Cyclopalladated Compounds derived from Ferrocenylimines. Crystal Structure of $[\mathrm{Pd}\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3CH{=}N(CH_2)_2Ph]\}Cl(PEt_3)]$†

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Reactions of ferrocenylimines of general formula $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH{=}N(CH_2)_nPh\}]$ (n = 1 **1a** or 2 **1b**) with palladium(II) salts have been studied. The dimeric cylopalladated complexes $[\{\mathrm{Pd}[(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nPh\}]Cl\}_2]$ **2a** and **2b** were obtained when the reactions were carried out in the presence of sodium acetate and using $Na_2[PdCl_4]$ as starting material. Addition of phosphine ligands PR_3 (R = Ph or Et) or 1,2-bis(diphenylphosphino)ethane (dppe) to acetone suspensions of these dinuclear compounds produced the more soluble mononuclear complexes $[\mathrm{Pd}\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nPh]\}Cl(PR_3)]$ with R = Ph (**3a** and **3b**) and Et (**4a** and **4b**) and $[\mathrm{Pd}\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nPh]\}(dppe)]Cl$ (**5a** and **5b**). Proton and ^{31}P NMR spectroscopic studies on these compounds confirm the formations of *endo* five-membered metallocycles. Mössbauer spectra of compounds **1b**–**5b** have also been recorded. The first crystal structure of a cyclopalladated complex derived from ferrocenylimines has been determined. The compound $[\mathrm{Pd}\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2CH_2Ph)\}Cl(PEt_3)]$ **4b** is monoclinic, space group $P2_1/a$, with a = 15.944(3), b = 12.425(2), c = 12.682(2) Å, β = 100.19(2)° and Z = 4. The structure confirms the formation of an *endo* five-membered metallocycle on the ferrocene moiety.

Since 1968, when Cope and Friedrich[1] reported the first example of a cyclopalladated compound containing *N,N*-dimethylbenzylamine, interest in complexes of this kind, in particular those involving N-donor ligands, has increased exponentially. For instance, during the last decade a wide variety of five-membered palladocycles containing $Pd\text{–}C_{aromatic}$ bonds and a few six-membered derivatives even with $Pd\text{–}C_{aliphatic}$ bonds have been reported.[2] For these systems it is widely accepted that the formation of the metallocycle from palladium(II) salts takes place in two steps. Co-ordination of the N-donor ligand, and electrophilic attack of the palladium(II) species on the carbon atom to afford the metallocycle. Previous studies on cyclopalladation reactions of pure organic ligands containing the functional group C=N have been very useful to clarify some of the factors which control the cyclometallation processes. Though the early rules established for this sort of reactions indicated a high tendency to the formation of five-membered metallocycles, containing $M\text{–}C_{aromatic}$ bonds, later studies have revealed that other factors, such as the substituents in the phenyl ring and the inclusion of the iminic bond in the metallocycle (*endo* effect), can be important enough to determine the position at which metallation takes place.[3]

Following our studies[3,4] on the cyclopalladation of phenylazines, -imines and hydrazones, we initiated a parallel study of the analogous N-donor ligands derived from ferrocene. These new substrates will allow us to achieve the following aims. (*i*) The elucidation of the influence of the nature of the carbon atom involved in the process, since it is well known that ferrocene is less resistant to electrophilic attack than phenyl derivatives. (*ii*) To extend the type of cyclopalladated compounds described so far to the ferrocene derivatives, which have hardly been studied and of which only a few refer to N-donor ligands {mainly amines[5] $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CHRNMe_2)]$-$[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4C_5H_4N)]$}. To the best of our knowledge there is only one case in which the N-donor ligand contains the C=N moiety and this involves the hydrazone[6] $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NNHCOMe)]$. In all these cases the metallation can exclusively occur at the cyclopentadienyl ring. (*iii*) To estimate the importance of the additional strain involved in fusing to five-membered rings (C_5H_5 and metallocycle) in relation to systems containing a five- or six-membered ring (metallocycle) fused to a six-membered ring (phenylic).

As a first approach to the problem we have undertaken a study of the cyclopalladation of the imine ligands derived from ferrocene of general formula $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH{=}N(CH_2)_nPh\}]$ (n = 1 **1a** or 2 **1b**). If metallation is to occur in these systems we could expect two different types of metallocycles *a priori* (Fig. 1). The first **I** could arise from the electrophilic attack of the palladium(II) species on the cyclopentadienyl ligand, in which case the C=N bond would be included in the metallocycle (*endo* type) and produce bicyclic systems containing two five-membered rings. In the second type of complex **II**, however, the iminic bond would not be included in the ring (*exo* type), but would rather produce a five- or a six-membered metallocycle with a $\sigma(Pd\text{–}C_{phenyl})$ bond for ligands **1a** and **1b**, respectively.

Results and Discussion

The general procedure described for the cyclopalladation of organic imines, which consists in the treatment of the free ligand with palladium(II) acetate in glacial acetic acid, was used at different temperatures (from room temperature to reflux) and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, issue 1, pp. xx–xxv.

in all cases was unsuccessful owing to the instability of the ferrocenylimine ligands in that solvent. When the reactions were carried out under milder experimental conditions, free ligand and $PdCl_2$ in ethanol for short reaction periods (2 h), no cyclopalladated complexes were obtained since the insoluble products formed reacted with PPh_3 yielding the $[PdCl_2(PPh_3)_2]$ complex. For the longest periods studied, dimeric cyclometallated compounds **2a** or **2b** were isolated as by-products. The major components of the mixtures were co-ordination compounds of general formula $[PdCl_2(amine)_2]$. This suggested that slow hydrolyses of the imine ligands had taken place. This result had already been pointed out by Peet and Rockett,[7] who studied hydrolyses of some ferrocenylimines. In order to improve the synthesis of the cyclometallated complex we used a method described by Gaunt and Shaw[5a] for the cyclopalladation of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$ which consisted of the reaction between the ligand and $Na_2[PdCl_4]$ in the presence of sodium acetate, using methanol as solvent. For imine ligands **1a** or **1b** longer reaction periods were used (24 h) and the insoluble materials formed were a mixture of the co-ordination compound and the dinuclear cyclopalladated complex **2a** and **2b** in Scheme 1.

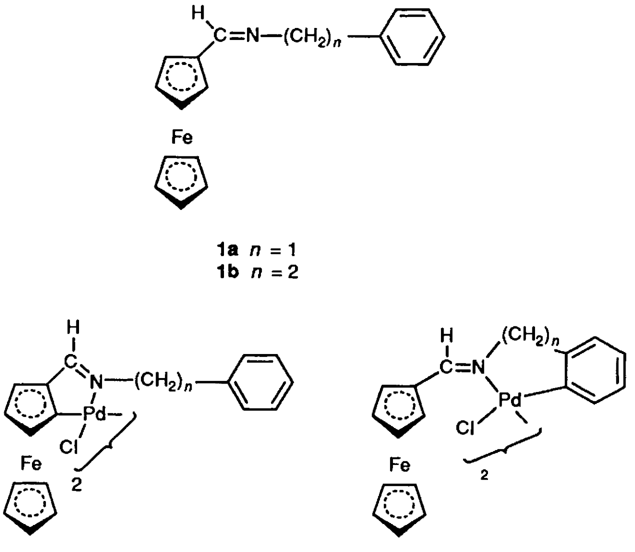


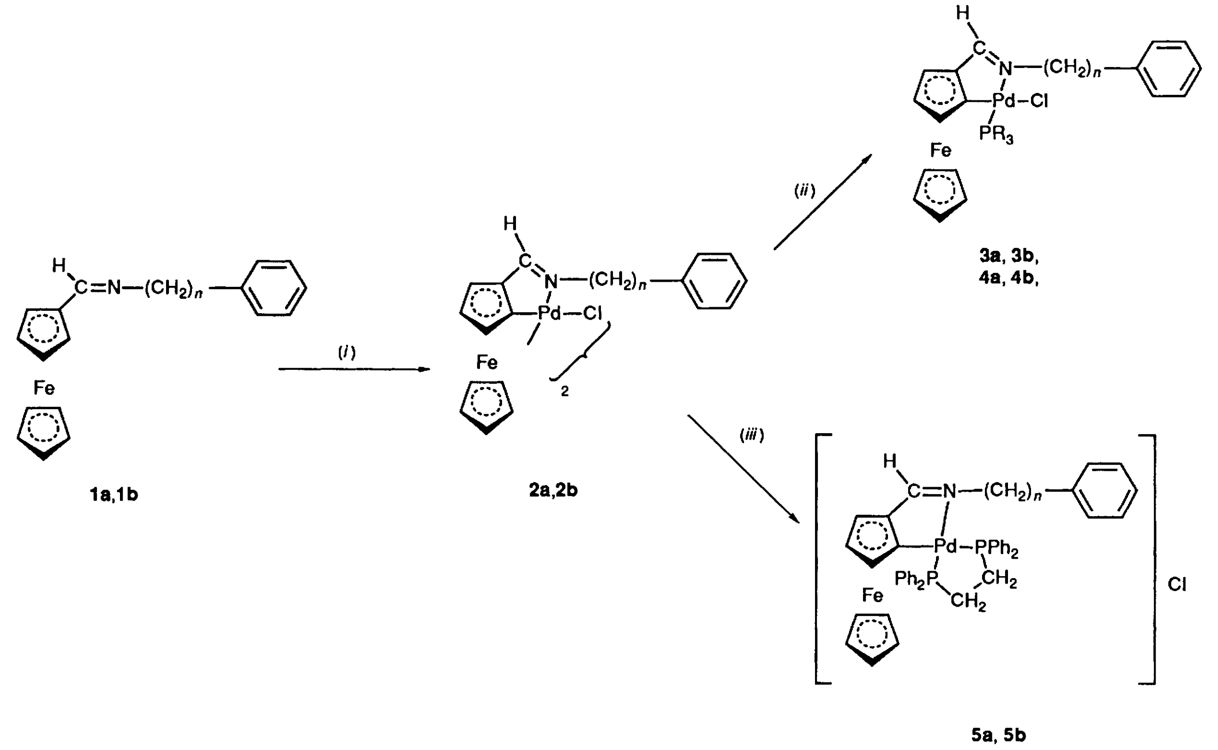
Fig. 1 Molecular scheme of compounds **1a** and **1b** and the two different types of metallocycles that can be formed from them: *endo* (**I**) and *exo* (**II**)

Addition of an excess of phosphine ligands (PPh_3, PEt_3) to acetone suspensions of the dimeric complexes **2a** or **2b** produced cleavage of the μ-Cl bridges and formation of the monomeric derivatives **3a**, **3b** and **4a**, **4b** respectively. The most outstanding feature of the dinuclear cyclopalladated complexes **2a**, **2b** is the high stability of the Pd–N bond. The formation of bis(phosphine)derivatives was not observed even when the PEt_3 : Pd molar ratio was 6 : 1. These results contrast with those found for the analogous cyclopalladated complexes derived from *N*-benzylideneamines in which an excess of PEt_3[3a,8] produced cleavage of the Pd–N bond. On the other hand, addition of 1,2-bis(diphenylphosphino)ethane (dppe) to an acetone suspension of the dimeric complexes produced the cationic cyclometallated compounds **5a**, **5b** in which the P-donor ligand acts as a chelate.

Characterization.—The new cyclopalladated complexes are air-stable orange-red solids. The monomeric compounds **3a**–**5a** and **3b**–**5b** are very soluble in chloroform, dichloromethane, slightly soluble in methanol, ethanol and diethyl ether, and insoluble in water and alkanes, while the dimeric complexes **2a** and **2b** exhibit low solubility in the most common solvents.

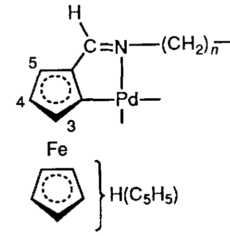
Comparison of the infrared spectra of all the compounds reveals that the band due to the asymmetric stretching of the C=N bond appears at lower frequencies for the cyclometallated complexes. This fact, which has been also reported for other five-membered cyclopalladated compounds was ascribed to a decrease in the C=N bond order.

Proton NMR data for all the complexes are summarized in Table 1. Comparison of the chemical shifts of the ligands and those of the complexes studied in the range δ 3.00–6.00 shows that the two doublets, due to the pairs H^2, H^5 and H^3, H^4 of



Scheme 1 (*i*) $Na_2[PdCl_4]$, NaO_2CMe, in methanol, at room temperature; (*ii*) PR_3, in acetone; (*iii*) dppe, in acetone

Table 1 Proton and ^{31}P NMR data[a] for compounds **1a**–**5a** and **1b**–**5b**



	^1H NMR								
			Palladated C_5H_3-ring						
Complex	HC=N	$H(C_5H_5)$	H^3	H^4	H^5	NCH_2	CH_2	^{31}P NMR[b]
1a	8.24	4.17	4.38	4.38	4.68	4.68[c]	—	—
2a	7.80	4.19	4.17	4.31	4.60[d]	4.60[d]	—	—
						5.21	—	37.50[g]
3a	7.98[e]	3.67	3.30	4.00	4.30	4.65[f]	—	
						5.45[f]	—	30.57[g]
4a	7.95[e]	4.01	4.27	4.35	4.37	4.60[f]	—	
						5.30[f]	—	43.08[g,h]
5a	8.13[e]	3.93	3.69	4.18	4.23	4.63[f]	—	59.35[g]
							—	—
1b	7.99	4.04	4.35	4.35	4.57	3.71[c]	2.97[c]	—
2b	7.77	4.31	4.39	4.39	4.56	3.86[d]	3.12[d]	—
						4.06[d]	2.97[d]	37.46[j]
3b	8.03[e]	3.82	3.31	4.06	4.32	4.05[i]	2.96[i]	
						3.87[i]	3.32[i]	30.11[j]
4b	7.89[e]	4.12	4.31	4.35	4.42	3.95[j]	3.05[i]	
							3.12[i]	44.58[g,j]
5b	8.12[e]	3.90	3.52	4.15	4.28	3.90[j]	2.90[i]	59.24[g,h]
							3.28[i]	

[a] Numbering of the H atoms of the ferrocenyl moiety as shown. [b] Referred to H_3PO_4. [c] Triplets. [d] Complex multiplet. [e] Doublet, ^4J(P–H) = 7.5 Hz. [f] AB quartet pattern due to the non-equivalence of the two protons in the NCH_2 moiety; the values given refer to the mid-points of each of the two doublets of doublets. [g] Doublet ^2J(P–P) = 24.6 Hz. [h] P *cis* to the iminic nitrogen. [i] Two overlapped multiplets. [j] P *trans* to the iminic nitrogen.

Table 2 Bond lengths (Å) for compound **4b** with estimated standard deviations (e.s.d.s) in parentheses

P–Pd	2.243(2)	C(5)–C(4)	1.370(14)
Cl–Pd	2.390(2)	C(7)–C(6)	1.439(8)
C(6)–Pd	1.999(6)	C(10)–C(6)	1.434(9)
N(12)–Pd	2.148(5)	C(8)–C(7)	1.435(10)
C(1)–Fe	2.040(8)	C(9)–C(8)	1.435(10)
C(2)–Fe	2.035(8)	C(10)–C(9)	1.415(10)
C(3)–Fe	2.074(8)	C(11)–C(10)	1.467(9)
C(4)–Fe	2.079(8)	N(12)–C(11)	1.280(8)
C(5)–Fe	2.063(8)	C(13)–N(12)	1.456(7)
C(6)–Fe	2.088(6)	C(14)–C(13)	1.507(9)
C(7)–Fe	2.055(6)	C(15)–C(14)	1.532(9)
C(8)–Fe	2.040(6)	C(16)–C(15)	1.386(10)
C(9)–Fe	2.047(7)	C(20)–C(15)	1.370(9)
C(10)–Fe	2.026(7)	C(17)–C(16)	1.407(11)
C(21)–P	1.827(7)	C(18)–C(17)	1.391(13)
C(23)–P	1.829(7)	C(19)–C(18)	1.353(13)
C(25)–P	1.817(7)	C(20)–C(19)	1.422(11)
C(2)–C(1)	1.376(14)	C(22)–C(21)	1.532(12)
C(5)–C(1)	1.433(16)	C(24)–C(23)	1.537(13)
C(3)–C(2)	1.418(13)	C(26)–C(25)	1.539(12)
C(4)–C(3)	1.426(13)		

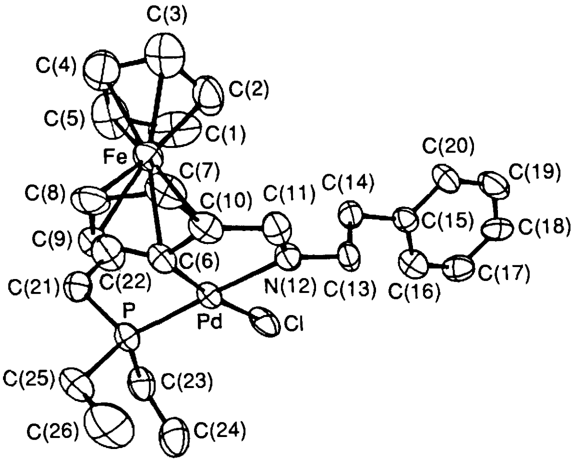


Fig. 2 Molecular structure and atom labelling scheme for compound **4b**

the imines, split into three signals upon cyclometallation, thus confirming the formation of *endo*-type metallocycles. The assignment of each of the resonances due to the three non-equivalent protons of the metallated ring (H^3, H^4 and H^5) was unequivocally undertaken by comparing the ^1H NMR spectra of the compounds containing PPh_3 (**3a**, **3b**), and PEt_3 (**4a**, **4b**). The iminic proton resonances shift upfield upon cyclometallation and for the monomeric complexes appear as doublets, thus confirming the formation of *endo*-type metallocycles, and a *trans* orientation of the phosphine group *versus* the N atom. The ^1H NMR resonance of the NCH_2 protons appears as a doublet of doublets (AB pattern) for complexes **2a**–**5a** and a doublet of multiplets for **2b**–**5b**. The differences in the chemical shifts of the two groups of signals in each of the metallated complexes is big enough (*ca.* ≈0.5–0.7 ppm) to rule out that such splitting is induced by the chirality of the C_5H_3 plane.[9] Consequently, these splittings, also observed for cyclopalladated complexes derived from benzylideneamines,[3b] may be ascribed to inhibition of the rotation around the N–CH_2 bond.

For compounds **3a** and **3b** and **4a** and **4b**, the ^{31}P NMR

Table 3 Bond angles (°) for compound **4b**, with e.s.d.s in parentheses

Cl–Pd–P	95.5(1)	Fe–C(2)–C(1)	70.5(3)	C(7)–Fe–C(6)	40.6(2)	C(8)–C(9)–C(10)	106.5(8)
C(6)–Pd–P	91.2(2)	Fe–C(2)–C(3)	71.3(3)	C(8)–Fe–C(1)	163.3(4)	Fe–C(10)–C(6)	71.9(3)
C(6)–Pd–Cl	172.4(2)	C(1)–C(2)–C(3)	108.3(6)	C(8)–Fe–C(2)	156.1(4)	Fe–C(10)–C(9)	70.5(3)
N(12)–Pd–P	170.0(1)	Fe–C(3)–C(2)	68.3(3)	C(8)–Fe–C(3)	121.8(3)	C(6)–C(10)–C(9)	110.4(8)
N(12)–Pd–Cl	92.5(1)	Fe–C(3)–C(4)	70.1(3)	C(8)–Fe–C(4)	110.0(3)	Fe–C(10)–C(11)	118.0(3)
N(12)–Pd–C(6)	81.1(2)	C(2)–C(3)–C(4)	106.4(6)	C(8)–Fe–C(5)	126.0(3)	C(6)–C(10)–C(11)	116.9(8)
C(2)–Fe–C(1)	39.5(4)	Fe–C(4)–C(3)	69.7(3)	C(8)–Fe–C(6)	68.4(2)	C(9)–C(10)–C(11)	132.3(8)
C(3)–Fe–C(1)	66.8(4)	Fe–C(4)–C(5)	70.0(3)	C(8)–Fe–C(7)	40.6(3)	C(10)–C(11)–N(12)	117.0(7)
C(3)–Fe–C(2)	40.4(4)	C(3)–C(4)–C(5)	109.6(6)	C(9)–Fe–C(1)	154.2(4)	Pd–N(12)–C(11)	112.9(3)
C(4)–Fe–C(1)	66.3(4)	Fe–C(5)–C(1)	68.7(3)	C(9)–Fe–C(2)	120.4(3)	Pd–N(12)–C(13)	127.1(3)
C(4)–Fe–C(2)	67.2(3)	Fe–C(5)–C(4)	71.3(3)	C(9)–Fe–C(3)	108.9(3)	C(11)–N(12)–C(13)	120.0(7)
C(4)–Fe–C(3)	40.2(4)	C(1)–C(5)–C(4)	106.9(6)	C(9)–Fe–C(4)	128.0(3)	N(12)–C(13)–C(14)	112.0(7)
C(5)–Fe–C(1)	40.9(4)	Pd–C(6)–Fe	122.1(2)	C(9)–Fe–C(5)	163.4(4)	C(13)–C(14)–C(15)	111.0(7)
C(5)–Fe–C(2)	67.8(4)	Pd–C(6)–C(7)	141.9(3)	C(9)–Fe–C(6)	68.9(3)	C(14)–C(15)–C(16)	119.4(7)
C(5)–Fe–C(3)	67.0(4)	Fe–C(6)–C(7)	67.5(3)	C(9)–Fe–C(7)	68.9(3)	C(14)–C(15)–C(20)	121.8(7)
C(5)–Fe–C(4)	38.6(4)	Pd–C(6)–C(10)	111.9(3)	C(9)–Fe–C(8)	41.1(3)	C(16)–C(15)–C(20)	118.8(7)
C(6)–Fe–C(1)	107.3(0)	Fe–C(6)–C(10)	67.3(3)	Pd–P–C(21)	114.4(4)	C(15)–C(16)–C(17)	120.8(7)
C(6)–Fe–C(2)	124.9(3)	C(7)–C(6)–C(10)	105.9(8)	Pd–P–C(23)	115.5(3)	C(16)–C(17)–C(18)	119.2(7)
C(6)–Fe–C(3)	162.8(3)	Fe–C(7)–C(6)	70.9(3)	C(21)–P–C(23)	103.1(3)	C(17)–C(18)–C(19)	120.6(7)
C(6)–Fe–C(4)	154.2(3)	Fe–C(7)–C(8)	69.1(3)	Pd–P–C(25)	115.7(3)	C(18)–C(19)–C(20)	119.8(7)
C(6)–Fe–C(5)	120.0(3)	C(6)–C(7)–C(8)	108.6(8)	C(21)–P–C(25)	103.6(4)	C(15)–C(20)–C(19)	120.8(8)
C(7)–Fe–C(1)	125.8(4)	Fe–C(8)–C(7)	70.3(3)	C(23)–P–C(25)	102.8(3)	P–C(21)–C(22)	112.6(4)
C(7)–Fe–C(2)	161.9(4)	Fe–C(8)–C(9)	69.7(3)	Fe–C(1)–C(2)	70.1(3)	P–C(23)–C(24)	114.9(4)
C(7)–Fe–C(3)	155.9(3)	C(7)–C(8)–C(9)	108.7(8)	Fe–C(1)–C(5)	70.4(3)	P–C(25)–C(26)	116.7(4)
C(7)–Fe–C(4)	121.2(3)	Fe–C(9)–C(8)	69.2(3)	C(2)–C(1)–C(5)	108.9(8)		
C(7)–Fe–C(5)	107.8(3)	Fe–C(9)–C(10)	68.9(3)				

Table 4 Fractional atomic coordinates for non-hydrogen atoms ($\times 10^4$; Pd and Fe, $\times 10^5$) for compound **4b** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	18 576(3)	25 479(3)	28 272(3)
Fe	34 353(5)	29 466(7)	11 802(7)
P	2 448(1)	1 272(1)	3 974(1)
Cl	1 095(1)	3 407(2)	4 055(2)
C(1)	3 727(8)	4 186(9)	2 236(8)
C(2)	3 488(5)	4 583(7)	1 214(9)
C(3)	4 073(6)	4 179(7)	580(7)
C(4)	4 666(5)	3 535(7)	1 264(8)
C(5)	4 459(6)	3 510(7)	2 267(8)
C(6)	2 497(4)	2 021(5)	1 707(5)
C(7)	3 221(4)	1 378(5)	1 572(5)
C(8)	3 335(4)	1 459(5)	489(6)
C(9)	2 695(5)	2 165(6)	−71(5)
C(10)	2 202(5)	2 516(4)	688(5)
C(11)	1 547(4)	3 352(5)	648(5)
N(12)	1 279(3)	3 553(4)	1 520(4)
C(13)	655(4)	4 403(5)	1 552(5)
C(14)	1 051(4)	4 393(5)	2 121(6)
C(15)	373(4)	6 244(5)	2 215(5)
C(16)	−161(5)	6 100(6)	2 955(6)
C(17)	−787(5)	6 870(6)	3 067(7)
C(18)	−868(5)	7 781(7)	2 419(8)
C(19)	−354(6)	7 928(6)	1 689(7)
C(20)	286(5)	7 155(6)	1 596(6)
C(21)	3 574(5)	1 490(7)	4 524(7)
C(22)	3 738(9)	2 581(8)	5 086(10)
C(23)	1 969(5)	1 105(7)	5 172(6)
C(24)	1 039(6)	716(9)	4 958(8)
C(25)	2 425(6)	−86(6)	3 437(6)
C(26)	1 644(8)	−390(8)	2 591(8)

signals (Table 1) appear at higher fields than for their analogues derived from benzylideneamines,[3] but are shifted downfield from those of the cyclopalladated ferrocenylthione recently reported.[10]

The molecular structure of compound **4b** and the atom labelling scheme are presented in Fig. 2. Bond distances, angles and atomic coordinates for non-hydrogen atoms are given in Tables 2, 3 and 4. The structure consists of discrete molecules linked by van der Waals forces. The palladium atom is in a slightly distorted square-planar environment co-ordinated to Cl, P, N(12) and the C(6) atom of the ferrocenyl group. The deviations from the plane are Pd, 0.018(2); P, −0.091(3); N(12), −0.016(6); Cl, 0.075(3); and C(6); 0.105(6) Å. Except for the Pd–N bond length which is clearly greater than that calculated for a single bond (Pd 1.31 and N sp^2 0.7 Å), the other palladium–ligand bond lengths are similar to those found in other five-membered cyclopalladated compounds.[11–16] Bond angles between adjacent atoms in the co-ordination sphere of the palladium lie in the range 81.1(2) [N(12)–Pd–C(6) to 95.5(1)° (Cl–Pd–P). The palladium deviates from the plane defined by the four atoms linked to it by 0.095(2) Å, towards the opposite site of the unsubstituted C_5H_5 ring.

The metallocycle is practically planar and contains the iminic C=N bond, thus confirming the *endo* structure predicted by ^1H NMR spectroscopy. The dihedral angle formed by the two fused rings is 7.14°. The C=N bond distance is similar to those found in other *endo*, and even *exo*, cyclopalladated complexes and slightly larger than the value for $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NPh)]$ [1.251(8) Å].[17] As a first approach to the evaluation of the strain involved in the formation of the five-membered metallocycle we have compared the C(6)–C(10)–C(11) and C(9)–C(10)– C(11) bond angles in complex **4b** with those for the above ferrocenylimine [123.0(7) and 128.8(8)°, respectively [17]]. The formation of the palladocycle involves a small variation in both angles (≈4.8°).

The average C–C bond length in both cyclopentadienyl rings is 1.417(1) Å, in good agreement with values reported for other ferrocene derivatives.[11] The Fe–C(ring) bond distances vary from 2.026(7) Å for Fe–C(10) to 2.088(6) Å for Fe–C(6) bonds. These two carbons are the ones shared by the C_5H_3 ring and the metallocycle. The two cyclopentadienyl rings are parallel, nearly eclipsed (tilt angle of 1.8, and −7.4° skewed from an eclipsed configuration). The NCH_2CH_2Ph moiety is nearly planar and forms a dihedral angle of 98.0° with the co-ordination plane of palladium. The distance between the two metals is 3.577(2) Å.

The crystal structure of complex **4b** is the first example reported so far in which a five-membered *endo*-type metallocycle is fused with a pentagonal ring. The unique crystal structure of a bicyclic system formed by a five-membered palladocycle and a cyclopentadienyl ligand of the ferrocene group reported to date

Table 5 Bond lengths (Å) and selected bond angles (°) in some five-membered cyclopalladated complexes containing σ{Pd–C(sp^2)} bonds

Compound	Pd–N	N–C(11)	C(11)–C(10)	C(10)–C(6)	C(6)–Pd	N–Pd–C(6)	Pd–N–C(11)
I σ[Pd–C(sp^2)cyclopentadienyl] cyclometallated ferrocenyl derivatives							
4b $[Pd\{(\eta^5-C_5H_5)Fe[\eta^5-C_5H_3CH=N(CH_2)_2Ph]\}-Cl(PEt_3)]$[a]	2.148(5)	1.280(8)	1.467(9)	1.434(9)	1.999(6)	81.1(2)	112.9(3)
6 $[Pd\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3CHMeNMe_2)\}-(acac)]$[b,c]	2.10(3)	1.572(3)	1.46(8)	1.50(2)	1.96(7)	82(4)	108(6)
II σ[Pd–C(sp^2)phenyl] *endo*-type metallocycles							
7 $[\{Pd(C_6H_4CH=NPh)-(\mu-NCOC_2H_4CO)\}_2]\cdot CH_2Cl_2$[d]	2.049(10)	1.298(16)	1.441(18)	1.436(18)	1.972(12)	81.4(5)	113.2(11)
8 $[\{Pd[3,4-(MeO)_2C_6H_2CH=NC_6H_{11}](\mu-Br)\}_2]$[e]	2.048(9)	1.275(12)	1.475(12)	1.475(12)	1.998(10)	81.4(5)	113.1(7)
9 $[\{Pd(o-MeOC_6H_4CH=NC_6H_4Me-p\ (\mu-O_2CMe)\}_2]$[f]	2.039(6)	1.281(9)	1.44(1)	1.41(1)	1.951(8)	80.9(3)	114.7(5)
10 $[Pd(C_6H_4CH=NCH_2CH_2NH_2)(en)][PF_6]$[b,g]	2.02(2)	1.25(3)	1.41(4)	1.40(4)	1.98(2)	81.2(9)	115.5(20)
11 $[Pd(C_6H_4CH=NCH_2Ph)(acac)]$[h]	2.008(5)	1.28(1)	1.45(1)	1.41(1)	1.955(7)	81.4(3)	115.2(58)
exo-type metallocycle							
12 $[Pd(C_6H_4CH_2N=CHPh)(acac)]$[i]	2.03(1)	1.49(3)	1.49(3)	1.38(2)	1.95(1)	81.0(8)	112.3(8)

[a] This work. [b] Average value for the two non-equivalent molecules. [c] Ref. 18. [d] Ref. 12. [e] Ref. 13. [f] Ref. 3. [g] en = $H_2NCH_2CH_2NH_2$. [h] Ref. 15. [i] Ref. 16.

Table 6 Iron-57 Mössbauer parameters (at room temperature) for the ferrocenylimine **1b** and the cyclopalladated complexes **2b**–**5b**

Complex	i.s.*/mm s^{-1}	q.s./mm s^{-1}
1b	0.44	2.34
2b	0.44	2.21
3b	0.45	2.16
4b	0.44	2.21
5b	0.44	2.13

* Isomer shift values are referred to metallic iron at room temperature.

was solved, but poorly refined (R = 0.11) by Kuz'min *et al.*,[18] and is $[Pd\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3CHMeNMe_2)\}(acac)]$ **6** (acac = acetylacetonate). The Pd–C bond lengths in the two complexes are similar [1.999(6), **4b**; 1.96(7) Å, **6**], but the Pd–N bond is clearly shorter in the cyclometallated amine complex [2.10(3) Å] (Table 5). Other outstanding structural differences between the two compounds are those related to the C atoms shared by the two fused rings [C(6) and C(10)], *i.e.* the C(6)–C(10) bond length is larger [1.50(2) Å] in **6**. The differences observed in metallocycle bond lengths and angles can be also explained in terms of the changes in hybridization of the N and C(11) atoms (sp^2 in **4b** and sp^3 in **6**). The larger distance between the two metals in complex **6** [3.595(2) Å][19] may be attributed to the envelope-like conformation of the metallocycle.

The most outstanding structural parameters of some five-membered metallocycles[12–16] are summarized in Table 5. The Pd–N bond in complex **4b** is longer than the values obtained for the *endo* (**7**, **11**), and *exo* five-membered metallocycles **12**, but very similar to that [2.138(4) Å] found in the *endo* six-membered complex with a σ(Pd–$C_{aliphatic}$) bond $[Pd\{1-CH_2(HC=NPh)-3,5-Me_2C_6H_2\}Br(PPh_3)]$ **13**, where the metallocycle has a half-skew chair conformation with the palladium atom −1.235 Å out of the plane.[19] The Pd–C bond in complex **4b** is similar to the value [2.009(3) Å] reported for [Pd(HL)Cl(PPh$_3$)] (HL = 7-chloro-1-(cyclopropylmethyl)-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-one,[20] where the metallocycle is involved in a tricyclic system being fused simultaneously to a phenyl and a seven-membered ring, and very close to that [2.060(5) Å] found in complex **13**.

As can easily be seen in Table 5, the bites of the ligands do not seem to be much affected either by the type of structure of the ring formed (*endo* or *exo*), nor by the nature of the metallated carbon atom (sp^2 of a phenyl group or sp^2 of a cyclopentadienyl ligand). Finally, in the five-membered metallocycles with σ[Pd–$C_{sp^2(phenyl)}$] reported previously[13–16] the two fused rings are practically coplanar, while in complex **4b** the two planes are slightly bent (forming an angle of 7.14°).

Mössbauer Spectra.—The ^{57}Fe Mössbauer spectra of the complexes **1b**–**5b** consists of a single quadrupole doublet. The isomer shift (i.s.) and the quadrupole splitting (q.s.) values are summarized in Table 6. The i.s. values are roughly identical for all the complexes (0.44–0.45 mm s^{-1}) and very similar, moreover, to those reported for $[\{\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)\}_2PCl]$,[21] [2]ferrocenophane[22] and its mercury(II) adduct.[22] Recent Mössbauer studies of several ferrocenyl-amines and -phosphines reveal that the isomer shifts obtained for these compounds are not significantly affected by the nature of the atom which is directly bound to the ferrocenyl moiety.[23] The quadrupole splitting parameter seems to be more affected by the nature of the substituent of the ferrocenyl moiety.

According to basic Mössbauer theory,[24] the differences observed for the q.s. values could be ascribed to two major causes: (*a*) the formation of the metallocycle might modify the symmetry of the iron environment and (*b*) a change in the electron donor (or electron withdrawing) nature of the substituent. Recently, the variations observed in the q.s. of ferrocene derivatives of the type $[Fe(C_5H_5)_2X]$[25] have been related to the distortions of the ferrocene moiety, reflected in the value of the tilt angle, and to the intensity of the Fe–X interaction. For instance, for complexes with tilt angles in the range 16–26° the decrease in q.s. in relation to ferrocene ($\Delta \approx -0.4$) has been attributed to the existence of weak interactions between Fe and the X group, while compounds with a q.s. larger than that of ferrocene ($\Delta \approx +0.3$ to $+0.9$) exhibited a strong Fe–X interaction, which produced a larger tilt angle (even exceeding 30°) and consequently modified the molecular orbital scheme.

The crystal structure of compound **4b** reveals that the formation of the metallocycle produces only tiny distortions in the ferrocene moiety, thus the q.s. values seem to reflect mainly the electronic effects of the substituents on the iron atom. The decrease observed shows an electron-withdrawing character of the palladium atom. According to the qualitative approach proposed to explain the substituent effects in ferrocene derivatives,[26] the decrease in the q.s. values produced by electron-withdrawing substituents can be attributed to an increase in the electron population of e_1 orbitals due to a stronger back donation. In order to clarify the effect of cyclopalladation upon the iron environment further studies on the variation of q.s. as a function of temperature, as well as molecular orbital calculations for these systems, need to be undertaken.

For the ferrocenylimines studied, we can conclude that palladation occurs on the cyclopentadienyl ring yielding *endo* five-membered metallocycles; no evidence of cyclopalladation of the phenyl moiety was found. These results are in sharp contrast with those reported by Crawford and Kaesz,[27] who studied the cyclomanganation of benzoylferrocene by $[MnMe(CO)_5)]$; in this case metallation occurred on the phenyl ring, giving $[Mn\{C_6H_4C(O)C_5H_4Fe(C_5H_5)\}(CO)_4]$. This fact was explained in terms of the higher strain energy involved in the fusion of the two pentagonal rings *versus* the formation of a bicyclic [5,6] system. Metallation did not occur at the ferrocene moiety even when benzoylferrocene was replaced by dimethylaminomethylferrocene.[28] The product of the reaction was $[Mn\{CH_2N(Me)CH_2C_5H_4Fe(C_5H_5)\}(CO)_4]$, formed by metallation of a methyl group. However, when dimethylbenzylamine was used the five-membered compound $[Mn(C_6H_4CH_2NMe_2)(CO)_4]$ was formed.[27,29] These results suggest that the formation of systems in which a five-membered ring is fused to a six-membered ring is preferred to the formation of a three-membered ring which in turn is preferred to formation of two fused five-membered rings.

Our results agree with those obtained in the cyclopalladation of *N*-benzylideneamines where the formation of *endo* five-membered metallocycles is favoured.[3b] Therefore, in the palladium derivatives, despite the fact that metallation at the phenyl ring would produce the fusion of a five- and a six-membered ring, the strain due to the formation of two five-membered fused rings does not prevent the formation of *endo* metallocycles. It is not possible to exclude that the larger atomic radius of palladium may decrease the strain of these fused systems. The reaction of $[ReMe(CO)_5]$[27] with dimethylaminomethylferrocene results in metallation of the cyclopentadienyl ring and the formation of five-membered derivatives. Recently, Nicholson and co-workers have reported the crystal structures of cyclomanganated complexes derived from *N*-acetylindol[30] and substituted acetylthiophenes,[31] containing two five-membered fused rings. The angles of the manganocycle in these systems are similar to those obtained for compound **4b**, and do not differ significantly from the normal values, thus suggesting that the strain imposed by fusing two five-membered rings is not very large.

Experimental

Elemental analyses (C, H and N) were carried out at the Institut de Química Bio-Orgànica de Barcelona (C.S.I.C). Infrared spectra were obtained from KBr pellets with a Perkin Elmer 1330 spectrophotometer, ^1H NMR spectra at *ca.* 20 °C on a Gemini-200 MHz instrument using $CDCl_3$ (99.8%) and $SiMe_4$ as solvent and internal standard, respectively, and operating at 80.2 MHz, and $^{31}P\{^1H\}$-NMR spectra with a Bruker WP80-50 spectrophotometer using $CHCl_3$ and H_3PO_4 (85%) as solvent and standard, respectively. Ultraviolet spectra of the complexes (10^{-3} and 10^{-4} mol dm^{-3} CH_2Cl_2 solutions) were recorded with a Shimadzu-UV160A spectrometer at room temperature. Conductivities of 10^{-3} mol dm^{-3} acetone solutions of the new compounds were measured with a Radiometer CDM3 conductivity bridge. The ^{57}Fe Mössbauer spectra were recorded at room temperature with a constant-acceleration spectrometer, using 10mCi ^{57}Co in a rhodium matrix as source. The calibration was performed with iron (25 mm thick). The spectral data were fitted by a least-squares method assuming that the two Lorentzian lines of the quadrupole doublet had the same intensity and width.

Materials and Syntheses.—Ferrocenecarbaldehyde and the amines $C_6H_5(CH_2)_nNH_2$ (n = 1 or 2) were obtained from standard sources and used as received. Some of the preparations described below involve the use of triethylphosphine and benzene which should be handled with caution. All the solvents were dried and distilled prior to use.

$[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH{=}N(CH_2)_nPh\}]$ (n = 1 **1a** *or* 2 **1b**). Ferrocenecarbaldehyde (1.0 g, 4.67 mmol) was dissolved in benzene (30 cm^3) at room temperature. Once the starting material had dissolved completely, the corresponding amine (4.67 mmol) was added. The flask containing the reaction mixture was connected to a condenser equipped with a Dean-Stark apparatus (10 cm^3). The red solution was refluxed on an ethylene glycol bath until 9.0–10.0 cm^3 of liquid (benzene–water mixture) had condensed on the Dean-Stark. The hot solution was carefully filtered and the filtrate reduced to dryness on a rotary evaporator. Addition of hexane to the oily material followed by a vigorous stirring at room temperature produced the precipitation of the imines **1a** and **1b**. The compounds were recrystallized from CH_2Cl_2–hexane (1:1). Yields: 88 and 71%, respectively. Compound **1a** [Found (Calc.) for $C_{18}H_{17}FeN$: C, 71.4 (71.3); H, 5.7 (5.3); N, 4.6 (4.6)%]: IR(KBr pellets) $\nu_{max}(C{=}N)$ 1632 cm^{-1}; UV/VIS (CH_2Cl_2) $\lambda_{max}(\log \varepsilon)$: 450.0(3.7) and 325.0(1.88) nm. Compound **1b** [Found (Calc.) for $C_{19}H_{19}FeN$: C, 71.9 (71.5); H, 6.1 (6.0); N, 4.6 (4.4)%]: IR(KBr pellets) $\nu_{max}(C{=}N)$ 1635 cm^{-1}; UV/VIS (CH_2Cl_2) $\lambda_{max}(\log \varepsilon)$ 452(1.09) and 326.0(1.89) nm.

$[\{Pd[(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nPh\}]Cl\}_2]$ (n = 1 **2a** *or* 2 **2b**). The imine **1a** or **1b** (1.7 mmol) was added to a methanolic (20 cm^3) solution containing $Na_2[PdCl_4]$ (0.51 g, 1.7 mmol) and sodium acetate trihydrate (0.23 g, 1.7 mmol). The resulting mixture was stirred at room temperature for 24 h and the wine-red precipitate was collected by vacuum filtration and air-dried. Then the solid was dissolved in benzene (50 cm^3) and filtered. The undissolved materials were discarded and the organic solution washed with three portions (30 cm^3) of water. The organic layer was extracted, dried over Na_2SO_4 (anhydrous) and concentrated on a rotary evaporator to dryness. The residue was treated with benzene (*ca.* 60 cm^3), and addition of hexane followed by slow evaporation of the solvent at room temperature resulted in the precipitation of a solid, which was filtered off and air-dried. Compound **2b** was purified by SiO_2 column chromatography using $CHCl_3$ as eluent. Yields: 63 and 45%, respectively. Compound **2a** [Found (Calc.) for $C_{36}H_{32}Cl_2Fe_2N_2Pd_2$: C, 48.8 (48.7); H, 3.65 (3.6); N, 3.2 (3.15%)]: IR(KBr pellets) $\nu_{max}(C{=}N)$ 1590 cm^{-1}; UV/VIS (CH_2Cl_2) $\lambda_{max}(\log \varepsilon)$ 469.0(0.89) and 379.0(sh) nm; Λ(acetone) = 12 Ω^{-1} cm^2 mol^{-1}. Compound **2b** [Found (Calc.) for $C_{36}H_{32}Cl_2Fe_2N_2Pd_2$: C, 49.9 (49.8); H, 4.1 (3.95); N, 3.15 (3.05)%]: IR(KBr pellets) $\nu_{max}(C{=}N)$ 1585 cm^{-1}; UV/VIS (CH_2Cl_2) $\lambda_{max}(\log \varepsilon)$ 470.5(0.94) and 380.0(sh) nm; Λ(acetone) = 15 Ω^{-1} cm^2 mol^{-1}.

$[Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nPh]\}Cl(PPh_3)]$ (n = 1 **3a** *or* 2 **3b**). Triphenylphosphine (1.2 mmol) was added to an acetone suspension (10 cm^3) containing the dimeric complex **2a** and **2b** (0.3 mmol). The resulting mixture was refluxed for 30 min. After cooling to room temperature the solution was filtered and the filtrate concentrated to dryness on a rotary evaporator. Addition of diethyl ether to the residue resulted in precipitation of the desired compound which was recrystallized from CH_2Cl_2–methanol (2:1). Yields: 69 and 58%. Compound **3a** [Found (Calc.) for $C_{36}H_{31}ClFeNPPd$: C, 60.95 (61.2); H, 4.4 (4.6); N, 1.9 (2.0)%]: IR(KBr pellets) $\nu_{max}(C{=}N)$ 1605 cm^{-1}; UV/VIS (CH_2Cl_2) $\lambda_{max}(\log \varepsilon)$ 471.0(1.1) and 381.5(sh) nm; Λ(acetone) = 8 Ω^{-1} cm^2 mol^{-1}. Compound **3b** [Found (Calc.) for $C_{37}H_{33}ClFeNPPd$: C, 61.3 (61.6): H, 4.6

(4.4); N, 1.9 (1.9)%]: IR(KBr pellets) ν_{max}(C=N) 1600 cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}(log ε) 472.5(0.98) and 382.0(1.7) nm; Λ(acetone) = 15 Ω^{-1} cm^2 mol^{-1}.

$[Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nPh]\}Cl(PEt_3)]$ (*n* = 1 **4a** *or* 2 **4b**). Compound **2a** or **2b** (0.3 mmol) was suspended under nitrogen in distilled acetone (15 cm^3) and then triethylphosphine (0.09 cm^3, 0.61 mmol) was added with caution. The reaction mixture was refluxed for 30 min and cooled to room temperature. The red-brown solution formed was filtered and the solvent removed on a rotary evaporator. Addition of ethanol to the oil formed resulted in precipitation of the desired complex, which was filtered off and dried. Yields: 83 and 73%, respectively. Compound **4a** [Found (Calc.) for $C_{24}H_{31}ClFeNPPd$: C, 51.1 (51.2); H, 5.3 (5.55); N, 2.6 (2.5)%]: IR(KBr pellets) ν_{max}(C=N) 1600 cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}(log ε) 470.0(0.97) and 380.5(sh) nm; Λ(acetone) = 20 Ω^{-1} cm^2 mol^{-1}. Compound **4b** [Found (Calc.) for $C_{25}H_{33}ClFeNPPd$: C, 52.3 (52.1); H, 5.8 (5.8); N, 2.5 (2.4)%]: IR(KBr pellets) ν_{max}(C=N) 1595 cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}(log ε) 471.0(1.04) and 381.0(1.10) nm; Λ(acetone) = 14 Ω^{-1} cm^2 mol^{-1}.

$[Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nPh]\}(dppe)]Cl$ (*n* = 1 **5a** *or* 2 **5b**). 1,2-Bis(diphenylphoshinoethane (dppe) (0.6 mmol) was added to an acetone suspension (50 cm^3) of the corresponding dimeric complex **2a** or **2b** (0.3 mmol). The resulting mixture was refluxed for 45 min. During this period the starting material dissolved gradually. Then the reaction flask was set aside to cool to room temperature and the solution filtered. Concentration of the filtrate to dryness on a rotary evaporator produced a red oil, which was treated with ether (*ca.* 10 cm^3) and stirred vigorously for 20 min at room temperature. The reddish solid obtained was collected by vacuum filtration and air-dried. Yields: 59 and 67%, respectively. Compound **5a** [Found (Calc.) for $C_{44}H_{40}ClFeNP_2Pd$: C, 62.6 (62.7); H, 5.0 (4.8); N, 1.65 (1.7)%]: IR(KBr pellets) ν_{max}(C=N) 1602 cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}(log ε) 474.0(0.93) and 387.0(1.03) nm; Λ(acetone) = 116 Ω^{-1} cm^2 mol^{-1}. Compound **5b** [Found (Calc.) for $C_{45}H_{42}ClFeNP_2Pd$: C, 63.2 (63.1); H, 4.9 (5.0); N, 1.7 (1.9)%]: IR(KBr pellets) ν_{max}(C=N) 1598 cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}(log ε) 475.0(1.09) and 389.0(1.02) nm; Λ(acetone) = 122 Ω^{-1} cm^2 mol^{-1}.

Crystallography for Compound **4b**.—*Crystal data.* $C_{25}H_{33}ClFeNPPd$, $M = 576.67$, monoclinic. space group $P2_1/a$, $a = 15.944(3)$, $b = 12.425(2)$, $c = 12.682(2)$ Å, $\beta = 100.19(2)^\circ$, $U = 2473(1)$ Å^3, $D_c = 1.550$ g cm^{-3}, $Z = 4$, $F(000) = 1180.0$, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 14.97 cm^{-1}, 298 K.

Data collection and processing. A prismatic crystal (0.1 × 0.1 × 0.15 mm) was selected and mounted on a Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($8 \leqslant \theta \leqslant 12^\circ$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-Kα radiation using the ω–2θ scan technique. 4445 Reflections were measured in the range $2 \leqslant \theta \leqslant 25^\circ$ ($\pm h,k,l$) of which 3668 were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$; R(int.) on F was 0.033. Three reflections were measured every 2 h as orientation and intensity control, and no significant decay was observed. Lorentz-polarization, but not absorption, corrections were made.

Structure analysis and refinement. The structure was solved by Patterson synthesis, using the SHELXS 86 [32] and DIRDIF 84 computer programs.[33] The structure was refined by the full-matrix least-squares method with the SHELX 76 computer program.[34] The function minimized was $\Sigma w||F_o| - |F_c||^2$ where $w = [\sigma^2(F_o) + 0.0106|F_o|^2]^{-1}$; f, f' and f'' were taken from ref. 35. Non-hydrogen atoms were refined anisotropically and the positions of 27 H atoms were obtained from a difference synthesis and refined with an overall isotropic thermal parameter. The final R and R' factors were calculated according to the expressions $(\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$ and $[(\Sigma w||F_o| - |F_c||^2)/(\Sigma w|F_o|^2)]^{\frac{1}{2}}$ giving 0.052 and 0.056 for all observed reflections; 353 parameters were refined. Maximum shift/e.s.d. = 0.1, maximum and minimum peaks in the final difference synthesis 0.4 and −0.4 e Å^{-3}, respectively.

Additional material available fro the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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