DALTON
FULL PAPER

A comparative study of the reactivity of the σ(Pd–$C_{sp^2,\ ferrocene}$) and σ(Pd–$C_{sp^2,\ biphenyl}$) bonds in cyclopalladated complexes derived from [Fe(η^5-C_5H_5)(η^5-$C_5H_4CH{=}NC_6H_4C_6H_5$-2)]

Mónica Benito,[a] Concepción López,*[a] Xavier Morvan,[a] Xavier Solans[b] and Mercè Font-Bardía[b]

[a] *Departament de Química Inorgànica, Universitat de Barcelona, Martí Franquès 1-11, E-08028, Barcelona, Spain. E-mail: conchi.lopez@qi.ub.es*
[b] *Departament de Cristal·lografía, Mineralogía i Dipòsits Minerals, Martí Franquès s/n., E-08028 Barcelona, Spain*

Received 18th September 2000, Accepted 2nd October 2000
First published as an Advance Article on the web 15th November 2000

A study has been made of the reactivity of the σ(Pd-C_{sp^2}) bond in the di-μ-chloro-bridged cyclopalladated complexes [Pd{(η^5-$C_5H_3CH{=}NC_6H_4C_6H_5$-2)Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ **1a** and [Pd{(C_6H_4-2-C_6H_4)N=CH(η^5-C_5H_4)Fe(η^5-C_5H_5)}-(μ-Cl)]$_2$ **1b** {which differ in the nature of the metallated carbon atom $C_{sp^2,\ ferrocene}$ or $C_{sp^2,\ biphenyl}$, respectively} towards the alkynes, $R^1C{\equiv}CR^2$ {with $R^1 = R^2 =$ Et; $R^1 =$ H, Me or Ph, and $R^2 =$ Ph; or $R^1 = R^2 = CO_2Me$}. Thus palladacycles containing seven-, eight-, nine- and ten-membered rings have been isolated and characterized. The crystal structure of [Pd{(EtC=CEt)$_2$(C_6H_4-2-C_6H_4)N=CH(η^5-C_5H_4)Fe(η^5-C_5H_5)}Cl] has also been determined and confirms the presence of a [6, 6, 10] tricyclic system arising from fusion of the two hexagonal rings of the biphenyl group and a ten-membered palladacycle generated through bis(insertion) of hex-3-yne into the σ(Pd–$C_{sp^2,\ biphenyl}$) bond in **1b**.

Introduction

The syntheses, characterization and study of cyclopalladated complexes[1–4] has attracted great interest during the last decade due to a wide variety of interesting applications in different areas.[5–13] Some examples of metallomesogens or antitumor drugs containing palladacycles have been reported.[6–8] More recently, the applications of chiral cyclopalladated complexes for the determination of enantiomeric excesses of chiral reagents or for their discrimination have been described.[11–15] However, one of the main interests of this sort of compounds is based on their use as precursors for organic or organometallic synthesis.[16–29] For instance, cyclopalladated complexes show high reactivity towards a wide variety of substrates, such as CO, isocyanides, alkenes or alkynes.[16–28] Reactions of this kind have provided new procedures for the syntheses of novel organic compounds. Several examples of mono-, bis- and even tris-(insertions) of alkynes into the σ(Pd–$C_{sp^2,\ aryl}$) bond have been reported for cyclopalladated complexes derived from organic N-donor ligands.[16–23] However, only a few articles involving insertions of alkynes into the σ(Pd–$C_{sp^2,\ ferrocene}$) bond have been reported so far,[25–30] and most of them focus exclusively on the insertion of diphenylacetylene.

On the other hand, studies on the insertion of alkynes into the σ(Pd–$C_{sp^2,\ aryl}$) bond have shown that differences in the reactivity of the σ(Pd–C) bond in cyclopalladated derivatives may be related to a wide variety of factors, including: (*a*) the lability of the Pd–N bond, (*b*) the nature of the substituents on the alkyne ligand, (*c*) the structure of the metallacycle, and (*d*) the remaining ligands bound to the palladium.[17–19] However, the relative importance of these factors has yet to be clarified.

Table 1 Electronic and steric parameters of the substituents on the alkyne[a]

R^1 or R^2	σ_I	σ_R	Es'CH
H	0.0	0.0	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

[a] σ_I and σ_R are the inductive (*para*) and mesomeric (*para*) parameters of the substituents R^1 and R^2. Positive σ values indicate the electron-withdrawing character of the substituent, negative electron donor groups. The Es'CH values are Chartons's steric parameters for R^1 and R^2 substituents calculated according to structural data. All the values presented in this table were taken from reference 32.

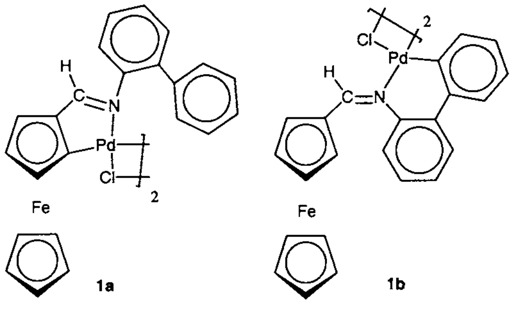


Fig. 1 Schematic view of the two di-μ-chloro-bridged cyclopalladated complexes **1a** and **1b**.

Furthermore, it has recently been reported that cyclopalladation of the ferrocenyl Schiff base [Fe(η^5-C_5H_5)(η^5-$C_5H_4CH{=}NC_6H_4C_6H_5$-2)] produces two types of metallacycle [Pd{(η^5-$C_5H_3CH{=}NC_6H_4C_6H_5$-2)Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ **1a** and [Pd{(C_6H_4-2-C_6H_4)N=CH(η^5-C_5H_4)Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ **1b** (Fig. 1)[31] which differ in the nature of the metallated carbon atom {$C_{sp^2,\ ferrocene}$ in **1a** or $C_{sp^2,\ biphenyl}$ in **1b**}. Here we compare the reactivity of the two types of σ(Pd–C) bond *versus* a wide variety of alkynes $R^1C{\equiv}CR^2$ {with $R^1 = R^2 =$ Et; $R^1 =$ H, Me or Ph and $R^2 =$ Ph; or $R^1 = R^2 = CO_2Me$} which differ in the electronic and steric properties[32] of the substituents R^1 and R^2 (Table 1). This type of study could be useful to elucidate the relative influence of (*i*) the substituents on the alkyne {electron-donor/electron-withdrawing character and/or their

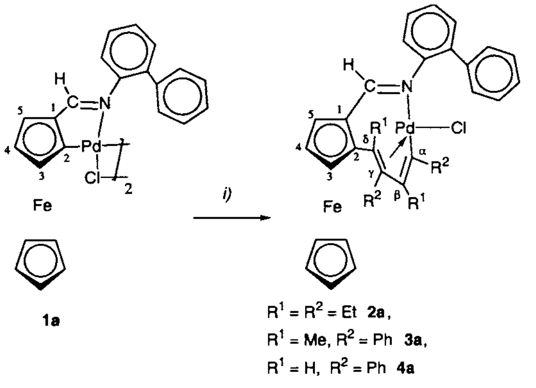
DOI: 10.1039/b007537j

bulk} and (*ii*) the structure of the metallacycle upon the final product.

Results and discussion

Alkyne insertions

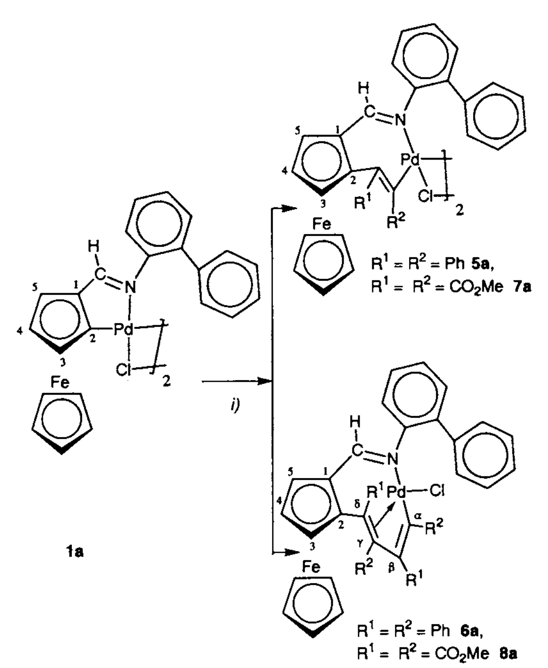
When $[Pd\{(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)_2]$ **1a** was treated separately with the alkynes $R^1C{\equiv}CR^2$ {with $R^1 = R^2 = Et$; $R^1 = Me$, $R^2 = Ph$; or $R^1 = H$, $R^2 = Ph$} in a 1 : 4 molar ratio in refluxing $CHCl_3$ for 1.5 h a brown-red solution was obtained and compounds $[Pd\{(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ **2a**–**4a** (Scheme 1) were isolated by SiO_2 column chromatography. Compounds **2a**–**4a** arose from the bis(insertion) of the corresponding alkyne into the $\sigma(Pd\text{–}C_{sp^2,\,ferrocene})$ bond. These results are in good agreement with previous studies on compounds $[Pd\{(\eta^5\text{-}C_5H_3C(R){=}NCH_2C_6H_5)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {with R = H or Me}, which also react with hex-3-yne giving bis(insertion) products.[27,28]



Scheme 1 (*i*) 4 $R^1C{\equiv}CR^2$ in refluxing $CHCl_3$, followed by SiO_2 column chromatography.

The bis(insertion) of the asymmetric alkynes $R^1C{\equiv}CPh$ (with $R^1 = Me$ or H) into the $\sigma(Pd\text{–}C_{sp^2,\,ferrocene})$ bond of compound **1a** has an additional interest since the two terminal groups have different electronic and steric properties which may be important in determining the nature of the final product. Depending on the relative arrangement of the substituents (Me or H) and phenyl groups in the η^3-butadienyl moiety of the nine-membered rings of $[Pd\{(R^1C{=}CPh)_2(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ ($R^1 = Me$ or H) this reaction may produce different isomeric species. In addition, previous studies on bis(insertions) of symmetric alkynes into the $\sigma(Pd\text{–}C_{sp^2,\,ferrocene})$ bond of $[Pd\{(\eta^5\text{-}C_5H_3CH_2NMe_2)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ allowed the isolation and characterization of two isomers of $[Pd\{(R^1C{=}CR^2)_2(\eta^5\text{-}C_5H_3CH_2NMe_2)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ {with $R^1 = R^2 = Et$} which differed in the orientation of the nine-membered ring with respect to the iron(II).[33] On this basis, the bis(insertion) of the alkynes $R^1C{\equiv}CPh$ into the $\sigma(Pd\text{–}C_{sp^2,\,ferrocene})$ bond of **1a** could provide additional information about the importance of the properties of the substituents (R^1 and Ph) in determining the nature of the final products formed in the process, *i.e.* the number of isomers of $[Pd\{(R^1C{=}CPh)_2(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ and their relative abundance. One- and two-dimensional NMR spectra of **3a** and **4a** (see below) revealed that only one species was present in solution. This suggested that the formation of one of the isomers occurred preferentially and consequently bis(insertion) of the alkynes $R^1C{\equiv}CPh$ proceeded with a higher degree of selectivity. For **3a** and **4a**, the arrangement of the substituents (R^1 and Ph) depicted in Scheme 1 is consistent with the NMR studies discussed below.

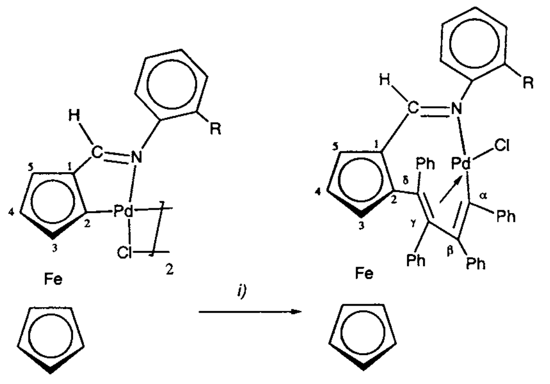
When the reaction was carried out using diphenylacetylene (Scheme 2), under identical experimental conditions, two compounds (**5a** and **6a**) were isolated by SiO_2 column chromatography. Elution with $CHCl_3$ gave a red band which contained the minor component. According to its elemental analyses and NMR spectra {^1H and ^{13}C} it was identified as $[Pd\{(PhC{=}CPh)(\eta^5\text{-}C_5H_3)CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ **5a**. This complex contains a [5,7] bicyclic system derived from fusion of the C_5H_3 ring and a seven-membered metallacycle, which is formed through the insertion of one molecule of $PhC{\equiv}CPh$ into the $\sigma(Pd\text{–}C_{sp^2,\,ferrocene})$ bond (Scheme 2). The major component was obtained from elution with $CHCl_3$–methanol (100 : 2), and its characterization (see Experimental section) was consistent with that expected for $[Pd\{(PhC{=}CPh)_2(\eta^5\text{-}C_5H_3\text{-}CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ **6a** which contains a nine-membered palladacycle generated in the bis(insertion) process.



Scheme 2 (*i*) 4 $R^1C{\equiv}CR^2$ in refluxing $CHCl_3$, followed by SiO_2 column chromatography.

These results are in contrast with those reported previously,[27,28] which have shown that the cyclopalladated compounds $[Pd\{(\eta^5\text{-}C_5H_3C(R){=}NCH_2C_6H_5)Fe(\eta^5\text{-}C_5H_5)\}\text{-}(\mu\text{-}Cl)]_2$ {with R = H (**1c**) or Me (**1d**)} react with $PhC{\equiv}CPh$ {in a 1 : 4 molar ratio} to produce the bis(insertion) compounds $[Pd\{(Ph\text{–}C{=}C\text{–}Ph)_2(\eta^5\text{-}C_5H_3C(R){=}NCH_2C_6H_5)Fe(\eta^5\text{-}C_5H_5)\}\text{-}Cl]$ {with R = H (**6c**) or Me (**6d**)}, and no evidence of the formation of any other complex was detected by ^1H or $^{13}C\text{-}\{^1H\}$ NMR. These findings suggest that the presence of the two phenyl rings on the alkyne might introduce significant steric effects which may hinder insertion of the second molecule of $PhC{\equiv}CPh$. According to mechanistic studies on alkyne insertions reported by Ryabov *et al.*[19] a *cis* ⟶ *trans* isomerization of the olefinic fragment (of the monoinsertion product) takes place during insertion of the second molecule of the alkyne. The use of molecular models of **5a** reveals that in the seven-membered palladacycle, where the two phenyl groups of the >C=C< moiety are in a *cis* arrangement, the environment of the metallacycle is crowded due to the arrangement of the ferrocenyl, phenyl and biphenyl groups. This arrangement of ligands may play an important role in the insertion of the second alkyne molecule. In a first attempt to elucidate whether the different reactivity of compound **1a** compared to those of **1c** and **1d** could be related to the presence of a bulky substituent bound to the imine nitrogen, we studied the reactions of compounds $[Pd\{(\eta^5\text{-}C_5H_3CH{=}NC_6H_4R\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {R = H (**1e**) or Me (**1f**)} previously reported.[34,36] These compounds can be visualized as derived from **1a** by replacement of the *ortho* phenyl ligand by either a hydrogen (in **1e**) or a methyl (in **1f**). According to the literature the basicity of the N-donor atom does not differ significantly in the three complexes.[37] Besides, the stability of the σ(Pd–N) bond in **1e**, **1f** is similar to that of **1a**.[31,34–36] On this basis, comparison of the reactions of compounds **1a**, **1e** and **1f** could show whether an increase in the effective bulk of the substituent in the *ortho* site is important to the nature of the products formed in the reaction of these di-μ-chloro-bridged derivatives with diphenylacetylene.

When complex **1e** or **1f** was treated with an excess of PhC≡CPh {in a molar ratio alkyne : Pd^{II} = 2 : 1} in refluxing chloroform for 1.5 h a deep red solution was obtained. In each case only one band was released by column chromatography and its concentration to dryness produced an orange-red solid. The elemental analyses and NMR data (see Experimental section) were consistent with those expected for the bis(insertion) derivatives $[Pd\{(PhC{=}CPh)_2(\eta^5\text{-}C_5H_3CH{=}NC_6H_4R\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ {R = H (**6e**) or Me (**6f**)} (Scheme 3), and there was no evidence of formation of the corresponding monoinserted derivatives. These results suggest that an increase in the effective bulk of the substituent {*E*s′CH[32] = 0 for H, 1.0 for Me and 3.0 for Ph, Table 1} in the adjacent position to the N-phenyl bond hinders insertion of the second molecule of the alkyne in **1a**.



R = H **1e**, Me **1f**

R = H **6e**, Me **6f**

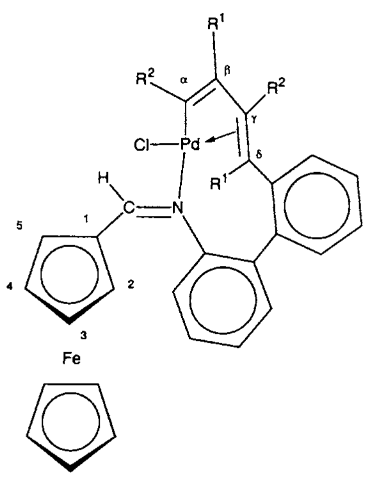
Scheme 3 (*i*) 4 PhC≡CPh in refluxing $CHCl_3$, followed by SiO_2 column chromatography.

Complex **5a**, which is obtained in a higher yield when the reaction is carried out using **1a** and PhC≡CPh in a 1 : 2 molar ratio, also reacts with an additional mole of the alkyne to give **6a**.

Although $MeO_2CC{\equiv}CCO_2Me$ is more reactive[38,39] than any of the other alkynes used in this work, its reaction with **1a** in a 4 : 1 molar ratio (Scheme 2) also produced a mixture of the mono- and bis-(insertion) products (**7a** and **8a**, respectively). This result is similar to that found in the reaction of **1a** with $MeO_2CC{\equiv}CCO_2Me$ (described above) and suggests that in **7a** the two CO_2Me (which are bulkier than the Ph groups) in a *cis* arrangement may hinder insertion of the second molecule of the alkyne. Complex **7a** was also isolated in a higher yield by decreasing the amount of the initial alkyne by 50%.

When these reactions were carried out using compound **1b** as starting material and the alkynes hex-3-yne, 1-phenylprop-1-yne or phenylacetylene, $[Pd\{(R^1C{=}CR^2)_2(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ {$R^1 = R^2$ = Et (**2b**); R^1 = Me, R^2 = Ph (**3b**) or R^1 = H, R^2 = Ph (**4b**)} (Fig. 2) were isolated exclusively, and their characterization data revealed that they contain a tricyclic [6, 6, 10] system formed by the two aryl rings of the biphenyl group and a ten-membered palladacycle {generated in a bis(insertion) process}. The crystal structure of **2b** (see below) confirmed these results. These findings suggest that the two types of σ(Pd–C) bond in **1a** or **1b** show similar reactivity to these three alkynes.

Similarly to what was mentioned above for compounds **3a** and **4a**, bis(insertion) of the asymmetric alkynes 1-phenylprop-1-yne or phenylacetylene into the σ(Pd–$C_{sp^2,\ biphenyl}$) bond may produce different isomers depending on the relative arrangement of the R^1 (Me or H) and Ph groups in the η^3-butadienyl fragment of the ten-membered palladacycles $[Pd\{(R^1C{=}CPh)_2(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ with R^1 = Me or H. However, the (^{1}H and ^{13}C) NMR spectra of **3b** and **4b** (see below) revealed that only one of the isomers was present in solution, suggesting that bis(insertion) of the alkynes $R^1C{\equiv}CPh$ {R^1 = Me or H} took place with a high degree of selectivity.



R^1	R^2	Compound
Et	Et	**2b**
Me	Ph	**3b**
H	Ph	**4b**
Ph	Ph	**6b**
CO_2Me	CO_2Me	**8b**

Fig. 2 Schematic view of the ten-membered palladacycles obtained in bis(insertion) of the alkynes $R^1C{\equiv}CR^2$ {where $R^1 = R^2$ = Et, Ph or CO_2Me; or R^1 = H or Me and R^2 = Ph} into the σ(Pd–$C_{sp^2,\ biphenyl}$) bond of complex **1b**.

When the acetylene was PhC≡CPh the reaction was more complex and the mono- and bis-(insertion) products $[Pd\{(PhC{=}CPh)(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ **5b** and $[Pd\{(PhC{=}CPh)_2(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ **6b** were isolated by SiO_2 column chromatography. In order to confirm this result the reaction was repeated using a Pd : PhC≡CPh molar ratio of 1 : 1, and in this case **5b** was obtained exclusively. Further treatment of **5b** with the stoichiometric amount of the corresponding alkyne in refluxing $CHCl_3$ also allowed us to isolate the bis(insertion) product **6b**.

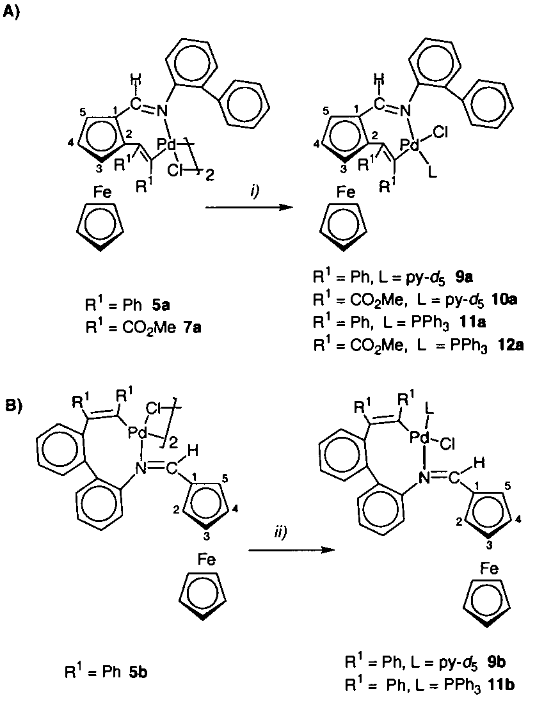
In contrast to the results obtained for **1a**, when $MeO_2CC{\equiv}CCO_2Me$ and the di-μ-chloro-bridged cyclopalladated complex **1b** (in a 4 : 1 molar ratio) were refluxed in chloroform for 1.5 h only the bis(insertion) derivative $[Pd\{(MeO_2CC{=}CCO_2Me)_2(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl]$ **8b** was obtained.

As mentioned above, the differences observed in the reactivity of the σ(Pd–C) bond in cyclopalladated derivatives may be related to a wide variety of factors. Previous studies on the reactivity of compound **1a** or **1b** with PPh_3 have demonstrated that the Pd–N bond is highly stable since no evidence of its cleavage was detected in either **1a** or **1b**.[31] In spite of this poor lability the insertion of the alkynes $R^1C{\equiv}CR^2$ takes place, which suggests that the reaction is not initiated through cleavage of this bond, in agreement with the results reported by Ryabov *et al.*[19] on the insertion of alkynes into the σ(Pd–$C_{sp^2,\ phenyl}$) bond of cyclopalladated derivatives containing *N*,*N*-dimethylbenzylamines $[Pd[RC_6H_3CH_2N(CH_3)_2](\mu\text{-}X)]_2$ (R = H, 4-MeO, 5-Me, or 5-F; X = Cl or I), which contain a more labile Pd–N bond.

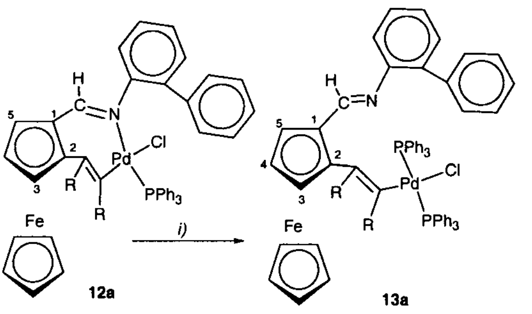
Study of the reactivity of the “Pd(μ-Cl)$_2$Pd” fragments in the monoinsertion compounds *versus* neutral ligands

Potentially bidentate chelating ligands $[C,X]^-$ {where X = N, P, O or S} may adopt different bonding modes and hapticities, which is relevant to catalytic processes. Previous studies on five- and six-membered cyclopalladated complexes derived from Schiff bases have shown that the ease with which the Pd–N bond cleaves depends on the nature of the metallacycle, the relative position of the functional C(R)=N group and the basicity of the nitrogen.[40–46] As mentioned above, the ring of the metallacycle in compounds **1a** and **1b** is unlikely to open, as this would involve cleavage of the Pd–N bond. In this study we isolated and characterized di-μ-chloro-bridged cyclopalladated complexes containing seven- or eight-membered palladacycles: $[Pd\{(R^1C{=}CR^2)(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ $\{R^1 = R^2 = Ph$ (**5a**) or CO_2Me (**7a**)} and $[Pd\{(PhC{=}CPh)(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}(\mu{-}Cl)]_2$ **5b**. On this basis, we examined whether the incorporation of the >C=C< unit into the five- or six-membered metallacycles could modify the lability of the Pd–N bond. With this aim the reactions of the monoinsertion complexes (**5a**,**5b** and **7a**) with deuteriated pyridine (py-d_5) and PPh_3 were studied and the results compared with those for the starting materials **1a**,**1b**.

The addition of an excess of py-d_5 to the monoinsertion products **5a**,**5b** or **7a** produced $[Pd\{(R^1C{=}CR^2)(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}Cl(py\text{-}d_5)]$ $\{R^1 = R^2 = Ph$ (**9a**) or CO_2Me (**10a**)} (Scheme 4, A) or $[Pd\{(PhC{=}CPh)(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(py\text{-}d_5)]$ **9b** (Scheme 4, B). These complexes arise from cleavage of the “Pd(μ-Cl)$_2$Pd” and co-ordination of pyridine to the palladium. Similarly, the corresponding reaction with PPh_3 (in a 1:2 molar ratio) in benzene at room temperature produced cleavage of the “Pd(μ-Cl)$_2$Pd” units and formation of $[Pd\{(R^1C{=}CR^2)(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ $\{R^1 = R^2 = Ph$ (**11a**) or CO_2Me (**12a**)} or $[Pd\{(PhC{=}CPh)(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ **11b** (Scheme 4, A and B). When compounds **11a** and **11b** were treated separately with larger excesses of PPh_3 {in a **11**:PPh_3 molar ratio 2:1} (in $CDCl_3$) no significant variation was observed in their ^{31}P NMR spectra, thus suggesting the poor lability of the Pd–N bond in **11a** and **11b**. In contrast to these results, when the reaction was carried out using **12a** as starting material, the $^{31}P\text{-}\{^1H\}$NMR spectrum was significantly different: the singlet due to the starting material (at δ 27.19) was not observed and a new signal at δ 12.10 appeared. This finding suggested the formation of $[Pd\{(MeO_2CC{=}CCO_2Me)(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2]$ **13a** (Scheme 5) which arose from cleavage of the Pd–N bond and incorporation of a second PPh_3 molecule in the co-ordination sphere of palladium(II). The multiplicity and number of signals detected in the ^1H NMR spectra were also consistent with those expected for **13a**. Comparison of the results obtained in the reactions of complexes **11a**,**11b** and **12a** shows the greater lability of the Pd–N bond in **12a**, which may be related to the stronger electron-withdrawing nature of the CO_2Me group when compared with that of phenyl.[32]



Scheme 4 (*i*) py-d_5 in $CDCl_3$ for **9a** and **10a**, or PPh_3 in benzene for **11a** and **12a** at room temperature; (*ii*) py-d_5 in $CDCl_3$ for **9b** or PPh_3 in benzene for **11b** at room temperature (20 °C).



Scheme 5 R = CO_2Me. (*i*) PPh_3 in $CDCl_3$ at room temperature.

Characterization of the compounds

All the compounds used in this study are orange or dark red solids at room temperature. The mononuclear complexes are highly soluble in $CHCl_3$, CH_2Cl_2, benzene and toluene, but practically insoluble in alkanes and methanol. However, the di-μ-chloro-bridged compounds are less soluble. Elemental analyses are consistent with the proposed formulae (see Experimental section). Infrared spectra of all the compounds show a sharp intense band in the range 1650–1500 cm^{-1}, which is attributed to stretching of the imine group.

Proton NMR studies on five- or six-membered cyclopalladated compounds derived from Schiff bases have shown that the variation observed in the position of the imine hydrogen in the free imine upon *ortho*-palladation reveals the structure (*endo*- or *exo*-cyclic) and conformation of the ligand (*anti* or *syn*) in the cyclopalladated derivatives.[40–58] For palladacycles containing the >C=N group (which can be formed if the imine has an *anti* conformation) the signal is shifted to high field;[50–58] on this basis in **2a**–**13a**, the >C=N group is endocyclic and the imine retains the *anti* conformation. For the exocyclic derivatives the ligand can adopt either conformation (*syn* or *anti*), but for the *syn* the proximity of the methinic proton to the palladium usually produces a downfield shift of the signal of the CH=N proton;[43,46] if the ligand maintains the *anti* conformation of the resonance does not vary appreciably from the position observed for the free imines. Consequently, we can conclude that in compounds **2b**–**11b** the conformation of the imine is *syn*. This type of arrangement provides less steric hindrance between the ligands bound to the palladium and the ferrocenyl fragment. Therefore, in these cases the formation of the palladacycle requires *anti* ⟶ *syn* isomerization of the ligand. It has recently been reported that the enthalpy for isomerization of the ligand (ΔH_{isom}) in $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH{=}NCH_2CH_2NMe_2)\}Cl_2]$ is small (-4.32 kcal mol^{-1}).[56]

These findings are consistent with the number and multiplicities of signals due to protons of the ferrocenyl moiety in the palladium(II) compounds. For instance, four signals of relative

Table 2 ^{13}C-{^{1}H} NMR chemical shifts (in ppm) of the alkylic or alkoxylic carbon nuclei of the R^1 and R^2 groups, of those belonging to the substituted pentagonal ring of the ferrocenyl fragment [C^1–C^5] and the imine carbon atom [CH=N] for compounds **2a**–**8a**, **11a**–**13a** and **2b**–**4b**. Labelling of the atoms corresponds to those shown in Schemes 1–4

Compound	R^1/R^2					C^1	C^2	C^3	C^4	C^5	CH=N
2a^a	Me	12.14	14.30	14.78	15.12	92.99	80.91	71.81	72.15	72.30	167.14
	CH$_2$	23.15	23.35	28.10	30.90						
3a^{b,c}	Me	18.65	28.80			90.43	85.54	71.19	73.04	71.95	168.36
4a$^{b–e}$						92.99	80.91	71.81	74.38	72.65	167.10
6a^{b,c,f}						^{g}	^{g}	70.30	72.54	72.47	168.80
7a^h	OMe	51.44	51.75			87.02	69.90	73.81	75.35	71.90	159.60
8a^h	OMe	51.84	51.93	52.17	52.55	^{g}	^{g}	68.26	75.95	73.08	170.21
11a^{b,f,c}						^{g}	69.66	71.74	73.22	70.83	170.02
12a^h	OMe	51.44	51.75			^{g}	69.66	71.74	73.22	70.83	170.02
13a^h	OMe	51.01	51.19			^{g}	^{g}	70.83	72.61	71.75	170.02
2b^a	Me	12.43	14.47	15.37	15.95	92.57	80.60	71.93	71.93	72.52	165.21
	CH$_2$	22.36	27.59	27.59	31.30						
3b^{b,c}	Me	18.75	28.80			^{g}	85.42	72.70	73.35	72.46	168.29
4b^{d,i}						97.97	80.82	71.73	74.11	72.55	168.01

^{a} R^1 = R^2 = Et. ^{b} R^2 = Ph. ^{c} See text. ^{d} R^1 = H. ^{e} Additional signals at δ 138.60 and 138.97 due to the C$^\alpha$ and C$^\gamma$ carbons of the η^3-butadienyl unit. ^{f} R^2 = Ph. ^{g} Not observed. ^{h} R^1 = R^2 = CO$_2$Me. ^{i} Additional signals at δ 136.67 and 138.90 due to the C$^\alpha$ and C$^\gamma$ carbons of the η^3-butadienyl unit.

intensities 1 : 1 : 1 : 5 in the range δ 3.0–5.0 were detected in the NMR spectra of compounds **2a**–**13a**, which contain a 1,2-disubstituted ferrocenyl moiety, while for **2b**–**9b** and **11b** a set of five signals of intensities 1 : 1 : 1 : 1 : 5 was detected in the same area of the spectrum.

The ^{13}C-{^{1}H}NMR spectra of selected compounds were also recorded, and a summary of the most relevant data is presented in Table 2. The signals due to the carbon nuclei of the CH$_2$, Me or OMe groups belonging to the R^1 or R^2 substituents were easily identified in the high field region of the spectra and provided additional evidence of incorporation of one or two molecules of the alkynes R^{1}C≡CR^2 into the σ(Pd–C) bond in **1a** or **1b**. The positions of these signals were in good agreement with results reported for related palladacycles arising from the mono- or bis-(insertion) of the alkynes under study into the σ(Pd–C$_{\text{sp}^2\text{, aryl}}$) bond having a similar arrangement of the R^1 and R^2 groups.[24,36] Besides that, the signals due to carbon atoms of the ferrocenyl fragment appeared in the range δ 65.0–100.0 (Table 2). For the two families of compounds, the signals due to the *ipso* carbon of the ferrocenyl fragment (C^1) exhibited low intensity and a similar feature was also observed for the resonance of the metallated carbon (C^2) in derivatives arising from insertion of the alkyne into the σ(Pd–C$_{\text{sp}^2\text{, ferrocene}}$) bond. The resonances due to the carbon nuclei of the biphenyl group, the phenyl rings of substituents (R^1 or R^2) or of the PPh$_3$ ligand as well as those of the quaternary carbons (C$^\alpha$, C$^\beta$, C$^\gamma$ and C$^\delta$) of the inserted fragment appeared in a narrow interval and precluded their assignment unambiguously. The signal due to the imine carbon (>C=N) appeared in the range δ 150–171.

In a first attempt to elucidate the relative arrangement of the substituents R^1 (Me or H) and Ph in [Pd{(R^{1}C=CPh)$_2$-(η^5-C$_5$H$_3$CH=NC$_6$H$_4$C$_6$H$_5$-2)Fe(η^5-C$_5$H$_5$)}Cl] {R^1 = Me (**3a**) or H (**4a**)} and [Pd{(R^{1}C=CPh)$_2$(C$_6$H$_4$-2-C$_6$H$_4$)N=CH(η^5-C$_5$H$_4$)Fe-(η^5-C$_5$H$_5$)}Cl] {R^1 = Me (**3b**) or H (**4b**)} their two dimensional [ROESY (rotating-frame Overhauser enhancement spectroscopy) and heteronuclear ^{1}H–^{13}C] NMR spectra were recorded. The most relevant feature observed in the ROESY spectra of **3a** and **4a** was the existence of cross peaks between the H^3 proton of the C$_5$H$_3$ unit and the protons of the methyl group (in **3a**) or the hydrogen in **4a** of the R^1 substituent. Thus suggesting that in compounds **3a** or **4a** the substituent on the carbon directly attached to the ferrocenyl fragment in the nine-membered ring C$^\delta$ is a Me in **3a** and a H in **4a**. Comparison of the position of the signals due to the protons of the other R^1 group with data reported for the two isomers of compound [Pd{(MeC=CPh)$_2$-C$_6$H$_4$CH$_2$NMe$_2$}Cl][24] suggested that the second R^1 is bound to the C$^\beta$ carbon, and consequently the phenyl groups are attached to the C$^\alpha$ and C$^\gamma$ carbons. The arrangement of the Me and Ph groups in **3a** is formally identical to that reported for [Pd-{(MeC=CPh)$_2$(η^5-C$_5$H$_3$CH$_2$NMe$_2$)Fe(η^5-C$_5$H$_5$)}Cl][25] and for one of the isomers of [Pd{(MeC=CPh)$_2$C$_6$H$_4$CH$_2$NMe$_2$}Cl].[24] For the ten-membered palladacycles **3b** and **4b**, analysis of the cross-peaks detected in the two dimensional NMR spectra suggested also close vicinity of the R^1 group (Me in **3b** and H in **4b**) and the CH bond adjacent to the carbon which participated in the formation of the C–C bond in the insertion process. Consequently, the results obtained from these experiments suggested that the smaller substituents (R^1 = Me or H) are linked to the C$^\beta$ and C$^\delta$ atoms of the η^3-butadienyl unit in compounds **3a**, **3b** and **4a**, **4b**.

Phosphorus-31 NMR spectra of compounds containing seven- or eight-membered palladacyles have also been recorded. For **11a**, **11b** and **12a** only one singlet {in the range δ 25.0–29.0} was detected. The position of the signal is consistent with a *trans* arrangement of the PPh$_3$ ligand and the imine nitrogen.[52–60] The high-field shift of the resonance of the phosphorus **11a**, **11b** and **12a**, when compared with those of five- or six-membered palladacycles [Pd{(η^5-C$_5$H$_3$CH=NC$_6$H$_4$R-2)-Fe(η^5-C$_5$H$_5$)}Cl(PPh$_3$)] **14a** {δ 34.29[31]} and [Pd{(C$_6$H$_4$-2-C$_6$H$_4$)N=CH(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}Cl(PPh$_3$)] **14b** {δ 33.86[31]}, obtained in the reaction of **1a** or **1b** with PPh$_3$, can be attributed to the different influence of the chelated ligand in each case. ^{31}P-{^{1}H} NMR spectra of **13a**, which contains two PPh$_3$ ligands bound to the palladium, showed one singlet at higher fields (δ 12.10), in good agreement with values reported for [PdL(Cl)(PPh$_3$)$_2$].[45,58–60]

Crystal structure of [Pd{(EtC=CEt)$_2$(C$_6$H$_4$-2-C$_6$H$_4$)N=CH-(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}Cl] 2b

A perspective drawing of the molecular structure of compound **2b** together with the atom numbering scheme is shown in Fig. 3 and a selection of bond lengths and angles is presented in Table 3. The structure consists of discrete molecules of [Pd{(EtC=CEt)$_2$(C$_6$H$_4$-2-C$_6$H$_4$)N=CH(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}-Cl] separated by van der Waals contacts. The palladium atom is four-co-ordinated, since it is bound to a chlorine, the nitrogen atom, the terminal carbon of the η^3-butadienyl fragment [C(12)] and the middle point of the segment defined by atoms C(18) and C(21), hereinafter referred to as χ. A slightly distorted square-planar environment is the result. The Pd–Cl bond length [2.3186(9) Å] is similar to those found for related complexes, and clearly larger than values reported for related palladacycles with a σ(Pd–C$_{\text{sp}^2\text{, ferrocene}}$) bond. This complex contains a tricyclic system which is formed by fusion of the metallacycle and the two hexagonal rings of the biphenyl

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

Pd–N	2.146(2)	Pd–Cl	2.3186(9)
Pd–C(12)	2.004(3)	Pd–C(15)	2.581(3)
Pd–C(18)	2.180(3)	Pd–C(21)	2.232(3)
C(10)–C(11)	1.447(4)	C(11)–N	1.279(4)
C(12)–C(13)	1.482(5)	C(12)–C(15)	1.321(5)
C(12)–Pd–N	176.67(12)	N–Pd–C(18)	109.30(11)
C(12)–Pd–C(21)	84.84(13)	N–Pd–C(21)	90.42(10)
C(18)–Pd–C(21)	37.31(12)	C(12)–Pd–Cl	95.26(10)
N–Pd–Cl	89.93(7)	C(18)–Pd–Cl	150.35(9)
C(21)–Pd–Cl	170.17(9)	C(12)–Pd–C(15)	30.28(12)
N–Pd–C(15)	144.46(11)	C(18)–Pd–C(15)	35.26(11)
C(21)–Pd–C(15)	61.68(11)	Cl–Pd–C(15)	121.42(8)
C(11)–N–C(35)	121.27(3)	C(11)–N–Pd	128.9(2)
C(35)–N–Pd	108.1(2)	C(9)–C(10)–C(11)	130.1(3)
N–C(11)–C(10)	129.7(3)	C(13)–C(12)–Pd	128.5(3)

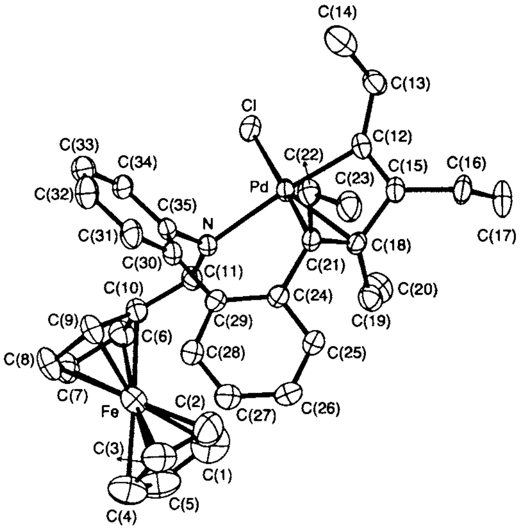


Fig. 3 Molecular structure and atom labelling scheme for compound **2b**.

group. The iminic group is not contained in the metallacycle (exocyclic), and the >C=N bond length {1.279(4) Å} is similar to those found in related ferrocenylmines, which range from 1.24 to 1.26 Å.[61–63]

The ligand has a *syn* conformation as reflected in the torsion angle C(10)–C(11)–N–C(35) 7.8°, thus confirming the conclusions reached from the ^{1}H NMR studies. The double bond of the η^3-butadienyl fragment closest to the biphenyl group is bound unsymmetrically to the palladium, as reflected in the two Pd–C bond distances. This arrangement, also detected in $[Pd\{(PhC{=}CPh)_2(\eta^5\text{-}C_5H_3CH{=}NCH_2Ph)Fe(\eta^5\text{-}C_5H_5)\}Cl]$[27] is different from those reported for most nine-membered metallacycles arising from bis(insertion) of alkynes, and provides less steric hindrance between the remaining substituents.[26,28–30] The distance between the two metals Fe and Pd {5.941 Å} is clearly longer than those reported for cyclopalladated compounds derived from bis(insertion) of hex-3-yne or diphenylacetylene into the $\sigma(Pd\text{–}C_{sp^2,\ ferrocene})$ bond of $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)C(R){=}NCH_2Ph\}(\mu\text{-}Cl)]_2$ (with R = H or Me).[28] The bond distances and angles of the ferrocenyl fragment are in good agreement with those reported for most ferrocene derivatives.[63] The two pentagonal rings of the ferrocenyl fragment are planar and nearly parallel (tilt angle: 0.8°), and their relative orientation is intermediate between the ideal eclipsed and staggered conformations (average value of the twist angle: 17.7°).

Conclusions

The results reported here reveal that for the two di-μ-chloro-bridged derivatives **1a** and **1b** {which differ in the metallated carbon atom: $C_{sp^2,\ ferrocene}$ in **1a** or $C_{sp^2,\ biphenyl}$ in **1b**} the nature of the substituents on the alkynes $R^1C{\equiv}CR^2$ plays a crucial role in determining the size of the metallacycle formed by the insertion. For instance, for $R^1C{\equiv}CR^2$ with non-bulky electron donor groups {such as $R^1 = R^2 =$ Et, R^1 = Me, R^2 = Ph or R^1 = H, R^2 = Ph, Table 1} the reaction produces bis(insertion) products containing nine- {in **2a**–**4a**} or ten-membered {in **2b**–**4b**} metallacycles, and there was no evidence of the formation of compounds arising from monoinsertion of these alkynes {which would yield to seven- or eight-membered rings}. However, when the reactions were carried out using diphenylacetylene, a mixture of products arising from the mono- (**5a** or **5b**) and bis-(insertion) (**6a** or **6b**) of this alkyne into the $\sigma(Pd\text{–}C_{sp^2,\ ferrocene})$ bond (for **1a**) or $\sigma(Pd\text{–}C_{sp^2,\ biphenyl})$ (for **1b**) was obtained. Consequently, the presence of two phenyl rings in the alkyne allowed us to isolate not only the bis(insertion) products, but also the monoinsertion derivatives in both cases. Comparison of the result obtained in the reaction of **1a** with PhC≡CPh and those obtained for the closely related cyclopalladated derivatives of general formulae $[Pd\{(\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nC_6H_5)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {*n* = 1 or 2} and $[Pd\{(\eta^5\text{-}C_5H_3CH{=}NC_6H_4R\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {R = H (**1e**) or Me (**1f**)} (under identical experimental conditions) reveals the importance of the bulky biphenyl substituent in **1a**. These factors suggest that the nature of the substituents bound to the imine nitrogen may also be important in the reactions of the $\sigma(Pd\text{–}C_{sp^2})$ bond *versus* alkynes. According to mechanistic studies on reactions of this type reported by Ryabov *et al.*[19] the formation of the bis(insertion) product requires $cis \longrightarrow trans$ isomerization of the fragment $(R^1)C{=}C(R^2)$. On this basis, it is reasonable to assume that the presence of bulky substituents on the alkyne and on the imine nitrogen will hinder insertion of the second PhC≡CPh molecule.

On the other hand, comparison of the results obtained in the reaction of compound **1a** or **1b** with $MeO_2CC{\equiv}CCO_2Me$ suggests that for **1b** the formation of the bis(insertion) product **8b** is preferred over **1a**, which reacts under identical experimental conditions to produce a mixture of the mono- and bis-(insertion) derivatives {**7a** and **8a**}. This finding can be ascribed to several factors, including the electron-pulling nature and the large bulk of the CO_2Me substituents on the alkene formed in the insertion, which may affect the ease with which the second molecule of the alkyne is inserted.

The use of SPARTAN 5.0 computer program[64] for the mono(insertion) derivatives of general formula $[Pd\{(R^1C{=}CR^2)(\eta^5\text{-}C_5H_3CH{=}NC_6H_4C_6H_5\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {with R^1 = Ph and a nearly orthogonal arrangement of the >C=C< fragment and the co-ordination plane of the palladium and a *cis* orientation of the R^1 and R^2 substituents} reveals that the biphenyl group cannot be coplanar with the imine moiety. For these systems a coplanar arrangement would involve short distances between the C_6H_5 ring and the imine proton or one of the chlorines bound to the palladium, which would make the complex unstable. In addition, the presence of bulky substituents on the >C=C< fragment reduces the free space available for approach of one additional molecule of the alkyne $R^1C{\equiv}CR^2$ to be inserted. This effect may be responsible for the formation of mixtures of monoinsertion and bis(insertion) products in the reaction of **1a** with alkynes having bulky Ph or CO_2Me groups.[32] Finally, the reactions of the di-μ-chloro-bridged cyclopalladated complexes **5a**, **5b** with py-d_5 or PPh_3 suggest low lability of the Pd–N bond. However, for **7a**, in which the seven-membered metallacycle contains two electron-withdrawing groups {CO_2Me} as pendant arms, the addition of excesses of PPh_3 produced cleavage of the Pd–N bond and opening of the metallacycle. This suggests that electron-pulling groups enhance the lability of the Pd–N imine bond.

Experimental

General comments

Triphenylphosphine, deuteriated pyridine (py-d_5, 99.8%) and the alkynes $R^1C\equiv CR^2$ {with $R^1 = R^2 = Et$; $R^1 = Me$, $R^2 = Ph$; $R^1 = H$, $R^2 = Ph$; $R^1 = R^2 = Ph$ or $R^1 = R^2 = CO_2Me$} were obtained from commercial sources and used as received. The di-μ-chloro-bridged cyclopalladated complexes $[Pd\{(\eta^5\text{-}C_5H_3\text{-}CH{=}NC_6H_4R\text{-}2)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ {with $R = C_6H_5$ (**1a**), H (**1e**) or Me (**1f**)} and $[Pd\{(C_6H_4\text{-}2\text{-}C_6H_4)N{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ **1b** were prepared as described elsewhere.[31,34,35] The solvents, except benzene, were dried and distilled before use. Some of the preparations described below require the use of **HAZARDOUS MATERIALS**, such as benzene, which should be handled with **CAUTION**. Elemental analyses (C, H and N) were carried out at the Serveis Cientifico-Tècnics (Universitat de Barcelona). Infrared spectra were obtained with a Nicolet-500-FTIR instrument using KBr pellets. Routine ^{1}H NMR spectra were recorded at 20 °C on a Gemini 200 MHz instrument using $CDCl_3$ (99.9%) as solvent and $SiMe_4$ as internal standard, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} spectra with a Bruker-250DXR instrument using the same solvents. $P(OCH_3)_3$ was used as internal reference for the ^{31}P-{^{1}H} NMR spectra [δ^{31}P for $P(OCH_3)_3$: 141.17]. High resolution ^{1}H and two-dimensional NMR spectra were recorded with either a Varian VRX-500 or a Bruker Advance-DMX 500 MHz instrument.

Preparations

Compounds 2–4. The appropriate di-μ-chloro-bridged cyclopalladated complex (**1a** or **1b**) (0.500 g, 4.94×10^{-3} mol) was suspended in 20 cm^3 of chloroform, and then the corresponding alkyne $R^1C\equiv CR^2$ (1.98×10^{-3} mol) added dropwise at room temperature and with continuous stirring. After the addition, the reaction mixture was refluxed for 1.5 h, allowed to cool to room temperature, and the reddish solution filtered. The undissolved materials were discarded and the filtrate was concentrated to *ca.* 5 cm^3 on a rotary evaporator. The brownish red solutions were then passed through an SiO_2 column (10 mm × 250 mm) using $CHCl_3$–CH_3OH {100:1 for **2a**–**4a** or 100:3 for **2b**–**4b**}. The orange or reddish bands eluted in each case were concentrated to dryness on a rotary evaporator, and the solids were collected, washed in n-hexane and air-dried. Yields: 72 (**2a**), 40 (**2b**), 86 (**3a**), 49 (**3b**), 80 (**4a**) and 45% (**4b**). Compound **2a** (Found: C, 62.9; H, 5.6 and N, 2.2. $C_{35}H_{38}ClFeNPd$ requires: C, 62.7; H, 5.7 and N, 2.1%): IR $\tilde{\nu}_{max}$/cm^{-1} 1625 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 4.15 [s, 5H, C_5H_5], 4.42 [s, 1H, H^3], 4.53 [s, 1H, H^4], 4.60 [s, 1H, H^5]; 7.90 [s, 1H, CH=N]; 1.43 [t, 3H, Me], 1.07 [t, 3H, Me], 0.92 [t, 3H, Me], 0.39 [t, 3H, Me] and 1.90–2.06 [m, 8H, CH_2] and 7.1–7.5 [m, 9H, aromatic]. Compound **2b** (Found: C, 62.7; H, 5.6 and N, 2.2. $C_{35}H_{38}ClFeNPd$ requires: C, 62.7; H, 5.7 and N, 2.1%): IR $\tilde{\nu}_{max}$/cm^{-1} 1625 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 3.98 [s, 5H, C_5H_5], 3.76 [s, 1H, H^2], 4.24 [s, 1H, H^3], 4.28 [s, 1H, H^4], 3.88 [s, 1H, H^5]; 7.89 [s, 1H, CH=N], 1.62 [t, 3H, Me], 1.06 [t, 3H, Me], 0.95 [t, 3H, Me], 0.44 [t, 3H, Me], 2.02–2.52 [br. m, 8H, CH_2] and 7.10–7.45 [m, 8H, aromatic]. Compound **3a** (Found: C, 66.4; H, 4.8 and N, 1.9. $C_{41}H_{34}ClFeNPd$ requires: C, 66.7; H, 4.6 and N, 1.9%): IR $\tilde{\nu}_{max}$/cm^{-1} 1621 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 4.35 [s, 5H, C_5H_5], 4.28 [s, 1H, H^3], 4.39 [s, 1H, H^4], 4.40 [s, 1H, H^5], 8.08 [s, 1H, CH=N], 2.02 [s, 3H, Me], 2.28 [s, 3H, Me] and 6.4–7.6 [m, 19H, aromatic]. Crystal data:^{66} Monoclinic, with $a = 10.795(8)$, $b = 35.439(6)$, $c = 10.973(5)$ Å, $\alpha = 89.9(2)$, $\beta = 106.2(4)$ and $\gamma = 90.0(3)°$. Compound **3b** (Found: C, 61.3; H, 4.4 and N, 1.8. $C_{41}H_{34}ClFeNPd{\cdot}CH_2Cl_2$ requires C, 61.3; H, 4.4 and N, 1.7%): IR $\tilde{\nu}_{max}$/cm^{-1} 1624 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 4.06 [s, 5H, C_5H_5], 3.65 [s, 1H, H^2], 4.35 [s, 1H, H^3], 4.42 [s, 1H, H^4], 4.25 [s, 1H, H^5]; 5.12 [s, 2H, CH_2Cl_2], 8.08 [s, 1H, CH=N], 1.93 [s, 3H, Me], 2.06 [s, 3H, Me] and 6.7–7.9 [m, 18H, aromatic]. Compound **4a** (Found: C, 65.8; H, 4.2 and N, 2.1. $C_{39}H_{30}ClFeNPd$ requires: C, 65.9; H, 4.3 and N, 2.0%): IR $\tilde{\nu}_{max}$/cm^{-1} 1616 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 3.69 [s, 5H, C_5H_5], 3.25 [s, 1H, H^3], 4.23 [s, 1H, H^4], 4.35 [s, 1H, H^5], 8.21 [s, 1H, CH=N], 4.85 [s, 1H, CH=] and 4.69 [s, 1H, CH=] and 6.4–8.0 [m, 19H, aromatic]. Compound **4b** (Found: C, 65.6; H, 4.5 and N, 1.7. $C_{39}H_{30}ClFeNPd$ requires: C, 65.9; H, 4.3 and N, 2.0%): IR $\tilde{\nu}_{max}$/cm^{-1} 1616 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 3.68 [s, 5H, C_5H_5], 3.17 [s, 1H, H^2], 4.24 [s, 1H, H^3], 4.29 [s, 1H, H^4], 4.19 [s, 1H, H^5], 8.06 [s, 1H, CH=N], 5.35 [s, 1H, CH=], 5.06 [s, 1H, CH=] and 6.7–7.5 [m, 18H, aromatic].

Compounds 5. The corresponding di-μ-chloro-cyclopalladated complex (**1a** or **1b**) (250 mg, 2.47×10^{-4} mol) was suspended in 10 cm^3 of $CHCl_3$ and then 89 mg (5.0×10^{-4} mol) of $PhC\equiv CPh$ were added dropwise at room temperature under continuous stirring. Once the addition had finished the reaction mixture was refluxed for 1.5 h and allowed to cool to room temperature. The solution was then passed through a SiO_2 column. Elution with $CHCl_3$ gave a red solution, which was then concentrated to dryness on a rotary evaporator. The residue was treated with n-hexane at room temperature for 30 min, the solid collected by filtration and air-dried. Compound **5a** was recrystallized in a 1:1 mixture of CH_2Cl_2 and n-hexane. Yields: 70 for **5a** and 76% for **5b**. Compound **5a** (Found: C, 63.3; H, 4.1 and N, 1.9. $C_{74}H_{56}Cl_2Fe_2N_2Pd_2{\cdot}\frac{1}{2}CH_2Cl_2$ requires C, 63.3; H, 4.1 and N, 2.0%): IR $\tilde{\nu}_{max}$/cm^{-1} 1564 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 4.05 [s, 10H, C_5H_5], 4.20 [s, 2H, H^3], 4.50 [s, 2H, H^4], 4.45 [s, 2H, H^5], 5.12 [s, 1H, CH_2Cl_2], 8.09 [s, 2H, CH=N], and 6.6–7.6 [m, 38H, aromatic]. Compound **5b** (Found: C, 60.6; H, 4.01 and N, 2.2. $C_{74}H_{56}Cl_2Fe_2N_2Pd_2{\cdot}CHCl_3$ requires: C, 60.5; H, 3.9 and N, 1.9%): IR $\tilde{\nu}_{max}$/cm^{-1} 1564 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 3.95 [s, 10H, C_5H_5], 4.27 [s, 2H, H^2], 3.75 [s, 2H, H^3], 4.12 [s, 2H, H^4], 4.50 [s, 2H, H^5]; 8.46 [s, 2H, CH=N] and 6.0–7.8 [m, 36H, aromatic].

Compounds 6. These compounds were prepared using the same procedure described for **5a**, but using the corresponding di-μ-chloro bridged derivative (2.5×10^{-4} mol of **1a**, **1b**, **1e** or **1f**) and 177 mg (10×10^{-4} mol) or diphenylacetylene as starting materials. The final solution obtained after the reflux was then passed through an SiO_2 column. When the starting material was **1a** or **1b** elution with $CHCl_3$ gave two bands. In contrast, when the reaction was performed using **1d** or **1e** only one band was released. For **1a** or **1b** the first eluted red band was collected and produced after concentration to dryness small amounts of **5a** or **5b** (yields: *ca.* 8 and 10%, respectively). Compounds **6a** and **6b** were obtained from the second band, which was released using a $CHCl_3$–CH_3OH (100:2) mixture as eluent. In contrast, when the reaction was performed using **1e** or **1f** only one band was released. In all cases the bands were collected and concentrated to *ca.* 5 cm^3 on a rotary evaporator. Further treatment with n-hexane followed by vigorous stirring for 15 min at room temperature produced precipitation of the complexes. The solids were collected by filtration, air-dried and recrystallized using CH_2Cl_2–n-hexane (1:1). Yields: 67, 58, 85 and 78% for **6a**, **6b**, **6e** and **6f**, respectively. Compound **6a** (Found: C, 65.9; H, 4.2 and N, 1.7. $C_{51}H_{38}ClFeNPd{\cdot}1CH_2Cl_2$ requires; C, 65.9; H, 4.3 and N, 1.5%): IR $\tilde{\nu}_{max}$/cm^{-1} 1618 (>C=N); ^{1}H NMR^{54} ferrocenyl moiety δ 4.16 [s, 5H, C_5H_5], 3.83 [s, 1H, H^3], 4.39 [s, 1H, H^4], 4.04 [s, 1H, H^5]; 5.12 [s, 2H, CH_2Cl_2], 8.00 [s, 1H, CH=N] and 6.6–7.6 [m, 29H, aromatic]. Compound **6b** (Found: C, 67.2; H, 4.3 and N, 1.6. $C_{51}H_{38}ClFeNPd{\cdot}0.75CH_2Cl_2$ requires: C, 67.2; H, 4.2 and N, 1.5%): IR $\tilde{\nu}_{max}$/cm^{-1} 1629 (>C=N); ^{1}H NMR^{65} ferrocenyl moiety δ 3.97 [s, 5H, C_5H_5], 4.28 [s, 1H, H^2], 3.72 [s, 1H, H^3], 4.14 [s, 1H, H^4], 4.33 [s, 1H, H^5]; 5.12 [s, 1.5H, CH_2Cl_2], 8.40 [s, 1H, CH=N] and 6.0–7.8 [m, 28H, aromatic]. Compound **6e** (Found: C, 68.8; H, 4.4 and N, 1.8. $C_{45}H_{34}ClFeNPd$ requires: C, 68.7; H, 4.4 and N, 1.8%): IR $\tilde{\nu}_{max}$/cm^{-1} 1572 (>C=N). ^{1}H NMR^{65} ferrocenyl moiety 3.96 [s, 5H, C_5H_5], 4.02 [s, 1H, H^3], 4.55 [s, 1H, H^4], 4.32 [s, 1H, H^5]; 8.20 [s, 1H, CH=N] and 6.4–7.8 [m, 25H, aromatic]. Compound **6f**: Found (C, 68.9; H, 4.5 and N, 1.7. $C_{46}H_{36}$-ClFeNPd requires: C, 69.0; H, 4.5 and N, 1.7%): IR $\tilde{\nu}_{max}$/1575 cm^{-1} (>C=N); ^1H NMR[65] ferrocenyl moiety δ 3.99 [s, 5H, C_5H_5], 4.08 [s, 1H, H^3], 4.60 [s, 1H, H^4], 4.40 [s, 1H, H^5]; 2.41 [s, 3H, Me]; 8.19 [s, 1H, CH=N] and 6.90–7.91 [m, 24H, aromatic].

Compound 7a. This complex was prepared according to the procedure described above for **5a** but using the stoichiometric amount of $MeO_2CC{\equiv}CCO_2Me$ as starting material (yield: 58%). Found: C, 52.8; H, 3.8 and N, 2.1. $C_{58}H_{48}Cl_2Fe_2N_2O_8$-$Pd_2{\cdot}CH_2Cl_2$ requires: C, 52.7; H, 3.7 and N, 2.1%. IR: $\tilde{\nu}_{max}/cm^{-1}$ 1565 (>C=N). ^1H NMR[65] ferrocenyl moiety δ 4.60 [s, 10H, C_5H_5], 4.70 [s, 2H, H^3], 5.02 [s, 2H, H^4], 4.85 [s, 2H, H^5]; 5.12 [s, 2H, CH_2Cl_2]; 8.26 [s, 2H, CH=N], 3.65 [s, 6H, OMe], 3.39 [s, 6H, OMe] and 6.80–8.02 [m, 18H, aromatic].

Compounds 8. This complex was prepared using the same procedure as described for **5**, but using the alkyne MeO_2-$CC{\equiv}CO_2Me$ and an alkyne: **1a** (or **1b**) molar ratio 2 : 1 (yields: 70 and 49%, respectively). Compound **8a** (Found: C, 51.0; H, 3.9 and N, 1.8. $C_{35}H_{30}ClFeNO_8Pd{\cdot}\frac{1}{2}CH_2Cl_2$ requires: C, 51.2; H, 3.8 and N, 1.7%): IR $\tilde{\nu}_{max}/cm^{-1}$ 1595 (>C=N); ^1H NMR[65] ferrocenyl moiety δ 4.60 [s, 5H, C_5H_5], 4.70 [s, 1H, H^3], 5.02 [s, 1H, H^4], 4.84 [s, 1H, H^5]; 5.12 [s, 1H, CH_2Cl_2], 8.26 [s, 1H, CH=N]; 4.48 [s, 3H, OMe], 4.39 [s, 3H, OMe], 3.65 [s, 3H, OMe], 3.46 [s, 3H, OMe] and 6.8–7.8 [m, 9H, aromatic]. Compound **8b** (Found: C, 53.5; H, 3.9 and N, 1.7. $C_{35}H_{30}$-$ClFeNO_8Pd$ requires: C, 53.2; H, 3.8 and N, 1.8%): IR $\tilde{\nu}_{max}/cm^{-1}$ 1572 (>C=N); ^1H NMR[65] ferrocenyl moiety δ 4.30 [s, 5H, C_5H_4], 4.48 [s, 2H, H^2 and H^5], 4.39 [s, 2H, H^3 and H^4]; 8.56 [s, 1H, CH=N], 3.97 [s, 3H, OMe], 3.88 [s, 3H, OMe], 3.80 [s, 3H, OMe], 3.74 [s, 3H, OMe] and 6.2–7.8 [m, 9H, aromatic].

Compounds 9. These complexes were prepared *in situ* as follows: **5a** or **5b** (46 mg, 3.09 × 10^{-5} mol) was suspended in 0.7 cm^3 of $CDCl_3$. Then an excess of deuteriated pyridine (5 × 10^{-3} cm^3, 6.2 × 10^{-5} mol) was added. The reaction mixture was shaken vigorously for *ca.* 2 min to dissolve **5a** or **5b**, which produced a pale orange solution. Compound **9a**: ^1H NMR[65] ferrocenyl moiety δ 3.96 [s, 5H, C_5H_5], 4.02 [s, 1H, H^3], 4.55 [s, 1H, H^4], 4.32 [s, 1H, H^5]; 8.20 [s, 1H, CH=N], and 6.4–7.8 [m, 19H, aromatic]. Compound **9b**: ^1H NMR[65] ferrocenyl moiety δ 4.29 [s, 5H, C_5H_5], 3.66 [s, 1H, H^2], 4.38 [s, 1H, H^3], 4.66 [s, 1H, H^4], 3.96 [s, 1H, H^5]; 8.32 [s, 1H, CH=N] and 6.4–7.8 [m, 18H, aromatic].

Compound 10a. This compound was prepared *in situ* as follows: **7a** (10 mg, 8.4 × 10^{-6} mol) was suspended in 0.7 cm^3 of $CDCl_3$. Then an excess of deuteriated pyridine (5 × 10^{-3} cm^{-3}, 6.2 × 10^{-5} mol) was added. The reaction mixture was shaken vigorously for *ca.* 2 min to dissolve **7a**, which produced an orange solution. ^1H NMR[65] ferrocenyl moiety δ 4.07 [s, 5H, C_5H_5], 4.08 [s, 1H, H^3], 4.39 [s, 1H, H^4], 4.71 [s, 1H, H^5]; 7.65 [s, 1H, CH=N], 3.29 and 3.42 [s, 3H, OMe] and 6.6–7.8 [m, 9H, aromatic].

Compounds 11. Triphenylphosphine (18 mg, 6.8 × 10^{-5} mol) was added to a suspension containing 50 mg (3.36 × 10^{-5} mmol) of compound **5a** or **5b** and 5 cm^3 of benzene. The reaction mixture was stirred at room temperature (*ca.* 20 °C) for 1 h, and then concentrated to dryness on a rotary evaporator. The solid obtained was dissolved in the minimum amount of CH_2Cl_2 and filtered. Then n-hexane (*ca.* 10 cm^3) was added, the mixture stirred at room temperature for 1 h and the orange-reddish solid formed filtered out and air-dried. Yield: 86% for **11a** and 76% for **11b**. Compound **11a** (Found: C, 66.4; H, 4.3 and N, 1.3. $C_{55}H_{43}ClFeNPPd{\cdot}CH_2Cl_2$ requires: C, 66.5; H, 4.5 and N, 1.4%): IR $\tilde{\nu}_{max}/cm^{-1}$ 1564 (>C=N); ^1H NMR[65] ferrocenyl moiety δ 4.28 [s, 5H, C_5H_5], 3.35 [s, 1H, H^3], 4.23 [s, 1H, H^4], 4.42 [s, 1H, H^5]; 5.12 [s, 2H, CH_2Cl_2]; 9.60 [d, 1H, CH=N] and 6.5–7.8 [m, 34H, aromatic]; ^{31}P NMR δ 28.95. Compound **11b** (Found: C, 68.4; H, 4.3 and N, 1.4. $C_{55}H_{43}ClFeNPPd$ requires: C, 68.6; H, 4.5 and N, 1.5%): IR $\tilde{\nu}_{max}/cm^{-1}$ 1564 (>C=N); ^1H NMR[65] ferrocenyl moiety δ 3.99 [s, 5H, C_5H_5], 4.47 [s, 1H, H^2], 4.70 [s, 1H, H^3], 5.19 [s, 1H, H^4], 4.55]s, 1H, H^5]; 8.47 [d, 1H, CH=N] and 6.0–7.7 [m, 33H, aromatic]; ^{31}P data δ 25.90.

Table 4 Crystal data and details of the refinement of the crystal structure of compound **2b**. Standard deviations are given in parentheses

Chemical formula	$C_{35}H_{38}ClFeNPd$
Formula weight	670.36
Crystal system	Tetragonal
Space group	$I4_1/a$
a/Å	34.337(5)
b/Å	34.337(5)
c/Å	11.335(2)
V/Å^3	13364(4)
T/K	293(2)
Z	16
μ/mm^{-1}	1.074
No. measured reflections	9299
No. independent reflections	9299
Final $R1$, $wR2$ {for $I > 2\sigma(I)$}	0.0365, 0.0780
(all data)	0.1134, 0.1397

Compound 12a. Triphenylphosphine (18 mg, 6.8 × 10^{-5} mol) was added to a suspension containing 41 mg (3.43 × 10^{-5} mol) of compound **7a** and 5 cm^3 of benzene. The reaction mixture was stirred at room temperature (*ca.* 20 °C) for 30 min and then concentrated to dryness on a rotary evaporator. The solid obtained was dissolved in the minimum amount of CH_2Cl_2 and filtered. Then n-hexane {*ca.* 10 cm^3} was added, the mixture stirred at room temperature for 1 h and the orange-reddish solid formed filtered out and air-dried. Yield: 86%. Found: C, 61.9; H, 4.3 and N, 1.4. $C_{47}H_{39}ClFeNO_8PPd$ requires: C, 62.0; H, 4.3 and N, 1.5%. IR: $\tilde{\nu}_{max}/cm^{-1}$ 1615 (>C=N). ^1H NMR[65] ferrocenyl moiety δ 4.24 [s, 5H, C_5H_5], 3.70 [s, 1H, H^3], 4.40 [s, 1H, H^4], 4.38 [s, 1H, H^5]; 8.25 [s, 1H, CH=N], 3.28 [s, 3H, OMe], 3.36 [s, 3H, OMe] and 6.2–7.8 [m, 24H, aromatic]. ^{31}P NMR δ 27.19.

Compound 13a. This complex was prepared in solution and characterized by its ^1H NMR spectrum. A 21 mg amount of **12a** (2.30 × 10^{-5} mol) was dissolved in 0.7 cm^3 of $CDCl_3$, then the stoichiometric amount of PPh_3 (6 mg, 2.29 × 10^{-5} mol) was added and shaken vigorously at room temperature (*ca.* 20 °C) for 2 min, giving a bright orange solution. ^1H NMR[65] ferrocenyl moiety δ 4.46 [s, 5H, C_5H_5], 3.67 [s, 1H, H^3], 4.74 [s, 1H, H^4], 4.34 [s, 1H, H^5]; 7.77 [s, 1H, CH=N], 3.95 [s, 3H, OMe], 3.46 [s, 3H, OMe] and 6.4–7.7 [m, 39H, aromatic]. ^{31}P NMR δ 12.10.

Crystal structure determination and refinement

A prismatic crystal of compound **2b** was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Crystal data are given in Table 4. Lorentz polarization corrections were made, but absorption corrections are not. The structure was solved by direct methods using the SHELXS computer program[67] and refined by full-matrix least-squares method using SHELX 93.[68] Twenty six hydrogen atoms were located from difference synthesis and refined with an overall isotropic thermal parameter and eight were computed and refined with an overall isotropic thermal parameter using a riding model.

CCDC reference number 186/2209.

See http://www.rsc.org/suppdata/dt/b0/b007537j/ for crystallographic files in .cif format.

Acknowledgements

We are grateful to the Ministerio de Educación y Cultura of Spain and to the Generalitat de Catalunya for financial support (Grants PB97-0164 and 1999-SGR-0045).

References

1 R. G. Newkome, G. E. Puckett, V. K. Gupta and G. E. Keifer, *Chem. Rev.*, 1986, **86**, 451 and references therein.
2 V. V. Dunina, O. A. Zalevskaya and V. M. Potatov, *Russ. Chem. Rev.*, 1988, **57**, 250 and references therein.
3 A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403 and references therein.
4 I. Omae, *Coord. Chem. Rev.*, 1988, **83**, 137 and references therein.
5 I. Omae, *Applications of Organometallic Compounds*, John Wiley, Chichester, 1998, Ch. 20, p. 423.
6 P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano and E. Sola, *Coord. Chem. Rev.*, 1992, **117**, 215 and references therein.
7 N. J. Thompson, J. L. Serrano, M. J. Baena and P. Espinet, *Chem. Eur. J.*, 1996, **2**, 214 and references therein.
8 A. G. Quiroga, J. M. Pérez, I. López Solera, J. R. Masaguer, A. Luque, P. Roman, A. Edwards, C. Alonso and C. Navarro-Ranninger, *J. Med. Chem.*, 1998, **41**, 1399, and references therein.
9 A. J. Klaus, *Modern Colorants*: *Synthesis and Structure*, eds. A. E. Peters and H. S. Freeman, Blackie Academic professional, London, 1995, vol. 3, p. 1.
10 A. Bose and C. R. Saha, *J. Mol. Catal.*, 1989, **49**, 271.
11 B. S. Wild, *Coord. Chem. Rev.*, 1997, **116**, 291 and references therein.
12 V. V. Dunina, L. G. Kuz'mina, M. Y. Rubina, Y. K. Grishin, Y. A. Veits and E. I. Kazankova, *Tetrahedron*: *Asymmetry*, 1999, **10**, 1483 and references therein.
13 C. López, R. Bosque, D. Sainz, X. Solans and M. Font-Bardía, *Organometallics*, 1997, **16**, 3261.
14 J. Albert, J. M. Cadena, J. Granell, G. Muller, J. I. Ordinas, D. Panyella, C. Puerta, C. Sañudo and P. Valerga, *Organometallics*, 1999, **18**, 3511.
15 P. Leung, G. H. Quek, H. Lang, A. M. Liu, K. F. Mok, A. J. White, D. J. Williams, N. Rees and W. McFarlane, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1639.
16 J. Spencer and M. Pfeffer, *Adv. Metal-Org. Chem.*, 1998, **6**, 103.
17 M. Pfeffer, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 567.
18 A. D. Ryabov, *Synthesis*, 1985, 233.
19 A. D. Ryabov, R. van Eldik, G. Le Borgne and M. Pfeffer, *Organometallics*, 1993, **12**, 1386.
20 J. Vicente, J. A. Abad, J. Gil-Rubio and P. G. Jones, *Organometallics*, 1995, **14**, 2677.
21 J. Vicente, I. Saura-Llamas and M. C. R. de Arellano, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2529.
22 J. Vicente, I. Saura-Llamas and M. C. R. Arellano, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2535.
23 A. Albinati, P. S. Pregosin and R. Rüedi, *Helv. Chim. Acta*, 1985, **68**, 2045.
24 A. Bahsoun, J. Dehand, M. Pfeffer, M. Zinsius, S. E. Bouaoud and G. Le Borgne, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 547.
25 M. Pfeffer, J. P. Sutter, A. De Cian and J. Fischer, *Organometallics*, 1993, **12**, 1167.
26 M. Pfeffer, M. A. Rotteveel, J. P. Sutter, A. de Cian and J. Fischer, *J. Organomet. Chem.*, 1989, **371**, C21.
27 C. López, D. Tramuns and X. Solans, *J. Organomet. Chem.*, 1994, **471**, 265.
28 C. López, R. Bosque, X. Solans, M. Font-Bardía, J. Silver and G. Fern, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1839.
29 G. Zhao, Q. G. Wang and T. C. W. Mak, *J. Organomet. Chem.*, 1999, **574**, 311.
30 M. Benito, C. López, X. Solans and M. Font-Bardía, *Tetrahedron*: *Asymmetry*, 1998, **9**, 4219.
31 M. Benito, C. López and X. Morvan, *Polyhedron*, 1999, **19**, 2583.
32 C. Hansch, A. Leo and D. Koekman, *Exploring QSAR. Hydrophobic*, *Electronic and Steric Constants*, ACS Professional reference Books, Washington, 1995.
33 J. P. Sutter, M. Pfeffer, A. de Cian and J. Fischer, *Organometallics*, 1992, **11**, 386.
34 C. López, J. Sales, R. Zquiak and X. Solans, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 2321.
35 R. Bosque, C. López, J. Sales, X. Solans and M. Font-Bardía, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 735.
36 R. Bosque, M. Font-Bardía, C. López, J. Sales, J. Silver and X. Solans, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 747.
37 *Beilstein Handbuch der Organische Chemie*, Vierte Auflage, Bande 12–14, Springer Verlag, Heidelberg, 1988.
38 *Comprehensive Organic Chemistry*: *The Syntheses and Reactions of Organic Compounds*, eds. D. Barton and W. D. Ollis, Pergamon Press, Exeter, 1979, vol. 1.
39 *Comprehensive Organic Functional Group Transformations*, eds. A. R. Katrizky, O. Meth-Cohn and C. W. Rees, Pergamon Press, Cambridge, 1995, vol. 1.
40 H. Onue and I. Moritani, *J. Organomet. Chem.*, 1972, **43**, 431.
41 B. N. Cockburn, D. V. Howe, T. Keating and B. F. G. Lewis, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 404.
42 J. Albert, J. Granell, J. Sales, M. Font-Bardía and X. Solans, *Organometallics*, 1995, **14**, 1393.
43 R. G. Miller, R. D. Stuffer, D. R. Fahey and D. R. Pernell, *J. Am. Chem. Soc.*, 1970, **92**, 1511.
44 J. Albert, J. Granell, J. Sales, X. Solans and M. Font-Bardia, *Organometallics*, 1985, **5**, 2567.
45 J. Albert, J. Granell and J. Sales, *J. Organomet. Chem.*, 1984, **273**, 393.
46 J. Albert, R. M. Ceder, M. Gómez, J. Granell and J. Sales, *Organometallics*, 1992, **4**, 1541.
47 R. M. Ceder, M. Gómez and J. Sales, *J. Organomet. Chem.*, 1989, **361**, 391.
48 J. Granell, R. Moragas, J. Sales, M. Font-Bardía and X. Solans, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1237.
49 C. López, R. Bosque, X. Solans and M. Font-Bardía, *J. Organomet. Chem.*, 1997, **539**, 99.
50 C. López and R. Bosque, *J. Organomet. Chem.*, 1996, **524**, 247.
51 G. Zhao, F. Xiu, Z. Y. Zhang and T. C. W. Mak, *Organometallics*, 1997, **16**, 4021.
52 R. Bosque, C. López, J. Sales and X. Solans, *J. Organomet. Chem.*, 1994, **483**, 61.
53 R. Bosque, C. López and J. Sales, *J. Organomet. Chem.*, 1995, **498**, 147.
54 R. Bosque, C. López, X. Solans, M. Font-Bardía, J. Silver and G. Fern, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1839.
55 R. Bosque, C. López, J. Sales, X. Solans and J. Silver, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3195.
56 A. Caubet, C. López, R. Bosque, X. Solans and M. Font-Bardía, *J. Organomet. Chem.*, 1999, **577**, 292.
57 C. López, R. Bosque, X. Solans and M. Font-Bardía, *New J. Chem.*, 1998, **22**, 977.
58 J. Granell, R. Moragas, J. Sales, M. Font-Bardía and X. Solans, *J. Organomet. Chem.*, 1992, **431**, 359.
59 M. T. Pereira, J. M. Vila, A. Suarez and M. Gayoso, *Gazz. Chim. Ital.*, 1988, **118**, 783.
60 J. Albert, M. Gómez, J. Granell, J. Sales and X. Solans, *Organometallics*, 1990, **9**, 1405.
61 C. López, R. Bosque, X. Solans and M. Font-Bardía, *New J. Chem.*, 1996, **20**, 1285.
62 S. Q. Huo, C. X. Du, Y. Zhu, H. Z. Yuan and X. A. Mao, *J. Organomet. Chem.*, 1994, **483**, 139.
63 T. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 146.
64 SPARTAN 5.0, Wavefunction Inc., Irvine, CA, 1995.
65 Labelling of the atoms refers to those shown in Fig. 2 and in Schemes 1–4.
66 The crystal structure of this complex could not be resolved because the single crystals degraded under X-ray radiation (at 293 and 198 K).
67 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
68 G. M. Sheldrick, SHELX 93, A computer program for determination of crystal structures, University of Göttingen, 1994.