Influence of substituents on the electrochemical properties of nine-membered palladacycles of general formula $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$

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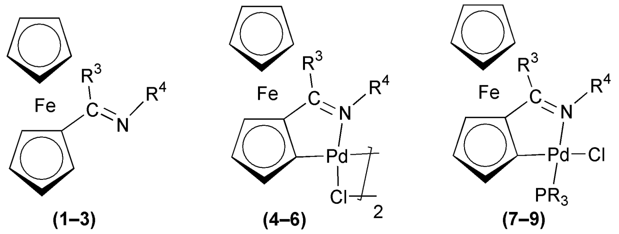
The reactions of the di-μ-chloro-bridged cyclopalladated complex $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ with several alkynes, $R^1C{\equiv}CR^2$, in a 1 : 4 molar ratio are described. They led to novel nine-membered palladacycles of general formula $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$, and to the di-μ-chloro-bridged derivative $[Pd\{[(EtO_2CC{=}CPh)(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$, which contains a seven-membered palladacycle. A comparative study of the electrochemical properties of a wide variety of nine-membered palladacycles containing ferrocenyl units of general formula $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ {with R^3 = H or Me and R^4 = Ph, CH_2Ph, CH(Me)Ph, CH_2CH_2OH or $C_6H_4C_6H_5$-2} is also reported. Molecular orbital calculations at a DFT level have also been carried out to rationalize the influence of the nature of the substituents R^1, R^2, R^3 and R^4 in the nine-membered rings on the electrochemical properties of these two types of palladacycles.

Introduction

Heteropolynuclear compounds containing ferrocenyl units have attracted great interest in the last decade. The presence of a transition metal in the vicinity of iron(II) may modify the properties of the ferrocenyl fragment, *i.e.* its reactivity, its proclivity to be oxidized, *etc.*[1] Among the heteronuclear complexes reported so far, palladium compounds, and to a lesser extent platinum(II) derivatives, with a σ(M–C sp², ferrocene) bond have become particularly interesting due to their applications in different areas.[2–4]

Most of the studies reported so far have involved monomeric or dimeric palladium(II) complexes formed by activation of the *ortho* σ(C sp², ferrocene H) bond of ferrocenyl aldimines or ketimines of general formula $[Fe\{\eta^5\text{-}C_5H_4C(R^3){=}NR^4\}(\eta^5\text{-}C_5H_5)]$ {with R^3 = H (**1**), Me (**2**) or Ph (**3**) and R^4 = phenyl, benzyl or naphthyl}. These reactions have led to dimeric or monomeric complexes of general formula $[Pd\{[\eta^5\text{-}C_5H_3C(R^3){=}NR^4]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ **4**–**6** or $[Pd\{[\eta^5\text{-}C_5H_3C(R^3){=}NR^4]Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$ **7**–**9** {R^3 = H, Me or Ph; R^4 = phenyl, benzyl or naphthyl; L = a phosphine ligand}, Scheme 1.[5] Electrochemical studies based on cyclic voltammetry of the palladium(II) compounds have revealed that in the free imines (**1**–**3**) the ferrocenyl unit is less prone to oxidation than in the palladium(II) complexes (**4**–**9**). Furthermore, only tiny changes in the nature of the substituents (R^3 and R^4) or in the neutral ligand, L, are needed to modify the half-wave potential of iron(II) in these systems.[6]

It is well known that many cyclopalladated complexes are useful precursors in the synthesis of organic or organometallic compounds.[4a,b,7] Most of these reactions involve the insertion of small molecules, *i.e.* alkynes, alkenes or CO, into the σ(Pd–C) bond.[8–12] However, articles focusing on the reactivity of the σ(Pd–C sp², ferrocene) bond are not common. Some examples of bis(insertion) of symmetric alkynes $R^1C{\equiv}CR^1$, R^1 being Et or Ph, into the σ(Pd–C sp², ferrocene) bond of $[Pd\{[\eta^5\text{-}C_5H_3C(R^3){=}NR^4]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {R^3 = H or Me and R^4 = CH_2Ph} have recently been reported. These reactions lead to nine-membered palladacycles containing a η³-butadienyl fragment directly attached to the C_5H_3 ring of the ferrocenyl unit of general formula $[Pd\{[(R^1C{=}CR^1)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ {R^1 = Et or Ph, R^3 = H or Me and R^4 = C_6H_5 or $CH_2C_6H_5$}, Scheme 2. However, studies based on the reactivity of cyclopalladated complexes containing σ(Pd–C sp², ferrocene) bonds towards asymmetric or internal alkynes $R^1C{\equiv}CR^2$ having one or two electron-withdrawing groups, *i.e.* R^1 or R^2 = CO_2Me or CO_2Et, are not so common[12] and the influence of the electron-donor or withdrawing nature of the substituents in the nine-membered palladacycles on the properties of this sort of compound, *i.e.* the proclivity of iron(II) to be oxidized, has not yet been established.



(1–3) **(4–6)** **(7–9)**

R3	R4	
H	CH_2Ph	**1a**
H	CH(Me)Ph	**1b**
H	$C_6H_4C_6H_5$-2	**1c**
Me	CH_2Ph	**2a**
Ph	CH_2Ph	**3a**

R3	R4	
H	CH_2Ph	**4a**
H	CH(Me)Ph	**4b**
H	$C_6H_4C_6H_5$-2	**4c**
Me	CH_2Ph	**5a**
Ph	CH_2Ph	**6a**

R3	R4	
H	CH_2Ph	**7a**
H	CH(Me)Ph	**7b**
H	$C_6H_4C_6H_5$-2	**7c**
Me	CH_2Ph	**8a**
Ph	CH_2Ph	**9a**

Scheme 1 Ferrocenyl Schiff bases $[Fe\{\eta^5\text{-}C_5H_4C(R^3){=}NR^4\}(\eta^5\text{-}C_5H_5)]$ **1**–**3** and their dimeric or monomeric derivatives containing five-membered palladacycles of general formula $[Pd\{[\eta^5\text{-}C_5H_3C(R^3){=}NR^4](Fe\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ **4**–**6** and $[Pd\{[\eta^5\text{-}C_5H_3C(R^3){=}NR^4]Fe(\eta^5\text{-}C_5H_5)\}(L)Cl]$ **7**–**9** (L = phosphine).

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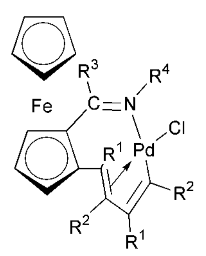


R^1	R^2	R^3	R^4
Et	Et	H	CH_2Ph
Et	Et	H	CH(Me)Ph
Et	Et	H	$C_6H_4C_6H_5$-2
Et	Et	Me	CH_2Ph
Ph	Ph	H	CH_2Ph
Ph	Ph	H	CH(Me)Ph
Ph	Ph	H	$C_6H_4C_6H_5$-2
Ph	Ph	Me	CH_2Ph
CO_2Me	CO_2Me	H	CH(Me)Ph
CO_2Me	CO_2Me	H	$C_6H_4C_6H_5$-2

Scheme 2 Nine-membered metallacycles formed by bis(insertion) of $R^1C{\equiv}CR^2$ {$R^1 = R^2 =$ Et, Ph or CO_2Me} into the σ(Pd–C sp^2, ferrocene) bond.

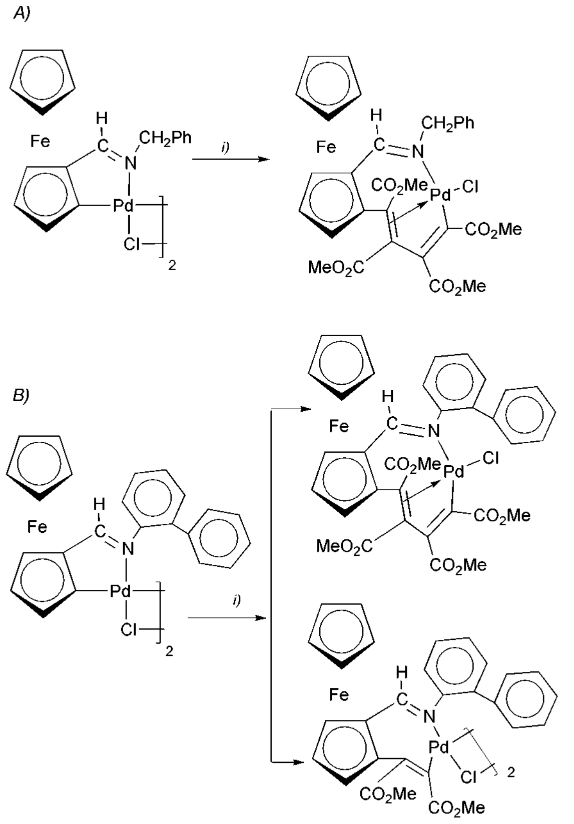
In this work we present the results from the reaction of $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ with four different alkynes of general formula $R^1C{\equiv}CR^2$ {$R^1 = R^2 = CO_2Me$, $R^1 = CO_2Et$, $R^2 = Ph$, $R^1 = Me$, $R^2 = Ph$ and $R^1 = H$, $R^2 = Ph$} whereby four new nine-membered metallacycles and a dinuclear complex, $[Pd\{[(EtO_2CC{=}CPh)(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$, have been isolated and characterized. Furthermore, a comparative study of the electrochemical properties ofthe new compounds and those of related palladacycles containing nine-membered rings of general formula $[Pd\{[(R^1C{=}CR^2)_2\text{-}(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ {$R^3 =$ H, Me or Ph, $R^4 = CH_2Ph$}, Scheme 2, has been performed. Theoretical studies using density functional theory (DFT) calculations, have also been carried out in order to elucidate the factors that may permit tuning of the electrochemical properties of this sort of palladacycle by appropriate selection of the substituents (R^1, R^2, R^3 or R^4).

Results and discussion

Syntheses and characterization

When $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ [5a,b] was treated with $MeO_2CC{\equiv}CCO_2Me$ in a 1 : 4 molar ratio in refluxing $CHCl_3$ for 1.5 h a dark brown soluwas obtained from which $[Pd\{[(MeO_2CC{=}CCO_2Me)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (Scheme 3, *A*) could be isolated by SiO_2 column chromatography in a yield of 67.5%. This compound, which contains a nine-membered palladacycle, arises by bis(insertion) of the alkyne into the σ(Pd–C sp^2, ferrocene) bond. No evidence of the mono(insertion) derivative could be detected by NMR spectroscopy in the course of the reaction. This finding differs from what is observed in the reaction of $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NC_6H_4C_6H_5\text{-}2]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ with $MeO_2CC{\equiv}CCO_2Me$ under identical experimental conditions by which both the mono- and bis(insertion) derivatives were formed (Scheme 3, *B*).[12a] This suggests that the presence of the bulky 2-biphenyl group on the imine nitrogen atom hinders at least partially the insertion of the second alkyne molecule.

Reactions of cyclopalladated complexes with asymmetric alkynes, $R^1C{\equiv}CR^2$, are also interesting from the point of view that they may lead to a wide variety of compounds depending on not only the number of alkynes molecules being inserted into the σ(Pd–C) bond but also on the relative arrangement of the R^1 and R^2 groups in the final products. As a first approach to evaluate the importance of the electronic and steric properties (Table 1)[13] of the substituents R^1 and R^2 in the alkynes on the nature of the final products we decided to study the reactivity of the di-μ-chloro-bridged cyclopalladated compound $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ towards $R^1C{\equiv}CPh$, R^1 being CO_2Et, Me or H, compounds that differ only in the nature of the R^1 group.



Scheme 3 (*i*) 4 $MeO_2CC{\equiv}CCO_2Me$ in refluxing chloroform (1.5 h) followed by SiO_2-column chromatography.

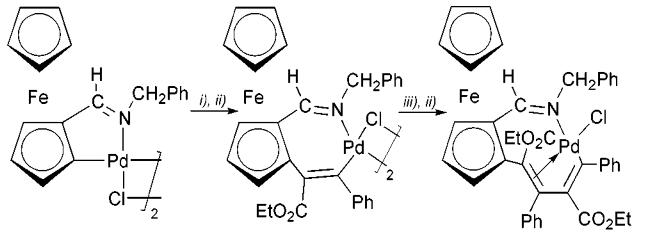
In order to elucidate the importance of the substituents (R^1 or Ph) on the stereoselectivity of the insertion process we studied the reaction of $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ and $EtO_2CC{\equiv}CPh$ (in a 1 : 4 molar ratio) in refluxing $CHCl_3$ for 1.5 h. This reaction, after work-up by column chromatography, led to a red solid with elemental analyses (see Experimental) as well as NMR data suggesting the product to be a di-μ-chloro-bridged cyclopalladated complex, $[Pd\{[(EtO_2CC{=}CPh)(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]\text{-}Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ (Scheme 4). This product arises by monoinsertion of the alkyne into the σ(Pd–C sp^2, ferrocene) bond and contains a seven-membered palladacycle. No evidence of the bis(insertion) complex could be detected by NMR spectroscopy.

A comparison of the chemical shifts of the protons of the CO_2Et fragment in this complex and in related derivatives formed by insertion of one molecule of $EtO_2CC{\equiv}CPh$ into the σ(Pd–C sp^2, aryl) bond[9c,14] allowed us to postulate the arrangement of the CO_2Et and Ph groups as depicted in Scheme 4. This is consistent with the fact that in the majority

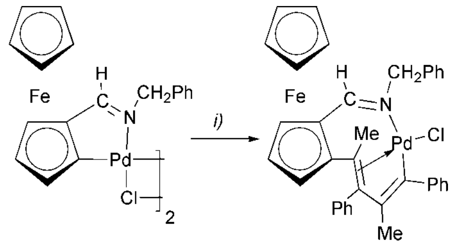
Table 1 Electronic and steric parameters[a] of the substituents R^1 and R^2 in $R^1C{\equiv}CR^2$

R^1 or R^2	σ_I	σ_R	ES-CH
H	+0.00	+0.00	0.0
Me	−0.08	−0.15	1.0
Et	−0.01	−0.14	2.0
Ph	0.12	0.10	3.0
CO_2Me	0.21	0.16	4.0
CO_2Et	0.21	0.16	4.0

[a] σ_I and σ_R are inductive (*para*) and mesomeric (*para*) parameters of substituents R^1 and R^2. Positive σ values indicate electron-withdrawing character of the substituent, negative values refer to electron-donor properties. The ES-CH values are Charton's steric parameters calculated according to structural data for R^1 and R^2. The parameters shown in this table are from ref. 13.



Scheme 4 (*i*) 4 $EtO_2CC{\equiv}CPh$ in refluxing chloroform (1.5 h); (*ii*) SiO_2-column chromatography; (*iii*) 2 $EtO_2CC{\equiv}CPh$ in refluxing chloroform (24 h).



Scheme 5 (*i*) 4 $MeC{\equiv}CPh$ in refluxing chloroform (1.5 h) followed by SiO_2-column chromatography.

of the cases for which this kind of reaction has been studied the insertion reaction proceeds in such a way that the ester group ends up away from the palladium atom.

These results are in sharp contrast with those reported for $[Pd\{[\eta^5\text{-}C_5H_3CH_2NMe_2]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ when reacting with $EtO_2CC{\equiv}CPh$ in a 1 : 4 molar ratio under milder experimental conditions, in CH_2Cl_2 at room temperature for 3 h, to give the bis(insertion) derivative $[Pd\{[(EtO_2CC{=}CPh)_2(\eta^5\text{-}C_5H_3CH_2NMe_2)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$.[14] In order to compare the reactivity of the σ(Pd–C sp^2, ferrocene) bond in the two dimeric complexes, $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ was also the subject of treatment with $EtO_2CC{\equiv}CPh$ at room temperature in CH_2Cl_2 for varying periods, from 30 min to 5 h. However, in this case the corresponding mono- or bis-(insertion) products could not be detected and the starting material was recovered. This indicated that the σ(Pd–C sp^2, ferrocene) bond in $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ is significantly less reactive than the corresponding bond in $[Pd\{[\eta^5\text{-}C_5H_3CH_2NMe_2]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$.

Further treatment of the di-m-chloro-bridged complex $[Pd\{[(EtO_2CC{=}CPh)(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ with $EtO_2CC{\equiv}CPh$ in refluxing $CHCl_3$ for longer reaction periods (24 h) led to the bis(insertion) derivative $[Pd\{[(EtO_2CC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$. The chemical shifts of the protons of the CO_2Et groups in this complex are similar to those reported for $[Pd\{[(EtO_2CC{=}CPh)_2(\eta^5\text{-}C_5H_3CH_2NMe_2)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$[9c] suggesting the relative orientation of the CO_2Et and Ph groups in these compounds to be similar.

According to previous mechanistic studies on the double insertion of $R^1C{\equiv}CR^2$ into the σ(Pd–C sp^2, phenyl) bond of $[Pd(C_6H_4CH_2NMe_2)(\mu\text{-}X)]_2$, X = Cl or AcO, the reaction proceeds in two steps: the insertion of a first alkyne molecule followed by a *cis* → *trans* isomerization of the olefinic fragment during insertion of the second alkyne molecule.[15] In the latter step the steric effects arising from the relative arrangement of the R^1 and R^2 substituents and/or changes in the charge of the terminal carbon atom in the monoinsertion product may play an important role. Since it is known that $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ reacts under similar experimental conditions with diphenylacetylene to give the bis(insertion) complex $[Pd\{[(PhC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$, the results obtained in the reaction with $EtO_2CC{\equiv}CPh$ suggest that the presence of the electron-withdrawing and bulky CO_2Et group hinders at least partially the insertion of the second alkyne molecule.

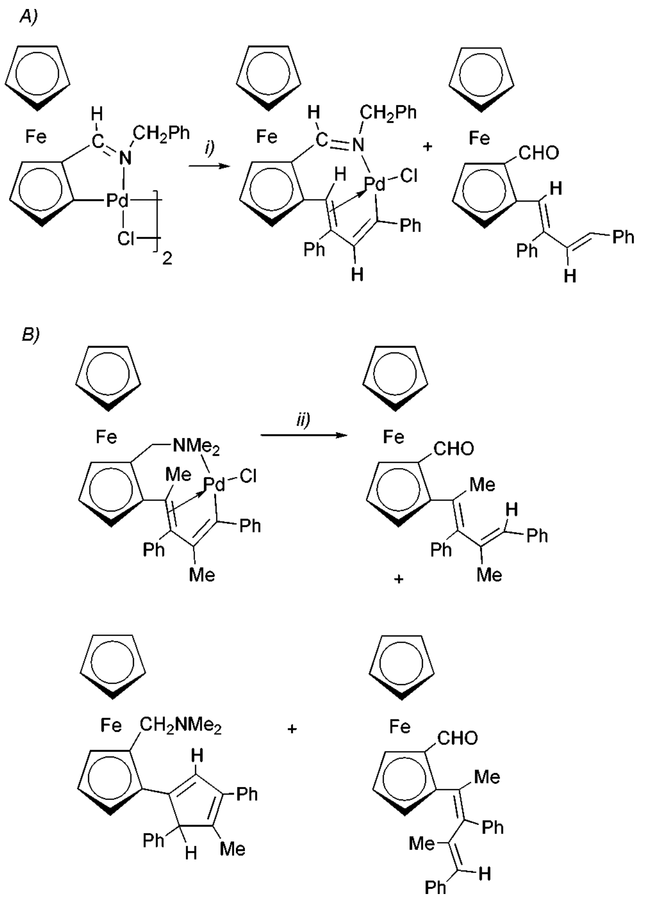
The reaction of $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ with $MeC{\equiv}CPh$, under experimental conditions as described above for $MeO_2CC{\equiv}CCO_2Me$, led to an orange solid. The elemental analyses (see below) were consistent with those expected for the bis(insertion) derivative, $[Pd\{[(MeC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$, Scheme 5. Depending on the relative arrangement of the Me and Ph groups, this product may exist in different isomeric forms. However, the proton and $^{13}C\text{-}\{^1H\}$ NMR spectra revealed that only one isomer was present in the solution suggesting a high degree of selectivity in the reaction. The NMR signals due to the methyl protons were similar to those reported for $[Pd\{[(MeC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NC_6H_4C_6H_5\text{-}2)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$[12a] suggesting a similar arrangement of the R^1 and Ph groups in these compounds.

Since $R^1C{\equiv}CPh$ differ only in the nature of the R^1 group[13] the differences detected in the nature of the final products from the reactions of $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ with $EtO_2CC{\equiv}CPh$, $MeC{\equiv}CPh$ and $PhC{\equiv}CPh$ suggest that in the monoinsertion complexes, $[Pd\{[(R^1C{=}CPh)(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$, the presence of the electron-withdrawing substituent, $R^1 = CO_2Et$,[13] may introduce significant variations in the net charge of the terminal atom bound to the phenyl in the seven-membered ring. This may be responsible for the inhibition of the insertion of the second alkyne molecule.

During the reaction of $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ with the monosubstituted alkyne, $HC{\equiv}CPh$, under identical experimental conditions, a larger amount of metallic palladium was observed. The ^1H NMR spectrum of the crude material exhibited highly complex patterns at δ 3.0–7.0 and at 7.9–10.5. Three singlets at δ 8.20, 9.75 and 10.2 were detected. However, the signal at higher fields could not be ascribed to the protons of the CH=N group of the free imine or the starting palladium(II) complex. The remaining two singlets, at δ 9.75 and 10.2, might suggest the presence of a CHO group, none of which, however, could be ascribed to ferrocenecarbaldehyde. Apparently, this reaction is far more complex than the ones described above and that at least three different compounds are formed. Unfortunately, only two compounds could be isolated by SiO_2-column chromatography and the characterization data of the major component, which was isolated as an orange–red solid, agreed with those expected for the bis(insertion) product: $[Pd\{[(HC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (Scheme 6, *A*). The other component was isolated as a yellow oily material with a ^1H NMR spectrum showing a singlet at δ *ca.* 9.75 and a group of 7 singlets, with relative intensities of 5 : 1 : 1 : 1 : 1 : 1 : 1 in the range δ 6.0–3.5. The infrared spectrum showed an intense band at 1689 cm^{-1}. On this basis and according to the microanalytical data,[16] combined with the results obtained for the depalladation of $[Pd\{[(MeC{=}CPh)_2(\eta^5\text{-}C_5H_3CH_2NMe_2)]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ (Scheme 6, *B*)[9c] which show a complexity of compounds, we may suggest that the minor component in the mixture is $[Fe[1\text{-}(CHO),2\text{-}\{C(H){=}C(Ph)C(H){=}C(Ph)H\}(\eta^5\text{-}C_5H_3)](\eta^5\text{-}C_5H_5)]$. The complexity of the reaction of $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ with $HC{\equiv}CPh$ may be related to the acidity of this alkyne[17] which may promote the hydrolysis of the imine and the depalladation reaction.

Influence of substituents on the proclivity of nine-membered palladacycles to oxidation

As a first approach to elucidate the influence of the nature of the substituents R^1 and R^2 (Table 1) on the nine-membered palladacycles of general formula $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ we decided to study the



Scheme 6 (*i*) 4 HC≡CPh in refluxing chloroform (1.5 h) followed by SiO_2-column chromatography (see text); (*ii*) PPh_3 in methanol [see ref. 9(*c*)].

electrochemical properties of the new nine-membered palladacycles and of related derivatives with $R^3 = H$ and $R^4 = C_6H_4C_6H_5$-2. Electrochemical data for all compounds were obtained by cyclic voltammetry of 10^{-3} M solutions in acetonitrile (HPLC grade). The cyclic voltammograms of the nine-membered palladacycles showed in all cases one anodic peak with a directly associated reduction peak in the reverse scan (Fig. 1) except for the compounds containing two electron-withdrawing groups $\{R^1 = R^2 = CO_2Me\}$ for which no reduction peak was detected in the reverse scan. This has also been observed for $[Pd\{[(MeO_2CC{=}CCO_2Me)_2(\eta^5\text{-}C_5H_3C(H){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$, $R^4 = CH(Me)Ph$ or CH_2CH_2OH,[11a,12] suggesting the oxidation to be electrochemically irreversible.

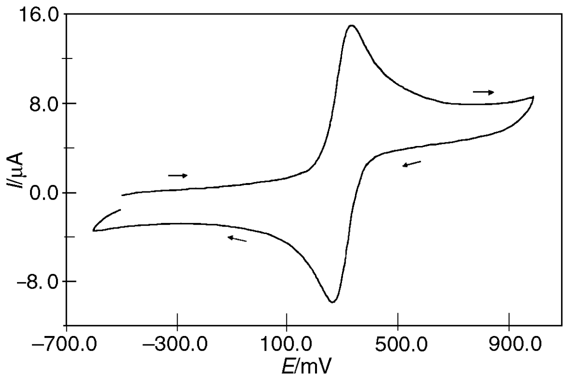


Fig. 1 Cyclic voltammogram of $[Pd\{[(MeC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$.

A summary of the electrochemical data for the compounds and the related nine-membered palladacycles is presented in Table 2. The data reveal that the nine-membered palladacycles are less prone to oxidation than the corresponding free ligands and the di-μ-chloro-bridged cyclopalladated complexes[6] while $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ are less prone to be oxidized than their analogues $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(H){=}NCH(Me)Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ containing identical R^3 and R^4 groups (Fig. 2). Additionally, for the two families of compounds the proclivity of the ferrocenyl unit to be oxidized is strongly dependent on the nature of the substituents R^1 and R^2 on the η^3-butadienyl moiety. In particular, electron-withdrawing groups, such as CO_2Me or CO_2Et, hinder the oxidation process. These findings are consistent with the conclusions reached by Zanello *et al.*[18] on the electrochemical behaviour of penta- and deca-substituted ferrocenes of general formula $[Fe(\eta^5\text{-}C_5R_5)(\eta^5\text{-}C_5R'_5)]$, $R = R' = H$, Me or Ph or $R = H$ and $R' =$ Me, Et or Ph, indicating that replacement of hydrogen atoms in the pentagonal rings by better electron-donor groups (*i.e.* Me or Et)[13] will facilitate oxidation of the iron centre.[18]

Table 2 Electrochemical data: anodic and cathodic potentials (E_{pa} and E_{pc}, respectively) and peak to peak separation: ΔE ($\Delta E = E_{pa} - E_{pc}$) (in mV) for the nine-membered palladacycles of general formula $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$

R^1	R^2	R^3	R^4	E_{pa}	E_{pc}	ΔE	Ref.
Et	Et	H	CH_2Ph	362	287	75	11(*a*)
Ph	Ph	H	CH_2Ph	383	297	86	11(*a*)
CO_2Me	CO_2Me	H	CH_2Ph	482	[a]	—	This work
CO_2Et	Ph	H	CH_2Ph	436	308	128	This work
Me	Ph	H	CH_2Ph	371	285	86	This work
H	Ph	H	CH_2Ph	390	298	92	This work
Et	Et	H	CH(Me)Ph	330	204	126	12
Ph	Ph	H	CH(Me)Ph	379	262	117	12
CO_2Me	CO_2Me	H	CH(Me)Ph	464	[a]	—	12
CO_2Et	Ph	H	CH(Me)Ph	417	293	126	12
H	Ph	H	CH(Me)Ph	373	251	122	12
Me	Ph	H	CH(Me)Ph	346	235	111	12
Et	Et	H	CH_2CH_2OH	318	201	117	11(*c*)
Ph	Ph	H	CH_2CH_2OH	336	231	105	11(*c*)
CO_2Me	CO_2Me	H	CH_2CH_2OH	375	[a]	—	11(*c*)
Et	Et	H	$C_6H_4C_6H_5$-2	293	203	90	This work
Ph	Ph	H	$C_6H_4C_6H_5$-2	329	253	76	This work
CO_2Me	CO_2Me	H	$C_6H_4C_6H_5$-2	420	[a]	—	This work
Et	Et	Me	CH_2Ph	364	275	89	11(*a*)
Ph	Ph	Me	CH_2Ph	352	247	135	11(*a*)

[a] No reduction peak detected in the reverse scan.

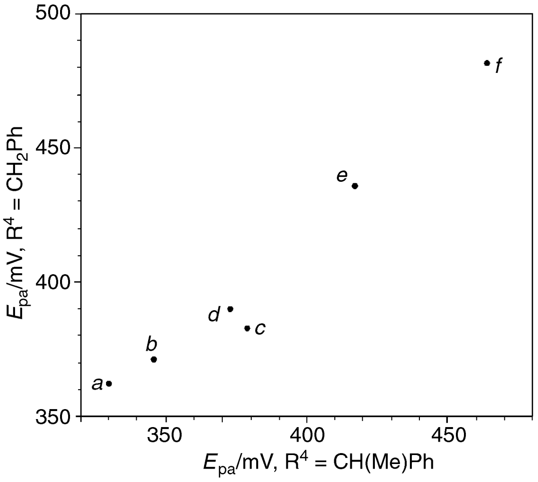


Fig. 2 Graphical representation of the anodic potentials (E_{pa}) for $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ *vs.* the values reported for (R_p,R)-$[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(H){=}NCH(Me)Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$[12b] with $R^1 = R^2$ = Et (*a*); R^2 = Ph and R^1 = Me (*b*), H (*c*), Ph (*d*) or CO_2Et (*e*) and $R^1 = R^2 = CO_2Me$ (*f*).

Theoretical approaches

In a first attempt to understand the effect of the substituents R^1 and R^2 on the η^3-butadienyl moiety, and on the imine fragment, R^3 and R^4, upon the electronic environment of the ferrocenyl unit we decided to perform molecular orbital (MO) calculations on simplified model complexes of general formula $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ {R^3 and R^4 = H or Me and $R^1 = R^2$ = Me, CO_2Me or CF_3; R^1 = H, Me or CO_2Me, R^2 = Ph}. The main differences between the model complexes and the real compounds were the replacement of both ethyl groups, R^1 or R^2, and the aryl or benzyl groups linked to the imine nitrogen by methyl groups. The first approach was undertaken in order to minimize problems that might arise due to the presence of the more flexible substituents.

The calculations were performed at a DFT level with the SPARTAN 5.0 suite of programs.[19] The HOMO and LUMO of the model compound $[Pd\{[(HC{=}CH)_2(\eta^5\text{-}C_5H_3C(H){=}NMe)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ are depicted in Fig. 3. The HOMO (Fig. 3) is mainly a combination of a π^* of the ferrocenyl moiety, the $d_{x^2-y^2}$ orbital of palladium and a small contribution of the p_z orbital of the imine nitrogen atom and the π-orbital of the butadienyl unit. This suggests that in the HOMO of the studied nine-membered palladacycles there is a lack of π conjugation between the $>\!C{=}N-$ group and the ferrocenyl fragment, contrary to the case in ferrocenyl Schiff bases and five-membered palladacycles for which the HOMO appears to contain a certain degree of conjugation between the functional group and the ferrocenyl fragment. These findings are consistent with results obtained by Mössbauer spectroscopy:[11a] the quadrupole splitting values of $[Pd\{[(EtC{=}CEt)_2(\eta^5\text{-}C_5H_3C(R^3){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ being 2.31(1) and 2.32(1) mm s^{-1} for R^3 = H and Me and larger than for the parent ligands $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4C(R^3){=}NCH_2Ph\}]$, quadrupole splitting = 2.24(1) for R^3 = H and 2.16(1) mm s^{-1} for R^3 = Me.[11a] This observation can only be explained by assuming that by incorporation of the η^3-butadienyl fragment a decrease of the π conjugation between the imine and ferrocenyl fragments in the nine-membered metallacycles will take place. The present calculations performed at a DFT level seem also to confirm this hypothesis.

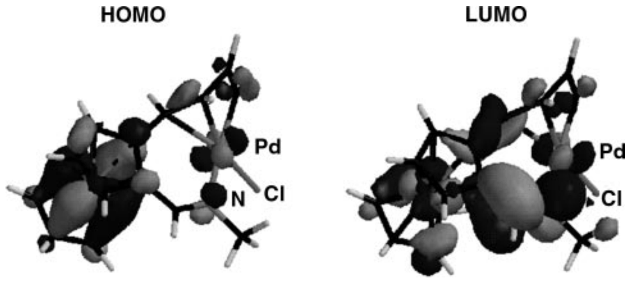


Fig. 3 HOMO and LUMO of $[Pd\{[(HC{=}CH)_2(\eta^5\text{-}C_5H_3C(H){=}NMe)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$.

In the studied systems the presence of electron-withdrawing groups, *i.e.* CO_2Me or CF_3, in the η^3-butadienyl moiety decreases the energy of the HOMO (Table 3). This is consistent with the experimental fact that these compounds are oxidized only at higher potentials. On the contrary, the presence of electron-donor groups facilitates the oxidation process. In addition, for compounds of the general type $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ with identical R^3 and R^4 groups the data shown in Table 3 also reveal that an increase of the electron-donor character of the R^3 group leads to an increase of the energy of the HOMO and, consequently, the oxidation will require smaller potentials. This is consistent with results obtained from a comparison of the anodic potentials (E_{pa}) for $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ with $R^4 = CH_2Ph$ and CH(Me)Ph shown in Fig. 2.

Conclusions

The present results reveal that the nine-membered palladacycles formed by the bis(insertion) of $R^1C{\equiv}CR^2$ into the σ(Pd–C sp^2, ferrocene) bond of $[Pd\{[\eta^5\text{-}C_5H_3C(R^3){=}NR^4]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ are more resistant to oxidation than the corresponding five-membered palladacycles. Futhermore, only minor changes in the nature of the substituents, R^1, R^2, R^3 and R^4, in the nine-membered metallacycles $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ are

Table 3 Values of the energies (in eV) obtained from the DFT calculations for the HOMO and LUMO orbitals and for the gap (ΔE_{gap}) for the nine-membered palladacycles of general formula $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$

R^1	R^2	R^3	R^4	*E*(HOMO)	*E*(LUMO)	ΔE_{gap}
H	H	H	Me	−5.004	−2.617	2.387
Me	Me	H	Me	−4.723	−2.487	2.236
CO_2Me	CO_2Me	H	Me	−5.084	−2.901	2.183
CF_3	CF_3	H	Me	−5.603	−3.647	1.956
Ph	Ph	H	Me	−4.926	−2.585	2.341
CO_2Me	CO_2Me	H	Me	−5.001	−2.728	2.273
H	Ph	H	H	−5.047	−2.738	2.309
Me	Ph	H	H	−4.998	−2.592	2.406
Me	Me	H	H	−4.971	−2.491	2.480

needed to influence the ease by which the oxidation process takes place. The theoretical calculations suggest that since the HOMO of $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ involves some conjugation between the η^3-butadienyl unit and the C_5H_3 ring of the ferrocenyl unit, the replacement of an electron-donor substituent in the inserted fragment by an electron-withdrawing group will modify the electronic ring current of the ferrocenyl moiety.

Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Científico-Tècnics de la Universitat de Barcelona. Infrared spectra were obtained with a Nicolet-520 FTIR instrument using KBr pellets, routine ^1H NMR spectra at 20 °C on a Gemini 200 MHz instrument using $CDCl_3$ (99.9%) as solvent and $SiMe_4$ as internal reference. High resolution ^1H-NMR spectra with a Varian 500 MHz and $^{13}C\text{-}\{^1H\}$NMR spectra with a Bruker 250DXR instrument using $CDCl_3$ as solvent and $SiMe_4$ as reference.

The alkynes, $R^1C{\equiv}CR^2$, with $R^1 = R^2 = CO_2Me$, $R^1 = CO_2Et$ and $R^2 = Ph$; $R^1 = Me$ and $R^2 = Ph$ or $R^1 = H$ and $R^2 = Ph$, were obtained from commercial sources and used as received. All solvents were dried over CaO and distilled before use, except acetonitrile which was of HPLC grade. The di-μ-chloro-bridged cyclopalladated complexes, $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$, and the compounds of general formula $[Pd\{[(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3C(R^3){=}NR^4)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ ($R^3 = H$, $R^4 = CH_2Ph$, $R^1 = R^2 = Et$ or Ph, $R^3 = H$, $R^4 = C_6H_4C_6H_5\text{-}2$, $R^1 = R^2 = Et$, Ph or CO_2Me; $R^3 = Me$, $R^4 = CH_2Ph$, $R^1 = R^2 = Et$) were prepared as described previously.[5–7,12]

Preparation of the compounds

$[Pd\{[(MeO_2CC{=}CCO_2Me)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$. $MeO_2CC{\equiv}CCO_2Me$, 138 μL, 11.2×10^{-4} mol, was added dropwise to a suspension of 250 mg (2.81×10^{-4} mol) $[Pd\{[\eta^5\text{-}C_5H_3CH{=}NCH_2Ph]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ in 20 mL of $CHCl_3$. The reaction mixture was finally refluxed for 1.5 h. The resulting solution was filtered to remove some insoluble black material and then concentrated to *ca.* 5 mL by a rotary evaporator. The deep brown solution was passed through a SiO_2 column (15 cm × 1.5 cm) using a $CHCl_3$–CH_3OH (100 : 1) mixture as eluent. The deep red band released during the elution was collected and evaporated to dryness on a rotary evaporator giving a red solid which was dried in vacuum. Yield: 276 mg, 67.5%. Anal. (%): C, 49.61; H, 4.02 and N, 1.98: $C_{30}H_{28}ClFeNO_8Pd$ requires: C, 49.48; H, 3.88 and N, 1.92. IR (KBr pellets): ν(C=O) at 1726 and ν(C=N) at 1632 cm^{-1}. ^1H NMR: δ 3.85 [s, 5H, C_5H_5], 4.82 [s, 1H, H^3], 5.06 [s, 1H, H^4], 4.46 [s, 1H, H^5], 4.71 and 5.46 [dd, 2H, CH_2]; 8.03 [s, 1H, CH=N], 3.53 [s, 3H, OMe], 3.69 [s, 3H, OMe], 4.09 [s, 3H, OMe], 4.34 [s, 3H, OMe] and 7.0–7.6 [m, 5H, aromatic].

$[Pd\{[(MeC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$. This compound was prepared as described above but using a stoichiometric amount of $MeC{\equiv}CPh$ (140 μL, 11.8×10^{-4} mol). After work-up an orange solid was obtained which was collected and dried in vacuum for 12 h. Yield: 210 mg, 55.2%. Anal. (%): C, 64.06; H, 4.82 and N, 2.10: $C_{36}H_{32}ClFeNPd$ requires: C, 63.93; H, 4.77 and N, 2.07. IR (KBr pellets): ν(C=N) at 1622 cm^{-1}. ^1H NMR: δ 4.28 [s, 5H, C_5H_5], 4.36 [s, 1H, H^3], 4.86 [s, 1H, H^4], 5.08 [s, 1H, H^5], 4.79 and 5.22 [dd, 2H, CH_2], 7.62 [s, 1H, CH=N], 2.73 [s, 3H, Me], 2.47 [s, 3H, Me], 6.7–7.4 [m, 15H, aromatic]. $^{13}C\text{-}\{^1H\}$ NMR: δ 71.16 [C_5H_5], 73.95 [C^3], 72.46 [C^4], 73.95 [C^5], 69.48 [NCH_2], 165.89 [CH=N], 12.43 [Me] and 14.18 [Me].

$[Pd\{[(EtO_2CC{=}CPh)(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$. To a suspension of the di-μ-chloro-bridged cyclopalladated complex $[Pd\{[\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph]\text{-}Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ (250 mg, 2.81×10^{-4} mol) in 15 mL of $CHCl_3$, $EtO_2CC{\equiv}CPh$ (78 μL, 5.6×10^{-4} mol) was added dropwise. After the addition was complete the reaction mixture was refluxed for 1 h. The resulting mixture was allowed to cool to room temperature and then filtered. Slow evaporation of the filtrate at room temperature led to an orange solid which was collected by filtration and air-dried. Yield: 296 mg, 74.1%. Anal. (%): C, 54.32; H, 4.0 and N, 2.2. $C_{60}H_{52}Cl_2Fe_2N_2O_8Pd_2$ requires: C, 54.41; H, 3.96 and N, 2.12. IR (KBr pellets): ν(C=O) at 1712 cm^{-1} and ν(C=N) at 1618 cm^{-1}. ^1H NMR: δ 4.34 [s, 10H, 2 C_5H_5], 4.20 [s, 2H, 2 H^3], 4.71 [s, 2H, 2 H^4], 5.12 [s, 2H, 2 H^5], 4.78 and 5.30 [dd, 4H, 2 CH_2], 7.67 [s, 1H, 2 CH=N], 3.86 [m, 4H, 2 CH_2 (CO_2Et)], 0.79 [t, 6H, 2 Me (CO_2Et)] and 6.92–7.5 [m, 32H, 2 CH=N and aromatic].

$[Pd\{[(EtO_2CC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$. The di-μ-chloro-bridged cyclopalladated complex $[Pd\{[(EtO_2CC{=}CPh)(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}\text{-}(\mu\text{-}Cl)]_2$, 100 mg, 7.5×10^{-5} mol, was suspended in 20 mL of $CHCl_3$, and $EtO_2CC{\equiv}CPh$, 25 μL, 1.5×10^{-4} mol, added dropwise. The reaction mixture was finally refluxed for 24 h. During this period a palladium mirror was formed. The resulting solution was filtered and concentrated to *ca.* 5 mL by a rotary evaporator and then passed through a SiO_2 column. Elution with $CHCl_3$–CH_3OH (100 : 1) led to the release of a red band which was collected and concentrated to dryness by a rotary evaporator. The solid formed was dried in vacuum for 24 h at room temperature. Yield: 45 mg, 37%. Anal. (%): C, 60.42; H, 4.20 and N, 1.80; $C_{40}H_{36}ClFeNO_4Pd$ requires: C, 60.63; H, 4.18 and N, 1.77. IR (KBr pellets): ν(CO) at 1708 cm^{-1} and ν(C=N) at 1627 cm^{-1}. ^1H NMR: δ 4.34 [s, 5H, C_5H_5], 4.39 [s, 1H, H^3], 4.67 [s, 1H, H^4], 5.06 [s, 1H, H^5], 4.12 and 5.23 [dd, 2H, CH_2], 7.67 [s, 1H, CH=N], 3.81 and 4.12 [m, 4H, 2 CH_2 (CO_2Et)], 0.79 and 1.26 [t, 6H, 2 Me (CO_2Et)] and 6.92–7.5 [m, 15H, aromatic]. $^{13}C\text{-}\{^1H\}$ NMR (selected): δ 72.21 [C_5H_5], 88.32 [C^1], 95.21 [C^2], 73.07 [C^3], 73.10 [C^4], 71.84 [C^5], 63.80 [NCH_2], 67.47 and 59.78 [CH_2 (CO_2Et)], 14.10 and 13.64 [Me (CO_2Et)] and 167.20 [CH=N].

$[Pd\{[(HC{=}CPh)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$. This compound was prepared as described above for $[Pd\{[(MeO_2CC{=}CCO_2Me)_2(\eta^5\text{-}C_5H_3C(H){=}NCH_2Ph)]\text{-}Fe(\eta^5\text{-}C_5H_5)\}Cl]$ but using a stoichiometric amount of $HC{\equiv}CPh$ (123 μL, 11.8×10^{-4} mol). Yield: 116 mg, 31.2%. Anal. (%): C, 63.1; H, 4.20 and N, 2.2. $C_{34}H_{28}ClFeNPd$ requires: C, 62.99; H, 4.35 and N, 2.16. ^1H NMR: δ 4.36 [s, 5H, C_5H_5], 4.92 [s, 1H, H^3], 5.12 [s, 1H, H^4], 4.58 [s, 1H, H^5], 4.48 and 5.46 [dd, 2H, CH_2], 8.20 [s, 1H, CH=N], 4.69 [s, 2H, $>$CH], 4.85 [s, 2H, $>$CH] and 6.85–7.40 [m, 15H, aromatic].

Electrochemical studies

Electrochemical data for the compounds were obtained by cyclic voltammetry under argon at 20 °C using acetonitrile (HPLC grade) as solvent and tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The measured potentials were referred to a Ag–$AgNO_3$ (0.1 M in acetonitrile) electrode separated by a medium porosity fritted disc. A platinum wire auxiliary electrode was used in conjunction with a platinum disc working electrode (TACUSSEL-EDI rotatory electrode) (3.14 mm^2). Cyclic voltammograms of

10^{-3} M solutions of the samples in acetonitrile were run and the measured potentials referred to ferrocene as internal standard to facilitate interpretation of the results. In all cases the experiments were carried out at different scan rates v, from 0.01 to 1.00 V s^{-1}.

Computational details

The DFT calculations were performed using the SPARTAN 5.0 suite of programs[19] implemented on a Silicon Graphics workstation (INDIGO-2 power XZ). No geometrical restrictions were imposed. They calculations were carried out at the BP86 level[20] using the basis set labelled as DN* in the program.[19] This is a numerical basis set that incorporates a polarization function on the non-hydrogen atoms.

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