Influences of the Substituents at the Iminic Carbon Atoms (Hydrogen *versus* Methyl) upon the Properties of Ferrocenylimines and their Cyclopalladated Derivatives†

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Ferrocenylimines of general formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ (R = Me, R′ = Ph **1a**, C_6H_4Me-2 **1b**, C_6H_4Me-4 **1c**, CH_2Ph **1d**, $CH_2C_6H_4Me$-2 **1e**, $CH_2C_6H_4Cl$-2 **1f**, CH_2CH_2Ph **1g** or 1-$C_{10}H_7$ **1h**; R = H, R′ = Ph **1i**, C_6H_4Me-2 **1j**, C_6H_4Me-4 **1k**, $CH_2C_6H_4Me$-2 **1l**, $CH_2C_6H_4Cl$-2 **1m** or 1-$C_{10}H_7$ **1n**) have been prepared and characterized. Addition of these ligands to methanolic solutions of $Na_2[PdCl_4]$, and sodium acetate trihydrate in a 1:1 molar ratio, results in the formation of the di-μ-chloro bridged cyclopalladated complex $[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CR{=}NR')](\mu\text{-}Cl)\}_2]$ **2a–2n**. Reaction of compounds **2a–2n** with triphenylphosphine in benzene yields more soluble monocyclopalladated derivatives $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CR{=}NR')\}Cl(PPh_3)]$ **3a–3n**. Proton, ^{13}C and ^{31}P NMR spectroscopic studies on these complexes reveal that cyclopalladation occurs on the ferrocenyl moiety, thus producing five-membered metallacycles containing the C=N bond (*endo*-type structures). The crystal structures of compounds **1a**, **1i** and **3g** have been determined. Complex **1a** is triclinic, space group $P\bar{1}$ with *a* = 10.152(3), *b* = 12.169(3), *c* = 12.239(3) Å, α = 90.45(2), β = 100.56(2) and γ = 102.72(2)°. Compound **1i** is monoclinic, space group *Cc*, with *a* = 5.876(3), *b* = 37.298(9), *c* = 12.640(4) Å and β = 103.26(4)°. The complex $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CMe{=}NCH_2CH_2Ph)\}Cl(PPh_3)]\cdot CH_2Cl_2$ **3g** is monoclinic, space group $P2_1/n$ with *a* = 20.343(2), *b* = 9.133(1), *c* = 19.714(2) Å and β = 97.17(1)°, and its crystal structure confirms the formation of a five-membered palladocycle fused with the ferrocenyl moiety. The influence of the substituents R (H or Me) and R′ upon the spectroscopic and structural properties of the free ligands and the cyclopalladated complexes is also discussed.

One of the areas of organometallic chemistry that has been widely developed during the last decade is the syntheses, characterization and reactivity of cyclometallated compounds, in particular those containing N-donor ligands and palladium. For instance, several reviews dealing with cyclopalladated complexes containing σ Pd–C(sp^2) (aromatic) and even σ Pd–C(sp^3) (aliphatic) bonds have appeared in the literature.[1] This sort of compound has been found to act as an interesting template in both organic and organometallic chemistry.[2]

According to the general scheme postulated for the cyclopalladation of N-donor ligands, the metallacycle formation takes place in two steps: (*a*) co-ordination of the N-donor ligand and (*b*) electrophilic attack of the palladium(II) species formed to the carbon atom. Recent studies on cyclopalladation of ligands containing the C=N functional group have shown that besides the tendency to form five-membered derivatives, other factors are also important enough to influence the ease and position of the metallation, particularly the inclusion of the iminic bond in the metallacycle (*endo* effect), the substituents in the phenyl ring and/or at the iminic carbon atom. For instance, though it is well known that organic imines exhibit a strong tendency to give five-membered *endo* derivatives,[3] for phenylhydrazones the structure of the metallacycle is highly dependent on the substituent at the methinic carbon atom, since hydrazones derived from ketones generally give *endo* metallacycles,[4] while those arising from aldehydes produce exocyclic cyclopalladated compounds.[5]

On the other hand, and although it is well known that ferrocene derivatives are more likely to undergo electrophilic attacks than aromatic ones, only a few examples of palladocycles containing σ Pd–C(sp^2) (ferrocene) bonds have been reported.[6,7] We have recently described two examples of cyclopalladation of Schiff bases derived from ferrocenecarbaldehyde of general formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NR')]$ [R′ = $(CH_2)_nPh$, *n* = 1 or 2],[7] in which the formation of *endo* five-membered metallocycles with σ Pd–C(sp^2) (ferrocene) bonds occurred exclusively.

In order to elucidate whether (*i*) the nature of the substituent at the iminic carbon atom (R) and (*ii*) the presence of substituents on the phenyl ring of the R′ moiety could be important enough to modify (*a*) the structure of the metallacycle and/or (*b*) the ease of the metallation, we have undertaken the study of imines of general formulae $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ (Fig. 1) derived from acetylferrocene (R = Me, **1a–1h**), and expanded our preliminary results on Schiff bases with R = H (**1i–1n**). For these systems metallation of the cyclopentadienyl ring would produce *endo* five-membered derivatives in all cases, but the formation of *exo* five- or six-membered metallacycles is also possible through activation of C–H bonds of the R′ substituent.

The two families of ferrocenylimines will allow us, moreover, to elucidate the influence of both substituents R (H or Me) and R′ upon the spectroscopic and structural properties of the ligands and their cyclopalladated derivatives.

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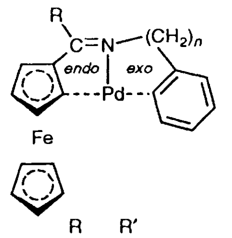
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



	R	R′
1a	Me	Ph
1b	Me	C_6H_4Me-2
1c	Me	C_6H_4Me-4
1d	Me	CH_2Ph
1e	Me	$CH_2C_6H_4Me$-2
1f	Me	$CH_2C_6H_4Cl$-2
1g	Me	CH_2CH_2Ph
1h	Me	1-$C_{10}H_7$
1i	H	Ph
1j	H	C_6H_4Me-2
1k	H	C_6H_4Me-4
1l	H	$CH_2C_6H_4Me$-2
1m	H	$CH_2C_6H_4Cl$-2
1n	H	1-$C_{10}H_7$

Fig. 1 Schematic view of the two different types of metallocycles (endo- and exo-cyclic) which could be formed from the ferrocenylimines $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ under study

Results and Discussion

Syntheses.—The preparation of the imines was carried out by condensation of acetylferrocene **1a**–**1h** or ferrocenecarbaldehyde **1i**–**1n** and the corresponding amines. The method reported previously[7] for the preparation of $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH{=}N(CH_2)_nPh\}]$ (n = 1 **1o** or 2 **1p**), based on the reaction of stoichiometric amounts of aldehyde and the amine using a Dean–Stark apparatus, allowed us to prepare ligands **1i**–**1n**, but it was unsuccessful for the syntheses of **1a**–**1h**. For these systems the presence of molecular sieves (5 Å) and large excess of amines were needed to force the displacement of the equilibria. The difficulties of preparing **1a**–**1h** might be ascribed to the larger bulk of the methyl substituent at the iminic carbon atom *versus* hydrogen.

On the other hand, ligands with R = Me **1a**–**1h** decompose at lower temperatures than those with R = H (**1i**–**1n**) and within each of the two series an increase in the basicity of the nitrogen is reflected in a lower value of the decomposition point. Stabilities of the two sorts of imine are markedly different, since ligands derived from ferrocenecarbaldehyde are more stable than compounds **1a**–**1h**, which undergo slow decomposition, even at 20 °C, yielding the corresponding amine and acetylferrocene.

The complexes $[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CR{=}NR')](\mu\text{-}Cl)\}_2]$ **2a**–**2n** were prepared according to the general procedure described for cyclopalladation of ferrocenylamines[6] and ferrocenylimines[7] (based on the reaction of the free ligands with stoichiometric amounts of $Na_2[PdCl_4]$ and $Na(O_2CMe)\cdot 3H_2O$, using methanol as solvent at *ca.* 20 °C). One outstanding feature of these reactions is that for ferrocenylimines with R = Me, **1a**–**1h**, the formation of the palladocycle is achieved faster (reaction time *ca.* 3 h) than for **1i**–**1n**, for which the partial activation of the C–H bond becomes evident only after a minimum of 18 h. Addition of triphenylphosphine to benzene or acetone suspensions of **2a**–**2h** or **2i**–**2n** respectively produced the cleavage of the μ-Cl bridges giving monomeric compounds $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CR{=}NR')\}Cl(PPh_3)]$ **3a**–**3n**. Evidence of the cleavage of the Pd–N bond was not observed in any of the cases, even when large excess of phosphine (up to fourfold molar ratio) was used. Besides, the reaction of more basic phosphine ligands such as PEt_3 and cyclopalladated complexes $[\{Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3CH{=}N(CH_2)_nPh]\}(\mu\text{-}Cl)\}_2]$ (n = 1 or 2) in a 6 : 1 molar ratio did not produce the cleavage of the metallacycle,[7] showing that for these cyclometallated complexes, the Pd–N bond is very unreactive. This finding is in contrast with previous work on cyclopalladation of organic imines such as $PhCH{=}N(CH_2)_nPh$, for which the formation of complexes containing one or two phosphine ligands per palladium unit was dependent on the basicity of the nitrogen atom.[3a] Addition of excess of PPh_3 to the di-μ-bridged dimeric complexes containing less basic nitrogen atoms (n = 0) produced cleavage of the Pd–N bond, while for those in which an alkylic chain is intercalated between the phenyl ring and the donor atom (thus enhancing the basic character of the nitrogen) ring opening and the incorporation of a second phosphine ligand in the co-ordination sphere of palladium was not observed.

Characterization.—Except for **1g**, which is an oil, the remaining complexes described here are solids at room temperature and their colours vary from yellow-orange for **1a**–**1n**, to dark red for the cyclometallated derivatives **2a**–**2n** and **3a**–**3n**. In all cases elemental analyses were consistent with the proposed formulae (Experimental section). Compounds **1** and **3** exhibit high solubility in most common solvents (chloroform, dichloromethane, acetone, benzene or toluene), are slightly soluble in alcohols, and practically insoluble in alkanes; while the di-μ-chloro bridged derivatives **2** are less soluble.

The infrared spectra of the free imines show an intense, sharp band in the range 1620–1640 cm^{-1} (**1a**–**1h**) and 1600–1620 cm^{-1} (**1i**–**1n**) assigned to the stretching of the C=N bond. For the cyclopalladated complexes this band appears at lower wavenumbers in both families of compounds. This variation in the infrared spectra has also been described in previous studies on cyclopalladation of Schiff bases,[3] and explained as derived from a decrease in the bond order of the imine bond upon cyclopalladation.

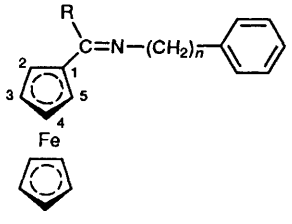
Proton and ^{13}C NMR data for the free imines **1a**–**1n** as well as for the related complexes $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NR')]$,[7,8] (R′ = CH_2Ph **1o**, CH_2CH_2Ph **1p**, C_6H_4-F-4 **1q**, C_6H_4Cl-4 **1r**, C_6H_4Br-4 **1s** or C_6H_4OMe-4 **1t**) in the range δ 1.00–6.00 are summarized in Tables 1 and 2. The most outstanding feature is that for the two series of compounds $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ (R = Me **1a**–**1h** or H **1i**–**1t**), the chemical shifts of the substituted C_5H_4 ring of the ferrocenyl moiety are clearly influenced by the nature of the two substituents, R and R′, *i.e.* for a given R group the ^1H and ^{13}C resonances of the C_5H_4 ring are shifted upfield as the basicity of the N-donor atom increases.[9] Furthermore, the iminic carbon resonances appear at higher fields for the compounds containing R = Me (*ca.* δ 166.5–169.0), than in their analogues with R = H (δ *ca.* 160.0–163.0) according to the differences of the σ-donor abilities of H and Me [$\sigma_I(H) = 0.0$, $\sigma_I(Me) = -0.07$].[10]

Comparison of the ^1H NMR data shown in Tables 1 and 3 allows us to deduce that cyclometallation has occurred on the C_5H_4 ring in all cases. The assignment of the signals is consistent with previous work on cyclopalladation of ferrocenylimines,[7] where the high-field shielding of the resonance due to the H^4 protons was interpreted in terms of the anisotropy due to the phenyl substituents of the phosphine ligand.

The resonance due to the NCH_2 protons, which appears as a triplet for **1d**–**1f** and **1l**–**1m**, splits into a doublet of doublets (AB pattern system) in the spectra of **3d**–**3f** and **3l**–**3m**. This fact, also observed in the ^1H NMR spectra of $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2Ph)\}Cl(PPh_3)]$ **3o** was attributed to the inhibition of the rotation around the NCH_2 bond.[7] For complex **3g**, the four protons of the two CH_2 groups appear as four multiplets and each one of these signals was unequivocally assigned with the aid of decoupling experiments.

As mentioned above, the H^4 resonance is under the influence of two effects simultaneously, the ring current of the C_5H_3 moiety of the ferrocene, and the anisotropy of the aromatic rings of the PPh_3 ligand. In all cases, the resonances of the H^2 and H^3

Table 1 Proton NMR data[a] for compounds **1a**–**1n** and for the ferrocenylimines $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NR')]$ (R′ = CH_2Ph **1o**, CH_2CH_2Ph **1p**, C_6H_4F-4 **1q**, C_6H_4Cl-4 **1r**, C_6H_4Br-4 **1s** or C_6H_4OMe-4 **1t**) in the range δ 1.00–6.00



Compound	Me	H^2,H^5	H^3,H^4	C_5H_5	NCH_2	CH_2	Me(R′)	HC=N
1a	2.39	4.87[b]	4.47[b]	4.24	—	—	—	—
1b[c]	2.03	4.82[b]	4.43[b]	4.22	—	—	2.14	—
1c	2.07	4.80[b]	4.41[b]	4.21	—	—	2.34	—
1d	2.19	4.73[b]	4.34[b]	4.14	4.65	—	—	—
1e	2.17	4.74[b]	4.35[b]	4.15	4.58	—	2.37	—
1f	2.21	4.79[b]	4.39[b]	4.17	4.69	—	—	—
1g	2.02	4.62[b]	4.30[b]	4.10	3.64[d]	2.99[d]	—	—
1h[c]	2.07	4.94[b]	4.50[b]	4.30	—	—	—	—
1i	—	4.80[b]	4.49[b]	4.25	—	—	—	8.33
1j	—	4.84[b]	4.50[b]	4.25	—	—	2.34	8.22
1k	—	4.75[b]	4.47[b]	4.23	—	—	2.33	8.32
1l	—	4.65[b]	4.38[b]	4.13	4.62	—	2.33	8.19
1m	—	4.69[b]	4.39[b]	4.19	4.74	—	—	8.24
1n	—	4.90[b]	4.53[b]	4.29	—	—	—	8.42
1o[e]	—	4.68	4.38	4.17	4.68	—	—	8.24
1p[e]	—	4.57	4.35	4.04	3.71	2.97	—	7.99
1q[f]	—	4.78	4.46	4.21	—	—	—	8.38
1r[f]	—	4.79	4.49	4.23	—	—	—	8.40
1s[f]	—	4.82	4.52	4.26	—	—	—	8.43
1t[f]	—	4.76	4.43	4.20	—	—	*g*	8.38

[a] Labelling refers to the scheme shown. [b] Triplets ^2J(H–H) = 1.8–2.0 Hz. [c] Two superimposed spectra were obtained, which correspond to the two rotameric species present in solution. [d] Triplets ^2J(H–H) = 7.5 Hz. [e] Data from ref. 7. [f] Data from ref. 8. [g] Data not given.

protons are shifted upfield upon cyclopalladation, thus indicating that the palladium atom produces a decrease in the ring current of the substituted pentagonal ring of the ferrocenyl moiety.

On the other hand, since cyclopalladation reactions involve the replacement of a σ C–H bond by a σ Pd–C bond, such interchange is expected to modify the chemical and the symmetrical environments of the carbon nuclei included in the ring fused with the metallacycle. However, ^{13}C NMR studies on this field are scarce.[11] In order to clarify the effect of the palladium atom upon the ring current of the metallated moiety, ^{13}C NMR spectra of the cyclopalladated compounds were recorded (Table 4).

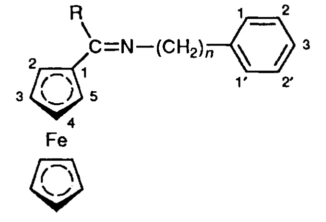
Comparison of data summarized in Tables 2 and 4 shows the splitting of the resonance due to the C^3,C^4 pair of carbon atoms, since the formation of the metallacycle involves a decrease in the symmetry of the substituted cyclopentadienyl ring. Further, the resonance of the Me at the imine carbon atom is shifted upfield and appears as a doublet [^4J(P–C) = 10–15 Hz] due to phosphorus coupling in **3a**–**3g**, while the singlet due to the iminic carbon atom of the free imines (δ *ca.* 166.5–169.0) shifts downfield and splits into a doublet, when observable, in the cyclopalladated complexes. This result is in sharp contrast with those obtained for *N*-benzylideneamines and their cyclopalladated derivatives, for which the resonance of the C atom in the C=N group did not shift appreciably upon cyclopalladation.[3b] The signal due to the metallated carbon atom exhibits low intensity due to the nuclear Overhauser effect and in most cases it was not observed. However, when present, it appears as a doublet and is downfield shifted. This shift (*ca.* 20 ppm) is smaller than those observed in cyclopalladated compounds with σ Pd–C(sp^2) phenyl bonds (*ca.* 30 ppm).[12] These three facts indicate that the coupling takes place through the metallacycle iminic bond.

The ^{31}P NMR spectra of **3a**–**3n** exhibit a singlet in the range δ 36.00–38.00, which is consistent with a *trans* arrangement of the phosphine and iminic nitrogen atom. This signal appears at lower fields than that reported for the cyclopalladated complex derived from ferrocenecarbothioamide[13] (δ 32.0), but is shifted upfield as compared with those derived from *N*-benzylideneamines (δ *ca.* 39.0–43.0).[3] This variation clearly reflects the influence of the *trans* ligand upon the ^{31}P NMR spectra of the PPh_3 group.

Crystal Structures of Compounds **1a**, **1i** *and* **3g**.—A perspective drawing of the molecular structures of compounds **1a** and **1i**, and the atom labelling schemes are presented in Figs. 2 and 3 respectively.

The structures of **1a** and **1i** consist of discrete molecules of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NPh)]$ (R = Me or H respectively), held together by van der Waals forces, and two non-equivalent molecules are present in their crystal structures. Selected bond lengths and angles for these complexes are summarized in Table 5. The high estimated standard deviations (e.s.d.s) are consistent with some large differences found in the two non-equivalent molecules present in the crystal structures. These differences may be expected given the size and orientation of some ellipsoids, *i.e.* C(1), C(4), C(5) in Figs. 2 and 3. Comparison of the data shows clearly that the replacement of a hydrogen by a methyl group at the iminic carbon atom is reflected in a variation of several bond lengths and angles. For instance, the larger bulk of the Me substituent *versus* H involves the closing of the C(10)–C(11)–N bond angle [from 125(1)° in **1i** to 119.0(7)° in **1a**]. This variation can be attributed to steric repulsions between the C_5H_4 ring and the Me substituent. The relative orientation between the phenyl and C_5H_4 rings is markedly different in the two cases [the angles defined by their planes are 93.9(3) and 19.0(5)° for **1a** and **1i**, respectively]. The nearly orthogonal arrangement of these two rings in **1a** rules out any conjugation effect between the phenyl ring and the

Table 2 Carbon-13 NMR spectroscopic data[a] for the ferrocenylimines of general formulae $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CR{=}NR')]$ **1a**–**1n**, and for complexes $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CH{=}NR')]$ ($R' = CH_2Ph$ **1o**, CH_2CH_2Ph **1p**, C_6H_4F-4 **1q**, C_6H_4Cl-4 **1r**, C_6H_4Br-4 **1s** and C_6H_4OMe-4 **1t**)



	Ferrocenyl moiety				R′ moiety							
Complex	Me	C^3,C^4	C^2,C^5	C_5H_5	NCH_2	CH_2	C_{ipso}	C^1,$C^{1'}$	C^2,$C^{2'}$	C^3	Me(R′)	C=N
1a	18.09	71.27	68.85	69.97	—	—	151.69	128.87	122.99	119.76	—	167.83
1b	18.16	70.65	68.28	69.37	—	—	*b*	130.28	126.30	118.95	17.95	166.53
								b	123.00			
1c	18.46	71.13	68.77	69.91	—	—	149.77	129.90	120.12	119.17	20.90	167.98
1d	16.47	70.22	67.87	69.16	54.98	—	*b*	*b*	128.36	127.51	—	
1e	16.39	70.25	67.87	69.15	53.05	—	*b*	*b*	130.02	126.50	19.39	*b*
									127.31	125.70		
1f	16.59	70.24	67.86	69.17	52.46	—	148.28	133.04	127.61	126.75	—	168.49
								b	129.00			
1g	15.58	70.00	67.64	69.15	53.48	37.31	*b*	129.03	127.03	129.20	—	*b*
1h	18.30	70.93	68.48	69.48	—	—	*c*	*c*	*c*	*c*	*c*	168.97
1i	—	71.29	69.29	69.50	—	—	*b*	129.11	120.63	125.20	—	161.43
1j	—	71.21	69.06	69.35	—	—	*b*	130.19	118.07	126.77	17.95	160.61
								131.26	124.95			
1k	—	71.24	69.01	68.28	—	—	134.92	129.74	120.53	*b*	21.02	160.67
1l	—	70.96	69.01	69.53	62.87	—	138.51	136.61	126.73	128.86	19.82	162.76
								130.75	127.62			
1m	—	70.57	68.59	69.58	62.03	—	137.30	129.65	126.89	129.65	—	163.41
								129.25	128.15			
1n	—	70.52	68.28	69.61	—	—	—	*d*	*d*	*d*	*d*	*d*
1o[e]	—	70.41	68.57	69.21	65.01	—	141.80	128.48	127.39	127.87	—	162.88
1p[e]	—	70.07	68.08	68.83	63.01	37.172	140.06	128.92	126.05	128.40	—	161.43
1q[f]	—	71.47	69.31	69.49	—	—	149.74	122.46	115.19	160.91	—	161.42
1r[f]	—	71.56	69.40	69.51	—	—	152.22	122.56	129.37	130.10	—	162.21
1s[f]	—	72.09	70.04	69.94	—	—	153.10	123.47	132.84	118.39	—	162.70
1t[f]	—	71.11	69.08	69.39	—	—	146.28	122.02	114.60	158.10	55.20	159.25

[a] Labelling refers to the scheme shown. [b] Not observed. [c] Not assigned. [d] Data not given. [e] Data from ref. 7. [f] Data from ref. 8.

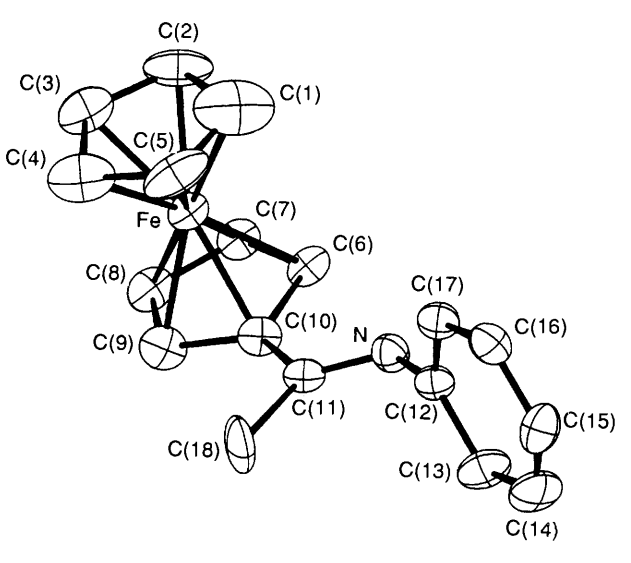


Fig. 2 Molecular structure and atom numbering scheme for $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CMe{=}NPh)]$ **1a**

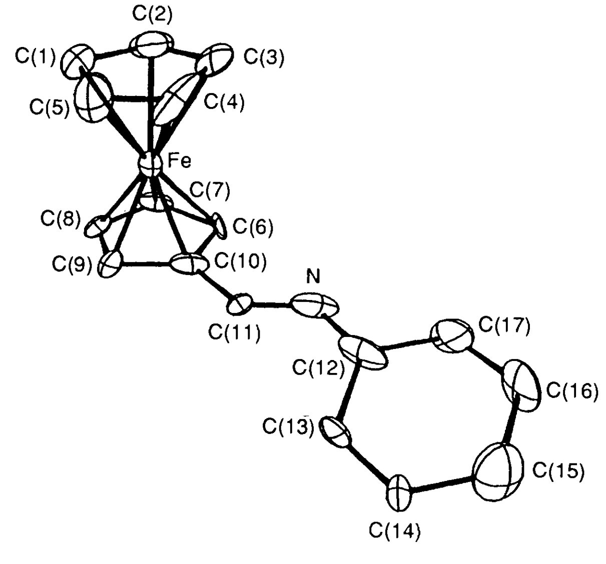
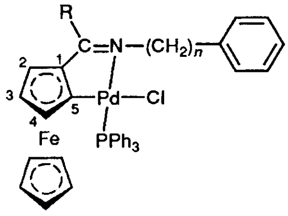


Fig. 3 Molecular structure and atom numbering scheme for $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CH{=}NPh)]$ **1i**

ferrocenyl moiety. This fact may be also responsible for the enlargement of the N–C(12) bond length in **1a** [1.41(1) Å] as compared with that found in **1i** [1.35(4) Å], which could also be attributed to steric hindrance. Furthermore, in **1a**, the methyl carbon is not coplanar with the C_5H_4 ring, since it is displaced by 0.294 Å (average value for the two non-equivalent molecules) towards the iron centre.

In both cases, the two pentagonal rings are planar and nearly

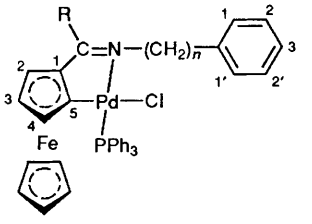
Table 3 Proton NMR data[a] for compounds **3a**–**3n** and for the cyclopalladated complexes $[\overline{\mathrm{Pd}\{(\eta^5\text{-}C_5H_5)\mathrm{Fe}[(\eta^5\text{-}C_5H_3)CH{=}N}\text{-}(CH_2)_n\mathrm{Ph}]\}\mathrm{Cl}(\mathrm{PPh}_3)]$ (n = 1 **3o** or 2 **3p**), in the range δ 1.50–6.00



Compound	Me	H^2	H^3	H^4	C_5H_5	NCH_2	CH_2	Me(R′)	HC=N
3a	2.06	4.47	4.13	3.93	3.92	—	—	—	—
3b	2.02	4.47	4.13	3.33	3.94	—	—	2.30	—
3c	2.07	4.47	4.13	3.38	3.95	—	—	2.32	—
3d	2.16	4.30	4.00	3.26	3.69	4.71[b] 5.70[b]	—	—	—
3e	2.07	4.36	4.06	3.29	3.89	4.92[b] 5.16[b]	—	2.39	—
3f	2.09	4.35	4.05	3.31	3.82	5.05[b] 5.54[b]	—	— —	—
3g[c]	2.15	4.35	4.03	3.34	3.83	4.22[d] 3.91[d]	3.31[d] 2.81[d]	— —	—
3h	1.99	4.51	4.20	3.48	—	—	—	—	
3i	—	4.52	4.19	3.49	3.97	—	—	—	8.29[e]
3j	—	4.53	4.21	3.44	4.00	—	—	2.53	8.20[e]
3k	—	4.53	4.20	3.51	3.97	—	—	2.54	8.32
3l	—	4.31	4.10	3.86	3.36	4.82[b] 5.18[b]	—	2.40	*f*
3m		4.30	4.03	3.77	3.31	4.98[b] 5.35[b]	—	—	7.95[e]
3n	—	4.55	4.24	3.50	4.08	—	—	—	8.33[e]
3o[g]	—	4.32	4.06	3.33	3.67	4.65[b] 5.45[b]	—	—	7.98[e]
3p[g]	—	4.30	4.00	3.45	3.67	4.05[d] 3.87[d]	3.32[d] 2.96[d]	—	8.08[e]

[a] Labelling refers to the scheme shown. [b] Doublet of doublets (AB pattern) centred at the values given. [c] Additional signal at δ 5.120 due to the CH_2Cl_2 molecule of solvation. [d] Complex multiplets centred at the values given. [e] Doublet ^3J(P–H) = 7.3 Hz. [f] Overlapped by the resonance of the phenyl rings. [g] Data from ref. 7.

Table 4 Carbon-13 NMR spectroscopic data[a] for the cyclopalladated compounds: $[\overline{\mathrm{Pd}\{(\eta^5\text{-}C_5H_5)\mathrm{Fe}(\eta^5\text{-}C_5H_3CMe{=}N}R')\}\mathrm{Cl}(\mathrm{PPh}_3)]$[b]



	Ferrocenyl moiety					R′ moiety							
	Me[c]	C^2	C^3	C^4	C_5H_5	NCH_2	CH_2	C_{ipso}	C^1,$C^{1'}$	C^2,$C^{2'}$	C^3	Me(R′)	C=N[c]
3a	17.032	69.149	67.065	69.218	70.532	—	—	*d*	128.274	123.543	125.342	—	*d*
3b[e]	17.021	69.094	67.056	69.165	—	—	—	145.210	128.901	123.343	*d*	21.114	181.420
3d	16.461	68.630	66.955	68.702	70.649	54.181		139.785	130.973	127.449	*d*	—	*d*
3e	16.106	68.658	66.854	68.673	70.662	51.921	—	138.101	128.945 130.613	126.803 126.402	120.075	—	*d*
3f[f]	15.862	68.312	66.478	68.389	70.077	50.240	—	137.251	130.409 130.602	126.935 126.080	127.793	22.681	184.569
3g	15.078	68.611	66.949	68.690	70.963	53.676	37.064	140.21	129.914	128.647	126.692	—	181.026

[a] Numbering of the carbon atoms refers to the scheme shown. [b] Four additional doublets are observed in all these spectra and are due to the four types of carbon nuclei present in the phenyl rings of the PPh_3 ligand [δ 131(C_{ipso}), 135(C^{α}), 129(C^{γ}) and 128(C^{β})]. [c] Doublet due to phosphorus coupling. [d] Not observed. [e] Two additional signals were oberved at δ 101.719 [doublet assigned to the metallated carbon atom, C(1)], and a singlet at δ 90.121 (due to the *ipso* carbon atom of the C_5H_3 ring). [f] Two more resonances were observed at δ 101.719 [doublet, assigned to the metallated carbon atom, C(1)], and a singlet at δ 91.188 due to the *ipso* carbon atom of the C_5H_3 ring.

parallel as reflected in the tilt angles (Table 5). The conformation of these rings can be deduced from the value of the twist angle as defined by Palenik and Giordano.[14] The imines have an *anti* conformation derived from the *trans* arrangement of the phenyl and ferrocenyl substituents (Figs. 2 and 3); a *syn* conformation would involve important steric repulsions between the two substituents.

More interesting is the crystal structure of complex **3g**,

Table 5 Selected bond lengths (Å) and angles (°) for [Fe(η^5-C_5H_5)(η^5-$C_5H_4CR{=}NPh$)] (R = Me **1a** or H **1i**).[a] Estimated standard deviations (e.s.d.s) are given in parentheses[b]

Compound	**1a**	**1i**
N–C(11)	1.269(5)	1.25(3)
N–C(12)	1.413(10)	1.35(4)
C(6)–C(10)	1.426(6)	1.489(8)
C(9)–C(10)	1.433(6)	1.45(6)
C(10)–C(11)	1.469(5)	1.460(8)
C(12)–C(13)	1.39(1)	1.462(5)
C(12)–C(17)	1.379(7)	1.42(3)
C(11)–C(18)	1.502(3)	—
C–C (C_5H_4 ring)	1.42(1)	1.44(5)
C–C (C_5H_5 ring)	1.37(5)	1.4(1)
Fe–C (average value)	2.03(2)	2.06(3)
C(9)–C(10)–C(11)	125(3)	128.8(6)
C(6)–C(10)–C(11)	127(1)	123(1)
C(10)–C(11)–N	119.0(7)	125(1)
N–C(12)–C(13)	120(2)	125.5(4)
N–C(12)–C(17)	120.4(3)	118(3)
C(11)–N–C(12)	121(1)	121.4(7)
Tilt angle[c]	1.56	1.66
Twist angle[d]	0.05	−9.32

[a] Average values for the two non-equivalent molecules. [b] The e.s.d.s were calculated according to the expression e.s.d. = $\{[n(\Sigma x^2) - (\Sigma x)^2]/[n(n-1)]\}^{\frac{1}{2}}$, where x represents the bond length or angle. [c] Angle between the planes defined by the two pentagonal rings of the ferrocenyl moiety. [d] For the definition of this angle see ref. 14.

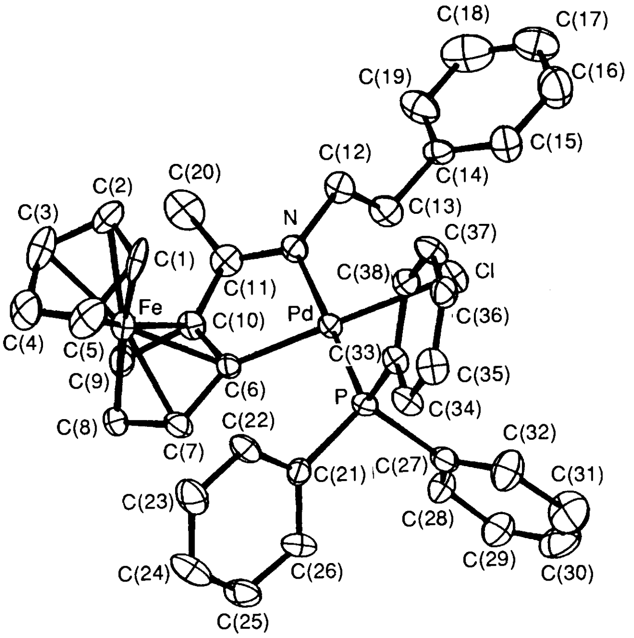


Fig. 4 Molecular structure and atom numbering scheme for [Pd{η^5-C_5H_5)Fe(η^5-$C_5H_3CMe{=}NCH_2CH_2Ph$)}Cl(PPh_3)]·CH_2Cl_2 **3g**

Table 6 Selected bond lengths (Å) and angles (°) for [Pd{(η^5-C_5H_5)Fe(η-$C_5H_3CMe{=}NCH_2CH_2Ph$)}Cl(PPh_3)]·CH_2Cl_2 **3g**, with e.s.d.s in parentheses

Cl–Pd	2.385(2)	P–Pd	2.247(2)
N–Pd	2.130(6)	C(6)–Pd	1.984(6)
C(1)–Fe	2.041(11)	C(2)–Fe	2.046(9)
C(3)–Fe	2.038(10)	C(4)–Fe	2.057(11)
C(5)–Fe	2.062(12)	C(6)–Fe	2.077(7)
C(7)–Fe	2.042(7)	C(8)–Fe	2.032(8)
C(9)–Fe	2.021(9)	C(10)–Fe	2.012(8)
C(2)–C(1)	1.397(17)	C(5)–C(1)	1.416(15)
C(3)–C(2)	1.384(14)	C(4)–C(3)	1.386(17)
C(5)–C(4)	1.462(17)	C(7)–C(6)	1.436(10)
C(10)–C(6)	1.428(11)	C(8)–C(7)	1.430(10)
C(9)–C(8)	1.393(14)	C(10)–C(9)	1.435(9)
C(11)–C(10)	1.418(11)	C(11)–N	1.305(9)
C(20)–C(11)	1.510(13)	C(12)–N	1.458(10)
P–Pd–Cl	88.5(1)	N–Pd–Cl	92.4(2)
N–Pd–P	177.8(2)	C(6)–Pd–Cl	170.1(2)
C(6)–Pd–P	98.5(2)	C(6)–Pd–N	80.8(3)
C(3)–C(2)–C(1)	107.3(10)	C(4)–C(3)–C(2)	111.0(10)
C(5)–C(4)–C(3)	106.3(9)	C(4)–C(5)–C(1)	105.9(10)
C(5)–C(1)–C(2)	109.4(9)	C(8)–C(7)–C(6)	107.8(7)
C(9)–C(8)–C(7)	109.9(6)	C(10)–C(9)–C(8)	106.3(7)
C(6)–C(10)–C(9)	105.7(6)	C(10)–C(6)–C(7)	105.8(6)
C(10)–C(11)–N	114.7(7)	C(11)–C(10)–C(6)	119.3(6)
C(11)–C(10)–C(9)	130.7(8)	C(11)–N–Pd	113.6(5)
C(12)–N–C(11)	121.9(7)	C(12)–N–C(11)	121.9(7)
C(13)–C(12)–N	110.7(6)	C(20)–C(11)–N	123.9(7)
C(20)–C(11)–C(10)	121.4(7)	C(21)–P–Pd	120.1(2)
C(27)–P–Pd	115.0(3)	C(33)–P–Pd	108.0(3)
C(33)–P–Pd	108.0(3)		

which consists of discrete molecules of [Pd{(η^5-C_5H_5)Fe(η^5-$C_5H_3CMe{=}NCH_2CH_2Ph$)}Cl(PPh_3)] (Fig. 4), packed by van der Waals forces and a molecule of CH_2Cl_2 as solvate. A selection of the most relevant bond lengths and angles is presented in Table 6.

The palladium atom is in a slightly distorted square-planar environment co-ordinated to a chlorine, the phosphorus of the PPh_3 ligand, the iminic nitrogen and the C(6) atom of the ferrocenyl group (Fig. 4). Except for the Pd–N bond length (Table 6), which is clearly larger than the calculated single bond [Pd: 1.31 Å and N(sp^2) 0.7 Å], the remaining Pd–ligand bond lengths are similar to those found in other five-membered cyclopalladated compounds containing organic imines. Bond angles between adjacent atoms in the co-ordination sphere of the palladium vary from 80.8(3)° [C(6)–Pd–N] to 98.5(2)° [C(6)–Pd–P] (Table 6). The palladium atom deviates from the plane defined by the four atoms linked to it by −0.047 Å towards the iron centre.*

The metallacycle is formed by the palladium atom, the nitrogen and carbon atoms involved in the iminic bond and two carbons [C(6),C(10)] of the ferrocenyl moiety, thus confirming the formation of *endo* five-membered metallacycles containing σ Pd–C(sp^2) (ferrocene) bonds. The palladocycle is practically planar,† but the bicyclic system formed by this ring and the C(6)–C(10) ring is slightly bent, as deduced from the angle formed by their planes of 9.27°.

The C=N bond in **3g** is clearly longer [1.305(9) Å] than that reported for ferrocenylimines derived from formyl- and acetylferrocene {**1i** [1.25(3) Å] and **1a** [1.269(5) Å], Table 5}. This lengthening of the C=N bond upon cyclopalladation is consistent with the decrease of the ν(C=N) frequency observed in the infrared spectra. The carbon atom of the methyl group is out of the plane defined by the metallated ring of the ferrocenyl moiety. The magnitude of the displacement is 0.256 Å towards the iron atom in the same direction as described above for **1a**.

The Fe–C(ring) bond distances vary from 2.012(7) Å [for C(9) and C(10)] to 2.077(7) Å [for C(6)]; these atoms are those shared by the metallacycle and the C(6)–C(10) ring. This

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* The least-squares equation of the plane defined by Cl, P, N and C(6) is $0.2249x + 0.8535y + -0.4701z = -1.7821$. The deviations of the plane are as follows: Cl, +0.077, P +0.079, N −0.094 and C(6) +0.096 Å.

† The equation of the plane defined by the five atoms involved in the metallacycle is $0.1449x + 0.8401y + -0.5228z = -2.6794$. The deviations from this plane are +0.008, +0.010, −0.026, +0.039 and −0.030 Å for Pd, N, C(6), C(10) and C(11) respectively.

type of distortion was also observed in the crystal structure of $[Pd\{\eta^5-C_5H_5)Fe[(\eta^5-C_5H_3CH=N(CH_2)_2Ph]\}Cl(PEt_3)]$ **4p**.[7]

The average C–C bond lengths in the pentagonal rings of the ferrocenyl moiety are also consistent with the values reported for other ferrocene derivatives.[15] The two pentagonal rings C(1)–C(5) and C(6)–C(10) are planar,* nearly parallel (tilt angle = 0.86°), and their conformation is eclipsed as reflected in the angle of twist (average value 1.2°).

In order to clarify the influences of (*a*) the substituent (H *versus* Me) at the imine carbon atom and (*b*) the nature of the N-donor atom (sp^2 or sp^3) upon the metallacycle, we have compared bond lengths, angles and other outstanding structural parameters in **3g**, with those reported for the cyclopalladated complex **4p**[7] and $[Pd\{(\eta^5-C_5H_5)Fe[\eta^5-C_5H_3CH(Me)NMe_2]\}(acac)]$ **5** (acac = acetylacetonate) in which the nitrogen has an sp^3 hybridization.[16]

Except for the C(11)–C(10) bond length which is clearly shorter in **3g** [1.418(11) Å] than in **4p** [1.467(9) Å], the remaining bond angles of the metallacycle do not differ significantly from those obtained for **4p**, in which the ferrocenylimine has a smaller substituent (hydrogen) at the iminic carbon atom. More influenced by the substituent are bond angles involving the C(11) atom, that is to say: C(6)–C(10)–C(11), C(10)–C(11)–N and C(9)–C(10)–C(11).

As a first approach, the strain involved in the fusion of the two pentagonal rings, the palladocycle and the C_5H_3 moiety can be evaluated by comparing the angles C(6)–C(10)–C(11) and C(10)–C(11)–N in **3g** [114.7(7)°] and **4p** [117.07(7)°] and in the related ferrocenylimines {**1a** [119.0(7)°], **1i** [125(1)°], Table 5}. In both cases the formation of the palladocycle involves the closing of these angles, but the variations are clearly smaller in complexes with methyl substituents (*ca.* 4.3 *versus* 8.0°) at the iminic carbon atom. This fact may be responsible for the different ease with which the two types of ferrocenylimines $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CR=NR')]$ (R = Me or H) undergo cyclopalladation, short reaction periods only being observed for R = Me, for which the formation of the metallacycle involves a smaller variation of the angles around the iminic carbon. We can therefore conclude that the fusion of the two rings involves a lower strain in cyclopalladated compounds containing ferrocenylimines with R = Me than in their analogues with R = H.

Final Remarks.—The studies described in this work have allowed us not only to establish general pathways for the preparation of $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CR=NR')]$ compounds, but also to elucidate the influences of the nature of the substituents R (H or Me) and R′ upon their spectroscopic and structural properties. Furthermore, cyclopalladation reactions of these Schiff bases reveal that, although metallation of a phenyl ring would yield bicyclic systems derived from the fusion of a five- or a six-membered *exo* type metallacycle (depending on the R′ substituent) and a phenyl ring, the metallation occurs exclusively at the ferrocenyl moiety. In all cases metallacycles containing a σ Pd–C(sp^2) (ferrocene) bond and the functional group C=N (*endo*-type structures) are formed, in good agreement with the results obtained for *N*-benzylideneamines which have shown a strong tendency to form endocyclic derivatives.[3] However, our results are in contrast with those obtained in cyclopalladation of phenylhydrazones,[4,5] for which the replacement of an H by a Me at the imine carbon atom is important enough to modify the structure of the palladocycle.

On the other hand, for ligands **1a**–**1n**, the formation of the metallacycle involves the conversion of a σ C–H (ferrocene) bond into a σ Pd–C(sp^2) (ferrocene) bond; the different ease of the ferrocenylimines with R = Me and H to undergo cyclopalladation may be interpreted in terms of the variation of the bond angle formed by the C=N group and the *ipso* carbon atom of the ferrocene moiety [C(10)–C(11)–N] in the cyclopalladation process. For substrates **1a**–**1h** with R = Me the formation of the metallacycle is achieved faster and involves a smaller variation of the angle C(10)–C(11)–N {of *ca.* 4.3°} than for the Schiff bases derived from ferrocenecarbaldehyde (*ca.* 8.0°). As mentioned above different factors such as the number of members of the metallacycle, the nature of the carbon and nitrogen atoms involved, the type of the structure (endo- or exo-cyclic), the electronic and/or the steric effects of the substituent in the rings susceptible to undergo cyclometallation, the strain involved in the fusion of the two rings (the metallacycle and the C_5H_5 or phenyl rings) play important roles in the cyclopalladation process. For the ferrocenylimines under study, the higher ease of ferrocene derivatives to undergo electrophilic attack relative to the phenyl group and/or the so-called *endo* effect seem to be the driving force for the formation of these palladocycles. Cyclopalladation reactions of ferrocenylimines derived from benzoylferrocene need to be studied in order to clarify which one of the two effects described above has more importance. These systems may yield two different types of *endo* five-membered metallacycles depending whether the metallation occurs at the ferrocenyl moiety or at the phenyl ring on the iminic carbon atom.

Experimental

Elemental analyses (C, H and N) were carried out at the Instituto de Química Bio-Orgánica (C.S.I.C., Barcelona). Infrared spectra were obtained with a Nicolet 520-FTIR spectrophotometer using KBr pellets or NaCl discs for solid and liquid samples respectively. Proton and $^{13}C-\{^1H\}$ NMR spectra were recorded at *ca.* 20 °C on a GEMINI-200 MHz spectrophotometer, using $CDCl_3$ (99.8%) and $SiMe_4$ as solvent and internal standard, respectively. $^{31}P-\{^1H\}$ NMR spectra were recorded with a Bruker WP80-SY spectrophotometer (32.8 MHz), using $CHCl_3$ as solvent and $P(OMe)_3$ as standard. Decomposition points of the complexes were determined with a Buchi 510 melting-point instrument.

Materials and Syntheses.—Acetylferrocene, ferrocenecarbaldehyde and the amines were obtained from standard sources and used as received. All the solvents, except benzene, were dried and distilled before use.

Preparations.—$[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CMe=NR')]$ (R′ = Ph **1a**, C_6H_4Me-2 **1b** *or* C_6H_4Me-4 **1c**). Acetylferrocene (1.14 g, 5.0 mmol), 5 Å molecular sieve (2.0 g) and the stoichiometric amount of the corresponding amine were suspended in dried diethyl ether (5.0 cm^3), and the reaction mixtures were stirred at 20 °C for 5-6 d. In order to control the progress of the condensation reaction the infrared spectra of the solutions were recorded. Daily addition of small quantities of the amines (*ca.* 0.5 cm^3) and molecular sieves (5 Å) was needed to force the displacement of the equilibria. This procedure was repeated for 5–6 d until the infrared spectra of the samples did not exhibit the band due to the asymmetrical stretching of the C=O group of the acetylferrocene [ν(C=O) 1661 cm^{-1}]. Then, the molecular sieves (5 Å) were removed by vacuum filtration and washed with ether until the washings became colourless. The orange-red solutions were concentrated to dryness on a rotary evaporator, and the oil formed was treated with *n*-hexane (*ca.* 30 cm^3). The solids formed were filtered off and air-dried (yields: 70, 66 and 83% for **1a**–**1c**, respectively). Compound **1a** [Found (Calc.) for $C_{18}H_{17}FeN$: C, 71.05 (71.30); H, 5.9 (5.65); N, 4.3 (4.60)%]: IR(KBr) pellet) $\tilde{\nu}_{max}$(C=N) 1620 cm^{-1}, m.p. 94–96 °C (decomp.). Compound **1b** [Found (Calc.) for $C_{19}H_{19}FeN$: C, 71.95 (71.95); H, 6.05 (6.05); N, 4.35 (4.40)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1630

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* The least-squares equation of the plane defined by the atoms C(6), C(7), C(8), C(9) and C(10) is $0.0690x + 0.8568y - 0.05110z = -3.0708$. Maximum deviations were found for C(8) (−0.011 Å) and C(7) (−0.013 Å). The equation of the plane defined by the atoms C(1)–C(5) is $0.0723x + 0.8640y - 0.4983z = -6.2197$. Maximum deviations are found for C(1) (0.007 Å) and C(5) (−0.007 Å).

cm^{-1}, m.p. 102–106 °C (decomp.). Compound **1c** [Found (Calc.) for $C_{19}H_{19}FeN$: C, 71.8 (71.95); H, 6.1 (6.05); N, 4.4 (4.40)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1625 cm^{-1}, m.p. 118–121 °C (decomp.).

$[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMe{=}NR')]$, ($R' = CH_2Ph$ **1d**, $CH_2C_6H_4Me\text{-}2$ **1e**, $CH_2C_6H_4Cl\text{-}2$ **1f**, CH_2CH_2Ph **1g** *or* $C_{10}H_7$ **1h**). The preparation of these imines was carried out using a similar procedure to that described above for **1a**–**1c**. The condensation reactions were carried out using benzene as solvent (15 cm^3) instead of dried ether, and in all cases the initial suspensions were refluxed. Except for these details the procedure was identical to that described in the previous paragraph, compound **1g** was isolated as an oily material (yields: 68, 72, 65, 48 and 61% for **1d**–**1h**, respectively). Compound **1d** [Found (Calc.) for $C_{19}H_{19}FeN$: C, 71.7 (71.95); H, 6.15 (6.05); N, 4.4 (4.40)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1620 cm^{-1}, m.p. 48–52 °C (decomp.). Compound **1e** [Found (Calc.) for $C_{20}H_{21}FeN$: C, 72.5 (72.55); H, 6.55 (6.40); N, 4.3 (4.25)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1620 cm^{-1}, m.p. 56–58 °C (decomp.). Compound **1f** [Found (Calc.) for $C_{19}H_{18}ClFeN$: C, 64.8 (64.9); H, 5.3 (5.15); N, 3.8 (4.00)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1621 cm^{-1}, m.p. 58–60 °C (decomp.). Compound **1g** [Found (Calc.) for $C_{20}H_{21}FeN$: C, 72.5 (72.50); H, 6.2 (6.40); N, 4.7 (4.25)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1620 cm^{-1}. Compound **1h** [Found (Calc.) for $C_{22}H_{19}FeN$: C, 74.6 (74.80); H, 5.4 (5.40); N, 3.9 (3.95)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1616 cm^{-1}, m.p. 160–165 °C (decomp.).

$[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NR')]$ ($R' = Ph$ **1i**, $C_6H_4Me\text{-}2$ **1j**, $C_6H_4Me\text{-}4$ **1k**, $CH_2C_6H_4Me\text{-}2$ **1l**, $CH_2C_6H_4Cl\text{-}2$ **1m** *or* $C_{10}H_7$ **1n**). Ferrocenecarbaldehyde (1.0 g, 4.57 mmol) was dissolved in benzene (30 cm^3) at 20 °C. Once the starting material had dissolved completely, the corresponding amine (4.67 mmol) was added, and the resulting mixture was connected to a condenser equipped with a Dean–Stark condenser (10 cm^3). The red solution was then refluxed on an ethylene glycol bath until 8 cm^3 had condensed on the Dean–Stark. The hot solution was carefully filtered 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 produced the precipitation of the imines. The solids were filtered off and air-dried. Recrystallization of the imines was carried out by dissolving 0.6 g in the minimum amount of CH_2Cl_2. The solution was filtered and *n*-hexane (*ca.* 20 cm^3) was added to the filtrate. Slow evaporation of the solvents at *ca.* 4 °C produced microcrystals which were collected and air-dried (yields: 88, 79, 87, 79, 73 and 84% for **1i**–**1n**, respectively). Compound **1i** [Found (Calc.) for $C_{17}H_{15}FeN$: C, 70.2 (70.60); H, 5.2 (5.20); N, 4.8 (4.85)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1612 cm^{-1}, m.p. 116–119 °C (decomp.). Compound **1j** [Found (Calc.) for $C_{18}H_{17}FeN$: C, 71.35 (71.30); H, 5.7 (5.60); N, 4.7 (4.60)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1618 cm^{-1}, m.p. 122–126 °C (decomp.). Compound **1k** [Found (Calc.) for $C_{18}H_{17}FeN$: C, 71.3 (71.30); H, 5.55 (5.60); N, 4.6 (4.60)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1615 cm^{-1}, m.p. 130–132 °C (decomp.). Compound **1l** [Found (Calc.) for $C_{19}H_{19}FeN$: C, 71.8 (71.95); H, 6.15 (6.05); N, 4.6 (4.40)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1620 cm^{-1}, m.p. 83–86 °C (decomp.). Compound **1m** [Found (Calc.) for $C_{18}H_{16}ClFeN$: C, 64.0 (64.05); H, 4.7 (4.75); N, 3.9 (4.15)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1622 cm^{-1}, m.p. 79–83 °C (decomp.). Compound **1n** [Found (Calc.) for $C_{21}H_{18}FeN$: C, 74.3 (74.60); H, 5.05 (5.30); N, 4.15 (3.80)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1609 cm^{-1}, m.p. 182–186 °C (decomp.).

$[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CR{=}NR')](\mu\text{-}Cl)\}_2]$ ($R = Me$, $R' = Ph$ **2a**, $C_6H_4Me\text{-}2$ **2b**, $C_6H_4Me\text{-}4$ **2c**, CH_2Ph **2d**, $CH_2C_6H_4Me\text{-}2$ **2e**, $CH_2C_6H_4Cl\text{-}2$ **2f**, CH_2CH_2Ph **2g** *or* $C_{10}H_7$ **2h**; $R = H$, $R' = Ph$ **2i**, $C_6H_4Me\text{-}2$ **2j**, $C_6H_4Me\text{-}4$ **2k**, $CH_2C_6H_4Cl\text{-}2$ **2m** *or* $C_{10}H_7$ **2n**). The reagents $Na_2[PdCl_4]$ (0.294 g, 1 mmol), $Na(O_2CMe){\cdot}3H_2O$ (0.130 g, 1 mmol) and a stoichiometric amount (1 mmol) of the corresponding imine (freshly prepared) were suspended in methanol (30 cm^3). The reaction mixture was stirred in an open vessel at *ca.* 20 °C for 3 h **2a**–**2h** or 24 h (**2i**–**2n**) to accomplish the formation of the metallacycle. The violet-red solid formed was filtered off, washed with methanol and air-dried. The purification of the dimeric complexes was carried out by dissolving the crude material in benzene (50 cm^3), then the undissolved brown-black products were removed by filtration and discarded. The deep red solution was concentrated to dryness on a rotary evaporator. Addition of *n*-hexane to the oil formed, followed by vigorous stirring produced the precipitation of the dimeric compounds, which were then filtered out and air-dried. Compound **2m** was purified by SiO_2 column chromatography using $CHCl_3$ as eluent (yields: 62, 55, 65, 70, 75, 72, 51, 48, 52, 61, 56, 45 and 39% respectively). Compound **2a** [Found (Calc.) for $C_{36}H_{32}Cl_2Fe_2N_2Pd_2$: C, 48.7 (48.65); H, 3.7 (3.60); N, 3.5 (3.15)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1600 cm^{-1}, m.p. 178–180 °C (decomp.). Compound **2b** [Found (Calc.) for $C_{38}H_{36}Cl_2Fe_2N_2Pd_2$: C, 49.4 (49.75); H, 3.8 (3.90); N, 2.9 (3.05)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1570 cm^{-1}, m.p. 181–186 °C (decomp.). Compound **2c** [Found (Calc.) for $C_{38}H_{36}Cl_2Fe_2N_2Pd_2$: C, 49.6 (49.75); H, 4.0 (3.90); N, 3.0 (3.05)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1535 cm^{-1}, m.p. 190–200 °C (decomp.). Compound **2d** [Found (Calc.) for $C_{38}H_{36}Cl_2Fe_2N_2Pd_2$: C, 49.7 (49.75); H, 4.05 (3.90); N, 3.1 (3.05)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1570 cm^{-1}, m.p. 218–224 °C (decomp.). Compound **2e** [Found (Calc.) for $C_{40}H_{40}Cl_2Fe_2N_2Pd_2$: C, 49.5 (50.85); H, 4.15 (4.25); N, 3.0 (2.95)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1570 cm^{-1}, m.p. 227–229 (decomp.). Compound **2f** [Found (Calc.) for $C_{38}H_{34}Cl_4Fe_2N_2Pd_2$: C, 45.9 (46.30); H, 3.5 (3.45); N, 2.8 (2.85)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1560 cm^{-1}, m.p. 198–207 °C (decomp.). Compound **2g** [Found (Calc.) for $C_{40}H_{40}Cl_2Fe_2N_2Pd_2$: C, 51.0 (50.85); H, 4.6 (4.25); N, 2.9 (2.95)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1575 cm^{-1}, m.p. 198–207 °C (decomp.). Compound **2h** [Found (Calc.) for $C_{38}H_{36}Cl_2Fe_2N_2Pd_2$: C, 55.3 (55.40); H, 3.6 (3.80); N, 2.8 (2.95)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1557 cm^{-1}, m.p. 227–231 °C (decomp.). Compound **2i** [Found (Calc.) for $C_{34}H_{38}Cl_2Fe_2N_2Pd_2$ C, 47.6 (47.40); H, 3.5 (3.30); N, 3.1 (3.25)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1576 cm^{-1}, m.p. 182–184 °C (decomp.). Compound **2j** [Found (Calc.) for $C_{36}H_{32}Cl_2Fe_2N_2Pd_2$: C, 48.8 (48.60); H, 3.7 (3.65); N, 3.2 (3.15)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1572 cm^{-1}, m.p. 187–190 °C (decomp.). Compound **2k** [Found (Calc.) for $C_{36}H_{32}Cl_2Fe_2N_2Pd_2$: C, 48.5 (48.60); H, 3.75 (3.65); N, 3.1 (3.15)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1580 cm^{-1}, m.p. 195–198 °C (decomp.). Compound **2m** [Found (Calc.) for $C_{36}H_{30}Cl_4Fe_2N_2Pd_2$: C, 44.9 (44.15); H, 3.3 (3.15); N, 2.9 (2.90)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1578 cm^{-1}, m.p. 221–225 °C (decomp.). Compound **2n** [Found (Calc.) for $C_{42}H_{30}Cl_2Fe_2N_2Pd_2$: C, 52.9 (52.60); H, 3.3 (3.15); N, 3.1 (2.90)%]: IR(KBr pellet) $\tilde{\nu}_{max}(C{=}N)$ 1575 cm^{-1}, m.p. 230–235 °C (decomp.).

$[\{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2C_6H_4Me\text{-}2)](\mu\text{-}Cl)\}_2]$ **2l**. $Na_2[PdCl_4]$ (0.51 g, 1.7 mmol) and $Na(O_2CMe){\cdot}3H_2O$ (0.23 g, 1.7 mmol) were suspended in methanol (15 cm^3) and stirred at room temperature. Once the starting materials had dissolved $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3CH{=}NCH_2C_6H_4Me\text{-}2)]$ **1l** (0.52 g, 1.7 mmol) was added. The resulting suspension was stirred at *ca.* 20 °C for a further 24 h. During this period the suspension changed gradually from brown to deep red. The solid formed was collected by vacuum filtration using a no. 4 funnel, washed with three portions (10 cm^3) of water and air-dried (yield: 78%) [Found (Calc.) for $C_{36}H_{32}Cl_2Fe_2N_2Pd_2$: C, 49.8 (48.40); H, 4.0 (4.05); N, 3.15 (3.15)%]: IR (KBr pellet) $\tilde{\nu}_{max}(C{=}H)$ 1582 cm^{-1}, m.p. 186–190 °C (decomp.).

$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CMe{=}NR')\}Cl(PPh_3)]$ ($R' = Ph$ **3a**, $C_6H_4Me\text{-}2$ **3b**, $C_6H_4Me\text{-}4$ **3c**, CH_2Ph **3d**, $CH_2C_6H_4Me\text{-}2$ **3e**, $CH_2C_6H_4Cl\text{-}2$ **3f**, CH_2CH_2Ph **3g** *or* $C_{10}H_7$ **3h**). Triphenylphosphine (0.130 g, 0.50 mmol) was added to a benzene suspension (9 cm^3) of the corresponding dimeric compound **2a**–**2h**. The resulting mixture was stirred at *ca.* 20 °C

Table 7 Crystallographic data and details of refinements for compounds **1a**, **1i** and **3g**

Formula	$C_{18}H_{17}FeN$	$C_{17}H_{15}FeN$	$C_{38}H_{35}ClFeNPPd{\cdot}CH_2Cl_2$
M	303.19	289.16	830.32
Crystal size/mm	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	*Cc*	$P2_1/n$
a/Å	10.152(3)	5.876(3)	20.342(2)
b/Å	12.169(3)	37.298(9)	9.133(1)
c/Å	12.239(3)	12.640(4)	19.714(2)
α/°	90.45(2)	90.00	90.00
β/°	100.56(2)	103.26(4)	97.17(1)
γ/°	102.72(2)	90.00	90.00
U/Å^3	1448(1)	2696(2)	3634(1)
D_c/g cm^{-3}	1.390	1.424	1.499
Z	4	8	4
F(000)	632.0	1200.0	1668.0
λ(Mo-Kα)/Å	0.710 69	0.710 69	0.710 69
μ(Mo-Kα)/cm^{-1}	10.57	11.31	11.86
No. of measured reflections	5247	3108	3547
No. of reflections with $I \geqslant 2.5\sigma(I)$	4257	2457	2812
Range of θ/°	2–25	8–12	2–25
Method	Patterson	MULTAN and DIRDIF	Patterson
k in weighting scheme	0.0	0.0	0.0007
No. of hydrogens	All computed	All computed	23
R	0.066	0.044	0.039
R'	0.076	0.055	0.040
No. of refined parameters	363	341	507
Maximum shift/e.s.d.	+0.1	+0.1	+0.1
Maximum and minimum peaks in final difference map/e Å^{-3}	±0.3	±0.4	±0.3

Table 8 Final atomic coordinates (× 10^5 for Fe, × 10^4 for other atoms) for complex **1a**

	Molecule A			B		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe	17 595(6)	37 606(4)	20 698(4)	−47 626(5)	−17 099(4)	24 543(4)
N	1 138(3)	611(3)	1 882(3)	−3 141(3)	1 446(3)	3 370(3)
C(1)	814(7)	4 381(6)	3 170(6)	−5 463(15)	−1 097(7)	985(5)
C(2)	1 978(6)	5 178(4)	3 065(4)	−4 330(7)	−1 471(8)	913(5)
C(3)	3 124(6)	4 710(6)	3 322(5)	−4 681(10)	−2 675(7)	1 132(5)
C(4)	2 706(11)	3 626(7)	3 662(5)	−5 974(10)	−2 860(8)	1 297(5)
C(5)	1 257(9)	3 406(6)	3 584(5)	−6 376(12)	−1 915(18)	1 233(6)
C(6)	305(5)	3 228(4)	695(4)	−3 095(4)	−939(3)	3 620(3)
C(7)	1 322(6)	4 142(4)	418(4)	−3 484(5)	−2 083(3)	3 848(3)
C(8)	2 597(5)	3 837(4)	670(4)	−4 880(5)	−2 318(3)	4 020(3)
C(9)	2 410(4)	2 720(3)	1 076(3)	−5 330(5)	−1 290(4)	3 878(3)
C(10)	966(4)	2 343(3)	1 071(3)	−4 231(4)	−431(3)	3 631(3)
C(11)	373(4)	1 274(3)	1 527(3)	−4 627(4)	750(3)	3 412(3)
C(12)	665(4)	−382(3)	2 410(4)	−3 129(4)	2 587(3)	3 123(3)
C(13)	87(5)	−1 414(4)	1 813(5)	−2 735(4)	3 400(3)	3 986(3)
C(14)	−237(6)	−2 380(4)	2 340(4)	−2 666(5)	4 556(3)	3 724(4)
C(15)	41(5)	−2 390(4)	3 508(5)	−3 036(5)	4 834(3)	2 647(4)
C(16)	587(4)	−1 390(4)	4 098(4)	−3 390(5)	4 008(4)	1 790(5)
C(17)	920(4)	−396(4)	3 560(4)	−3 449(4)	2 884(3)	2 042(3)
C(18)	−1 150(5)	1 041(5)	1 501(6)	−5 648(4)	1 043(4)	3 217(4)

for 3 h. The solution was filtered off and the filtrate was concentrated to dryness on a rotary evaporator. The oil formed was quenched by adding 5 cm^3 of *n*-hexane, and the solid formed was collected by filtration and air-dried. All these monomeric cyclopalladated compounds were recrystallized from CH_2Cl_2-*n*-hexane (1 : 1) (yields: 74, 68, 79, 75, 66, 63, 77 and 56% for **3a**–**3h**). Compound **3a** [Found (Calc.) for $C_{36}H_{31}ClFeNPPd$: C, 61.1 (61.15); H, 4.6 (4.40); N, 2.0 (2.00)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1575 cm^{-1}, ^{31}P NMR δ 37.87, m.p. 178–184 °C (decomp.). Compound **3b** [Found (Calc.) for $C_{37}H_{33}ClFeNPPd$ C, 61.6 (61.65); H, 4.7 (4.60); N, 1.9 (1.95%): IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1580 cm^{-1}, ^{31}P NMR δ 37.53, m.p. 192–200 °C (decomp.). Compound **3c** [Found (Calc.) for $C_{37}H_{33}ClFeNPPd$: C, 61.4 (61.65); H, 4.7 (4.60); N, 1.8 (1.95)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1570 cm^{-1}, ^{31}P NMR δ 37.64, m.p. 200–205 °C (decomp.). Compound **3d** [Found (Calc.) for $C_{37}H_{33}ClFeNPPd$: C, 61.85 (61.65); H, 4.7 (4.60); N, 1.85 (1.95)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1585 cm^{-1}, ^{31}P NMR δ 37.48, m.p. 180–186 °C (decomp.). Compound **3e** [Found (Calc.) for $C_{38}H_{35}ClFeNPPd$: C, 62.05 (62.15); H, 4.9 (4.80); N, 1.8 (1.90)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1580 cm^{-1}, ^{31}P NMR δ 37.28, m.p. 168–172 °C (decomp.). Compound **3f** [Found (Calc.) for $C_{37}H_{32}Cl_2FeNPPd$: C, 58.6 (58.65); H, 4.3 (4.25); N, 1.7 (1.85)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1582 cm^{-1}, ^{31}P NMR δ 37.40, m.p. 138–145 °C (decomp.). Compound **3g** [Found (Calc.) for $C_{38}H_{35}ClFeNPPd{\cdot}CH_2Cl_2$: C, 57.0 (57.15); H, 4.5 (4.55); N, 1.6 (1.75)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1580 cm^{-1}, ^{31}P NMR δ 37.15, m.p. 194–196 °C (decomp.). Compound

3h [Found (Calc.) for $C_{40}H_{30}ClFeNPPd$: C, 58.4 (58.50); H, 4.2 (4.20); N, 1.6 (1.65)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1565 cm^{-1}, ^{31}P NMR δ 37.48, m.p. 198–201 °C (decomp.).

Table 9 Final atomic coordinates (×10^5 for Fe, ×10^4 for other atoms) for complex **1i**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(A)	0	2 084(2)	0
Fe(B)	95 121(18)	22 924(2)	90 501(4)
N(A)	3 524(13)	829(1)	−1 579(4)
N(B)	14 570(9)	1 678(1)	10 680(4)
C(1A)	−2 426(9)	−191(1)	−6(5)
C(2A)	−93(16)	−331(2)	192(8)
C(3A)	747(13)	−261(2)	−731(7)
C(4A)	−1 120(13)	−40(2)	−1 447(5)
C(5A)	−2 875(19)	−14(3)	−987(10)
C(6A)	3 158(9)	488(1)	538(5)
C(7A)	2 037(12)	388(1)	1 465(4)
C(8A)	−65(10)	553(2)	1 292(6)
C(9A)	−639(12)	734(2)	252(6)
C(10A)	1 303(12)	693(1)	−217(5)
C(11A)	1 684(10)	857(1)	−1 216(5)
C(12A)	3 694(11)	995(2)	−2 491(7)
C(13A)	2 267(12)	1 299(2)	−2 994(6)
C(14A)	2 571(13)	1 451(2)	−3 963(6)
C(15A)	4 450(15)	1 320(2)	−4 420(4)
C(16A)	5 836(12)	1 016(2)	−3 977(7)
C(17A)	5 539(13)	875(2)	−2 988(8)
C(1B)	7 577(10)	2 484(1)	10 109(4)
C(2B)	6 988(27)	2 675(2)	9 086(13)
C(3B)	9 363(17)	2 849(2)	8 964(7)
C(4B)	10 986(14)	2 765(2)	9 829(6)
C(5B)	10 011(12)	2 510(2)	10 639(7)
C(6B)	12 135(8)	2 018(1)	8 576(5)
C(7B)	10 195(9)	2 097(1)	7 667(4)
C(8B)	8 133(10)	1 948(1)	7 814(4)
C(9B)	8 562(10)	1 766(2)	8 828(6)
C(10B)	11 108(13)	1 796(1)	9 333(5)
C(11B)	12 427(11)	1 666(2)	10 379(5)
C(12B)	15 738(12)	1 524(2)	11 629(4)
C(13B)	14 925(11)	1 215(2)	12 147(5)
C(14B)	16 161(12)	1 062(2)	13 048(6)
C(15B)	18 395(15)	1 187(2)	13 555(6)
C(16B)	19 355(13)	1 477(2)	13 076(8)
C(17B)	17 966(15)	1 647(2)	12 158(8)

[Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CH=NR′)}Cl(PPh_3)] (R′ = Ph **3i**, C_6H_4Me-2 **3j**, C_6H_4Me-4 **3k**, $CH_2C_6H_4$Me-2 **3l**, $CH_2C_6H_4$Cl-2 **3m** *or* $C_{10}H_7$ **3n**). Triphenylphosphine (0.32 g, 1.2 mmol) was added to an acetone suspension (10 cm^3) of **2i**–**2n** (0.3 mmol) and the resulting mixture was refluxed for 30 min. After cooling to room temperature, the solution was filtered and the filtrate was concentrated to dryness on a rotary evaporator. Addition of diethyl ether to the residue resulted in precipitation of the solids (yields: 58, 62, 71, 62, 71 and 65% for **3i**–**3m**, respectively). Compound **3i** [Found (Calc.) for $C_{35}H_{29}ClFeNPPd$: C, 60.6 (60.70); H, 4.4 (2.20); N, 2.1 (2.00)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1598 cm^{-1}, ^{31}P NMR δ 37.35, m.p. 187–192 °C (decomp.). Compound **3j** [Found (Calc.) for $C_{36}H_{31}ClFeNPPd$: C, 61.2 (61.15); H, 4.4 (4.40); N, 2.0 (2.00)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1601 cm^{-1}, ^{31}P NMR δ 36.07, m.p. 181–186 °C (decomp.). Compound **3k** [Found (Calc.) for $C_{36}H_{31}ClFeNPPd$: C, 61.2 (61.15); H, 4.5 (4.40); N, 1.9 (2.00)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1600 cm^{-1}, ^{31}P NMR δ 37.55, m.p. 196–200 °C (decomp.). Compound **3l** [Found (Calc.) for $C_{37}H_{33}ClFeNPPd\cdot 0.5CH_2Cl_2$: C, 59.1 (59.00); H, 4.4 (4.25); N, 1.7 (1.75)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1605 cm^{-1}, ^{31}P NMR δ 37.29, m.p. 178–182 °C (decomp.). Compound **3m** [Found (Calc.) for $C_{36}H_{30}Cl_2FeNPPd$: C, 58.1 (58.35); H, 4.1 (4.10); N, 1.8 (2.00)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1599 cm^{-1}, ^{31}P NMR δ 37.62, m.p. 212–216 °C (decomp.). Compound **3n** [Found (Calc.) for $C_{37}H_{33}ClFeNPPd$: C, 61.3 (61.65); H, 4.6 (4.60); N, 1.85 (1.95)%]: IR(KBr pellet) $\tilde{\nu}_{max}$(C=N) 1600 cm^{-1}, ^{31}P NMR δ 37.36, m.p. 209–214 °C (decomp.).

Crystal Structure Determination and Refinement.—Prismatic crystals of compounds **1a**, **1i** and **3g** were selected and mounted on an Enraf-Nonius CAD-4 (**1a** and **1i**) or on a Philips PW-1100 (**3g**) diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections in the ranges given in Table 7, and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo-Kα radiation using the ω–2θ scan technique. Three reflections were measured every 2 h as orientation and intensity control, and no significant variation was observed in any of the cases. The number of collected reflections and the ranges are listed in Table 7. Lorentz–polarization corrections, but not for absorption were made.

The structures were solved by the methods given in Table

Table 10 Final atomic co-ordinates (×10^4) for complex **3g**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	2 223(1)	1 653(1)	4 740(1)
Fe	3 743(1)	−175(2)	5 539(1)
Cl	1 137(1)	1 894(3)	4 136(2)
P	1 875(1)	2 903(3)	5 610(2)
N	2 558(4)	397(9)	3 941(5)
C(1)	3 112(6)	−1 560(17)	5 943(10)
C(2)	3 411(7)	−2 294(13)	5 440(8)
C(3)	4 087(7)	−2 265(15)	5 645(10)
C(4)	4 235(7)	−1 544(17)	6 262(9)
C(5)	3 601(9)	−1 082(15)	6 468(8)
C(6)	3 180(4)	1 550(11)	5 091(6)
C(7)	3 664(5)	2 045(11)	5 628(6)
C(8)	4 303(4)	1 644(13)	5 463(7)
C(9)	4 237(5)	864(13)	4 855(7)
C(10)	3 542(5)	800(12)	4 619(6)
C(11)	3 193(6)	121(12)	4 036(6)
C(12)	2 132(5)	−144(12)	3 346(6)
C(13)	2 097(5)	948(14)	2 759(7)
C(14)	1 610(6)	530(12)	2 152(7)
C(15)	942(6)	818(14)	2 167(7)
C(16)	498(8)	381(19)	1 604(11)
C(17)	721(11)	−265(20)	1 056(11)
C(18)	1 387(12)	−553(18)	1 062(9)
C(19)	1 826(7)	−155(16)	1 612(9)
C(20)	3 541(6)	−872(15)	3 582(7)
C(21)	2 453(3)	3 335(8)	6 365(4)
C(22)	2 605(4)	2 264(10)	6 841(5)
C(23)	3 059(5)	2 520(12)	7 410(6)
C(24)	3 385(5)	3 869(13)	7 482(6)
C(25)	3 245(5)	4 917(11)	7 018(6)
C(26)	2 764(4)	4 689(9)	6 454(5)
C(27)	1 209(3)	2 046(8)	5 996(5)
C(28)	1 012(4)	2 573(9)	6 596(5)
C(29)	488(4)	1 931(10)	6 870(5)
C(30)	173(4)	765(10)	6 558(7)
C(31)	360(4)	207(10)	5 989(6)
C(32)	879(4)	807(9)	5 699(5)
C(33)	1 563(4)	4 686(8)	5 282(5)
C(34)	970(5)	5 242(11)	5 425(6)
C(35)	759(7)	6 632(14)	5 122(8)
C(36)	1 159(9)	7 344(12)	4 727(8)
C(37)	1 728(6)	6 782(11)	4 594(6)
C(38)	1 928(4)	5 442(9)	4 850(5)
C(39)	−609(8)	4 903(14)	6 723(9)
Cl(2)	110(9)	5 907(25)	7 138(16)
Cl(2′)	−59(12)	5 837(33)	7 328(21)
Cl(3)	−1 000(4)	3 565(8)	7 204(7)
Cl(3′)	−1 021(21)	4 279(44)	7 155(25)

7[17–20] and refined by full-matrix least-squares method with the SHELX 76 computer program.[18] The function minimized was $\Sigma w[|F_o| - |F_c|]^2$ where $w = \sigma^{-2}(F_o)$, $w = \sigma^2(F_o)$ and $[\sigma^2(F_o) + 0.0007|F_o|^2]^{-1}$ for **1a**, **1i** and **3g**, respectively; f, f' and f'' were obtained from ref. 21. The positions of 23 H atoms were located from a difference syntheses and those of 25 H were computed in the crystal structure of complex **3g**. All hydrogens were refined with an overall isotropic thermal parameter using a riding model for computed atoms. The final R and R' factors were calculated according to the expressions $R = (\Sigma||F_o| - k|F_c||)/(\Sigma|F_o|)$ and $R' = [(\Sigma w||F_o| - k|F_c||^2)/(\Sigma w|F_o|^2)]^{\frac{1}{2}}$, and their values are presented in Table 7, together with the number of refined parameters for each of the structures and the maximum and minimum peaks in the final difference synthesis. Atomic coordinates for **1a**, **1i** and **3g** are given in Tables 8–10.

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

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