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A bis(cyclopalladated) tetranuclear derivative of methyl ferrocenyl ketone azine: $[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CMe{=}N]Cl(PPh_3)\}_2]$

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The bis(cyclopalladated) tetranuclear compound $[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CMe{=}N]Cl(PPh_3)\}_2]$ has been prepared and characterized. Proton and ^{31}P NMR spectra reveal the presence of four diastereomers in solution. The crystal structure of the *meso* form has been determined by X-ray crystallography. This confirms the existence of two five-membered palladacycles with a $\sigma(Pd\text{–}C_{sp^2,\mathrm{ferrocene}})$ bond. Electrochemical studies, based on cyclic voltammetry, and Mössbauer spectra are also reported.

Since 1968, when Cope and Friedrich[1] began the study of cyclopalladated compounds containing N-donor ligands, interest in complexes of this kind has increased enormously.[2] Most examples described so far refer to palladacycles containing a five- or six-membered ring and a $\sigma(Pd\text{–}C_{sp^2,\mathrm{phenyl}})$ or a $\sigma(Pd\text{–}C_{sp^3,\mathrm{aliphatic}})$ bond. During the last few years several cyclopalladated compounds in which the palladium atom is linked to a $C_{sp^2,\mathrm{ferrocene}}$ atom have also been prepared and characterized.[3,4] However, the literature reporting double cyclopalladation of an N-donor ligand is scarce,[5] and only in one paper the activation of two $\sigma(C_{sp^2,\mathrm{ferrocene}}\text{–}H)$ bonds in 1,1′-ferrocenedylbis(hydrazones) has been proposed.[5h] More recently, Butler[3h] reported further attempts to achieve a double cyclopalladation of 1,1′-bis(2,2′-bipyridin-6-yl)ferrocene. However, all these experiments failed and only monocyclopalladated complexes with $\sigma(Pd\text{–}C_{sp^2,\mathrm{ferrocene}})$ bonds were obtained in all cases.

In the light of these findings we attempted to determine whether methyl ferrocenyl ketone azine $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CMe{=}N]_2$ **1** could undergo cyclopalladation on the two ferrocenyl moieties simultaneously, thus providing polymetallic cyclopalladated derivatives. In this paper we report the first examples of mono- and bis-(cyclopalladated) complexes with $\sigma(Pd\text{–}C_{sp^2,\mathrm{ferrocene}})$ bonds derived from ferrocenylazines.

Results and Discussion

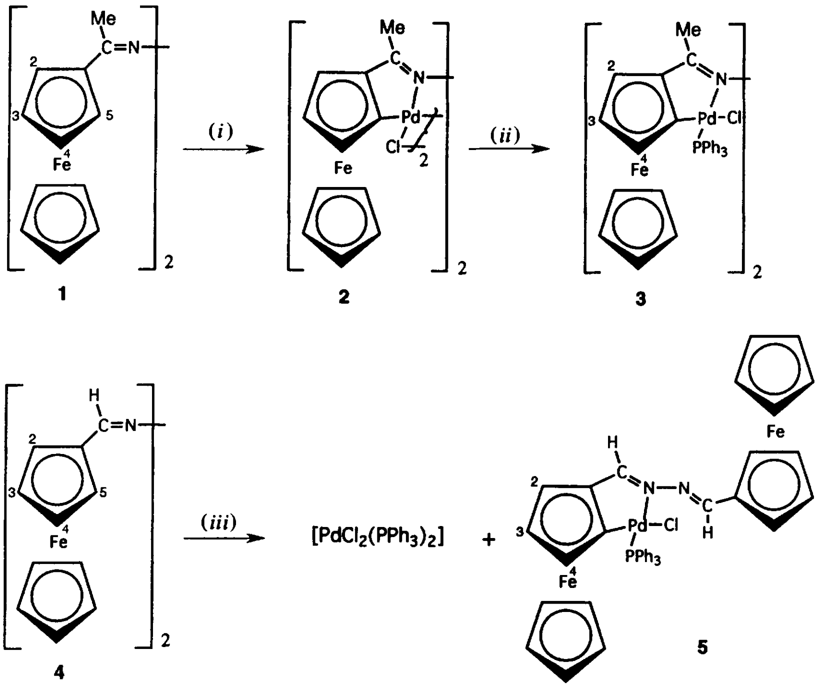
Syntheses and characterization

The $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CMe{=}N]_2$ **1**[6,7] reacts with $Na_2[PdCl_4]$ in the presence of $Na(O_2CMe)\cdot 3H_2O$ in a 1:2:2 molar ratio in methanol giving the di-μ-chloro-bridged derivative $[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CMe{=}N](\mu\text{-}Cl)\}_2]$ **2** (Scheme 1). The structure proposed is consistent with the elemental analyses and has been tentatively assigned by analogy with recently results[5j] which have demonstrated (by X-ray analyses) that double cyclopalladation of bis(*N*-benzylidene)-1,4-phenylenediamine yields a non-polymeric tetranuclear halide-bridged compound. Addition of triphenylphosphine to benzene suspensions of complex **2** results in cleavage of the chloride bridges and the formation of $[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CMe{=}N]Cl(PPh_3)\}_2]$ **3**. However, when $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH{=}N]_2$ **4** was used as starting material (Scheme 1) the reaction produced $[PdCl_2(PPh_3)_2]$ and only small amounts (*ca.* 5%) of the trimetallic cyclopalladated complex $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CH{=}NN{=}CH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ **5**. Attempts to obtain the monometallated derivative from **1** were unsuccessful even when the reagents were used in a 1:1:1 molar ratio and no evidence of its formation was detected by NMR spectroscopy.

Compounds **2**, **3** and **5** are dark red solids at room temperature. All except **2** are highly soluble in the most common solvents. Elemental analyses are consistent with the proposed formulae. Proton and ^{31}P NMR spectra of **3** and **5** have also been recorded. Although the ^1H NMR pattern recorded for **5** was that expected, proton and ^{31}P NMR spectra of **3** exhibited higher complexity (Fig. 1 and Table 1) than expected, as compared with those of related compounds $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CMe{=}NR\}Cl(PPh_3)]$.[4b]

As a first approach to explain the existence of four signals in the ^{31}P NMR spectrum and the complex pattern in the proton NMR spectrum (Fig. 1) molecular models were used. They showed that four diastereomers could be formed. As shown in Fig. 2, this molecule can easily be visualized as derived from the fusion of two fragments '$Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CMe{=}N\}Cl(PPh_3)$' (hereinafter referred to as **I** and **II**) linked through the nitrogen. In this compound the planar chirality of the two 1,2-disubstituted ferrocenyl moieties can be opposite (*R*,*S*) or identical [(*R*,*R*) or (*S*,*S*)] [Fig. 2, **A** (*meso* form) and **B** (*rac*), respectively]. Consequently, if **3** consists of a mixture of **A** and **B**, two singlets (in the ^{31}P NMR spectrum) and two sets of superimposed signals (in the proton NMR spectrum) would also be expected. In addition, in each of the isomers (**A** and **B**) the environment around the $>C{=}N\text{–}$ groups and the palladium atoms is so crowded (see also the crystal structure described below) that free rotation around the N–N bond is prevented. Indeed, the presence of rotameric species for more simple related cyclopalladated complexes of general formulae $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CR'{=}NR\}Cl(PPh_3)]$ (with bulky R substituents)[4b] or for $[\{Pd(C_6H_4CH{=}N)L\}_2]$ (L = diethyldithiocarbamate)[5k] has been reported.

In order to test whether rotation around the N–N bond could be promoted by temperature, proton and ^{31}P NMR spectra of the mixture of isomers **3** were recorded at different temperatures from 330 to 298 K. However, no significant variations of the positions of the signals, their shapes or their



Scheme 1 (*i*) $Na_2[PdCl_4]$, $Na(O_2CMe)$, MeOH, room temperature (r.t.); (*ii*) $4PPh_3$, C_6H_6, r.t.; (*iii*) (*a*) $Na_2[PdCl_4]$, $Na(O_2CMe)$; (*b*) PPh_3, C_6H_6

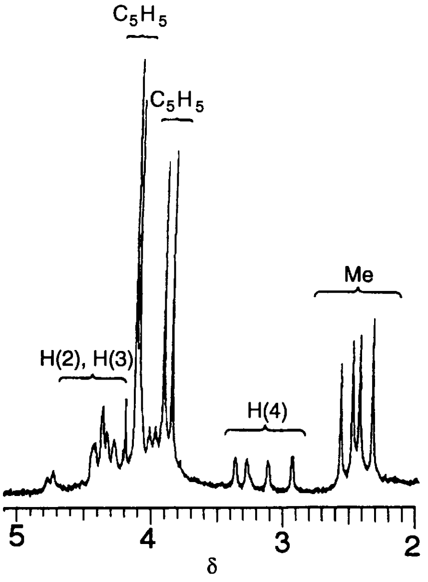


Fig. 1 Proton NMR spectrum of compound **3** in the range δ 2.0–5.0

Table 1 Selected ^1H NMR spectroscopic data (δ). Atom numbering as in Scheme 1

Compound	H(2)	H(3)	H(4)	C_5H_5	CH_3	CH=N
1	4.73	4.37[a]	4.37[a]	4.29	2.18	—
3 *meso*	4.44	3.96	3.26	4.11	2.47	—
	4.36	4.07	3.15	3.91	2.42	—
rac	4.33	3.93	3.27	4.09	2.56	—
	4.28	4.01	2.91	3.64	2.32	—
4	4.83	4.54[a]	4.54[a]	4.29	—	7.38
5	4.24[b]	4.12[b]	3.49[b]	3.94[b]	—	8.51[c]
	4.76[d]	4.45[a,d]	4.45[a,d]	4.31[d]	—	9.36[e]

[a] Atoms H(3) and H(4) are equivalent for the metallated ferrocenyl moiety. [b] Metallated ferrocenyl unit. [c] Corresponds to the proton bound to the >C=N– group contained (*endo*) in the palladacycle, and appears as a doublet due to coupling with the P atom of the PPh_3 ligand. [d] Due to the protons of $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$. [e] Due to the proton of the CH=N group bound to the non-metallated ferrocenyl moiety.

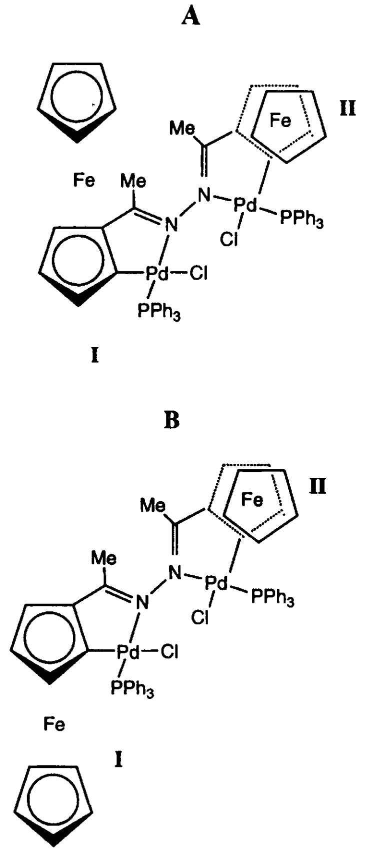


Fig. 2 Schematic view of two of the diastereomers **A** and **B** (*meso* and *rac* forms, respectively) formed by activation of $\sigma(Pd\text{–}C_{sp^2,ferrocene})$ bonds in compound **3**. The two halves of the molecule (**I** and **II**) are orthogonal and the ferrocenyl moiety in **II** has been simplified to facilitate understanding and viewing of the two isomers. The dashed pentagonal ring indicates that the C_5H_5 group is in a lower plane

relative intensities were observed. This finding signifies that the environment around the azine group is so crowded that rotation of the two halves of the molecule is precluded on steric grounds, even at 330 K. For **3**, the inhibition of the rotation around the

N–N bond introduces axial chirality, and consequently two *meso*-[(*S*)-(*RS*) and (*R*)-(*RS*)] forms and two *rac* pairs could be expected. On this basis the ^{31}P NMR spectrum of a mixture containing the four isomers would exhibit four singlets (two for the *rac* and two for the *meso* forms). When the ^{31}P NMR spectrum was recorded at lower temperatures (240 K) the intensities of the two signals assigned to the *meso* form (see below) decreased; such a change was also consistent with the decrease in the relative intensity of the set of signals due to this component in the proton NMR spectra. In the two experiments the formation of a solid was detected, thus suggesting that the isomers may exhibit different solubility in $CDCl_3$.

Fractional crystallization of compound **3** in CH_2Cl_2–hexane (1 : 1) allowed us to obtain good-quality crystals of the *meso* form. Comparison of the ^1H and ^{31}P NMR spectra of the mixture and that of the *meso* form allowed us to assign unambiguously the signals due to the racemic forms.

Crystal structure of the *meso* form of compound 3

A perspective drawing of the molecular structure is shown in Fig. 3, and selected bond lengths and angles are given in Table 2. The structure consists of discrete molecules of $[\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)CMe{=}N]Cl(PPh_3)\}_2]$ separated by van der Waals forces, and also contains a CH_2Cl_2 molecule as solvate. As mentioned above, the molecule can be visualized as derived from the fusion of the two fragments **I** and **II** through the nitrogen, each of which contains four-co-ordinated palladium(II) atom [Pd(1) or Pd(2)] bound to the phosphorus of the triphenylphosphine [P(1) or P(2)], the nitrogen [N(1) or N(2)] and one of the carbon atoms of the ferrocenyl unit [C(9) or C(19), for fragments **I** and **II**, respectively]. These findings confirm the double cyclopalladation of the azine.

The co-ordination around the palladiums [Pd(1) or Pd(2)] is slightly different in each of units **I** and **II**, as reflected in the palladium–ligand bond lengths, such as Pd(1)–P(1) [2.256(2)] and Pd(2)–P(2) [2.224(1) Å] (Table 2). More significant are the differences in bond angles around the palladium [*i.e.* N(1)–Pd(1)–P(1) 177.3(1) or N(2)–Pd(2)–P(2) 166.1(1)°] and even for Cl(1)–Pd(1)–P(1) or Cl(2)–Pd(2)–P(2) which clearly exceed 3σ. The two palladium atoms are in a distorted square-planar environment but the Pd(2) centre presents a stronger tetrahedral distortion than the Pd(1).* Furthermore, the torsion angles C(10)–C(11)–N(1)–N(2) and C(13)–C(12)–N(2)–N(1) are also different (−178.8 and 167.6°), thus showing once more that, from the structural point of view, the two halves of the molecule are not identical.

The distances between the two metals (Fe and Pd) in each fragment are consistent with data reported for other five-membered palladacycles with $\sigma(Pd\text{–}C_{sp^2,\text{ferrocene}})$ bonds (3.45–3.65 Å).[3b,h–j,4]

The molecule contains two endocyclic five-membered palladacycles, one of which is defined by the atoms Pd(1), N(1), C(9), C(10) and C(11), the other by Pd(2), N(2), C(13), C(15) and C(19). The two metallacycles are essentially planar and form angles of 2.3 and −7.2° with the plane of the C_5H_3 units in the two fragments. The relative orientation of the two palladacycles can easily be defined by the angle between the normals to their planes (82.9°), thus providing a quasi-orthogonal arrangement.

In each ferrocenyl moiety the $Fe\text{–}C_{ring}$ and $C\text{–}C_{ring}$ bond distances are consistent with those expected for ferrocene derivatives.[8] The pentagonal rings are planar and practically parallel. However, the two ferrocenyl units have different conformations (eclipsed and staggered for fragments **I** and **II**, respectively, as reflected in the twist angles,[9] 32.7 and −7.0°).

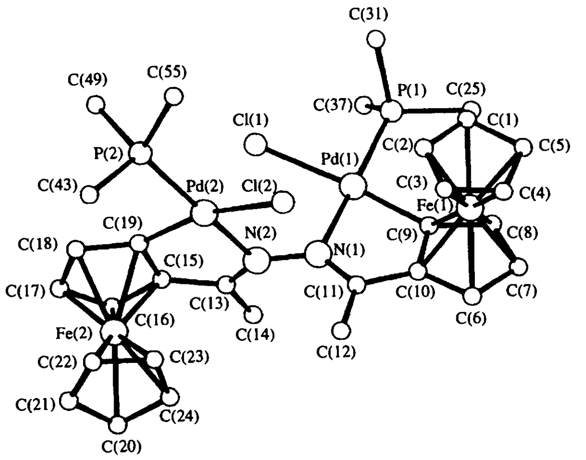


Fig. 3 View of the molecular structure of the *meso* form of complex **3**, together with the atomic numbering scheme. Some of the C atoms of the PPh_3 groups have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for compound **3** with estimated standard deviations in parentheses

Pd(1)–P(1)	2.256(2)	Pd(2)–P(2)	2.224(1)
Pd(1)–Cl(1)	2.376(2)	Pd(2)–Cl(2)	2.361(2)
Pd(1)–N(1)	2.121(4)	Pd–N(2)	2.154(4)
Pd(1)–C(9)	2.000(5)	Pd(2)–C(19)	1.983(6)
N(1)–C(11)	1.292(7)	N(2)–C(13)	1.303(7)
C(9)–C(10)	1.444(7)	C(19)–C(15)	1.444(7)
C(10)–C(11)	1.456(8)	C(13)–C(15)	1.451(7)
C(11)–C(12)	1.490(9)	C(13)–C(14)	1.475(8)
Fe(1) ··· Pd(1)	3.610(1)	Fe(2) ··· Pd(2)	3.472(1)
Fe(1) ··· Fe(2)	8.425(1)	Pd(1) ··· Pd(2)	4.477(1)
Pd(1)–Pd(1)–Cl(1)	89.9(1)	P(2)–Pd(2)–Cl(2)	95.7(1)
N(1)–Pd(1)–C(9)	79.8(2)	N(2)–Pd(2)–C(19)	80.3(2)
C(9)–Pd(9)–P(1)	99.1(2)	C(19)–Pd(2)–P(2)	91.0(2)
N(1)–Pd(1)–C(1)	90.9(1)	N(2)–Pd(2)–Cl(2)	95.4(1)
N(1)–C(11)–C(10)	112.2(5)	N(2)–C(13)–C(15)	113.4(4)
C(11)–C(10)–C(9)	119.0(5)	C(13)–C(15)–C(19)	118.8(5)
C(10)–C(9)–Pd(1)	111.4(4)	C(15)–C(19)–Pd(2)	112.2(4)
Pd(1)–N(1)–N(2)	122.6(3)	Pd(2)–N(2)–N(1)	127.2(3)

This crystal structure confirms that the distribution of ligands around the palladiums is rather crowded and may be responsible for the inhibition of rotation around the N–N bond, mainly due to steric repulsion between the methyl group on one half of the molecule and the ligands bound to the palladium in the other.

In order to confirm the inhibition of the rotation around the N–N bond the program EHMACC[10] was used to calculate the total energy of the *meso* form of compound **3** for different values of the torsion angle C(11)–N(1)–N(2)–C(13), hereafter referred to as Φ. The atomic coordinates for all atoms obtained from the X-ray studies were used to generate the internal coordinates; the independent variable introduced was the torsion angle Φ. Fig. 4 shows the variation of the total energy as a function of Φ. These calculations revealed that for $\Phi > -90°$ (or smaller than −140°) the total energy increased substantially due to short contacts between the substituents belonging to each half of the molecule. This finding is in good agreement with the conclusions reached from the NMR data. Furthermore, the minimum of the plot corresponds to $\Phi = -120.8°$, which is quite close to the experimental value [−112.7(6)°] obtained from the X-ray studies.

Iron-57 Mössbauer spectra of compounds **1** and **4** showed a single quadrupole doublet. The isomer shifts (i.s.) and quadrupole splitting (q.s.) (Table 3) are in good agreement with those of ferrocenylimines of general formula $[Fe(\eta^5\text{-}C_5H_5)\{(\eta^5\text{-}$

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* The deviations of the atoms C(19), N(2), P(2) and Cl(2) from the mean plane are 0.254, 0.023, 0.200 and −0.176 Å, while those of C(9), N(1), P(1) and Cl(1) from the mean plane are 0.028, −0.028, −0.022 and 0.022 Å.

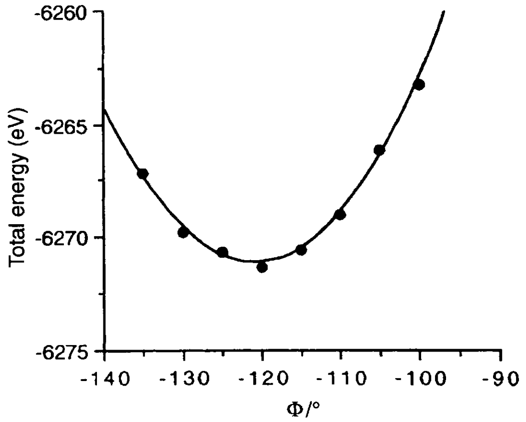

Fig. 4 Plot of the total energy of the molecule *versus* the torsion angle Φ defined by the atoms C(11)–N(1)–N(2)–C(13); eV ≈ 1.60×10^{-19} J

Table 3 Mössbauer parameters (mm s^{-1}) at 78 K

Compound	i.s.	q.s.	Γ*
1	0.51(1)	2.29(1)	0.17(1)
3	0.51(1)	2.25(1)	0.13(1)
4	0.52(1)	2.27(1)	0.15(1)

* Linewidth.

$C_5H_4)CR'$=NR}].[4c,11] For compound **3** a single quadrupole doublet was also obtained and its linewidth was similar to those obtained for **1**, **4** and related derivatives, thus allowing us to rule out the existence of two overlapping quadrupole doublets. Consequently, the electronic properties of the iron(II) in each of the isomers of **3** are not expected to be different. These findings reveal that the structural differences in the two fragments of the molecule in the *meso* form of **3** do not affect the electronic environment of the iron(II) centres. This suggests that the structural differences are purely due to steric effects and can be accommodated without upsetting the electronic structure of the entire molecule.

The substitution of two σ($C_{sp^2,ferrocene}$–H) bonds in compound **1** by σ(Pd–$C_{sp^2,ferrocene}$) bonds is reflected in a decrease in the q.s. value, thus allowing us to attribute an electron-withdrawing character to the palladium moiety bound to the ferrocenyl group. This finding is in excellent agreement with our previous work on the Mössbauer spectra of ferrocenylimines and their cyclopalladated derivatives; [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)CR'=NR}Cl(PPh$_3$)].

In order to test how the formation of the metallacycle could affect the electrochemical behaviour of the two iron centres cyclic voltammograms[12] of compounds **1** and **4** and the metallated complexes were recorded. For **1** and **4** only one wave was detected, thus indicating that the two moieties are independent. The cyclic voltammogram of **3** was similar to that of **1**, except for the position of the wave which appears at lower potentials [$E_{\frac{1}{2}}$ = 0.10 and 0.17 V for **3** and **1**. *vs.* ferrocene–ferrocenium respectively], and it is consistent with previous electrochemical studies of ferrocenylimines of general formula [Fe(η^5-C_5H_5){(η^5-C_5H_4)CR'=NR}] and their cyclopalladated derivatives [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)CR'=NR}Cl(PPh$_3$)], which showed that the formation of the palladacycle facilitates oxidation of iron(II).[13] The cyclic voltammogram for complex **5** showed two independent waves ($E_{\frac{1}{2}}$ = 0.09 and 0.22 V). The less anodic peak, which is shifted to more negative potentials than for **4** ($E_{\frac{1}{2}}$ = 0.12 V), is attributed to the oxidation of iron(II) of the metallated moiety, while the second peak, at higher potentials, corresponds to the oxidation of the other iron(II). Consequently, in this case the two iron(II) centres which are in different chemical environments exhibit different proclivity to undergo oxidation-reduction processes. Only after one iron centre is oxidized the other feels an additional electronic effect and needs a higher potential to oxidize.

Experimental

Elemental analyses of C, H and N were carried out at the Institut de Química Bio-Orgànica (Consejo Superior de Investigaciones Cientificas, Barcelona). Infrared spectra were recorded using KBr discs on a Nicolet 520-FTIR spectrophotometer, ^1H NMR spectra on a GEMINI 200 MHz spectrometer using $CDCl_3$ (99.8%) as solvent and $SiMe_4$ as standard and ^{31}P-{^1H} NMR spectra on a Bruker 250 MHz spectrometer using $CHCl_3$ as solvent and $P(OMe)_3$ [δ(^{31}P) 140.17] as reference. Variable-temperature NMR experiments were carried out in the range 240–330 K using the Bruker 250 MHz spectrometer.

Materials and syntheses

The ferrocenylazines [(η^5-C_5H_5)Fe(η^5-C_5H_4)CR=N]$_2$ (R = Me **1** or H **4**) were prepared as described previously.[6] All the solvents were dried and distilled before use. **CAUTION**: some of the preparations described involve the use of benzene which should be handled with care.

[{Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3)CMe=N](μ-Cl)}$_2$] 2. The ferrocenylazine **1** (1.58 g, 3.73 mmol), $Na_2[PdCl_4]$ (2.06 g, 7.0 mmol) and $Na(O_2CMe)\cdot 3H_2O$ (0.956 g, 7.0 mmol) were suspended in methanol (140 cm^3). The reaction mixture was protected from the light with aluminium foil and stirred at room temperature (*ca.* 20 °C) for 3 h. After this period the dark red solid formed was filtered off, washed with methanol (until colourless washings were obtained) and finally air-dried. Yield: 45% [Found (Calc. for $C_{48}H_{44}Cl_4Fe_4N_4Pd_4$): C, 39.2 (38.9); H, 3.00 (3.05); N, 3.80 (3.80)%]. IR: $\tilde{\nu}_{max}$(C=N) 1537 cm^{-1}.

[{Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3)CMe=N]Cl(PPh$_3$)}$_2$] 3. Complex **2** (0.460 g, 0.31 mmol) and triphenylphosphine (0.328 g, 1.25 mmol) were suspended in benzene (20 cm^3). The reaction mixture was stirred at room temperature for 30 min and then the undissolved materials were filtered off and discarded. The dark wine-coloured solution was concentrated to dryness in a rotary evaporator. Addition of hexane followed by vigorous stirring resulted in precipitation of compound **3** Yield: 80% [Found (Calc. for $C_{60}H_{52}Cl_2Fe_2N_2P_2Pd_2\cdot CH_2Cl_2$): C, 54.55 (54.7); H, 4.05 (4.20); N, 2.10 (2.20)%]. IR: $\tilde{\nu}_{max}$(C=N) 1560 cm^{-1}. ^{31}P NMR: δ 40.03, 39.64, 38.03 and 37.61. Slow evaporation of CH_2Cl_2–hexane (1 : 1) solutions of **3** gave the *meso* form as the less-soluble fraction. ^{31}P NMR: δ 39.64 and 37.61.

[Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)CH=NN=CH(η^5-C_5H_4)Fe(η^5-C_5H_5)}Cl(PPh$_3$)] 5. Compound **4** (1.50 g, 3.5 mmol), $Na_2[PdCl_4]$ (2.09 g, 7.0 mmol) and $Na(O_2CMe)\cdot 3H_2O$ (0.96 g, 7.0 mmol) were suspended in methanol (40 cm^3), and the mixture protected from light with aluminium foil. The solid formed after this period (24 h) was filtered off, washed with methanol and air-dried. Then this material was suspended in benzene (20 cm^3) and treated with triphenylphosphine (0.185 g, 0.7 mmol). The reaction mixture was stirred at room temperature for 30 min. The undissolved materials were then filtered out and the filtrate was concentrated to dryness on a rotary evaporator. The oily residue was treated with hexane to induce precipitation and the solid formed was filtered out and air-dried. This material was suspended in the minimum volume of CH_2Cl_2 to remove the major component $[PdCl_2(PPh_3)_2]$ and the red filtrate obtained was then treated again with hexane to induce precipitation. The solid formed was filtered off and air-dried. Yield: 5% [Found. (Calc. for $C_{40}H_{34}Fe_2N_2PPd$): C, 58.05 (58.2); H, 4.10 (4.20); N,

Table 4 Crystallographic data for compound **3**

Formula	$C_{60}H_{52}Cl_2Fe_2N_2P_2Pd_2\cdot CH_2Cl_2$
M	1342.4
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	13.333(2)
b/Å	13.864(2)
c/Å	15.759(3)
α/°	78.26(2)
β/°	88.68(2)
γ/°	84.78(1)
U/Å^3	2840(1)
Z	2
D_c/g cm^{-3}	1.569
λ(Mo-Kα)/Å	0.710 69
μ(Mo-Kα)/cm^{-1}	13.99
F(000)	2756.0
R	0.050
R′	0.057
No. reflections collected	10 113
No. observed reflections	8422

3.40 (3.60)%]. IR: $\tilde{\nu}_{max}$(C=N) 1609 and 1605 cm^{-1}. ^{31}P NMR: δ 38.9.

Crystallography

A summary of the crystal data for the *meso* form of complex **3** is given in Table 4. A prismatic red crystal (0.1 × 0.1 × 0.1 mm) was selected and mounted on an Enraf-Nonius CAD-4 diffractometer. Unit-cell parameters were calculated from accurate settings of 25 automatically centred reflections in the range $12 \leqslant \theta \leqslant 16°$ and refined by the least-squares method. Intensities were collected with graphite-monochromated Mo-Kα radiation using ω–2θ scans. The numbers of collected reflections in the range $2 \leqslant \theta \leqslant 25°$ and those assumed as observed [$I \geqslant 2.5\sigma(I)$] are given in Table 4. Three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz-polarization corrections were made but not for absorption. The structure was solved by Patterson synthesis using the SHELXS 86[14] computer program and refined by full-matrix least squares with SHELX 76.[15] The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.0030|F_o|^2]^{-1}$. Values of *f*, *f′* and *f″* were taken from ref. 16. All the hydrogen atoms were located from a difference synthesis and refined with an overall isotropic thermal parameter. The number of parameters refined was 790. Maximum shift/e.s.d. = 0.1, maximum and minimum peaks in the final difference syntheses 0.3 and −0.3 e Å^{-3}.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/111.

Electrochemical studies

Cyclic voltammetry was performed at 293 K under nitrogen using acetonitrile (HPLC grade) as solvent and tetrabutylammonium hexafluorophosphate as supporting electrolyte (10^{-3} mol dm^{-3}). The half-wave potentials were referred to an Ag–AgNO$_3$ (0.1 mol dm^{-3} in acetonitrile) electrode separated from the solution by a medium-porosity fritted disc. A platinum-wire auxiliary electrode was used in conjunction with a platinum-disc TACUSSEL-EDI rotatory electrode (area 3.14 mm^2). The DACFAMOV potentiostat was described previously.[17] Cyclic voltammograms of ferrocene were recorded before and after each sample solution, in order to check the viability and reproducibility, especially to test the stability of the Ag–AgNO$_3$ electrode.[18] Three cyclo-voltammograms of 10^{-3} mol dm^{-3} solutions of the samples were run and the average values of the measured $E_{\frac{1}{2}}$ were later referred to ferrocene, which was used as standard. Working under these experimental conditions the standard error of $E_{\frac{1}{2}}$ was ± 5 mV.

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,[19] was calibrated with natural iron absorber 25 mm thick, which was used as a zero for the isomer shift measurements. The spectral data were computed fitted.

Acknowledgements

Financial support was generously provided by the Dirección General de Investigación Científica y Técnica (Grants Nos. PB89-0254 and PB-93-0804). We are also grateful to Dr. Eliseo Ruiz for helping us with the EHMACC program.[10]

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Received 12*th April* 1996; *Paper* 6/02576E