Effects of the Nature of the Nitrogen Donor Atom (sp^2 *versus* sp^3) upon the Properties and Chemistry of Palladated Complexes with σ(Pd–C_{sp^2}, ferrocene) Bonds†

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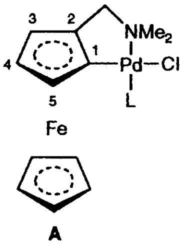
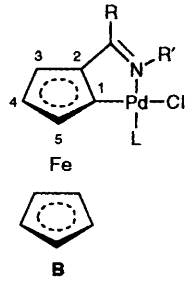
The NMR and Mössbauer spectra and electrochemistry of the N-donor ferrocenyl ligands $[Fe(\eta^5\text{-}C_5H_5)\{(\eta^5\text{-}C_5H_4CH{=}NCH_2Ph)\}]$ and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$ as well as their mononuclear derivatives with σ(Pd–C_{sp2}, ferrocene) bonds $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2Ph)\}Cl(L)]$, $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(L)]$ [L = 1-methylimidazole (mim) or PPh_3], and $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(PPh_3)_2]$ have been studied. Comparison of the data allows an understanding of the influence of the nature of the N-donor atom of the ferrocenyl moiety (sp^2 *versus* sp^3) upon the properties of these compounds. In particular, the differences observed in the quadrupole splitting parameters obtained from Mössbauer spectroscopy reveal not only that the palladium(II) acts as an electron-withdrawing group in all these cyclometallated derivatives, but also that most of the electron density is withdrawn from the imine CH=N moiety in the derivatives containing ferrocenyl Schiff bases as ligands. The crystal structures of $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2Ph)\}Cl(PPh_3)]$ and $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(mim)]$ have been determined.

An important area of organometallic chemistry is that concerning compounds containing polydentate ligands bound to metals through carbon and other donor atoms, especially nitrogen, phosphorus, oxygen, sulfur, *etc.* During the last decade several reviews[1] on this type of compound (usually known as *cyclometallated*) have appeared. Amongst the wide variety of cyclometallated complexes described those containing N-donor atoms and σ(Pd–C_{sp^2}, phenyl) or even σ(Pd–C_{sp^3}, aliphatic) bonds are particularly interesting in view of their novel applications.[2–6] For example, it is well established that cyclopalladated compounds provide new methods for regio- and stereo-selective synthesis of organic and organometallic substrates.[2] Compounds of this kind also exhibit antitumoural activity.[3] More recently, several examples of metallomesogens (liquid crystals containing co-ordinated metals) containing five-membered palladacyclic derivatives have been described.[4] Finally applications of such derivatives in homogeneous catalysis have been reported.

Previous studies on cyclopalladated compounds have shown that their properties are dependent on several factors: the nature of the metallated carbon atom (sp^2 or sp^3), the size and structure of the metallacycle, and the nature of the N-donor atom (*i.e.* its basicity). Although it is widely accepted that (*a*) the formation of a metallacycle from palladium(II) salts takes place in two steps, one of which involves electrophilic attack of the co-ordinated palladium(II) species to the carbon, and (*b*) metallocenes are more reactive towards electrophilic substrates than is benzene,[7] only a few examples of cyclopalladated compounds with N-donor ligands and σ(Pd–C_{sp^2}, ferrocene) bonds have been reported.[8–12] Most of these contain (dimethylaminomethyl)ferrocene, $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$ **A**. Recently, we have described novel endocyclic five-membered metallacycles derived from ferrocenylimines, $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$[10–12] **B**, and studied the influence of the substituents R and R′ upon their properties.



A



B

Interestingly, although the two metallacycles **A** and **B** (R = H, R′ = CH_2Ph) contain a σ(Pd–C_{sp^2}, ferrocene) bond, they exhibit different reactivity *versus* alkynes.[13,14] In particular, the insertion of two molecules of diphenylacetylene into the σ(Pd–C_{sp^2}, ferrocene) bond takes place under milder experimental conditions for cyclopalladated derivatives containing the ferrocenylamine **A** than when the ligand is the Schiff base **B**.[13] These findings suggest that other factors such as the nature of the N-donor atom and the structure of the metallacycle (*i.e.* its conformation and/or its flexibility) may also have an important effect on the properties of cyclopalladated derivatives containing σ(Pd–C_{sp^2}, ferrocene) bonds.

In this paper we report the results of a comparative study of the two types of compound shown, in an attempt to clarify the influences of (*a*) the N-donor atom (sp^2 *versus* sp^3) of the

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

ferrocenyl moiety, and (*b*) the remaining ligands on the co-ordination sphere of the palladium atoms [1-methylimidazole (mim) *versus* PPh_3] upon their properties. We concentrate, in particular, on the iron centres, mainly reflected in the Mössbauer spectra and their redox potentials.

Preliminary Mössbauer spectroscopic studies[10,12] of several Schiff bases of general formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ (R = H, Me or Ph) and a few palladacycles of the type $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CR{=}N}R')\}Cl(PR_3)]$ led to the conclusion that the '$PdCl(PR_3)$' units act as electron-acceptor substituents. However, the data available, which refer exclusively to the Schiff-base derivatives,[10,12] were not sufficient to clarify the mechanism involved. Three possible pathways were suggested: (1) directly from the substituted pentagonal ring, (2) through the iminic C(R)=N bond or (3) both (1) and (2) simultaneously.[12] Comparison of the Mössbauer parameters of the ligands $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NCH_2Ph)]$ **1a** and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$ **2a** and those of the palladated complexes $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}N}CH_2Ph)\}Cl(L)]$, $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2N}Me_2)\}Cl(L)]$ (L = mim or PPh_3), and $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(PPh_3)_2]$ reported in this work appears to be the key to this problem. Since the formation of the palladated compounds from ligands **1a** and **2a** can be interpreted as arising from the substitution of a $\sigma(H\text{-}C_{sp^2}$, ferrocene) bond by a $\sigma(Pd\text{-}C_{sp^2}$, ferrocene) bond, such replacement is expected to modify the ring current of the substituted pentagonal ring of the ferrocenyl moiety. Consequently, these variations should be reflected not only in the ^{13}C NMR spectra, but also in the Mössbauer parameters and the redox behaviour of the iron centre. A systematic study of these spectroscopic and redox properties may be a useful tool to clarify the effects of the palladium atom, its ligands and the heteroatom of the ferrocenyl moiety upon the iron environment in compounds containing $\sigma(Pd\text{-}C_{sp^2}$, ferrocene) bonds.

Another aspect that has inspired further study of ferrocenyl ligands and their metal complexes is the fact that some ferrocenium derivatives have antitumoural activity, while the parent ferrocene does not.[15] Preliminary work in this field reveals that the antitumoural activity of these compounds depends on several factors, especially their redox properties.[16] Consequently, further synthesis and electrochemical studies of ferrocene derivatives are necessary for the successful design of novel derivatives with the desired properties.

Results and Discussion

Synthesis and Characterization.—Ferrocenylimine **1a** was prepared by condensation of ferrocenecarbaldehyde and benzylamine according to the general procedure described for $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NR')]$.[10,11] The di-μ-chloro-bridged cyclopalladated compounds $[\{\overline{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}N}CH_2Ph)](\mu\text{-}Cl)\}_2]$ **1b** and $[\{\overline{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2N}Me_2)](\mu\text{-}Cl)\}_2]$ **2b** were synthesized using Gaunt's method.[8a] For these dinuclear complexes, the addition of neutral L ligands (*i.e.* mim or PPh_3) in a molar ratio palladium complex : entering L ligand of 1 : 2 produces cleavage of the μ-chloro bridges giving $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}N}CH_2Ph)\}Cl(L)]$ and $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2N}Me_2)\}Cl(L)]$ with L = mim **1c**, **2c** or PPh_3 **1d**, **2d**. However, the two dinuclear compounds **1b** and **2b** exhibit different reactivities towards larger excesses of phosphine ligands. When complex **2b** was treated with PPh_3 in a 1 : 4 molar ratio cleavage of the Pd–N bond was also observed and this produced the metallated compound $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(PPh_3)_2]$ **2e**. This complex can also be obtained directly using the cyclopalladated compound **2d** and the stoichiometric amount of PPh_3. However, when the reaction was carried out using **1b** no evidence of the incorporation of a second phosphine ligand in the co-ordination sphere of the palladium atom was detected, even when excesses of more basic phosphine ligands (such as PEt_3) were used. These results reveal the higher lability of the Pd–N bond in the cyclopalladated compounds derived from (dimethylaminomethyl)ferrocene as compared with their analogues containing ferrocenyl Schiff bases.

All the cyclopalladated compounds were orange-red solids, except for **2c** and **2e** which are yellow. In all cases the elemental analyses were consistent with the proposed formulae. Compounds **1c**, **1d** and **2c**, **2e** were soluble in chloroform, dichloromethane, benzene and practically insoluble in hexane.

Proton NMR data for the free ferrocenyl derivatives and compounds containing $\sigma(Pd\text{-}C_{sp^2}$, ferrocene) bonds are summarized in Table 1. The resonances of the CH_2 protons which appear as singlets for the free ferrocenyl derivatives split into an AB quartet pattern for the cyclometallated complexes **1c**, **1d** and **2c**, **2d**, thus indicating their non-equivalence. Furthermore, two resonances are also observed for the methyl protons of the NMe_2 group in the spectra of compounds **2c** and **2d**. These two findings can be ascribed to the different environments of the protons belonging to the CH_2 and NMe_2 groups, above and below the metallacycle. Such splitting, which was also observed for cyclopalladated complexes derived from benzylidenebenzylamines,[17] may be ascribed to inhibition of the rotation around the $N\text{-}CH_2$ bond.

For complex **2e** the resonances arising from the protons of the CH_2 and NMe_2 moieties appear as singlets, as a consequence of the cleavage of the Pd–N bond, which results in opening of the metallacycle and pemits free rotation of the amine substituent at the C_5H_3 ring.

The variations observed in the ^{31}P NMR chemical shifts of compounds **1d** (δ 37.50), **2d** (δ 39.71) and $[\overline{Pd\{[\eta^5\text{-}C_5H_3C(S}){\text{-}}NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ (δ 32.9[18]) allow us to establish the influence of the *trans*-donor ligand [N(sp^2, or sp^3) and S] upon the ^{31}P NMR spectra of five-membered palladocycles with phosphine ligands. The shift of the signal to higher fields can be summarized according to the nature of the heteroatom of the chelated ferrocenyl ligand, as follows: ferrocenylamine (N_{sp^3}) < ferrocenylimine (N_{sp^2}) < ferrocenylcarbothioamide.

A summary of the ^{13}C NMR spectroscopic data for compounds **1a**, **2a** and the palladated derivatives **1c**, **1d** and **2c**–**2e** is presented in Table 2. Several relevant conclusions can be drawn from the variations observed in the spectra of **1a**, **2a** upon metallation. The two signals due to C(1)–C(3) and C(4),C(5) split due to the formation of the $\sigma(Pd\text{-}C_{sp^2}$, ferrocene) bond. The signal due to the metallated carbon atom exhibits low intensity due to the nuclear Overhauser effect, and is shifted downfield (*ca.* 25–34 ppm) as compared with those for **1a**, **2a**. This downfield shift is similar to those observed for related compounds containing $\sigma(Pd\text{-}C_{sp^2}$, ferrocene) bonds (*ca.* 30 ppm).[11]

Crystal Structures.—Perspective drawings of the molecular structures of compounds **1d** and **2c** as well as their atom labelling schemes are shown in Figs. 1 and 2. These structures consist of discrete molecules of $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}N}CH_2Ph)\}Cl(PPh_3)]$ **1d** and $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2N}Me_2)\}Cl(mim)]$ **2c** with only van der Waals forces operating in the molecular packing; four CH_2Cl_2 molecules are also contained in the unit cell of complex **2c**. The most relevant bond lengths, angles and other outstanding structural parameters for **1a**,[11] complexes **1d** and **2c** and two other five-membered cyclopalladated compounds $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}N}CH_2CH_2Ph)\}Cl(PEt_3)]$ **3e** and $[\overline{Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CHMeN}Me_2)\}(acac)]$ **4f**

Table 1 Most relevant ^1H NMR data for the ferrocenyl (**1a**, **2a**) and palladated compounds (**1c**, **1d** and **2c**–**2e**)

Compound	$H(C_5H_5)$	H^3	H^4	H^5	NCH_2 [a]	CH=N	NMe_2 [b]	CH_2N [a]
1a $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NCH_2Ph)]$	4.17	4.68	4.38	4.38	4.68 [c]	8.24	—	—
1c $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2Ph)\}Cl(mim)]$	4.13	4.19	4.26	4.37	4.65 5.45	8.07	—	—
1d $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2Ph)\}Cl(PPh_3)]$	3.67	4.30	3.90	3.30	5.21 4.69	7.90 [d]	—	—
2a $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$	4.10	4.17	4.15	4.15	—	—	2.17 [c]	3.27 [c]
2c $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(mim)]$	4.18	4.15	3.95	3.54	—	—	3.14 2.89	3.21 3.42
2d $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(PPh_3)]$	3.79	4.00	3.75	3.60	—	—	2.57 2.60	3.24 3.00
2e $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(PPh_3)_2]$	4.12	4.57	4.24	3.78	—	—	2.60	4.14

[a] Doublet of doublets (AB quartet pattern), except as noted. The values given refer to the midpoints of each of the two doublets. [b] Doublet, except as noted. [c] Singlet. [d] Doublet due to phosphorus coupling.

Table 2 Most relevant ^{13}C NMR data

Compound	C_5H_5	C^1	C^2	C^3	C^4	C^5	NCH_2	CH=N
1a [a]	69.21	70.41	84.38	70.41	68.57	68.57	65.01	163.88
1c [b]	70.18	99.20	84.31	68.54	66.44	63.28	62.09	174.34
1d [c]	69.80	104.18	87.57	69.35	66.48	69.42	59.10	172.38 [d]
	C_5H_5	C^1	C^2	C^3	C^4	C^5	CH_2N	NMe_2
2a [a]	64.95	70.56	83.84	70.57	68.49	68.49	59.69	45.29
2c [b]	69.38	94.93	93.55	68.08	67.81	64.62	61.57	53.62 53.25
2d [c]	69.39	97.22	95.17	69.73	65.30	69.58	60.57	53.01 51.25
2e [c]	69.17	93.97	80.71	72.43	70.99	70.24	62.64	50.44

[a] For complexes **1a** and **2a** C^1 is equivalent to C^3 and C^4 to C^5. For **2a** the protons of the two methyl groups are also equivalent. [b] Four additional resonances due to the carbons of mim: δ 140.25, 131.30, 119.96 and 34.53. [c] Four additional doublets centred at δ 134.98, 131.93, 130.38 and 128.02, assigned to the four types of carbon nuclei on the phenyl rings of the PPh_3 ligand. [d] Doublet due to the coupling with the phosphorus of PPh_3.

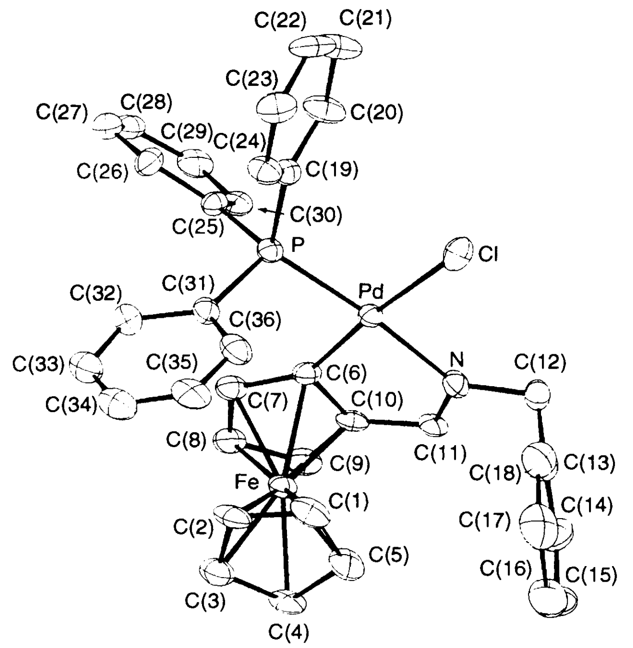

Fig. 1 Molecular structure and atom labelling scheme for the compound $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CH{=}NCH_2Ph)\}Cl(PPh_3)]$ **1d**

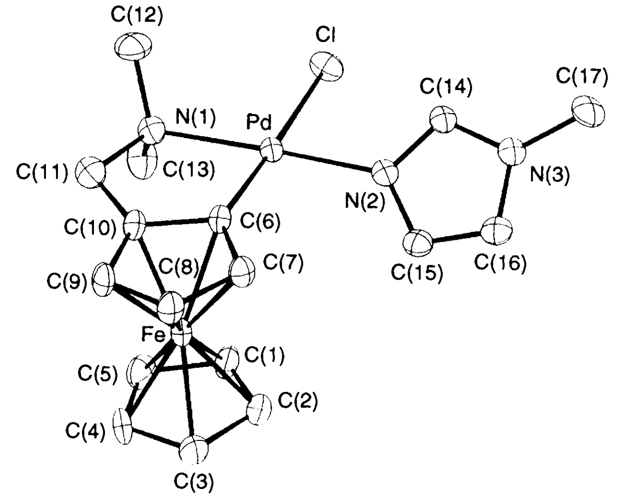

Fig. 2 Molecular structure and atom labelling scheme for the compound $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(mim)]$ **2c**

(acac = acetylacetonate) which also contain σ(Pd–C_{sp^2}, ferrocene) bonds[8c,10] are summarized in Table 3.

In compounds **1d** and **2c** the palladium atom is bound to chloride, the heteroatom of the neutral ligand [P in **1d** and N(2) in **2c**], the nitrogen and the C(6) atom of the ferrocenyl moiety. This confirms the formation of a bicyclic system arising from the fusion of the substituted pentagonal ring of the ferrocenyl ligand and the metallacycle defined by the atoms: Pd, C(6), C(10), C(11) and N.

The most interesting structural differences between the two families of cyclopalladated derivatives containing ferrocenylimines (**1d** and **3e**) and ferrocenylamines (**2c** and **4f**) are found in the Pd–N and Pd–C(6) bond lengths and the metallacycle angles. The variations observed in the former can be attributed to the different basicities of the nitrogen bound to the palladium. Furthermore, Pd–C(6) in complex **1d** is clearly longer than in **2c**, and this increase is compensated by the enlargement of the Pd–Cl bond in a *trans* arrangement. The remaining differences

Table 3 Most relevant structural parameters (lengths in Å, angles in °)[a] with estimated standard deviations (e.s.d.s) in parentheses

	1a[b]	**1d**	**2c**	**3e**[c]	**4f**[d]
Pd–N	—	2.146(6)	2.112(3)	2.148(5)	2.10(3)
Pd–Cl	—	2.368(2)	2.411(1)	2.390(2)	2.07(3)[e]
Pd–C(6)	—	2.004(5)	1.967(3)	1.999(6)	1.96(4)
Pd–L[f]	—	2.247(2)	2.029(2)	2.243(2)	2.05(2)
N–C(11)	1.262(4)	1.279(7)	1.526(5)	1.280(8)	1.57(5)
C(6)–C(10)	1.430(8)	1.430(9)	1.429(5)	1.434(9)	1.50(2)
C(10)–C(11)	1.420(8)	1.475(9)	1.495(5)	1.467(9)	1.46(5)
Fe–C[g]	2.032(5)	2.051(7)	2.046(3)	2.055(7)	2.064(5)
C–$C_{ferrocenyl}$[g]	1.048(8)	1.417(10)	1.420(5)	1.418(10)	1.45(1)
Fe $\cdots$ Pd	—	3.589(1)	3.560(1)	3.577(2)	3.595(3)
N–Pd–C(6)	—	80.8(2)	83.5(1)	81.1(2)	89.0(2)
N–Pd–Cl	—	92.8(1)	93.1(1)	92.5(1)	—
C(6)–Pd–L[f]	—	91.0(2)	94.0(1)	91.2(2)	92.5(3)
Cl–Pd–L[f]	—	95.4(1)	89.3(1)	95.5(1)	91.7(2)
N–C(11)–C(10)	122.8(5)	115.2(3)	108.8(3)	117.0(7)	101.0(3)
C(11)–C(10)–C(6)	125.6(5)	118.0(3)	120.1(3)	116.9(8)	121.0(3)
C(10)–C(6)–Pd	—	111.5(2)	114.2(2)	111.9(3)	107.0(2)
Pd–N–C(11)	—	114.3(2)	112.5(2)	112.9(2)	108.0(6)

[a] The labelling of the atoms refers to the schemes in Figs. 1 and 2. [b] From ref. 12. Average values for the two non-equivalent molecules. [c] From ref. 10. [d] From ref. 8(*c*). [e] In this case the distance refers to the Pd–O (acac) bond in a *trans* arrangement to the Pd–C(6) segment. [f] L = P of the PR_3 ligands in compounds **1d** and **3e**, N(2) of the 1-methylimidazole ligand in **2c**, or the oxygen of the acac group in **4f**. [g] Average values.

[*i.e.* C(10)–C(11) and C(11)–N bond lengths] may be interpreted in terms of the hybridizations of the C(11) and N atoms: sp^2 (in **1d** and **3e**) and sp^3 (in **2c** and **4f**). In all cases the Fe–C and C–C bond lengths of the ferrocenyl substituent are consistent with values reported for other ferrocene derivatives.[19]

The metallacycle in complex **1d** is smaller [perimeter 8.334(8) Å] than in **2c** [8.529(3) Å], but the distance between the two metals Fe $\cdots$ Pd is shorter in **2c**. This can be attributed to the different conformations of the metallacycles, practically planar in **1d** and a half-skew chair conformation in **2c**, which can be explained as arising from the higher flexibility of the CH_2NMe_2 moiety *versus* the imine group C(H)=NR′.

The different N–Pd–C(6) angles observed in the ferrocenylimines and ferrocenylamines correspond to small variations in their bites (Table 4). It is interesting that the typical bite for such ligands is one of the largest found for five-membered chelate rings. The typical bites for oxalate, tropolonate (2-hydroxycyclohepta-2,4,6-trien-1-onate) dioximate, bipyridyl and ethylenediamine ligands are 2.51, 2.52, 2.54, 2.56 and 2.78 Å, respectively.[21,22] The small variations in the bites of the bidentate ligands (Table 4) are compensated by tiny differences in the Pd–N and Pd–C(6) bonds, resulting in a practically constant normalized bite, *b*, which falls within the range expected for bidentate ligands forming five-membered rings (Table 4).[23]

Electrochemical Studies.—Electrochemical data for the ligands and the palladated compounds were obtained from cyclic voltammetric studies of 10^{-3} mol dm^{-3} solutions in acetonitrile. The half-wave potentials referred to ferrocene [$E_{\frac{1}{2}}$(ferrocene)] for the compounds and related derivatives are summarized in Table 5. In all cases the electrochemical parameters (ΔE, I_{pc}/I_{pa}) were coincident with those obtained for ferrocene itself under identical experimental conditions.

The half-wave potentials of the compounds **1a** and **2a** are consistent with those recently reported for the bis(ferrocenyl)-diimine **5** and the diamine **6**[24] (Table 5). In both cases the ferrocenyl Schiff bases exhibit higher $E_{\frac{1}{2}}$(ferrocene) values than those of the corresponding amines. This result is in good agreement with the different nature of the two functional groups: amino (electron donor) and imino (electron withdrawing). The half-wave potentials for the five-membered palladocyclic complexes containing (dimethylaminomethyl)-ferrocene **2c** and **2d** are also clearly more anodic than those obtained for their analogues **1c** and **1d**.

Furthermore, the redox potentials for the five-membered palladacycles are less positive than those of compounds **1a** and **2a**. This result is similar to that reported by Nonoyama and co-workers[25] for the mono- and di-cyclopalladated complexes containing *N*,*N*-dimethylferrocenecarbothioamide **7** and *N*,*N*,*N*′,*N*′-tetramethylferrocene-1,1′-dicarbothioamide **8**. Moreover, the oxidation potentials of the five-membered metallacycles containing ferrocenylimines are similar to those obtained for their carbothioamide analogues.

On the other hand the co-ordination of the ferrocenylamine **2a** as a monodentate ligand to the palladium atom solely through the nitrogen in $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH{=}NMe_2)\}_2Cl_2]$ **2f** or only through the carbon in **2e** clearly inhibits oxidation of the iron centre (Table 5). This suggests that the '$PdCl_2$' and '$PdCl(PPh_3)_2$' units in these complexes act as electron-withdrawing substituents.

Furthermore, the data in Table 5 also reveal that the $E_{\frac{1}{2}}$(ferrocene) potentials of the palladocyclic derivatives are clearly influenced by the nature of the neutral ligand L (mim or PPh_3) bound to the palladium. The L ligands are *trans* to the N-donor atom of the chelated ferrocenyl ligand. Replacement of the PPh_3 moiety by mim facilitates oxidation of the iron centre.

Mössbauer Spectra.—The ^{57}Fe Mössbauer spectra of the compounds consist of single quadrupole doublets. The isomer shifts (i.s.), quadrupole splittings (q.s.) and the linewidths (Γ) are summarized in Table 6. The large value of the linewidth obtained for **2a** is due to the fact that the spectrum was obtained from a frozen solution.

The variations in the Mössbauer parameters obtained for compounds **1a** and **2a** are consistent with the results obtained from the electrochemical studies described above, and arise from the different nature of the two substituents bound to the ferrocenyl moiety. Compared to ferrocene itself, the CH_2NMe_2 fragment in the amine ligand has an electron-donor ability, while the $CH{=}NCH_2Ph$ in the Schiff base acts as electron-withdrawing group. We have previously shown a relationship between oxidation potential and quadrupole splitting, and the current electrochemical data fit this well.[27]

More interesting is the comparison of the quadrupole splitting values obtained for compounds **1a** and **2a** and the cyclopalladated derivatives. For **2a** the replacement of a $\sigma(H\text{–}C_{sp^2}$, ferrocene) bond by a $\sigma(LClPd\text{–}C_{sp^2}$, ferrocene) bond introduces only a slight lowering of the quadrupole splitting, which appears to be independent of the nature of the neutral L

Table 4 Selection of Pd–N, Pd–C(6) bond lengths (Å), bites (N ··· C) of the chelated ferrocenylamines or ferrocenylimines, and the corresponding normalized bites b^a for cyclopalladated compounds containing σ(Pd–C_{sp^2}, ferrocene) bonds and N-donor ligands

Compound	Pd–N	Pd–C(6)	N ··· C(6)	b
1d	2.146(6)	2.004(5)	2.692(7)	1.297(7)
3e[b]	2.148(5)	1.999(6)	2.699(8)	1.301(6)
2c	2.112(3)	1.967(3)	2.720(5)	1.334(4)
4f[c]	2.10(3)	1.96(4)	2.76(2)	1.35(3)
$[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NC_6H_2Me_3\text{-}2,4,6)](\mu\text{-}MeCO_2)_2]$[d]	2.05(1) 2.02(2)	1.93(3) 1.93(3)	2.65(3) 2.56(3)	1.33(3) 1.30(3)

[a] Calculated according to the expression $b = N \cdots C/\frac{1}{2}(Pd–N + Pd–C)$. [b] From ref. 10. [c] From ref. 8(*c*). [d] This compound contains two five-membered rings with a σ(Pd–C_{sp^2}, ferrocene) bond.[20]

Table 5 Oxidation potentials $E_{\frac{1}{2}}$(ferrocene)[a]

Compound		$E_{\frac{1}{2}}$(ferrocene)[a]/ V
(*a*) Ligands		
1a		0.13
2a		−0.01
5	$[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH{=}NCH_2CH_2N{=}CHC_5H_4\text{-}\eta^5)Fe(\eta^5\text{-}C_5H_5)]$[b]	0.14
6	$[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2NHCH_2CH_2NHCH_2C_5H_4\text{-}\eta^5)Fe(\eta^5\text{-}C_5H_5)]$[b]	−0.05
7	$[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4C(S)NMe_2\}]$[c]	0.08
8	$[Fe\{\eta^5\text{-}C_5H_4C(S)NMe_2\}_2]$[c]	0.16
(*b*) Palladium compounds with σ(Pd–C_{sp^2}, ferrocene) bonds		
1c		0.02
1d		0.05
2c		−0.20
2d		−0.16
2e		0.02
7a	$[Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3C(S)\text{-}NMe_2]\}(acac)]$	0.03
8b	$[Pd_2\{Fe[(\eta^5\text{-}C_5H_3C(S)NMe_2]_2\}(acac)_2]$[c,d]	0.04
8b′	$[Pd_2\{Fe[(\eta^5\text{-}C_5H_3C(S)NMe_2]_2\}(acac)_2]$[c,e]	0.03
(*c*) Palladium compound without σ(Pd–C_{sp^2}, ferrocene) bonds		
2f[f]		0.14

[a] Referred to ferrocene (E = 0.00 V). The e.s.d. is $\pm 5 \times 10^{-3}$ V (see Experimental section). [b] From ref. 24. [c] From ref. 25. [d] *meso* Form. [e] Racemic form. [f] Data from ref. 26.

Table 6 Iron-57 Mössbauer spectroscopic parameters[a]

Compound	i.s.	q.s.	Γ	T/K
1a[b]	0.54(1)	2.29(1)	0.15(1)	78
1c	0.52(1)	2.24(1)	0.13(1)	78
2a	0.53(1)	2.42(1)	0.22(1)[c]	78
2c	0.54(1)	2.41(1)	0.13(1)	78
	0.45(1)	2.39(1)	0.12(1)	295
2d	0.53(1)	2.39(1)	0.15(1)	78

[a] All in mm s^{-1}. [b] From ref. 12. [c] The large value is probably due to the fact that the spectrum of the free amine was obtained from a frozen solution.

ligand (PPh_3 or mim) in a *trans* arrangement to the N-donor atom of the ferrocenylamine. This suggests that in the cyclopalladated complexes the 'PdClL' moiety takes little electron density from the ferrocenyl unit, and must therefore satisfy its requirements from the lone pair of the N-donor atom of the amine. Thus, if a change of around 0.02 mm s^{-1} (as a measure of the electron density taken directly from the ferrocene) is assumed, and if we compare the values obtained for compound **1c** and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NCH_2Ph)]$ **1a** we can assume that *ca.* 0.03 mm s^{-1} is removed by the 'PdClL' entity *via* the CH=N pathway.

Similar arguments allow analogous conclusions for a number of our previous results.[12] Table 7 shows the differences observed for the quadrupole splittings obtained for the cyclopalladated compounds and their parent ligands [Δ = q.s. (cyclopalladated complex) − q.s. (free ligand)] and the estimated electron withdrawing contribution of the PdClL unit reflected in the differences (Δ −0.02 mm s^{-1}) for the imine derivatives. The results support the following conclusions: (*a*) the C(R)=N unit is an electron sink, (*b*) most of the electron density is withdrawn *via* the imine bond to the palladium, and only around 0.02 mm s^{-1} can be attributed to the electron density which is removed directly from the ferrocenyl unit to the palladium and (*c*) the palladium withdraws more electron density from the C(R)=N bond than do the substituents (R′) on the nitrogen in the free ferrocenyl derivatives.

Conclusion

The results reported here for the two N-donor ligands derived from ferrocene, $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}NCH_2Ph)]$ **1a** and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$ **2a**, and for their palladium(II) compounds containing a σ(Pd–C_{sp^2}, ferrocene) bond have cast light on the influence and the nature of the N-donor atoms, not only upon their spectroscopic and structural properties but also on their chemical reactivity. For instance, the two dinuclear compounds **1b** and **2b** exhibit different reactivity *versus* phosphine ligands. The reaction of $[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)](\mu\text{-}Cl)\}_2]$ and PPh_3 in a 1 : 4 molar ratio led to cleavage of the Pd–N bond, *via* opening of the metallacycle and with incorporation of a second phosphine ligand in the co-ordination sphere, producing $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(PPh_3)_2]$, whereas the formation of the analogous compound derived from the Schiff base was not even detected in the course of the reaction. These findings allow us to conclude that in cyclopalladated compounds containing the imine as the chelate ligand the Pd–N bond is clearly less reactive than those containing the amine.

Electrochemical studies reveal that the formation of the metallacycles facilitates oxidation of the iron centre in every case. Furthermore, for the palladocyclic compounds **1c**, **1d**, **2c** and **2d** changes in the neutral L ligand (three bonds distant from the iron) introduce significant variations (*ca.* 30–40 mV) in the redox potentials. Mössbauer spectroscpic studies on these compounds indicate that most of the electron density withdrawn from the ferrocenyl group by the palladium is taken through the imine bond.

Consequently, the study of these ferrocene derivatives has allowed an understanding of the effects of the binding of palladium(II) to ferrocene and indicates approaches to controlling the oxidation potential of the metallocene. These factors should aid in the design of ferrocenyl ligands with antitumoural activity. It should be noted that similar compounds could be formed containing platinum instead of palladium and two monodentate N-donor ligands instead of phosphine and chloride. This would give a molecule with two

Table 7 Comparison of the quadrupole splitting parameters (in mm s^{-1}) obtained for cyclopalladated compounds and the corresponding parent ligand, as well as the estimated withdrawal effect of the palladium

	q.s.			
Complex	Cyclopalladated complex	Ligand	Δ(q.s.)[a]	Δ(q.s.) − 0.02
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2CH_2Ph)\}Cl(PEt_3)]$	2.21[b]	2.34[b]	0.13	0.11
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2CH_2Ph)\}Cl(PPh_3)]$	2.16[b]	2.34[b]	0.18	0.16
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2CH_2Ph)\}Cl(dppe)]$	2.13[b]	2.34[b]	0.21	0.19
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CMe{=}NC_6H_4Me\text{-}4)\}Cl(PPh_3)]$	2.20[c]	2.29[c]	0.09	0.07
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NPh)\}Cl(PPh_3)]$	2.19[c]	2.31[c]	0.12	0.10
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4Me\text{-}4)\}Cl(PPh_3)]$	2.24[c]	2.30[c]	0.06	0.04
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NCH_2C_6H_4Me\text{-}2)\}Cl(PPh_3)]$	2.21[c]	2.29[c]	0.08	0.06
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NCH_2C_6H_4Cl\text{-}2)\}Cl(PPh_3)]$	2.22[c]	2.35[c]	0.13	0.11
$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_{10}H_7)\}Cl(PPh_3)]$	2.23	2.26	0.03	0.01

dppe = $Ph_2PCH_2CH_2PPh_2$. [a] Δ(q.s.) = (cyclopalladated complex) − q.s. (free ligand). [b] From ref. 10. [c] From ref. 12.

possible centres for antitumour activity, *viz*. the ferrocene and the platinum.

Experimental

Elemental analyses (C, H and N) were carried out at the Instituto de Química Bioorganica (C.S.I.C., Barcelona). Infrared spectra were obtained with a Nicolet-520-FTIR spectrophotometer using KBr pellets, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra at *ca.* 20 °C on a Gemini-200 MHz spectrophotometer, using $CDCl_3$ (99.8%) and $SiMe_4$ as solvent and internal standard respectively. For complexes **1d**, **2d** and **2e** the $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded with a Brucker WP-80-SY spectrophotometer (32.8 MHz) using $CHCl_3$ as solvent and $P(OMe)_3$ as standard. Decomposition points were obtained with a Buchi 510 melting-point instrument. All the solvents, except benzene, were dried and distilled before use.

Materials and Syntheses.—(Dimethylaminomethyl)ferrocene **2a** and ferrocenecarbaldehyde were obtained from standard sources and used as received. The Schiff base **1a** was prepared by condensation of benzylamine and ferrocenecarbaldehyde, using the general procedure described for $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ (R = H or Me).[10] The di-μ-chloro-bridged derivatives **1b**, **2b** as well as complexes **1d**, **2d** were synthesized according to the methods described in the literature.[8a,10] Characterization data: **1a** [Found (Calc.) for $C_{18}H_{17}FeN$: C, 71.4 (71.35); H, 5.50 (5.60) and N, 4.60 (4.60)%]; IR $\nu_{max}(C{=}N)$ 1632 cm^{-1}; **1b** [Found (Calc.) for $C_{38}H_{32}Cl_2Fe_2N_2Pd_2$: C, 49.9 (50.0); H, 3.50 (3.50); N, 2.95 (3.05)%]; IR $\nu_{max}(C{=}N)$ 1590 cm^{-1}; **1d** [Found (Calc.) for $C_{36}H_{31}ClFeNPPd$: C, 60.95 (61.2); H, 4.40 (4.60); N, 2.00 (1.90)%]; IR $\nu_{max}(C{=}N)$ 1605 cm^{-1}; ^{31}P NMR, δ 37.50; **2b** [Found (Calc.) for $C_{26}H_{32}Cl_2Fe_2N_2Pd_2$: C, 43.0 (43.15); H, 2.95 (3.05); N, 3.95 (3.85)%]; **2d** [Found (Calc.) for $C_{31}H_{31}ClFeNPPd$: C, 57.6 (57.55); H, 4.85 (4.80); N, 2.10 (2.15)%]; ^{31}P NMR δ 39.71.

$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH{=}NCH_2Ph)\}Cl(mim)]$ **1c**. 1-Methylimidazole (65 mm^3, 0.81 mmol) was added to an acetone suspension (10 cm^3) containing compound **1b** (0.355 g, 0.4 mmol). The resulting mixture was refluxed for 30 min. After cooling to room temperature *ca.* 20 °C, the solution was filtered and the filtrate concentrated to dryness on a rotary evaporator. Addition of diethyl ether to the oily residue precipitated compound **1c** which was recrystallized from CH_2Cl_2–hexane (1 : 2). Yield: 76% [Found (Calc.) for $C_{22}H_{22}ClFeN_3Pd$: C, 50.3 (50.20); H, 4.10 (4.20); N, 7.95 (8.00)%]; IR $\nu_{max}(C{=}N)$ 1607 cm^{-1}.

$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(mim)]\cdot 0.5CH_2Cl_2$ **2c**. To a suspension containing compound **2b** (0.307 g, 0.4 mmol) in benzene (10 cm^3) was added 1-methylimidazole (65 mm^3, 0.81 mmol). The resulting mixture was stirred at room temperature for 45 min and filtered. The filtrate was concentrated to dryness on a rotary evaporator. The oily residue was dissolved in CH_2Cl_2 (5 cm^3) and filtered. The resulting yellowish solution was treated with hexane until turbidity. Slow evaporation of the solvents at *ca.* 20 °C produced crystals of compound **2c**. Yield: 88.1% [Found (Calc.) for $C_{18}H_{22}ClFeN_3Pd\cdot 0.5CH_2Cl_2$: C, 35.7 (35.80); H, 3.75 (3.70); N, 6.80 (6.75)%].

$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)\}Cl(PPh_3)_2]$ **2e**. This complex can be prepared using the dimeric complex **2b** or the mononuclear phosphine derivative **2d** as starting materials.

Method A. Triphenylphosphine (0.419 g, 1.6 mmol) was added to a benzene suspension (10 cm^3) containing the dimeric compound **2b** (0.307 g, 0.4 mmol). The reaction mixture was stirred at room temperature for 1 h. The undissolved materials were filtered out and discarded, and the filtrate was concentrated to *ca.* 5 cm^3 on a rotary evaporator. Addition of hexane (*ca.* 10 cm^3), followed by slow evaporation of the solvents, produced yellow plates of the complex. The microcrystals were filtered off and air-dried. Yield 69.2%.

Method B. Triphenylphosphine (81 mg, 0.31 mmol) was added to a CH_2Cl_2 solution (10 cm^3) containing compound **2d** (0.200 g, 0.31 mmol). The reaction mixture was stirred at room temperature for 2 h. During this period it changed from deep orange to bright yellow. Then the solution was concentrated on a rotary evaporator to *ca.* 5 cm^3. Addition of hexane precipitated complex **2e**, which was filtered off and air dried. Yield 88.4% [Found (Calc.) for $C_{49}H_{46}ClFeNP_2Pd\cdot 0.5CH_2Cl_2$: C, 64.55 (64.75); H, 5.10 (5.05); N, 1.40 (1.50)%]; ^{31}P NMR δ 28.03.

Crystal Structure Determination and Refinement.—Prismatic crystals (0.1 × 0.1 × 0.2 mm) of compounds **1d** and **2c** were selected and mounted on a Phillips (**1d**) and an Enraf-CAD4 diffractometer (**2c**). Unit-cell parameters (Table 8) were determined from automatic centring of 25 reflections in the range $8 \leqslant \theta \leqslant 16°$ and refined by the least-squares method. Intensities were collected with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å), using the ω–2θ scan technique. Three reflections were measured every 2 h as orientation and intensity controls, and no significant decay was observed. Lorentz polarization but not absorption corrections were made.

The structures were solved by the Patterson method[28] and refined by full-matrix least-squares method with the SHELX 76 computer program.[29] The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|$, where $w = [\sigma^2(F_o) + k(F_o)^2]^{-1}$; f, f' and f'' were obtained from ref. 30. The number of hydrogens located from difference syntheses, the final R and R' values {calculated according to $(\Sigma||F_o| - |F_c|)/(\Sigma|F_o|)$ and $[(\Sigma|w|F_o| - |F_c||^2)/(\Sigma w|F_o|^2)]^{\frac{1}{2}}$, respectively} are given in Table 8 together with the number of parameters refined for each structure and the maximum and minimum peaks in the final difference syntheses. The positions of all the hydrogens were refined with an overall isotropic thermal parameter.

Final atomic coordinates for non-hydrogens atoms in compounds **1d** and **2c**, are given in Tables 9 and 10, respectively.

Table 8 Crystallographic data and details of the refinements for compounds **1d** and **2c**

	1d	**2c**
Formula	$C_{36}H_{31}ClFeNPPd$	$C_{18}H_{22}ClFeN_3Pd\cdot 0.5CH_2Cl_2$
M	706.33	520.56
Crystallographic system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	13.252(3)	36.095(4)
b/Å	11.077(2)	7.712(1)
c/Å	10.791(2)	14.384(2)
α/°	73.99(2)	90.0
β/°	88.52(3)	105.97(3)
γ/°	85.42(3)	90.0
U/Å^{-3}	1517.7(9)	3849(1)
D_c/g cm^{-3}	1.545	1.796
Z	2	8
μ(Mo-Kα)/mm^{-1}	12.38	19.69
No. of reflections measured	8287	5300
R_{int} (on F)	—	0.010
No. of reflections with $I \geqslant 2.5\sigma(I)$	4318	4729
θ Range/°	0–30	0–30
Weighting scheme	—	0.004
Number of hydrogens located	Computed	All
Final R	0.055	0.044
R'	0.061	0.049
No. of parameters refined	373	294
Maximum shift/e.s.d.	0.1	0.1
Maximum and minimum peaks/e Å^{-3}	+0.3	+0.5 and −0.6
F(000)		2088.0

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

Electrochemical Studies.—Electrochemical data were obtained by cyclic voltammetry under N_2 at 20 °C, using acetonitrile (HPLC grade) as solvent and 10^{-1} mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte. The redox half-wave potentials, $E_{\frac{1}{2}}$, were referred to an Ag–AgNO$_3$ (10^{-1} mol dm^{-3} in acetonitrile) electrode separated from the solution by a medium-porosity fritted disc. A platinum-wire auxiliary electrode was used in conjunction with a platinum-disc working electrode and Tacussel EDI rotating electrode (area 3.14 mm^2). Further details concerning the DACFAMOV apparatus were as described previously.[29]

Cyclic voltammograms of 10^{-3} mol dm^{-3} solutions of the samples in acetonitrile were run and the average values of the

Table 10 Final atomic coordinates (× 10^4, except × 10^5 for Pd, Fe, Cl and N) for non-hydrogen atoms in compound **2c**, with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c
Pd	67 228(1)	59 005(3)	28 067(1)
Fe	57 895(1)	48 737(6)	12 934(3)
Cl(1)	72 464(2)	52 446(12)	42 117(6)
Cl(2)	48 489(8)	−8 676(24)	14 648(13)
N(1)	68 667(8)	38 635(36)	19 885(20)
N(2)	65 640(8)	78 778(31)	35 448(19)
N(3)	66 231(8)	100 969(34)	45 268(20)
C(1)	5 778(1)	3 460(6)	2 489(3)
C(2)	5 473(1)	4 653(5)	2 272(3)
C(3)	5 236(1)	4 299(6)	1 315(3)
C(4)	5 401(1)	2 905(6)	958(3)
C(5)	5 733(1)	2 362(5)	1 664(4)
C(6)	6 297(1)	6 283(4)	1 633(2)
C(7)	5 972(1)	7 387(4)	1 298(2)
C(8)	5 764(1)	6 859(5)	345(3)
C(9)	5 959(1)	5 404(5)	789(2)
C(10)	6 284(1)	5 068(4)	875(2)
C(11)	6 606(1)	3 803(5)	963(3)
C(12)	7 268(1)	4 051(7)	1 936(4)
C(13)	6 835(2)	2 223(5)	2 470(3)
C(14)	6 809(1)	8 951(4)	4 121(2)
C(15)	6 236(1)	9 743(5)	4 191(3)
C(16)	6 203(1)	8 356(5)	3 588(3)
C(17)	6 794(1)	11 511(6)	5 179(3)
C(18)	5 000(0)	356(7)	2 500(0)

Table 9 Final atomic coordinates (× 10^4, except × 10^5 for Pd, Fe and P) for non-hydrogen atoms in compound **1d**, with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c
Pd	19 449(3)	−7 212(4)	12 842(2)
Fe	15 204(7)	−38 619(7)	31 567(8)
P	30 762(12)	−2 136(14)	25 365(13)
Cl	2 490(2)	657(2)	−666(2)
N	764(4)	−1 348(5)	344(5)
C(1)	2 647(5)	−4 200(7)	1 956(7)
C(2)	2 957(6)	−4 662(6)	3 228(8)
C(3)	2 315(6)	−5 591(6)	3 894(8)
C(4)	1 583(5)	−5 687(6)	3 008(8)
C(5)	1 773(7)	−4 813(7)	1 789(8)
C(6)	1 353(5)	−1 921(5)	2 821(6)
C(7)	1 518(5)	−2 532(6)	4 141(6)
C(8)	738(6)	−3 354(6)	4 630(6)
C(9)	91(5)	−3 296(6)	3 616(7)
C(10)	468(5)	−2 418(5)	2 486(6)
C(11)	191(5)	−2 094(5)	1 112(6)
C(12)	579(6)	−1 137(7)	−1 063(6)
C(13)	1 033(6)	−2 251(7)	−1 495(6)
C(14)	2 007(7)	−2 248(9)	−1 954(8)
C(15)	2 465(8)	−3 333(12)	−2 254(9)
C(16)	1 927(9)	−4 405(11)	−2 102(10)
C(17)	949(8)	−4 361(9)	−16 592(10)
C(18)	473(7)	−3 280(8)	−1 387(8)
C(19)	3 864(5)	1 088(6)	1 784(6)
C(20)	3 374(6)	2 290(7)	1 399(8)
C(21)	3 928(8)	3 320(8)	881(10)
C(22)	4 949(8)	3 156(8)	721(9)
C(23)	5 429(7)	1 988(9)	1 068(9)
C(24)	4 884(5)	960(7)	1 583(7)
C(25)	2 579(5)	295(5)	3 896(5)
C(26)	1 534(5)	461(6)	4 092(6)
C(27)	1 178(6)	915(7)	5 115(7)
C(28)	1 840(7)	1 156(6)	5 991(7)
C(29)	2 867(6)	1 015(7)	5 782(7)
C(30)	3 231(6)	622(7)	4 758(6)
C(31)	4 021(5)	−1 543(6)	3 141(6)
C(32)	4 245(5)	−2 060(7)	4 486(6)
C(33)	4 966(6)	−3 058(7)	4 834(9)
C(34)	5 494(6)	−3 526(8)	3 905(9)
C(35)	5 279(6)	−3 011(7)	2 640(9)
C(36)	4 548(6)	−2 040(7)	2 252(7)

measured $E_{\frac{1}{2}}$ then referred to ferrocene [$E_{\frac{1}{2}}$(ferrocene)] to aid interpretation of the results. In all cases the separation between the anodic and cathodic peaks ($\Delta E = E_a - E_c$) as well as the I_{pa}/I_{pc} ratio were similar to those obtained for ferrocene itself under identical experimental conditions. Cyclic voltammograms of ferrocene were recorded before and after each sample to ensure the viability and reproducibility of the results.[32] Under these experimental conditions the standard error of the oxidation potential was ± 5 mV.

Mössbauer Spectra.—Mössbauer spectra were recorded using solid samples in aluminium holders. The samples were placed in liquid N_2, quenched to 78 K and transferred to a cryostat. The spectrometer, previously described,[33] was calibrated with a natural iron absorber 25 mm thick, which was used as zero for the isomer shift measurements. The spectral data were computed fitted.

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