Activation of σ(C–H) bonds in ferrocenylhydrazones derived from acetylferrocene

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Abstract

The synthesis and characterization of the novel ferrocenylhydrazones: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)\text{=}N\text{-}NHR\}]$ (R = C_6H_4-4-NO_2 (**1a**), C_6H_4-4-Cl (**1b**), C_6H_4-2-CH_3 (**1c**), C_6H_3-2,4-$(NO_2)_2$ (**1d**) or C_6H_3-2,5-Cl_2 (**1e**)) is described. These compounds react in methanol with $Na_2(PdCl_4)$ and sodium acetate trihydrate in a 1:1:1 molar ratio at room temperature, giving the di-μ-chlorobridged cyclopalladated complexes: $[Pd\{[(\eta^5\text{-}C_5H_3)\text{-}C(CH_3)\text{=}N\text{-}NHR]Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)\}]_2$ (**2**). Addition of triphenylphosphine (PPh_3) to benzene suspensions of compounds **2**, produced the cleavage of the di-μ-chlorobridges and the formation of $[Pd\{[(\eta^5\text{-}C_5H_3)\text{-}C(CH_3)\text{=}N\text{-}NHR]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)\}]$ (**3**). NMR studies (^{1}H and ^{31}P) on compound **3** revealed the formation of a (5,5) bicyclic system derived from the fusion of a five-membered palladacycle and the ferrocenyl moiety. The X-ray crystal structure of $[Pd\{[(\eta^5\text{-}C_5H_3)\text{-}C(CH_3)\text{=}N\text{-}NH(C_6H_3\text{-}2,5\text{-}Cl_2)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)\}]$ (**3e**) is also reported and confirms the formation of a five-membered palladacycle with a $\sigma(Pd\text{-}C_{sp^2,ferrocene})$ bond. © 1997 Elsevier Science S.A.

1. Introduction

Cyclopalladation reactions of N-donor ligands such as imines, amines, azines, oximes and hydrazones have been described in the literature. [1] Some years ago, a parallel study on analogous N-donor substrates derived from ferrocene was initiated [6–20]. Up to now, cyclopalladation studies of ferrocenylamines [6–10], imines [11–17], azines and azo derivatives [18,19] and oximes [20] have allowed the isolation of a novel kind of palladocyclic complex with $\sigma(Pd\text{-}C_{sp^2,ferrocene})$ bonds. However, to our knowledge, only two examples of cyclopalladation of ferrocenylhydrazones (Fig. 1) have been reported [21].

The presence of substituents is an especially important factor regulating cyclopalladation. For instance, although the ferrocenylimine $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH_2\text{-}N\text{=}CH(C_6H_4\text{-}2\text{-}Cl)\}]$ undergoes cyclopalladation at the aryl ring giving $[Pd\{[(C_6H_3\text{-}2\text{-}Cl)\text{-}CH\text{=}N\text{-}CH_2\text{-}(\eta^5\text{-}C_5H_4)]Fe\{\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$, when the chloro group is replaced by a hydrogen atom the reaction produces a mixture of two cyclopalladated complexes: $[Pd\{[(C_6H_3\text{-}2\text{-}Cl)\text{-}CH\text{=}N\text{-}CH_2\text{-}(\eta^5\text{-}C_5H_4)]Fe\{\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ and $[Pd\{(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3)\text{-}CH_2\text{-}N\text{=}CH(C_6H_4\text{-}2\text{-}Cl)]\}(\mu\text{-}Cl)]_2$, which contain a $\sigma(Pd\text{-}C_{sp^2,phenyl})$ bond and a $\sigma(Pd\text{-}C_{sp^2,ferrocene})$ bond respectively [22]. In the light of this, we decided to study the cyclopalladation of several ferrocenylhydrazones of the general formula $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)\text{=}N\text{-}NHR\}]$ (R = C_6H_4-4-NO_2 (**1a**), R = C_6H_4-4-Cl (**1b**), R = C_6H_4-2-CH_3 (**1c**), R = C_6H_3-2,4-$(NO_2)_2$ (**1d**) or R = C_6H_3-2,5-Cl_2 (**1e**)). Depending on the nature of the $\sigma(C\text{–}H)$ bond to be activated ($C_{sp^2,ferrocene}\text{–}H$ or $C_{sp^2,phenyl}\text{–}H$) these ferrocenylhydrazones (**1**) could produce different compounds (Fig. 2).

2. Results and discussion

2.1. The ligands

The ferrocenylhydrazones $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)\text{=}N\text{-}NHR\}]$ **1** were prepared by condensation of equimolar amounts of acetylferrocene and

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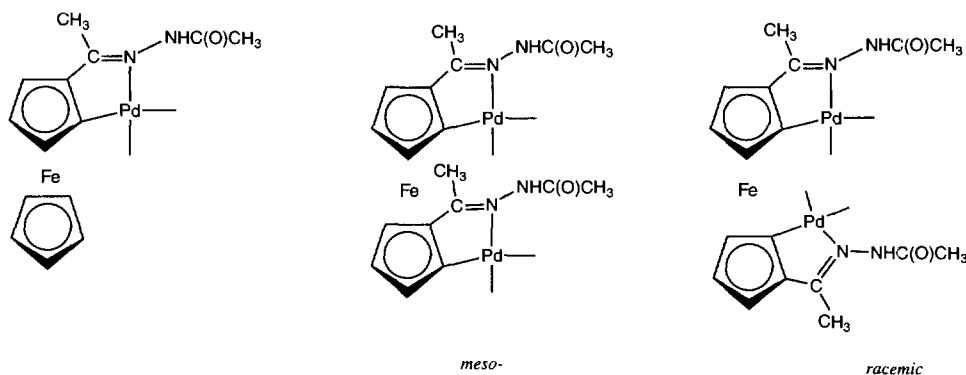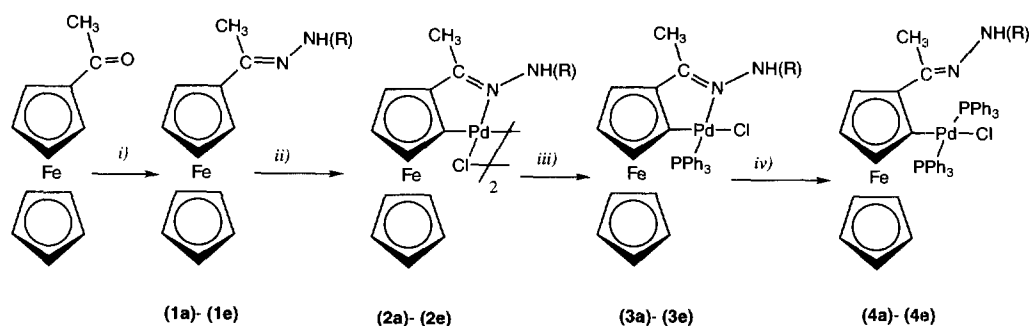[1] For reviews concerning the cyclopalladation reaction see [1–5].

Fig. 1. Schematic view of the two cyclopalladated complexes derived from ferrocenylhydrazones described so far.

Scheme 1. (i) $H_2N–NH(R)$ in ethanol. (ii) $Na2[PdCl_4]$, and $Na(CH_3COO) \cdot 3H_2O$, in methanol at room temperature. (iii) PPh_3 in benzene, at room temperature, followed by SiO_2-column chromatography using $CHCl_3$:methanol 100:1 as eluant. (iv) PPh_3, in $CDCl_3$ at room temperature.

their corresponding hydrazines in ethanol and in the presence of glacial acetic acid (Scheme 1).

These compounds are orange–red solids (except **1d** which is dark red) and exhibit high solubility in benzene, chloroform or dichloromethane. The new ferrocenylhydrazones (**1**) were characterized by elemental analyses, infrared spectroscopy and proton NMR spectroscopy. In all cases the elemental analyses were consistent with the expected values (see Section 3). The IR spectra showed a sharp intense band in the range of

Fig. 2. Schematic view of the different types of palladacycles (*endo*- or *exo*-) which can be formed through activation of a $\sigma(C_{sp^2,ferrocene}–H)$ bond or a $\sigma\{C_{sp^2,phenyl}–H\}$ bond in the substrates under study in relation to the conformation of the ferrocenylhydrazone.

$1590–1620$ cm^{-1}, due to the asymmetric stretching of the $> C=N$- group and the typical stretching band of the N–H fragment within the range $3300–3400$ cm^{-1}.

Proton NMR spectra of compounds **1** (Table 1) show a singlet and two triplets in the region $3.00–5.00$ ppm, which are ascribed to the three types of protons of the ferrocenyl unit. A signal due to the methyl protons of the $-C(CH_3)=N$-fragment is also observed within the region $2.15–2.30$ ppm. For compounds **1a–1c** and **1e**, the resonance of the amine proton appears as a singlet in the range $7.00–8.00$ ppm. For **1d**, the signal is strongly shifted to lower fields (ca. 11.30 ppm). This finding, which was also observed for related *ortho* nitro-substituted organic hydrazones ($RR'C=N–NH\{C_6H_{4-x}R''_x-2-NO_2\}$) [23,24], is believed to be derived from the presence of a strong hydrogen bond between the amine proton and the NO_2 substituent in the *ortho* site. In fact, the X-ray crystal structures of 2-nitro substituted hydrazones confirm this type of interaction [25].

In order to compare the influence of the substituent $-C(CH_3)=N–NHR$ on the redox ability of iron(II), and the electron-giving/electron withdrawing power of the hydrazone $\{-C(CH_3)=N–NHR\}$ and the imine $\{-C(CH_3)=N–R\}$ groups, we carried out electrochemical studies on compounds **1**. In all cases the cyclic voltammograms exhibited one anodic peak with a directly associated cathodic peak in the reverse scan. The half-
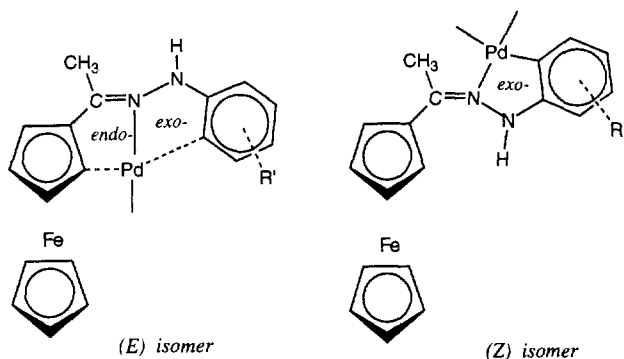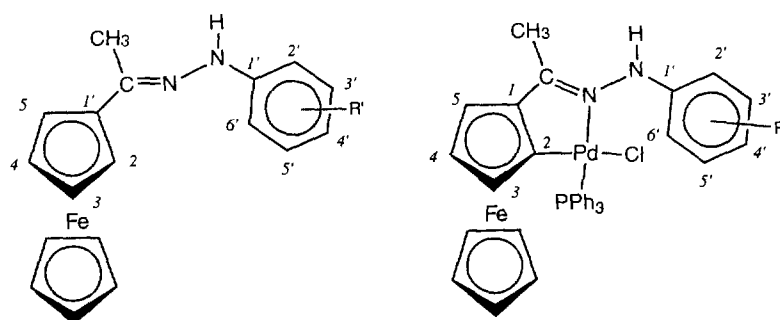
Table 1
Proton and ^{31}P NMR data (in ppm) for compounds under study

R'	^{1}H NMR				^{31}P NMR
	Phenyl	–NH–	Ferrocenyl	Aliphatic	
1a 4-NO$_2$	7.12, d, H$^{2'}$,H$^{6'}$ 8.19, d, H$^{3'}$, H$^{5'}$	7.70, s	4.19, s, Cp 4.67, t, H^2, H^5 4.39, t, H^3, H^4	2.22, s, CH$_3$	–
1b 4-Cl	7.21, d, H$^{2'}$, H$^{6'}$ 7.04, d, H$^{3'}$, H$^{5'}$	7.12, s	4.16, s, Cp 4.61, t, H^2, H^5 4.31, t, H^3, H^4	2.14, s, CH$_3$	–
1c 2-CH$_3$	7.54, d, H$^{6'}$ 7.18, d, H$^{5'}$ 7.09, d, H$^{3'}$ 6.78, t, H$^{4'}$	7.55, s	4.15, s, Cp 4.65, t, H^2, H^5 4.31, t, H^3, H^4	2.24, s, CH$_3$ 2.14, s, CH$_3$(R')	–
1d 2,4(NO$_2$)$_2$	9.18, d, H$^{5'}$ 8.02, d, H$^{6'}$ 8.37, dd, H$^{3'}$	11.30, s	4.21, s, Cp 4.73, t, H^2, H^5 4.47, t, H^3, H^4	2.34, s, CH$_3$	–
1e 2,5-(Cl)$_2$	7.54, d, H$^{6'}$ 7.18, d, H$^{3'}$ 6.72, d, H$^{4'}$	7.59, s	4.19, s, Cp 4.67, t, H^2, H^5 4.36, t, H^3, H^4	2.20, s, CH$_3$	–
3a 4-NO$_2$	6.80, d, H$^{2'}$, H$^{6'}$ 8.10, d, H$^{3'}$, H$^{5'}$ 7.20–7.85, br m, PPh$_3$	8.60, d	3.92 s, Cp 3.40, d, H^3 4.10, t, H^4 4.50, d, H^5	2.28, s, CH$_3$	36.4
3b 4-Cl	7.20, H$^{2'}$, H$^{6'}$ 7.03, H$^{3'}$, H$^{5'}$ 7.30–7.85, br m, PPh$_3$	8.40, d	3.92, s, Cp 3.32, d, H^3 4.13, t, H^4 4.43, d, H^5	2.17, s, CH$_3$	36.2
3c 2-CH$_3$	6.72, d, H$^{6'}$ 6.90, d, H$^{5'}$ 7.17, d, H$^{4'}$ 7.30–7.85, br m, H$^{3'}$ and PPh$_3$	8.10, d	3.94, s, Cp 3.37, d, H^3 4.12, t, H^4 4.45, t, H^5	2.30, s, CH$_3$ 2.16, s, CH$_3$ (R')	36.3
3d 2,4(NO$_2$)$_2$	8.30, d, H$^{3'}$, 9.15, d, H$^{5'}$, 7.30–7.8, br. m, H^6 and PPh$_3$	10.10, br.	3.99, s, Cp 3.53, d, H^3 4.33, t, H^4 4.57, d, H^5	2.32, s, CH$_3$	37.1
3e 2,5-(Cl)$_2$	7.20, d, H$^{3'}$ 6.80, d, H$^{4'}$ 7.30–7.80, br. m, H$^{6'}$ and PPh$_3$	8.18, d	3.97, s, Cp 3.37, d, H^3 4.18, t, H^4 4.42, d, H^5	2.12, s, CH$_3$	36.5

wave potentials $E_{1/2}(F_c)$ for compounds **1** (Table 2) were smaller than those previously reported for the ferrocenylimines $[(\eta^5$-C$_5$H$_5)$Fe$\{(\eta^5$-C$_5$H$_4)$–C(R')=N–R$\}]$ (with R' = H, CH$_3$ or C$_6$H$_5$, and R = phenyl or benzyl groups) [26].

According to the general knowledge on ferrocene derivatives, the propensity of Fe(II) to undergo oxidation is strongly dependent on the nature of the sub-stituents. For instance, it is well known that electron-donor groups facilitate the oxidation of Fe(II), while electron-pulling groups reduce the proclivity of the Fe(II) to undergo oxidation [27–31]. Thus, the compari-son of the $E_{1/2}(F_c)$ for **1c** and for $[(\eta^5$-C$_5$H$_5)$Fe$\{(\eta^5$-C$_5$H$_4)$–C(CH$_3$)=N–(C$_6$H$_4$-2-CH$_3)\}]$ clearly shows that the incorporation of an –NH– fragment favours the oxidation of Fe(II). Moreover, according to the general

Table 2

Half-wave potentials (in V) referred to ferrocene, $E_{1/2}(F_c)$, for some of the ferrocenylhydrazones under study and the ferrocenylimines: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}R\}]^a$

	$E_{1/2}(F_c)$
(A) Ferrocenylhydrazones:	
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}NH(C_6H_4\text{-}4\text{-}NO_2)\}]$ **(1a)**	0.03
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}NH(C_6H_4\text{-}4\text{-}Cl)\}]$ **(1b)**	−0.01
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}NH\text{-}(C_6H_4\text{-}2\text{-}CH_3)\}]$ **(1c)**	−0.03
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}NH[C_6H_3\text{-}2,4\text{-}(NO_2)_2]\}]$ **(1d)**	0.07
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}NH\text{-}(C_6H_3\text{-}2,5\text{-}Cl_2)\}]$ **(1e)**	0.02
(B) Ferrocenylimines of general formula: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}R'\}]$	
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}C_6H_5\}]$	0.15
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}(C_6H_4\text{-}2\text{-}CH_3)\}]$	0.14
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}(C_6H_4\text{-}4\text{-}CH_3)\}]$	0.14
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}(CH_2\text{-}C_6H_5)\}]$	0.09
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}(CH_2\text{-}C_6H_4\text{-}2\text{-}CH_3)\}]$	0.09
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}(CH_2\text{-}C_6H_4\text{-}2\text{-}Cl)\}]$	0.09
$[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(CH_3)=N\text{-}(CH_2\text{-}CH_2\text{-}C_6H_5)\}]$	0.08

ᵃ Data from Ref. [26].

rules of the electrochemistry of ferrocene derivatives [27–31], the imine group $-C(CH_3)=N-R$ has a stronger electron-pulling effect on the ferrocenyl moiety than $-C(CH_3)=N-NHR$. In fact, the effect of the latter group is comparable to that of the substituents $(CH_2)_n-N=CHR$ (with $n = 1$ or 2) in $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}(CH_2)_n\text{-}N=CHR\}]$ [26].

2.2. Cyclopalladation reactions

Compounds **1** reacted with $Na_2(PdCl_4)$ and $Na(CH_3COO) \cdot 3H_2O$ in a 1:1:1 molar ratio in methanol giving the dimeric cyclopalladated complexes $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(CH_3)=N\text{-}NHR]\}(\mu\text{-}Cl)]_2$ **(2)** (Scheme 1). Further treatment of compounds **2** with PPh_3, in benzene at room temperature for 1 h produced the cleavage of the '$Pd(\mu\text{-}Cl)_2Pd$' units and the formation of the more soluble monomeric derivatives $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(CH_3)=N\text{-}NHR]\}Cl(PPh_3)]$ **(3)**. When compounds **3** were treated with larger excesses of PPh_3 (up to molar ratios PPh_3:**3** equal to 6:1) in refluxing benzene, no evidence for the formation of compounds $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}C(CH_3)=N\text{-}NHR]\}Cl(PPh_3)_2]$ **(4)** (which would arise from the cleavage of the Pd–N bond) was detected by ^1H or ^{31}P NMR spectroscopy. This indicates the poor lability of the Pd–N bond in compounds **3**.

Compounds **2** and **3** are orange or red air-stable solids. The dimeric complexes **2** show poor solubility in the most common solvents, while the monomeric derivatives **3**, are highly soluble in chloroform, dichloromethane and benzene, and insoluble in alkanes. The IR spectra of **2** and **3** give the typical bands of the hydrazones; however, the absorption due to the asymmetric stretching of the $>C=N-$ bond appears at a lower wave number consistent with the coordination of the imine nitrogen.

Proton NMR spectra data for compounds **3** are summarized in Table 1. The comparison of the positions and multiplicities of the signals due to the protons of the ferrocenyl moiety in the free ligands **1** and in **3** affords conclusive evidence of the palladation position. In all the metallocycles the ligand is in the *anti* form; this shows that although two different types of palladacycles could be obtained for this conformation (depending on the nature of the C–H bond to be activated) (Fig. 2), the
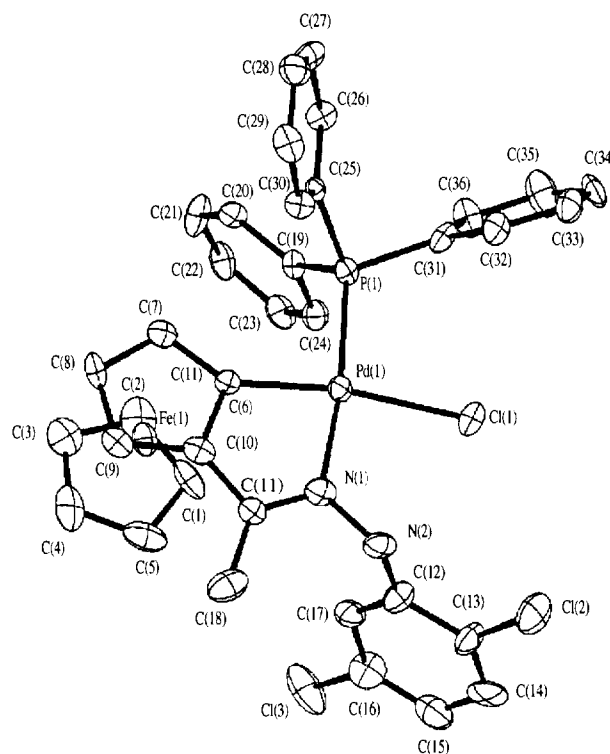

Fig. 3. Molecular structure and atom numbering scheme for complex **3e**.

Table 3
Final atomic coordinates (1×10^4) for non-hydrogen atoms for compound **3e**. (Standard deviations are given in parenthesis)

	x	y	z
Pd(1)	2794(1)	4437(1)	8015(1)
Fe(1)	−587(2)	3992(1)	7564(2)
P(1)	2903(3)	5246(2)	7104(3)
Cl(1)	5053(4)	4189(2)	7858(4)
Cl(2)	6129(5)	2859(3)	9598(4)
Cl(3)	2198(6)	1956(3)	6516(4)
N(1)	2460(13)	3731(6)	8933(8)
N(2)	3480(13)	3350(6)	9269(10)
C(1)	174(19)	3560(9)	6407(14)
C(2)	−703(19)	3990(10)	6091(13)
C(3)	−1966(18)	3894(10)	6486(12)
C(4)	−1877(18)	3402(10)	7068(13)
C(5)	−585(22)	3177(8)	7001(14)
C(6)	852(13)	4508(6)	8224(9)
C(7)	−281(15)	4854(7)	8002(10)
C(8)	−1416(14)	4616(8)	8437(11)
C(9)	−1042(16)	4117(7)	8972(11)
C(10)	361(15)	4046(7)	8866(10)
C(11)	1283(15)	3609(7)	9187(11)
C(12)	3800(16)	2891(8)	8667(11)
C(13)	5016(16)	2578(8)	8747(13)
C(14)	5326(21)	2101(8)	8225(14)
C(15)	4404(21)	1889(9)	7561(16)
C(16)	3256(21)	2199(9)	7446(13)
C(17)	2957(17)	2689(7)	7945(12)
C(18)	856(20)	3091(8)	9740(13)
C(19)	1983(12)	5176(6)	5981(9)
C(20)	930(14)	5526(6)	5724(9)
C(21)	311(14)	5427(9)	4834(10)
C(22)	739(14)	5013(8)	4216(11)
C(23)	1747(15)	4653(7)	4462(11)
C(24)	2347(14)	4723(7)	5356(10)
C(25)	2371(12)	5936(6)	7692(9)
C(26)	2468(14)	6457(6)	7201(9)
C(27)	2253(15)	6966(7)	7679(12)
C(28)	2014(16)	6959(8)	8631(13)
C(29)	1913(16)	6447(8)	9170(12)
C(30)	2108(14)	5924(7)	8682(10)
C(31)	4565(14)	5461(7)	6714(11)
C(32)	4981(15)	5518(8)	5786(11)
C(33)	6258(18)	5683(10)	5561(15)
C(34)	7155(15)	5778(7)	6265(14)
C(35)	6739(16)	5763(8)	7207(13)
C(36)	5475(14)	5611(7)	7442(11)
Pd(2)	2720(1)	3818(1)	2060(1)
Fe(2)	6141(2)	4315(1)	2539(1)
P(2)	2550(3)	2975(2)	2885(3)
Cl(4)	424(3)	4011(2)	1831(3)
Cl(5)	−538(4)	5363(2)	346(3)
Cl(6)	2992(5)	6222(2)	3719(3)
N(3)	3195(10)	4529(5)	1127(8)
N(4)	2142(12)	4919(5)	760(8)
C(37)	5327(16)	4859(8)	3576(12)
C(38)	6019(16)	5195(8)	2912(12)
C(39)	7386(16)	4994(8)	2900(13)
C(40)	7433(15)	4551(8)	3613(13)
C(41)	6205(18)	4455(10)	4009(11)
C(42)	4691(12)	3761(8)	1993(9)
C(43)	5891(13)	3447(6)	2306(11)
C(44)	6982(15)	3654(6)	1795(12)
C(45)	6618(14)	4101(8)	1164(11)

Table 3 (continued)

	x	y	z
C(46)	5233(13)	4185(7)	1277(10)
C(47)	4353(14)	4608(7)	861(10)
C(48)	1712(14)	5359(6)	1412(11)
C(49)	498(15)	5632(7)	1236(11)
C(50)	104(17)	6081(8)	1813(14)
C(51)	859(20)	6283(8)	2567(14)
C(52)	2071(16)	6004(8)	2738(11)
C(53)	2487(15)	5561(7)	2147(10)
C(54)	4759(16)	5080(8)	190(11)
C(55)	1032(12)	2783(6)	3575(9)
C(56)	9(13)	3170(7)	3703(11)
C(57)	−1057(16)	2999(8)	4287(12)
C(58)	−1077(17)	2485(8)	4739(10)
C(59)	−38(17)	2160(7)	4627(11)
C(60)	1003(16)	2265(8)	4019(12)
C(61)	3786(12)	2835(6)	3817(10)
C(62)	4424(14)	2309(7)	3926(11)
C(63)	5241(14)	2218(9)	4758(14)
C(64)	5369(15)	2663(8)	5417(11)
C(65)	4700(18)	3171(10)	5337(12)
C(66)	3946(16)	3268(7)	4508(11)
C(67)	2705(13)	2398(6)	1986(10)
C(68)	3892(14)	2268(8)	1538(11)
C(69)	3955(17)	1854(8)	837(13)
C(70)	2866(18)	1555(8)	549(12)
C(71)	1688(19)	1688(7)	955(13)
C(72)	1544(15)	2096(6)	1685(13)

formation of the *endocyclic* derivatives is strongly preferred.

^{31}P NMR spectra of compounds **3** show one singlet in the range 36.0–37.5 ppm. The position of this signal is consistent with previous studies for [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)–C(R')=N–R]}Cl(PPh$_3$)] (R' = H, CH$_3$ or C$_6$H$_5$ and R = phenyl, benzyl) and with a *trans*-arrangement between the imine nitrogen and the phosphine ligand [11–17].

2.3. Description of the crystal structure of compound 3e

The molecular structure of compound [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)–C(CH$_3$)=N–NH(C$_6$H$_3$-2,5-Cl$_2$)]}Cl(PPh$_3$)] **3e** together with the atom labelling scheme is shown in Fig. 3. Final atomic coordinates for non-hydrogen atoms are given in Table 3, and a selection of bond lengths and angles is presented in Table 4.

The structure consists of discrete molecules of [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)–C(CH$_3$)=N–NH(C$_6$H$_3$-2,5-Cl$_2$)]}Cl(PPh$_3$)] separated by van der Waals contacts. The palladium is in a slightly distorted square planar environment (coordinated to Cl(1), P(1), N(1) and the C(6) atom of the ferrocenyl group in one of the two non-equivalent molecules and to Cl(4), P(2), N(3) and C(43) in the other).

The metallocycle is practically planar and contains the >C=N- group, thus confirming the *endo*-type

Table 4
Selected bond lengths (in Å) and bond angles (in degrees) for compound 3e. (Standard deviations are given in parenthesis)

(A) Bond lengths			
Pd(1)–N(1)	2.084(14)	Pd(2)–N(3)	2.115(11)
Pd(1)–P(1)	2.243(2)	Pd(2)–P(2)	2.251(4)
Pd(1)–Cl(1)	2.360(4)	Pd(2)–Cl(4)	2.376(3)
Pd(1)–C(6)	1.988(13)	Pd(2)–C(42)	1.995(12)
N(1)–N(2)	1.43(2)	N(3)–N(4)	1.41(2)
N(1)–C(11)	1.27(2)	N(3)–C(47)	1.33(2)
C(11)–C(18)	1.48(2)	C(47)–C(54)	1.48(2)
Cl(2)–C(13)	1.74(2)	Cl(5)–C(49)	1.72(2)
Cl(3)–C(16)	1.75(2)	Cl(6)–C(52)	1.71(2)
(B) Bond angles			
P(1)–Pd(1)–Cl(1)	95.7(2)	P(2)–Pd(2)–Cl(4)	98.65(14)
N(1)–Pd(1)–Cl(1)	91.5(4)	N(3)–Pd(2)–Cl(4)	87.6(3)
C(6)–Pd(1)–N(1)	79.2(5)	C(42)–Pd(2)–N(3)	80.6(5)
C(6)–Pd(1)–P(1)	93.7(4)	C(42)–Pd(2)–P(2)	92.6(5)
N(1)–C(11)–C(10)	111.4(14)	N(3)–C(47)–C(46)	112.7(13)
N(1)–C(11)–C(18)	122.(2)	N(3)–C(47)–C(54)	122.4(14)
N(1)–N(2)–C(12)	116.4(12)	N(3)–N(4)–C(48)	115.9(10)

structure predicted by ^{1}H NMR spectroscopy. The metallocycle is practically coplanar with the C_5H_3 ring (the dihedral angle formed by the two fused rings is 0.26° and 4.57° for the two independent molecules). The >C=N-distance (average value for the two molecules: 1.30(4) Å) is similar to that found in related five-membered palladacycles with $\sigma(Pd–C_{sp^2,ferrocene})$ bonds.

As a first approach to elucidate the effect of the palladium on the structures of the free ligand, structural data of ferrocenylhydrazones derived from acetylferrocene [25] and those of 3e have been compared. This study reveals that the formation of the palladacycle does not significantly affect bond lengths involving the C_{ipso}–C(CH$_3$)=N-fragment. The differences clearly do not exceed 3σ; for instance, the >C=N-bond distance is 1.30(4) Å (average value for the two non-equivalent molecules) in complex 3e and for the free hydrazones the distance is 1.28–1.31 Å. The variations detected in bond angles around the hydrazone fragment are more significant; for instance, the C_{ipso}–C=N-bond angle is clearly smaller (ca. 4°) in 3e than in the ferrocenylhydrazones.

Bond lengths and angles in the ferrocenyl fragment are in good agreement with those reported for other ferrocene derivatives [25]. The two pentagonal rings are planar, nearly parallel (average value of the tilt angle for the two non-equivalent molecules: 4.0°), and their conformation is intermediate between the ideal staggered and eclipsed conformations (average value of the twist angle: 11.3°). The aryl ring of the hydrazone is nearly orthogonal to the C_5H_3 ring. The long distance between Fe(II) and Pd(II) (average value for the two molecules: 3.61(3) Å) suggests that there is no direct interaction.

2.4. Conclusions

The results reported in this work have allowed us to prepare and characterize five novel ferrocenylhydrazones of the general formula: $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-C(CH_3)=N-NHR\}]$ (1). The electrochemical studies revealed that the Fe(II) has a greater propensity to oxidize in 1 than in the ferrocenylimines: $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-C(CH_3)=N-R\}]$. This indicates that the $-C(CH_3)=N-NHR$ fragment has a stronger electron-donor character than the $-C(CH_3)=N-R$ moiety. In addition, the reaction of compounds 1 with $Na_2(PdCl_4)$ and $Na(CH_3COO)\cdot 3H_2O$, produced the di-μ-chlorobridged cyclopalladated compounds 2, which contain a five-membered metallacycle with a $\sigma(PdC_{sp^2,ferrocene})$ bond. Thus, although compounds 1 have two sites susceptible to metallation (Fig. 2), the formation of the endocyclic five-membered metallacycles is strongly favoured. These results are in agreement with those reported for organic hydrazones derived from acetophenone, $C_6H_{5-x}R_x-C(CH_3)=N-NHR$, for which the formation of the endocyclic derivatives is also preferred.

3. Experimental section

Elemental analyses (C, H and N) were carried out at the Serveis Cientifico-Técnics de la Universitat de Barcelona. Infrared spectra were obtained with a Nicolet-IMPACT-400 spectrophotometer using KBr pellets. Proton NMR spectra were recorded at ca. 20°C on a GEMINI-250MHz instrument using CDCl$_3$ (99.9%) as solvent and Si(CH$_3$)$_4$ as internal standard. ^{31}P NMR spectra of compounds 3, were recorded with a Bruker-250DRX instrument using CDCl$_3$ as solvent and trimethylphosphite as reference (δ ^{31}P (P(OCH$_3$)$_3$)=141.17 ppm).

3.1. Materials and synthesis

Acetylferrocene (98%) and the organic hydrazines or their hydrochlorides were obtained from commercial sources. The hydrochlorides were transformed into the corresponding hydrazines before use. ^{2} The solvents, except benzene, were distilled before use as follows: chloroform and dichloromethane, over CaO; ethanol and methanol, over CaCl$_2$.

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^{2} The hydrochlorides were treated with aqueous NaOH and then the hydrazines were extracted from the solution with chloroform. The organic layer was then dried over anhydrous Na$_2$SO$_4$ and filtered out. Concentration of the filtrate to dryness on a rotary evaporator allowed the corresponding hydrazines as oily materials.

3.1.1. Preparation of the ferrocenylhydrazones: [(H^5-C$_5$H$_5$)Fe{(H^5-C$_5$H$_4$)-C(CH$_3$)= N-NHR}] {R = C$_6$H$_4$-4-NO$_2$ (1a), C$_6$H$_4$-4-Cl (1b), C$_6$H$_4$-2-CH$_3$ (1c), C$_6$H$_3$-2,4-(NO$_2$)$_2$ (1d) or C$_6$H$_3$-2,5-Cl$_2$ (1e)}

Acetylferrocene (1.0 g, 4.4 mmol) was added to 20 ml of ethanol and stirred at room temperature until complete dissolved. Then the stoichiometric amount of the corresponding hydrazine (4.4 mmol), and 0.5 ml of glacial acetic acid were poured into the solution. For compounds 1a–1c and 1e, the reaction mixture was stirred at room temperature for 1 h. The solid formed after this period was collected by filtration, washed with three portions of 5 ml of cold ethanol and air-dried. For ligand 1d, the reaction mixture was refluxed for 20 min to favour the dissolution of the 2,4-dinitrophenylhydrazine. After this period the reaction mixture was filtered and the filtrate was allowed to cool to room temperature. Slow evaporation of the solvent produced the precipitation of compounds 1, which were filtered out and air-dried. Yields: 77 (1a), 82 (1b), 68 (1c), 68 (1d) and 57% (1e).

Characterization data for: 1a: Anal. (%) calcd. for C$_{18}$H$_{17}$N$_3$O$_2$Fe (found): C, 59.52 (59.4); H, 4.72 (4.7) and N, 11.72 (11.6). IR: ν(N–H) = 3351 cm^{-1} and ν(> C=N–) = 1609 cm^{-1}. 1b: Anal. (%) calcd. for C$_{18}$H$_{17}$N$_2$ClFe (found): C, 61.31 (61.15); H, 4.86 (4.75) and N, 7.94 (7.7). IR: ν(N–H) = 3361 cm^{-1} and ν(> C=N–) = 1597 cm^{-1}. 1c: Anal. (%) calcd. for C$_{19}$H$_{20}$N$_2$Fe (found): C, 69.69 (69.7); H, 6.07 (6.1) and N, 8.43 (8.4). IR: ν(N–H) = 3382 cm^{-1} and ν(> C=N–) = 1600 cm^{-1}. 1d: Anal. (%) calcd. for C$_{18}$H$_{16}$N$_4$O$_4$Fe (found): C, 59.96 (59.6); H, 3.95 (3.93) and N, 13.72 (13.72). IR: ν(N–H) = 3307 cm^{-1} and ν(> C=N–) = 1617 cm^{-1}. 1e: Anal. (%) calcd. for C$_{18}$H$_{16}$N$_2$Cl$_2$Fe (found): C, 55.84 (55.75); H, 4.14 (4.2) and N, 7.23 (7.25). IR: ν(N–H) = 3370 cm^{-1} and ν(> C=N) = 1593 cm^{-1}

3.1.2. Preparation of [Pd{(H^5-C$_5$H$_5$)Fe[(H^5-C$_5$H$_3$)-C(CH$_3$)= N-NHR]}(μ-Cl)]$_2$ {R = C$_6$H$_4$-4-NO$_2$ (2a), C$_6$H$_4$-4-Cl (2b), C$_6$H$_4$-2-CH$_3$ (2c) or C$_6$H$_3$-2,4-(NO$_2$)$_2$ (2d), C$_6$H$_3$-2,5-Cl$_2$ (2e)}

Sodium tetrachloropalladate(II), Na$_2$(PdCl$_4$) (0.300 g, 1.02 mmol), Na(CH$_3$COO) · 3H$_2$O (0.139 g, 1.02 mmol) and 1.02 mmol of the corresponding ferrocenylhydrazone 1 were suspended in 20 ml of methanol. The reaction flask was protected from light with aluminium foil and stirred at room temperature for 24 h. The brown (for 2a–2d) or red solid (for 2b, 2c or 2e) that formed was then filtered out and washed with three (5-ml) portions of methanol, and air-dried. Yields: 73 (2a), 80 (2b), 78 (2c), 62 (2d) and 55% for (2e)).

Characterization data for 2a: Anal. (%) calcd. for C$_{36}$H$_{32}$N$_6$Cl$_2$O$_4$Fe$_2$Pd$_2$ (found): C, 42.89 (43.0); H, 3.20 (3.3) and N, 8.34 (8.5). IR: ν(N–H) = 3312 cm^{-1} and ν(> C=N–) = 1602 cm^{-1}. 2b: Anal. (%) calcd.

for C$_{36}$H$_{32}$N$_4$Cl$_4$Fe$_2$Pd$_2$ (found): C, 43.81 (43.7); H, 3.27 (3.3) and N, 5.68 (5.7). IR: ν(N–H) = 3307 cm^{-1} and ν(> C=N–) = 1596 cm^{-1}. 2c: Anal. (%) calcd. for C$_{38}$H$_{38}$N$_4$Cl$_2$Fe$_2$Pd$_2$ (found): C, 46.89 (47.0); H, 4.15 (4.20) and N, 6.07 (6.1). IR: ν(N–H) = 3318 cm^{-1} and ν(> C=N–) = 1595 cm^{-1}. 2d: Anal. (%) calcd. for C$_{36}$H$_{30}$N$_8$O$_8$Cl$_2$Fe$_2$Pd$_2$ (found): C, 39.38 (39.4); H, 2.75 (2.8) and N, 10.20 (10.0). IR: ν(N–H) = 3300 cm^{-1} and ν(> C=N–) = 1614 cm^{-1}. 2e: Anal. (%) calcd. for C$_{36}$H$_{30}$N$_4$Cl$_6$Fe$_2$Pd$_2$ (found): C, 40.95 (41.05); H, 2.86 (3.0) and N, 5.31 (5.4). IR ν(N–H) 3348 cm^{-1} and ν(> C=N–) = 1562 cm^{-1}.

3.1.3. Preparation of [Pd{(H^5-C$_5$H$_5$)Fe[(H^5-C$_5$H$_3$)-C(CH$_3$)= N-NHR]}Cl(PPh$_3$)] {with R = C$_6$H$_4$-4-NO$_2$ (3a), C$_6$H$_4$-4-Cl (3b), C$_6$H$_4$-2-CH$_3$ (3c), C$_6$H$_3$-2,4-(NO$_2$)$_2$ (3d) or C$_6$H$_3$-2,5-Cl$_2$ (3e)}

Triphenylphosphine (100 mg, 0.38 mmol) was added to a suspension containing 0.38 mmol of the corresponding di-μ-chloro-bridged cyclopalladated complex 2, in 20 ml of benzene. The reaction mixture was stirred at room temperature for 1 h, then the undissolved materials were filtered out and discarded, and the dark red filtrate was concentrated on a rotary evaporator to dryness. The residue was then dissolved in a minimum amount of chloroform (ca. 5 ml) and passed through a SiO$_2$ column (10 × 250 mm), using CHCl$_3$:CH$_3$OH (100:1) as the eluant. The first band eluted was collected and concentrated to dryness on a rotary evaporator. The residue was then treated with 10 ml of n-hexane and stirred at room temperature for 30 min. The solid formed was collected by filtration and air-dried. Yields: 72 (3a), 80 (3b), 67 (3c), 70 (3d) and 75% for (3e).

Characterization data for 3a: Anal. (%) calcd. for C$_{36}$H$_{31}$N$_3$ClO$_2$FePdP · 1/2CH$_2$Cl$_2$ (found): C, 54.10 (54.0); H, 3.96 (4.0) and N, 5.19 (5.05). IR: ν(N–H) = 3308 cm^{-1} and ν(> C=N–) = 1609 cm^{-1}. 3b: Anal. (%) calcd. for C$_{36}$H$_{31}$N$_2$Cl$_2$FePdP (found): C, 57.21 (57.2); H, 4.13 (4.2) and N, 3.71(3.65). IR: ν(N–H) = 3306 cm^{-1} and ν(> C=N–) = 1596 cm^{-1}. 3c: Anal. (%) calcd. for C$_{37}$H$_{34}$N$_2$ClFePdP (found): C, 55.11 (55.05); H, 4.25 (4.35) and N, 3.47 (3.5). IR: ν(N–H) = 3300 cm^{-1} and ν(> C=N–) = 1600 cm^{-1}. 3d: Anal. (%) calcd. for C$_{36}$H$_{30}$N$_4$O$_4$ClFePdP (found): C, 53.29 (53.35); H, 3.72 (3.8) and N, 6.91 (6.8). IR: ν(N–H) = 3309 cm^{-1} and ν(> C=N–) = 1608 cm^{-1}. 3e: Anal. (%) calcd. for C$_{36}$H$_{30}$N$_2$Cl$_3$FePdP (found): C, 54.72 (54.5); H, 3.82 (3.8) and N, 3.54 (3.5). IR: ν(N–H) = 3351 cm^{-1} and ν(> C=N–) = 1583 cm^{-1}.

3.2. Electrochemical studies

Electrochemical data for the hydrazones 1 were obtained by cyclic voltammetry under argon at 20°C using acetonitrile (HPLC-grade) as solvent and tetrabutylammonium hexafluorophosphate (0.1 M) as supporting

Table 5
Crystal data and details of the refinement of the crystal structure of compound **3e**. (Standard deviations are given in parentheses)

Empirical formula	$C_{36}H_{30}Cl_3FeN_2PPd$
Crystal size (mm mm mm)	$0.1 \times 0.1 \times 0.1$
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	$a = 10.086(2)$ Å, $b = 22.952(4)$ Å, $c = 13.770(9)$ Å
	$\alpha = 90°$
	$\beta = 90.30(3)°$
	$\gamma = 90°$
Volume (Å^3)	3188(2)
Z	4
Density$_{Calcd}$ (g cm^{-3})	1.647
Absorption coefficient (mm^{-1})	1.351
Θ range for data collection (°)	from 2.02 to 30.13
Index ranges	$-14 \leq h \leq 14, -6 \leq k \leq 32, -2 \leq l \leq 19$
N of reflections collected	9938
N of independent reflections	9468 ($R_{int} = 0.0465$)
Refinement method	Full-matrix least squares on F^2
Data/N of restrains/N of parameters	6662/1/797
Goodness of fit on F^2	1.058
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0591, wR2 = 0.1274$
R indices all data	$R1 = 0.1975, wR2 = 0.2009$
Absolute structure parameter	0.10(5)
Extinction coeficient	0.000(3)
Largest difference peak and hole (e Å^{-3})	0.810 and 0.828
Temperature (K)	293(2)

electrolyte. The half-wave potentials were referred to an Ag/AgNO$_3$ (0.1 M, in acetonitrile) electrode separated from the solution by a medium porosity fritted disk. A platinum wire auxiliary electrode was used in conjunction with a platinum disk working electrode, TACUSSEL-EDI rotatory electrode (3.14 mm^2). Cyclic voltammograms of 1×10^{-3} M solutions of the samples in acetonitrile were recorded with a VersaStat, EG&G Princeton Applied Research potentiostat.

3.3. Crystal structure determination and refinement

A prismatic crystal (sizes in Table 5) was selected and mounted on an Enraf–Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections in the range $12° < \Theta < 21°$) and refined by a least squares method. Intensities were collected with a graphite monochromatized Mo Kα radiation, using $\omega/2\Theta$ scan-technique. There were 9938 reflections measured in the range $2.02° < \Theta < 30.13°$ of which 9468 were non-equivalent by symmetry [R_{int} (on I) = 0.046] and 4544 were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed. Corrections were made for Lorentz polarization but not for absorption.

The structure was solved by direct methods, using SHELXS computer program [32] and refined by full-

matrix least-squares method using SHELX93 computer program [33]. The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0807P)^2 + 0.6527P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from Ref. [34]. The absolute configuration of the structure was defined from the Flack coefficient [35], which is equal to 0.10(5) for the results given. Fifty-eight hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final R (on F) and wR (on F^2) factors were 0.059 and 0.127, respectively. Further details concerning the resolution and refinement of the crystal structure of complex **3e** are also presented in Table 5.

Acknowledgements

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