

# Novel cyclopalladated ferrocenyl Schiff base compounds with bridging and chelating diphosphines. Crystal and molecular structure of $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{N}-2,4,6\text{-Me}_3\text{C}_6\text{H}_2]\} - \{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{-}P,P\}][\text{PF}_6]$ ( $n = 1, 2$ )

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## Abstract

The reaction of the ferrocenylimine  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{H})=\text{NR}$  ( $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) (**a**), with  $\text{Pd}(\text{AcO})_2$  or with  $\text{Li}_2[\text{PdCl}_4]$  leads to the heterotetrametallic compounds  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\}(\mu\text{-O}_2\text{CMe})_2]$  (**1**) and  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\}(\mu\text{-Cl})_2]$  (**2**), respectively. Compound **2** may also be obtained by treatment of **1** with aqueous sodium chloride. Compound **2** reacts with tertiary diphosphines in 1:1 or 1:2 molar ratio to give  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}]\text{Cl}\}_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$  ( $n = 1, \mathbf{3}; n = 2, \mathbf{4}; n = 3, \mathbf{5}; n = 4, \mathbf{6}$ ),  $[\{\text{Pd}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}]\text{Cl}\}_2(\mu\text{-Ph}_2\text{PC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{PPh}_2)]$  (**7**), and  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{-}P,P\}][\text{PF}_6]$  ( $n = 1, \mathbf{8}; n = 2, \mathbf{9}; n = 3, \mathbf{10}; n = 4, \mathbf{11}$ ),  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\}(\text{Ph}_2\text{PC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{PPh}_2\text{-}P,P)][\text{PF}_6]$  (**12**), respectively. The crystal structures of compounds **8** and **9** have been determined by X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Cyclometallation; Palladium; Imine

## 1. Introduction

The discovery of ferrocene by Kealy and Pauson [1] was a milestone in organometallic chemistry; moreover, the description of the chemical bond in ferrocene was of paramount importance in the understanding of the new bonding mode hitherto unknown [2,3]. This has led to the synthesis of a great deal of analogous sandwiched compounds with transition metals other than iron and with related ligands, the result of which yielded the wide variety of species known to date. Among these are the cyclometallated class of complexes [4] derived from ligands that bear the ferrocenyl moiety, such as Schiff bases, which contain a  $\sigma(\text{M}-\text{C}_{\text{sp}^2})$  bond to the five-membered ring. In previous work we have shown that mono- and bidentate imines may be readily

metallated by palladium(II) giving compounds with a  $\sigma(\text{M}-\text{C}_{\text{sp}^2})$  bond to the phenyl ring [5–7]; as the number of donor atoms to the metal atom increases metallation of the phenyl ring seems to proceed under milder reaction conditions. Thus, potentially terdentate Schiff bases [8,9], semicarbazones [10] and thiosemicarbazones [11,12] undergo facile metallation with palladium(II), as well as with palladium(0) and platinum(II) yielding compounds with two five-membered fused rings at the metal center. In the case of ferrocenyl ligands the more aromatic character of the ferrocene ring as opposed to its phenyl counterparts should facilitate the electrophilic attack of the  $\text{sp}^2$  carbon atom by palladium(II) [13–15] giving reactions that proceed smoothly at room temperature [16–18]. Consequently, in the last years numerous papers concerning cyclometallation of ferrocene moieties by transition metals have appeared [19–21]. Inasmuch as a wide variety of complexes are now known, little if any work has been carried out

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related to their reactivity with diphosphines; probably due to decomposition processes that cyclometallated palladium(II) complexes containing phosphines or diphosphines seem to undergo, especially in solution [22]. Examples of cyclopalladated ferrocene derivatives with diphosphines are scarce and to the best of our knowledge only two examples with chelating bis(diphenylphosphino)ethane or bis(diphenylphosphino)-1,1'-naphthyl have been reported [19,23,24], whilst compounds with bridging diphosphines remain outstanding. In the present work we describe the reactions of the heterotetranuclear compound  $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\{\mu\text{-Cl}\}]_2$  with the diphosphines  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1\text{--}4$ ) and 1,1'-bis(diphenylphosphino)ferrocene to give novel multinuclear complexes containing bridging or chelating phosphorus ligands. The first crystal structures of two such compounds are also reported.

## 2. Results and discussion

### 2.1. Synthesis and characterization

The ligand  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{H})=\text{N-2,4,6-Me}_3\text{C}_6\text{H}_2$  (**a**) was prepared by reaction of ferrocenecarboxaldehyde and 2,4,6-trimethylaniline in refluxing chloroform (see Section 4 and Table 1). The IR spectrum showed the expected value of the  $\nu\text{C}=\text{N}$  stretch at  $1627\text{ s cm}^{-1}$ . The  $^1\text{H-NMR}$  spectrum showed a singlet at  $\delta 8.06$  due to the  $\text{HC}=\text{N}$  proton. Two apparent triplets at  $\delta 4.79$  and  $\delta 4.47$  were ascribed to the H2, H5 and H3, H4 protons, respectively, of the substituted ferrocenyl ring; a singlet at  $\delta 4.26$  was assigned to the  $\text{C}_5\text{H}_5$  ring protons. It should be noted that although in previous papers authors tend to give the  $\text{C}_5\text{H}_4$  resonances in the  $^1\text{H-NMR}$  spectrum as two multiplets, the  $\text{C}_5\text{H}_4$  protons constitute an AA'XX' spin system for which two apparent triplets appear due to simplification of the 20 lines of the theoretical spectrum [25].

Compounds **1** and **2** have been previously reported by us [16]. Compound **1** was made by treating ligand **a** with  $\text{Na}_2[\text{PdCl}_4]$  and reaction of **1** with silver acetate yielded **2**. Furthermore, no account of the IR spectra was given. We now report new syntheses for these compounds, together with the IR data, and we also include a more complete and detailed discussion of the  $^1\text{H-NMR}$  spectra. Thus, treatment of ligand **a** with palladium(II) acetate in boiling toluene for 8 h gave a residue from which the tetranuclear compound  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\}\{\mu\text{-O}_2\text{CMe}\}]_2$  (**1**) was isolated after column chromatography as an orange air-stable solid (see Section 4 and Scheme 1). The  $\nu(\text{C}=\text{N})$  band shift towards lower wavenumbers [26,27] and the upfield shift of the  $\text{HC}=\text{N}$  resonance in the  $^1\text{H-NMR}$  spectrum supports nitrogen coordination to

the metal center [28]. Metallation of the ligand is manifest from the absence of the AA'XX' system of the  $\text{C}_5\text{H}_4$  ring; three proton resonances were assigned for the  $\text{C}_5\text{H}_3$  group (see Table 1). The  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  values were in agreement with bridging acetate groups [29]; the singlet resonance at  $\delta 2.25$  in the spectrum was assigned to the equivalent methyl acetate protons, in accordance with a *trans* geometry of the cyclometallated moieties.

In a typical metathesis reaction, treatment of **1** with aqueous sodium chloride gave the corresponding chloro-bridged tetranuclear dimer compound  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\}\{\mu\text{-Cl}\}]_2$  (**2**) as an air-stable solid which was fully characterized (see Section 4 and Table 1). The IR spectrum showed the absence of the acetate bands, and two bands at  $350$  and  $262\text{ cm}^{-1}$  were assigned to the differing  $\nu(\text{Pd-Cl})_b$  vibrations of the asymmetric  $\text{Pd}_2\text{X}_2$  bridging unit. Alternatively, compound **2** could be made by reaction of **a** with  $\text{Li}_2[\text{PdCl}_4]$  and  $\text{Na}(\text{AcO})$  in methanol for 48 h at room temperature. In subsequent syntheses of compound **2**, this method was preferred owing to the higher yield obtained and because it involves only one reaction step. The activation of the  $\text{C}_{\text{sp}^2}\text{-H}$  bond in ferrocene introduces planar chirality ( $R_p$  or  $R_s$ ) [19] and papers dealing with the chirality of cyclopalladated ferrocenyl compounds have appeared [23,30,31]. However, we have detected but one set of signals in the  $^1\text{H-NMR}$  spectra for compounds **1** and **2**.

Treatment of **2** with tertiary diphosphines in 1:1 molar ratio gave the tetranuclear compounds  $[\{\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\}\text{Cl}\}]_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$  ( $n = 1, \mathbf{3}; n = 2, \mathbf{4}; n = 3, \mathbf{5}; n = 4, \mathbf{6}$ ), and the pentanuclear species  $[\{\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{NR}\}\text{Cl}\}]_2\{\mu\text{-Ph}_2\text{PC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{PPh}_2\}]$  (**7**) with the phosphine ligand bridging the two palladium centers, as pure air-stable solids which were fully characterized (see Section 4, Scheme 2 and Table 1). To the best of our knowledge these are the first ferrocenylimine cyclopalladated compounds with bridging diphosphine ligands. The  $^1\text{H-NMR}$  spectra showed the H4 resonance was shifted to lower frequency and coupled to the phosphorus nucleus (in compound **7** this shift is slightly towards higher frequency). The  $^{31}\text{P}$  resonance was a singlet signal in accordance with centrosymmetric compounds [32]; the chemical shift values were consistent with a phosphorus *trans* to nitrogen geometry.

Cyclopalladated ferrocene compounds with chelating diphosphines are limited to bis(diphenylphosphino)ethane [19] or to bis(diphenylphosphino)-1,1'-naphthyl as a reagent for chiral recognition [23]. Furthermore, it has been claimed that the use of bis(diphenylphosphino)ethane (dppe) frequently results in decomposition of the materials prepared. In particular, the cyclopalladated compound  $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)\text{C}(\text{H})=\text{N}(\text{C}_6\text{H}_4\text{-2-C}_6\text{H}_5)\}\{\mu\text{-Cl}\}]_2$  reacted with

Table 1  
<sup>31</sup>P<sup>a</sup>- and <sup>1</sup>H<sup>b</sup>-NMR data<sup>c</sup>

Compound	<sup>31</sup> P	<sup>1</sup> H	
		Cp	Others
<b>a</b>		4.79 (t, 2H, H <sup>2</sup> , H <sup>5</sup> ) 4.47 (t, 2H, H <sup>3</sup> , H <sup>4</sup> ) 4.26 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	8.06 (s, 1H, HC=N) 6.87 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.76 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.28 (s, 6H, Me) 2.15 (s, 3H, Me)
<b>1</b>		4.90 (br, 1H, H <sup>2</sup> ) 4.52 (br, 1H, H <sup>3</sup> ) 4.20 (br, 1H, H <sup>4</sup> ) 4.39 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	7.84 (s, 1H, HC=N) 6.81 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.79 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.43 (s, 3H, Me) 2.25 (s, br, 6H, Me <sup>d</sup> ) 2.17 (s, 3H, Me)
<b>2</b>		4.65 (br, H <sup>2</sup> , H <sup>3</sup> , H <sup>2</sup> ) 4.50 (br, 1H, H <sup>3</sup> ) 4.21 (br, 1H, H <sup>4</sup> ) 4.42 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	7.75 (s, 1H, HC=N) 6.91 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.90 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.52 (s, 3H, Me) 2.24 (s, 3H, Me) 2.17 (s, 3H, Me)
<b>3</b>	25.1s	4.30 (d, 1H, H <sup>2</sup> , 2.3 <sup>e</sup> ) 4.04 (t, 1H, H <sup>3</sup> , 2.3 <sup>e</sup> ) 3.41 (m, 1H, H <sup>4</sup> ) 3.57 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	7.85 (d, 1H, HC=N, 7.4 <sup>f</sup> ) 6.93 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.86 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.50 (s, 3H, Me) 2.29 (s, 3H, Me) 2.09 (s, 3H, Me)
<b>4</b>	29.2s	4.39 (d, 1H, H <sup>2</sup> , 2.3 <sup>e</sup> ) 4.15 (t, 1H, H <sup>3</sup> , 2.3 <sup>e</sup> ) 3.45 (m, 1H, H <sup>4</sup> ) 3.89 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	7.95 (d, 1H, HC=N, 7.8 <sup>f</sup> ) 6.88 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.84 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.40 (s, 3H, Me) 2.28 (s, 3H, Me) 2.14 (s, 3H, Me)
<b>5</b>	26.2s	4.40 (d, 1H, H <sup>2</sup> , 2.3 <sup>e</sup> ) 4.15 (m, 1H, H <sup>3</sup> ) 3.40 (dd, 1H, H <sup>4</sup> , 2.3 <sup>d</sup> , 30.0 <sup>f</sup> ) 3.85 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	7.96 (d, 1H, HC=N, 7.4 <sup>f</sup> ) 6.90 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.86 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.36 (s, 3H, Me) 2.29 (s, 3H, Me) 2.08 (s, 3H, Me)
<b>6</b>	27.2s	4.39 (d, 1H, H <sup>2</sup> , 2.3 <sup>e</sup> ) 4.14 (m, 1H, H <sup>3</sup> ) 3.46 (dd, 1H, H <sup>4</sup> , 2.3 <sup>e</sup> , 28.6 <sup>f</sup> ) 3.86 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	7.96 (d, 1H, HC=N, 7.4 <sup>f</sup> ) 6.88 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.83 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.40 (s, 3H, Me) 2.27 (s, 3H, Me) 2.17 (s, 3H, Me)
<b>7</b>	22.4s	4.76 (m, 2H, H <sup>2</sup> , H <sup>3</sup> ) 4.41 (d, 1H, H <sup>4</sup> , 13.4 <sup>f</sup> ) 4.14 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	8.02 (d, 1H, HC=N, 7.8 <sup>f</sup> ) 6.87 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.85 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.48 (s, 3H, Me) 2.17 (s, 3H, Me) 2.17 (s, 3H, Me)
<b>8</b>	−11.4d 38.2d (61.0) <sup>g</sup>	4.67 (d, 1H, H <sup>2</sup> , 2.3 <sup>e</sup> ) 4.62 (m, 1H, H <sup>3</sup> ) 4.17 (m, 1H, H <sup>4</sup> ) 4.13 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	8.05 (d, 1H, HC=N, 7.8 <sup>f</sup> ) 6.66 (br, 2H, C <sub>6</sub> H <sub>2</sub> ) 2.30 (s, 3H, Me) 2.23 (s, 3H, Me) 2.01 (s, 3H, Me)
<b>9</b>	52.6d 37.9d (18.8) <sup>g</sup>	4.64 (d, 1H, H <sup>2</sup> , 2.3 <sup>e</sup> ) 4.48 (m, 1H, H <sup>3</sup> , 2.3 <sup>e</sup> ) 3.77 (m, 1H, H <sup>4</sup> , 2.3 <sup>e</sup> ) 4.01 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	8.00 (d, 1H, HC=N, 7.4 <sup>f</sup> ) 6.36 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 6.15 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.15 (s, 3H, Me) 2.06 (s, 3H, Me) 1.74 (s, 3H, Me)
<b>10</b>	14.5d −11.2d	4.66 (d, 1H, H <sup>2</sup> , 2.7 <sup>e</sup> ) 4.40 (m, 1H, H <sup>3</sup> , 2.7 <sup>e</sup> )	7.94 (d, 1H, HC=N, 7.8 <sup>f</sup> ) 6.36 (s, 1H, C <sub>6</sub> H <sub>2</sub> )

Table 1 (Continued)

Compound	<sup>31</sup> P	<sup>1</sup> H	
		Cp	Others
	(18.7) <sup>g</sup>	3.61 (m, 1H, H <sup>4</sup> ) 3.99 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	6.02 (s, 1H, C <sub>6</sub> H <sub>2</sub> ) 2.26 (s, 3H, Me) 2.04 (s, 3H, Me) 1.84 (s, 3H, Me)
<b>11</b>	13.2d	4.67 (d, 1H, H <sup>2</sup> , 2.3 <sup>c</sup> )	7.95 (d, 1H, HC=N, 7.4 <sup>f</sup> )
	20.5d	4.39 (m, 1H, H <sup>3</sup> )	6.40 (s, 1H, C <sub>6</sub> H <sub>2</sub> )
	(19.2) <sup>g</sup>	3.74 (m, 1H, H <sup>4</sup> )	6.18 (s, 1H, C <sub>6</sub> H <sub>2</sub> )
		3.98 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	2.15 (s, 3H, Me) 2.11 (s, 3H, Me) 1.84 (s, 3H, Me)
<b>12</b>	30.0d	4.75 (br, 1H, H <sup>2</sup> )	8.02 (d, 1H, HC=N, 7.8 <sup>f</sup> )
	22.3d	4.48 (br, 1H, H <sup>3</sup> )	6.32 (s, 1H, C <sub>6</sub> H <sub>2</sub> )
	(14.1) <sup>g</sup>	4.15 (br, 1H, H <sup>4</sup> )	6.19 (s, 1H, C <sub>6</sub> H <sub>2</sub> )
		4.13 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	2.49 (s, 3H, Me) 2.27 (s, 3H, Me) 1.96 (s, 3H, Me)

<sup>a</sup> In CDCl<sub>3</sub> unless otherwise stated. Measured at 100.6 MHz (ca. 20 °C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H<sub>3</sub>PO<sub>4</sub>.

<sup>b</sup> In CDCl<sub>3</sub> unless otherwise stated. Measured at 250 or 300 MHz; chemical shifts (δ) in ppm (± 0.01) to high frequency of SiMe<sub>4</sub>.

<sup>c</sup> Coupling constants in Hz. s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt doublet of triplets; dq, doublet of quadruplets; m, multiplet; br, broad; oc, occluded.

<sup>d</sup> Includes the MeCOO resonance.

<sup>e</sup>  $N = {}^3J(\text{HH})$ .

<sup>f</sup>  ${}^4J(\text{HP})$ .

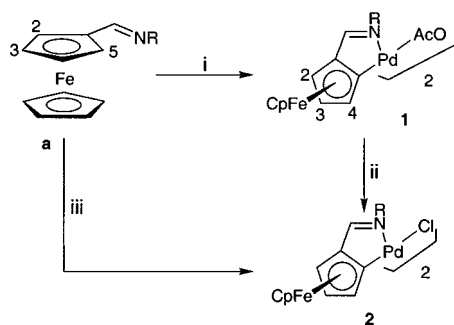
<sup>g</sup>  ${}^nJ(\text{PP})$ .

Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub> (dppe) at room temperature to give the coordination complex [PdCl<sub>2</sub>(dppe)] [19]. Therefore, we sought out to find if this was a general tendency of diphosphines similar to dppe, as well as the behavior of the related 1,1'-bis(diphenylphosphino)ferrocene. Thus, treatment of **2** with tertiary diphosphines in 1:2 molar ratio and ammonium hexafluorophosphate gave the dinuclear compounds [Pd{(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)C(H)=NR}{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>-P,P}][PF<sub>6</sub>] (*n* = 1, **8**; *n* = 2, **9**; *n* = 3, **10**; *n* = 4, **11**), and the trinuclear species [Pd{(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)C(H)=NR}{(Ph<sub>2</sub>PC<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>-P,P)}][PF<sub>6</sub>] (**12**) as orange air-stable solids. Characteristic microanalytical and spectroscopic data are given in Section 4 and in Table 1. The complexes were 1:1 electrolytes, as shown by molar conductivity measurements in dry acetonitrile. The <sup>31</sup>P-NMR spectra showed two doublets for the two non-equivalent phosphorus nuclei. The resonance at lower frequency was assigned to the phosphorus nucleus *trans* to the carbon atom in agreement with the relative *trans* influence of the imine nitrogen atom and the sp<sup>2</sup> carbon atoms [33].

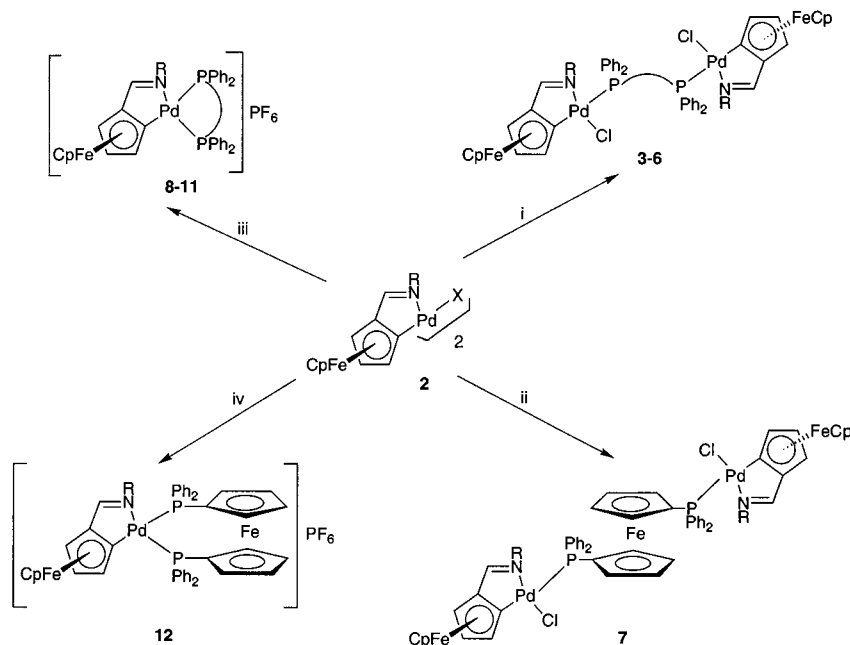
Although cyclometallated complexes bearing phosphine ligands at the metal center tend to decompose in solution to give typical phosphine coordination compounds (vide supra) [22,24], in the present case we have not observed the appearance of coordination species consequent upon decomposition.

## 2.2. Molecular structures of compounds **8** and **9**

Suitable crystals of compounds **8** and **9** were grown by slowly evaporating chloroform solutions. The molecular structure for each cation with the numbering scheme is illustrated in Figs. 1 and 2, respectively. Crystal data are given in Table 2. Selected bond lengths and angles are listed in Table 3. The structures consist of discrete molecules separated by van der Waals distances. The palladium(II) atom in each compound is in a slightly distorted square-planar environment bonded to two phosphorus atoms of the diphosphine ligand, the nitrogen atom and the C(12), **8**, and C(1), **9**, atom of the ferrocenyl moiety. The deviations from the mean



Scheme 1. (i) Pd(AcO)<sub>2</sub>–toluene; (ii) aqueous NaCl; (iii) Li<sub>2</sub>[PdCl<sub>4</sub>]–MeOH. R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.



Scheme 2. (i)  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  (1:1 molar ratio), acetone; (ii)  $\text{Ph}_2\text{PC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{PPh}_2$  (1:1 molar ratio), acetone; (iii)  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  (1:2 molar ratio) +  $\text{NH}_4\text{PF}_6$ , acetone; (iv)  $\text{Ph}_2\text{PC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{PPh}_2$  (1:2 molar ratio) +  $\text{NH}_4\text{PF}_6$ , acetone.

plane are as follows: Pd(1) 0.0037, C(12) 0.0762, N(1)  $-0.2327$ , P(1)  $-0.0213$ , P(2) 0.0052 Å (8), and Pd(1) 0.0032, C(1)  $-0.1934$ , N(1)  $-0.1776$ , P(1) 0.1518, P(2)  $-0.1709$  Å (9). The angles between adjacent atoms in the coordination sphere are close to the expected value of  $90^\circ$  with a somewhat reduced bond angle C(12)–Pd(1)–N(1) of  $80.0(2)^\circ$  for compound 8 and C(1)–Pd(1)–N(1) of  $81.09(19)^\circ$  for compound 9 consequent upon chelation. This is reflected in the C(13)–C(12)–Pd(1) angle,  $140.9(5)^\circ$  (8), and in the C(2)–C(1)–Pd(1) angle,  $144.3(4)^\circ$  (9). The angles of the five-membered chelate ring Pd(1)P(1)C(21)C(22)P(2) in compound 9 are close to the expected values for  $\text{C}_{\text{sp}^3}$ ,  $\text{P}_{\text{sp}^3}$ ,  $109.5^\circ$ , and square-planar Pd(II),  $90^\circ$ . However, in compound 8 the four-membered chelate ring at palladium imposed by the short bite diphosphine,  $\text{Ph}_2\text{PCH}_2\text{-PPh}_2$ , accounts for strong deviations from the theoretical values in the angles centered at P(1), C(61) and P(2),  $96.8(2)$ ,  $96.0(3)$ ,  $90.7(2)$ , respectively, and at Pd(1),  $72.33^\circ$ . The sum of angles about palladium in compound 8 is  $360.21^\circ$ , and in compound 9,  $361.48^\circ$ . The Pd–C bond lengths Pd(1)–C(12)  $2.023(6)$  Å (8) and Pd(1)–C(1)  $2.044(5)$  Å (9) are shorter than the expected value of  $2.081$  Å based on the sum of the covalent radii of carbon ( $\text{sp}^2$ ) and palladium,  $0.771$  and  $1.31$  Å, respectively [34], but longer than those found in other cyclopalladated compounds where partial multiple-bond character of the Pd–C bond was assumed [35,36], as a consequence of the *trans* influence of the phosphine ligand. The Pd–N bond lengths Pd(1)–N(1)  $2.142(5)$  Å (8) and Pd(1)–N(1)  $2.129(4)$  Å (9) are longer than the single bond value of  $2.01$  Å calculated from the covalent

radii of  $\text{N}_{\text{sp}^2}$   $0.70$  Å, palladium  $1.31$  Å, which is consistent with the *trans* influence of the phosphine ligands. The distinct Pd–P bond lengths Pd(1)–P(1)  $2.2359(17)$ , Pd(1)–P(2)  $2.4141(19)$  Å (8) and Pd(1)–P(1)  $2.3447(14)$ , Pd(1)–P(2)  $2.2418(15)$  Å (9) arise from the differing *trans* influence of the metallated  $\text{C}_{\text{sp}^2}$  and nitrogen atoms of the ferrocenylimine. These values [except Pd(1)–P(2)  $2.4141(19)$  Å (8)] are shorter than the sum of the single bond radii for palladium and phosphorus,  $2.41$  Å [34], as observed before [37]. The metallated pentagonal ring of the ferrocenyl moiety and the five-membered palladacycle are nearly co-planar

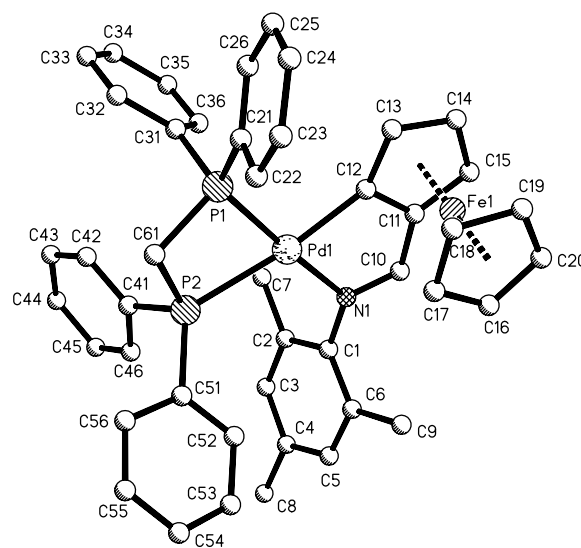


Fig. 1. Crystal structure of compound 8 with the labeling scheme. Hydrogen atoms and the  $\text{PF}_6$  anions have been omitted for clarity.

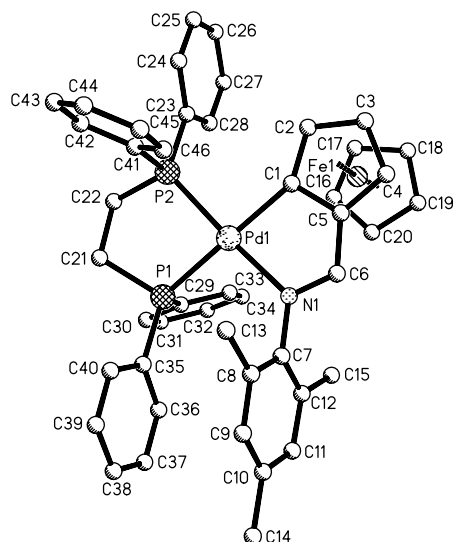


Fig. 2. Crystal structure of compound **9** with the labeling scheme. Hydrogen atoms and the  $\text{PF}_6^-$  anions have been omitted for clarity.

with angles between mean planes of  $2.2^\circ$  (**8**) and  $1.4^\circ$  (**9**). The two  $\text{C}_5\text{H}_5$  rings are parallel, nearly eclipsed with tilt angles of  $0.9^\circ$  (**8**) and  $3.4^\circ$  (**9**); with  $8.4^\circ$  (**8**) and  $9.6^\circ$  (**9**) skewed from an eclipsed configuration. Irrespective of the chirality introduced by activation of the  $\text{C}_{\text{sp}^2}\text{-H}$  bond in ferrocene, in compound **9** a further source of chirality stems from the non-planarity of the chelated five-membered ring at palladium, Pd(1)–P(1)–C(21)–C(22)–P(2), related to the differing conformations of the chelate ring as has been described by Bailar et al. [38]. In any case, whichever is the source of chirality, the space group of the crystal structures (see Table 2) indicates that both enantiomers are present in the solid state in compounds **8** and **9**.

### 3. Conclusions

The results reported in the present paper show that the ferrocenyl Schiff base  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{H})=\text{N}-2,4,6\text{-Me}_3\text{C}_6\text{H}_2$  may be smoothly metallated to give the corresponding cyclopalladated tetranuclear acetato-bridged complex **1**, which may be converted into the corresponding chloro-bridged compound **2** by a simple metathesis reaction. However, higher yields of **2** are achieved by direct metallation of the ligand with  $\text{Li}_2[\text{PdCl}_4]$ . The reaction of compound **2** with diphosphines (1:1 molar ratio) afforded the first cyclopalladated ferrocenyl compounds with bridging diphosphines as centrosymmetric species; and also (1:2 molar ratio) compounds with the diphosphine as a chelating ligand. In both cases the complexes were air-stable solids and no decomposition processes were observed in solution or in the solid state.

## 4. Experimental

### 4.1. Materials and instrumentation

Solvents were purified by standard methods [39]. Chemicals were reagent grade. Palladium(II) acetate and palladium(II) chloride were purchased from Alfa Products. The phosphines  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm),  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$  (dppe),  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$  (dppp),  $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$  (dppb),  $\text{Ph}_2\text{PC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{PPh}_2$  (dppf) were purchased from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental

Table 2  
Crystal data for compounds **8** and **9**

	<b>8</b>	<b>9</b>
Empirical formula	$\text{C}_{45}\text{H}_{42}\text{F}_6\text{FeNP}_3\text{Pd}$	$\text{C}_{47}\text{H}_{45}\text{Cl}_3\text{F}_6\text{FeP}_3\text{Pd}$
Formula weight	965.96	1099.35
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal color	orange	yellow
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
<i>a</i> (Å)	10.7021(12)	11.3911(6)
<i>b</i> (Å)	11.3405(22)	22.2331(12)
<i>c</i> (Å)	17.9757(20)	19.5426(11)
$\alpha$ (°)	77.689(17)	90
$\beta$ (°)	81.046(11)	100.7240(10)
$\gamma$ (°)	84.908(12)	90
<i>V</i> (Å <sup>3</sup> )	2102.0(5)	4862.9(5)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (Mg m <sup>3</sup> )	1.526	1.502
Absorption coefficient (mm <sup>-1</sup> )	0.947	0.988
<i>F</i> (000)	980	2224
Crystal size (mm)	0.40 × 0.32 × 0.20	0.55 × 0.25 × 0.05
Theta range for data collection (°)	2.56–30.41	1.40–25.00
Index ranges	–15 < <i>h</i> < 15, –16 < <i>k</i> < 0, –25 < <i>l</i> < 25	–13 < <i>h</i> < 13, –26 < <i>k</i> < 26, –20 < <i>l</i> < 23
Reflections collected	13 298	25 776
Independent reflections	12 713 [ <i>R</i> <sub>int</sub> = 0.0694]	8556 [ <i>R</i> <sub>int</sub> = 0.0538]
Completeness to 2 $\theta$ (%)	99.9	99.8
Max/min transmission	0.8332, 0.7032	0.9523, 0.6125
Refinement method	full-matrix-block least-squares on <i>F</i> <sup>2</sup>	
Data/restraints/parameters	12713/0/517	8556/70/633
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0716, <i>wR</i> <sub>2</sub> = 0.1691	<i>R</i> <sub>1</sub> = 0.0560, <i>wR</i> <sub>2</sub> = 0.1371
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.2372, <i>wR</i> <sub>2</sub> = 0.2221	<i>R</i> <sub>1</sub> = 0.0912, <i>wR</i> <sub>2</sub> = 0.1587
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.961	0.986
Largest difference peak and hole (e Å <sup>-3</sup> )	2.100 and –1.154	1.1574 and –0.541

Table 3  
Selected bond lengths (Å) and angles (°)

<i>Bond distances for 8</i>			
Pd(1)–C(12)	2.023(6)	Pd(1)–N(1)	2.142(5)
Pd(1)–P(1)	2.2359(17)	Pd(1)–P(2)	2.4141(19)
C(11)–C(12)	1.427(9)	C(10)–C(11)	1.442(9)
N(1)–C(10)	1.279(8)	N(1)–C(1)	1.431(7)
P(1)–C(61)	1.844(7)	P(1)–C(21)	1.799(6)
P(1)–C(31)	1.796(6)	P(2)–C(61)	1.855(6)
P(2)–C(41)	1.815(7)	P(2)–C(51)	1.810(6)
<i>Bond distances for 9</i>			
Pd(1)–C(1)	2.044(5)	Pd(1)–N(1)	2.129(4)
Pd(1)–P(1)	2.3447(14)	Pd(1)–P(2)	2.2418(15)
C(1)–C(5)	1.443(7)	C(5)–C(6)	1.445(8)
N(1)–C(6)	1.283(7)	N(1)–C(7)	1.454(7)
P(1)–C(21)	1.841(6)	P(1)–C(29)	1.816(6)
P(1)–C(35)	1.813(6)	P(2)–C(22)	1.285(6)
P(2)–C(23)	1.808(6)	P(2)–C(41)	1.807(6)
C(21)–C(22)	1.520(9)		
<i>Bond angles for 8</i>			
C(12)–Pd(1)–N(1)	80.0(2)	C(12)–Pd(1)–P(1)	98.35(18)
N(1)–Pd(1)–P(1)	172.75(14)	C(12)–Pd(1)–P(2)	170.43(18)
N(1)–Pd(1)–P(2)	109.53(15)	P(2)–Pd(1)–P(1)	72.33(6)
C(10)–N(1)–Pd(1)	113.7(4)	C(13)–C(12)–Pd(1)	140.9(45)
C(11)–C(12)–Pd(1)	112.0(4)	C(12)–C(11)–C(10)	117.0(6)
N(1)–C(10)–C(11)	117.2(6)	C(61)–P(1)–Pd(1)	96.8(2)
C(61)–P(2)–Pd(1)	90.7(2)	P(1)–C(61)–P(2)	96.0(3)
<i>Bond angles for 9</i>			
C(1)–Pd(1)–N(1)	81.09(19)	C(1)–Pd(1)–P(2)	93.88(16)
N(1)–Pd(1)–P(2)	168.93(12)	C(1)–Pd(1)–P(1)	170.89(16)
N(1)–Pd(1)–P(1)	101.25(12)	P(2)–Pd(1)–P(1)	85.26(5)
C(6)–N(1)–Pd(1)	113.7(4)	C(2)–C(1)–Pd(1)	144.3(4)
C(5)–C(1)–Pd(1)	109.9(4)	C(1)–C(5)–C(6)	118.1(5)
N(1)–C(6)–C(5)	117.2(2)	C(21)–P(1)–Pd(1)	106.0(2)
C(22)–P(2)–Pd(1)	108.8(2)	C(22)–C(21)–P(1)	108.3(4)
C(21)–C(22)–P(2)	110.2(4)		

at the University of Santiago using a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or KBr discs on a Perkin–Elmer 1330 and on a Mattson spectrophotometer. NMR spectra were obtained as CDCl<sub>3</sub> solutions and referenced to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H}) and were recorded on Bruker WM250 and AMX-300 spectrometers. All chemical shifts are reported downfield from standards.

The synthesis of (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)C(H)=NR (R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (**a**) was performed by heating a CHCl<sub>3</sub> solution of the appropriate quantities of ferrocenecarboxaldehyde and 2,4,6-trimethylaniline in a Dean–Stark apparatus under reflux. After cooling to room temperature (r.t.) the solvent was evaporated to dryness, and the residue was dried under vacuum to give an oily red product which resulted to be the desired ligand. Yield 99.62%. Anal. Found: C, 72.66; H, 6.20; N, 4.38. Calc. for C<sub>20</sub>H<sub>21</sub>NFe: C, 72.52; H, 6.39; N, 4.23%. IR: (C=N) 1627s cm<sup>-1</sup>.

## 4.2. Preparations

### 4.2.1. [Pd{(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)C(H)=NR}(μ-O<sub>2</sub>-CMe)<sub>2</sub>] (**1**)

(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)C(H)=N-2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**a**) (200 mg, 0.6 mmol) and palladium(II) acetate (130 mg, 0.6 mmol) were added to 40 cm<sup>3</sup> of toluene to give a clear solution, which was heated under reflux for 8 h. After cooling to r.t., the solvent was removed under vacuum and the residue was chromatographed on a column packed with silica gel. Elution with CH<sub>2</sub>Cl<sub>2</sub>–EtOH (3%) afforded product **1** as an orange solid after concentration. Yield 45.85%. Anal. Found: C, 52.72; H, 4.38; N, 2.47. Calc. for C<sub>44</sub>H<sub>46</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>4</sub>Pd<sub>2</sub>·0.33CH<sub>2</sub>Cl<sub>2</sub>: C, 52.23; H, 4.61; N, 2.75%. IR: ν(C=N) 1565m, ν<sub>as</sub>(COO) 1564m, ν<sub>s</sub>(COO) 1412m cm<sup>-1</sup>.

### 4.2.2. [Pd{(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)C(H)=NR}(μ-Cl)]<sub>2</sub> (**2**)

**4.2.2.1. Method a.** To a solution of **1** in Me<sub>2</sub>CO (25 cm<sup>3</sup>) aqueous sodium chloride was added (ca. 10<sup>-2</sup> M) and the mixture was stirred at r.t. for 3 h. The resulting precipitate was filtered off and recrystallized from CHCl<sub>3</sub>–*n*-hexane. Yield 41.6%. Anal. Found: C, 50.74; H, 4.75; N, 2.88. Calc. for C<sub>40</sub>H<sub>40</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>Pd<sub>2</sub>: C, 50.88; H, 4.27; N, 2.97%. IR: ν(C=N) 1563s, ν(Pd–Cl *trans*-N) 350m, ν(Pd–Cl *trans*-C) 262s cm<sup>-1</sup>.

**4.2.2.2. Method b.** To a stirred solution of palladium(II) chloride (89 mg, 0.50 mmol) and lithium chloride (26 mg, 0.60 mmol) in MeOH (40 cm<sup>3</sup>) (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)C(H)=N-2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**a**) (100 mg, 0.30 mmol) and AcONa (24 mg, 0.30 mmol) were added. The mixture was stirred for 48 h at r.t. under N<sub>2</sub>. The yellow precipitate was filtered off, washed with EtOH and dried. Yield 58.5%.

### 4.2.3. [{Pd[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)C(H)=NR]Cl}]<sub>2</sub>{μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2}}</sub> (**3**)

To a suspension of **2** (30 mg, 0.31 mmol) in Me<sub>2</sub>CO (10 cm<sup>3</sup>) Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (12 mg, 0.031 mmol) was added. The mixture was stirred for 24 h at r.t. and the resulting precipitate was filtered off and dried in vacuo. Yield 55.2%. Anal. Found: C, 57.90; H, 4.27; N, 2.01. Calc. for C<sub>65</sub>H<sub>62</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub>·0.33CH<sub>2</sub>Cl<sub>2</sub>: C, 57.84; H, 4.66; N, 2.06%. IR: ν(C=N) 1581s, ν(Pd–Cl) 282m cm<sup>-1</sup>.

Compounds **4–7** were prepared as orange air-stable solids following a similar procedure.

### 4.2.4. [{Pd[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)C(H)=NR]Cl}]<sub>2</sub>{μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2}}</sub> (**4**)

Yield 45.11%. Anal. Found: C, 58.24; H, 4.67; N, 1.98. Calc. for C<sub>66</sub>H<sub>64</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub>·0.33CH<sub>2</sub>Cl<sub>2</sub>: C, 58.13; H, 4.76; N, 2.04%. IR: ν(C=N) 1582s, ν(Pd–Cl) 284m cm<sup>-1</sup>.

4.2.5. [ $\{Pd[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)C(H)=NR]Cl\}_2\{\mu-Ph_2P(CH_2)_3PPh_2\}$ ] (**5**)

Yield 56.86%. Anal. Found: C, 58.25; H, 4.81; N, 2.00. Calc. for  $C_{67}H_{66}Cl_2Fe_2N_2P_2Pd_2 \cdot 0.33CH_2Cl_2$ : C, 58.40; H, 4.85; N, 2.02%. IR:  $\nu(C=N)$  1584s,  $\nu(Pd-Cl)$  283m  $cm^{-1}$ .

4.2.6. [ $\{Pd[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)C(H)=NR]Cl\}_2\{\mu-Ph_2P(CH_2)_4PPh_2\}$ ] (**6**)

Yield 40.27%. Anal. Found: C, 58.46; H, 4.89; N, 2.00. Calc. for  $C_{68}H_{68}Cl_2Fe_2N_2P_2Pd_2 \cdot 0.33CH_2Cl_2$ : C, 58.67; H, 4.95; N, 2.00%. IR:  $\nu(C=N)$  1582s;  $\nu(Pd-Cl)$  283m  $cm^{-1}$ .

4.2.7. [ $\{Pd[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)C(H)=NR]Cl\}_2(\mu-Ph_2PC_5H_4FeC_5H_4PPh_2)$ ] (**7**)

Yield 40.27%. Anal. Found: C, 58.85; H, 5.04; N, 1.87. Calc. for  $C_{74}H_{68}Cl_2Fe_3N_2P_2Pd_2$ : C, 59.31; H, 4.57; N, 1.87%. IR:  $\nu(C=N)$  1583s;  $\nu(Pd-Cl)$  305s  $cm^{-1}$ .

4.2.8. [ $Pd\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)C(H)=NR\}\{Ph_2-PCH_2PPh_2-P,P\}][PF_6]$ ] (**8**)

To a suspension of **1** (30 mg, 0.031 mmol) in  $Me_2CO$  (10  $cm^3$ )  $Ph_2PCH_2PPh_2$  (24 mg, 0.062 mmol) was added. The mixture was stirred for 2 h at r.t., after which ammonium hexafluorophosphate was added and the mixture was stirred for another 2 h. The resulting solution was reduced to half volume and the precipitate that formed was filtered off and recrystallized from  $CHCl_3-n$ -hexane. Yield 69.72%. Anal. Found: C, 56.19; H, 4.90; N, 1.48. Calc. for  $C_{45}H_{42}F_6FeNP_3Pd$ : C, 55.95; H, 4.38; N, 1.45%. IR:  $\nu(C=N)$  1568  $cm^{-1}$ .

Compounds **9–12** were prepared as orange air-stable solids following a similar procedure.

4.2.9. [ $Pd\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)C(H)=NR\}\{Ph_2-P(CH_2)_2PPh_2-P,P\}][PF_6]$ ] (**9**)

Yield 73.22%. Anal. Found: C, 56.53; H, 5.18; N, 1.53. Calc. for  $C_{46}H_{44}F_6FeNP_3Pd$ : C, 56.38; H, 4.53; N, 1.43%. IR:  $\nu(C=N)$  1570m  $cm^{-1}$ .

4.2.10. [ $Pd\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)C(H)=NR\}\{Ph_2-P(CH_2)_3PPh_2-P,P\}][PF_6]$ ] (**10**)

Yield 88.49%. Anal. Found: C, 56.67; H, 4.41; N, 1.62. Calc. for  $C_{47}H_{46}F_6FeNP_3Pd$ : C, 56.79; H, 4.66; N, 1.41%. IR:  $\nu(C=N)$  1573m  $cm^{-1}$ .

4.2.11. [ $Pd\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)C(H)=NR\}\{Ph_2-P(CH_2)_4PPh_2-P,P\}][PF_6]$ ] (**11**)

Yield 51.87%. Anal. Found: C, 57.31; H, 4.95; N, 1.48. Calc. for  $C_{48}H_{48}F_6FeNP_3Pd$ : C, 57.19; H, 4.80; N, 1.39%. IR:  $\nu(C=N)$  1581m  $cm^{-1}$ .

4.2.12. [ $Pd\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)C(H)=NR\}(Ph_2-PC_5H_4FeC_5H_4PPh_2-P,P)][PF_6]$ ] (**12**)

Yield 89.43%. Anal. Found: C, 57.15; H, 4.37; N, 1.34. Calc. for  $C_{54}H_{48}F_6Fe_2NP_3Pd$ : C, 57.09; H, 4.26; N, 1.23%. IR:  $\nu(C=N)$  1580m  $cm^{-1}$ .

### 4.3. Single-crystal X-ray diffraction analysis

Three-dimensional, room temperature X-ray data were collected on an Enraf–Nonius CAD4 (**8**) and a Siemens SMART charge coupled device (CCD) detector system (**9**) single-crystal X-ray diffractometers using graphite monochromated Mo– $K_\alpha$  radiation at 298 K by the  $\omega/2\theta$  (**8**) and the  $\omega$  (**9**) scan methods. The 12 713 ( $R_{int} = 0.0694$ ) (**8**) and 8556 ( $R_{int} = 0.0538$ ) (**9**) independent reflections (of the 13 298 measured, completeness to  $\theta = 30.41$ , 99.9% (**8**) and 25 776 measured, completeness to  $\theta = 25.00$ , 99.8% (**9**)) were corrected for Lorentz and polarization effects and for absorption by an empirical method [40] (**8**) and a semi-empirical method based on symmetry-equivalent and repeated reflections (**9**) (maximum and minimum transmission coefficients 0.8332 and 0.7032 (**8**) and 0.9523 and 0.6125 (**9**)). The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  with allowance for thermal anisotropy of all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined in riding mode. The structure solution and refinement were carried out using the program package SHELX-97 [41].

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 154873 and 154978 for compounds **8** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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## References

- [1] T.J. Kealy, P.L. Pauson, *Nature* 168 (1951) 1039.
- [2] G. Wilkinson, M. Rosenblum, M.C. Whiting, R.B. Woodward, *J. Am. Chem. Soc.* 74 (1952) 2125.
- [3] E.O. Fischer, W. Pfab, *Z. Naturforsch. B* 7 (1952) 377.
- [4] For general papers concerning cyclometallated compounds see: (a) I. Omae, *Organometallic-Coordination Compounds*, Elsevier, Amsterdam, 1986;



- (b) O.A. Dunina, V.M. Zalewska, V.M. Potapov, *Russ. Chem. Rev.* 57 (1988) 250;
- (c) A.D. Ryabov, *Chem. Rev.* 90 (1990) 403.
- [5] J.M. Vila, M. Gayoso, M.T. Pereira, A. Romar, J.J. Fernández, M. Thornton-Pett, *J. Organomet. Chem.* 401 (1991) 385.
- [6] J.M. Vila, M. Gayoso, M.T. Pereira, M. López-Torres, J.J. Fernández, A. Fernández, J.M. Ortigueira, *J. Organomet. Chem.* 506 (1996) 165.
- [7] J.M. Vila, M. Gayoso, M.T. Pereira, M. López-Torres, J.J. Fernández, A. Fernández, J.M. Ortigueira, *Z. Anorg. Allg. Chem.* 623 (1997) 844.
- [8] J.M. Vila, M. Gayoso, M.T. Pereira, M. López-Torres, J.J. Fernández, A. Fernández, J. Ortigueira, H. Adams, *J. Organomet. Chem.* 532 (1997) 171.
- [9] J.M. Vila, M.T. Pereira, J.M. Ortigueira, D. Lata, M. López-Torres, J.J. Fernández, A. Fernández, H. Adams, *J. Organomet. Chem.* 566 (1998) 93.
- [10] J.M. Vila, T. Pereira, J.M. Ortigueira, M. López-Torres, A. Castiñeiras, D. Lata, J.J. Fernández, A. Fernández, *J. Organomet. Chem.* 556 (1998) 21.
- [11] J.M. Vila, T. Pereira, J.M. Ortigueira, M. López-Torres, D. Lata, M. Graña, A. Suárez, J.J. Fernández, A. Fernández, *J. Chem. Soc. Dalton Trans.* (1999) 4193.
- [12] D. Vázquez-García, A. Fernández, J.J. Fernández, M. López-Torres, A. Suárez, J.M. Ortigueira, J.M. Vila, H. Adams, *J. Organomet. Chem.* 595 (2000) 199.
- [13] A.D. Ryabov, A.K. Yatsimirski, *Inorg. Chem.* 789 (1984) 23.
- [14] A.D. Ryabov, I.K. Sakodinskaya, A.K. Yatsimirski, *J. Chem. Soc. Dalton Trans.* (1985) 2629.
- [15] A.D. Ryabov, *Inorg. Chem.* 26 (1987) 1252.
- [16] J. Blanco, E. Gayoso, J.M. Vila, M. Gayoso, C. Maichle-Mössmer, J. Strähle, *Z. Naturforsch. B* 48 (1993) 906.
- [17] R. Bosque, C. López, J. Sales, X. Soláns, *J. Organomet. Chem.* 483 (1994) 61.
- [18] Y.J. Wu, Y.H. Liu, K.L. Ding, H.Z. Yuan, X.A. Mao, *J. Organomet. Chem.* 505 (1995) 37.
- [19] M. Benito, C. López, X. Morván, *Polyhedron* 18 (1999) 2583 (and references therein).
- [20] P.B. Hitchcock, D.L. Hughes, G.J. Leigh, J. Roger Sanders, J.S. de Souza, *J. Chem. Soc. Dalton Trans.* (1999) 1611.
- [21] K. McGrouther, D.K. Weston, D. Fenby, B.H. Robinson, J. Simpson, *J. Chem. Soc. Dalton Trans.* (1999) 1965.
- [22] J.M. Vila, T. Pereira, A. Amoedo, M. Graña, J. Martínez, M. López-Torres, A. Fernández, *J. Organomet. Chem.*, in press.
- [23] C. López, R. Bosque, D. Sainz, X. Soláns, M. Font-Bardía, *Organometallics* 16 (1997) 3261.
- [24] C. López, J. Sales, X. Soláns, R. Zquiak, *J. Chem. Soc. Dalton Trans.* (1992) 2321.
- [25] H. Günther, *NMR Spectroscopy*, 2nd ed., Wiley, New York, 1995.
- [26] H. Onoue, I. Moritani, *J. Organomet. Chem.* 43 (1972) 431.
- [27] H. Onoue, K. Minami, I. Moritani, *Bull. Chem. Soc. Jpn.* 43 (1970) 3480.
- [28] Y.A. Ustinyuk, V.A. Chertov, I.V. Barinov, *J. Organomet. Chem.* 29 (1971) C53.
- [29] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, 1997.
- [30] R. Bosque, C. López, X. Soláns, M. Font-Bardía, *Organometallics* 18 (1999) 1267.
- [31] G. Zhao, Q.G. Wang, T.C. Mak, *J. Chem. Soc. Dalton Trans.* (1998) 3785.
- [32] J.M. Vila, M. Gayoso, A. Fernández, N. Bailey, H. Adams, *J. Organomet. Chem.* 448 (1993) 233.
- [33] P.S. Pregosin, R.W. Kuntz,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR of Transition Metal Phosphine Complexes, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), *NMR 16*, Springer, Berlin, 1979.
- [34] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, New York, 1960.
- [35] J.M. Vila, M. Gayoso, M.T. Pereira, A. Romar, J.J. Fernández, M. Thornton-Pett, *J. Organomet. Chem.* 401 (1991) 385.
- [36] J. Selbin, K. Abboud, S.F. Watkins, M.A. Gutiérrez, F.R. Fronczek, *J. Organomet. Chem.* 241 (1983) 259.
- [37] J. Albert, J. Granell, J. Sales, X. Soláns, M. Font-Altaba, *Organometallics* 5 (1986) 2567.
- [38] E.J. Corey, J.C. Bailar, *J. Am. Chem. Soc.* 81 (1959) 2620. For a more recent discussion see also, *Comprehensive Coordination Chemistry*, Pergamon, Oxford, vol. 1, 1987, p. 179.
- [39] D.D. Perrin, W.F.L. Armarego, D.L. Perrin, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, London, 1988.
- [40] A.C.T. North, D.C. Phillips, F.S. Mathews, *Acta Crystallogr. A* 24 (1968) 351.
- [41] G.M. Sheldrick, *SHELXL-97*, An Integrated System for Solving and Refining Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.