

Schiff bases derived from aminomethylferrocene and their cyclopalladated derivatives

Ramón Bosque, Concepción López ^{*}, Joaquim Sales ^{*}

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028-Barcelona, Spain

Received 25 November 1994

Abstract

Synthesis and characterization of novel Schiff bases derived from aminomethylferrocene of general formula: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N=CH}(\text{C}_6\text{H}_4\text{-2-R}))]$ with $\text{R}=\text{Cl}$ (**1a**) and H (**1b**) are reported. These react with $\text{Na}_2[\text{PdCl}_4]$ and $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ in methanol at room temperature producing di- μ -chloro-bridged cyclopalladated compounds $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N=CH}(\text{C}_6\text{H}_4\text{-2-R}))(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$ (**2a**, **2b**) which contain a $\sigma(\text{Pd-C}_{\text{sp}^2, \text{phenyl}})$ bond. However, for (**1b**), the activation of the $\sigma(\text{C}_{\text{sp}^2, \text{ferrocene}}\text{-H})$ bond also takes place giving $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N=CH}(\text{C}_6\text{H}_5)](\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})\}_2]$ (**2b'**). These dinuclear complexes react with triphenylphosphine (PPh_3) with cleavage of the $\mu\text{-Cl}$ bridges, yielding mononuclear derivatives $[\text{Pd}(\text{C}(\text{N})\text{Cl})(\text{PPh}_3)]$ (**3**). The results obtained show the strong influence of the so-called “endo effect” in cyclopalladation reactions of *N*-donor ferrocenyl ligands.

Keywords: Iron; Palladium; Cyclopalladation; Aminoferrocenes; Schiff bases

1. Introduction

One of the areas of organometallic chemistry that has attracted great interest during the last few decades is that concerning the syntheses, characterization and study of cyclopalladated compounds, in particular those containing a nitrogen and a $\sigma(\text{Pd-C}_{\text{sp}^2, \text{phenyl}})$ bond, or, to a lesser extent a $\sigma(\text{Pd-C}_{\text{sp}^3})$ bond [1,2]. It is generally accepted that the cyclopalladation process takes place by electrophilic attack of the palladium atom previously coordinated to the nitrogen on the carbon atom. Recent studies [3] on cyclopalladation of ligands containing the $>\text{C=N-}$ functional group have shown that the formation of palladacycles containing the imine moiety (*endocyclic*) is especially favoured.

Although it is well known that ferrocene derivatives are more likely to undergo electrophilic attack than aromatic ones [4], only a few examples of palladacycles containing $\sigma(\text{Pd-C}_{\text{sp}^2, \text{ferrocene}})$ bonds have been reported [5,6] so far.

In order to evaluate the relative importance of the *endo* effect vs. the proclivity to undergo electrophilic attack in the cyclopalladation process, we have studied

the Schiff bases derived from 1-aminomethylferrocene: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-NH}_2)]$ of general formula: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N=CH}(\text{C}_6\text{H}_4\text{-2-R}))]$ with $\text{R}=\text{Cl}$ (**1a**) and H (**1b**) (Fig. 1). These could undergo metallation at two different sites (Fig. 1), the substituted pentagonal ring of the ferrocenyl moiety, giving exocyclic five-membered palladacycles with a $\sigma(\text{Pd-C}_{\text{sp}^2, \text{ferrocene}})$ bond, or the phenyl ring that would yield endocyclic palladacycles with a $\sigma(\text{Pd-C}_{\text{sp}^2, \text{phenyl}})$ bond, but of the same size.

Furthermore, since **1a** and **1b** can be visualized as being derived from *N*-benzylidenbenzylamines $[\text{C}_6\text{H}_5\text{-CH}_2\text{-N=CH}(\text{C}_6\text{H}_4\text{-2-R})]$ ($\text{R}=\text{Cl}$, or H) by replacement of the phenyl ring by the ferrocenyl moiety, the study of their cyclopalladation reactions would also allow us to compare the reactivity of these two types of Schiff base.

2. Results and discussion

2.1. Syntheses

The new Schiff bases $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N=CH}(\text{C}_6\text{H}_4\text{-2-R}))]$ with $\text{R}=\text{Cl}$ (**1a**) or H (**1b**) were synthesized by condensation of the corresponding

^{*} Corresponding authors.

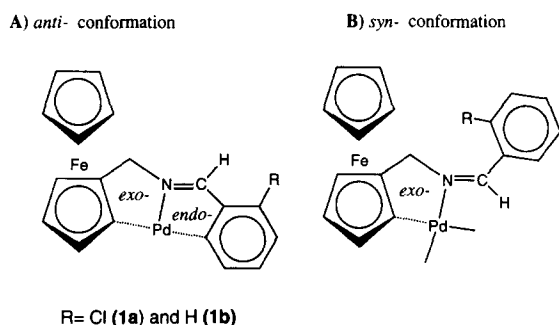


Fig. 1. Schematic view of the two possible conformations (*anti*- and *syn*-) of the Schiff bases under study (**1a**, **1b**), showing the two types of palladacycle that might be expected.

aldehyde and freshly prepared aminomethylferrocene, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-NH}_2\}]$ [**7**] (Scheme 1). The success of these syntheses is highly dependent on the purity of the aminomethylferrocene, which degra-

dates quite easily [4] and should be used immediately after preparation.

In order to study cyclopalladation reactions of imines (**1a**, **1b**), the general procedure described for related *N*-donor ferrocenyl derivatives was used [5,6]. This consists of the reaction of stoichiometric amounts of the base, $\text{Na}_2[\text{PdCl}_4]$ and $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ in methanol at room temperature.

When the reaction was carried out using $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}=\text{CH}(\text{C}_6\text{H}_4\text{-2-Cl})\}]$ (**1a**), the cyclopalladated compound $[\text{Pd}\{[(2\text{-Cl-C}_6\text{H}_3\text{-CH}=\text{N-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$ (**2a**) was formed (Scheme 1). ^1H and ^{13}C NMR studies (see Section 2.2.) suggest that this complex contains a {five, six} bicyclic system derived from the fusion of the phenyl ring and an endocyclic, five-membered metallacycle. Therefore although ferrocene derivatives are more likely to undergo electrophilic attack than benzene [4],

Table 1

Most relevant ^1H NMR data ^a (ppm) for the *N*-donor ligands and for the cyclopalladated compounds ^b used in this work

	Cp	H(2),H(5)	H(3),H(4)	-CH ₂ -	-CH=N- ^c
<i>N</i>-donor ligands					
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-NH}_2\}]$	4.18	4.24	4.20	4.01	—
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}_3\}]$	4.13	4.10	4.07	3.53	—
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}=\text{CH}(\text{C}_6\text{H}_4\text{-2-Cl})\}]$ (1a)	4.16	4.24	4.23	4.58	8.75
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}=\text{CH}(\text{C}_6\text{H}_5)\}]$ (1b)	4.16	4.15	4.21	4.55	8.29
<i>Cyclopalladated compounds</i>					
$[\text{Pd}\{[(2\text{-Cl-C}_6\text{H}_3\text{-CH}=\text{N-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-Cl})_2\}]$ (2a) ^d	4.21	4.23	4.35	4.94	8.36
$[\text{Pd}\{[(\text{C}_6\text{H}_4\text{-CH}=\text{N-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-Cl})_2\}]$ (2b) ^d	4.20	4.22	4.31	4.96	7.67 ^e
$[\text{Pd}\{[(2\text{-Cl-C}_6\text{H}_3\text{-CH}=\text{N-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)\}]$ (3a)	4.17	4.22	4.33	5.05	8.39 ^d
$[\text{Pd}\{[(\text{C}_6\text{H}_4\text{-CH}=\text{N-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)\}]$ (3b)	4.18	4.23	4.30	5.06	7.87 ^e
$[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_3)\text{-CH}_2\text{-N}=\text{CH}(\text{C}_6\text{H}_5)\}]\text{Cl}(\text{PPh}_3)\}]$ (3b')	3.74 ^f	4.40	3.79 ^g 3.30 ⁱ	4.98 ^h —	9.00 ^e —
	4.00 ^f		3.95 ^g 3.52 ⁱ	5.03 ^h	

^a Labelling refers to the scheme shown below.

^b Most relevant ^1H NMR-spectral data (in ppm) for the *exocyclic* complex are as follows: for **2b'** {the values given below were obtained from the ^1H NMR spectrum of the mixture. **2b**, **2b'** in CDCl_3 , and in the presence of py-d_5 , followed by the identification of the signals due to the pure **2b**: 9.3 ppm (broad m) $\text{HC}=\text{N}$; 3.5 ppm, broad {Cp}, 3.8; 3.9 and 4.2 (complex multiplets) H(4), H(3) and H(2) of the C_5H_3 -ring; 5.1 and 4.5-ppm (doublet of doublets) $-\text{CH}_2-$.

^c Singlet except where quoted.

^d The ^1H NMR spectra of these derivatives were recorded in the presence of deuterated pyridine (py-d_5).

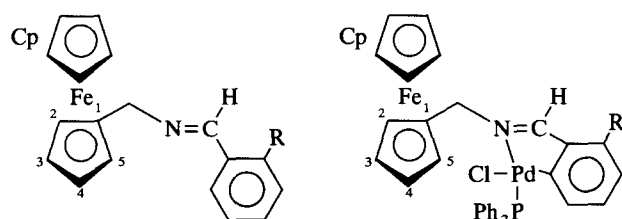
^e Doublet due to phosphorus coupling.

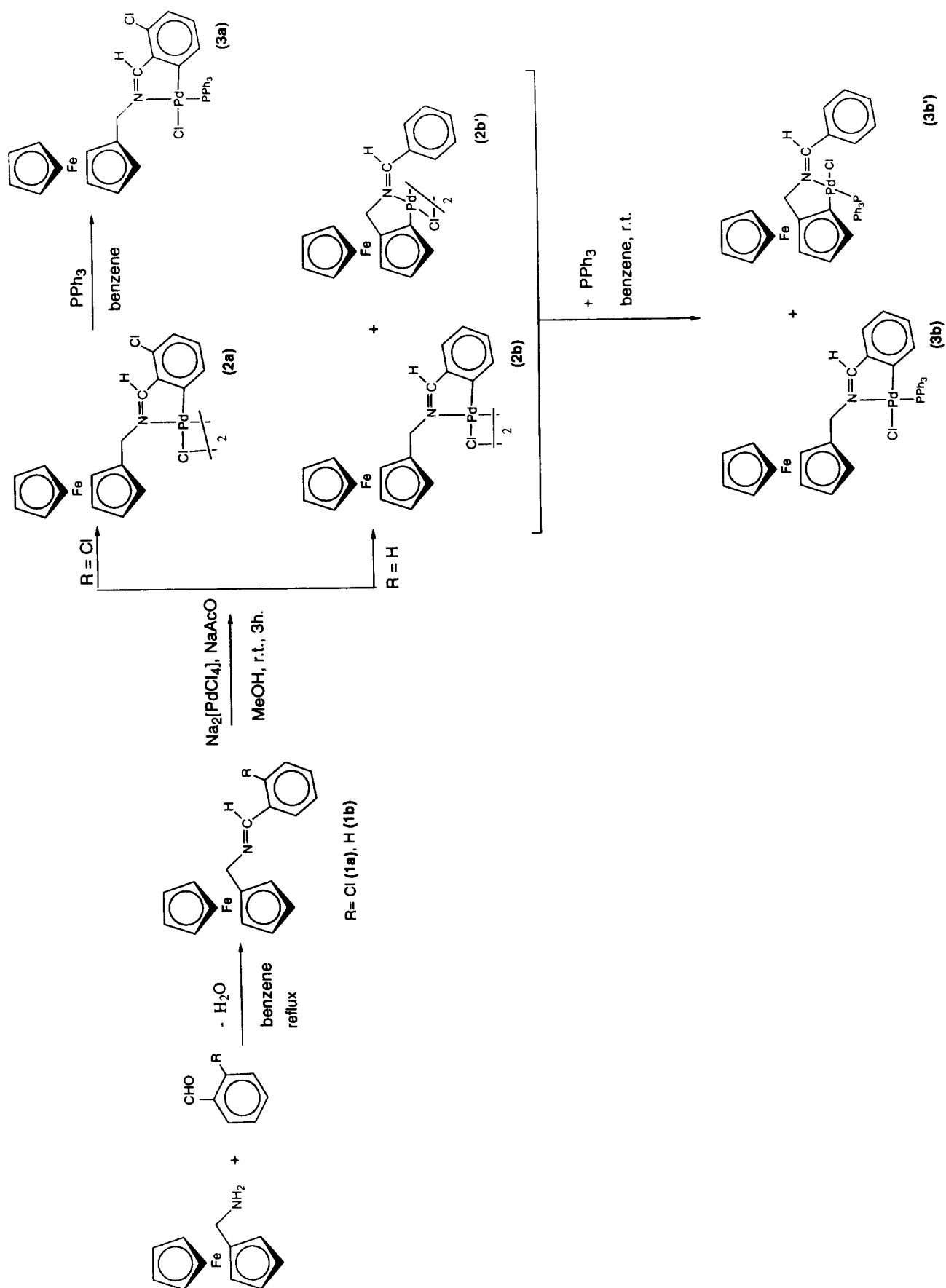
^f See text.

^g H(3).

^h Doublet of doublets.

ⁱ H(4).





Scheme 1.

in this case the *endo* effect is strong enough to induce electrophilic attack of the palladium(II) species (formed after the coordination of the nitrogen) on the phenyl ring.

Cyclopalladation of the ferrocenylimine (**1b**) exhibits several and outstanding differences. When the reaction was carried out under identical experimental conditions as for (**1a**), the elemental analyses of the solid formed were consistent with those expected for a di- μ -chloro-bridged cyclopalladated compound $[\{\text{Pd}(\text{C}=\text{N})(\mu\text{-Cl})\}_2]$, but its ^1H NMR spectrum revealed two components (**2b** and **2b'**, in Scheme 1) in a 60:40 molar ratio. Two bands due to the asymmetric stretching of the $>\text{C}=\text{N}$ -functional group were also observed in the IR spectrum. In an attempt to separate and characterize the two components, the mixture (**2b**, **2b'**) was dissolved in chloroform and passed through a SiO_2 column, using CHCl_3 as eluant. The first band eluted was concentrated to dryness in vacuum and then treated with hexane. The yellow solid obtained was characterized as (**2b**). However, the remaining bands gave ^1H NMR spectra suggesting that the isolated solid was a mixture of **2b** and **2b'**. Attempts to isolate complex **2b'** from the mixture were unsuccessful.

As is well known, di- μ -chloro-bridged cyclopalladated complexes react with neutral *N*- or *P*-donors *L*, producing: $[\text{Pd}(\text{C}=\text{N})\text{Cl}(\text{L})]$ or $[\text{Pd}(\text{C}=\text{N})\text{Cl}(\text{L})_2]$ [**3**], which are more soluble than the dinuclear ones, and consequently easier to characterize. In order to confirm the results obtained, the pure di-nuclear derivatives (**2a**, **2b**) were treated with triphenylphosphine in a 1:2 molar ratio, to give the mononuclear compounds: $[\text{Pd}(\{2\text{-R-C}_6\text{H}_3\text{-CH}=\text{N-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)}\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{-Cl}(\text{PPh}_3)]$ (**3a**, **3b**). However, when this reaction was undertaken using the mixture (**2b**, **2b'**) (60:40), spectroscopic studies of the final product revealed two components (**3b**, **3b'**). In particular, the ^{31}P NMR spectrum showed two singlets, one of which was coincident with that of complex **3b**, while the other can be assigned to the exocyclic derivative: (**3b'**). Compounds (**3b**, **3b'**) were separated by SiO_2 -column chromatography, and their characterization data are consistent with the structures proposed.

2.2. Characterization

All the compounds described here are solids at room temperature and their colours vary from bright yellow (**1a,b**, **2a,b** and **3a,b**) to orange (**3b'**). In all cases elemental analyses are consistent with the proposed formula (Section 3). The Schiff bases and their monomeric derivatives exhibit high solubility in chloroform, dichloromethane, acetone, benzene and toluene, and they are slightly soluble in alkanes. The di- μ -chloro-bridged derivatives are less soluble.

The IR spectra of the ferrocenylimines show an intense and sharp band at 1630 cm^{-1} for (**1a**) and 1638 cm^{-1} for (**1b**), assigned to the asymmetric stretching of the $>\text{C}=\text{N}$ -bond. For the cyclopalladated derivatives this band appears at lower wavenumbers but the shift is clearly smaller for the exocyclic derivatives (1628 cm^{-1}).

^1H NMR data for the free bases (**1a**, **b**) are summarized in Table 1. Only one isomer of the base was detected by proton NMR spectroscopy. The positions of the signals are consistent with those observed for related ferrocenylimines which have an *anti* conformation, thus allowing us to assign the same conformation to **1a** and **1b**. The outstanding feature of in the spectra is four signals in the range 3.5–5.5 ppm, of relative intensities 2:2:5:2, which are assigned to the $-\text{CH}_2-$ protons and to the three types of non equivalent protons in the ferrocenyl moiety. Furthermore, the resonance of the imine proton appears as a singlet at 8.75 ppm (for **1a**) and 8.29 (for **1b**). The difference between these signals is similar to that reported for the *N*-benzylidenebenzylamines $[\text{C}_6\text{H}_5\text{-CH}_2\text{-N}=\text{CH}(\text{C}_6\text{H}_4\text{-2-R})]$ (*R* = Cl or H, $\delta\ ^1\text{H}(-\text{CH}=\text{N-})$ = 8.9 and 8.2 ppm, respectively [**3d,e**]). This may be ascribed to different orientations of the aryl ring with respect to the imine moiety.

All the structural studies so far of the Schiff bases derived from ferrocene show that the fragment formed by the $>\text{C}=\text{N}$ -functional group and the phenyl ring of the *R*-group (in $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-N}=\text{CH}(\text{R})\}]]$ [**8**]) or the substituted five-membered ring of the ferrocenyl group in $[\{(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH}=\text{N-R'}\}]]$ [**6b,d**]) are nearly coplanar. If we assume that in (**1a**) the units $-\text{N}=\text{CH-C}_{\text{ipso}}(\text{R})$ and the $\text{C}_6\text{H}_4\text{-2-Cl}$ ring are also coplanar, there are two possible orientations of *ortho*-chlorine with respect to the imine nitrogen. In one methyne hydrogen and chlorine are on the same side of the molecule, while for the other these two atoms are on opposite sites of the phenyl and consequently, the chlorine is rather close to the lone pair of the nitrogen. The X-ray crystal structure of $[\{(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-N}=\text{CH}(\text{C}_6\text{H}_4\text{-2-OH})\}]]$ [**8**] shows that the orientation of the OH substituent is such that it provides an intramolecular hydrogen interaction between the nitrogen and the alcohol function. The replacement of the OH group by Cl will introduce significant differences. Since it is well known that the $\text{C}_{\text{phenyl}}\text{-Cl}$ bond is longer than $\text{C}_{\text{phenyl}}\text{-O}$, the chlorine would be brought closer to the nitrogen, which should be unstable due to repulsions between the lone pairs on Cl and N. For the other orientation, the chlorine atom will be quite close to the methyne proton, thus facilitating hydrogen bonding. These explanations are consistent with the conclusions reached from molecular models for (**1a**) and with the changes observed in the IR spectrum of these compounds.

The ^1H NMR spectra of compounds (**2a,b**) and

(**3a,b**) (Table 1) show that the relative intensities and the multiplicities of the signals due to the $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)]$ moiety do not change appreciably upon cyclopalladation, indicating that metallation did not take place on the ferrocenyl unit.

The chemical shift of the methyne proton is useful for the structural characterization of cyclopalladated compounds. This signal is shifted to high field (0.3–1.3 ppm) relative to that of the free imine in the *endo* derivatives [3c,d,e,9]. In the exocyclic metallacycles, if the imine adopts a *syn* form, the signal is shifted to low field (due to the paramagnetic anisotropy of the metal) [10], but when the ligand has an *anti*-conformation, this signal appears very near to that of the free base. On this basis it is clear that compounds **2a** and **2b**, **3a** and **3b** are endocyclic.

However for complexes **2b'** and **3b'** the signal due to the methyne proton appears shifted ca. 0.4 ppm to low field, suggesting that *anti* → *syn* isomerization of the imine has taken place. Isomerization of the base has also been postulated in the cyclopalladation of *N*-benzylidenebenzylamines $[\text{C}_6\text{H}_5\text{-CH}_2\text{-N=CH}(\text{C}_6\text{H}_5\text{-2-R,6-R'})]$ containing the *ortho* positions of the aryl ring blocked by either methyl or chlorine [3b,d,e].

The ^1H NMR spectrum of complex **3b'** showed sharp and well defined signals in the range 6.00–9.00 ppm, but the resonances due to the protons of the C_5H_5 ring appeared as two broad signals which partially overlapped one of the resonances of the protons of the

metallated pentagonal ring. In a first attempt to elucidate the cause of this broadening, the spectrum was recorded from –50 to 40°C. Although a sharpening of the signals was observed at lower temperatures, it was not possible to achieve a clear resolution.

Since ^1H NMR spectra of related cyclopalladated complexes of general formula $[\text{Pd}((\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_3)\text{-C(R)=N-R')}] \text{Cl}(\text{PPh}_3))]$ (with R = H, CH_3 or C_6H_5) [6a–c] exhibit well defined signals in the range 3.0–6.0 ppm, it seemed reasonable that the complexity of signals due to the ferrocenyl-moiety protons might be related to the geometry of the palladacycle. The X-ray crystal structures of $[\text{Pd}((\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_3)\text{-C(R)=N-R')}] \text{Cl}(\text{PPh}_3))]$ have shown that the metallacycle is planar [6a–c], but for complex **3b'** the palladacycle is expected to be nonplanar and quite similar to that found in $[\text{Pd}((\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_3)\text{-CH}(\text{CH}_3)\text{-N}(\text{CH}_3)_2]) \text{Cl}(\text{PPh}_3))]$ (acac) (envelope-like conformation) [11]. Thus, the interconversion of the two possible envelope-like conformations of the ring would clearly affect the relative positions of the C_5H_5 ring and one of the phenyl groups in the PPh_3 , and so the influence of the paramagnetic anisotropy of the C_6H_5 ring upon the C_5H_5 protons should be different in the two conformations. The ^1H NMR spectra of $[\text{Pd}((\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_3)\text{-CH}_2\text{-N}(\text{CH}_3)_2]) \text{Cl}(\text{PPh}_3))]$ exhibit clear, well defined signals in the region 3.0–6.0 ppm [5a], though in this case the five-membered metallacycle is also flexible. This may be related to the different environment of the nitrogen atom.

The ^{13}C NMR spectra (Table 2) of complexes **3a** and **3b** show the same number of signals as the free bases in the range 50–85 ppm, confirming that metallation did not take place on the ferrocenyl moiety. Furthermore, the resonance of the imine carbon shifts downfield for the palladacycles. A similar trend is found for the metallated carbon atom of the phenylic ring. These observations, as well as the assignments, are consistent with previous ^{13}C NMR studies on cyclopalladated complexes containing a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{phenyl}})$ or a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$ bond [3,6a–c]. However, for compound **3b'** the signals due to the carbon atoms of the ferrocenyl moiety are more complex. For instance, there are two resonances due to the C_5H_5 and their intensities are lower than those of the phenyl carbon atoms. The complexity of this spectrum can also be explained using the argument above for the interpretation of the proton NMR spectrum.

The ^{31}P NMR spectra of compounds **3** exhibit a singlet, its position consistent with a *trans* arrangement between the PPh_3 and the imine nitrogen [3,6a–c].

2.3. Final remarks

The studies summarized in this work have lead to the preparation and characterization of novel kinds of Schiff

Table 2

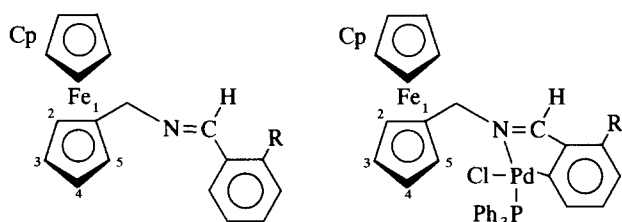
Selection of ^{13}C NMR data ^a (ppm) for the Schiff bases derived from ferrocene (**1a,b**) and their cyclopalladated compounds (**3a,b**) ^b

	1a	1b	3a	3b
–C(H)=N–	158.27	160.87	172.30 ^c	174.17 ^c
Cp	69.06	68.54	68.79	69.36
C(1)	86.20	84.95	82.09	82.47
C(2),C(5)	68.74	68.03	69.98	70.67
C(3),C(4)	68.41	67.86	68.87	70.67
–CH ₂ –	60.90	60.03	57.13	57.10
C _{ipso,phenyl}	135.64	130.59	144.94 ^c	148.82 ^c
C α	131.98	128.56	159.55 ^c	158.08 ^c
C α'	133.75	128.56	137.02	138.70
C β	130.26	128.13	136.54	138.59
C β'	128.85	128.13	124.80	124.85

^a Labelling refers to the schemes shown below.

^b For these compounds four additional doublets due to the four types of carbon nuclei of the PPh_3 (at ca. 131, 129, 135 and 128 ppm) were also observed.

^c Doublet due to phosphorus coupling.



base derived from 1-aminomethylferrocene, and their cyclopalladation.

Consistent with the higher proclivity of ferrocene derivatives to undergo electrophilic attack [4], and the fact that the formation of the metallacycle occurs through the electrophilic attack of the palladium(II) on the carbon, the formation of five-membered *exocyclic* metallacycles through the activation of a $\sigma(\text{C}_{\text{sp}^2, \text{ferrocene}}-\text{H})$ bond could not be excluded in principal. However, for the two compounds under study $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}=\text{CH}(\text{C}_6\text{H}_4\text{-2-R})\}]$ (**1a**, **1b**) cyclopalladation took place mainly at the phenyl ring. This shows not only the strong influence of the *endo* effect in cyclopalladation of *N*-donors containing the functional group $>\text{C}=\text{N}-$, but also proves that the proclivity of a given carbon atom to undergo electrophilic attack is not necessarily the main driving force controlling the cyclopalladation reactions. Other more subtle factors, such as the *endo* effect and the substituents may be important enough to determine the site of palladation. The exclusive formation of the endocyclic palladacycles from **1a** may be attributed to the interaction between the imine hydrogen and the *ortho* chlorine which precludes the rotation of the aryl ring and facilitates electrophilic attack of the coordinated palladium, thus reinforcing the *endo* effect. However, for substrate **1b** free rotation around the $\text{N}-\text{C}_{\text{ipso}}(\text{phenyl})$ bond is possible, and in this case the higher proclivity of ferrocene derivatives to undergo electrophilic attack is strong enough to counteract the *endo* effect, giving mixtures of the *endo*- and *exocyclic* derivatives.

3. Experimental details

Elemental analyses (C, H and N) were carried out at the Institut de Química Bio-Orgànica (C.S.I.C. Barcelona) and at the Serveis Científic-Tècnics de la Universitat de Barcelona. IR spectra were obtained with KBr pellets using a NICOLET-520 FTIR spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at ca. 20°C on a varian Gemini 200 MHz spectrometer, using CDCl_3 (99.8%) as solvent and TMS as internal standard in both cases. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained with a Bruker WP80-SY spectrometer using CHCl_3 as solvent and $\text{P}(\text{OCH}_3)_3$ as standard.

3.1. Materials and synthesis

N,N-(Dimethylaminoethyl)ferrocene, benzaldehyde and 2-chlorobenzaldehyde were obtained from commercial sources and used as received. The synthesis of 1-aminomethylferrocene involves the use of the highly HAZARDOUS MATERIALS, NaN_3 and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}_3\}]$ which may explode.

Consequently, they should be handled with EXTREME CAUTION. All the solvents were dried and distilled before use. The ferrocenylamine $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-NH}_2\}]$ was prepared according to the literature method [7].

3.1.1. Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}=\text{C}(\text{H})(\text{C}_6\text{H}_4\text{-2-Cl})\}]$ (**1a**)

2-Chlorobenzaldehyde (0.520 g, 3.7 mmol) was added to a solution containing the stoichiometric amount of freshly prepared $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-NH}_2\}]$ [7]. The reaction mixture was heated under reflux using a Dean–Stark apparatus until ca. 5 ml. of the azeotrope had condensed. Then the brownish suspension was filtered off and the undissolved dark materials were discarded. The yellowish filtrate was concentrated to dryness on a rotary evaporator. Addition of hexane (ca. 10 ml) to the oily residual, followed by vigorous stirring at room temperature produced precipitation of the desired ferrocenylimine. The yellow solid was collected by filtration and air-dried (yield 38%). Characterization data: Anal. Calc. for $\text{C}_{18}\text{H}_{16}\text{ClFeN}$ (found): C, 64.04 (64.18), H, 4.74 (4.90) and N, 4.15 (4.06)%. IR: $\nu(\text{C}=\text{N})$: 1630 cm^{-1} m.p.: 102–105°C, decomp.

3.1.2. Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}=\text{C}(\text{H})(\text{C}_6\text{H}_5)\}]$ (**1b**)

This compound was prepared using the procedure described for **1a** but using benzaldehyde (0.326 g, 3.08 mmol) and the stoichiometric amount of freshly prepared aminomethylferrocene as starting materials (yield 37%). Characterization data: Anal. Calc. for: $\text{C}_{18}\text{H}_{17}\text{FeN}$ (found): C, 71.33 (71.58), H, 5.61 (5.72) and N, 4.62 (4.55)%. IR (KBr pellets), $\nu(\text{C}=\text{N})$: 1638 cm^{-1} , m.p.: 72–76°C, decomp.

3.1.3. Preparation of $[\text{Pd}\{(\text{2-Cl-C}_6\text{H}_3)\text{-CH}=\text{N-CH}_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2]$ (**2a**)

The imine $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N}=\text{CH}(\text{C}_6\text{H}_4\text{-2-Cl})\}]$ (**1a**) (0.300 g, 0.89 mmol), $\text{Na}_2[\text{PdCl}_4]$ (0.262 g, 8.9 mmol) and $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ (0.121 g, 0.89 mmol) were suspended in 20 ml of methanol. The reaction mixture was stirred at room temperature for 3 h and the pale brownish solid formed was collected by filtration and air-dried (yield 38%). The compound was purified by SiO_2 column chromatography using CHCl_3 as eluant. The yellow band was collected and concentrated to dryness on a rotary evaporator. Further treatment of the gummy material with hexane followed by vigorous stirring at room temperature produced a bright yellow solid which was then filtered off and air-dried (yield 43%). Characterization data: Anal. Calc. for: $\text{C}_{36}\text{H}_{30}\text{Cl}_4\text{Fe}_2\text{N}_2\text{P}_2\text{Pd}_2$ (found): C, 45.12 (45.10), H, 3.13 (3.14) and N, 2.92 (2.86)%. IR: $\nu(\text{C}=\text{N})$: 1605 cm^{-1} .

3.1.4. Preparation of $[Pd\{\overline{[(C_6H_4)-CH=N-CH_2-(\eta^5-C_5H_4)]Fe(\eta^5-C_5H_5)}\}(\mu-Cl)]_2$ (2b**) and $[Pd\{\overline{[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH_2-N=CH(C_6H_5)\}}\}(\mu-Cl)]_2$ (**2b'**)**

0.300 g (9.9 mmol) of the ferrocenylimine $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH_2-N=C(H)(C_6H_5)\}]$ (**1b**), 0.291 g (9.9 mmol) of $Na_2[PdCl_4]$ and 0.135 g (0.99 mmol) of $Na(CH_3COO) \cdot 3H_2O$ were suspended in 10 ml of methanol. The resulting mixture was stirred at room temperature for 3 h and the precipitate formed was then filtered off and air dried (yield 46%). This solid contained compounds **2b** and **2b'** in the ratio 60:40. Characterization data: Anal. (**2b**, **2b'**). Calc. for $C_{36}H_{32}Cl_2Fe_2N_2P_2Pd_2$ (found): C, 48.69 (48.5); H, 3.61 (3.75) and N, 3.15 (2.8). IR: $\nu(C=N)$: 1610 and 1620 cm^{-1} . Complex **2b** can be partially separated from the mixture by SiO_2 column chromatography using $CHCl_3$ as eluant. The first band which contained complex **2b** exclusively was concentrated under vacuum on a rotary evaporator and treated with hexane (ca. 10 ml) to induce the precipitation of the complex (yield: 18%). Characterization data: (**2b**) Anal. Calc. for $C_{36}H_{32}Cl_2Fe_2N_2P_2Pd_2$ (found): C, 48.69 (48.8); H, 3.61 (3.7) and N, 3.15 (3.0)%. IR: $\nu(C=N)$: 1610 cm^{-1} .

3.1.5. Preparation of $[Pd\{\overline{[(2-Cl-C_6H_3)-CH=N-CH_2-(\eta^5-C_5H_4)]Fe(\eta^5-C_5H_5)}\}Cl(PPh_3)]$ (3a**)**

To a suspension of 0.45 g (0.150 mmol) of $[Pd\{\overline{[(2-Cl-C_6H_3)-CH=N-CH_2-(\eta^5-C_5H_4)]Fe(\eta^5-C_5H_5)}\}(\mu-Cl)]_2$ (**2a**) in 10 ml of benzene, triphenylphosphine (80 mg, 0.3 mmol) was added. The resulting yellow brown mixture was stirred at room temperature for 45 min and filtered. The filtrate was taken to dryness on a rotary evaporator, and the residual was then treated with hexane. The yellow solid was filtered off and air-dried (yield 72%). Characterization data: (**3a**) Anal. (%) Calc. for $C_{36}H_{30}Cl_2FeNPPd$ (found): C, 58.25 (58.4); H, 4.07 (4.0) and N, 1.89 (1.9)%. IR: $\nu(C=N)$: 1620 cm^{-1} . ^{31}P NMR: 41.6 ppm m.p. $218\text{--}225^\circ\text{C}$, decomp.

3.1.6. Preparation of $[Pd\{\overline{[(C_6H_4)-CH=N-CH_2-(\eta^5-C_5H_4)]Fe(\eta^5-C_5H_5)}\}Cl(PPh_3)]$ (3b**)**

This complex was prepared using the procedure described for **3a** but with the stoichiometric amount of **2a** as starting material (yield 56%). Characterization data: (**3b**) Anal. Calc. for $C_{36}H_{31}ClFeNPPd$ (found): C, 61.22 (61.3); H, 4.39 (4.4) and N, 1.98 (2.05)%. IR: $\nu(C=N)$: 1621 cm^{-1} . ^{31}P NMR: 43.0 ppm m.p.: $205\text{--}215^\circ\text{C}$, decomp.

3.1.7. Preparation of $[Pd\{\overline{[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_3)-CH_2-N=CH(C_6H_5)\}}\}Cl(PPh_3)]$ (3b'**)**

This complex was prepared using the procedure described above for compound (**3a**), but using the mixture **2b**: **2b'** (60:40) (see Section 3.1.4) as starting material.

The final solid was dissolved in the minimum amount of $CHCl_3$ and resulting solution was passed through an SiO_2 column (10 mm $\times$ 200 mm), using $CHCl_3$ as eluant. The yellow fraction was collected and taken to dryness on a rotary evaporator. Addition of hexane (ca. 20 ml) to the bright yellow solution precipitated complex **3b**, which was collected by filtration and air-dried. Complex **3b'** was obtained from the second band eluted, by taking the orange solution to dryness, followed by the addition of hexane. The orange solid was collected by filtration and air-dried. Characterization data for (**3b'**) Anal. Calc. for $C_{36}H_{31}ClFeNPPd$ (found): C, 61.22 (61.2); H, 4.39 (4.5) and N, 1.98 (1.82)%. IR: $\nu(C=N)$: 1631 cm^{-1} . ^{31}P NMR: 34.5 ppm.

Acknowledgements

We are indebted to the Dirección General de Investigación Científica y Técnica (D.G.C.Y.T.) for financial support (Grant No. PB89-0254 and PB93-0804) and to Johnson Matthey Inc. for the loan of palladium chloride.

References and notes

- [1] For reviews concerning cyclopalladated compounds, see (a) G.R. Newkome, W.E. Puckett, V.K. Gupta, G.E. Kiefer, *Chem. Rev.*, **86** (1986) 451; (b) I. Omae, *Coord. Chem. Rev.*, **83** (1988) 137; (c) V.V. Dunina, O.A. Zaleskaya and V.M. Potatov, *Russ. Chem. Rev.*, (1988) 250; (d) A.D. Ryabov, *Chem. Rev.*, **90** (1990) 403.
- [2] For recent applications of cyclopalladated compounds see: (a) P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano and E. Sola, *Coord. Chem. Rev.*, **15** (1992) 215, and references therein; (b) M. Pfeffer, *Recl. Trav. Pays-Bas*, **109** (1990) 567, and references therein; (c) J.D. Higgins, *J. Inorg. Biochem.*, **49** (1993) 149; (d) C. Navarro-Ranninger, J. López Solera, J.M. Pérez, J.M. Massaguer and C. Alonso, *Appl. Organomet. Chem.*, **7** (1993) 57; (e) A. Bose and C.H. Saha, *J. Mol. Catal.*, **49** (1989) 271; (f) P.K. Santra and C.H. Saha, *J. Mol. Cat.*, **39** (1987) 279; (g) Y. Wakatsuki, H. Yamazaki, P.A. Gutsch, M. Southanan and C. Kutal, *J. Am. Chem. Soc.*, **107** (1985) 8153; (h) M. Maestri, D. Sandrini and V. Balzani and A. von Zelewsky, *Helv. Chim. Acta*, **71** (1988) 134; (i) C. Cornioley-Deschel, T. Ward and A. von Zelewsky, *Helv. Chim. Acta*, **71** (1988) 130.
- [3] (a) J. Albert, J. Granell, J. Sales, X. Solans and M. Font, *Organometallics*, **5** (1986) 2567; (b) J. Albert, R.M. Ceder, M. Gómez, J. Granell and J. Sales, *Organometallics*, **11** (1992) 1536; (c) J. Albert, J. Barro and J. Granell, *J. Organomet. Chem.*, **408** (1991) 115; (d) J. Albert, M. Gómez, J. Granell, J. Sales and X. Solans, *Organometallics*, **9** (1990) 1405; (e) J. Albert, J. Granell and J. Sales, *J. Organomet. Chem.*, **273** (1984) 393.
- [4] *Gmelin Handbuch der Anorganische Chemie, Eisen Organische Verbindungen*, Ferrocen 1, Teil A, Springer, Heidelberg, Germany, 1976.
- [5] (a) J.C. Gaunt and B.L. Shaw, *J. Organomet. Chem.*, **102** (1975) 511; (b) V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, *J. Organomet. Chem.*, **182** (1979) 537; (c) V.I. Sokolov, L.L. Troitskaya and N. Khurscheava, *Zh. Org. Khim.*, **18** (1982)

- 2606; (d) V.I. Sokolov, L.L. Troitskaya and T.I. Rozhkova, *Gazz. Chim. Ital.*, 117 (1987) 525; (e) A. Kasahara, T. Izumi and M. Maemura, *Bull. Chem. Soc. Jpn.*, 50 (1977) 1878; (f) M. Nonoyama, *Inorg. Nucl. Chem. Lett.*, 14 (1968) 337; (g) M. Nonoyama and M. Sugimoto, *Inorg. Chim. Acta*, 35 (1979) 131; (h) I. Butler, *Organometallics*, 11 (1992) 74.
- [6] (a) C. López, J. Sales, X. Solans and R. Zquiak, *J. Chem. Soc., Dalton Trans.*, (1992) 2321; (b) R. Bosque, C. López, J. Sales, M. Font-Bardía and X. Solans, *J. Chem. Soc., Dalton Trans.*, (1994) 735; (c) R. Bosque, C. López, J. Sales, M. Font-Bardía and X. Solans, *J. Organomet. Chem.*, (1994) in press; (d) R. Bosque, M. Font-Bardía, C. López, J. Sales, X. Solans and J. Silver, *J. Chem. Soc., Dalton Trans.* (1994) 747.
- [7] (a) J.K. Lindsay and C.R. Hauser, *J. Org. Chem.*, 22 (1957) 355; (b) J.M. Osgerby and P.L. Pauson, *J. Chem. Soc.*, (1958) 656; (c) D.E. Bublitz, *J. Organomet. Chem.*, 23 (1970) 225.
- [8] M. Bracci, C. Ercolani, B. Floris, M. Bassetti, A. Chesi-Vila and C. Guastini, *J. Chem. Soc., Dalton Trans.*, (1990) 1357.
- [9] (a) I. Onue and I. Moritani, *J. Organomet. Chem.*, 43 (1972) 433; (b) J. Granell, D. Sainz, J. Sales, X. Solans and M. Font-Bardía, *J. Chem. Soc., Dalton Trans.*, (1986) 1785.
- [10] R.G. Miller, R.D. Stuffer, D.R. Fahey and D.R. Parnell, *J. Am. Chem. Soc.*, 92 (1970) 1511.
- [11] L.G. Kuzm'in, Y.T. Struchkov, L.L. Troitskaya, V.I. Sokolov and O.A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 1417.