Activation of σ(C–H) Bonds in Ferrocenyl- and Bis(ferrocenyl)-imines promoted by Palladium†

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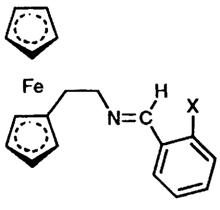
Ferrocenylimines of general formula $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2CH_2N{=}CR(R')\}]$ [R = H, R′ = Ph **1a**, C_6H_4Cl-2 **1b**, $C_6H_3Cl_2$-2,6 **1c**, $C_6H_2Me_3$-2,4,6 **1d** or $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ **1e**, R = Me, R′ = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ **1f**] were prepared by condensation of 2-ferrocenylethylamine and the corresponding aldehyde (**1a**–**1e**) or acetylferrocene (**1f**). Cyclopalladation reactions of these substrates gave different kinds of metallacycle depending on the nature of the ligand. In particular, endocyclic five-membered palladacycles containing a $\sigma(Pd\text{–}C_{sp^2,\,phenyl})$ or a $\sigma(Pd\text{–}C_{sp^2,\,ferrocene})$ were obtained from **1a**, **1b** and **1e**, **1f** respectively. However, for the ferrocenylimines in which the *ortho* positions of the aryl ring are blocked by either chlorine (**1c**) or methyl (**1d**) groups, mixtures of palladated compounds containing a $\sigma(Pd\text{–}C_{sp^2,\,ferrocene})$ and a $\sigma(Pd\text{–}C_{sp^2,\,phenyl})$ (for **1c**) or a $\sigma(Pd\text{–}C_{sp^3,\,aliphatic})$ bond (for **1d**) were obtained. The molecular structure of $[\overbrace{Pd\{C_6H_4CH{=}N}CH_2CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]\cdot CH_2Cl_2$ was determined by X-ray crystallography: triclinic, space group $P\bar{1}$, with $a = 9.995(1)$, $b = 11.308(2)$, $c = 15.747(2)$ Å, $\alpha = 96.85(1)$, $\beta = 99.05(1)$ and $\gamma = 95.99(1)°$. This confirms the formation of a five-membered palladacycle fused with the phenyl ring.

During the last years the interest in cyclopalladated compounds derived from N-donor ligands has increased exponentially,[1] mainly due to their novel and outstanding applications.[2] To date, most of these systems contain organic amines, imines, and to a lesser extent hydrazones and azo-derivatives, bound to the palladium through nitrogen and a C_{sp^2} or C_{sp^3} carbon atom, and only a few examples of cyclopalladated complexes containing N-donor ferrocenyl ligands have been reported.[3]

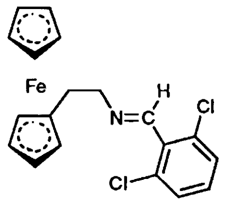
After studying cyclopalladation reactions of phenyl- and benzyl-imines in detail,[4,5] we recently initiated a 'parallel' study with Schiff bases derived from ferrocene, of general formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ (R = H, Me or Ph)[6] and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2N{=}CHR)]$.[7] Though the former type of compound produced endocyclic five-membered palladacycles with $\sigma(Pd\text{–}C_{sp^2,\,ferrocene})$ bonds in all cases,[6] the results obtained in cyclopalladation of the ferrocenylimines $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2N{=}CHR)]$ revealed that minor changes on the R group at the iminic carbon atom are important enough to modify the structure of the metallacycle formed (endo- or exo-cyclic).[7]

In order to study the influence of the size of the metallacycle and the nature of the iminic nitrogen in relation to the higher propensity to undergo electrophilic substitutions at the $C_{sp^2,\,ferrocene}$ atoms[8] *versus* the $C_{sp^2,\,phenyl}$ atoms, we have prepared some Schiff bases derived from 2-ferrocenylethylamine of general formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2CH_2N{=}CRR')]$ (R = H, R′ = Ph **1a**, C_6H_4Cl-2 **1b**, $C_6H_3Cl_2$-2,6 **1c** or $C_6H_2Me_3$-2,4,6 **1d**). Their cyclopalladation reactions were also studied. Furthermore, since **1a**–**1d** could be visualized as derived from *N*-benzylidene(2-phenylethyl)amines by replacement of the Ph ring by the ferrocenyl unit, these studies would allow comparison between the two types of imine.

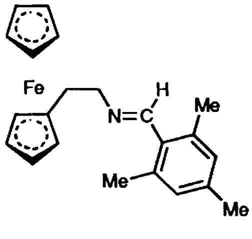
The interest of these substrates lies in the fact that they possess two different C–H bonds susceptible to activation, and thus could produce two types of palladacycle: (*a*) exocyclic six-membered metallacycles, which would arise from the activation of the $\sigma(C_{sp^2,\,ferrocene}\text{–}H)$, and (*b*) endocyclic derivatives containing a $\sigma(Pd\text{–}C_{sp^2,\,phenyl})$ (for **1a**, **1b**) or a $\sigma(Pd\text{–}C_{sp^3,\,aliphatic})$ bond (**1d**). For **1c**, in which the two *ortho* sites of the phenyl ring are blocked by chlorine, endocyclic metallacycles can only be formed if an oxidative addition of the *ortho*-C–Cl bond of the aryl ring to the palladium(0) species (formed during the process) takes place, a process which has been observed in similar cases.[4,5]



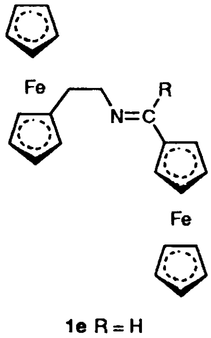
1a X = H
1b X = Cl



1c



1d



1e R = H
1f R = Me

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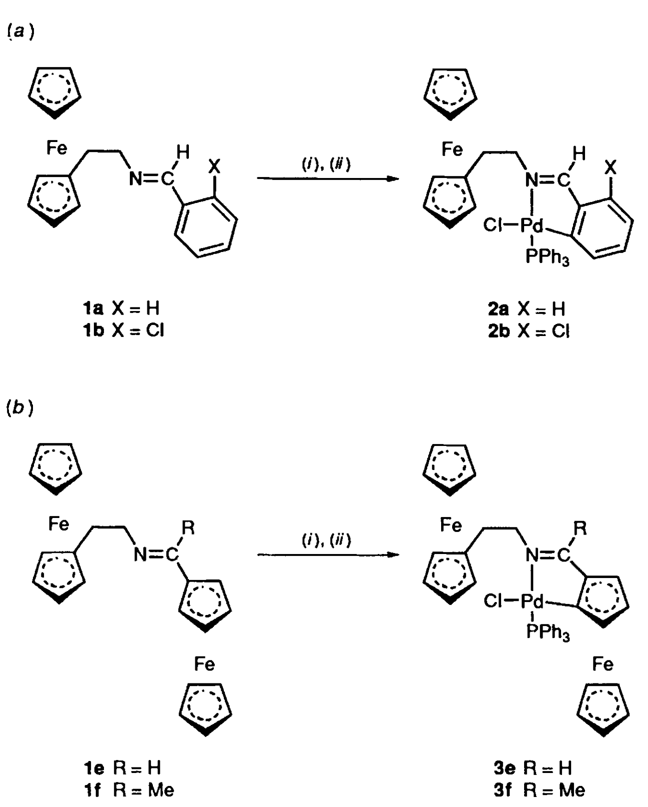
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 (*i*) $Na_2[PdCl_4]$, $Na(O_2CMe)$, MeOH, room temperature (r.t.), 3 h; (*ii*) PPh_3, C_6H_6

We have also studied $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2CH_2N{=}CR(R')\}]$ with R′ = $\eta^5\text{-}C_5H_4Fe(\eta^5\text{-}C_5H_5)$ and R = H **1e** or Me **1f**, which permits comparison of the relative stability of two cyclopalladated derivatives containing a [5,5] or [5,6] bicyclic system, which arise from fusion of the C_5H_3 ring and an endocyclic five-membered or an exocyclic six-membered palladocycle, respectively.

Results and Discussion

Syntheses of the Ferrocenyl Schiff Bases.—The 2-ferrocenylethylamine $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2CH_2NH_2)]$ was prepared from dimethylaminomethylferrocene, $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$, using the three-step sequence previously described,[9] and purified by vacuum distillation. The Schiff bases **1a**–**1f** were synthesized by condensation of freshly prepared 2-ferrocenylethylamine and the corresponding aldehyde (for **1a**–**1e**) or ketone (for **1f**), using a 1 : 1 molar ratio of the reactants and benzene as solvent. In all cases the reaction mixtures were refluxed in an ethylene glycol bath and the benzene–water azeotrope was removed with the aid of a Dean–Stark apparatus. It is worth noting that the success of these preparations is highly dependent on the purity of the amine, which degrades quite easily, and consequently should be used immediately after preparation to avoid the formation of by-products arising from its low stability.

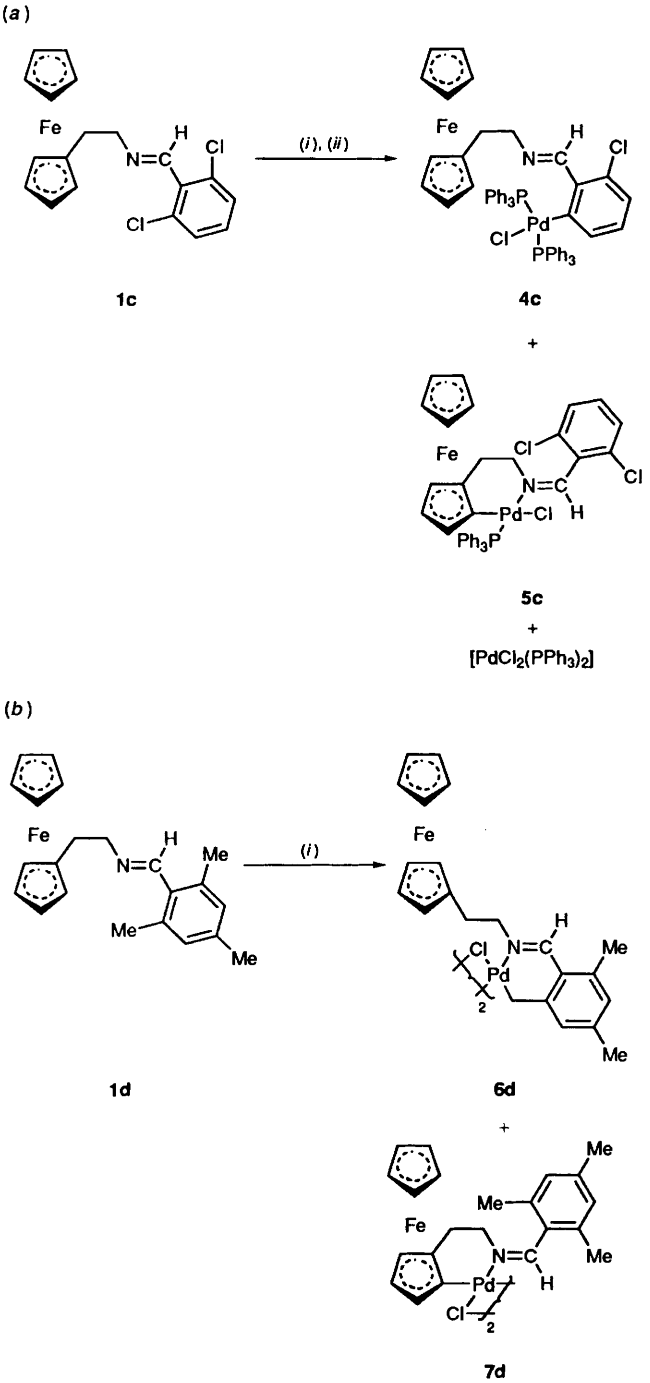
Cyclopalladation Reactions.—In order to study this sort of reaction, the general procedure described for most ferrocenyl ligands was used.[3,6,7] This consists of the reaction of equimolar amounts of the N-donor (hereafter referred to as HL), $Na_2[PdCl_4]$ and $Na(O_2CMe)\cdot 3H_2O$ in methanol at room temperature, which produces dichloro-bridged cyclopalladated complexes $[\{PdL(\mu\text{-}Cl)\}_2]$. Owing to the high insolubility of this kind of compound, they are usually treated with neutral ligands L′ such as phosphines and pyridine in benzene and converted into more soluble monomeric derivatives [PdLCl(L′)] or $[PdLCl(L')_2]$. All the cyclopalladation reactions undertaken in this work are summarized in Schemes 1 and 2.

When compounds **1a** and **1b** were treated with $Na_2[PdCl_4]$ and $Na(O_2CMe)\cdot 3H_2O$ in methanol for 3 h dark yellow solids were obtained. These materials reacted with PPh_3 in benzene producing compounds **2a** and **2b**, which contain endocyclic five-membered metallacycles with a $\sigma(Pd\text{–}C_{sp^2,\ phenyl})$ bond, exclusively. No evidence of the formation of compounds containing a $\sigma(Pd\text{–}C_{sp^2,\ ferrocene})$ bond was detected. Although it is widely accepted that one of the steps in the cyclopalladation reaction consists of the electrophilic attack of the species formed after co-ordination of the palladium to the N-donor atom to the σ(C–H) bond, and that ferrocene derivatives are more liable than their benzene analogues to undergo electrophilic attacks,[8] the activation of the $\sigma(C_{sp^2,\ ferrocene}\text{–}H)$ bond does not occur. These findings are clearly different from those obtained in the cyclopalladation of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2N{=}CHPh)]$, for which a 60 : 40 mixture of endo- and exo-cyclic cyclopalladated compounds was obtained.[7] Consequently, the incorporation of an additional CH_2 unit between the ferrocenyl moiety and the iminic nitrogen precludes the formation of six-membered exocyclic derivatives with a $\sigma(Pd\text{–}C_{sp^2,\ ferrocene})$ bond. This finding can be explained according to the lower stability of six-membered palladacycles.

Cyclopalladation reactions of compounds **1c** and **1d** are more complex and will be discussed below. For Schiff bases **1e** and **1f**, only the activation of $\sigma(C_{sp^2,\ ferrocene}\text{–}H)$ bonds is possible, and also in these cases, the endocyclic five-membered palladacycles **3e**, **3f** were obtained exclusively. These results are in good agreement with those described in the previous paragraph for **1a**, **1b**. It is worth noting that in these cases the formation of a [5,5] bicyclic system is highly preferred to that arising from the fusion of a six-membered exocyclic palladacycle and the C_5H_3 ring.

When the reaction was carried out using the Schiff base **1c** the solid obtained consisted of a mixture of the three products shown in Scheme 2 [equation (*a*)]: the co-ordination compound $[PdCl_2(PPh_3)_2]$ and two derivatives containing a σ(Pd–C) bond (**4c** and **5c** in a *ca.* 3 : 1 ratio), which could be separated by SiO_2-column chromatography. In one of these complexes the palladium is bound to a chlorine, two PPh_3 ligands and a $C_{sp^2,\ phenyl}$ carbon atom (**4c**); while the other **5c** is characterized by the presence of a six-membered metallacycle fused with the ferrocenyl moiety. It is interesting that these results contrast with those reported for related organic Schiff bases, such as 2,6-dichlorobenzylidene(2-phenylethyl)amine, for which metallation occurred exclusively at the aryl ring giving $[\{\overline{Pd(3\text{-}ClC_6H_3CH{=}N}CH_2CH_2Ph)(\mu\text{-}X)\}_2]$.[4] The formation of this product was interpreted as arising from an oxidative addition of the *ortho*-C–Cl bond of the aryl ring to the palladium(0) formed *in situ*. Some facts indicate that this argument may also be used to explain the formation of complex **4c**, among which the reductive nature of the ligand and the formation of a palladium mirror in the course of the reaction are the most significant. On the other hand, the formation of the exocyclic compound **5c** can easily be understood according to the higher proclivity of ferrocene derivatives to undergo electrophilic attacks.[8]

The reaction of imine **1d** with $Na_2[PdCl_4]$ and $Na(O_2CMe)\cdot 3H_2O$ (in a 1 : 1 : 1 molar ratio) in methanol for 3 h [equation (*b*)] in Scheme 2 produced a brown precipitate. This material consisted of palladium metal and a 1 : 1 mixture of two dichloro-bridged cyclopalladated complexes in a *ca.* 1 : 1 molar ratio. One of them contains an endocyclic six-membered palladacycle with a $\sigma(Pd\text{–}C_{sp^3,\ aliphatic})$ bond (**6d**) fused with the benzene ring, while for the other component there is also an identically sized metallacycle fused with the ferrocenyl moiety (**7d**). Consequently, in this case the metallacycle does not contain the funtional group >C=N– (exocyclic). These findings are particularly important, since they reveal that the *endo* effect is strong enough partially to induce activation of a



Scheme 2 (*i*) $Na_2[PdCl_4]$, $Na(O_2CMe)$, MeOH, r.t., 3 h; (*ii*) PPh_3, C_6H_6

$\sigma(C_{sp^3,\ aliphatic}–H)$ bond *versus* that of a $\sigma(C_{sp^2,\ ferrocene}–H)$ bond, which is more liable to undergo electrophilic attacks.[8] Early studies based on cyclopalladation of $PhCH_2CH_2N{=}CH(C_6H_2Me_3$-2,4,6) have shown that, although there were also two different kinds of C–H bond which could be activated ($C_{sp^2,\ phenyl}$–H or C_{sp^3}–H) for this substrate, the endocyclic six-membered metallacycles with a $\sigma(Pd–C_{sp^3})$ bond were obtained exclusively, with no evidence of the formation of the exocyclic metallacycles, through activation of the $C_{sp^2,\ phenyl}$–H bonds.[5] Consequently, the formation of complex **7d** can be explained in terms of the higher proclivity of ferrocene derivatives, when compared with their benzene analogues, to undergo electrophilic attacks.[8]

To sum up, the results summarized in Schemes 1 and 2 reveal the importance of the *endo* effect in the cyclopalladation of ferrocenyl Schiff bases of general formula $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4CH_2CH_2N{=}CR(R')\}]$. Of all the reactions described in this work, cyclopalladation of compound **1d** is probably the best example to illustrate this fact. For this substrate, two identically sized [six-membered endo- (**6d**) and exo-cyclic (**7d**)] palladacycles, which differ in the nature of the metallated C atom ($C_{sp^2,\ ferrocene}$ or C_{sp^3}) were obtained. It is worth noting that in this case the *endo* effect is so strong that it even permits the activation of a $\sigma(C_{sp^3}–H)$ bond (**6d**), which is less reactive.

Characterization.—All the compounds prepared in this work are yellow-orange solids at room temperature (*ca.* 20 °C), and exhibit high solubility in most common solvents, except for the dichloro-derivatives **6d** and **7d**, which are more insoluble. Elemental analyses (see Experimental section) for all the compounds are consistent with the formulae proposed. The most relevant feature of the infrared spectra of the **1a**–**1f** is the presence of a sharp absorption band in the range 1630–1650 cm^{-1}, which is assigned to the asymmetric stretching of the $>C{=}N–$ group. For the palladated derivatives this band appears at lower wavenumbers.

Proton NMR data for compounds **1a**–**1f** and the palladium compounds are presented in Table 1. It should be noted that only one conformer of **1a**–**1f** was detected and the positions of the signals are consistent with those reported for related ferrocenylimines,[6,7,10] for which an *anti* conformation has been postulated. The most outstanding feature is the presence of two triplets at *ca.* δ 2.6–2.8 and 3.0–3.6 (assigned to the two CH_2 entities) and a group of three signals with relative intensities 2:5:2 in the range δ 3.5–4.5 (due to the three types of proton of the ferrocenyl moiety: H^2, H^5; C_5H_5; and H^3, H^4). For imines **1e** and **1f** the number of signals observed in this area is higher due to the presence of two $(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)$ fragments.

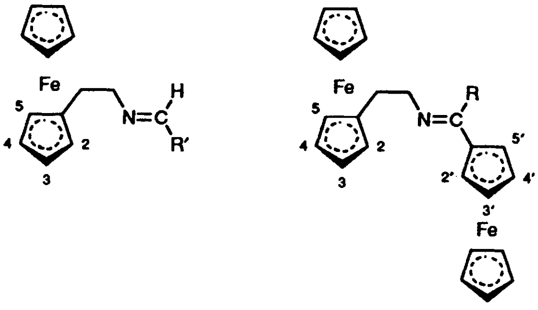
Proton NMR studies on cyclopalladated compounds derived from ligands containing the –CH=N– moiety have shown that the variation observed in the position of the iminic hydrogen in the free imines upon cyclopalladation is indicative of the structure (endo- or exo-cyclic) and conformation of the ligand (*anti* or *syn*) in the metallated complex.[11,12] It is well known that for the endocyclic palladacycles (which can be formed only if the imine has an *anti* conformation) the signal is shifted to high field,[4,5] thus on this basis we can deduce that in compounds **2a**, **2b**, **3e** and **6d** the metallacycle contains the functional group. Furthermore, we have previously shown that for the endocyclic five-membered cyclopalladated complexes of general formula $[Pd\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3CMe{=}NR')\}Cl(PPh_3)]$ the resonance of the methyl protons is shifted downfield,[6b] in the same direction as that observed in the comparison of the ^1H NMR spectra of **1f** and complex **3f**. Consequently, we can also postulate that in this case the metallacycle is also endocyclic.

For the exocyclic derivatives the ligand can adopt the two conformations, but for the *syn* conformation the proximity of the methinic proton to the palladium usually produces a downfield shift of the signal,[4,5] while if the ligand maintains the *anti* conformation this resonance does not vary appreciably from the position observed for the free imine.[11,12] Consequently, we can conclude that in the exocyclic compounds **5c** and **7d** the conformation of the imine is *syn*. This type of arrangement provides less steric hindrance between the ligands bound to the palladium and the aryl ring. Therefore, in these cases the cyclopalladation reaction involves the *anti* ⟶ *syn* isomerization of the ligand.

Carbon-13 NMR data for the ligands and some cyclopalladated complexes are presented in Table 2, and in all cases the number of signals and their multiplicities are consistent with the structures proposed.

Compounds **2a**, **2b**, **3e**, **3f** and **5c** have also been characterized by ^{31}P NMR spectroscopy. In all cases the spectrum showed a singlet in the range δ 30–45 (see Experimental section) the

Table 1 Selected ^1H NMR data (in ppm) for the Schiff bases **1a**–**1f** and the palladated compounds



1a–**1d**

1e R = H
1f R = Me

Compound	CH=N	H^2, H^5	H^3, H^4	C_5H_5	$CH_2{}^a$	CH_2N^a	CH_3
1a	8.04	3.97	3.96	3.99	2.63	3.02	—
1b	8.64	4.10	4.02	4.11	2.75	3.80	—
1c	8.38	4.16	4.07	4.13	2.79	3.86	—
1d	8.46	4.13	4.05	4.12	2.74	3.76	2.27^b
							2.35
1e	8.04	4.07^c	4.06^c	4.13^c	2.70	3.59	—
		4.62	4.37	4.16	2.70	3.59	—
1f	—	4.20^c	*c*	4.08^c	2.74	3.53	2.05
		4.70	4.35	4.13			
2a	7.80^d	4.04	4.10	4.13	2.92	*e*	—
2b	8.33^d	4.07	4.12	4.14	2.95	3.82	—
3e	7.97^d	4.05^c	4.13^c	4.15^c	2.70^f	4.09^g	—
		4.37	4.20^h	3.85	3.15^f	3.90^g	
			3.34^i				
3f	—	4.02^c	4.09^c	4.17^c	2.55^f	*e*	2.10
		4.30	4.15^h	3.82	3.05^f	*e*	
			3.28^i				
4c	8.37	4.07	4.16	4.14	2.81	3.88	—
5c	8.70	4.05	4.08	4.13	2.71^f	3.52	—
			3.70		3.23^f		
6d	8.09	4.23	4.15	4.30	2.82^f	*e*	2.33
							2.22
							3.40
7d	8.70	3.97	4.10	3.84	2.82	*e*	2.47
			3.87				2.16

[a] Triplets, except where noted. [b] Methyl groups at positions 2 and 6. [c] These resonances correspond to the protons of the (η^5-C_5H_5)$FeC_5H_4CH_2$ unit. [d] Doublet due to phosphorus coupling. [e] Overlapped by the signal due to the C_5H_5 protons. [f] Broad; the two protons are not equivalent. [g] Partially overlapped. [h] $H^{4'}$. [i] $H^{3'}$.

Table 2 Selected ^{13}C NMR spectral data (in ppm)[a] for the new ferrocenyl Schiff bases and some of the cyclopalladated complexes

Compound	>C=N–	C_5H_5	C^2, C^5	C^3, C^4	CH_2N	CH_2
1b	158.00	68.53	67.37	68.41	63.01	31.30
1c	157.35	69.65	69.00	67.88	64.17	31.57
1d	161.18	68.56	67.34	64.17	64.17	31.64
1e	161.64	68.51	69.49	67.35	62.91	31.38
		69.13^b	70.49^b	*b*, *c*		
1f[d]	*e*	68.52	67.75	67.29	53.11	30.96
		69.19^b	67.30^b	70.18^b		
2a[f]	176.01^g	68.80	68.60	67.41	60.56	31.15
3e[h]	*e*	70.08	70.52	67.87	59.49	31.18
		69.36^b	*b*, *c*	68.87^b		
3f[i]	180.12^g	70.33^b	68.66^b	66.29^b	52.43	30.14
		69.19	69.04	67.83		

[a] Labelling refers to the schemes shown in Table 1. [b] Carbon atoms belonging to the (η^5-C_5H_5)Fe(η^5-$C_5H_4CR{=}N$) moiety. [c] Partially overlapped by the remaining signals of the two C_5H_4 rings. [d] Additional signal at δ 11.96 due to the methyl group at the iminic carbon atom. [e] Not observed due to its low intensity. [f] Additional signals at: δ 128.06, 130.63, 131.4 and 135.04, due to the carbon atoms of the PPh_3 ligand, and at δ 123.80, 128.06 and 135.50 due to the phenyl carbon atoms. [g] Doublets due to phosphorus coupling. [h] Additional signals: four doublets at δ 128.01, 130.41, 131.74 and 134.86 due to the four types of carbon nuclei of the PPh_3 ligand. [i] Additional signals at δ 15.24 (d) due to the CH_3 carbon, and four doublets at δ 127.98, 129.92, 131.52 and 134.89 due to the phenyl carbon atoms of the phosphine.

position of which is consistent with the values reported for related five-membered cyclopalladated derivatives containing a σ($Pd{-}C_{sp^2,\ phenyl}$) or a σ($Pd{-}C_{sp^2,\ ferrocene}$) bond in which the iminic nitrogen and the phosphine ligand are in a *trans*

Table 3 Final atomic coordinates [× 10^5 for Pd, Fe, Cl(1), P; × 10^4 others] for non-hydrogen atoms in compound **2a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	6 005(2)	15 471(2)	16 086(1)
Fe	44 839(4)	−18 853(4)	27 161(3)
Cl(1)	−13 019(8)	1 807(7)	17 011(6)
P	−1 041(7)	30 563(6)	24 321(4)
N	1 424(3)	224(2)	882(2)
Cl(2)	9 531(2)	−2 195(1)	4 047(1)
Cl(3)	11 207(2)	42(1)	3 999(1)
C(1)	3 444(4)	−2 433(4)	3 642(3)
C(2)	4 151(6)	−3 347(4)	3 316(3)
C(3)	5 553(6)	−2 877(6)	3 488(4)
C(4)	5 667(5)	−1 695(6)	3 899(3)
C(5)	4 385(5)	−1 470(4)	3 991(3)
C(6)	4 020(3)	−433(3)	2 133(2)
C(7)	5 366(4)	−626(4)	2 080(3)
C(8)	5 330(4)	−1 762(5)	1 632(3)
C(9)	3 943(4)	−2 292(4)	1 405(2)
C(10)	3 115(3)	−1 461(3)	1 721(2)
C(11)	1 604(3)	−1 575(3)	1 573(2)
C(12)	1 013(3)	−1 066(3)	768(2)
C(13)	2 459(3)	623(3)	589(2)
C(14)	2 961(3)	1 884(3)	812(2)
C(15)	4 134(4)	2 389(4)	555(2)
C(16)	4 599(3)	3 574(4)	804(2)
C(17)	3 898(3)	4 264(3)	1 324(2)
C(18)	2 735(3)	2 772(3)	1 583(2)
C(19)	2 220(3)	2 560(3)	1 349(2)
C(20)	1 154(3)	3 711(3)	3 389(2)
C(21)	911(4)	4 647(4)	3 968(3)
C(22)	1 847(5)	5 080(4)	4 717(3)
C(23)	3 019(4)	4 582(4)	4 896(2)
C(24)	3 252(4)	3 658(4)	4 346(3)
C(25)	2 336(4)	3 219(4)	3 590(2)
C(26)	−1 595(3)	2 664(2)	2 923(2)
C(27)	−1 443(3)	2 162(3)	3 678(2)
C(28)	−2 555(4)	1 838(3)	4 058(2)
C(29)	−3 824(4)	2 027(4)	3 682(3)
C(30)	−3 994(4)	2 527(4)	2 938(3)
C(31)	−2 887(3)	2 842(4)	2 548(2)
C(32)	−644(3)	4 254(2)	1 823(2)
C(33)	−896(6)	4 025(4)	953(2)
C(34)	−1 409(6)	4 878(5)	464(3)
C(35)	1 692(4)	4 076(4)	−844(3)
C(36)	−1 398(7)	6 163(4)	1 688(4)
C(37)	−897(8)	5 325(4)	2 189(3)
C(38)	9 610(6)	−768(6)	3 719(4)

Table 4 Selected bond lengths (Å) and angles (°) for complex **2a** with e.s.d.s in parentheses

Cl(1)–Pd	2.356(1)	P–Pd	2.258(1)
N–Pd	2.091(3)	C(19)–Pd	2.008(3)
C(2)–C(1)	1.404(7)	C(3)–C(2)	1.418(8)
C(4)–C(3)	1.399(9)	C(5)–C(1)	1.361(6)
C(5)–C(4)	1.358(8)	C(7)–C(6)	1.399(5)
C(8)–C(7)	1.384(7)	C(9)–C(8)	1.424(6)
C(10)–C(6)	1.417(4)	C(10)–C(9)	1.413(5)
C(11)–C(10)	1.481(4)	C(12)–C(11)	1.516(5)
C(12)–N	1.455(4)	C(13)–N	1.261(4)
C(14)–C(13)	1.443(4)	C(15)–C(14)	1.389(5)
C(16)–C(15)	1.361(5)	C(17)–C(16)	1.383(5)
C(18)–C(17)	1.377(5)	C(19)–C(14)	1.418(4)
C(19)–C(18)	1.397(4)		
P–Pd–Cl(1)	92.9(1)	N–Pd–Cl(1)	91.5(1)
N–Pd–P	175.1(1)	C(19)–Pd–Cl(1)	171.0(1)
C(19)–Pd–P	94.9(1)	C(19)–Pd–N	80.9(1)
C(11)–C(10)–C(6)	126.3(3)	C(11)–C(10)–C(9)	127.4(3)
C(12)–C(11)–C(10)	112.8(3)	C(11)–C(12)–N	109.6(2)
C(14)–C(13)–N	118.3(3)	C(15)–C(14)–C(13)	122.2(3)
C(14)–C(19)–Pd	111.7(2)	C(18)–C(19)–Pd	133.1(2)

arrangement.[4–7] For complex **4c**, which contains two PPh_3 ligands bound to the palladium, the singlet appears at higher fields (δ 29.36), in good agreement with the values reported for compounds $[PdLCl(PPh_3)_2]$.[4,5]

Crystal Structure of Compound **2a**.—A perspective drawing of the molecular structure of compound **2a** and the atom labelling scheme are presented in Fig. 1. Final atomic coordinates for non-hydrogen atoms as well as a selection of bond lengths and angles are given in Tables 3 and 4 respectively. The structure consists of discrete molecules of $[Pd\{C_6H_4CH{=}NCH_2CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ packed by van der Waals forces. Two molecules of CH_2Cl_2 as solvate are also contained in the unit cell.

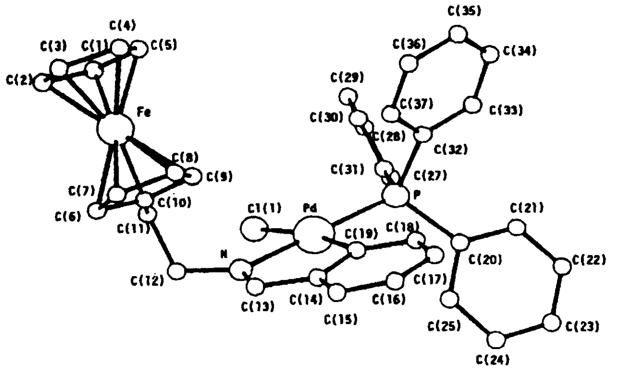


Fig. 1 Molecular structure and atom labelling scheme for the compound $[Pd\{C_6H_4CH{=}N(CH_2)_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]\cdot CH_2Cl_2$ **2a**

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(19) atom of the phenyl ring (Fig. 1, Table 4). Maximum deviations from the least-squares plane defined by Pd, P, Cl(1), N and C(19) are +0.016 (Pd), +0.053 (P), −0.060 [Cl(1)], +0.067 (N) and −0.076 Å [C(19)]. The metallacycle is formed by the palladium atom, the nitrogen and carbon atoms involved in the iminic bond and two carbons [C(14) and C(19)] of the phenyl ring, thus confirming the formation of an *endo* five-membered ring containing a $\sigma(Pd\text{–}C_{sp^2,\ phenyl})$ bond. It is practically co-planar with the metallated aryl ring as reflected in the angle defined by their planes, 2°.

The imine ligand has an *anti* conformation, as reflected in the torsion angle defined by the atoms C(12), N, C(13) and C(14) [−171.5°]. The Fe–C(ring) bond distances (Table 4) as well as the average C–C bond distance [1.398(7) Å] in the pentagonal rings of the ferrocenyl moiety are in good agreement with the values reported for other ferrocene derivatives.[13]

The two pentagonal rings [C(1)–C(5)] and [C(6)–C(10)] are planar and parallel (tilt angle 3.0°) and their conformation is nearly eclipsed, as reflected in the average value of the twist angle (−3.93°) defined by Palenik and Giordano.[14] The benzene ring [C(14)–C(19)] is planar and its mean plane forms an angle of 1.0° with the metallacycle.

The Pd–N bond length in complex **2a** [2.091(3) Å] is larger than the values obtained for related complexes with a $\sigma(Pd\text{–}C_{sp^2,\ phenyl})$ bond,[15–22] [2.039(6)–2.051(8) Å], but clearly shorter than in the monomeric cyclopalladated complexes with a $\sigma(\mathrm{Pd{-}C_{sp^2,\ ferrocene}})$ bond[6,23,24] [2.03(2)–2.146(5) Å], and for which the >C=N– bond length is clearly larger than in complex **2a**. This fact may be related to the different basicity of the nitrogen atom in these two types of ferrocenyl Schiff base. On the other hand the Pd–C bond length in **2a** is one of the largest reported so far for endocyclic five-membered metallacycles,[15–24] and it is practically identical to the value [2.009(3) Å] obtained for $[\mathrm{Pd(L'')Cl(PPh_3)}]$ (HL″ = 7-chloro-1-cyclopropylmethyl-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-one),[25] in which the palladacycle is involved in a tricyclic system, being fused simultaneously to a phenyl and a seven-membered ring.

Experimental

Elemental analyses (C, H and N) were carried out at the Institut de Química BioOrgànica (Consejo Superior de Investigaciónes Cientificas, Barcelona). Infrared spectra were obtained with a Nicolet 520-FTIR spectrophotometer using KBr pellets, proton and ^{13}C-{^{1}H} 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 and ^{31}P-{^{1}H} NMR spectra with a Bruker WP50-SY spectrophotometer (32.8 MHz) using $CHCl_3$ as solvent and $P(OMe)_3$ as standard.

Materials and Syntheses.—Dimethylaminomethylferrocene, ferrocenecarbaldehyde, acetylferrocene and the organic aldehydes were obtained from standard sources and used as received.

2-Ferrocenylethylamine was prepared as described in the literature[9] and purified by vacuum distillation. **CAUTION**: Most of the preparations described below require the use of benzene which should be handled with care. All the solvents, except benzene, were dried and distilled before use.

Syntheses.—$[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\{\eta^5\text{-}\mathrm{C_5H_4CH_2CH_2N{=}CR(R')}\}]$ **1a**–**1f**. The corresponding aldehyde (for **1a**–**1e**) or ketone (for **1f**) (2.0 mmol) was added to a solution containing freshly prepared 2-ferrocenylethylamine (0.45 g, 2.0 mmol) in benzene (15 cm^3). The reaction flask was connected to a condenser and a Dean-Stark apparatus, and the contents refluxed in an ethylene glycol bath until *ca.* 10 cm^3 of the benzene–water azeotrope had condensed on the Dean–Stark apparatus. Then the reaction mixture was concentrated to dryness on a rotary evaporator. Addition of hexane to the oily residue followed by vigorous stirring at room temperature produced the precipitation of the ferrocenyl Schiff bases, yields 55, 50, 50, 40, 50 and 30% for **1a**–**1f**, respectively: **1a** [Found (Calc. for $C_{19}H_{19}FeN$): C, 72.3 (71.95); H, 6.4 (6.0); N, 4.2 (4.4)%], IR ν(C=N) 1634 cm^{-1}; **1b** [Found (Calc. for $C_{19}H_{18}ClFeN$): C, 65.1 (64.90); H, 5.3 (5.15); N, 3.7 (3.9)%], IR ν(C=N) 1620 cm^{-1}; **1c** [Found (Calc. for $C_{19}H_{17}Cl_2FeN$): C, 59.2 (59.1); H, 4.7 (4.45); N, 3.4 (3.6)%], IR ν(C=N) 1647 cm^{-1}; **1d** [Found (Calc. for $C_{22}H_{25}FeN$): C, 73.4 (73.55); H, 7.1 (7.0); N, 3.9 (3.9)%], IR ν(C=N): 1636 cm^{-1}; **1e** [Found (Calc. for $C_{23}H_{23}Fe_2N$): C, 65.0 (65.0); H, 5.6 (5.45); N, 3.0 (3.3)%], IR ν(C=N) 1640 cm^{-1}; **1f** [Found (Calc. for $C_{24}H_{25}Fe_2N$): C, 65.8 (65.6); H, 5.7 (5.75); N, 3.3 (3.2)%], IR ν(C=N) 1630 cm^{-1}.

$[\mathrm{Pd\{3\text{-}XC_6H_3CH{=}NCH_2CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)}]$ (X = H **2a** *or* Cl **2b**). The corresponding imine (**1a** or **1b**) (1.0 mmol), $Na_2[PdCl_4]$ (1.0 mmol, 0.294 g) and $Na(O_2CMe){\cdot}3H_2O$ (1.0 mmol) were suspended in methanol (20 cm^3). The reaction flask was protected from the light (with aluminium foil) and the mixture stirred for 3 h at room temperature. The solid formed was washed with methanol until the washings were colourless, and air-dried. Later, this yellowish material was suspended in benzene (10 cm^3) and treated with triphenylphosphine (1.0 mmol). The resulting solution was stirred at room temperature for 30 min, and the undissolved black material was filtered off and discarded. The yellow filtrate was concentrated to dryness on a rotary evaporator and the oily gummy residue treated with hexane to precipitate the compound. The microcrystalline product formed was filtered off and air-dried. Yields: 40% for **2a** and 15% for **2b**. These complexes were recrystallized by slow evaporation of CH_2Cl_2–hexane (1:1) mixtures. **2a** [Found (Calc. for $C_{37}H_{33}ClFeNPPd{\cdot}CH_2Cl_2$): C, 56.5 (56.8); H, 4.4 (4.35), N, 1.7 (1.7)%], IR ν(C=N) 1618 cm^{-1}, ^{31}P NMR δ 43.04; **2b** [Found (Calc. for $C_{37}H_{32}Cl_2FeNPPd$): C, 58.6 (58.85); H, 4.3 (4.3); N, 2.1 (1.85)%], IR ν(C=N) 1614 cm^{-1}, ^{31}P NMR δ 41.6.

$[\mathrm{Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3C(R){=}NCH_2CH_2(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)}]$ (R = H **3e** *or* Me **3f**). Equimolar amounts of the imine **1e** (0.44 g, 1.05 mmol), $Na_2[PdCl_4]$ (0.30 g, 1.0 mmol) and $Na(O_2CMe){\cdot}3H_2O$ (0.13 g, 1.0 mmol) were suspended in methanol (20 cm^3). The reaction mixture was protected from the light (with aluminium foil) and stirred at room temperature for 3 h. Then the solid formed was filtered off, washed with three (10 cm^3) portions of methanol and air-dried. This material was suspended in benzene (15 cm^3) and triphenylphosphine (1.05 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and the undissolved materials were filtered off and discarded. The red-orange filtrate was concentrated to dryness on a rotary evaporator. Addition of hexane to the oily residue produced a precipitate of complex **3e**. Yield: 45% [Found (Calc. for $C_{41}H_{37}ClFe_2NPPd$): C, 55.8 (55.25); H, 4.5 (4.3); N, 1.7 (1.5)%], IR ν(C=N) 1635 cm^{-1}, ^{31}P NMR δ 37.29.

Compound **3f** was prepared similarly, but using the stoichiometric amount of **1f** as starting material. Yield: 40% [Found (Calc. for $C_{42}H_{39}ClFe_2NPPd$): C, 59.3 (59.4); H, 4.5 (4.45); N, 1.6 (1.7)%], IR ν(C=N) 1602 cm^{-1}, ^{31}P NMR δ 35.67.

$[\mathrm{Pd\{3\text{-}ClC_6H_4CH{=}NCH_2CH_2C_5H_4Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)_2}]$ **4c** *and* $[\mathrm{Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3CH_2CH_2N{=}CHC_6H_3Cl_2\text{-}2,6]\}Cl(PPh_3)}]$ **5c**. The Schiff base: **1c** (0.386 g, 1.0 mmol), $Na_2[PdCl_4]$ (0.294 g, 1.0 mmol) and $Na(O_2CMe){\cdot}3H_2O$ (0.136 g, 1.0 mmol) were suspended in methanol (20 cm^3) and stirred at room temperature for 3 h. During this period the reaction vessel was protected from the light with aluminium foil. The solid formed was filtered off, washed with methanol and air-dried. Then this material was treated with triphenylphosphine (1.0 mmol, 0.262 g) in benzene (10 cm^3) for 30 min. The undissolved materials were filtered off and discarded, and the filtrate was concentrated to dryness in a rotary evaporator. The brownish residue was then dissolved in the minimum amount of chloroform and passed through a SiO_2 column, using $CHCl_3$ as eluent. Three fractions were collected, and each concentrated to dryness on a rotary evaporator and treated with hexane to induce precipitation. The first band eluted gave the co-ordination compound $[\mathrm{PdCl_2(PPh_3)_2}]$. Compounds **4c** and **5c** were obtained from the second and third eluted fractions respectively. Yields: 15% **4c** and *ca.* 5% **5c**: **4c** [Found (Calc. for $C_{55}H_{47}ClFeNP_2Pd$): C, 65.2 (64.95); H, 4.7 (4.6); N, 1.3 (1.4)%], ^{31}P NMR δ 29.24; **5c** [Found (Calc. for $C_{37}H_{31}Cl_2FeNPPd$): C, 56.4 (56.1); H, 5.9 (6.05); N, 2.2 (2.2)%], ^{31}P NMR δ 37.58.

$[\{\mathrm{Pd[(CH_2C_6H_2Me_2\text{-}3,5)CH{=}NCH_2CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)}\}_2]$ **6d** *and* $[\{\mathrm{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2CH_2N{=}CHC_6H_2Me_3\text{-}2,4,6)](\mu\text{-}Cl)}\}_2]$ **7d**. Compound **1d** (0.90 g, 2 mmol), $Na_2[PdCl_4]$ (0.735 g, 2.5 mmol) and $Na(O_2CMe){\cdot}3H_2O$ (0.325 g, 2.5 mmol) were suspended in methanol (30 cm^3). The reaction mixture was protected from the light and stirred at room temperature for 3 h. The insoluble material formed was filtered off, washed with three (10 cm^3) portions of methanol and air-dried. The solid was then

Table 5 Crystallographic data and details of refinement for compound **2a**

Formula	$C_{37}H_{33}ClFeNPPd \cdot CH_2Cl_2$
M	805.29
Crystal size/mm	0.1 × 0.1 × 0.1
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.995(1)
b/Å	11.308(2)
c/Å	15.747(2)
α/°	96.85(1)
β/°	99.05(1)
γ/°	95.99(1)
U/Å^3	1731.2(7)
D_c/g cm^{-3}	1.544
Z	2
F(000)	816.0
λ(Mo-Kα)/Å	0.710 69
μ(Mo-Kα)/cm^{-1}	12.43
No. of measured reflections	9886
No. of reflections with $I \geqslant 2.5\sigma(I)$	7265
Range of θ/°	2–30
R	0.036
R'	0.037
No. of refined parameters	514
Maximum shift/e.s.d.	0.1
Maximum and minimum peaks in the final difference map/e Å^{-3}	+0.3 and −0.3

dissolved in chloroform and passed through an SiO_2-column chromatograph using $CHCl_3$ as eluent. The yellow band was collected and concentrated to dryness in vacuum, and later treated with hexane, followed by vigorous stirring for 1 h at room temperature. The microcrystalline solid obtained (a 1 : 1 mixture of complexes (**6d** and **7d**) was filtered off and air-dried. Yield 20%: **6d**, **7d**. [Found (Calc. for $C_{37}H_{33}ClFeNPd$): C, 53.0 (52.85); H, 4.7 (4.65); N, 2.6 (2.8)%], IR ν(C=N) 1612 (**6d**, *endo*), 1638 cm^{-1} (**7d**, *exo*).

Crystal Structure Determination and Refinement.—A prismatic crystal of compound **2a** was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were determined from the automatic centring of 25 reflections in the range $16 \leqslant \theta \leqslant 21°$ and refined by the least-squares method. Intensities were collected with graphite-monochromated Mo-Kα radiation using the ω–2θ scan technique. Three reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed. The number of collected reflections and the ranges are listed in Table 5. Corrections were applied for Lorentz-polarization but not for absorption.

The structure was solved by Patterson synthesis using the SHELXS computer program[26] and refined by a full-matrix least-squares method with SHELX 76.[27] The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.003|F_o|^2]^{-1}$. Values of f, f' and f'' were taken from ref. 28. All hydrogen atoms were found from a difference synthesis and refined with an overall isotropic thermal parameter, while the positions of the remaining atoms were refined anisotropically. The final R and R' factors were calculated according to the expresions $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $[\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, and their values are presented in Table 5 together with the number of parameters refined and the maximum and minimum peaks in the final difference synthesis.

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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