Palladium(II)-induced Preferential Activation of the $\sigma[C_{sp^2}$(phenyl)–Cl] Bond *versus* $\sigma[C_{sp^2}$(ferrocene)–H]. Crystal Structure of $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4CH_2N{=}CH(C_6H_3Cl_2-2,6)\}]$†

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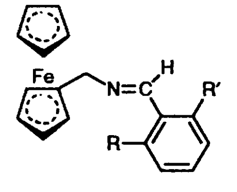
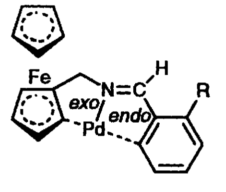
The ferrocenylimine $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4CH_2N{=}CH(C_6H_3Cl_2-2,6)\}]$ has been prepared by condensation of aminomethylferrocene and 2,6-dichlorobenzaldehyde, and characterized by IR, NMR (^1H and ^{13}C) spectroscopy and X-ray diffraction. The compound is triclinic, space group $P\bar{1}$, with a = 7.553(3), b = 11.763(2), c = 18.148(2) Å, α = 89.94(1), β = 98.90(2) and γ = 91.91(2)°. It reacts with $Na_2[PdCl_4]$ and $NaO_2CMe{\cdot}3H_2O$ in a 1:1:1 molar ratio, producing the di-μ-chloro-bridged cyclopalladated complex $[\{Pd[(3-ClC_6H_3)CH{=}NCH_2(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)](\mu-Cl)\}_2]$. Further treatment of this compound with triphenylphosphine results in cleavage of the 'Pd(μ-Cl)$_2$Pd' units, yielding the monomeric derivative $[Pd\{(3-ClC_6H_3)CH{=}NCH_2(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)\}Cl(PPh_3)]$. These compounds contain an endocyclic five-membered palladocycle fused with the phenyl ring and arise by activation of a σ(C–Cl) bond. The reactivity of *N*-(2,6-dichlorobenzylidene)benzylamine and the analogous ferrocenyl Schiff bases is compared.

Ferrocene derivatives containing atoms with good donor abilities (*i.e.* nitrogen, sulfur, oxygen, phosphorus, *etc.*) have attracted much interest, as the co-ordination of a metal to these heteroatoms generates multicentre molecules which have potential in many different areas.[1] In compounds of this type the presence of proximal metals having different environments and oxidation/spin states may influence the mutual co-operation of these metals in a wide variety of processes, including their reactivity towards external substrates. For instance, it is well known that palladium compounds containing $\sigma[Pd-C_{sp^2}$(ferrocene)] bonds derived from (dimethylaminomethyl)ferrocene or Schiff bases of general formula $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CR{=}NR')]$ (R = H, Me or Ph, R′ = Ph, C_6H_4Me-2, C_6H_4Me-4, CH_2Ph, $CH_2C_6H_4Cl-2$, $CH_2C_6H_4Me-2$ or CH_2CH_2Ph) have provided new pathways for the syntheses of novel ferrocene derivatives,[2] some of which are analogues of prostaglandins or oestradiol.[3]

We have recently reported the synthesis and cyclopalladation reactions of two novel ferrocenyl Schiff bases derived from aminomethylferrocene of general formula $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4CH_2N{=}CH(C_6H_4R_2-2)\}]$ (R = H **1a** or Cl **1b**),[4,5]. In the two cases metallation occurs at the aryl ring, *via* activation of a $\sigma[C_{sp^2}$(phenyl)–H] bond, giving $[\{Pd[(3-RC_6H_3)CH{=}NCH_2(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)](\mu-Cl)\}_2]$ (R = H **2a** or Cl **2b**) and the formation of small amounts of the exocyclic five-membered metallacycle $[\{Pd[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3)CH_2N{=}CHPh](\mu-Cl)\}_2]$ **2a′** was detected only for substrate **1a** (Scheme 1). From these results it was decided to prepare the ferrocenylimine $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4CH_2N{=}CH(C_6H_3Cl_2-2,6)\}]$ **1c** and to study its cyclopalladation reaction. Since, in this substrate, the two *ortho* positions of the phenyl ring are occupied by chlorines, if metallation takes place, the formation of the exocyclic palladocycle through activation of a $\sigma[C_{sp^2}$(ferrocene)–H] bond should be expected. However, the so-called *endo* effect is strong enough to induce the activation of the $\sigma[C_{sp^2}$(phenyl)–Cl] bond instead of the expected $\sigma[C_{sp^2}$(ferrocene)–H].



R = H, R′ = H **1a** or Cl **1b**
R = R′ = Cl **1c**



Results and Discussion

The new ferrocenyl Schiff base $[Fe\eta^5(C_5H_5)\{\eta^5-C_5H_4CH_2N{=}CH(C_6H_3Cl_2-2,6)\}]$ **1c** was prepared by condensation of 2,6-dichlorobenzaldehyde and freshly prepared aminomethylferrocene,[5] using a 1:1 molar ratio and benzene as solvent. The success of the syntheses is highly dependent on the quality of the ferrocenylamine. The imine **1c** is a yellow solid at room temperature and is highly soluble in most common solvents such as chloroform, benzene, dichloromethane and alcohols, but practically insoluble in hexane. It has been characterized by elemental analyses, IR and NMR (^1H and ^{13}C) spectroscopies and its crystal structure has also been solved and refined. Elemental analyses are consistent with the proposed formula (see Experimental section). The infrared spectrum shows a sharp intense band due to the asymmetric stretching of the $\rangle C{=}N-$group at *ca.* 1644 cm^{-1}.

One of the most relevant features observed in the ^1H NMR spectrum of compound **1c** is the existence of four signals of relative intensities 2:2:2:5 in the range δ 3.7–5.0, which are

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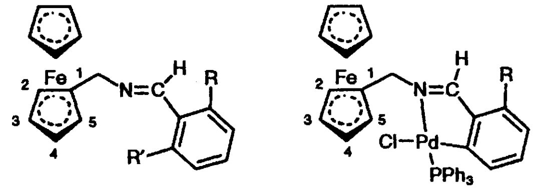
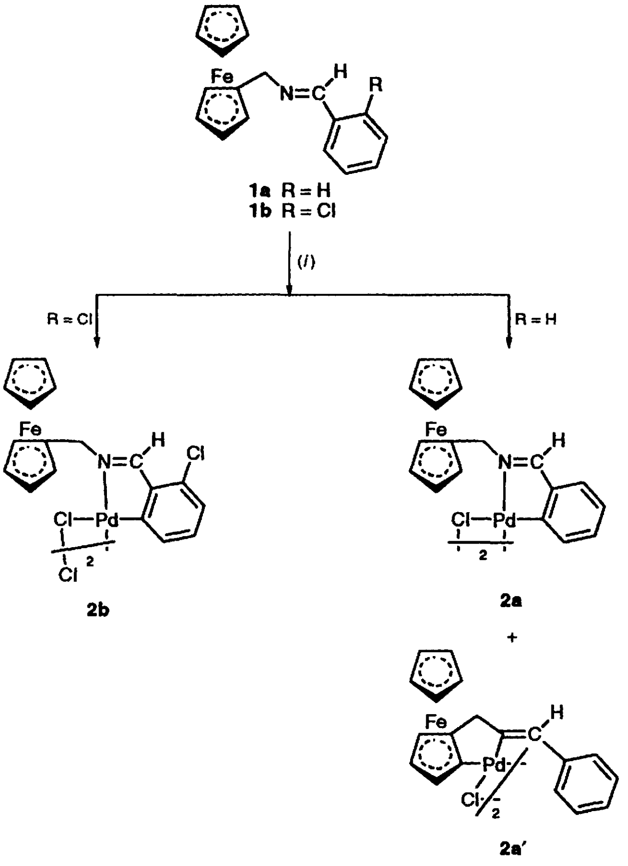
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Most relevant ^1H NMR data (in ppm)[a] for the ferrocenylimines $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2N{=}CHR)]$ **1a**–**1c** and the cyclopalladated complexes



	C_5H_5	H(2), H(5)	H(3), H(4)	CH_2	CH=N
Ferrocenylimines					
1a $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2N{=}CHPh)]$[b]	4.16	4.24	4.23	4.58	8.75
1b $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2N{=}CH(C_6H_4Cl\text{-}2)\}]$[b]	4.16	4.15	4.21	4.55	8.29
1c $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2N{=}CH(C_6H_3Cl_2\text{-}2,6)\}]$	4.17	4.16	4.24	4.66	8.44
Cyclopalladated complexes					
2a $[\{\overline{Pd[C_6H_4CH{=}N}CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)\}_2]$[c]	4.20	4.22	4.31	4.96	7.67
2b $[\{\overline{Pd[(3\text{-}ClC_6H_3)CH{=}N}CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)\}_2]$[b,c]	4.21	4.23	4.35	4.94	8.36
3a $[\overline{Pd\{C_6H_4CH{=}N}CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$[b]	4.18	4.23	4.30	5.06	7.87[d]
3b $[\overline{Pd\{(3\text{-}ClC_6H_3)CH{=}N}CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$	4.17	4.22	4.33	5.05	8.39[d]

[a] Labelling refers to the schemes shown. [b] Data from ref. 4. [c] Spectrum recorded in the presence of deuteriated pyridine C_5D_5N. [d] Doublet due to phosphorus coupling.



Scheme 1 (*i*) $Na_2[PdCl_4]$, $NaO_2CMe{\cdot}3H_2O$, MeOH, room temperature, 3 h

assigned to the CH_2 protons, the pairs H(2), H(5) and H(3), H(4) and the C_5H_5 ring, respectively (Table 1). At lower fields a singlet due to the imine proton is also observed. The position of the signal depends on the nature of the substituent at the iminic carbon atom (C_6H_5, C_6H_4Cl-2 or $C_6H_3Cl_2$-2,6) (Table 1). This feature has also been observed for the analogous *N*-(benzylidene)benzylamines previously reported.[6] The ^{13}C NMR spectrum (Table 2) is also consistent with those reported for related ferrocenyl Schiff bases.[4,7]

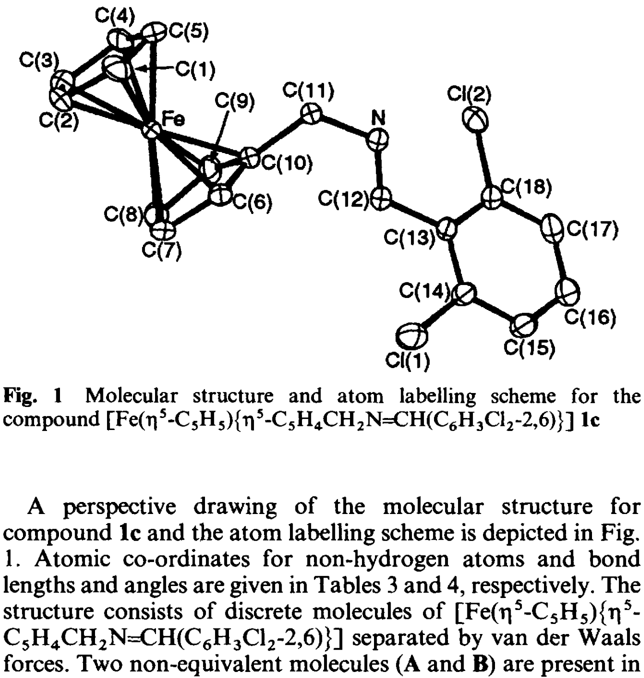


Fig. 1 Molecular structure and atom labelling scheme for the compound $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2N{=}CH(C_6H_3Cl_2\text{-}2,6)\}]$ **1c**

A perspective drawing of the molecular structure for compound **1c** and the atom labelling scheme is depicted in Fig. 1. Atomic co-ordinates for non-hydrogen atoms and bond lengths and angles are given in Tables 3 and 4, respectively. The structure consists of discrete molecules of $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2N{=}CH(C_6H_3Cl_2\text{-}2,6)\}]$ separated by van der Waals forces. Two non-equivalent molecules (**A** and **B**) are present in the unit cell. The geometry of the $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$ moiety has averaged $Fe\text{–}C_{ring}$ and $C\text{–}C_{ring}$ bond lengths, in good agreement with data reported for ferrocene and other ferrocene derivatives.[8] The two pentagonal rings of the ferrocenyl moiety are planar and nearly parallel [tilt angles: 0.8(3) and 3.7(3)° for **A** and **B** respectively], their conformation is eclipsed as reflected in averaged twist angles[9] of 0.4(3) and −6.5(3)° for the two non-equivalent molecules.

The $\rangle C{=}N\text{–}$ bond length [average 1.234(4) Å] is slightly shorter than those obtained for ferrocenylimines of general formulae $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$[7,10] as well as for $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4N{=}CH(C_6H_4OH\text{-}2)\}]$.[11] The imine has an *anti* conformation, as reflected in the torsion angles C(11A)–N(A)–C(12A)–C(13A) and C(11B)–N(B)–C(12B)–C(13B) 176.8(3) and 177.2(3)°. Molecular models reveal that this type of arrangement provides less steric hindrance. A *cis* arrangement of the two non-hydrogen substituents of the functional group $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, and $C_6H_3Cl_2$-2,6 may be prohibited by steric factors arising

Table 2 Selected ^{13}C NMR data (in ppm)[a] for the ferrocenylimines **1a**–**1c** and the cyclopalladated complexes

	CH=N	CH_2	C(1)	C(2),C(5)	C(3),C(4)	C_5H_5
Ferrocenylimines						
1a[b]	160.87	60.03	84.95	68.03	67.86	68.54
1b[b]	158.27	60.90	86.20	68.74	68.41	69.06
1c	156.95	60.90	86.15	68.32	68.32	68.61
Cyclopalladated complexes						
3a	174.17	57.10	82.47	70.67	70.67	69.36
3b	172.30	57.13	82.09	69.98	68.79	68.79

[a] Labelling refers to the schemes in Table 1. [b] Data from ref. 4.

Table 3 Final atomic coordinates (× 10^3) for non-hydrogen atoms of compound **1c** with estimated standard deviations in parentheses

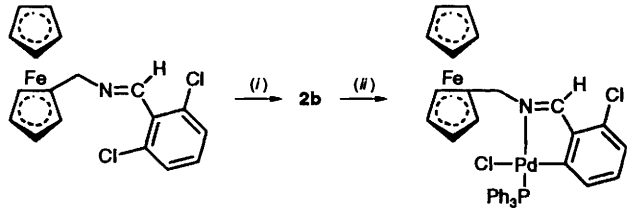
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(A)	1 717(1)	368(1)	3 376(1)	Fe(B)	3 936(1)	6 737(1)	8 868(1)
Cl(1A)	1 834(2)	−5 214(1)	3 538(1)	Cl(1B)	9 741(1)	11 032(1)	9 371(1)
Cl(2A)	2 958(2)	−3 856(1)	6 424(1)	Cl(2B)	3 479(1)	12 458(1)	7 818(1)
N(A)	2 102(5)	2 573(2)	4 941(2)	N(B)	4 375(4)	10 532(2)	8 948(2)
C(1A)	−197(6)	1 423(4)	3 419(2)	C(1B)	2 547(5)	5 956(3)	9 618(2)
C(2A)	894(5)	1 761(3)	289(2)	C(2B)	3 179(4)	5 142(3)	9 166(2)
C(3A)	776(5)	930(3)	2 358(2)	C(3B)	2 456(4)	5 368(3)	8 413(2)
C(4A)	−365(5)	36(3)	2 537(2)	C(4B)	1 382(4)	6 328(3)	8 409(2)
C(5A)	−985(4)	358(4)	3 203(3)	C(5B)	1 447(4)	6 687(3)	9 153(3)
C(6A)	3 179(5)	148(3)	4 401(2)	C(6B)	5 917(4)	7 773(3)	9 431(2)
C(7A)	4 307(4)	510(3)	3 880(2)	C(7B)	6 665(4)	6 906(3)	9 046(3)
C(8A)	4 180(4)	−335(3)	3 324(2)	C(8B)	5 993(5)	7 001(3)	8 282(3)
C(9A)	3 016(5)	−1 216(3)	3 506(2)	C(9B)	4 801(5)	7 925(3)	8 177(2)
C(10A)	2 394(5)	−913(3)	4 177(2)	C(10B)	4 785(4)	8 401(2)	8 896(2)
C(11A)	1 155(6)	−1 610(3)	4 563(2)	C(11B)	3 671(4)	9 376(2)	9 062(2)
C(12A)	1 553(4)	−3 524(3)	4 720(2)	C(12B)	5 853(4)	10 662(2)	8 735(2)
C(13A)	2 349(4)	−4 609(3)	4 989(2)	C(13B)	6 638(4)	11 802(2)	8 599(2)
C(14A)	2 444(5)	−5 478(3)	4 480(2)	C(14B)	8 444(4)	12 042(3)	8 853(2)
C(15A)	3 084(5)	−6 540(3)	4 684(3)	C(15B)	9 272(5)	13 080(3)	8 730(2)
C(16A)	3 626(5)	−6 750(3)	5 424(3)	C(16B)	8 265(5)	13 906(3)	8 338(2)
C(17A)	3 571(5)	−5 924(3)	5 945(2)	C(17B)	6 500(5)	13 702(3)	8 076(2)
C(18A)	2 948(5)	−4 859(3)	5 728(2)	C(18B)	5 703(4)	12 666(2)	8 203(2)

from the proximity of one of the *o*-chlorines and the protons of the CH_2 moiety.

The phenyl ring is planar and the angle defined by its plane and the C(13)–C(12)–N in each of the two non-equivalent molecules is 39.34(3) and 43.47(3)° for **A** and **B**, respectively. This arrangement is similar to that reported for $4\text{-MeC}_6H_4N{=}CH(C_6F_5)$.[12]

The 2,6-dichlorophenyl ring is asymmetrically bound to the C(12) carbon atom, as reflected in the bond angles C(12)–C(13)–C(14) and C(12)–C(13)–C(18) [averages for the two molecules 119.1(3) and 124.8(3)°, respectively]. Furthermore, the larger C(13)–C(18)–Cl(2) bond angle [as compared with C(17)–C(18)–Cl(2)] suggests that the Cl(2) atom tends to move away from the imine nitrogen and thus reduce the electronic repulsion between the lone pairs on these atoms [N and Cl(2)]. This type of distortion has also been found for the organic imine $4\text{-MeC}_6H_4N{=}CH(C_6F_5)$,[12] in which the *ortho* positions of the aryl ring are occupied by fluorine. The distance between the imine hydrogen and the Cl(2) atom is clearly smaller [2.728(5) and 2.638(5) Å] than the sum of the van der Waals radii of these two atoms (Cl, 1.75, H, 1.20 Å).[13] However, the two C–Cl bond distances [averages C(14)–Cl(1) 1.733(4) and C(18)–Cl(2) 1.722(4) Å] are only slightly different (if significant, since they do not clearly exceed 3σ).

In order to study the cyclopalladation of compound **1c** the general procedure described before for $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$[14] and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$[7] was used. The method was based on the reaction of the ferrocenyl Schiff base **1c**, $Na_2[PdCl_4]$ and $NaO_2CMe{\cdot}3H_2O$ in a 1 : 1 : 1 molar ratio at room temperature in methanol (for 3 h) (Scheme 2). During the course of the reaction the formation of metallic palladium was detected. The dark ochre solid formed was collected and purified by SiO_2-column chromatography using $CHCl_3$ as eluent. The band eluted was concentrated in a rotary evaporator and the residue treated with hexane at room temperature. The bright yellow solid formed was characterized by elemental analyses, infrared and ^1H NMR spectroscopies. These data are consistent with the formation of the di-μ-chloro-bridged compound $[\{\overline{Pd[(3\text{-}ClC_6H_3)CH{=}N}CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)\}_2]$ **2b** through activation of a σ(C–Cl) bond. No evidence of the formation of the dimeric exocyclic derivative $[\{\overline{Pd[\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CH_2N}{=}CH(C_6H_3Cl_2\text{-}2,6)](\mu\text{-}Cl)\}_2]$ **2c′** was detected. In order to confirm this result compound **2b** was treated at room temperature with triphenylphosphine (in a 1:2 molar ratio) giving $[\overline{Pd\{(3\text{-}ClC_6H_3)CH{=}N}CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ **3b**, which exhibits higher solubility. Proton and ^{13}C NMR spectroscopic data (Tables 1 and 2) for this complex are



1c **3b**

Scheme 2 (*i*) $Na_2[PdCl_4]$, $NaO_2CMe{\cdot}3H_2O$, MeOH, room temperature, 3 h; (*ii*) PPh_3, C_6H_6

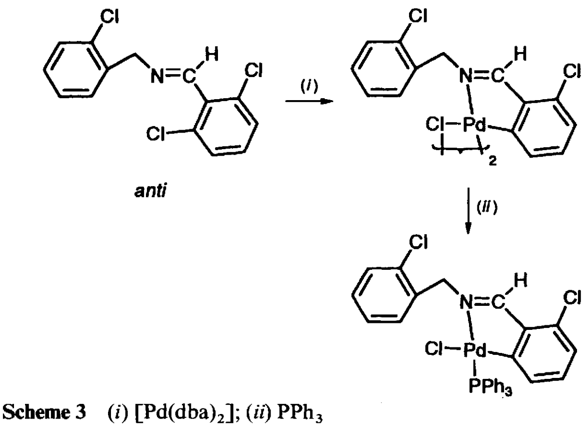
Table 4 Selected bond lengths (Å) and angles (°) for complex **1c** with e.s.d.s in parentheses

	Molecule A	Molecule B		Molecule A	Molecule B
Fe–C(1)	2.027(3)	2.043(3)	C(7)–C(8)	1.408(6)	1.406(6)
Fe–C(2)	2.033(3)	2.040(3)	C(8)–C(9)	1.408(5)	1.428(5)
Fe–C(3)	2.037(3)	2.030(3)	C(9)–C(10)	1.420(5)	1.426(4)
Fe–C(4)	2.025(3)	2.022(3)	C(10)–C(6)	1.430(5)	1.425(4)
Fe–C(5)	2.023(3)	2.024(3)	C(10)–C(11)	1.479(5)	1.490(4)
Fe–C(6)	2.023(3)	2.044(3)	C(11)–N	1.471(4)	1.470(4)
Fe–C(7)	2.038(3)	2.040(3)	C(12)–N	1.226(5)	1.242(4)
Fe–C(8)	2.028(3)	2.030(3)	C(12)–C(13)	1.480(4)	1.484(4)
Fe–C(9)	2.027(3)	2.035(3)	C(13)–C(14)	1.389(5)	1.390(4)
Fe–C(10)	2.029(3)	2.032(3)	C(14)–C(15)	1.384(5)	1.387(5)
C(1)–C(2)	1.401(6)	1.404(5)	C(15)–C(16)	1.367(6)	1.382(6)
C(2)–C(3)	1.372(5)	1.419(5)	C(16)–C(17)	1.362(6)	1.357(6)
C(3)–C(4)	1.406(5)	1.411(5)	C(17)–C(18)	1.387(5)	1.377(4)
C(4)–C(5)	1.418(6)	1.409(6)	C(18)–C(13)	1.381(5)	1.392(4)
C(5)–C(1)	1.399(7)	1.404(6)	Cl(1)–C(14)	1.732(4)	1.735(4)
C(6)–C(7)	1.413(6)	1.418(5)	Cl(2)–C(18)	1.719(4)	1.726(3)
C(1)–C(2)–C(3)	108.3(4)	108.0(3)	N–C(12)–C(13)	125.6(3)	122.4(3)
C(2)–C(3)–C(4)	109.2(3)	107.7(3)	C(12)–C(13)–C(14)	119.1(3)	119.5(3)
C(3)–C(4)–C(5)	106.7(4)	107.8(3)	C(12)–C(13)–C(18)	124.8(3)	124.5(3)
C(4)–C(5)–C(1)	107.7(3)	108.5(3)	C(13)–C(14)–C(15)	123.3(3)	122.5(3)
C(6)–C(7)–C(8)	107.4(3)	108.5(3)	C(14)–C(15)–C(16)	118.3(4)	118.7(3)
C(7)–C(8)–C(9)	108.2(3)	109.0(3)	C(15)–C(16)–C(17)	120.7(3)	120.6(2)
C(8)–C(9)–C(10)	108.3(3)	106.8(3)	C(16)–C(17)–C(18)	120.1(4)	119.8(4)
C(9)–C(10)–C(6)	107.0(3)	108.2(3)	C(17)–C(18)–C(13)	121.6(3)	122.5(3)
C(9)–C(10)–C(6)	107.0(3)	108.2(3)	Cl(1)–C(14)–C(13)	119.0(3)	119.4(2)
C(6)–C(10)–C(11)	127.3(3)	125.9(3)	Cl(1)–C(14)–C(15)	117.6(3)	118.0(3)
C(9)–C(10)–C(11)	125.7(3)	125.9(3)	Cl(2)–C(18)–C(13)	121.4(3)	120.7(2)
C(10)–C(11)–N	109.9(3)	118.0(2)	Cl(2)–C(18)–C(17)	117.0(3)	116.8(3)
C(11)–N–C(12)	116.2(4)	119.4(3)			

also consistent with a five-membered palladocycle fused with the aryl ring. The ^{31}P NMR spectrum showed a singlet at δ 41.6 the position of which is consistent with the values obtained for related $[\mathrm{Pd(CN)Cl(PPh_3)}]$ derivatives with a σ[Pd-$\mathrm{C_{sp^2}}$(phenyl)] bond and a *trans* arrangement between the iminic nitrogen and the phosphine ligand.[6,7] This finding is clearly different from the results obtained in cyclopalladation of *N*-(2,6-dichlorobenzylidene)benzylamine[6] for which (*a*) metallation required stronger experimental conditions (*b*) the process produced a five-membered exocyclic palladacycle, thus showing that the presence of two chloro substituents on the *ortho* positions of the benzyl ring precluded the formation of the endocyclic metallacycle {consequently for this substrate the activation of a σ[$\mathrm{C_{sp^2}}$(phenyl)–H] is preferred to that of σ[$\mathrm{C_{sp^2}}$(phenyl)–Cl]} and (*c*) *anti* ⟶ *syn* isomerization of the ligand took place during the reaction.

Although the mechanism of the cyclopalladation of N-donor ligands has not been clearly established, it is widely accepted that the reaction takes place in two steps, co-ordination of the N-donor ligand to the palladium and subsequent electrophilic attack of the species formed on the carbon atom.[15] The results summarized in this work reveal that the activation of the σ[$\mathrm{C_{sp^2}}$(ferrocene)–H] bond does not take place, although ferrocene derivatives have greater proclivity to undergo electrophilic attack.[16] Consequently, the formation of the metallacycle from compound **1c** must be achieved through a different pathway. The results reported here are similar to those obtained in cyclopalladation of the *N*-benzylidene-(2-phenylethyl)amine $(4\text{-}\mathrm{RC_6H_4)CH_2CH_2N{=}CH(C_6H_3Cl_2}\text{-}2,6)$ (R = H or OMe) where the formation of $[\{\mathrm{Pd[(3\text{-}ClC_6H_3)CH{=}NCH_2CH_2(C_6H_4R\text{-}4)](\mu\text{-}Br)}\}_2]$ took place *via* activation of a σ(C–Cl) bond.[6] In this case the results were also interpreted as arising from an oxidative addition of the ligand to the palladium(0) formed during the reaction. This sort of reaction has been postulated in the catalytic arylation of olefins and organic halides.[17]

Previous studies, based on oxidative additions of substituted *N*-(benzylidene)benzylamines to palladium(0) compounds, have shown that when $\mathrm{2,6\text{-}Cl_2C_6H_3CH{=}NCH_2C_6H_4Cl\text{-}2}$ was treated with $[\mathrm{Pd(dba)_2}]$ (dba = dibenzylideneacetone) or $[\mathrm{Pd(PPh_3)_4}]$ the reaction produced the endocyclic five-membered cyclopalladated compound $[\{\mathrm{Pd[(3\text{-}ClC_6H_3)CH{=}NCH_2C_6H_4Cl\text{-}2](\mu\text{-}Cl)}\}_2]$[18] (Scheme 3). The nature of the present product $[\{\mathrm{Pd[(3\text{-}ClC_6H_3)CH{=}NCH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)](\mu\text{-}Cl)}\}_2]$ is analogous and consequently an oxidative addition of the ligand to the palladium(0) produced during the reaction (see above and Experimental section) cannot be disregarded, especially when the redox properties of the free imine are taken into account.[19]



Scheme 3 (*i*) $[\mathrm{Pd(dba)_2}]$; (*ii*) $\mathrm{PPh_3}$

Mössbauer Spectra.—Iron-57 Mössbauer spectroscopic parameters of the compounds and related derivatives are presented in Table 5. In all cases isomer shifts are consistent with data reported in the literature for ferrocenyl compounds.[20,21] The quadrupole splittings, q.s. for **1a**–**1c** are clearly larger than those obtained for ferrocenyl Schiff bases of

Table 5 Mössbauer parameters [isomer shift, (i.s.), quadrupolar splitting, (q.s.), and linewidths (Γ, in mm s^{-1})] for ferrocenylimines **1a**–**1c** and $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2N{=}CH(C_6H_3Cl_2\text{-}2,6)\}]$ and the cyclopalladated derivatives **2a** and **2b**

Ferrocenylimines	i.s.	q.s.	Γ
1a	0.50(1)	2.37(1)	0.12(1)
1b	0.50(1)	2.39(1)	0.13(1)
1c	0.50(1)	2.37(1)	0.13(1)
$[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2CH_2N{=}CH\text{-}(C_6H_3Cl_2\text{-}2,6)\}]$	0.52(1)	2.41(1)	0.18(1)
Cyclopalladated complexes			
2a	0.49(1)	2.38(1)	0.13(1)
2b	0.49(1)	2.35(1)	0.12(1)

general formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ [in the range 2.20(1)–2.35(1) mm s^{-1} [7c,f]], in good agreement with the stronger electron-attracting nature of the substituent $C(R){=}NR'$ *versus* $\text{–}CH_2N{=}CHR'$. This is also reflected in a comparison of the q.s. values obtained for **1c** and $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2CH_2N{=}CH(C_6H_3Cl_2\text{-}2,6)\}]$, which only differ in the length of the $(CH_2)_n$ chain. The incorporation of an additional CH_2 group between the nitrogen and the ferrocenyl unit produces an increase in the quadrupolar splitting parameter, which is consistent with the finding that the CH_2CH_2 unit is a better electron donor.

The q.s. values of the palladium complexes do not differ significantly from those of the free imines (the differences clearly do not exceed 3σ). This finding is in contrast with the results obtained previously for $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ and their cyclopalladated complexes of general formula $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CR{=}NR'\}Cl(L)]$, for which the replacement of a $\sigma[C_{sp^2}(\text{ferrocene})\text{–}H]$ by a $\sigma[Pd\text{–}C_{sp^2}(\text{ferrocene})]$ bond produced a decrease in the q.s. This variation has been interpreted in terms of the electron-attracting character of the 'PdCl(L)' unit directly bound to the ferrocenyl fragment. For the present compounds the formation of the palladacycle takes place further away from the ferrocenyl moiety and the CH_2 units linked to the ferrocenyl group isolate the two fragments of the molecule, and consequently the q.s. for the free imines and their palladium derivatives do not vary significantly.

Experimental

Elemental analyses (C, H and N) were carried out at the Institut de Química Bio-Orgànica (C. S. I. C., Barcelona) and at the Serveis Cientifico-Tècnics (Universitat de Barcelona). Infrared spectra were obtained from KBr pellets using a Nicolet 520FTIR spectrometer, and $^{13}C\text{-}\{^1H\}$ NMR spectra at *ca.* 20 °C on a Gemini 200 MHz spectrophotometer using $CDCl_3$ (99.9%) as solvent and $SiMe_4$ as internal standard in both cases. The ^{31}P NMR spectrum of complex **3b** was recorded with a Bruker WP80-SY, using chloroform as solvent and trimethyl phosphite as internal reference $\{\delta[P(OMe)_3]$ 140.17$\}$.

Materials and Syntheses.—Aminomethylferrocene, $[Fe(\eta^5\text{-}C_5H_5(\eta^5\text{-}C_5H_4CH_2NH_2)]$, was prepared as described previously[5] using (dimethylaminomethyl)ferrocene, $[Fe(\eta^5\text{-}C_5H_5(\eta^5\text{-}C_5H_4CH_2NMe_2)]$, as starting material. **CAUTION**: This procedure requires the use of highly hazardous materials, such as NaN_3 and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2N_3)]$, consequently they should be handled with extreme caution. 2,6-Dichlorobenzaldehyde and (dimethylaminomethyl)ferrocene, were obtained from standard sources and used as received. Some of the preparations described below require benzene which should be used with caution. All the solvents were dried and distilled before use.

Preparations.—$[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2N{=}CH(C_6H_3\text{-}Cl_2\text{-}2,6)\}]$ **1c**. 2,6-Dichlorobenzaldehyde (0.408 g, 2.33 mmol) was added to a solution containing freshly prepared aminomethylferrocene.[5] (0.500 g, 2.33 mmol) in benzene (20 cm^3). The reaction mixture was connected with a Dean–Stark apparatus and refluxed on an ethylene glycol bath until *ca.* 8–9 cm^3 of the benzene–water azeotrope had condensed on the Dean-Stark. Then the pale yellowish solution was filtered out and the filtrate concentrated to dryness on a rotary evaporator. Addition of hexane (*ca.* 20 cm^3) to the gummy material formed, followed by vigorous stirring at room temperature for 1 h, resulted in the precipitation of the Schiff base. The yellow solid was filtered off and air-dried. Yield: 68%. Good quality crystals of this ferrocenylimine were obtained by slow evaporation (*ca.* 1 week) of a saturated solution of the complex in benzene [Found (Calc. for $C_{18}H_{15}Cl_2FeN$): C, 58.25 (58.10); H, 4.10 (4.05); N, 3.85 (3.75%)]. IR: ν(>C=N–) 1644 cm^{-1}.

$[\{Pd[(3\text{-}ClC_6H_3)CH{=}NCH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)](\mu\text{-}Cl)\}_2]$ **2b**. Compound **1c** (0.371 g, 1 mmol), $Na_2[PdCl_4]$ (0.294 g, 1 mmol) and $NaO_2CMe{\cdot}3H_2O$ (0.136 g, 1 mmol) were suspended in methanol (20 cm^3). The resulting mixture was stirred at room temperature in an open vessel for 3 h. Then the solid formed was filtered off, washed with two portions of methanol (*ca.* 5 cm^3) and air-dried. Afterwards the solid was suspended in chloroform (25 cm^3) and stirred at room temperature for 30 min. The undissolved deep brown materials were filtered off and discarded. The filtrate was concentrated on a rotary evaporator to *ca.* 5 cm^3 and purified by SiO_2 column (10.0 × 250.0 mm) chromatography, using $CHCl_3$ as eluent. The bright yellow band was collected and concentrated to dryness on a rotary evaporator. Addition of hexane followed by vigorous stirring resulted in the precipitation of the compound, which was filtered off and air-dried. Yield: 52% [Found (Calc. for $C_{36}H_{30}Cl_4N_2Fe_2P_2Pd_2$): C, 45.10 (45.10); H, 3.15 (3.15), N, 2.85 (2.90%)]. IR: ν(>C=N–) 1605 cm^{-1}.

$[Pd\{(3\text{-}ClC_6H_3)CH{=}NCH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ **3b**. To a suspension containing compound **2b** (0.450 g, 0.150 mmol) in benzene (10 cm^3) was added triphenylphosphine (80 mg, 0.30 mmol). The resulting suspension was stirred at room temperature for 45 min and filtered. The filtrate was concentrated to dryness on a rotary evaporator and the gummy residue treated with hexane (*ca.* 10 cm^3) and stirred vigorously at room temperature for 30 min. The solid formed was filtered off and air-dried. Yield: 75% [Found (Calc. for $C_{36}H_{30}\text{-}Cl_2FeNPd$): C, 58.4 (58.25); H, 4.05 (4.05); N, 1.9 (1.9%)]. IR ν(>C=N–) 1620 cm^{-1}. ^{31}P NMR: δ 41.6.

Crystal Structure Determination and Refinement.—A prismatic crystal of compound **1c** was selected and mounted on a Enraf-Nonius CAD4 diffractometer. Unit-cell parameters (Table 6) were determined from automatic centring of 25 reflections ($12 \geqslant \theta \geqslant 21°$), 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 collected every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz polarization corrections were made, but not absorption.

The structure was solved by Patterson synthesis using the SHELXS computer program[22] and refined by full-matrix least squares on F^2 using the SHELXL 93 computer program.[23] The function minimized was $\Sigma\big||F_o|^2 - |F_c|^2\big|^2$, where $w = [\sigma^2(F_o^2) + 0.1254P^2 + 2.1781P]^{-1}$ and $P = (F_o^2 + 2F_c^2)^{\frac{1}{3}}$. Values of f, f' and f'' were taken from ref. 24. The positions of the hydrogen atoms were computed and refined with an overall isotropic thermal parameter, using a riding model. The final $R1$, $wR2$ and S factors, as well as the number of refined parameters, and other details concerning the refinement of the crystal structure are presented in Table 6.

Table 6 Crystallographic data and details of the refinement of the crystal structure of $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4CH_2N{=}CH(C_6H_3Cl_2-2,6)\}]$ **1c**

Empirical formula	$C_{18}H_{15}Cl_2FeN$
M	372.06
Crystal size/mm	0.1 × 0.1 × 0.1
Crystallographic system	Triclinic
Space group	$P\bar{1}$
a/Å	7.553(3)
b/Å	11.763(2)
c/Å	18.148(2)
α/°	89.94(1)
β/°	98.90(2)
γ/°	91.91(2)
Z	4
D_c/g cm^{-3}	1.552
U/Å^3	1592.2(7)
μ/mm^{-1}	1.277
λ(Mo-Kα)/Å	0.710 69
F(000)	760
θ range for data collection/°	1.14–30.01
h, k, l, Ranges	−10 to 10, −16 to 16, 0–25
Reflections collected	9310
Independent reflections	9210
R_{int}	0.0264
No. of data	9160
No. parameters	399
Goodness of fit on F^2	0.845
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0513$, $wR_2 = 0.1573$
(all data)	$R1 = 0.0953$, $wR_2 = 0.2220$
Extinction coefficient	0.006(2)
Largest difference peak and hole */ e Å^{-3}	0.709, 0.721
T/K	293(2)

* The highest peak in the final difference syntheses was located 0.4 Å from the iron.

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

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

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References

1 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21; D. M. Burland, *Chem. Rev.*, 1994, **84**, 1; E. C. Constable, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 407; E. C. Constable, A. J. Edwards, R. Martínez-Mañez, P. R. Raithby and A. W. Cargill-Thompson, *J. Chem. Soc., Dalton Trans.*, 1994, 645; R. W. Wagner, P. A. Brown, T. E. Thompson and S. L. Lindsey, *J. Chem. Soc., Chem. Commun.*, 1991, 1463; C. Kollmar, M. Couty and O. Khan, *J. Am. Chem. Soc.*, 1991, **113**, 7994; K. M. Chi, J. C. Calabrese, W. M. Reiff and J. S. Miller, *Organometallics*, 1991, 10, 688; A. Werner and W. Friedrich, *J. Chem. Soc., Chem. Commun.*, 1994, 365; L. V. Popova, V. N. Babin, Y. A. Belousov, Y. S. Nekrasov, A. Snergireva, N. P. Borodina, G. P. Shoposnikova, O. B. Bychenko, P. M. Raevskii, N. B. Mozorova, A. I. Ilyna and K. G. Shitkov, *Appl. Organomet. Chem.*, 1993, 7, 85; B. Belaoux-Nicot, R. Mathieu, D. Mountazon, G. Lavigne and J. P. Majoral, *Inorg. Chem.*, 1994, **33**, 434; A. Togni, M. Hobi, O. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech and H. Keller, *Organometallics*, 1994, **13**, 1224; T. Y. Dong, T. Y. Lee, G. H. Lee and S. M. Peng, *Organometallics*, 1994, **13**, 2337.

2 M. Pfeffer, J. P. Sutter, A. de Cian and J. J. Fischer, *Inorg. Chim. Acta*, 1994, **220**, 115; M. Pfeffer, M. Roteveell, J. P. Sutter, A. de Cian and J. J. Fisher, *J. Organomet. Chem.*, 1989, **371**, C21; C. López, X. Solans and D. Tramuns, *J. Organomet. Chem.*, 1994, **471**, 265; C. López, R. Bosque, X. Solans, M. Font-Bardía, J. Silver and G. Fern, *J. Chem. Soc., Dalton Trans.*, 1995, 1839.

3 V. I. Sokolov, L. L. Troitskaya and N. S. Khrushchova, *J. Organomet. Chem.*, 1983, **439**, 250; M. Gruselle, B. Malezieux, V. I. Sokolov and L. L. Troitskaya, *Inorg. Chim. Acta*, 1994, **222**, 51.

4 R. Bosque, C. López and J. Sales, *J. Organomet. Chem.*, 1995, **498**, 147.

5 J. K. Lindsay and R. C. Hauser, *J. Org. Chem.*, 1975, **22**, 355; J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 1958, 656; D. E. Bublitz, *J. Organomet. Chem.*, 1970, **23**, 225.

6 J. Albert, M. Gómez, J. Granell, J. Sales and X. Solans, *Organometallics*, 1990, **9**, 1405; J. Albert, J. Granell and J. Sales, *J. Organomet. Chem.*, 1984, **273**, 393.

7 (*a*) C. López, J. Sales, X. Solans and R. Zquiak, *J. Chem. Soc., Dalton Trans.*, 1992, 2321; (*b*) R. Bosque, C. López, J. Sales, M. Font-Bardía and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1994, 735; (*c*) R. Bosque, M. Font-Bardía, C. López, J. Sales, J. Silver and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1994, 747; (*d*) R. Bosque, C. López, J. Sales, X. Solans and M. Font Bardía, *J. Organomet. Chem.*, 1994, **483**, 61; (*e*) R. Bosque, C. López, J. Sales, D. Tramuns and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1995, 2445; (*f*) C. López, R. Bosque, X. Solans, M. Font-Bardía, D. Tramuns, G. Fern and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1994, 3039.

8 F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146.

9 G. P. Palenik and T. J. Giordano, *J. Chem. Soc., Dalton Trans.*, 1987, 1175.

10 J. Silver, J. R. Miller, A. Houlton and M. T. Ahmet, *J. Chem. Soc., Dalton Trans.*, 1994, 3355; A. Houlton, J. R. Miller, J. Silver, N. Jassim, T. L. Axon, D. Bloorm and G. H. Cross, *Inorg. Chim. Acta*, 1993, **205**, 67.

11 M. Bracci, C. Ercolani, B. Floris, M. Bassetti, A. Chesi-Vila and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1990, 1357.

12 A. J. Adamson, Y. Archambean, R. E. Banks, B. Beagley, M. Helliwell, R. G. Pritchard and A. E. Tipping, *Acta Crystallogr. Sect. C*, 1994, 967.

13 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063; A. Bondi, *J. Chem. Phys.*, 1964, 441; A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, London, 1973.

14 J. C. Gaunt and B. L. Shaw, *J. Organomet. Chem.*, 1975, **102**, 511.

15 G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kiefer, *Chem. Rev.*, 1986, **86**, 451; I. Omae, *Coord. Chem. Rev.*, 1988, **83**, 137; V. V. Dunina, O. A. Zalewskaya and V. M. Potatov, *Russ. Chem. Rev.*, 1988, **57**, 250; A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.

16 *Gmelin, Handbuch der Anorganische Chemie; Eisen organische Verbindunge, Ferrocen*, 1, Teil A, Springer, Heidelberg, 1976.

17 R. F. Heck, *Org. React.*, 1982, **17**, 345.

18 J. Albert, J. Barro and J. Granell, *J. Organomet. Chem.*, 1991, **408**, 115.

19 R. Bosque, C. López and J. Sales, *Inorg. Chim. Acta*, in the press.

20 A. Houlton, J. R. Miller, R. M. G. Roberts and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1990, 2421.

21 A. Houlton, J. R. Miller, R. M. G. Roberts and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1991, 467.

22 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

23 G. M. Sheldrick, University of Göttingen, 1993.

24 *International Tables of X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 100 and 149.

25 M. Y. Hamed, R. C. Hider and J. Silver, *Inorg. Chim. Acta*, 1982, **66**, 13.

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