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# Schiff bases derived from benzoylferrocene and their cyclopalladated derivatives. X-Ray crystal structure of $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)\text{=}N\text{-}C_6H_5]\}Cl(PPh_3)]$

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## Abstract

We report the syntheses, characterization, and study of cyclopalladated complexes derived from ferrocenylimines $[(\eta^5\text{-}C_5H_5)\text{-}Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(C_6H_5)\text{=}N\text{-}R'\}]$ ($R' = C_6H_5$ (**1a**), $C_6H_4\text{-}2\text{-}CH_3$ (**1b**), $C_6H_4\text{-}4\text{-}CH_3$ (**1c**), $CH_2\text{-}C_6H_5$ (**1d**), $CH_2\text{-}C_6H_4\text{-}2\text{-}CH_3$ (**1e**), or $CH_2\text{-}C_6H_4\text{-}2\text{-}Cl$ (**1f**)). Addition of these ferrocenylamines to methanolic solutions of $Na_2[PdCl_4]$ and sodium acetate trihydrate in a 1:1 molar ratio results in the formation of the di-$\mu$-chloro-cyclopalladated complexes $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)\text{=}N\text{-}R]\}(\mu\text{-}Cl)]_2$ (**2a–2f**). More soluble complexes $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)\text{=}N\text{-}R]\}Cl(PPh_3)]$ (**3a–3f**) were obtained by the reaction of compounds **2a–2f** with triphenylphosphine. $^1H$, $^{13}C$, and $^{31}P$-NMR spectroscopic studies of these complexes reveal that cyclometallation occurs on the ferrocenyl-moiety, producing five-membered metallacycles which contain the >C=N bond (*endo*-type structures). The X-ray crystal structure of $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)\text{=}N\text{-}C_6H_5]\}Cl(PPh_3)] \cdot 2H_2O$ (**3a**) is also reported. This complex is monoclinic with $a = 18.184(3)$, $b = 11.631(2)$, $c = 19.499(3)$ Å, $\beta = 112.55(2)°$, space group $P2_1/c$, and its crystal structure confirms the formation of a five-membered metallacycle, which contains a $\sigma\{Pd\text{-}C_{sp^2(ferrocene)}\}$ bond.

*Keywords:* Iron; Palladium; Cyclopalladation; X-ray structure; Schiff bases; Ferrocene

## 1. Introduction

An area of organometallic chemistry which has shown outstanding and rapid development in the last few years is that of cyclopalladated compounds [1]. Interest in complexes of this kind, which was initially related to their use in organic syntheses [2] is spreading to other areas of chemistry. Quite recently, some new applications of cyclopalladated compounds in photochemistry [3], catalysis [4], in the liquid crystal materials field [5], and in antitumoral materials [6] have been described. Most of these studies, which involve the use of palladocycles containing $\sigma(Pd\text{-}C_{sp^2}$ phenyl) or $\sigma(Pd\text{-}C_{sp^3}$ aliphatic) bonds and N-donor ligands, have shown that the properties of cyclopalladated complexes are dependent on several factors, the most important including the metallated carbon atom, the structure, and the size of the metallacycle [1].

Metallacycles with $\sigma(Pd\text{-}C_{sp^2}$ ferrocene) bonds have not been widely studied and only a few examples have been reported [7,8]. We have recently described [8] a few cyclopalladated complexes containing ferrocenylimines derived from formyl- and acetyl-ferrocene of general formula: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(R)\text{=}N\text{-}R'\}]$ (with $R = H$ or $CH_3$ and $R' = C_6H_5$, $C_6H_4\text{-}2\text{-}CH_3$, $C_6H_4\text{-}4\text{-}CH_3$, $CH_2\text{-}C_6H_5$, $CH_2\text{-}C_6H_4\text{-}2\text{-}CH_3$, $CH_2\text{-}C_6H_4\text{-}2\text{-}Cl$ or $CH_2\text{-}CH_2\text{-}C_6H_5$). The results obtained suggested that although most of these ligands may undergo cyclometallation at two sites, either in the substituted $C_5H_4$-ring of the ferrocenyl moiety, or in the aromatic ring of the R'-substituent, thus producing two types of metallacycle depending on whether the imine bond is contained within the palladocycle (*endocyclic* and *exocyclic* structures, respectively), in all cases the metallation occurred only on the ferrocene moiety, giving exclusively *endo*-type metallacycles. Conse-

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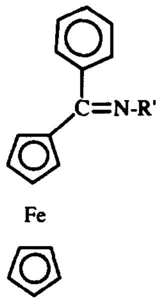


R'= $C_6H_5$ (1a), $C_6H_4$-2-$CH_3$ (1b), $C_6H_4$-4-$CH_3$(1c),

$CH_2$-$C_6H_5$ (1d), $CH_2$-$C_6H_4$-2-$CH_3$ (1e) and

$CH_2$-$C_6H_4$-2-Cl (1f).

Fig. 1. Schiff bases (1a–1f) derived from benzoylferrocene.

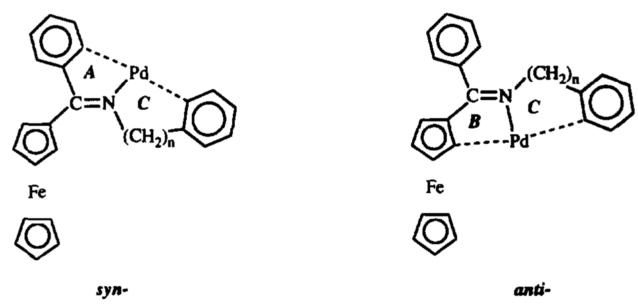


Fig. 2. Schematic view of the three types of metallacycle (A, B and C) that could be expected: (A) endocyclic five-membered ring with σ(Pd–$C_{sp^2}$, phenyl) bond; (B) endocyclic five-membered ring with σ(Pd–$C_{sp^2}$, ferrocene) bond; (C) exocyclic five- or six-membered rings with σ(Pd–$C_{sp^2}$, phenyl) bond.

quently, we decide to perform cyclopalladation reactions of analogous Schiff bases containing a phenyl group as substituent at the imine carbon atom: [($\eta^5$-$C_5H_5$)Fe{($\eta^5$-$C_5H_4$)–C($C_6H_5$)=N–R'}] {with R' = $C_6H_5$ (1a), $C_6H_4$-2-$CH_3$ (1b), $C_6H_4$-4-$CH_3$ (1c), $CH_2$–$C_6H_5$ (1d), $CH_2$–$C_6H_4$-2-$CH_3$ (1e) or $CH_2$–$C_6H_4$-2-Cl (1f)} (Fig. 1). These might yield three different sorts of metallacycle (Fig. 2), two with an *endocyclic* structure. The first, A, would involve the formation of a σ{Pd–$C_{sp^2}$, phenyl} bond, while the second, B, would arise from an electrophilic attack of the palladium(II) species on the C–H bond next to the substituent in the $C_5H_4$ of the ferrocenyl group, and would be characterized by a σ{Pd–$C_{sp^2}$, ferrocene} bond.

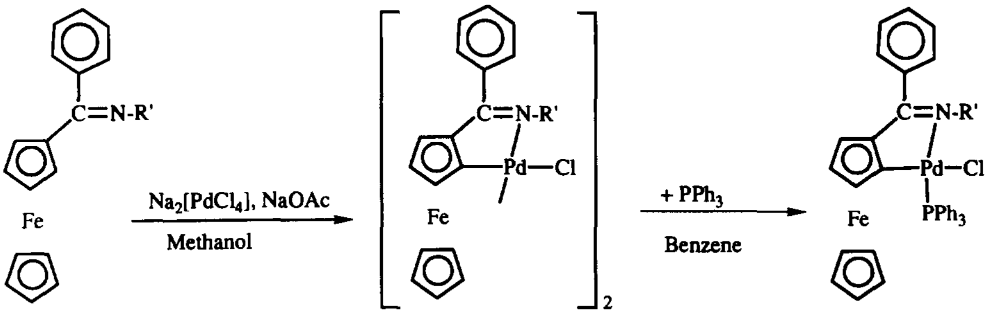
However, since the replacement of a hydrogen or a methyl group at the imine carbon by a bulkier substituent could also induce the formation of a third type of five- or six-membered metallacycle, C (depending on the length of the –$(CH_2)_n$– chain) which would not contain a > C=N– bond, then the formation of *exocyclic* derivatives cannot be disregarded *a priori*. According to our previous work [8], the formation of *endocyclic* derivatives is more likely, and if so the study of cyclopalladation of the Schiff bases [($\eta^5$-$C_5H_5$)-Fe{($\eta^5$-$C_5H_4$)–C($C_6H_5$)=N–R'}] would allow us to establish which carbon atom {$C_{sp^2}$ phenyl or $C_{sp^2}$ ferrocene} is more liable to be activated.

## 2. Results and discussion

### 2.1. Syntheses

Though a large number of Schiff bases $C_6H_5$–C($C_6H_5$)=N–R' derived from benzophenone has been described [9], reports dealing with the syntheses and characterization of analogous imines in which one of the phenyl groups has been replaced by ferrocenyl are scarce and in all cases the substituent at the imine nitrogen is either a phenyl or a naphthyl group [10–12].

The method reported by Cais et al. [10], for the synthesis of [($\eta^5$-$C_5H_5$)Fe{($\eta^5$-$C_5H_4$)–C($C_6H_5$)=N–$C_6H_5$}] (1a) based on the reaction of benzoylferrocene with a large excess of aniline {molar ratio 1:72} in the presence of $TiCl_4$ did not allow us to obtain **1b–1e**.



Compounds **1a-1f**

Compounds **2a-2f**

Compounds **3a-3f**

Scheme 1.

Furthermore, two general procedures described recently for the syntheses of analogous Schiff bases derived from formyl- and acetyl-ferrocene [8], respectively, were also unsuccessful when the aldehyde or ketone was benzoylferrocene. These results may be related to the steric hindrance induced by the larger bulk of the phenyl ring at the imine carbon as compared with the H or $CH_3$.

Only when the condensation reaction was carried out using benzoyl ferrocene and the corresponding amine in the presence of freshly activated $Al_2O_3$ [13], was isolation of products possible. In all cases, long reaction periods {ca. 5–7 d} and daily additions of volatile amine were needed to force the displacement of the equilibria.

The cyclopalladated complexes $[[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)\text{=}N\text{-}R']\}(\mu\text{-}Cl)]_2]$ (**2a–2f**) were prepared following Gaunt and Shaw [7a] based on the reaction of the free base, $Na_2[PdCl_4]$ and $NaAcO \cdot 3H_2O$ in 1 : 1 : 1 molar ratios (Scheme 1) using methanol as solvent at room temperature.

Our previous work on cyclopalladation reactions of ferrocenylimines [8], showed that the ease with which Schiff bases derived from formyl- and acetyl-ferrocene underwent palladation can be ascribed to steric effects. The replacement of an H by a $CH_3$ at the imine carbon involves the narrowing of the bond angle defined by the imine > C=N bond and the *ipso* carbon atom of the ferrocenyl moiety, and in this case metallation is faster. On this basis, **1a–1f**, which have a phenyl group (bulkier than H and $CH_3$) as substituent should facilitate the activation of the C–H bond. Evidence for the cyclopalladation of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(C_6H_5)\text{=}N\text{-}R'\}]$ was detected after short reaction periods (ca. 2–3 h).

Addition of triphenylphosphine to benzene suspensions of the dinuclear compounds (**2a–2f**) produced the cleavage of the Cl bridges and the formation of $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)\text{=}NR']\}Cl(PPh_3)]$ (**3a–3f**). However, when complexes **3a–3f** were treated with a larger excess of $PPh_3$, no evidence of the cleavage of the Pd–N bond was found consequently the metallacycle did not open up under these experimental conditions. These results are identical with those obtained for complexes $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(R)\text{=}N\text{-}R']\}Cl(PPh_3)]$, with R = H or $CH_3$ [8], and reveal that the Pd–N bond in cyclopalladated compounds derived from ferrocenylimines is more stable than in their analogues containing *N*-benzylideneamines [14].

## 2.2. Characterization

The complexes are orange–red solids at room temperature. In all cases the elemental analyses were consistent with the proposed formulae (Table 1). The ferrocenylimines **1** and the monocyclopalladated complexes **3** are highly soluble in chloroform, dichloromethane, acetone, benzene and toluene, slightly soluble in alcohols, and practically insoluble in alkanes. Complexes **2** are more insoluble.

The IR spectra of the free imines (**1a–1f**) exhibit an intense, sharp band in the range 1590–1625 $cm^{-1}$, which is assigned to the stretching of the imine bond. For the cyclopalladated complexes this band appears at lower wavelengths (Table 1). This variation in the IR

Table 1
Elemental analyses, decomposition points and IR data {ν(C=N)}

| Compound | Empirical formular | Elemental analysis | | | Decomp. point (°) | IR ν(C=N) ($cm^{-1}$) |
|---|---|---|---|---|---|---|
| | | % C<br>Calcd. (found) | % H<br>Calcd. (found) | % N<br>Calcd. (found) | | |
| **1a** | $C_{23}H_{19}FeN$ | 75.64(75.5) | 5.24(5.2) | 3.83(3.8) | 148–150 | 1585 |
| **1b** | $C_{24}H_{21}FeN$ | 75.99(75.8) | 5.59(5.5) | 3.69(3.7) | 132–135 | 1595 |
| **1c** | $C_{24}H_{21}FeN$ | 75.99(75.6) | 5.59(5.5) | 3.69(3.6) | 152–155 | 1621 |
| **1d** | $C_{24}H_{21}FeN$ | 75.99(75.5) | 5.59(5.6) | 3.69(3.4) | 68– 70 | 1615 |
| **1e** | $C_{25}H_{23}FeN$ | 76.35(76.7) | 5.90(6.0) | 3.56(3.5) | 112–118 | 1595 |
| **1f** | $C_{24}H_{20}ClFeN$ | 69.68(69.7) | 4.88(4.8) | 3.39(3.4) | 115–117 | 1621 |
| **2a** | $C_{46}H_{36}Cl_2Fe_2N_2Pd_2$ | 54.58(54.7) | 3.57(3.4) | 2.77(3.0) | 193–198 | 1560 |
| **2b** | $C_{48}H_{40}Cl_2Fe_2N_2Pd_2$ | 55.36(55.7) | 3.87(3.6) | 2.69(2.5) | 210–220 | 1561 |
| **2c** | $C_{48}H_{40}Cl_2Fe_2N_2Pd_2$ | 55.36(55.2) | 3.87(3.8) | 2.69(2.5) | 185–200 | 1531 |
| **2d** | $C_{48}H_{40}Cl_2Fe_2N_2Pd_2$ | 55.36(55.8) | 3.87(4.0) | 2.69(2.5) | 138–142 | 1548 |
| **2e** | $C_{50}H_{44}Cl_2Fe_2N_2Pd_2$ | 56.24(56.7) | 4.16(4.6) | 2.62(2.8) | 218–220 | 1545 |
| **2f** | $C_{48}H_{38}Cl_4Fe_2N_2Pd_2$ | 54.47(55.2) | 3.68(3.5) | 2.69(2.5) | 198–210 | 1572 |
| **3a** | $C_{41}H_{33}ClFeNPPd$ [1] | 61.22(61.4) | 4.60(4.7) | 1.74(1.7) | 210–214 | 1536 |
| **3b** | $C_{42}H_{35}ClFeNPPd$ [2] | 59.51(59.6) | 4.29(4.3) | 1.61(1.4) | 208–214 | 1546 |
| **3c** | $C_{42}H_{35}ClFeNPPd$ | 64.43(64.2) | 4.51(4.5) | 1.79(1.8) | 196–201 | 1544 |
| **3d** | $C_{42}H_{35}ClFeNPPd$ | 64.43(64.1) | 4.51(4.5) | 1.79(1.8) | 140–155 | 1564 |
| **3e** | $C_{43}H_{37}ClFeNPPd$ | 64.81(64.4) | 4.68(4.7) | 1.76(1.8) | 225–228 | 1585 |
| **3f** | $C_{42}H_{35}Cl_2FeNPPd$ | 61.64(61.6) | 4.31(4.3) | 1.71(1.7) | 216–222 | 1565 |

[1] $2H_2O$; [2] $1CH_2Cl_2$.

spectra has also been described in previous papers on cyclopalladation of Schiff bases, and explained as arising from a decrease in the bond order of the imine bond upon cyclopalladation [14].

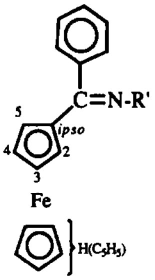
Tables 2 and 3 present the most relevant $^1$H-NMR data for the free bases (**1a–1f**) and for the metallocyclic compounds (**3a–3f**). The $^1$H-NMR spectra of compounds **3a–3f** show four singlets (with relative intensities 1 : 1 : 5 : 1) in the range 3.5–4.5 ppm, which are assigned to the four types of proton of the ferrocenyl moiety {H(5), H(4), H($C_5H_5$) and H(3), respectively}, showing that the formation of the palladocycle takes place through activation of a $\sigma(C_{sp^2}$ ferrocene–H) bond.

However, the resonance due to the H(3) and H($C_5H_5$) protons appeared shifted to high field in **3a–3f**, which may be interpreted in terms of the magnetic anisotropy induced by the phenyl rings of the phosphine. The N–$CH_2$– proton resonance which appears as a singlet in the free bases splits into a doublet of doublets due to the non-equivalence of these two protons in the cyclopalladated derivatives.

Table 2
$^1$H-NMR data (in ppm) for [($\eta^5$-$C_5H_5$)Fe{($\eta^5$-$C_5H_4$)-C($C_6H_5$)=N-R'}] (**1a–1f**) in the range 1.0–6.0 ppm

| Compound | Ferrocenyl moiety proton [1] | | | $CH_3$(R) | –N–$CH_2$– |
|---|---|---|---|---|---|
| | H($C_5H_5$) | H(2), H(5) | H(3), H(4) | | |
| **1a** | 4.26 | 4.71 | 4.45 | – | – |
| **1b** | 4.25 | 4.73 | 4.45 | 2.28 | – |
| **1c** | 4.28 | 4.70 | 4.46 | 2.22 | – |
| **1d** | 4.17 | 4.53 | 4.36 | – | 4.46 |
| **1e** | 4.19 | 4.55 | 4.35 | 2.34 | 4.40 |
| **1f** | 4.21 | 4.56 | 4.36 | – | 4.42 |

[1] Numbering refers to the scheme shown below.



Special attention should be paid to compound **3b**, for which two superimposed spectra of relative intensities (1 : 1) were observed. The two sets of signals (Table 3) are assigned to the two rotamers present in solution. This interpretation is consistent with the $^{13}$C- and $^{31}$P-NMR spectroscopic studies (see below). Furthermore, molecular models show clearly that the methyl substituent of the 2-$CH_3$-$C_6H_4$ ring stops free rotation around the N–R' bond. Moreover the structural studies of complex **1a** [15] revealed a rather crowded environment around the imine bond.

One of the most relevant differences observed in the $^{13}$C-NMR spectra of free **1a–1f** (Table 4) and in those

Table 3
$^1$H-NMR data in the range 1.0–6.0 ppm and $^{31}$P-NMR data for the monomeric cyclopalladated complexes [Pd{$\eta^5$-$C_5H_5$}Fe{($\eta^5$-$C_5H_3$)-C($C_6H_5$)=N-R'}Cl($PPh_3$)] (**3a–3f**)

| | Ferrocenyl moiety protons [1] | | | | $CH_3$(R) | –N–$CH_2$– | $^{31}$P-NMR δ (ppm) |
|---|---|---|---|---|---|---|---|
| | H($C_5H_5$) | H(3) | H(4) | H(5) | | | |
| **3a** | 3.92 | 3.51 | 4.14 | 4.19 | – | – | 37.85 |
| **3b** [2] | 3.94 | 3.50 | 4.13 | 4.19 | 2.20 | – | 37.50 |
| | 4.02 | 3.44 | 4.16 | 4.26 | 2.68 | – | 39.70 |
| **3c** | 3.94 | 3.48 | 4.11 | 4.17 | 2.19 | – | 37.70 |
| **3d** | 3.77 | 3.34 | 3.98 | 3.91 | – | 5.54 [3]<br>4.73 [3] | 37.30 |
| **3e** | 3.96 | 3.32 | [4] | 4.04 | 2.02 | 5.28 [3]<br>4.75 [3] | 37.30 |
| **3f** | 3.93 | 3.37 | 3.99 | 4.06 | – | 5.34 [3]<br>4.92 [3] | 37.50 |

[1] Numbering refers to the scheme shown above.
[2] Two rotameric forms were detected by $^1$H- and $^{31}$P-NMR (see Table 5 and text).
[3] Two doublets centered at the values given due to the non-equivalence of the –N–$CH_2$– protons.
[4] Overlapped by the H($C_5H_5$) resonance.

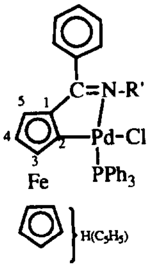
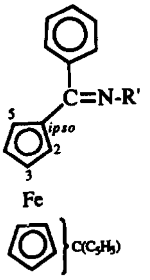


Table 4
Selection of $^{13}$C-NMR data (in ppm) for $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(C_6H_5)\text{=}N\text{-}R'\}]$ (**1a–1f**)

| | Ferrocenyl moiety [1] | | | $C_{ipso}$ | $-N-CH_2-$ | $CH_3(R')$ | $>C=N-$ |
|---|---|---|---|---|---|---|---|
| | $C(C_5H_5)$ | {C(2), C(5)} | {C(3), C(4)} | | | | |
| **1a** | 70.08 | 70.25 | [2] | [3] | – | – | [3] |
| **1b** | 69.60 | 69.90 | 70.92 | 83.65 | – | 19.03 | 169.99 |
| **1c** | 70.21 | 70.41 | 71.47 | 83.81 | – | 21.39 | 170.68 |
| **1d** | 69.33 | 69.07 | 70.25 | 84.06 | 54.27 | – | [3] |
| **1e** | 69.61 | 69.57 | 68.34 | 84.42 [4] | 53.99 | 18.57 | 170.69 |
| **1f** | 69.35 | 70.43 | 69.14 | 84.78 | 54.04 | – | 171.85 |

[1] Numbering refers to the scheme shown below.
[2] Overlapped by the $C(C_5H_5)$ and {C(2),C(5)} resonances.
[3] Not observed.
[4] Low intensity.

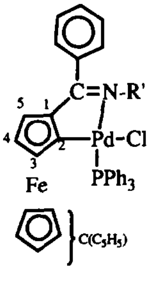


of the cyclopalladated compounds (**3a–3f**) (Table 5) is the splitting of the signal due to the {C(3), C(4)} pair of atoms, due to the non-equivalence of these two nuclei arising from the replacement of a $\sigma(C_{sp^2}$ ferrocene–H) bond by a $\sigma(Pd–C_{sp^2}$ ferrocene). On the other hand, the resonance of the iminic carbon atom is shifted

Table 5
Selection of $^{13}$C-NMR data (in ppm) for complexes $[Pd\{(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_3)\text{–}C(C_6H_5)\text{=}N\text{–}R'\}Cl(PPh_3)\}]$ (**3a–3f**)

| | Ferrocenyl moiety [1] | | | | $-N-CH_2-$ | $CH_3(R')$ | $-C=N-$ |
|---|---|---|---|---|---|---|---|
| | $C(C_5H_5)$ | C(3) | C(4) | C(5) | | | |
| **3a** | 70.81 | 70.25 | 69.92 | 70.02 | – | – | 183.437 |
| **3b** [2,3] | 70.94 | 70.12 | 69.84 | 69.71 | – | 20.56 | 183.802 |
| | 71.94 | 69.87 | 69.92 | 69.52 | – | 19.76 | 183.749 |
| **3c** [4] | 70.79 | 70.60 | 69.57 | 69.57 | – | 21.11 | 183.178 |
| **3d** [5] | 70.33 | 69.58 | 69.41 | [6] | 54.27 | – | 183.268 |
| **3e** [6] | 70.83 | 68.91 | 60.06 | 69.12 | 54.14 | 19.77 | [7] |
| **3f** [8] | 70.86 | 69.36 | 69.14 | 69.43 | 58.98 | – | [7] |

[1] Labelling refers to the scheme shown below.
[2] Two rotameric species present in solution, see Table 2 and text.
[3] Additional signals at 91.43 and 91.68 ppm {C(1)} and at
[4] 01.55 and 103.6 ppm {C(2)}.
[5] Other signals at 91.08 {C(1)} and 102.10, doublet, C(2).
[6] overlapped with the C(3) resonance.
[7] Not observed.
[8] Resonance at ca. 91.33 low intensity, C(1).



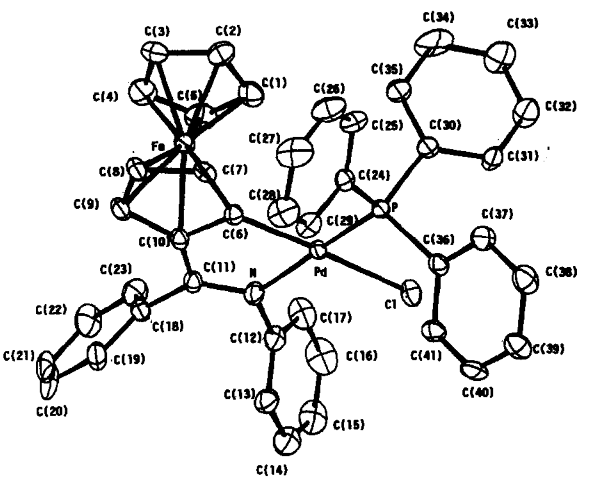


Fig. 3. Molecular structure and atom labelling scheme for complex [Pd{($\eta^5$-$C_5H_5$)Fe[($\eta^5$-$C_5H_3$)-C($C_6H_5$)=N-$C_6H_5$]}Cl($PPh_3$)] (**3a**).

downfield (ca. 13 ppm) upon cyclopalladation. As reported above, two superimposed spectra were obtained for complex **3b**, thus confirming the existence of two rotameric species in solution.

$^{31}$P-NMR spectra of complexes **3a**–**3f** exhibit a singlet in the range 36.00–40.00 ppm (Table 3). The spectrum of **3b** showed two singlets at *ca.* 37.52 and 37.74 ppm which are assigned to the two rotamers. These values are similar to those reported for [Pd{($\eta^5$-$C_5H_5$)Fe[($\eta^5$-$C_5H_3$)-C(R)=N-R′]}Cl($PR''_3$)] (with R = $CH_3$ R′ = $CH_2$-$CH_2$-$C_6H_5$, and R″ = $C_6H_5$ [8]), whose crystal structure revealed a *trans*-arrangement of the phosphine and the imine nitrogen. However, these chemical shifts are higher than the values reported for other palladocycles containing ferrocenes such as *N*,*N*-dimethylferrocenecarbothioamide [16], in which the metallacycle contains a Pd–S bond.

### 2.3. Description of the structure of compound 3a

The perspective drawing of the molecular structure of complex **3a** and the atom numbering scheme are presented in Fig. 3. Final atomic coordinates for non-hydrogen atoms are presented in Table 6.

The structure consists of discrete molecules of [Pd{($\eta^5$-$C_5H_5$)Fe[($\eta^5$-$C_5H_3$)-C($C_6H_5$)=N-$C_6H_5$]}Cl($PPh_3$)]. Two interstitial water molecules are also present in the unit cell. The palladium atom is tetracoordinate, since it is bound to a chloride, the phosphorus atom of the $PPh_3$, the imine nitrogen and the C(6) atom of the ferrocenyl moiety, giving a slightly distorted square planar environment around the palladium, as can be seen in the deviation from the plane [17] defined by the atoms Pd, Cl, P, N and C(6) {Pd = 0.006, P: 0.056(4), Cl: −0.057, N: 0.066 and C(6): −0.071 Å}. The Pd–ligand bond lengths (Table 7) are similar to those obtained in five-membered palladocyclic compounds [7b,7h,8,18].

The bond angles (Table 8) between adjacent atoms in the coordination sphere of the palladium lie in the range 80.4(2)°–97.98(14)°, and the minimum corre-

Table 6
Final atomic coordinates (×10$^4$) for non-hydrogen atoms and equivalent isotropic displacement parameters (Å$^2$ ×10$^3$) in compound: [Pd{($\eta^5$-$C_5H_5$)Fe[$\eta^5$-$C_5H_3$]-C($C_6H_5$)=N-$C_6H_5$]}Cl($PPh_3$)]·$2H_2O$ (**3a**)

| | $x$ | $y$ | $z$ | $U_{eq}$ [1] |
|---|---|---|---|---|
| Pd | 2939(1) | 910(1) | 2037(1) | 32(1) |
| Fe | 2114(1) | −1221(1) | 2854(1) | 40(1) |
| P | 3237(1) | 2403(1) | 2819(1) | 33(1) |
| Cl | 2679(1) | 2240(1) | 1056(1) | 51(1) |
| N | 2729(3) | −538(4) | 1333(2) | 42(1) |
| C(1) | 1263(4) | −1646(7) | 3253(5) | 73(1) |
| C(2) | 1093(4) | −2162(7) | 2559(5) | 71(2) |
| C(3) | 1012(4) | −1296(7) | 2026(5) | 64(2) |
| C(4) | 1103(4) | −233(6) | 2372(4) | 68(2) |
| C(5) | 1271(4) | −442(7) | 3137(4) | 34(1) |
| C(6) | 3069(3) | −336(4) | 2779(3) | 42(1) |
| C(7) | 3175(3) | −522(5) | 3533(3) | 51(1) |
| C(8) | 3157(4) | −1730(5) | 3655(4) | 47(1) |
| C(9) | 3024(3) | −2318(5) | 2992(3) | 39(1) |
| C(10) | 2969(3) | −1452(4) | 2446(3) | 39(1) |
| C(11) | 2785(3) | −1534(4) | 1661(3) | 47(1) |
| C(12) | 2584(4) | −494(4) | 554(3) | 70(2) |
| C(13) | 1832(6) | −233(6) | 54(4) | 89(3) |
| C(14) | 1719(6) | −196(7) | −698(4) | 91(3) |
| C(15) | 2302(7) | −379(7) | −927(4) | 80(2) |
| C(16) | 3050(6) | −646(6) | −422(5) | 61(2) |
| C(17) | 3183(5) | −706(5) | 322(4) | 43(1) |
| C(18) | 2697(3) | −2653(4) | 1271(3) | 61(2) |
| C(19) | 1973(4) | −2989(6) | 742(4) | 76(2) |
| C(20) | 1893(5) | −4026(6) | 368(5) | 80(2) |
| C(21) | 2546(6) | −4718(6) | 519(4) | 83(2) |
| C(22) | 3274(6) | −4399(6) | 1045(5) | 59(2) |
| C(23) | 3343(4) | −3379(5) | 1416(4) | 41(1) |
| C(24) | 3747(3) | 2153(5) | 3809(3) | 51(1) |
| C(25) | 4484(3) | 1589(5) | 4019(4) | 70(2) |
| C(26) | 4966(4) | 1459(7) | 4747(4) | 89(3) |
| C(27) | 4710(5) | 1879(9) | 5283(4) | 86(2) |
| C(28) | 3997(6) | 2383(9) | 5085(5) | 58(2) |
| C(29) | 3516(4) | 2543(6) | 4364(4) | 38(1) |
| C(30) | 3934(3) | 3459(4) | 2727(3) | 45(1) |
| C(31) | 4402(3) | 3233(5) | 2324(4) | 57(2) |
| C(32) | 5012(4) | 3992(6) | 2369(4) | 63(2) |
| C(33) | 5130(3) | 4974(6) | 2793(4) | 64(2) |
| C(34) | 4660(4) | 5218(6) | 3171(4) | 54(1) |
| C(35) | 4072(4) | 4456(5) | 3158(4) | 43(1) |
| C(36) | 2323(3) | 3182(5) | 2657(3) | 49(1) |
| C(37) | 2132(4) | 4151(5) | 2207(3) | 68(2) |
| C(38) | 1393(4) | 4669(7) | 2009(4) | 83(3) |
| C(39) | 849(4) | 4217(7) | 2253(5) | 81(3) |
| C(40) | 1021(4) | 3242(9) | 2695(5) | 81(2) |
| C(41) | 1759(3) | 2722(6) | 2897(4) | 60(2) |
| OW(1) | 334(3) | 1513(5) | 4434(3) | 87(2) |
| OW(2) | 140(3) | 3220(6) | 5425(3) | 101(2) |

[1] $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 7
Bond lengths (Å)[1] for compound [Pd{($\eta^5$-$C_5H_5$)Fe[($\eta^5$-$C_5H_3$)–C($C_6H_5$)=N–$C_6H_5$]}Cl($PPh_3$)]·$2H_2O$ (**3a**)

| | | | |
|---|---|---|---|
| P–Pd | 2.2356(13) | C(13)–C(12) | 1.376(9) |
| Cl–Pd | 2.3623(14) | C(17)–C(12) | 1.351(9) |
| N–Pd | 2.114(4) | C(14)–C(13) | 1.400(11) |
| C(6)–Pd | 1.997(5) | C(15)–C(14) | 1.316(13) |
| C(1)–Fe | 2.041(6) | C(16)–C(15) | 1.375(13) |
| C(2)–Fe | 2.040(6) | C(17)–C(16) | 1.378(10) |
| C(3)–Fe | 2.037(7) | C(19)–C(18) | 1.382(9) |
| C(4)–Fe | 2.064(6) | C(23)–C(18) | 1.385(8) |
| C(5)–Fe | 2.031(7) | C(20)–C(19) | 1.382(9) |
| C(6)–Fe | 2.072(5) | C(21)–C(20) | 1.370(12) |
| C(7)–Fe | 2.043(5) | C(22)–C(21) | 1.377(12) |
| C(8)–Fe | 2.029(6) | C(23)–C(22) | 1.370(10) |
| C(9)–Fe | 2.024(6) | C(25)–C(24) | 1.405(8) |
| C(10)–Fe | 2.017(5) | C(29)–C(24) | 1.379(8) |
| C(24)–P | 1.817(5) | C(26)–C(25) | 1.361(9) |
| C(30)–P | 1.811(5) | C(27)–C(26) | 1.386(11) |
| C(36)–P | 1.822(5) | C(28)–C(27) | 1.338(12) |
| C(11)–N | 1.308(7) | C(29)–C(28) | 1.354(10) |
| C(12)–N | 1.440(7) | C(31)–C(30) | 1.387(7) |
| C(2)–C(1) | 1.401(11) | C(35)–C(30) | 1.398(8) |
| C(5)–C(1) | 1.419(11) | C(32)–C(31) | 1.394(8) |
| C(3)–C(2) | 1.414(12) | C(33)–C(32) | 1.378(10) |
| C(4)–C(3) | 1.387(11) | C(34)–C(33) | 1.355(10) |
| C(5)–C(4) | 1.423(10) | C(35)–C(34) | 1.383(8) |
| C(7)–C(6) | 1.424(7) | C(37)–C(36) | 1.388(8) |
| C(10)–C(6) | 1.432(7) | C(41)–C(36) | 1.386(8) |
| C(8)–C(7) | 1.427(8) | C(38)–C(37) | 1.386(8) |
| C(9)–C(8) | 1.399(8) | C(39)–C(38) | 1.357(12) |
| C(10)–C(9) | 1.441(7) | C(40)–C(39) | 1.386(13) |
| C(18)–C(11) | 1.485(7) | C(41)–C(40) | 1.385(9) |

[1] Standard deviations are in parentheses.

sponds to the angle involving the two coordinated atoms of the chelating ligand {N–Pd–C(6)}.

The metallacycle is formed by the palladium atom, the nitrogen and carbon atoms involved in the imine bond and two carbon atoms of the ferrocenyl moiety {C(6) and C(10)}, thus confirming that cyclometallation had taken place on the ferrocenyl substituent. The two rings involved in the bicyclic system formed by the fusion of the metallacycle [19] and the $C_5H_3$ moiety [20] of the ferrocenyl are practically planar, and their planes form an angle of 4.0°.

The C=N bond length in free **1a** {1.308(9) Å [15]} and in complex **3a** {1.308(7) Å}, are practically identical, and consequently the coordination of the palladium atom to the nitrogen does not cause significant variations in the imine group. Furthermore, in both cases the C=N bond length is clearly greater than the typical value reported for organic Schiff bases [18]. The average C–C and Fe–C(ring) bond lengths {1.39(5) and 2.039(6) Å, respectively} are in good agreement with the values reported for other ferrocene derivatives [18]. The large distance between the two metal centres (3.574 Å) indicates that there is no direct interaction between them.

The two pentagonal rings [C(1)–C(5)] [21] and [C(6)–C(10)] [20] are planar and nearly parallel (tilt angle: 3.74°). Their relative conformation can be deduced from the angle of twist [22], 36.55°. The expected values of this angle for ideal eclipsed and staggered conformations are *ca.* 0.0° and 36.0°, respectively, and consequently in complex **3a** the two rings of the ferrocenyl substituent are staggered. The two phenyl substituents of the imine ligand [C(12)–C(17)] [23] and [C(18)–C(23)] are planar [24], and their planes form an angle of 119.9°. The ferrocenyl group and the [C(12)–C(17)] ring are in a *trans* position in relation to the imine bond (Fig. 3). The arrangement of these two groups is identical to that found for the free imines [15], showing that the *anti*- conformation of the ligand is retained during the cyclopalladation process.

## 2.4. Final remarks

The results described here and those obtained in cyclopalladation studies of analogous Schiff bases derived from formyl- and acetyl-ferrocene [8], confirm the strong tendency of ferrocenylimines to form endocyclic compounds. Furthermore, for substrates **1a–1f**, which could produce two different kinds of endocyclic five-membered palladocycles {A and B in Fig. 2}, metallation occurs exclusively at the ferrocenyl and consequently the formation of bicyclic systems arising from the fusion of the two pentagonal rings ($C_5H_3$-moiety and the metallacycle) is highly preferred to the activation of a $\sigma(C_{sp^2}$, phenyl–H) bond, which would produce bicyclic [5,6] systems. According to the theory accepted for cyclopalladation of *N*-donor, this reaction takes place in two steps: a) the coordination of the nitrogen to the palladium and b) electrophilic attack by the $Pd^{II}$ species thus formed, on the carbon atom. Consequently, for the compounds under study, the formation of the palladocycle with a $\sigma(Pd–C_{sp^2}$, ferrocene) bond is apparently driven by the proclivity of the ferrocene derivatives to undergo electrophilic attack [25] compared with phenyl. Furthermore, since the NMR-spectra of ferrocenylimines show that only one isomer is present in solution and the X-ray crystal structure of **1a** [15] and related imines [8b] confirm the *anti* conformation, the formation of a B-type endocyclic metallacycle through activation of $\sigma(C_{sp^2}$ ferrocene–H) must be favoured.

The activation of a $\sigma(C_{sp^2}$, phenyl–H) bond would require the *anti* → *syn* isomerization of the imine. However, even though this kind of conformational change has been observed in cyclopalladation of *N*-benzilideneamines [14], especially when the *ortho*-positions of the phenyl ring linked to the imine carbon atom are blocked by a Cl– or a $CH_3$– group, this process did not take place during cyclopalladation of the ferrocenylimines under study. The plane defined by

Table 8
Bond angles (degrees) [1] for compound [Pd{(η$^5$-$C_5H_5$)Fe[(η$^5$-$C_5H_3$)–C($C_6H_5$)=N–$C_6H_5$]}Cl($PPh_3$)]·$2H_2O$ (**3a**)

| | | | |
|---|---|---|---|
| Cl–Pd–P | 88.01(5) | Fe–C(6)–C(7) | 68.7(3) |
| N–Pd–P | 176.50(13) | Fe–C(6)–C(10) | 67.5(3) |
| N–Pd–Cl | 93.76(12) | C(7)–C(6)–C(10) | 105.9(4) |
| C(6)–Pd–P | 97.98(14) | Fe–C(7)–C(6) | 68.7(3) |
| C(6)–Pd–Cl | 173.28(14) | Fe–C(7)–C(8) | 68.9(3) |
| C(6)–Pd–N | 80.4(2) | C(6)–C(7)–C(8) | 108.6(5) |
| C(2)–Fe–C(1) | 40.2(3) | Fe–C(8)–C(7) | 70.0(3) |
| C(3)–Fe–C(1) | 68.4(3) | Fe–C(8)–C(9) | 69.6(3) |
| C(3)–Fe–C(2) | 40.6(3) | C(7)–C(8)–C(9) | 109.5(5) |
| C(4)–Fe–C(2) | 67.3(3) | Fe–C(9)–C(10) | 68.9(3) |
| C(4)–Fe–C(3) | 39.5(3) | C(8)–C(9)–C(10) | 106.3(5) |
| C(5)–Fe–C(1) | 40.8(3) | Fe–C(10)–C(6) | 71.6(3) |
| C(5)–Fe–C(2) | 67.3(3) | Fe–C(10–C(9)) | 69.3(3) |
| C(5)–Fe–C(3) | 67.5(3) | C(6)–C(10)–C(9) | 109.7(5) |
| C(5)–Fe–C(4) | 40.7(3) | Fe–C(10)–C(11) | 121.9(4) |
| C(6)–Fe–C(1) | 157.7(3) | C(6)–C(10)–C(11) | 118.7(4) |
| C(6)–Fe–C(2) | 160.8(3) | C(9)–C(10)–C(11) | 131.4(5) |
| C(6)–Fe–C(3) | 124.2(3) | B–C(11)–C(10) | 113.8(4) |
| C(6)–Fe–C(4) | 108.4(2) | N–C(11)–C(18) | 123.5(5) |
| C(6)–Fe–C(5) | 122.5(3) | C(10)–C(11)–C(18) | 122.6(4) |
| C(7)–Fe–C(1) | 120.9(3) | N–C(12)–C(13) | 119.0(6) |
| C(7)–Fe–C(2) | 158.4(4) | N–C(12)–C(17) | 120.1(6) |
| C(7)–Fe–C(3) | 158.1(3) | C(13)–C(12)–C(17) | 120.9(6) |
| C(7)–Fe–C(4) | 121.9(3) | C(12)–C(13)–C(14) | 117.0(8) |
| C(7)–Fe–C(5) | 105.6(3) | C(13)–C(14)–C(15) | 122.5(9) |
| C(7)–Fe–C(6) | 40.5(2) | C(14)–C(15)–C(16) | 119.9(7) |
| C(8)–Fe–C(1) | 104.9(3) | C(15)–C(16)–C(17) | 119.3(8) |
| C(8)–Fe–C(2) | 122.8(3) | C(12)–C(17)–C(16) | 120.3(5) |
| C(8)–Fe–C(3) | 160.6(3) | C(11)–C(18)–C(19) | 121.0(5) |
| C(8)–Fe–C(4) | 156.9(3) | C(11)–C(18)–C(23) | 121.0(5) |
| C(8)–Fe–C(5) | 120.1(3) | C(19)–C(18)–C(23) | 118.1(6) |
| C(8)–Fe–C(6) | 68.8(2) | C(18)–C(19)–C(20) | 121.1(6) |
| C(8)–Fe–C(7) | 41.0(2) | C(19)–C(20)–C(21) | 119.3(7) |
| C(9)–Fe–C(1) | 119.8(3) | C(20)–C(21)–C(22) | 120.5(6) |
| C(9)–Fe–C(2) | 108.0(3) | C(21)–C(22)–C(23) | 119.6(7) |
| C(9)–Fe–C(3) | 125.8(3) | C(18)–C(23)–C(22) | 121.4(7) |
| C(9)–Fe–C(4) | 162.2(3) | P–C(24)–C(25) | 115.2(4) |
| C(9)–Fe–C(5) | 155.3(3) | P–C(24)–C(29) | 126.6(5) |
| C(9)–Fe–C(6) | 70.0(2) | C(25)–C(24)–C(29) | 118.0(5) |
| C(9)–Fe–C(7) | 69.1(2) | C(24)–C(25)–C(26) | 121.1(6) |
| C(9)–Fe–C(8) | 40.4(2) | C(25)–C(26)–C(27) | 118.7(7) |
| Pd–P–C(24) | 119.5(2) | C(26)–C(27)–C(28) | 120.7(4) |
| Pd–P–C(30) | 116.9(2) | C(27)–C(28)–C(29) | 121.9(7) |
| C(24)–P–C(30) | 97.0(2) | C(24)–C(29)–C(28) | 120.0(6) |
| Pd–P–C(36) | 107.7(2) | P–C(30)–C(31) | 122.0(4) |
| C(24)–P–C(36) | 109.0(3) | P–C(30)–C(35) | 118.1(4) |
| C(30)–P–C(36) | 105.8(2) | C(31)–C(30)–C(35) | 119.8(8) |
| C(11)–N–C(12) | 119.8(4) | C(30)–C(31)–C(32) | 119.4(6) |
| Fe–C(1)–C(2) | 69.9(4) | C(31)–C(32)–C(33) | 119.9(6) |
| Fe–C(1)–C(5) | 69.2(4) | C(32)–C(33)–C(34) | 121.0(5) |
| C(2)–C(1)–C(5) | 106.3(7) | C(33)–C(34)–C(35) | 120.0(6) |
| Fe–C(2)–C(1) | 70.0(4) | C(30)–C(35)–C(34) | 120.1(6) |
| Fe–C(2)–C(3) | 69.6(4) | P–C(36)–C(37) | 120.4(4) |
| C(1)–C(2)–C(3) | 109.0(7) | P–C(36)–C(41) | 119.7(5) |
| Fe–C(2)–C(3) | 69.6(4) | C(37)–C(36)–C(41) | 119.2(5) |
| Fe–C(3)–C(4) | 71.3(4) | C(36)–C(37)–C(38) | 120.6(6) |
| C(2)–C(3)–C(4) | 108.6(7) | C(37)–C(38)–C(39) | 119.6(7) |
| Fe–C(4)–C(3) | 69.2(4) | C(38)–C(39)–C(40) | 120.9(6) |
| Fe–C(4)–C(5) | 68.4(4) | C(39)–C(40)–C(41) | 119.8(7) |
| C(3)–C(4)–C(5) | 107.1(7) | C(36)–C(41)–C(40) | 119.8(7) |
| Fe–C(5)–C(1) | 70.0(4) | Fe–C(5)–C(4) | 70.9(4) |
| C(1)–C(5)–C(4) | 108.9(7) | | |

[1] Standard deviations are given in parentheses.

the phenyl substituent at the imine carbon atom [C(18)–C(23)] in free **1a** forms an angle of 43.1(2)° with that defined by the imine moiety [C(18)–C(11)=N], and consequently, once the palladium coordinates to the imine nitrogen, the orientation of neither of the C–H bonds in the *ortho*-positions of the phenyl ring is suitable for its activation.

Quite recently, Knox and co-workers [26] described the cyclopalladation of phenylazoferrocene [(η$^5$-$C_5H_5$)Fe(η$^5$-$C_5H_4$)–N=N–$C_6H_5$]. For this compound metallation takes place at the phenyl ring, producing a five-membered endocyclic metallacycle, which contains a σ(Pd–$C_{sp^2}$, phenyl) giving [Pd{$C_6H_4$–N=N-(η$^5$-$C_5H_4$)Fe(η$^5$-$C_5H_5$)}Cl]$_2$. There is no activation of a σ($C_{sp^2}$, ferrocene–H) bond giving [Pd{(η$^5$-$C_5H_5$)-Fe(η$^5$-$C_5H_3$)–N=N–$C_6$}Cl]$_2$. These results have been rationalized in terms of the higher stability of the bicyclic [5,6] systems as compared with those derived from the fusion of two pentagonal rings {the metallacycle and the $C_5H_3$-moiety}. According to our findings, which show that metallation of the ferrocene moiety is highly preferred, the results described by Knox et al. [26] could also be interpreted in terms of the different basicities of the two nitrogen atoms of the phenylazoferrocene. The coordination of the palladium atom to the more basic nitrogen, (which is the one bound to the ferrocenyl moiety) may induce the activation of σ($C_{sp^2}$ phenyl–H) bonds, and consequently, lead to [[Pd{$C_6H_4$–N=N-(η$^5$-$C_5H_4$)Fe(η$^5$-$C_5H_5$)}Cl]$_2$].

## 3. Experimental section

Elemental analyses (C, H, and N) were carried out at the Instituto de Química Bio-Orgánica (CSIC, Barcelona). IR spectra were obtained from KBr pellets with a Nicolet-520-FTIR spectrophotometer. $^1H$ and $^{13}C\{^1H\}$-NMR spectra were recorded at *ca.* 20°C on a Gemini-200 MHz spectrometer, using $CDCl_3$ (99.8%) as solvent and TMS as internal standard in both cases. $^{31}P\{^1H\}$-NMR spectra were obtained with a Bruker WP80-SY spectrophotometer using $CDCl_3$ as solvent and $P(OCH_3)_3$ as standard. Decomposition points of all the complexes were determined with a Buchi 510 melting point instrument.

### *3.1. Materials and syntheses:*

Benzoylferrocene and the amines were obtained from commercial sources and used as received. The preparations described below involve the use of benzene which should be handled with caution. All the solvents were distilled before use.

### 3.1.1. $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(C_6H_5)=N\text{-}R\}]$ with $R = C_6H_5$ (1a), $R = C_6H_4\text{-}2\text{-}CH_3$ (1b), $C_6H_4\text{-}4\text{-}CH_3$ (1c), $CH_2\text{-}C_6H_5$ (1d), $CH_2\text{-}C_6H_4\text{-}2\text{-}CH_3$ (1e) or $CH_2\text{-}C_6H_4\text{-}2\text{-}Cl$ (1f)

Though compound **1a** can be synthesized using Cais' method [10], the procedure described here is also suitable. To a suspension containing 0.4 g of activated $Al_2O_3$ [14], 3.45 nmol of amine and 80 ml of toluene, 1.0 g (3.45 mmol) of benzoylferrocene was added. The reaction mixtures were heated under reflux for 5–7 days. The progress of the condensation was checked every day by the IR spectra of the supernatant solutions. In order to force the displacement of the equilibria, daily addition of small amounts (ca. 0.1 ml) of volatile amines were needed. This procedure was repeated until the IR spectrum of the samples did not exhibit any band due to the $>C{=}O$ group of the benzoylferrocene [$\nu(C{=}O) = 1630$ cm$^{-1}$]. Then the undissolved materials were removed by filtration and washed with toluene until colourless washings were obtained. The washings were combined with the filtrate giving a deep red solution, which was concentrated to dryness on a rotary evaporator. Addition of hexane (ca. 50 ml) to the oil followed by vigorous stirring effected precipitation of **1a–1f**. The solids were collected by filtration and air-dried (yields: 63, 52, 68, 55, 60 and 48%, respectively).

### 3.1.2. $[Pd\{(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)=N\text{-}R\}\}(\mu\text{-}Cl)]_2$ ($R = C_6H_5$ (2a), $C_6H_4\text{-}2\text{-}CH_3$ (2b), $C_6H_4\text{-}4\text{-}CH_3$ (2c), $CH_2\text{-}C_6H_5$ (2d), $CH_2\text{-}C_6H_4\text{-}2\text{-}CH_3$ (2e) or $CH_2\text{-}C_6H_4\text{-}2\text{-}Cl$ (2f)

0.294 g (1.1 mmol) of $Na_2[PdCl_4]$, 0.130 g (1.0 mmol) of sodium acetate trihydrate and the stoichiometric amount of the corresponding ferrocenylimine **1a–1f** were suspended in 30 ml of methanol. The reaction mixture was stirred in an open vessel at room temperature for three h. The red-violet solids were then collected by vacuum filtration and air-dried. The complexes were purified by dissolving the crude materials in benzene (40 ml), the undissolved materials were removed by filtration and discarded, and the filtrate was concentrated on a rotary evaporator. Addition of hexane followed by vigorous stirring at room temperature precipitated the solids, which were collected by filtration and air-dried. The yields of these preparation fall in the range 60–65%.

### 3.1.3. $[Pd\{(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)=N\text{-}R\}\}Cl(PPh_3)]$ ($R = C_6H_5$ (3a) $C_6H_4\text{-}2\text{-}CH_3$ (3b), $C_6H_4\text{-}4\text{-}CH_3$ (3c), $CH_2\text{-}C_6H_5$ (3d), $CH_2\text{-}C_6H_4\text{-}2\text{-}CH_3$ (3e) or $CH_2\text{-}C_6H_4\text{-}2\text{-}Cl$ (3f).

Two mmol of triphenylphosphine were added to a benzene (10 ml) suspension containing 1 mmol of the corresponding di-$\mu$-chloro-bridged cyclopalladated compounds **2a–2f**. The reaction mixture was stirred at room temperature for 2 h. After this the solution was filtered and the filtrate was concentrated to dryness. The oily residue was treated with hexane (ca. 10 ml) and stirred at room temperature for 30 min. The solid formed was collected by filtration and air-dried. The yields of these preparations varied from 75% to 80%. All these compounds can be recrystallized from $CH_2Cl_2$ : hexane (1 : 1) mixtures. Good quality X-ray crystals of compound **3a** were obtained by slow evaporation of acetone : water (3 : 1) mixtures.

Table 9
Crystal data and details of the refinement of the crystal structure of compound $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(C_6H_5)=N\text{-}(C_6H_5)]\}\text{-}Cl(PPh_3)]\cdot 2H_2O$ (**3a**)

| | **3a** |
|---|---|
| Empirical Formula | $C_{41}H_{33}ClFeNPPd\cdot 2H_2O$ |
| Formula weight | 768.40 |
| Crystal size (mm) | 0.1 × 0.1 × 0.1 |
| Crystallographic System | monoclinic |
| $a$ (Å) | 18.184(3) |
| $b$ (Å) | 11.631(2) |
| $c$ (Å) | 19.499(3) |
| $\beta$ (°) | 112.55(2) |
| Space Group | $P2_1/c$ |
| $V$ (Å$^3$) | 3808.7(11) |
| $Z$ | 4 |
| $D_x$(g × cm$^{-3}$) | 1.605 |
| λ(Mo Kα) (Å) | 0.71069 |
| Absorption coefficient | 1.011 mm$^{-1}$ |
| Temperature | 293(2) K |
| $F$(000) | 1864 |
| Q range for data collection | from 1.21 to 24.96° |
| Index ranges | $-21 \le h \le 19$<br>$-3 \le k \le 13$<br>$-2 \le l \le 23$ |
| Reflections collected | 6971 |
| Independent reflections | 6679 |
| $R$(int) | 0.0189 |
| Data/restraints/n parameters | 6629/0/435 |
| Goodnes of fit on $F^2$ | 0.870 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0504$, $wR_2 = 0.1498$ |
| $R$ indices (all data) | $R_1 = 0.0709$, $wR_2 = 0.2085$ |
| Extinction coefficient | 0.0010(3) |
| Largest difference peak and hole | 0.649 and −0.516 eÅ$^{-3}$ |

### 3.2. Data collection and refinement

A prismatic crystal (Table 9) of compound **3a** was selected and mounted on an Enraf CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections in the range $\{12° \le \Theta \le 16°\}$, and refined by a least-squares method. Intensities were collected with graphite monochromatized Mo $K_\alpha$ radiation using the $\omega/2\Theta$ scan technique. The ranges of $\Theta$, the numbers of reflections (collected and those with $I \ge 2.5\ \sigma(I)$, assumed as observed) are also given in Table 9. Three reflections were measured every two h as orientation and intensity control and no significant decay was observed. Lorentz-polarization corrections were applied, but not absorption corrections.

The structure was solved by Patterson synthesis, using the SHELXS computer program [27], and refined by least-squares, with the SHELX76 computer program [28]. The function minimized was $\Sigma w \| F_o | - | F_c \|^2$, where $w = (\sigma^2(F_o) + 0.0119 | F_o |^2)^{-1}$. $f$, $f'$ and $f''$ were taken from ref. 29. The positions of all H atoms were computed and refined with an overall isotropic temperature factor, using a riding model. The final $R$ and $wR$ indices as well as the number of parameters refined are summarized in Table 9.

## Supplementary materials

Tables containing hydrogen atomic coordinates, complete listings of bond lengths and angles, observed and calculated structure factors, anisotropic and thermal parameters for **3a** have been deposited with the Cambridge Crystallographic Data Centre and are available from the authors upon request.

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[20] The equation of the plane defined by C(6), C(7), C(8), C(9) and C(10) atoms is: (0.9881)XO + (−0.0577)YO + (−0.1423)ZO = 4.6394. Max. deviations are found for C(6) and C(10) (−0.008 and +0.007 Å, Respectively).

[21] Least-squares plane defined by C(1), C(2), C(3), C(4) and C(5) is: (0.9772)XO + (−0.0502)YO + (−0.2065)ZO = 1.0473. Max. deviations were found for C(1): +0.011 and C(2): −0.010 Å.

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[24] The least squares plane defined by C(18), C(19), C(20), C(21), C(22) and C(23) is: (−0.2242)XO + (−0.4613)YO + (0.8584)ZO = 0.9267. Max. deviations were found for C(22): 0.014 and C(21): −0.016 Å.

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