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Factors affecting the lability of the Pd–N bonds in palladacycles containing a $\sigma(Pd–C_{sp^2,\ ferrocene})$ bond. X-ray crystal structures of $[Pd\{[(\eta^5\text{-}C_5H_3)–C(Me)=N–R]Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$ {with $R = CH_2–C_6H_5$ and $L = PEt_3$ or $R = C_6H_4\text{-}4\text{-}Me$ and $L = PPh_2Et$}

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Abstract

The syntheses, characterization and molecular structures of the cyclopalladated complexes $[Pd\{[(\eta^5\text{-}C_5H_3)–C(Me)=N–CH_2–C_6H_5]Fe(\eta^5\text{-}C_5H_5)\}Cl(PEt_3)]$ (**1**) and $[Pd\{[(\eta^5\text{-}C_5H_3)–C(Me)=N–C_6H_4\text{-}4\text{-}Me]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_2Et)]$ (**2**) are reported. A comparative study of the reactivity of **1** and **2** in front of PEt_3, reveals that the Pd–N bond is more prone to cleavage in **2** than in **1**. These results have been interpreted on the basis of the differences detected in the structural characteristics of this sort of derivatives. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclopalladation; Ferrocenyl Schiff bases; Lability of Pd–N bonds; Metallation

1. Introduction

Cyclopalladated compounds containing a $\sigma(Pd–C_{sp^2,}$ ferrocene) bond have attracted great interest in the last decade due to their potential applications [1]. Among the variety of compounds of this kind reported so far, the mononuclear derivatives of general formula: $[Pd\{[(\eta^5\text{-}C_5H_3)–C(R)=N–R']Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$ (Fig. 1), {where R is an hydrogen, a methyl or a phenyl group; R′ represents a phenyl, benzyl or naphthyl group and L = neutral ligand} containing a five-membered palladacycle are probably the most widely studied [2–6]. In these compounds, L is in general triphenylphosphine (PPh_3) [2–4] or in a lesser extent an N-donor group such as pyridine or imidazole [5]. It is well known that the properties of compounds: $[Pd\{[(\eta^5\text{-}C_5H_3)–C(R)=N–R']Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$ in solution, i.e. their proclivity to undergo an oxidation process, are strongly dependent on the nature of the R and R′ substituents (on the imine group) and on the neutral L ligand {$L = PPh_3$, or an N-donor group} [6]. Besides that, the X-ray crystal structures of a wide variety of compounds of the type: $[Pd\{[(\eta^5\text{-}C_5H_3)–C(R)=N–R']$-

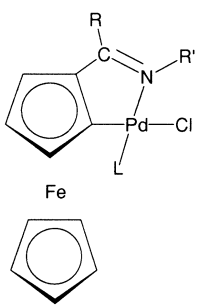

Fig. 1. Schematic view of some cyclopalladated complexes containing five-membered palladacycles with a $\sigma(Pd–C_{sp^2,\ ferrocene})$ bond of general formula: $[Pd\{[\eta^5\text{-}C_5H_3)–C(R)=N–R']Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$.

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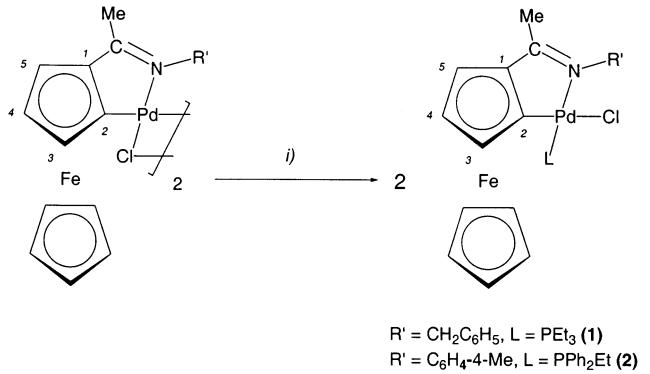

Scheme 1. *i*) L in benzene.

$Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ have shown that in all cases the phosphine and the imine nitrogen are in a *trans* arrangement [2–6]. This arrangement is formally identical to that found in related cyclopalladated complexes containing a $\sigma(Pd–C_{sp^2,\ aryl})$ bond of general formula: $[Pd\{C_6H_4–C(R)=N–R'\}(X)(L)]$ {with X = Cl, Br or I and L = P-donor group} [7,8] for which it has been reported that depending on: (a) the nature and size of the metallacycle; (b) the basicity of the imine; (c) the nature of remaining ligands bound to the palladium(II) and (d) the incoming ligand, the cleavage of the Pd–N bond, can be achieved [9]. On these basis and as a first attempt to elucidate the relative importance of: (a) the chelating ligand; and (b) the phosphine group bound to the palladium on the lability of the Pd–N bond in the cyclopalladated complexes with a $\sigma(Pd–C_{sp^2,\ ferrocene})$ bond, we decided to prepare several derivatives of the type: $[Pd\{[(\eta^5\text{-}C_5H_3)–C(Me)=N–R']Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$, holding different phosphine ligands (Fig. 1) and to compare their reactivity versus PEt_3. In order to elucidate whether the lability of the Pd–N bond in these compounds could be related to structural differences induced by the electronic or steric properties of the phosphine ligand or by the basicity of the chelating group, a comparative study of the crystal structures of a wide variety of palladacycles of general formula: $[Pd\{[(\eta^5\text{-}C_5H_3)–C(R)=N–R']Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$ {with R = Me, H or Ph, R′ = phenyl or benzyl groups and L = phosphine ligand} was also carried out.

2. Results and discussion

The new compounds were prepared by treatment of the corresponding di-μ-chloro-bridged derivative: $[Pd\{[(\eta^5\text{-}C_5H_3)–C(R)=N–R']Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {with R = Me, R′ = C_6H_4-4-Me and R = H, R′ = $CH_2C_6H_5$} [3] with the stoichiometric amount of the corresponding phosphine in benzene, followed by the subsequent purification of the residue obtained after the concentration of the solvent on a rotary evaporator, by SiO_2-column chromatography (Scheme 1).

The new compounds were characterized by elemental analyses, infrared and NMR spectroscopy. In the two cases, the elemental analyses were consistent with the proposed formulae (see Section 3). The infrared spectra of **1** and **2** showed a sharp and intense band at approximately 1590 (for **1**) and 1575 cm^{-1} (for **2**) which is assigned to the stretching of the >C=N– group of the ferrocenylimine. The typical bands of the coordinated phosphines (PEt_3 or PPh_2Et) [10] were also detected in the infrared spectra.

Compounds **1** and **2** have also been characterized by $\{^1H,\ ^{13}C$ and $^{31}P\}$ NMR spectroscopy. The signals observed in their ^1H NMR spectra were assigned with the aid of two-dimensional heteronuclear $\{^1H–^{13}C\}$ NMR experiments. Proton NMR spectra of compounds **1** and **2** (see Section 3) showed the typical pattern of 1,2-disubstituted ferrocene derivatives [2–6,11]: a group of four signals with relative intensities 5:1:1:1 in the range: 3.50–4.50 ppm. The chemical shift of the proton (H^3) in the adjacent position to the metallated carbon (C^2) in **2** appeared at higher fields [$\delta = 3.58$ ppm] than in **1** [$\delta = 4.28$ ppm]. This fact may be related to the proximity of the phenyl rings of the PPh_2Et ligand in **2**. A similar argument was used to explain the differences observed in the position of the signal due to the (H^3) proton in compounds $[Pd\{[(\eta^5\text{-}C_5H_3)–C(H)=N–CH_2–CH_2–C_6H_5]Fe(\eta^5\text{ - }C_5H_5)\}Cl(L)]$, with L = PPh_3 or PEt_3 [2]. The signal due to the diastereotopic protons of the –N–CH_2– moiety of **1** appeared as a doublet of doublets.

In the $^{13}C\{^1H\}$ NMR spectra of **1** and **2**, the signals due to the imine carbon and to the metallated carbon atom (C^2) exhibited low intensity, appeared as doublets (due to phosphorus coupling) and they were shifted to lower fields {at 182.44 in **1** and 182.95 ppm in **2**} when compared with the free imines [3]. A similar type of variation has also been found for cyclopalladated complexes derived from *N*-benzylideneanilines and *N*-benzylidenebenzylamines [12].

^{31}P NMR spectra of compounds under study showed a singlet in the range 30–37 ppm, which suggested, according to the literature [9,12], a *cis* arrangement of the metallated carbon atom (C^2) and the phosphine ligand.

Compounds **1** and **2** have also been characterized by X-ray diffraction. Their molecular structures together with their atom labeling schemes are shown in Figs. 2 and 3. A selection of the most relevant structural parameters of **1** and **2** is presented in Table 1.

The structures of **1** and **2** consist of discrete molecules of $[Pd\{[(\eta^5\text{-}C_5H_3)–C(Me)=N–CH_2C_6H_5]Fe(\eta^5\text{-}C_5H_5)\}Cl(PEt_3)]$ in (**1**) or $[Pd\{[(\eta^5\text{-}C_5H_3)–C(Me)=N–C_6H_4\text{-}4\text{-}Me]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_2Et)]$ in **2** separated by van der Waals contacts.

In each molecule the palladium atom is in a slightly distorted square-planar environment bound to a chlorine, the phosphorus (of the PEt_3 group in **1** or of the

PPh_2Et ligand in **2**), the nitrogen and the C(6) atom of the ferrocenyl unit.[1] The values of the P–Pd–N bond angles (Table 1): 172.36(12)° in **1** and 175.09(2)° in **2**, indicate a *trans* arrangement between the imine nitrogen and the phosphorus in good agreement with the results obtained from $^{31}P\{^1H\}$ NMR spectroscopy.

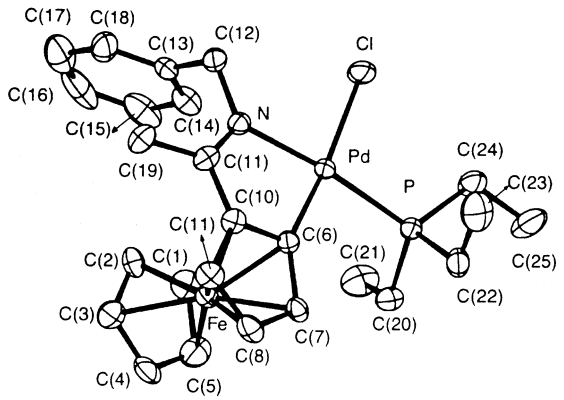

Fig. 2. Molecular structure and atom labeling scheme for [Pd{[(η^5-C_5H_3)–C(Me)=N–$CH_2C_6H_5$]Fe(η^5-C_5H_5)}Cl(PEt_3)] (**1**).

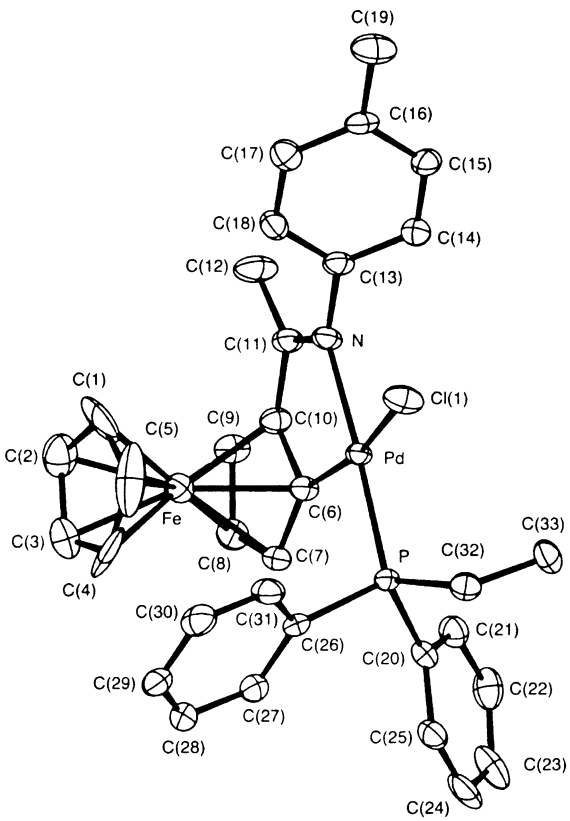

Fig. 3. Molecular structure and atom labeling scheme for [Pd{[(η^5-C_5H_3)–C(Me)=N–C_6H_4-4-Me]Fe(η^5-C_5H_5)}Cl(PPh_2Et)] (**2**).

The two compounds have a [5,5] bicyclic system in which the C_5H_3 ring shares the C(6)–C(10) bond with a practically planar five-membered palladacycle.[2]

The >C=N– functional group is contained in the metallacycle (endocyclic) and the >C=N– bond lengths (1.292(5) in **1** and 1.288(5) Å in **2**) are similar to those reported for the ketimines: [(η^5-C_5H_5)Fe[(η^5-C_5H_4)–C(R)=N–R′] {with R = H, Me or C_6H_5 and R′ = phenyl or benzyl groups} [13,14].

In the two structures the ligands adopt the *anti*-conformation as reflected in the values of the torsion angle C(10)–C(11)–N–C(13): −174.61° (for **1**) and −175.52° (in **2**).

The phenyl rings of the R′ group are planar[3] and their main planes form angles of 79.30° (in **1**) and 110.78° (in **2**) with the imine moiety.

The distances between the Fe and Pd atoms are: 3.6265 (in **1**) and 3.5544 Å (in **2**), thus suggesting that there is no direct interaction between the two metals. The average C–C bonds of the pentagonal rings are similar to those reported for most ferrocene derivatives [14]. The Fe–C ring bond lengths range from 2.015(5) to 2.064(3) Å (in **1**) and from 2.018(5) to 2.081(4) Å in **2**. The pentagonal rings of the ferrocenyl unit are planar[4] and nearly parallel (tilt angles: 2.27° (in **1**) and 0.76° (in **2**)), and their relative arrangement deviate by −0.90° (in **1**) and by 5.84° (in **2**) from the ideal eclipsed conformation.

[1] The least-squares equation of the plane defined by the atoms bound to the palladium in **1** and **2** are: $(0.4917)XO + (-0.0160)YO + (0.8706)ZO = 3.3719$ and $(0.7488)XO + (0.1404)YO + (-0.6477)ZO = 1.2236$, respectively. Deviations from these planes are: P, −0.025; Cl, 0.022; N, −0.029 and C(6), 0.031 Å in **1** and P, 0.064; Cl, −0.060, N, 0.075 and C(6), −0.079Å in **2**.

[2] The least-squares equation of the planes defined by the sets of atoms: Pd, N, C(6), C(10) and C(11) are: $(0.4753)XO + (-0.0634)YO + (0.8775)ZO = 4.1670$ in **1** (deviations from the main plane are: Pd, 0.039; N, −0.023; C(6), −0.064; C(10), 0.058 and C(11), −0.009 Å) and $(0.6941)XO + (0.1344)YO + (-0.7072)ZO = 0.9141$ in **2** (deviations from the main plane are: Pd, −0.001; N, −0.009; C(6), −0.060; C(10), 0.014 and C(11), −0.016 Å).

[3] The least-squares equation of the planes defined by the carbon atoms of the C_6H_5 rings in the imine fragment in **1** and **2** are: $(0.1839)XO + (0.9829)YO + (0.0053)ZO = 7.4275$ (for **1**) and $(0.2908)XO + (-0.7448)YO + (0.6005)ZO = -0.4605$ (for **2**). Maxima deviations: in **1** C(13), −0.002 and C(15): 0.002 Å and in **2**: C(15), −0.006 and C(16), 0.005 Å.

[4] The least-squares equation of the planes defined by the sets of atoms [C(1)–C(5)] and [C(6)–C(10)] in **1** and **2** are: for **1** $(-0.6578)XO + (-0.0887)YO + (0.7480)ZO = 2.6608$ and $(-0.6480)XO + (-0.0926)YO + (0.7560)ZO = -0.6422$, respectively. Maxima deviations were found for C(2): −0.008 and C(1): 0.008 Å. For **2**: $(0.3423)XO + (0.0399)YO + (0.9384)ZO = 0.7984$ and $(0.3802)XO + (0.0388)YO + (0.9241)ZO = 4.0889$, respectively. Maxima deviations were found for C(6): 0.007 and C(7): −0.007 Å.

Table 1
Selected bond lengths (Å) and bond angles (°) for compounds [Pd{[(η^5-C_5H_3)–C(Me)=N–$CH_2C_6H_5$]Fe(η^5-C_5H_5)}Cl(PEt_3)] (**1**), [Pd[{(η^5-C_5H_3)–C(Me)=N–C_4H_4-4-Me]Fe(η^5-C_5H_5)}Cl(PPh_2Et)] (**2**) and related derivatives of general formula: [Pd{[(η^5-C_5H_3)–C(R)=N–R′]Fe(η^5-C_5H_5)}Cl(L)], where L represents a phosphine ligand. For labeling of the atoms refer to Scheme 1

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
R =	Me	Me	Me	Me	Me	H	H
R′ =	$CH_2C_6H_5$	C_6H_4-4-Me	C_6H_4-4-Me	C_6H_4-4-Cl	$(CH_2)_2C_6H_5$	$CH_2C_6H_5$	$(CH_2)_2C_6H_5$
L =	PEt_3	PPh_2Et	PPh_3	PPh_3	PPh_3	PPh_3	PEt_3
Bond lengths							
Pd–P	2.2283(13)	2.2374(14)	2.2371(10)	2.2569(9)	2.247(2)	2.247(2)	2.243(2)
Pd–Cl	2.3878(14)	2.3669(18)	2.3414(9)	2.3600(9)	2.385(2)	2.368(2)	2.390(2)
Pd–N	2.131(4)	2.142(3)	2.136(3)	2.135(3)	2.130(6)	2.146(6)	2.148(5)
Pd–C(6)	1.989(4)	1.983(4)	1.998(3)	1.991(4)	1.984(6)	2.004(5)	1.999(6)
C(10)–C(11)	1.437(7)	1.443(6)	1.446(6)	1.450(6)	1.418(11)	1.475(9)	1.467(9)
C(11)–N	1.292(6)	1.288(5)	1.299(4)	1.296(5)	1.305(9)	1.279(7)	1.280(8)
Bond angles							
Cl–Pd–P	94.36(5)	91.69(12)	95.08(3)	94.37(3)	94.55(2)	95.4(1)	95.5(1)
P–Pd–C(6)	91.97(13)	94.68(12)	92.51(10)	94.8(1)	98.5(2)	91.0(2)	91.2(2)
C(6)–Pd–N	80.40(17)	80.41(14)	80.25(12)	79.9(1)	80.8(3)	80.8(2)	81.1(2)
N–Pd–Cl	93.27(12)	93.18(12)	93.02(7)	91.93(9)	92.4(2)	92.8(1)	92.5(1)
C(10)–C(11)–N	114.9(4)	114.8(4)	113.5(3)	113.8(3)	114.7(7)	115.2(3)	117.0(7)
C(6)–C(10)–C(11)	118.0(4)	118.1(4)	119.3(6)	117.8(3)	119.3(6)	118.0(3)	116.9(8)
Reference	this work	this work	[6c]	[1e]	[3]	[5]	[2]

2.1. Reactivity with triethylphosphine

Previous studies on the reactivity of the Pd–N bond in cyclopalladated complexes of the type [Pd{$C_6H_{4-x}R_x$–CH=N$-(CH_2)_n-C_6H_{5-y}R'_y$}Cl(PPh_3)], derived from *N*-benzylideneanilines {$n=0$} or *N*-benzylidenebenzylamines {$n=1$}, have shown that the stability of the Pd–N bond is highly dependent on the basicity of the nitrogen atom and on the properties of the incoming ligand [9]. For instance, compounds [Pd{$C_6H_{4-x}R_x$–CH=N–R″}Cl(PPh_3)] {with R″ = phenyl or ferrocenyl groups react with PPh_3 to give: [Pd{$C_6H_{4-x}R_x$–CH=N–(CH_2)–$C_6H_{5-x}R'_x$}Cl(PPh_3)$_2$] through cleavage of the Pd–N bond, while their analogues derived from *N*-benzylidenebenzylamines {$n=1$} do not undergo the opening of the metallacycle under identical experimental conditions [8c,9]. The replacement of the PPh_3 ligand by a more basic phosphine PEt_3 produced [Pd{$C_6H_{4-x}R_x$–CH=N–$(CH_2)_n$–$C_6H_{5-y}R'_y$}Cl(PEt_3)$_2$] {with $n=0$ or 1}. This type of reactions involves a change of the mode of coordination of the ligand {from $(C,N)^-$ bidentate to $(C)^-$ monodentate} which is relevant in the view of their potential applications in catalysis. In contrast with these results, it has been reported that compounds: [Pd{[(η^5-C_5H_3)–C(R)=N–$(CH_2)_n-C_6H_5$]Fe(η^5-C_5H_5)}-Cl(PPh_3)] {where R = H, CH_3 or Ph and $n=0$ or 1} do not react with large excesses of PPh_3 to give [Pd{[(η^5-C_5H_3)–C(R)=N–$(CH_2)_n$–C_6H_5]Fe(η^5-C_5H_5)}Cl(PPh_3)$_2$], thus suggesting the poor lability of the Pd–N bond in this sort of derivatives [2–4a].

In view of these findings, we decided to elucidate whether the replacement of the PPh_3 in the coordination sphere of the palladium and/or the use of a more basic incoming group (such as PEt_3) could be important to modify the lability of the Pd–N bond. As a first approach to this problem, solutions of compounds **1** or **2** (in $CDCl_3$) were treated separately on an NMR tube with different amounts of PEt_3 (molar ratios Pd:PEt_3 varying from 1:1 to 1:20} and the resulting solutions were characterized by ^1H and ^{31}P NMR spectroscopy. When the reactions were performed using compound **1**, in all cases, the spectra showed only two signals, the position of which were coincident with those expected for the free PEt_3 and complex **1**, thus suggesting, that even when larger excesses of the entering ligand (PEt_3) were used, the ring opening of the metallacycle did not take place.

Similar results were obtained when **2** was treated with PEt_3 in molar ratios varying from 1:1 to 1:5. However, the addition of larger excesses of PEt_3 (15–20 times the stoichiometric amount) produced significant variations in the $^{31}P\{^1H\}$ NMR spectra of the resulting solution, i.e., the signal due to the phosphorus nuclei of **2** decreased its intensity and three new signals were detected in the ^{31}P NMR spectra. The chemical shifts of two of them were coincident with those expected for the free PEt_3 and PPh_2Et [15]. This finding suggested that a chemical reaction involving the cleavage of the Pd–PPh_2Et bond had taken place.

The remaining signal observed in the $^{31}P\{^1H\}$ NMR spectra, which appeared at higher fields than in **2**, suggested, according to the literature [16] the formation

of a new complex containing two phosphine ligands bound to the palladium in a *trans* arrangement.

In order to confirm this finding, the reaction was scaled up and the residue obtained after the concentration to dryness of the solution on a rotary evaporator was passed through a SiO_2 column chromatography (see Section 3). After working up of the column an orange red solid was obtained and its characterization data (see Section 3) were coincident with those expected for $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}C_6H_4\text{-}4\text{-}Me]Fe(\eta^5\text{-}C_5H_5)\}Cl(PEt_3)_2]$ in which the ligand behaves as a monoanionic $(C)^-$ group.

In view of these results obtained in the reactions of compounds **1** or **2** with PEt_3, and in order to clarify the importance of the basicity of the chelating ligand in this sort of reaction, the experiments were repeated using $[Pd\{[(\eta^5\text{ - }C_5H_3)\text{–}C(H)\text{=}N\text{–}CH_2\text{–}C_6H_5]Fe(\eta^5\text{ - }C_5H_5)\}Cl(PEt_3)]$ (**6**) [2] and PEt_3 under identical experimental conditions and molar ratios varying from 1:1 to 1:20. According to previous electrochemical and theoretical studies, in complex **6** (which can be easily visualized as derived from **1** by replacement of the $–CH_3$ group in the imine carbon by an hydrogen) the donor ability of the chelating ligand is smaller than in **1** [6a,c]. However, there is no evidence for the formation of: $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(H)\text{=}N\text{–}CH_2\text{–}C_6H_5]Fe(\eta^5\text{-}C_5H_5)\}Cl(PEt_3)_2]$ (**6**) through cleavage of the Pd–N bond were detected by NMR spectroscopy in any of the cases studied.

Thus, the comparison of the results presented here, reveal that: (a) the higher lability of the Pd–N bond in complex **2** when compared with that of **1** and **6**; (b) despite the donor ability of the nitrogen atom and the chelating ligand, in **1** and **6** is markedly different, the Pd–N bond does not cleave even in the presence of large excesses of the more basic PEt_3 ligand [15]. Thus suggesting that for palladacycles containing $\sigma(Pd\text{–}C_{sp^2,\ ferrocene})$ in addition to the basicity of the ligand, other more subtle factors may also be important to determine the proclivity of the Pd–N bond to cleave. In order to elucidate whether the differences detected in reactivity of the Pd–N bond in compounds **1**, **2**, **6** could be related to structural features, a comparative study of the most relevant bond lengths and angles in compounds **1**, **2** and in related cyclopalladated derivatives of general formula: $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(R)\text{=}N\text{–}R']Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$ (with $L = PPh_3$, $R = Me$ and $R' = C_6H_4\text{-}4\text{-}Me$ (**3**) [6c], $C_6H_4\text{-}4\text{-}Cl$ (**4**) [1e] or $(CH_2)_2C_6H_5$ (**5**) [3]; $L = PPh_3$, $R = H$ and $R' = CH_2\text{–}C_6H_5$ (**6**) [5] and $L = PEt_3$, $R = H$ and $R' = (CH_2)_2C_6H_5$ (**7**) [2]) was carried out. Data presented in Table 1 show that changes of the neutral L ligand or the substituents on the imine group do not introduce significant variations in the Pd–N bond, since the differences do not clearly exceed three times the standard deviations.

In compounds **2** and **3**, holding $N\text{–}C_6H_4\text{-}4\text{-}R$ groups, the Pd–Cl bond length is shorter than in complexes containing one or two $–CH_2–$ fragments between the imine nitrogen and the phenyl ring. In the X-ray crystal structure of **1** the distance between the chloro ligand and one of the two hydrogen atoms {H(12A)} of the $–N–CH_2–$ moiety of the ferrocenylketimine is (2.652 Å) clearly smaller than the sum of the van der Waals radii of these atoms (Cl, 1.75 and H, 1.20 Å [17]), thus suggesting a weak C(12)–H(12A)···Cl interaction. A careful study of the structures of compounds **1**, **5**–**7**, and of the cyclopalladated complexes containing $\sigma(Pd\text{–}C_{sp^2,\ phenyl})$ rings of general formulae: $[Pd\{(C_6H_{4-x}R_x - C(R'')\text{=}N\text{–}(CH_2)_n\text{–}R'\}Cl(L)]$ {with $n = 1$ or 2, L = P-donor group, R' = phenyl or ferrocenyl groups and $R'' = H$, Me or Ph} previously reported [7,8,14], reveals that in all cases the Cl^- is also very close to one of the hydrogens of the $–CH_2–$ fragment attached to the imine nitrogen. Thus, suggesting also a weak C–H···Cl interaction. A similar type of interaction between the halide X group and one of the protons of the $–CH_2–$ fragment has also been recently reported in compounds $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(H)\text{=}N\text{–}CH_2\text{–}C_6H_5]Fe(\eta^5\text{ - }C_5H_5)\}X(PPh_3)]$ (X = Br or I) [18] which do not undergo the cleavage of the Pd–N bond in the presence of large excesses of phosphines. Consequently, for this sort of complex, the incorporation of the second phosphine ligand in the coordination environment of the palladium (which usually takes place in a *cis* arrangement to the chlorine), would require not only the approach of the entering ligand, but also the cleavages of the C–H···Cl interaction and of the Pd–N bond.

3. Conclusions

The results presented here reveal not only the low lability of the Pd–N bond in cyclopalladated complexes containing a $\sigma(Pd\text{–}C_{sp^2,\ ferrocene})$ bond, but also the importance of the substituent bound to the imine nitrogen (a phenyl or a benzyl group) in determining the ease with which the cleavage of the Pd–N bond takes place.

4. Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Cientifico-Tècnics de la Universitat de Barcelona. Infrared spectra were obtained with a Nicolet Impact 400 spectrophotometer using KBr pellets. Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at approximately 20°C on a Gemini-200 instrument using $CDCl_3$ (99.9%) as solvent and $SiMe_4$ as internal reference. High resolution ^1H NMR spectra and the two-dimensional NMR experiments were carried out with a Varian 500 MHz instrument. $^{31}P\{^1H\}$ NMR

spectra were obtained with a Bruker 250-DXR instrument using $CDCl_3$ as solvent and trimethylphosphite as reference: $\delta^{31}P[P(OMe)_3] = 140.17$ ppm.

4.1. Materials and synthesis

The di-μ-chloro-bridged cyclopalladated complexes: $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(R)\text{=}N\text{–}CH_2C_6H_5]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {with R = Me or H} and $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}C_6H_4\text{-}4\text{-}Me]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ were prepared as described previously [2,3]. The phosphine PPh_2Et was kindly provided by Dr D. Panyella (U.B.). The solvents used in the preparations, except benzene were dried and distilled before use. The preparations described below require the use of benzene which should be handled with caution!

4.2. Preparation of $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}CH_2C_6H_5]Fe(\eta^5\text{-}C_5H_5)\}Cl(PEt_3)]$ (1)

A 100 mg amount (1.1×10^{-3} mol) of the di-μ-chloro-bridged cyclopalladated complex: $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}CH_2\text{–}C_6H_5]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ [3] was suspended in 20 ml of benzene. Then, PEt_3 (2.2×10^{-3} mol) was carefully added. The resulting mixture was stirred at room temperature (r.t.) for 1.5 h. The undissolved materials were filtered off and discarded and the filtrate was concentrated to dryness on a rotary evaporator. The residue was then dissolved in the minimum amount of CH_2Cl_2 and then allowed to evaporate slowly at r.t. The reddish crystals formed were collected and air-dried (yield: 72%).

Characterization data. *Anal.* Found: C, 52.2; H, 5.8; N, 2.4. Calc. for $C_{25}H_{33}ClFeNPdP$: C, 52.07; H, 5.73; N, 2.43%. IR (cm^{-1}): $\nu(>C\text{=}N\text{–})$ 1590. ^1H NMR[5]: $\delta = 4.03$ (C_5H_5), 4.29 (H^3), 4.36 (H^4), 4.40 (H^5), 4.64, 4.55 (–N–CH_2–), 2.11 (Me), 1.30, 2.05 (br. m, 15H, –CH_2–CH_3), 7.22–7.60 (m, 5H, aromatic protons). $^{13}C\{^1H\}$ NMR (selected data)[5]: $\delta = 69.77$ (C_5H_5), 97.01 (C^1), 92.56 (C^2), 68.86 (C^3), 67.14 (C^4), 69.77 (C^5), 53.08 (–N–CH_2–), 182.44 (>C=N–). $^{31}P\{^1H\}$ NMR: $\delta =$ 30.40.

4.3. Preparation of $(Pd\{((\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}C_6H_4\text{-}4\text{-}Me)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_2Et))$ (2)

This compound was prepared according to the procedure described above for **1**, but using $(Pd\{((\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}C_6H_4\text{-}4\text{-}Me)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl))_2$ [3] as a starting material and PPh_2Et as an entering ligand (yield: 67%).

Characterization data. *Anal.* Found: C, 58.8; H, 4.95; N, 2.1. Calc. for $C_{33}H_{33}ClFeNPdP$: C, 58.96; H, 4.95; N, 2.08%. IR (cm^{-1}): $\nu(>C\text{=}N\text{–}) = 1575$. ^1H NMR[5]: $\delta = 3.81$ (C_5H_5), 3.58 (H^3), 4.13 (H^4), 4.41 (H^5), 2.04 (–C(Me) = N–), 2.36 (Me), 2.15–2.40 (–CH_2–), 0.9–1.40 (Me), 6.98 (H^a, $H^{a\prime}$), 7.19 (H^b, $H^{b\prime}$), 7.10–7.90 (m, H^c, aromatic protons of the phenyl rings of the PPh_2Et group). $^{13}C\{^1H\}$ NMR (selected data)[5]: $\delta = 70.81$ (C_5H_5), 101.61 (C^1), 91.23 (C^2), 69.64 (C^3), 67.33 (C^4), 69.42 (C^5), 182.95 (>C=N–). $^{31}P\{^1H\}$ NMR (in ppm): 36.52.

4.4. Preparation of $(Pd\{((\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}C_6H_4\text{-}4\text{-}Me)Fe(\eta^5\text{-}C_5H_5)\}Cl(PEt_3)_2)$

Compound **2** (100 mg, 1.49×10^{-4} mol) was dissolved in 20 ml of benzene, then a large excess of triethylphosphine (0.45 ml, 3.0×10^{-3} mol) was added carefully. The resulting reaction mixture was then refluxed for 1 h and filtered. The deep orange filtrate was concentrated to dryness on a rotary evaporator. The resulting deep brown residue was then dissolved in the minimum amount of chloroform and purified by SiO_2 column chromatography[6] (yield: 45%).

Characterization data. *Anal.* Found: C, 53.5; H, 7.1; N, 2.10. Calc. for $C_{31}H_{48}ClFeNPdP_2$: C, 53.6; H, 6.97; N, 2.02%. IR (cm^{-1}): $\nu(>C\text{=}N\text{–}) = 1603$. ^1H NMR[5]: $\delta = 4.24$ (C_5H_5), 4.35 (H^3), 4.47 (H^4), 4.52 (H^5), 2.10 (–C(Me)=N–), 2.17 (Me), 1.08 and 1.97 (br. M, 30H, –CH_2– and –CH_3), 6.82 (H^a, $H^{a\prime}$), 7.20 (H^b, $H^{b\prime}$). $^{31}P\{^1H\}$ NMR: $\delta = 19.17$.

5. Crystallography

A prismatic crystal of compound **1** or **2** (sizes in Table 2) was selected and mounted on a Enraf–Nonius CAD-4 four circle diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections in the range $12° < \theta < 21°$ and refined by least-squares method. Intensities were collected with graphite monochromatized Mo K_α radiation, using ω–2θ scan-technique. The number of reflections collected and of those assumed as observed applying the condition $I > 2\sigma(I)$ are presented in Table 2. In the two cases three reflections were collected for every 2 h as orientation and intensity control and significant intensity decay was not observed. Lorentz polarization corrections were made but not for absorption.

[5] Labeling of the atoms refers to those shown in Scheme 1.

[6] The preparation of the column was carried out as follows: 15 g of silica gel (Merck, 60 mesh) were suspended in 60 cm^3 of $CHCl_3$ and 0.5 cm^3 of NEt_3 were added. In the absence of NEt_3 the crude of the reaction formed by: $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}C_6H_4\text{-}4\text{-}Me]Fe(\eta^5\text{-}C_5H_5)\}Cl(PEt_3)_2]$ and free phosphines [PPh_2Et and PEt_3], decomposes, giving a mixture of $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(Me)\text{=}N\text{–}C_6H_4\text{-}4\text{-}Me]Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$ (L = PPh_2Et and PEt_3). This sort of process has also been reported for related palladacycles with $\sigma(Pd\text{–}C_{sp^2,\,aryl})$ bonds. See for instance Ref. [16].

The structures were solved by direct methods, using SHELXS computer program [20] and refined by full-matrix least-squares method [21]. The function minimized was $\Sigma w\left||F_o|^2-|F_c|^2\right|^2$, where $w=[\sigma^2(F_o)+(0.007|F_o|^2)^2]^{-1}$ for **1** and $w=[\sigma^2(I)+(0.0386P)^2]^{-1}$ for **2**, with $P=\{(|F_o|^2+2|F_c|^2)/3\}$. f, f' and f'' were obtained from the literature [22].

For **2**, 29 hydrogen atoms were located from a difference syntheses and refined with an overal isotropic temperature factor; the remaining hydrogen atoms of **2** and all the hydrogen atoms of **1** were computed and refined with an overal isotropic temperature factor using a riding model. The final R indices for the two structures as well as further details concerning their resolution and refinement are presented in Table 2.

6. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 152931 and 152930 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Table 2
Crystal data and details of the refinement of the crystal structures of compounds: **1** and **2**

	1	**2**
Empirical formula	$C_{25}H_{33}ClFeNPPd$	$C_{33}H_{33}ClFeNPPd$
Molecular weight	576.22	672.27
Temperature (K)	298(3)	298(3)
Wavelength (Mo Kα) (Å)	0.71069	0.71069
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/a$
Unit cell dimensions		
a (Å)	11.398(2)	16.386(15)
b (Å)	17.108(3)	11.170(5)
c (Å)	13.684(2)	17.717(7)
α (°)	90.0	90.0
γ (°)	90.0	90.0
β (°)	112.77(1)	117.48(4)
V (Å^3)	2460.4(7)	2877(3)
D_{calc} (Mg m^{-3})	1.556	1.552
Z	4	4
Absorption coefficient (mm^{-1})	1.506	1.301
$F(000)$	1176	1368
Crystal size (mm)	$0.1\times0.1\times0.2$	$0.1\times0.1\times0.2$
Reflections collected	7473	8705
Unique reflections	7135 [$R_{int}=0.0179$]	8347 [$R_{int}=0.0230$]
Parameters	272	459
Goodness-of-fit on F^2	1.276	0.988
R indices [$I>2\sigma(I)$]	$R_1=0.0599$, $wR_2=0.1455$	$R_1=0.0482$, $wR_2=0.0859$
R indices (all data)	$R_1=0.0768$, $wR_2=0.1666$	$R_1=0.1318$, $wR_2=0.1045$
Largest difference peak and hole (e Å^{-3})	0.467 and −0.474	0.457 and −0.655

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