

Mono- and bis(cyclopalladation) of the bis(ferrocenylimine) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}\}]_2$

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Abstract

The reaction of the novel bis(ferrocenylimine) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}\}]_2$ (**1**) with $\text{Na}_2[\text{PdCl}_4]$ and $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$ in methanol in a 1:2:2 or a 1:1:1 molar ratio produces the polynuclear di- μ -chloro-bridged cyclopalladated compounds $[\text{Pd}_2\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}\}]_2(\mu\text{-Cl})_2$ (**2a**) or $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-4-[(C}_6\text{H}_3\text{-2'-CH}_3\text{)-N=CH-(}\eta^5\text{-C}_5\text{H}_4\text{)]}\}\}(\mu\text{-Cl})_2$ (**2b**) respectively, which arise from the activation of two (for **2a**) or one (for **2b**) $\sigma(\text{C}_{\text{sp}^2, \text{ferrocene}}\text{-H})$ bonds. Addition of triphenylphosphine to benzene suspensions of compounds **2** produces the cleavage of the 'Pd($\mu\text{-Cl}$)₂Pd' units and the formation of $[\text{Pd}_2\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}\}]_2\text{Cl}_2(\text{PPh}_3)_2$ (**3a**), or $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-4-(C}_6\text{H}_3\text{-(2'-CH}_3\text{)-N=CH-(}\eta^5\text{-C}_5\text{H}_4\text{))}\}\}(\text{PPh}_3)]$ (**3b**). Proton and ³¹P NMR studies on compounds **3** confirm the existence of two (in **3a**) or one (in **3b**) five-membered palladocycles fused with the ferrocenyl units, and a trans arrangement of the PPh₃ ligand and the imine nitrogen. Electrochemical studies of these compounds are also reported.

Keywords: Cyclopalladation; Ferrocene; Electrochemistry

1. Introduction

Cyclopalladated compounds derived from N-donor ligands have been extensively studied during the last decade (for reviews concerning cyclometallation reactions see Ref. [1]), in particular those containing one metallacycle in which the palladium atom is bound to the nitrogen and to a C_{sp³}, to a C_{sp²,aryl} or, to a lesser extent, to a C_{sp²,ferrocene} carbon atom [2–7].

Doubly cyclopalladated derivatives containing an organic ligand with two nitrogen atoms (e.g. diamines, pyrazines, piperidines, pyrazoles, dioximes, diimines or benzylidene hydrazones) are not so common [8–10] and, in particular, those containing $\sigma(\text{Pd-C}_{\text{sp}^2, \text{ferrocene}})$ bonds are scarce. As far as we know only two articles on this kind of compound have been reported so far [11–13]. In 1976, Nonoyama and coworkers [11,12] described the double cyclopalladation of 1,1'-ferrocenylhydrazone; more recently, the syntheses and X-ray crystal structure of a bis(cyclopalladated) tetranuclear compound derived from acetylferroceneazine has been reported [13].

However, recent studies on cyclopalladation have shown that ferrocenylimines of general formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C(R)=N-R'}\}]$ (with R = H, CH₃, or C₆H₅) undergo the activation of $\sigma(\text{C}_{\text{sp}^2, \text{ferrocene}}\text{-H})$ bonds under mild experimental conditions, giving five-membered palladocycles with a $\sigma(\text{Pd-C}_{\text{sp}^2, \text{ferrocene}})$ bond in all cases [3–6]. On this basis, it seemed interesting to test whether related bifunctional ligands such as the bis(ferrocenylimine), $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}\}]_2$ (**1**) (Fig. 1), could undergo the activation of two $\sigma(\text{C-H})$ bonds.

Furthermore, ligand (**1**) could produce different kinds of cyclopalladated compounds, depending on (a) the number of C-H bonds to be activated (mono- or bis(cyclopalladated) derivatives) and (b) the nature of the metallated carbon atom C_{sp²,ferrocene} or C_{sp³} (endo- or exocyclic five-membered metallacycles respectively) (Fig. 1).

2. Results and discussion

The new bis(ferrocenylimine) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}\}]_2$ (**1**) was prepared by reaction between formylferrocene and 3,3'-dimethyl-

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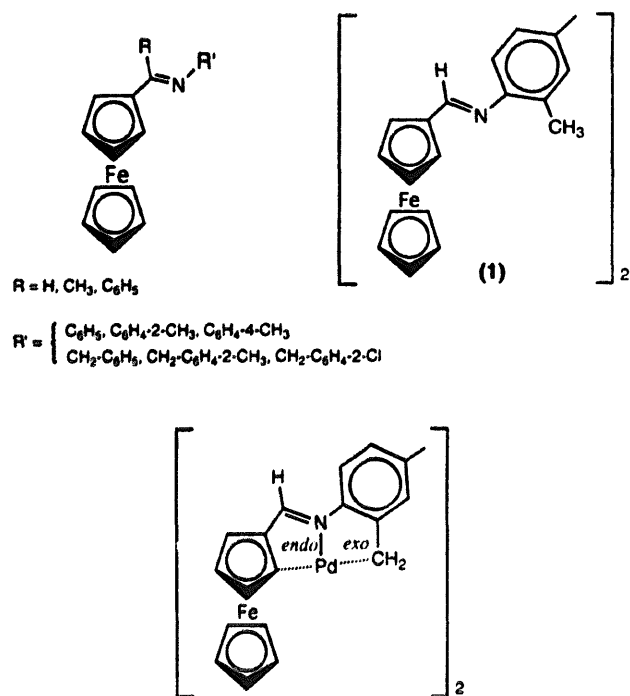


Fig. 1. Schematic view of the ferrocenylimines of general formulae $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-C(R)=N-R'})]$ and the bis(ferrocenylyimine) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-C(H)=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-})]_2$ (1) under study. The two sorts of palladacycle which may arise upon the activation of $\sigma(\text{C-H})$ bonds in ligand 1 are also shown.

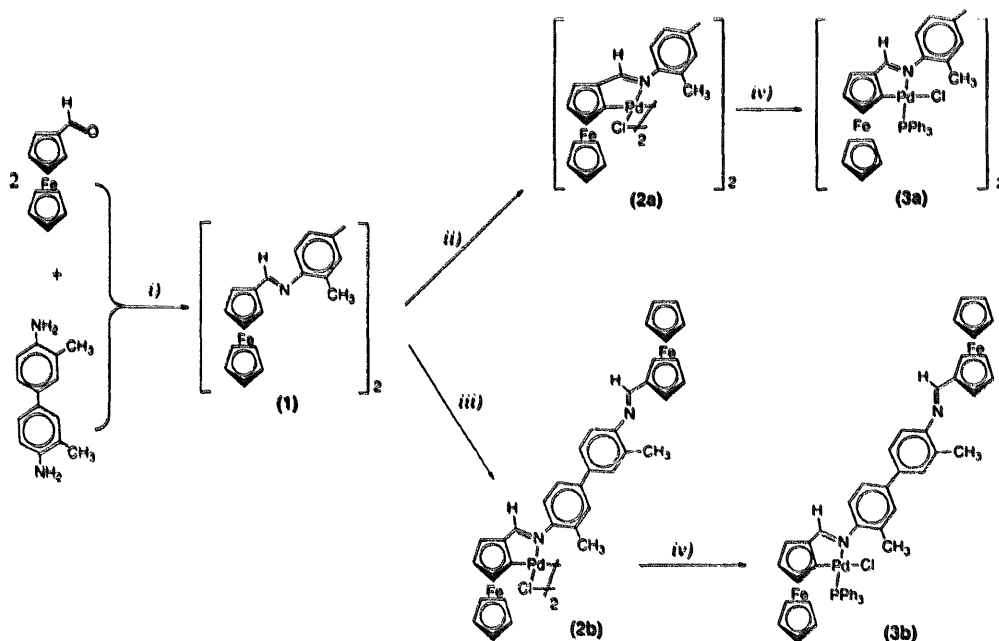
benzidine using a 1:2 molar ratio with benzene as solvent. The condensation reaction was carried out using a Dean–Stark apparatus to remove the H_2O –benzene azeotrope formed in the course of the process.

This substrate reacts at room temperature with $\text{Na}_2[\text{PdCl}_4]$ and $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ (in a 1:2:2 molar ratio) giving the di- μ -chloro-bridged cyclopalladated derivative $[\text{Pd}_2\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}]\}_2(\mu\text{-Cl})_2]$ (2a) (Scheme 1), which arises from the activation of two $\sigma(\text{C}_{\text{sp}^2, \text{ferrocene}}\text{-H})$ bonds. The tetrameric nature of complex 2a is postulated by analogy to the results obtained recently by Vila et al. [10], who have demonstrated by X-ray diffraction that double cyclopalladation of bis(*N*-benzylidene)-1,4-phenylenediamines) produce tetrameric species instead of polymeric species.

When equimolar amounts of ligand 1, $\text{Na}_2[\text{PdCl}_4]$ and $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ were used, the reaction yielded to the monometallated derivative $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-C}_6\text{H}_3\text{-(2-CH}_3\text{)-4-}[(\text{C}_6\text{H}_3\text{-2'-CH}_3\text{)-N=CH}(\eta^5\text{-C}_5\text{H}_4)]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\mu\text{-Cl})_2]$ (2b). It is worth noting that when the reaction periods were increased from 24 h to 3 days, small amounts (ca. 10%) of the dimetallated compound 2a were also detected.

Evidence of the formation of mono- or di-metallated complexes containing five-membered rings and a $\sigma(\text{Pd-C}_{\text{sp}^2})$ bond was not detected by proton-NMR spectroscopy in any case. This result is consistent with previous work on cyclopalladation of ferrocenylimines of general formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-C(R)=N-(C}_6\text{H}_4\text{-2-CH}_3\text{)-})]$, with $R = \text{H, CH}_3$ or C_6H_5 , for which endocyclic cyclopalladated complexes with $\sigma(\text{Pd-C}_{\text{sp}^2, \text{ferrocene}})$ were obtained exclusively [3–5].

These findings show, moreover, that for ligand 1 the activation of the $\sigma(\text{C}_{\text{sp}^2, \text{ferrocene}}\text{-H})$ bond is achieved



Scheme 1. (i) In refluxing benzene. (ii) $\text{Na}_2[\text{PdCl}_4]$ and $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ (using the molar ratio 1:Pd(II): $\text{CH}_3\text{COO}^- = 1:2:2$) in methanol at room temperature, 3 h. (iii) $\text{Na}_2[\text{PdCl}_4]$ and $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ (using the molar ratio 1:Pd(II): $\text{CH}_3\text{COO}^- = 1:1:1$) in methanol at room temperature, 3 h. (iv) Benzene at room temperature using PPh_3 :Pd(II) molar ratio of 1:1.

under milder experimental conditions than for bis(*N*-benzylidene)-1,4-phenylenediamines [9,10], for which the formation of the metallacycle required the use of $\text{Pd}(\text{AcO})_2$ in refluxing acetic acid. This is consistent with the higher proclivity of ferrocene derivatives to undergo electrophilic attacks [14]. Attempts to activate $\sigma(\text{C}-\text{H})$ bonds in **1** using stronger reaction conditions ($\text{Pd}(\text{AcO})_2$ and acetic acid) were unsuccessful, even at room temperature, owing to the high instability of ligand **1** in acidic medium, which produces the hydrolysis of the $-\text{C}(\text{H})=\text{N}-$ bond and the protonation of the aldehyde [14].

It is also worth noting that the results reported here differ from those obtained in cyclopalladation of the ferrocenylazine $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_4)-\text{C}(\text{H})=\text{N}-])_2]$, where only the monometallated complex was obtained; this fact can be related to steric effects arising from the higher proximity of the two nitrogen donor atoms in the azine [13].

When triphenylphosphine was added to benzene suspensions of compounds **2** in a $\text{Pd}:\text{PPh}_3$ molar ratio of 1:1, the cleavage of the ' $\text{Pd}(\mu-\text{Cl})_2\text{Pd}$ ' units took place, giving the corresponding mononuclear derivative $[\text{Pd}_2\{(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_4)-\text{CH}=\text{N}-(\text{C}_6\text{H}_3-2-\text{CH}_3)]\}_2\text{Cl}_2(\text{PPh}_3)_2]$ (**3a**) and $[\text{Pd}\{(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_4)-\text{CH}=\text{N}-\text{C}_6\text{H}_3-(2-\text{CH}_3)-4-(\text{C}_6\text{H}_3-2'-(\text{CH}_3)-\text{N}=\text{CH}(\eta^5-\text{C}_5\text{H}_4))]\text{Fe}(\eta^5-\text{C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ (**3b**).

When larger excesses of PPh_3 were used ($\text{Pd}:\text{PPh}_3$ molar ratio up to 1:3), no evidence of the cleavage of the $\text{Pd}-\text{N}$ bond was detected by ^1H or ^{31}P NMR in any case, thus suggesting the high stability of this bond. This finding is in contrast with the results reported on cyclopalladation of the analogous bis(*N*-benzylidene)-1,4-phenylenediamines in which an excess of phosphine ligands involved the opening of the metallacycle through cleavage of the $\text{Pd}-\text{N}$ bond, and the incorporation of a second PPh_3 group bound to the palladium [9,10].

All the compounds are orange-red solids at room temperature and, except **2a**, **2b**, they are soluble in most common solvents: chloroform, dichloromethane, ace-

tone and benzene; slightly soluble in alcohols and practically insoluble in hexane. In contrast, complexes **2a** and **2b** are only poorly soluble in benzene, dichloromethane and chloroform.

Elemental analyses of complexes **1–3** are consistent with the proposed formulae (see Section 3). The infrared spectrum of ligand (**1**) exhibits a sharp and intense band at 1617 cm^{-1} , which is assigned to the asymmetric stretching of the $>\text{C}=\text{N}-$ group. For the bis(cyclopalladated) complexes (**2a**, **3a**) this band appears at lower wavenumbers, in good agreement with the results reported for related palladacycles of general formula $[\text{Pd}\{(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_4)-\text{C}(\text{R})=\text{N}-\text{R}']\}\text{Cl}(\text{PPh}_3)]$ (with $\text{R} = \text{H}$, Me or Ph) [8]. However, infrared spectra of compounds **2b** and **3b**, showed two bands in the region ($1570\text{--}1625\text{ m}^{-1}$) due to the two types of $>\text{C}=\text{N}-$ group present.

The ^1H NMR spectrum of the free ligand showed two singlets at 8.27 and 2.40 ppm which were ascribed to the $-\text{C}(\text{H})=\text{N}-$ and CH_3 protons respectively. A singlet and two triplets (of relative intensities 5:2:2) were also observed in the area 3.00–5.00 ppm, and these signals are ascribed to the three types of non-equivalent protons of the ferrocenyl unit (Table 1).

The most relevant differences observed in the ^1H NMR spectrum of **3a** are: (a) the presence of four singlets of relative intensities 1:5:1:1 in the range 3.00–5.00 ppm, thus confirming that compound **3a** contains a five-membered palladacycle fused with the ferrocenyl unit through a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{ferrocene}})$; (b) the resonance of the imine proton appears as a doublet ($^4J(\text{P}-\text{H}) = 6.8\text{ Hz}$), due to phosphorus coupling, and high field shifted, thus indicating that the metallacycle contains the $>\text{C}=\text{N}-$ moiety; (c) the signal due to the H(3) proton appears at higher field due to the paramagnetic anisotropy of the aryl rings of the PPh_3 group. All these findings are consistent with the NMR-spectroscopic studies of the ferrocenylimine $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_4)-\text{C}(\text{H})=\text{N}-(\text{C}_6\text{H}_4-2-\text{CH}_3)]]$ (**4**) and its cyclopalladated derivative $[\text{Pd}\{(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_4)-\text{C}(\text{H})=\text{N}-(\text{C}_6\text{H}_4-2-\text{CH}_3)]\}\text{Cl}(\text{PPh}_3)]$ (**4a**) [4], which

Table 1

Selected proton data (ppm) for compounds under study, for the ferrocenylimine $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_4)-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2-\text{CH}_3)]]$ (**4**) and its cyclopalladated derivative $[\text{Pd}\{(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_4)-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2-\text{CH}_3)]\}\text{Cl}(\text{PPh}_3)]$ (**4a**); ^{31}P NMR data (ppm) for compounds **3a**, **3b** and **4a** are also included

	^1H NMR					^{31}P NMR	
	C_5H_5	H(2)	H(3)	H(4)	H(5)	$-\text{CH}=\text{N}-$	CH_3
1	4.24	4.72 ^a	4.48 ^a	4.48 ^a	4.72 ^a	8.27	2.40
4 ^c	4.25	4.84 ^a	4.50 ^a	4.50 ^a	4.84 ^a	8.22	2.34
3a	3.99	—	3.43	4.18	4.52	8.18 ^b	2.54
4a ^c	4.00	—	3.44	4.21	4.53	8.20 ^b	2.53
3b	4.29 ^d	4.70 ^d	4.50 ^d	4.50 ^d	4.70 ^d	8.70 ^d	2.38 ^d
	4.05	—	3.47	4.21	4.49	8.20 ^b	2.63

^a In the free ligands the protons H(2) and H(5) are equivalent, and the same occurs with the remaining two protons: H(3) and H(4). ^b Doublet due to phosphorus coupling. ^c Data from Ref. [4]. ^d This signal corresponds to the non-metallated ferrocenyl moiety of the compound.

Table 2

Half-wave potentials referred to ferrocene $E_{1/2}(\text{Fc})$ for: ligand **1**; ferrocenylimines $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-C(R)=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)})]$ (with $\text{R} = \text{H}$ (**4**), C_6H_5 (**5**) or CH_3 (**6**)); ferrocenylazines $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-C(R)=N-})]_2$ (with $\text{R} = \text{CH}_3$ (**7**) or H (**8**)) and their cyclopalladated complexes **3a**, **3b**, $[\text{Pd}((\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_3)\text{-C(R)=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)}))\text{Cl(PPh}_3\text{)}]$ (with $\text{R} = \text{H}$ (**4a**), C_6H_5 (**5a**) or CH_3 (**6a**)), $[\text{Pd}((\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_3)\text{-C(CH}_3\text{)=N-})\text{Cl(PPh}_3\text{)})]_2$ (**7a**) and the monometallated compound $[\text{Pd}((\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-N=CH-(}\eta^5\text{-C}_5\text{H}_4\text{)})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl(PPh}_3\text{)})]$ (**8b**)

Ferrocenyl ligands		Cyclopalladated compounds	
	$E_{1/2}(\text{Fc})$ (V)		$E_{1/2}(\text{Fc})$ (V)
1	0.14	3a	0.11
		3b	0.10
			0.22
4 ^a	0.15	4a ^a	0.10
5 ^a	0.17	5a ^a	0.13
6 ^a	0.14	6a ^a	0.08
7 ^a	0.17	7a ^b	0.10
8 ^b	0.12	8b ^b	0.09
			0.22

^a Data from Ref. [17]. ^b Data from Ref. [13].

could be visualized as the monomeric units of compounds **1** and **3a** respectively.

The spectrum of compound **3b** exhibited higher complexity, and two superimposed sets of signals were detected (Table 1). The positions and multiplicities of the signals for one of these sets were similar to those of the free ligand, while the other was coincident with those of compound **3a**, thus suggesting that in this case the activation of only one $\sigma(\text{C}_{\text{sp}^2, \text{ferrocene}}\text{-H})$ has taken place.

³¹P NMR spectra of **3a–3b** exhibit a singlet in the range 36–37 ppm (Table 1), which is consistent, according to the literature [3–7], with a trans arrangement between the imine nitrogen and the phosphine ligand.

Electrochemical studies based on cyclic voltammetry for compounds **1** and **3** were also carried out. The cyclic voltammogram of **1** exhibits one anodic peak with a directly associated reduction in the reverse scan; this fact indicates that the organic framework attached to the two ferrocenyl groups does not allow communication between the two centres and delocalization is not possible, making the two moieties independent [15]. The cyclic voltammogram of complex **3a** does not differ significantly from that of the free ligand except for the position of the wave, which appears at lower potentials (Table 2). This suggests that the formation of the metal-lacycle increases the proclivity of the iron(II) to undergo oxidation. This finding is in good agreement with previous work on cyclopalladated compounds derived from ferrocenylamines, ferrocenylimines [16,17], and ferrocenylazines [13].

In contrast to this situation, the cyclic voltammogram of complex **3b** showed two independent waves. The less anodic peak, which appears at lower potentials than in

the free ligand **1**, is attributed to the oxidation of the iron(II) of the metallated moiety; the other peak, at higher potentials, is due to the oxidation of the remaining Fe(II). Consequently, in this case the two Fe(II) centres exhibit different proclivity to undergo oxidation. On this basis complex (**3b**) resembles to the monocyclopalladated complex $[\text{Pd}((\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-N=CH-(}\eta^5\text{-C}_5\text{H}_4\text{)})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl(PPh}_3\text{)})]$ described recently [13].

2.1. Final remarks

The results reported here have allowed not only the preparation and characterization of the novel bis(ferrocenylimine) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}((\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-})]_2$ (**1**), but also the study of its reactivity vs. $\text{Na}_2[\text{PdCl}_4]$. These studies have enabled us, moreover, to obtain polymetallic mono- and bis(cyclopalladated) compounds containing five-membered palladacycles and one or two $\sigma(\text{Pd-C}_{\text{sp}^2, \text{ferrocene}})$ bonds. Electrochemical studies on all the compounds under study have also provided a method of fine tuning the oxidation potentials of the Fe(II), by replacement of one or two $\sigma(\text{C}_{\text{sp}^2, \text{ferrocene}}\text{-H})$ bonds by $\sigma(\text{Pd-C}_{\text{sp}^2, \text{ferrocene}})$ bonds. In particular, for compound **3b**, which contains two Fe(II) ions in a different electronic and chemical environment, it is possible to oxidize one of the ferrocenyl fragments exclusively. This result is particularly important since it may allow the preparation of polymetallic species containing mixed ferrocene–ferricinium units by the oxidation of one of the Fe(II) ions in compound (**3b**).

3. Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Científico-Tècnics de la Universitat de Barcelona. Infrared spectra were obtained with a Nicolet 520-FTIR spectrophotometer using KBr pellets. Routine ¹H and ¹³C-{¹H} NMR spectra were recorded at ca. 20°C on a Gemini-200 MHz instrument using CDCl₃ (99.8%) and Si(CH₃)₄ as solvent and internal standard respectively. The ³¹P-{¹H} NMR spectra of compounds **3** were recorded with a Bruker WP50-SY instrument (32.8 MHz), using CHCl₃ as solvent and P(OCH₃)₃ as standard.

3.1. Materials and syntheses

Formylferrocene, 3,3'-dimethylbenzidine and the remaining reagents were obtained from standard sources and used as-received. Some of the preparations described below involve the use of benzene which should be handled with CAUTION. All the solvents were dried and distilled before use.

3.2. Preparation of the compounds

3.2.1. Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}]_2$ (1)

Formylferrocene (1.0 g, 4.57 mmol) was dissolved in benzene (30 cm³) at 20°C. Once the starting material had dissolved completely, 3,3'-dimethylbenzidine (4.85 g, 2.29 mmol) was added, and the reaction flask was connected to a condenser equipped with a Dean-Stark apparatus (ca. 20 cm³). The wine-red solution was then refluxed on an ethylene glycol bath until ca. 10 cm³ had condensed in the Dean-Stark apparatus. The hot solution was carefully filtered out and the filtrate was concentrated to dryness in a rotary evaporator. Addition of *n*-hexane to the gummy material formed, followed by vigorous stirring at ca. 20°C precipitated the bis(ferrocenylimine) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_3\text{-2-CH}_3\text{)-}]_2$ (1). The orange solid was filtered off and air-dried. (Yield: 89%). *Characterization data.* Anal. (%) calc. (found) for C₃₆H₃₂Fe₂N₂: C, 71.51 (71.4); H, 5.33 (5.35); N, 4.64 (4.6). IR, $\nu(>\text{C=N-})$: 1623 cm⁻¹.

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

The bis(ferrocenylimine) (1), (0.603 g, 1.0 mmol), Na₂[PdCl₄] (0.590 g, 2.0 mmol) and Na(CH₃COO)·3H₂O (0.260 g, 2 mmol) were suspended in 50 cm³ of methanol. The reaction flask was protected from the light with aluminium foil and stirred in an open vessel at room temperature (ca. 20°C) for 24 h to accomplish the reaction. The deep red solid formed was filtered off and washed with methanol (until colourless washings were obtained) and air-dried. The compound was then purified by SiO₂ column chromatography (10.0 mm × 250.0 mm) using CHCl₃ as eluant. The red band was collected and concentrated to dryness on a rotary evaporator, and then treated with *n*-hexane (ca. 50 cm³). The mixture was stirred vigorously at room temperature for ca. 1 h. The microcrystalline solid was collected and air-dried. (Yield: 60%). *Characterization data.* Anal. (%) calc. (found) for C₇₂H₆₀Cl₄Fe₄N₄Pd₄: C, 48.87 (48.7); H, 3.42 (3.5); N, 3.17 (3.3). IR, $\nu(>\text{C=N-})$: 1590 cm⁻¹.

3.2.3. Preparation of $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-(CH}_3\text{)-4-(C}_6\text{H}_3\text{-2'-(CH}_3\text{)-N=CH-(}\eta^5\text{-C}_5\text{H}_4\text{)-}\})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{-(}\mu\text{-Cl)}\}]_2$ (2b)

This complex was prepared according to the procedure described in Section 3.2.2 for (2a), but using equimolar amounts (1 mmol) of the reagents. (Yield: 52%). *Characterization data:* Anal. (%) calc. (found) for C₇₂H₆₄Cl₂Fe₄N₄Pd₂: C, 57.99 (58.1); H, 4.30 (4.2); N, 3.76 (3.9). IR, $\nu(>\text{C=N-})$: 1595 and 1618 cm⁻¹.

3.2.4. Preparation of $[\text{Pd}_2\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-(CH}_3\text{)-}\}]_2\text{Cl}_2(\text{PPh}_3)_2$ (3a)

Triphenylphosphine (0.260 g, 1 mmol) was added to a benzene suspension (20 cm³) containing 0.5 mmol of the dimeric compound 2a. The resulting mixture was stirred at ca. 20°C for 3 h. The solution was then filtered out and the filtrate was concentrated to dryness in a rotary evaporator. The gummy material formed was dissolved in the minimum amount of CHCl₃ and purified by SiO₂ column chromatography (10.0 mm × 250.0 mm) using CHCl₃ as eluant. The red band was collected and concentrated to dryness in a rotary evaporator. The oil formed was quenched by adding *n*-hexane (10 cm³). The orange-red solid formed was collected by filtration and air-dried. (Yield: 70%). *Characterization data.* Anal. (%) calc. (found) for C₇₂H₆₀Cl₂Fe₂N₂P₂: C, 58.71 (58.7); H, 4.19 (4.18); N, 1.88 (1.95). IR, $\nu(>\text{C=N})$: 1613 cm⁻¹.

3.2.5. Preparation of $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-(CH}_3\text{)-4-(C}_6\text{H}_3\text{-2'-(CH}_3\text{)-N=CH-(}\eta^5\text{-C}_5\text{H}_4\text{)-}\})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{-(}\mu\text{-Cl)}\}]$ (3b)

This product was prepared as described for (3a) but using $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_3\text{-2-Cl)-4-(C}_6\text{H}_3\text{-2'-(CH}_3\text{)-N=CH-(}\eta^5\text{-C}_5\text{H}_4\text{)-}\})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{-(}\mu\text{-Cl)}\}]_2$ (2b) as starting material and a PPh₃:Pd molar ratio of 1:1. (Yield: 68%). *Characterization data.* Anal. (%) calc. (found) for C₅₄H₄₆ClFe₂N₂PPd: C, 64.41 (64.5); H, 4.61 (4.65); N, 2.78 (2.9). IR, $\nu(>\text{C=N})$: 1599 and 1619 cm⁻¹.

3.3. Electrochemical studies

Electrochemical data for the compounds under study were obtained by cyclic voltammetry under N₂ at 20°C using acetonitrile (HPLC grade) as solvent and tetrabutylammonium hexafluorophosphate (0.1 mol cm⁻³) as supporting electrolyte. The redox half-wave potentials *E*_{1/2} were referred to an Ag–AgNO₃ (0.1 M, in acetonitrile) electrode separated from the solution by a medium-porosity fritted disk. A platinum wire auxiliary electrode was used in conjunction with a platinum disk working electrode, Tacussel–EDI rotatory electrode (3.14 mm²). Further details concerning the DAC-FAMOV potentiostat are described elsewhere [18].

Cyclic voltammograms of ferrocene were recorded before and after each sample to ensure the viability and reproducibility of the results [19], in particular to test and control the stability of the Ag–AgNO₃ electrode. Three cyclic voltammograms of 10⁻³ M solution of the samples in acetonitrile were run and the average values of the *E*_{1/2} measured were then referred to ferrocene (*E*_{1/2}(Fc)), which was also used as internal standard to facilitate the interpretation of the results. In all cases the separation between the anodic and cathodic peaks $\Delta E = E_{\text{pa}} - E_{\text{pc}}$, and the ratio *i*_{pa}/*i*_{pc}, were similar to those

obtained for ferrocene alone under identical experimental conditions.

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