]. The two pentagonal rings are planar<sup>2</sup> and nearly parallel (tilt angle 4.3 $^\circ$ ), and their conformation is close to the ideal staggered type, as

<sup>1</sup> The least squares equation of the plane defined by the atoms Pd, N, C(6), C(10) and C(11) is  $(-0.0198)XO + (-0.5365)YO + (0.8437)ZO = -1.7983$ . Maximum deviations were found for C(10) ( $+0.057$  Å) and for C(6) ( $-0.056$  Å).

<sup>2</sup> (a) The least squares equation of the plane defined by the set of atoms C(1)–C(5) is  $(0.1272)XO + (-0.4839)YO + (0.8658)ZO = -4.7452$ . Maxima deviations were found for C(2) ( $+0.014$  Å) and for C(3) ( $-0.013$  Å). (b) The least squares equation of the plane defined by the set of atoms C(6)–C(10) is  $(0.0544)XO + (-0.5030)YO + (0.8626)ZO = -1.6207$ . Maxima deviations were found for C(7) ( $+0.002$  Å) and for C(8) ( $-0.002$  Å).

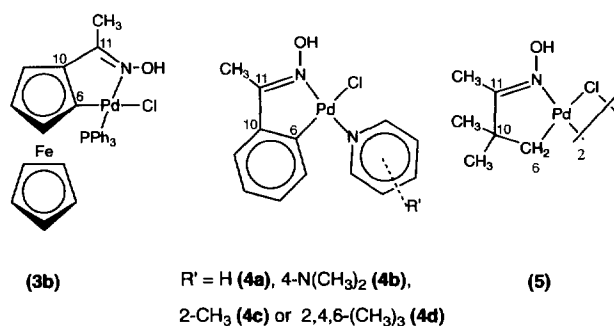


Fig. 4. Schematic formulae of the three types of cyclopalladated complex derived from oximes which have been characterized by X-ray analyses. In all cases the metallacycles are five-membered rings containing the  $>C=N-$  groups, but they differ in the nature of the metallated carbon atom:  $C_{sp^2}$ , (ferrocene) in **3b**,  $C_{sp^2}$ , (aryl) in **4** or  $C_{sp^3}$  in **5**.

reflected in the small value of the twist angle [18] (average value  $-4.6(4)^\circ$ ).

The distance between the two metals is slightly larger (3.635(3) Å) than those obtained for related cyclopalladated complexes of general formula  $[Pd\{[(\eta^5-C_5H_5)-C(R)=N-R']Fe(\eta^5-C_5H_5)]Cl(PPh_3)\}]$  ( $R = H, CH_3$  or  $C_6H_5$ ) or  $[Pd\{[(\eta^5-C_5H_5)-CH_2-N(CH_3)_2]Fe(\eta^5-C_5H_5)]Cl(L)\}]$ , which fall in the range 3.560(3)–3.595(3) Å [9].

In order to elucidate the influence of the nature of the metallated carbon atom upon the structures of the five-

membered palladacycles containing  $[CN]^-$  bidentate oxime ligands, comparison of bond lengths and angles in **3b** and in complexes of general formula  $[Pd\{C_6H_5-C(CH_3)=N(OH)\}Cl(L)]$  (**4**) [3] and  $[Pd\{CH_2-C(CH_3)_2-C(CH_3)=N(OH)\}(\mu-Cl)_2]$  (**5**) [2] (which contain  $\sigma[Pd-C_{sp^2}(aryl)]$  and  $\sigma[Pd-C_{sp^3}(aliphatic)]$  bonds respectively) (Fig. 4) was undertaken.

The most relevant structural differences are found (Table 4) in bond lengths and angles involving group N(OH). For instance, complex **3b** exhibits the largest N–O and Pd–N distances. This finding can be related to the different  $\sigma$ -donor ability of the three sorts of substituent bound to the  $-CH=N(OH)$  moiety, ferrocenyl, aryl or alkyl, which modify the basicity of the nitrogen

On the other hand, the small differences obtained for the bites of the three bidentate oxime ligands are compensated by the variations of the C(6)–Pd–N angles, thus resulting in a practically constant normalized bite for these systems which falls within the range expected for bidentate ligands forming five-membered rings [19].

#### 2.4. Final remarks

The results reported in this paper have allowed us to prepare and characterize the former examples of cyclopalladated compounds derived from ferrocenyl-oximes, which simultaneously contain a five-membered

Table 4

Selected bond lengths (Å) and angles (deg) for compound **3b** and for endocyclic five-membered palladacycles obtained through cyclopalladation of the aryloximes  $C_6H_5-C(CH_3)=NOH$  and  $(CH_3)_3C-C(CH_3)=NOH$ . Compounds **3**, **4** and **5** are schematically shown in Fig. 4 and they differ in the nature of the metallated carbon atom: Pd– $C_{sp^2}$ , ferrocene in **3b**, and Pd– $C_{sp^2}$ , aryl in **4a–e** and Pd– $C_{sp^3}$  in **5**<sup>a</sup>

	<b>3b</b>	<b>4a</b> <sup>b</sup>	<b>4b</b> <sup>b</sup>	<b>4c</b> <sup>b</sup>	<b>4d</b> <sup>b</sup>	<b>5</b> <sup>c</sup>
<b>Bond lengths</b>						
Pd–N	2.121(7)	1.993(5)	1.997(5)	1.988(6)	1.981(4)	1.997(4)
N–C(11)	1.288(13)	1.271(7)	1.293(7)	1.279(9)	1.302(8)	1.271(4)
C(11)–C(10)	1.372(14)	1.468(8)	1.450(7)	1.47(1)	1.466(7)	1.516(9)
C(10)–C(6)	1.453(11)	1.408(7)	1.432(6)	1.42(3)	1.395(7)	1.518(8)
N–O	1.422(12)	1.390(6)	1.384(6)	1.390(8)	1.393(6)	1.386(6)
C(11)–C(12)	1.516(10)	1.486(8)	1.483(9)	1.48(4)	1.48(2)	1.533(9)
Pd–C(6)	2.000(11)	1.983(5)	1.890(5)	1.978(7)	2.004(5)	2.023(6)
<b>Bite: N...C</b>	2.627(10)	2.544(7)	2.572(7)	2.542(7)	2.560(8)	2.579(9)
<b>Normalized bite</b>	1.381(13)	1.280(8)	1.323(6)	1.28(3)	1.285(7)	1.283(8)
<b>Bond angles</b>						
Pd–N–C(11)	116.6(7)	120.3(4)	118.9(4)	120.1(6)	120.0(4)	119.4(6)
N–C(11)–C(10)	112.8(8)	111.6(4)	112.4(5)	116.2(4)	110.9(5)	114.6(6)
C(11)–C(10)–C(6)	121.2(10)	115.4(4)	116.2(4)	115.2(6)	116.8(5)	108.1(4)
C(10)–C(6)–Pd	109.3(7)	112.8(4)	111.9(4)	113.1(6)	112.1(4)	109.6(4)
C(6)–Pd–N	79.2(4)	79.6(2)	80.6(2)	79.7(3)	80.0(2)	79.8(6)
Pd–N–O	122.3(7)	122.7(3)	123.9(4)	123.4(5)	123.3(3)	122.7(6)

<sup>a</sup> Labelling of the atoms refers to the scheme shown in Fig. 4.

<sup>b</sup> Data from Ref. [3].

<sup>c</sup> This compound is dimeric and contains two metallacycles, data from Ref. [4].

metallacycle with a  $\sigma$ [Pd–C<sub>sp<sup>2</sup></sub>(ferrocene)] bond and an oxime group. The structural characterization of complex [Pd{[( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)-C(CH<sub>3</sub>)=N(OH)]Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}Cl(PPh<sub>3</sub>)] (**3b**) and the comparison of bond lengths and angles in **3b** with those of related cyclopalladated complexes derived from aryl or alkyloximes has also allowed us to establish the influence of the nature of the metallated carbon atom, C<sub>sp<sup>2</sup></sub>(ferrocene), C<sub>sp<sup>2</sup></sub>(aryl) or C<sub>sp<sup>3</sup></sub>(aliphatic), upon the structures of these compounds.

On the other hand, the new cyclopalladated compounds **2** and **3** appear to be interesting substrates for further reactivity studies, such as insertions into the  $\sigma$ [Pd–C<sub>sp<sup>2</sup></sub>(ferrocene)] bond. Moreover, the hydrolyses of the Pd–Cl bonds in these substrates might generate substrates containing simultaneously two nucleophilic sites in close vicinity, the N–OH group and the OH bound to the palladium.

### 3. Experimental

Elemental analyses (C, H, and N) were carried out at the Institut de Química Bio-Orgànica de Barcelona (C.S.I.C.) and at the Serveis de Microanàlisi de la Universitat de Barcelona. Infrared spectra were obtained from KBr disks with a Nicolet-520 FTIR spectrophotometer. Proton NMR spectra were recorded at ca. 20 °C on a Varian Gemini 200 MHz instrument using CDCl<sub>3</sub> (99.8%) and Si(CH<sub>3</sub>)<sub>4</sub> as solvent and internal reference respectively. <sup>31</sup>P NMR were recorded on a Bruker 80-SY spectrometer using CHCl<sub>3</sub> as solvent and P(OCH<sub>3</sub>)<sub>3</sub> as internal reference.

#### 3.1. Materials and synthesis

The ferrocenyloximes [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)-C(R)=N(OH)], with R = H (**1a**) or CH<sub>3</sub> (**1b**) were prepared according to the procedure described previously [12].

#### 3.1.1. Preparation of [Pd{[( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)-C(R)=N(OH)]Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}( $\mu$ -Cl)]<sub>2</sub> (R = H (**2a**) or CH<sub>3</sub> (**2b**))

The corresponding ferrocenyloxime (1 mmol, 0.228 g of **1a** or 0.243 g of **1b**), Na<sub>2</sub>[PdCl<sub>4</sub>] (1 mmol, 0.294 g) and Na(CH<sub>3</sub>COO) · 3H<sub>2</sub>O (1 mmol, 0.136 g) were suspended in 40 cm<sup>3</sup> of methanol. The reaction mixture was protected from the light with aluminium foil and stirred at room temperature ca. 20 °C for 24 h (**2a**) or 3 h (**2b**). After this period, the orange solids formed were collected by filtration, washed in methanol (until colourless washing was obtained) and finally air-dried. Then the solids were suspended in the minimum amount of

CHCl<sub>3</sub> (ca. 30 cm<sup>3</sup>) and filtered off. The undissolved materials were discarded and the filtrate was passed through an SiO<sub>2</sub>-column (250 mm × 15 mm), using CHCl<sub>3</sub> as eluant. The first orange-yellow fraction was collected and then concentrated to dryness on a rotary evaporator. The gummy residual was treated with methanol to induce the precipitation of the complexes. The solids obtained were collected by filtration washed with methanol and air-dried. (Yields: 30% (**2a**) and 40% (**2b**)) Characterization data for **2a**. Anal. (%) Calcd. for C<sub>22</sub>H<sub>20</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub> (found): C, 35.71 (35.60); H, 2.70 (2.75); N, 3.80 (3.7). IR,  $\nu$ (C=): 1602 cm<sup>-1</sup>. **2b**: Anal. (%) Calcd. for C<sub>24</sub>H<sub>24</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub> (found): C, 37.53 (37.6); H, 3.13 (3.1); N, 3.65 (3.5). IR,  $\nu$ (C=): 1590 cm<sup>-1</sup>.

#### 3.1.2. Preparation of [Pd{[( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)-C(R)=N(OH)]Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}Cl(PPh<sub>3</sub>)] (R = H (**3a**) or CH<sub>3</sub> (**3b**))

Triphenylphosphine (1 mmol, 0.262 g) was added to a benzene suspension (10 cm<sup>3</sup>) containing 0.5 mmol of the corresponding di- $\mu$ -chloro-bridged complex (0.370 g for

Table 5

Crystal data and details of the refinement of the crystal structure of complex [Pd{[( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)-C(CH<sub>3</sub>)=N(OH)]Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}Cl(PPh<sub>3</sub>)] (**3b**). The e.s.d. values are given in parentheses

Empirical formula	C <sub>30</sub> H <sub>27</sub> ClFeNOPPd
Formula weight	646.20
Crystal size (mm <sup>3</sup> )	0.1 × 0.1 × 0.2
Crystallographic system	Monoclinic
Space group	C2/c
T (K)	293(2)
a (Å)	27.485(5)
b (Å)	9.964(2)
c (Å)	24.778(4)
$\alpha$ (deg)	90.0
$\beta$ (deg)	131.07
$\gamma$ (deg)	90.0
V (Å <sup>3</sup> )	5116(2)
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.678
Z	8
$\Theta$ range (deg)	2.18 < $\Theta$ < 25.02
F(000)	2608
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71069
Absorption coefficient (mm <sup>-1</sup> )	1.462
Index ranges	-32 ≤ h ≤ 24, 0 ≤ k ≤ 11, 0 ≤ l ≤ 29
No. of reflections collected	5063
No. of independent reflections	4508 [R(int) = 0.034]
No. of parameters	327
Refinement method	Full matrix least squares on F <sup>2</sup>
Goodness of fit on F <sup>2</sup>	0.776
Final R values [I > 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0519, wR <sub>2</sub> = 0.0661
Final R values for all data	R <sub>1</sub> = 0.1728, wR <sub>2</sub> = 1.7010
Extinction coefficient	0.00004(4)
Largest difference peak, hole (e <sup>-</sup> Å <sup>-3</sup> )	0.698, -0.615

**2a** or 0.380 g for **2b**). The reaction mixture was stirred at room temperature for 1 h and filtered. The resulting red solution was concentrated to ca. 3 cm<sup>3</sup> on a rotary evaporator and addition of *n*-hexane (ca. 10 cm<sup>3</sup>) followed by slow evaporation of the solvent produced orange-red microcrystals, which were collected by filtration and air-dried. (Yields: 68 and 75% for **3a** and **3b**.) Characterization data for **3a**. Anal. (%) Calcd. for C<sub>29</sub>H<sub>25</sub>ClFeNOPPd (found): C, 55.08 (54.9); H, 3.93 (3.9); N, 2.22 (2.2). IR,  $\nu(\text{C}=\text{N})$ : 1619 cm<sup>-1</sup>. <sup>31</sup>P NMR: 37.4 ppm. **3b**: Anal. (%) Calcd. for C<sub>30</sub>H<sub>27</sub>ClFeNOPPd (found): C, 55.71 (55.75); H, 4.18 (4.2); N, 2.17 (2.2). IR,  $\nu(\text{C}=\text{N})$ : 1610 cm<sup>-1</sup>. <sup>31</sup>P NMR: 38.6 ppm. <sup>13</sup>C NMR: 71.38 (C<sub>5</sub>H<sub>5</sub>), 68.22 (C(3), C<sub>5</sub>H<sub>3</sub>), 65.93 (C(4), C<sub>5</sub>H<sub>3</sub>), (C(5), C<sub>5</sub>H<sub>3</sub>), 101.21 (C<sub>ipso</sub>, C<sub>5</sub>H<sub>3</sub>), 181.22 (>C=N-, d, <sup>4</sup>J<sub>C-P</sub> 2 Hz), and four doublets centred at: 136.40, 131.88, 129.44 and 131.02 due to the four carbon atoms of the PPh<sub>3</sub> ligand.

### 3.2. Crystal structure determination and refinement

A prismatic crystal (sizes in Table 5) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections in the range  $8 \leq \theta \leq 12^\circ$  and refined by the least squares method. Intensities were collected with graphite monochromatized Mo K $\alpha$  radiation, using  $\omega$ -2 $\theta$  scan-technique. 4508 reflections were measured in the range  $2.18 \leq \theta \leq 25.02^\circ$ . Three reflections were measured every 2 h as orientation and intensity-control. Lorentz polarization corrections were made but not for absorption. The structure was solved by Patterson synthesis, using the SHELXS computer program [20] and refined by the full-matrix least squares method with SHELXL-93 computer program [21], using 4457 reflections (highly negative intensities ( $I < -10$ ) produced by asymmetric background were not assumed) and the SIMU instruction. The function minimized was  $\sum w||F_o|^2 - |F_c|^2|^2$ , where  $w = [\sigma^2(I) + (0.0597)P^2]^{-1}$ , and  $P = \{|F_o|^2 + 2|F_c|^2\}/3$ .  $f$ ,  $f'$  and  $f''$  were taken from the literature [22]. The extinction coefficient was 0.0011(1). Twenty-nine H-atoms were located from difference syntheses and refined with an overall isotropic temperature factor using a riding model. The final  $R$  parameters, the goodness of fit, and other relevant details concerning the X-ray crystal structure are summarized in Table 5.

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