Influence of the electronic effects of phosphine ligands upon the properties of cyclopalladated complexes containing a σ(Pd—$C_{sp}{}^2$, ferrocene)bond

X-Ray crystal structures of [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)C(Me)=N(C_6H_4-4-Me)]}Cl(PPh_3)] and [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)CH_2NMe_2]}Cl(PPh_3)]

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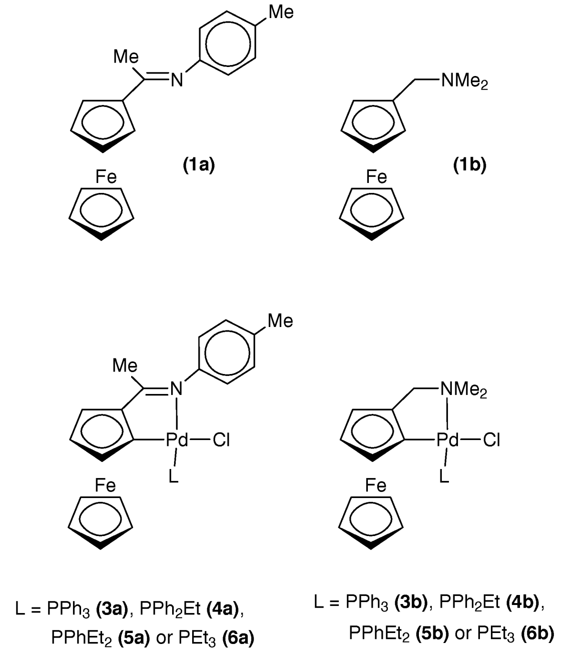
The synthesis, characterization and study of the properties of the cyclopalladated compounds [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)C(Me)=N(C_6H_4-4-Me)]}Cl(L)] and [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)CH_2NMe_2]}Cl(L)] (L = PPh_3, PPh_2Et, $PPhEt_2$ or PEt_3) are reported. The comparison of the electrochemical and electronic properties of these compounds has allowed us to elucidate the influence of the phosphine and chelate ligands upon the environment of the Fe^{II}. As a first approach to clarify the factors affecting the properties of these complexes, molecular orbital (MO) calculations using the PM3(tm) semiempirical method were also undertaken. [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)C(Me)=N(C_6H_4-4-Me)]}Cl(PPh_3)] (**3a**) and [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)CH_2NMe_2]}Cl(PPh_3)] (**3b**) have also been characterized structurally. Complex **3a** is triclinic, space group $P\bar{1}$, with $a = 12.795(2)$, $b = 11.534(2)$ and $c = 11.267(2)$ Å and $\alpha = 106.660(10)°$, $\beta = 98.660(10)°$ and $\gamma = 94.500(10)°$; compound **3b** is monoclinic, space group $P2_1/a$, with $a = 13.650(3)$, $b = 19.678(4)$ and $c = 10.169(2)$ Å and $\alpha = \gamma = 90.0°$ and $\beta = 94.69(2)°$. In both cases the molecules contain a [5,5] bicyclic system formed by a five-membered palladacycle and the C_5H_3 ring of the ferrocenyl moiety.

One of the areas of organometallic chemistry that has attracted great interest during the last few years is that concerning ferrocene derivatives containing heteroatoms with good donor abilities (*e.g.*, nitrogen, oxygen, sulfur, phosphorus, *etc.*) since the coordination of a metal to these heteroatoms produces polymetallic molecules.[1,2] In compounds of this kind the presence of proximal metals may affect the properties of the iron(II). For instance, recent electrochemical studies on ferrocene derivatives containing divalent transition metals and N-donor ferrocenyl units has shown that the proclivity of the iron(II) to oxidize depends on several factors,[3–7] including the nature of the transition metal and the mode of coordination of the ferrocenyl unit to it [*i.e.*, as a monodentate or bidentate $(C^\wedge N)^-$ or $(N^\wedge N)$ ligand]. For instance, in the coordination compounds [M{(η^5-C_5H_5)Fe[(η^5-C_5H_4)CH=N$CH_2CH_2NMe_2$]}Cl_2],[8] [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_4)CH_2NMe_2]}$_2Cl_2$], [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_4)CH=NNMe_2]}$_2Cl_2$] or [M{(η^5-C_5H_5)Fe[(η^5-C_5H_4)N=CH(C_4H_4-2-O)]$_2$}],[4] (M = Zn, Co, Cu or Ni) the Fe^{II} is more resistant to oxidation than in the corresponding free ligands, while in the cyclopalladated derivatives [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)CH_2NMe_2]}(μ-Cl)]$_2$ or [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)CH_2NMe_2]}Cl(PR_3)], in which the ligand acts as a $(C^\wedge N)^-$ bidentate ligand, the iron(II) is more prone to oxidize.[9]

Besides, previous electrochemical studies on cyclopalladated complexes containing N-donor ferrocenyl moieties suggested that the ligands bound to the palladium in the cyclopalladated derivatives (at a distance of three bond lengths) could also contribute to tune the redox ability of the Fe^{II}.[9]

For these reasons we decided to study the electrochemical and spectroscopic properties of the cyclopalladated complexes [Pd($C^\wedge N$)Cl(L)], in which ($C^\wedge N$) stands for either ferrocenylimine {(η^5-C_5H_5)Fe[(η^5-C_5H_4)C(Me)=N(C_6H_4-4-Me)]} (**1a**) or *N*,*N*-dimethylaminomethylferrocene(**1b**) which acts as a monoanionic bidentate ligand, and the neutral L group is PPh_3, PPh_2Et. $PPhEt_2$ or PEt_3. These studies may allow us to explain the influence of these neutral ligands bound to the



Scheme 1

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palladium upon the spectroscopic and electronic properties of the ferrocenyl unit.

Results and Discussion

Syntheses and characterization

The di-μ-chloro-bridged cyclopalladated complexes $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{C(Me){=}N(C_6H_4\text{-}4\text{-}Me)}]\}(\mu\text{-}\mathrm{Cl})]_2$ (**2a**)[10] and $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{CH_2NMe_2}]\}(\mu\text{-}\mathrm{Cl})]_2$ (**2b**)[11] react (in benzene and at room temperature) with a stoichiometric amount of the appropriate phosphine ligand, L, to give the monomeric derivatives $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{C(Me){=}N(C_6H_4\text{-}4\text{-}Me)}]\}\mathrm{Cl(L)}]$ (**3**–**6a**) and $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{CH_2NMe_2}]\}\mathrm{Cl(L)}]$ (**3**–**6b**). All these complexes are orange-red (**3**–**6a** and **3**, **4b**) or yellowish (**5**, **6b**) solids at room temperature and are highly soluble in the most common solvents: chloroform, dichloromethane, acetonitrile, acetone and benzene, but they are only poorly soluble in alcohols and practically insoluble in alkanes.

Elemental analyses of compounds **3**–**6a, b** are consistent with the proposed formulae (see Experimental). The infrared spectra of complexes **3**–**6a** showed a sharp intense band in the range 1570–1590 $\mathrm{cm^{-1}}$, which is assigned to the asymmetric stretching of the $\rangle\mathrm{C{=}N}-$ functional group. This absorption appears at lower wavenumbers than in free ferrocenylketimine[12] [$\nu(\rangle\mathrm{C{=}N}-)$: 1625 $\mathrm{cm^{-1}}$] owing to the coordination of the nitrogen. Compounds **3**–**6a, b** have been also characterized by ^{1}H and ^{13}C NMR spectroscopy (see Experimental). Phosphorus-31 NMR spectra of compounds **3**–**6** showed a singlet in the range 30–40 ppm (Table 1). The position of the signal is consistent, according to the literature,[10,12] with a *trans* arrangement between the phosphine group and the nitrogen of the ferrocenyl Schiff base. The X-ray crystal structures of compounds **3a** and **3b** described below confirm this type of arrangement.

Description of the crystal structures

The molecular structures of **3a** and **3b**, together with the atom labelling schemes, are presented in Fig. 1 and 2, respectively, and a selection of bond lengths and angles for these compounds is given in Table 2.

The structures consist of discrete molecules of $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{C(Me){=}N(C_6H_4\text{-}4\text{-}Me)}]\}\mathrm{Cl(PPh_3)}]$ in **3a** or $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{CH_2NMe_2}]\}\mathrm{Cl(PPh_3)}]$ in **3b**, separated by van der Waals contacts. In the two cases the palladium is in a slightly distorted square-planar environment, bound to a chlorine, the phosphorus, the nitrogen and the C(6) atom of the ferocenyl unit.† The two compounds contain a bicyclic system, which is formed by the substituted pentagonal ring of the ferrocenyl fragment and a five-membered metallacycle. In **3a** the metallacycle is practically planar and its mean plane forms an angle of 1.5° with the plane of the $\mathrm{C_5H_3}$ ring, while in **3b** the palladacycle has an envelope-like conformation.

Table 1 pK_a of the phosphine ligands and ^{31}P NMR data, halfwave potentials referenced to ferrocene and UV/VIS absorption wavelengths for the compounds under study.

Compound	L	pK_a[a]	$\delta\,^{31}$P	$E_{1/2}$(Fc)/mV	λ_1/nm	λ_2/nm
A. Cyclopalladated compounds derived from: $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{C(Me){=}N(C_6H_3\text{-}4\text{-}Me)}]\}\mathrm{Cl(L)}]$ (**3a**–**6a**)						
3a	$\mathrm{PPh_3}$	2.30	37.6	70	393	309
4a	$\mathrm{PPh_2Et}$	2.52	36.5	58	376	305
5a	$\mathrm{PPhEt_2}$	6.25	32.0	45	342	306
6a	$\mathrm{PEt_3}$	8.69	30.2	23	322	298
B. Cyclopalladated compounds of general formula: $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{CH_2NMe_2}]\}\mathrm{Cl(L)}]$ (**3b**–**6b**)						
3b	$\mathrm{PPh_3}$	2.30	39.7	−16	399	316
4b	$\mathrm{PPh_2Et}$	2.52	38.6	−18	385	312
5b	$\mathrm{PPhEt_2}$	6.25	34.4	−25	370	305
6b	$\mathrm{PEt_3}$	8.69	32.6	−33	352	307

[a] Data from ref. 13.

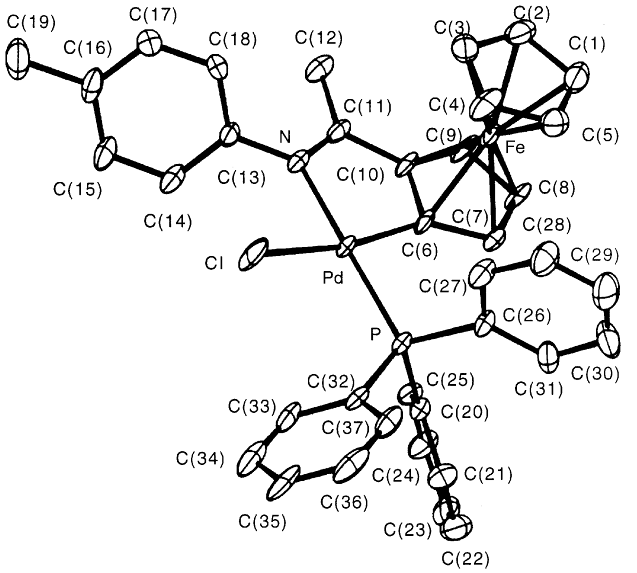

Fig. 1 Molecular structure and atom labelling scheme of $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{C(Me){=}N(C_6H_4\text{-}4\text{-}Me)}]\}\mathrm{Cl(PPh_3)}]$ (**3a**)

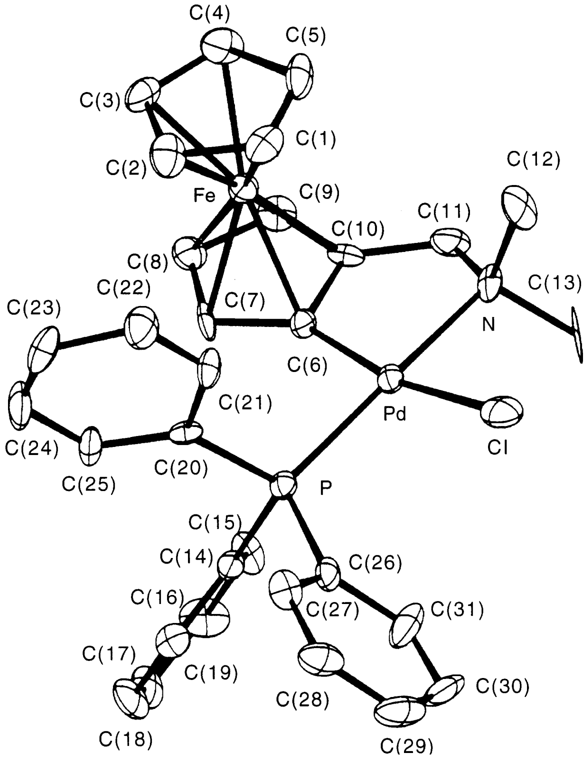

Fig. 2 Molecular structure and atom labelling scheme of $[\mathrm{Pd}\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}[(\eta^5\text{-}\mathrm{C_5H_3})\mathrm{CH_2NMe_2}\}\mathrm{Cl(PPh_3)}]$ (**3b**)

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† In compound **3a**, the least-squares equation of the plane defined by the atoms Pd, P, N, Cl and C(6) is (0.5884)XO − (0.2024)YO + (0.7829)ZO = 1.6688. The deviations from this plane are: Pd, +0.050; Pd, −0.120; N, −0.143; Cl, 0.110; C(6), 0.149 Å. In complex **3b**, the least-squares equation of the same plane is (0.2303)XO + (0.7220)YO − (0.6524)ZO = −1.3923. The deviations from this plane are: Pd, −0.087; P −0.396; Cl, 0.083; N, −0.011; C(6), 0.102 Å.

Table 2 Selected bond lengths (in Å) and angles (in degrees) for **3a** and **3b**. Standard deviations are given in parentheses

	3a	**3b**
Pd—C(6)	1.998(3)	1.983(10)
Pd—N	2.136(3)	2.170(10)
Pd—P	2.2371(10)	2.238(3)
Pd—Cl	2.3414(9)	2.395(3)
C(10)—C(11)	1.446(4)	1.50(2)
N—C(11)	1.299(4)	1.48(2)
N—C(13)	1.428(4)	1.468(14)
N—Pd—Cl	93.02(7)	90.1(3)
P—Pd—Cl	95.08(3)	95.59(11)
C(6)—Pd—N	80.25(12)	82.6(4)
C(6)—Pd—P	92.51(10)	92.6(3)
C(10)—C(11)—N	113.5(3)	109.4(9)
C(11)—N—C(13)	119.3(3)	109.0(10)

In compound **3a** the $>$C=N— functional group is *endocyclic* and the $>$C=N— bond length [1.299(4) Å] is similar to that reported for the free ligand.[12] The imine has an *anti* conformation as reflected in the C(10)—C(11)—N—C(13) torsion angle [178.5(4)°]. The plane defined by the phenyl group forms an angle of 63.5° with the C_5H_3 of the ferrocenyl moiety.

The distance between the Fe and the Pd is 3.592(2) Å for **3a** and 3.558(2) Å for **3b**, thus suggesting that there is no direct interaction between the two metals. In the two structures, the average C—C bond lengths in the two pentagonal rings [1.406(15) Å for **3a** and 1.42(2) Å for **3b**] are similar to the values reported for other ferrocene derivatives.[14] The Fe—C(ring) bond distances range from 2.011(3) to 2.065(3) Å in **3a** and from 2.015(11) to 2.087(10) Å in **3b**. The two pentagonal rings of the ferrocenyl moiety are planar,‡ nearly parallel (tilt angle) of 1.0° for **3a** and 3.1° for **3b**. The twist angle is 2.0° in **3a** and 6.7° in **3b**.

Electrochemical studies and UV/VIS spectra

Electrochemical data for the compounds under study were obtained from cyclic voltammetric studies of 10^{-3} M solutions in acetonitrile (HPLC grade). Cyclic voltammograms of compounds **3**–**6a,b** exhibit an anodic peak with a reduction in the reverse scan. The experiments were carried out at different scan rates from 0.05 to 1.0 V s^{-1} and the results were consistent with those expected for a simple and reversible one-electron transfer process.[15,16] The half-wave potentials referred to ferrocene [$E_{1/2}$(Fc)] are summarized in Table 1. Comparison of the data reveals that the cyclopalladated compounds are more prone to oxidize than the free ligands (138 mV for **1a**[15] and −10 mV for **1b**[16]). A similar trend has also been observed for other cyclopalladated and cycloplatinated complexes containing ferrocenyl units.[9,17] In addition, the proclivity of compounds **3**–**6a,b** towards oxidation is strongly dependent on the nature of the phosphine ligands bound to the palladium. In particular, in our two families of compounds the replacement of the PPh_3 by a more basic phosphine ligand[13] produces a decrease in $E_{1/2}$(Fc), that is to say the iron becomes more prone to oxidation. Besides, the half-wave potentials for compounds **3**–**6a** spread over a wider range (*ca.* 50 mV) than for compounds **3**–**6b** (*ca.* 17 mV) in which the substituent directly bound to the metallated ring is an sp^3-hybridized carbon atom. These results are similar to those reported by Silva *et al.*[18] for monosubstituted ferrocene derivatives of the type $\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)C(X){=}Y]\}$ (class A) or $\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)CHYZ]\}$ (class B). For these systems, it has been postulated that the stronger substituent effect of the —C(X)=Y moiety in class A compounds could be interpreted in terms of the interaction between the π system of the ferrocenyl group and the p_z orbital of the sp^2 carbon.

Several attempts to correlate UV/VIS spectroscopic data and the half-wave potentials ($E_{1/2}$) of the Fe^{II} in ferrocene derivatives have been reported.[18–21] Recent electrochemical studies for a large number of this type of compound have shown that for derivatives having the general formula $\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)C(X){=}Y]\}$ (class A),[18] an increase of the electron-withdrawing nature of the R group was reflected in an increase of the $E_{1/2}$(Fc) value and a decrease in energy of the d–d transition energy.

Since compounds **3**–**6a** included here also contain an sp^2 carbon atom attached to the ferrocenyl group, we decided to check whether the relationship between the electrochemical and UV/VIS spectroscopic data (λ^{-1}) obtained by Silva *et al.*[18] for the class A ferrocenes could also be extended to the palladium(II) compounds **3**–**6a**. UV/VIS spectral data for compounds **3**–**6a,b** are summarized in Table 1. Comparison of these data reveals that for **3**–**6a** the position of the band λ_1 is more sensitive to changes introduced in the phosphine ligands than for **3**–**6b**. In addition, for compounds **3**–**6a** an overall gross tendency appears to occur between $E_{1/2}$ and λ_1^{-1}, that is to say an increase in the redox potential (this is usually related[19–22] to an increase of the electronic acceptor character of the substituents) tends to correspond to a decrease in the energy of the d–d transition. These findings are similar to those reported for class A compounds.[18]

Theoretical approaches to clarify the influence of the phosphine ligands and the chelating group upon the electronic environment of the iron(II)

As a first attempt to understand the effect of the palladium and its ligands upon the electronic environment of the ferrocenyl fragment, we decided to undertake molecular orbital (MO) calculations on the ligands **1a** and **1b**, as well as on some model cyclopalladated complexes of the general formula $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)C(Me){=}N(C_6H_4\text{-}4\text{-}Me)]\}Cl(L)]$ and $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)CH_2NMe_2]\}Cl(L)]$ (Fig. 1, where L represents PPh_3, PPh_2Me, $PPhMe_2$, PMe_3 or PH_3) (**3a**, **4a′**–**7a′** and **3b**, **4**–**7b′**). The main difference between these model compounds and the complexes prepared in this work is the replacement of the ethyl group by a methyl or a hydrogen. This approach was undertaken in order to minimize the problems that may arise during the optimization of the geometry of these complexes owing to the flexibility of the ethyl fragments.

All the calculations were carried out with the PM3(tm) model of the SPARTAN 4.1 program[22] and the geometries of all the molecules used in this study were fully optimized before the calculation of the molecular orbitals. In order to test the validity of this program for the compounds under study the geometries of the imines $\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)C(R){=}NR']\}$ (with R = H, R′ = Ph and R = Me,

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‡ In compound **3a** the least-squares equation of the plane defined by the set of atoms C(1)–C(5) is (0.6419)XO − (0.2767)YO + (0.7151)ZO = 4.9479. The deviations from this plane are: C(1), 0.001; C(2), −0.003; C(3), 0.004; C(5), 0.001 Å. The least-squares equation of the plane defined by the set of atoms C(6)–C(10) is (0.6551)XO − (0.2741)YO + (0.7041)ZO = 1.6329. The deviations from this plane are: C(6), −0.013; C(7), 0.013; C(8), −0.009; C(9), 0.003; C(10), 0.008 Å.

In compound **3b**, the least-squares equation of the plane defined by the set of atoms C(1)–C(5) is (0.1430)XO + (0.7875)YO − (0.5955)ZO = 2.4029. The deviations from this plane are: C(1), 0.004; C(2). 0.003; C(3), −0.009; C(4), 0.011; C(5), −0.010 Å. The least-squares equation of the plane defined by the set of atoms C(6)–C(10) is (0.1239)XO + (0.8194)YO − (0.5597)ZO = −0.7655. The deviations from this plane are: C(6), −0.019; C(7), 0.131; C(8), −0.003; C(9), −0.009; C(10), 0.017 Å.

R′ = Ph or C_6H_4-4-Me) and of the cyclopalladated complexes **3a** and **3b** were optimized and compared with available X-ray data.[12] In all cases, the structural parameters (bond lengths, bond angles and the relative orientation of the rings) in the optimized geometries were in excellent agreement with the structural data obtained by X-ray diffraction, thus suggesting that for compounds of this kind the PM3(tm) method[22] gives fairly accurate optimized geometries. On this basis, it seemed reasonable to assume that this semiempirical method could also be used to optimize the geometries of the model complexes containing L = PPh_2Me, $PPhMe_2$, PMe_3 or PH_3, for which X-ray data are not available.

The MO calculation for the ferrocenylimine $\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)C(Me){=}N(C_6H_4\text{-}4\text{-}Me)]\}$ reveals that the HOMO is mainly a combination of the π orbital of the ferrocenyl fragment and the π orbital of the functional group $>$C=N—, while the LUMO is mainly the π^* orbital of the $>$C=N— group. In contrast, in the cyclopalladated complexes derived from the ferrocenylimine (**3a** and **4**–**7a′**), the HOMO is formed by a combination of the π^* orbital of the ferrocenyl moiety, a contribution from the orbitals of the chlorine ligand bound to the palladium, the $d_{x^2-y^2}$ orbital of the palladium atom and a small contribution from the p_z orbital of the imine nitrogen, while the LUMO is mainly formed by combination of two π^* orbitals: one of the ferrocenyl group and the other of the $>$C=N— group [Fig. 3(A)]. These findings allow us to confirm the results obtained by Silva *et al.*,[18] who postulated that the variations observed in the electrochemical and electronic properties of $\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)C(X){=}Y]\}$ [which contain an sp^2-hybridized carbon atom attached to the ferrocenyl group (class A)] could be related to a certain degree of conjugation between the π system of the ferrocenyl moiety and the —C(X)=Y fragment.

In the cyclopalladated complexes $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)CH_2NMe_2]\}Cl(L)]$ (L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3 or PH_3, **3b** and **4**–**7b′**) [Fig. 3(B)], the HOMO was very similar to that mentioned for compounds **3a** and **4**–**7a′** (except for the absence of the contribution of the p_z orbital of the amine nitrogen), while the LUMO was basically a π^* orbital of the ferrocenyl moiety.

For the two families of compounds, the formation of the σ(Pd—C) bond increases the energy of the HOMO, which is consistent with the fact that in the cyclopalladated complexes the Fe^{II} is more prone to oxidation than in the free ligands (**1a**, **1b**). Besides, and although the phosphine ligand is not directly involved in the HOMO, the energy of this level is sensitive to the nature of the phosphine. For the two families of compounds the energy of the HOMO increases according to the sequence $PPh_3 < PPh_2Me < PPhMe_2 < PMe_3$, and consequently the proclivity of Fe^{II} towards oxidation in the cyclopalladated complexes should be higher for compounds containing PMe_3 than for those with L = PPh_3. On the other hand, an increase in the basicity of the phosphine produces a destabilization of the palladium-based orbitals, which in turn could result in a greater electron density on the ferrocenyl moiety. These findings are consistent with the variations obtained for the half-wave potentials of compounds **3**–**6a,b** (Table 1).

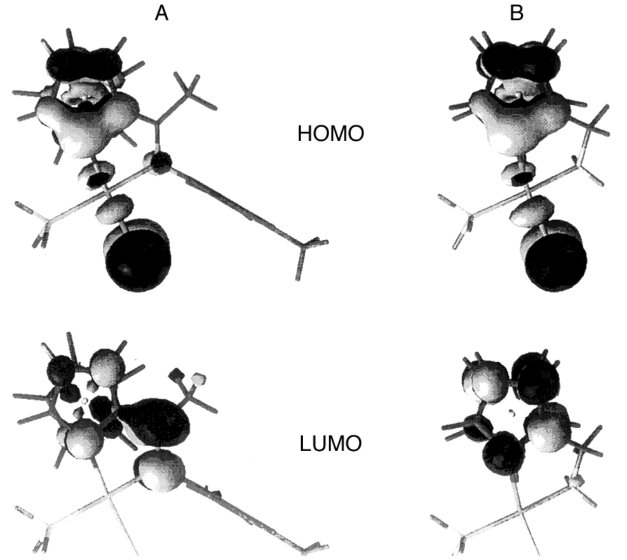

Fig. 3 HOMO and LUMO of (A) $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)C(Me){=}N(C_6H_4\text{-}4\text{-}Me)]\}Cl(PH_3)]$ (**7a′**) and (B) $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)CH_2NMe_2]\}Cl(PH_3)]$ (**7b′**)

Conclusions

The electrochemical studies show that the cyclopalladated compounds $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)C(Me){=}N(C_6H_4\text{-}4\text{-}Me)]\}Cl(L)]$ (L = PPh_3, PPh_2Et, $PPhEt_2$ or PEt_3, **3**–**6a**) are more sensitive to changes introduced in the phosphine ligands than those containing the ferrocenylamine **1b**. In addition, for the two families of compounds an increase in the basicity of the phosphine ligand enhances the proclivity of the Fe^{II} towards oxidation. MO calculations on the compounds $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)C(Me){=}N(C_6H_4\text{-}4\text{-}Me)]\}Cl(L)]$ (**3**–**6a**) and $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)CH_2NMe_2]\}Cl(L)]$ (**3**–**6b**) revealed that in compounds **3**–**6a** there is a certain degree of conjugation between the π system of the functional group and that of the ferrocenyl fragment, while in **3**–**6b**, where the carbon bound to the C_5H_4 ring has an sp^3 hybridization, this kind of interaction cannot take place.

Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Cientifico-Técnics de la Universitat de Barcelona. Infrared spectra were obtained with a Nicolet Impact-400 spectrophotometer using KBr pellets. ^1H and ^{13}C NMR spectra were recorded at *ca.* 20 °C on a Gemini 200 MHz instrument using $CDCl_3$ (99.9%) as solvent and $SiMe_4$ as internal standard. ^{31}P NMR spectra of compounds **3**–**6a,b** were obtained with a Bruker 250 DRX instrument using $CDCl_3$ as solvent and trimethylphosphite as reference $\{\delta^{31}P[P(OMe)_3] = 140.17\}$. UV/VIS spectra of the compounds in CH_2Cl_2 were recorded at 20 °C with a Shimadzu instrument.

Methods and materials

The di-μ-chloro-bridged cyclopalladated complexes $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)C(Me){=}N(C_6H_4\text{-}4\text{-}Me)]\}(\mu\text{-}Cl)]_2$ (**2a**) and $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)CH_2NMe_2]\}(\mu\text{-}Cl)]_2$ (**2b**) were prepared as described previously.[10,11] The phosphines PPh_2Et and $PPhEt_2$ were kindly provided by Dr. D. Panyella (Univ. Barcelona). $CHCl_3$ and CH_2Cl_2 were distilled (over CaO) before use. Some of the preparations described below require the use of benzene, which should be handled with CAUTION.

Syntheses of 3–6a

2a (100 mg, 0.11 mmol)[10] was suspended in 20 ml of benzene and then 0.220 mmol of the corresponding phosphine was added. The resulting mixture was stirred at room temperature 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 dissolved in the minimum

Table 3 Crystal data and details of the refinement of the crystal structures of [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)C(Me)=N(C_6H_4-4-Me)]}Cl(PPh_3)] (**3a**) and [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)CH_2NMe_2]}Cl(PPh_3)] (**3b**). Standard deviations are given in parentheses

	3a	**3b**
Empirical formula	$C_{37}H_{33}$ClFeNPPd	$C_{31}H_{31}$ClFeNPPd
Formula weight	720.31	646.24
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71069	0.71069
Crystal system	Triclinic	Monoclinic
Crystal size/(mm × mm × mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
Space group	$P\bar{1}$	$P2_1/a$
Unit cell dimensions	$a = 12.795(2)$ Å	$a = 13.650(3)$ Å
	$b = 11.534(2)$ Å	$b = 19.678(4)$ Å
	$c = 11.267(2)$ Å	$c = 10.169(2)$ Å
	$\alpha = 106.660(10)°$	$\alpha = 90°$
	$\beta = 98.660(10)°$	$\beta = 94.69(2)°$
	$\gamma = 94.500(10)°$	$\gamma = 90°$
Volume/Å^3	1561.8(5)	2722.3(10)
Z	2	4
Density calcd/g cm^{-3}	1.532	1.577
Absorption coefficient/mm^{-1}	1.204	1.371
Θ range for data collection/deg	2.23–30.00	3.70–24.98
Index ranges	$-17 \leqslant h \leqslant 17$	$-15 \leqslant h \leqslant 16$
	$-16 \leqslant k \leqslant 15$	$0 \leqslant k \leqslant 23$
	$0 \leqslant l \leqslant 15$	$0 \leqslant l \leqslant 11$
No. of reflections collected	9087	2550
No. of independent reflections	9087 [R_{int} (on F) = 0.000]	2424 [R_{int} (on F) = 0.1372]
Refinement method	Full-matrix least-squares on F^2	
No. of data/restraints/parameters	9036/0/479	2374/0/327
Goodness-of-fit on F^2	0.884	1.109
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0356$	$R_1 = 0.0483$
	$wR_2 = 0.0694$	$wR_2 = 0.1272$
R indices (all data)	$R_1 = 0.0847$	$R_1 = 0.0571$
	$wR_2 = 0.1538$	$wR_2 = 0.1944$
Largest diff. peak, hole/e Å^{-3}	0.826, −1.337	0.851, −1.282

amount of CH_2Cl_2 and then treated with 20 ml of *n*-hexane. The resulting mixture was stirred at room temperature for 30 min and the deep orange solids formed were collected by filtration and air-dried. (Yields: 83, 72, 81 and 75% for **3**–**6a**, respectively).

3a: Anal. (%) calcd (found) for $C_{37}H_{33}$NFePPdCl: C, 61.69 (61.7); H, 4.62 (4.7); N, 1.94 (2.05). IR(KBr pellets): ν($\rangle$C=N—) = 1570 cm^{-1}. ^{1}H NMR (in ppm): 3.75 [C_5H_5]. 3.38 [H^3], 4.13 [H^4]. 4.47 [H^5], 2.07 [—C(Me)=N—], 2.38 [Me], 7.10–7.90 [aromatic]. ^{13}C NMR (selected data in ppm): 70.53 [C_5H_5], 101.72 [C^1], 90.12 [C^2], 69.19 [C^3], 67.06 [C^4], 69.09 [C^5], 181.42 [$\rangle$C=N—].

4a: Anal. (%) calcd (found) for $C_{33}H_{33}$NFePPdCl: C, 58.96 (58.8); H, 4.95 (4.95); N, 2.08 (2.1). IR (KBr pellets): ν($\rangle$C=N—) = 1575 cm^{-1}. ^{1}H NMR (in ppm): 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$^\alpha$ and H$^{\alpha'}$], 7.19 [H$^\beta$ and H$^{\beta'}$], 7.10–7.90 [C_6H_5]. ^{13}C NMR (selected data in ppm): 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 [$\rangle$C=N—].

5a: Anal. (%) calcd (found) for $C_{29}H_{33}$NFePPdCl: C, 55.79 (55.7); H, 5.33 (5.3); N, 2.24 (2.2). IR (KBr pellets): ν($\rangle$C=N—) = 1583 cm^{-1}. ^{1}H NMR (in ppm): 3.99 [C_5H_5], 3.62 [H^3], 4.18 [H^4], 4.41 [H^5], 2.03 [—C(Me)=N—], 2.36 [Me], 2.06–2.38 [—CH_2—], 1.02–1.50 [Me], 6.98 [H$^\alpha$ and H$^{\alpha'}$], 7.19 [H$^\beta$ and H$^{\beta'}$], 7.36–8.10 [C_6H_5]. ^{13}C NMR (selected data in ppm): 71.20 [C_5H_5], 101.46 [C^1], 90.79 [C^2], 68.32 [C^3], 67.40 [C^4], 69.32 [C^5] 183.02 [$\rangle$C=N—].

6a: Anal. (%) calcd (found) for $C_{25}H_{33}$NFePPdCl: C, 52.11 (52.05); H, 5.77 (5.8); N, 2.43 (2.4). IR (KBr pellets): ν($\rangle$C=N—) = 1590 cm^{-1}. ^{1}H NMR (in ppm): 4.03 [C_5H_5], 4.35 [H^3], 4.29 [H^4], 4.40 [H^5], 2.08 [—C(Me)=N—], 2.37 [Me], 2.00–2.30 [—CH_2—], 0.95–1.30 [Me], 6.85 [H$^\alpha$ and H$^{\alpha'}$], 7.02 [H$^\beta$ and H$^{\beta'}$]. ^{13}C NMR (selected data in ppm): 71.21 [C_5H_5], 67.82 [C^3], 67.52 [C^4], 69.12 [C^5], 183.16 [$\rangle$C=N—].

Syntheses of 3–6b

These compounds were prepared using the same procedure as described above for **3**–**6a** but using **2b** as the starting material.[11] (Yields: 78, 75, 69 and 72% for **3**–**6b**, respectively).

3b: Anal. (%) calcd (found) for $C_{31}H_{31}$NFePPdCl: C, 57.61 (57.7); H, 4.83 (4.9); N, 2.17 (2.1). ^{1}H NMR (in ppm): 3.79 [C_5H_5], 3.60 [H^3], 3.75 [H^4], 4.00 [H^5], 3.54 and 3.00 [—CH_2N—], 2.57 and 2.60 [—N(Me)$_2$], 7.20–7.95 [aromatic]. ^{13}C NMR (selected data in ppm): 69.39 [C_5H_5], 97.22 [C^1], 95.17 [C^2], 69.73 [C^3], 65.30 [C^4], 69.58 [C^5], 60.57 [—CH_2N—], 51.23 [Me].

4b: Anal. (%) calcd (found) for $C_{27}H_{31}$NFePPdCl: C, 54.21 (54.3), H, 5.22 (5.2); N, 2.34 (2.3). ^{1}H NMR (in ppm): 3.72 [C_5H_5], 3.52 [H^3], 3.76 [H^4], 3.96 [H^5], 3.57 and 3.18 [—CH_2N—], 3.24 and 3.00 [—N(Me)$_2$], 2.10–2.40 [—CH_2—], 0.90–1.40 [—CH_3], 7.30–8.00 [C_6H_5]. ^{13}C NMR (selected data in ppm): 69.52 [C_5H_5], 97.01 [C^1], 95.42 [C^2], 69.82 [C^3], 65.54 [C^4], 69.80 [C^5], 61.40 [—CH_2N—], 51.18 [Me].

5b: Anal. (%) calcd (found) for $C_{23}H_{31}$NFePPdCl: C, 50.21 (49.8), H, 5.68 (6.6); N, 2.55 (2.45). ^{1}H NMR (in ppm): 3.88 [C_5H_5], 3.43 [H^3], 3.08 [H^4], 3.95 [H^5], 3.50 and 3.42 [—CH_2N—], 3.20 and 2.98 [2—N(Me)$_2$], 2.00–2.45 [—CH_2—], 1.00–1.40 [Me], 7.30–7.95 [C_6H_5]. ^{13}C NMR (selected data in ppm): 69.40 [C_5H_5], 97.12 [C^1], 94.92 [C^2], 69.31 [C^3], 65.96 [C^4], 69.85 [C^5], 61.42 [—CH_2N—], 50.02 [Me].

6b: Anal. (%) calcd (found) for $C_{19}H_{30}$NFePPdCl: C, 45.45 (45.4); H, 6.22 (6.1); N, 2.79 (2.7). ^{1}H NMR (in ppm): 3.90 [C_5H_5], 4.40 [H^3], 4.01 [H^4], 3.98 [H^5], 3.51 and 3.05

[$-CH_2N-$], 3.20 and 2.95 [$-N(Me)_2$], 2.00–2.30 [$-CH_2-$], 0.95–1.30 [Me]. ^{13}C NMR (selected data in ppm): 69.25 [C_5H_5], 68.86 [C^3], 65.68 [C^4], 69.70 [C^5], 61.50 [$-CH_2N-$], 50.93 [Me].

Electrochemical studies

Electrochemical data for the compounds under study were obtained by cyclic voltammetry under argon at *ca.* 20 °C, using acetonitrile (HPLC grade) as solvent and tetrabutylammonium hexafluorophosphate as supporting electrolyte. The redox half-wave potentials were referred to an $Ag/AgNO_3$ (0.1 M, in acetonitrile) electrode separated from the solution by a medium porosity fritted disc. A platinum wire auxiliary electrode was used in conjunction with a platinum disk working electrode, Tacussel EDI rotatory electrode (3.14 mm^2). Cyclic voltammograms of 10^{-3} M solutions of the samples in acetonitrile were recorded with a Versstat, EG&G Princeton Applied Research potentiostat.

Crystal structure resolution and refinement

Prismatic crystals of compounds **3a** and **3b** were selected and mounted on a Philips-110 four-circle diffractometer. Unit cell parameters were determined from automatic centering of 24 reflections in the range ($8° < \Theta < 21°$) and refined by the least-squares method. Intensities were collected with graphite monochromated MoKα radiation using $\omega - 2\Theta$ scan technique. The reflections (9087 for **3a** and 2550 for **3b**) were measured in the ranges of $2.23° \leqslant \Theta \leqslant 30.0°$ for **3a** and $3.70° \leqslant \Theta \leqslant 24.98°$ for **3b**. The number of independent reflections in the two cases are given in Table 3. In both cases, three reflections were measured every two hours for orientation and intensity control and no significant intensity decay was observed. Lorentz polarization corrections were made, but absorption corrections were not.

The structures were solved by direct methods using SHELX[23] and refined by the full-matrix least-squares method using SHELX93.[24] The function minimized was $\sum w||F_0|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + 0.0995P^2]^{-1}$ for **3a**, $w = [\sigma^2(F_0^2) + (0.1254P)^2 + 2.1781P]^{-1}$ for **3b** and $P = [|F_0|^2 + 2|F_c|^2]/3$. f, f' and f'' were taken from the literature.[25] The C(13) atom for **3b** gave an abnormal temperature factor and the short N—C(13) bond length suggests a possible disorder in its localization. Twenty-seven hydrogen atoms in **3a** (and all hydrogen atoms in **3b**) were located from a difference synthesis. For complex **3a** the remaining six hydrogen atoms were computed. All the hydrogen atoms (in **3a** and **3b**) were refined with an overall isotropic temperature factor using a riding model for computed H atoms. The final *R* indices and further details concerning the refinement of the structures are summarized in Table 3. CCDC reference number 440/048.

Computational details

The calculations were performed with the SPARTAN 4.1 suite of programs[22] using a Silicon Graphics workstation (INDIGO-2 power XZ). The PM3(tm) method was used with the default parameters provided by the program. Geometrical restrictions were not imposed in any case. The calculations were performed using the option SCF = converge. The number of geometry optimization cycles required was greater than the default value. A minimum of 1500 cycles was necessary in all cases.

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