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Stereochemical rigidity in a trimetallic complex. X-ray crystal structure of *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}CH{=}N\text{-}N(CH_3)_2]\}_2Cl_2]$

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Abstract

The reaction of the novel ferrocenylhydrazone $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH{=}N\text{-}N(CH_3)_2\}]$ (1) with $Na_2[PdCl_4]$ in methanol at room temperature produces the trimetallic complex *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}CH{=}N\text{-}N(CH_3)_2]\}_2Cl_2]$ (**2**). NMR spectra of complex **2** reveal the presence of two isomers in solution. The crystal structure of **2** has been determined from X-ray diffraction. This complex crystallizes in the orthorhombic system, space group *Pcab* with $a = 9.353(2)$, $b = 12.061(5)$, $c = 23.487(4)$ Å. The structure reveals that the two chlorine atoms and the two imine nitrogens of the ferrocenylhydrazones are located strictly in a plane; in addition, the hydrazone backbone {⟩C=N–N–} is forced into a position which is nearly orthogonal with the coordination plane. Electrochemical data, based on cyclic voltammetry, for the two compounds reveals that the coordination of the hydrazine ligand hinders the oxidation of the ferrocenyl unit. © 1997 Elsevier Science S.A.

Keywords: Ferrocene; Hydrazone; Electrochemistry; Palladium(II)

1. Introduction

One of the areas of organometallic chemistry that has undergone major developments in recent years is that concerning ferrocene derivatives. Interest in these compounds is not only related to their applications [1], but also to the fact that the presence of one or more heteroatoms with good donor abilities (such as nitrogen, phosphorus, oxygen, sulphur, etc.) or unsaturated fragments provides potential sites susceptible to which one or more metal ions might bind [2,3]. The coordination of metals to these substrates generates multicentre molecules {heterobis- and/or heteropolymetallic species} which have potential in many different areas. In addition, in these compounds the presence of proximal metals with varying environments and oxidations or spin rates may influence the mutual cooperation of these metals in a wide variety of processes. For instance, it is well known that in compounds $[M\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}NH_2]\}_2Cl_2]$ the proclivity of the Fe(II) to be oxidized is strongly dependent on the nature of the M(II) ion [3].

We therefore decided to prepare and characterize the novel ferrocenylhydrazone $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH{=}N\text{-}N(CH_3)_2\}]$ (1, Fig. 1) and to study its reaction with palladium(II) salts in order to isolate heteropolymetallic species containing ferrocenyl units, and to clarify the influence of the coordination of the palladium(II) on the properties of the ferrocenylhydrazone.

2. Results and discussion

The new ferrocenylhydrazone $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}CH{=}N\text{-}N(CH_3)_2\}]$ (1) was prepared at room temperature by condensation of equimolar amounts of ferrocenecarboxaldehyde and 1,1-dimethylhydrazine in ethanol. Compound **1** is a yellow solid at room temperature and exhibits high solubility in the most common solvents (i.e. $CHCl_3$, CH_2Cl_2, methanol, benzene), but it is insoluble in alkanes, and hydrolyzes quite quickly in aqueous or acidic media. Elemental analyses {see Section 3} are consistent with the proposed formula. The infrared spectrum shows a sharp intense band at ca. 1620 cm^{-1} due to the asymmetric stretching of the ⟩C=N– group.

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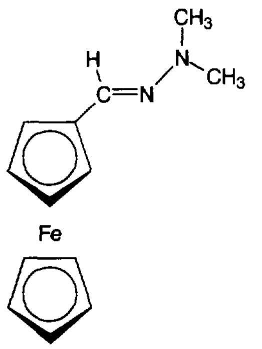


Fig. 1. Schematic view of the ferrocenylhydrazone under study.

Proton and carbon-13 NMR data (Table 1) are consistent with the typical patterns described previously for monosubstituted ferrocenyl derivatives, as well as for a *trans*-arrangement between the ferrocenyl group and the amine nitrogen (*anti*-conformation). Interestingly, the resonance due to the imine carbon atom appears {ca. 143.53 ppm} strongly shifted to higher fields than in related ferrocenyl imines of general formula [$(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{-}C(R){=}N\text{-}R'\}$] with R = H, CH_3 or C_6H_5 and R′ = phenyl, benzyl or naphthyl groups (in the range 160–170 ppm [4,5]). This indicates that the $N\text{-}N(CH_3)_2$ group has a superior donor ability than that of N–R′.

When compound **1** was treated at room temperature with $Na_2[PdCl_4]$ {in a 2:1 molar ratio} in methanol, the trimetallic complex was formed in good yield (80%), and an identical product was obtained when the molar ratio Pd(II):hydrazone was 1:1, but in this case the yield was significantly lower (30%).

Some recent studies of ferrocenyl Schiff bases have shown that when these substrates react with $Na_2[PdCl_4]$ and $Na(CH_3COO)\cdot 3H_2O$ in a 1:1:1 molar ratio, the reaction yields di-μ-chloro-bridged cyclopalladated complexes containing a $\sigma(Pd\text{-}C_{sp^2,\,\text{ferrocene}})$ bond [5–7]. However, for ligand **1**, attempts to obtain palladocyclic derivatives using these methods were unsuccessful. This finding is not surprising, since it is well known that the procedures described so far for the cyclopalladation of organic imines [8] usually fail when the starting materials are replaced by hydrazones [9].

The infrared spectrum of **2** shows one band assignable to the Pd–Cl stretching vibration, suggesting that the two chlorine atoms are mutually *trans* [10]. In addition the shift of the band due to the $\rangle C{=}N\text{-}$ group (at ca. 1611 cm^{-1}) indicates that the ligand binds to the metal through the lone pair of the imine nitrogen [11]. This is the most common mode of coordination of hydrazones to transition metals, and in particular to palladium(II) [12–19].

NMR spectra {^1H and ^{13}C} of **2** were rather complex, since for each type of equivalent nucleus {^1H or ^{13}C respectively} two resonances were observed (Table 1), thus suggesting the existence of two isomeric species in solution.

In an initial attempt to explain the complexity of the spectra a molecular model for the *trans* isomer of **2** was constructed, but its manipulations revealed that a coplanar arrangement between the '$PdCl_2$' fragment and the backbones of the hydrazones {$\rangle C{=}N\text{-}N$} was not possible since such an orientation would involve short contacts between the Cl groups and the *ortho* hydrogens of the C_5H_4 rings in each one of the ferrocenyl moieties. Consequently, this steric hindrance precludes the free rotation around the Pd–N bond. Furthermore, if rotation of the ferrocenyl fragments around the $C_{ipso}\text{-}C_{imine}$ bond occurred, it would bring the C_5H_5 rings too close to one or both of the two methyl groups bound to the amine nitrogen, leading to the destabilization of the system due to steric repulsions. Thus it would seem that the complexity of the NMR spectra might be due to the presence of two isomeric species in solution: **A** and **B** (Fig. 2), which only differ in the relative orientation of the two C_5H_5 rings of the two coordinated ferrocenyl ligands. Natile et al. [12] have also identified rotameric species in solution for palladium(II) compounds of general formula *trans*-[$Pd(R^1R^2C{=}N\text{-}NR^3R^4)_2Cl_2$] {with R^1 = H, CH_3, CH_3CH_2; $R^2 = CH_3$, CH_3CH_2 or ^iPr; $R^3 = CH_3$ or C_5H_5; $R^4 = CH_3$}.

In order to determine whether the interconversion of these isomers (by rotation around the Pd–N or the

Table 1
NMR spectral data {^1H and ^{13}C (ppm)} and electrochemical data for compounds under study (labelling of the atoms refers to the schemes shown below)

(A) *^1H NMR data*

	Cp	H^2,H^5	H^3,H^4	–CH=N	N–CH_3
1	4.13	4.51	4.24	7.14	2.83
2 [a]	4.33	5.88	4.70	8.15	3.19
	4.24	5.62	4.56	8.14	3.01

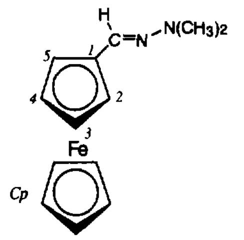
(B) *^{13}C NMR data*

	Cp	C^1	C^2,C^5	C^3,C^4	–CH=N	N–CH_3
1	69.00	82.12	72.12	73.45	143.53	43.36
2 [a]	70.49	[b]	73.75	73.11	166.48	49.71
	70.52	[b]	73.33	72.82	167.85	48.89

(C) *Electrochemical data: half-wave potentials $E_{1/2}(Fc)$ (V)*

	$E_{1/2}(Fc)$		$E_{1/2}(Fc)$
1	−0.03	**2**	0.32

[a] See text. [b] Not observed



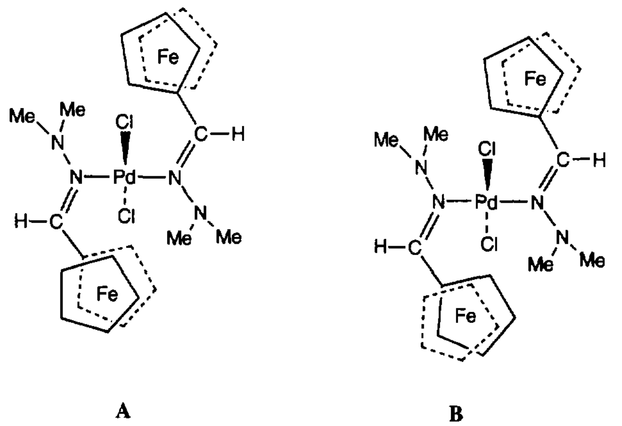


Fig. 2. Schematic view of the two isomers (**A** and **B**) of complex **2** present in solution. In the figure the dashed pentagonal rings and bonds indicate that the atoms are in a lower plane. The main difference between the two isomers is found on the relative orientations of the unsubstituted C_5H_5 rings. In **A** the two C_5H_5 rings are on the same side of one of the two chlorines; while in **B**, each one of the rings is facing a different chlorine, and in this case the whole molecule is centrosymmetric.

Table 2
Final atomic coordinates for non-hydrogen atoms ($\times 10^4$) in compound **2** (standard deviations are given in parentheses)

Atom	*x*	*y*	*z*
Pd	0	5000	0
Fe	2365(1)	4970(1)	1734(1)
Cl	−46(1)	3213(1)	−359(1)
N(1)	2197(4)	4931(3)	30(2)
N(2)	3074(4)	5293(3)	−442(2)
C(1)	2806(8)	6611(4)	1588(3)
C(2)	1412(7)	6500(4)	1800(3)
C(3)	1490(7)	5977(5)	2340(3)
C(4)	2948(6)	5780(4)	2457(2)
C(5)	3767(6)	6168(4)	1997(2)
C(6)	1106(4)	4025(4)	1224(2)
C(7)	1254(5)	3500(4)	1760(2)
C(8)	2729(5)	3309(4)	1869(2)
C(9)	3493(5)	3690(4)	1386(2)
C(10)	2501(4)	4134(3)	982(2)
C(11)	2974(4)	4600(4)	446(2)
C(12)	2908(7)	4525(5)	−916(3)
C(13)	2723(6)	6427(4)	−597(3)

C_{ipso}–C_{imine} bonds) could be promoted thermically, ^1H NMR spectra of **2** were recorded at different temperatures (from 298 to 330 K). However, no significant differences were detected in any of the cases. These findings reveal that the environment around the palladium atom in **2** is so crowded that the interconversion of the isomers is not possible, even at 330 K. This observation contrasts with the results reported by Natile et al. [12] for the *trans*-$[Pd(R^1R^2C{=}N{-}NR^3R^4)_2Cl_2]$ for which the coalescence of the system was achieved at lower temperatures (from −30 to 25 °C depending on the nature and bulk of the hydrazone ligand [12]). In compound **2**, one of the substituents bound to the imine carbon is ferrocenyl, which exhibits a larger effective bulk than any of the substituents R^1, R^2 of the ligands bound to palladium in Natile's compounds [12]. Thus, the rotation around the Pd–N bond should be considerably hindered in **2**, and consequently if the interconversion of the two isomers is to take place, a higher temperature of coalescence would be expected.

The molecular structure of **2** together with the atom labelling scheme are depicted in Fig. 3. Final atomic coordinates for non-hydrogen atoms, and a selection of bond lengths and angles for **2** are presented in Tables 2 and 3.

The structure consists of discrete molecules of *trans*-$[Pd\{(\eta^5C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}CH{=}N{-}N(CH_3)_2]\}_2Cl_2]$ separated by van der Waals contacts. The palladium atom, which is located on a crystallographic symmetry centre, is tetracoordinated bound to two chlorines: Cl(1) and Cl(1)′ in a *trans*-arrangement (in close agreement with infrared data) and the imine nitrogens of the two ferrocenylhydrazones (**1**) {N(1) and N(1)′}. The Pd–N and Pd–Cl bond lengths (Table 2) fall within the expected ranges {2.043(31) and 2.331(67) respectively [13]}.

The hydrazone backbone {C(11)–N(1)–N(2)} forms an angle of 91.0(5)° with the coordination plane of the

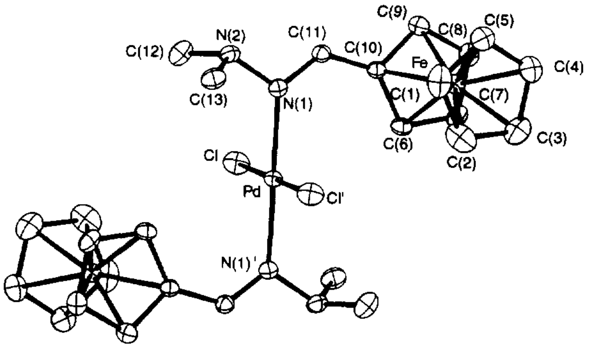


Fig. 3. Molecular structure and atom labelling scheme for *trans*-$[Pd\{(\eta^5C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{-}CH{=}N{-}N(CH_3)_2]\}Cl_2]$ (**2**). Thermal ellipsoids have been drawn with 50% probability.

Table 3
A selection of bond lengths (Å) and bond angles (deg) for **2** (standard deviations are given in parentheses)

(A) *Bond lengths*			
Pd–N(1)	2.058(4)	Pd–Cl	2.3152(14)
N(1)–C(11)	1.281(6)	N(1)–N(2)	1.447(5)
N(2)–C(13)	1.453(6)	N(2)–C(12)	1.457(7)
(B) *Selected bond angles*			
C(10)–C(11)–N(1)	127.6(4)	C(11)–N(1)–Pd	127.2(3)
N(1)–N(2)–C(11)	111.0(3)	N(1)–N(2)–C(12)	109.5(4)
N(1)–N(2)–C(13)	110.4(3)	N(1)–N(2)–Pd	121.8(3)
N(1)–Pd–Cl(1)	89.63(1)	N(1)–Pd–N(1′)	180.0

palladium. In addition, from the arrangement of the atoms shown in Fig. 3, it is evident that neither the rotation around the Pd–N nor the C_{ipso}–C_{imine} bonds is plausible, thus confirming the predictions deduced from the manipulations with the molecular models.

The ⟩C=N– bond distance is similar to those found in related ferrocenyl Schiff bases [3,4] as well as in other *trans*-[Pd{hydrazone}$_2$Cl$_2$]-containing organic hydrazones [12,14–18] (Table 4). The ligand has an *anti*-conformation as reflected in the value of the N(2)–N(1)–C(11)–C(10) torsion angle: −177.1(6)°. However, the ⟩C=N–N– bond angle is one of the narrowest described so far for *trans*-[Pd{hydrazone}$_2$Cl$_2$] complexes, suggesting that this variation might be related to the greater bulk of the ferrocenyl moiety. The opening of the ⟩C=N–N– bond angle would take one of the *ortho* hydrogens of the C_5H_4 ring too close to the $PdCl_2$ fragment.

As a result of the nearly orthogonal arrangement of the ferrocenylhydrazone in relation to the $PdCl_2$ unit and the nearly coplanar orientation of the C_5H_4 ring and the hydrazone group, there are two pairs of transanular Pd···H contacts: Pd···H(6), 2.64(3) Å and Pd···H(13), 2.85(3) Å. In the former case, the orientation of the two hydrogens involved {H(6) and H(6)′} is nearly orthogonal to the coordination plane {angles between [Cl, Pd and H(6)] 91(3)°, [N, Pd and H(6)] 82(3)°}. In addition, tiny rotations of the C_5H_4 ring around the C_{ipso}–C_{imine} bond would take the *ortho*-hydrogens {H(6) and H(6)′} further away from the palladium and, consequently, in this case the transanular contact would be avoided. This finding suggests that these interactions are attractive in nature. A similar kind of transanular Pd···H contact has also been reported for *trans*-[Pd{(R^1)(CH_3)C=N–N(CH_3)(Ph)}$_2$Cl$_2$] {with R^1 = CH_3 or ^{i}Pr} [12–15] as well as for the dinuclear complex [Pd_2Cl_4{(CH_3)$_2$N–N=CH–(CH_2)$_3$–CH–N–N(CH_3)$_2$}] [18].

The average C–C bond length as well as the Fe–C(ring) bond distances of the ferrocenyl moiety are in close agreement with those reported for other ferrocene derivatives [19]. The cyclopentadienyl rings are planar, parallel and nearly eclipsed {tilt angle 1.0(4)° and −1.9(4)° skewed from the ideal eclipsed conformation}. [The equation of the least-squares plane defined by the atoms C(1), C(2), C(3), C(4) and C(5) is (0.0703)XO + (0.8965)YO + (0.4374)ZO = 8.9671. Maximal deviations were found for C(2) {0.003 Å} and C(1) {−0.003 Å}. The equation of the least-squares plane defined by the atoms C(6), C(7), C(8), C(9) and C(10) is (0.0848)XO + (0.9002)YO + (0.44272)ZO = 5.6764. Maximal deviations were found for C(6) {0.010 Å} and C(7) {−0.010 Å}.] The hydrazone fragment N(2)–N(1)–C(11) is practically planar and forms a dihedral angle 5.5(4)° with the C_5H_4 ring.

The distance between the palladium and the iron(II) ions is (4.6349(7) Å), clearly larger than those reported for cyclopalladated compounds containing $\{CN\}^-$ bidentated ferrocenyl Schiff bases as ligands [5–7].

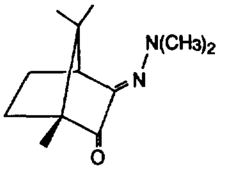
Electrochemical studies based on cyclic voltammetries on compounds **1** and **2** were also performed in order to clarify the effect of the hydrazone group as well as that of the coordination of the palladium upon the liability of the iron(II) to be oxidized. In the two cases the cyclic voltammograms exhibit an anodic peak with a directly asociated peak in the reverse scan.

Data in Table 1 show that complex **1** exhibits a lower half-wave potential than ferrocene. This finding suggests that the –CH=N–N(CH_3)$_2$ is a better electron donor group than the hydrogen since it is well known

Table 4
Selected bond lengths (Å) and angles (deg) for palladium(II) compounds containing coordinated hydrazone ligands

Compound	Pd–N	Pd–Cl	⟩C=N–	–N–N–	⟩C=N–N	Ref.
trans-[Pd{$CH_3C(^iPr)$=N–N(CH_3)(Ph)}$_2$Cl$_2$]	2.027(7)	2.312(6)	1.294(8)	1.425(6)	117.5(6)	[14]
trans-[Pd{$CH_3C(CH_3)$=N–N(CH_3)(Ph)}$_2$Cl$_2$]	2.047(12)	2.298(4)	1.288(21)	1.398(19)	117.8(18)	[12]
trans-[Pd{CH_3C(Ph)=N–N(CH_3)$_2$}$_2$Cl$_2$]	2.045(12)	2.309(4)	1.288(5)	1.433(6)	114.5(4)	[15]
trans-[Pd[(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–N(CH_3)$_2$}]$_2$Cl$_2$] (**2**)	2.058(4)	2.3152(14)	1.281(6)	1.447(5)	111.0(3)	this work
[Pd{C_2H_5OP(S)[(CH_3)N–N=CH–(η^5-C_5H_4)Fe(η^5-C_5H_4)]$_2$}Cl$_2$]	2.022(13)	2.299(1)	1.268(10)	1.393(9)	112.8(3)	[16]
	2.028(3)	2.301(1)	1.290(12)	1.389(9)	113.2(3)	
[Pd_2{(CH_3)$_2$N–N=CH–(CH_2)$_3$–CH=N–N(CH_3)$_2$}$_2$Cl$_4$]	2.035(3)	2.294(1)	1.274(4)	1.435(3)	115.3(2)	[18]
	2.057(3)	2.306(1)	1.274(4)	1.400(3)	121.1(13)	
trans-[Pd{L}$_2$Cl$_2$] [a]	2.065(3)	2.311(1)	1.255(5)	1.428(5)	113.7(5)	[17]
	2.052(3)	2.292(1)	1.279(4)	1.423(5)	114.8(5)	

[a] L represents



that this type of substituent produces a decrease of the $E_{1/2}$(Fc) [20]. On the contrary, the binding of the palladium(II) to the imine nitrogen of ligand **1** hinders the oxidation of the iron(II), thus suggesting that the fragment '–{CH=N–N(CH$_3$)$_2$}PdCl' acts as a stronger electron-withdrawing group. These results agree with those reported for [(η^5-C$_5$H$_5$)Fe{(η^5-C$_5$H$_4$)–CH$_2$–N(CH$_3$)$_2$}] and *trans*-[Pd{(η^5-C$_5$H$_5$)Fe[(η^5-C$_5$H$_4$)–CH$_2$–N(CH$_3$)$_2$]}$_2$Cl$_2$], which revealed that the coordination of the palladium to the amine nitrogen considerably reduced the proclivity of the iron(II) to be oxidized [21].

3. Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Cientifico-Tècnics de la Universitat de Barcelona. Infrared spectra were obtained with a NICOLET-Impact-400 spectrophotometer using KBr pellets. Proton and ^{13}C NMR spectra were recorded at ca. 20 °C on a GEMINI-200 MHz instrument using CDCl$_3$ (99.9%) as solvent and Si(CH$_3$)$_4$ as internal standard.

3.1. Materials and synthesis

Ferrocenecarboxaldehyde and the 1,1-dimethylhydrazine were obtained from commercial sources and used as received. The solvents (ethanol and methanol) were distilled over CaCl$_2$ before use.

3.1.1. Preparation of [(η^5-C$_5$H$_5$)Fe{(η^5-C$_5$H$_4$)–CH=N–N(CH$_3$)$_2$}] (1)

Ferrocenecarboxaldehyde (1.00 g, 4.1 mmol) was added to 10 ml of ethanol and stirred at room temperature for 5 min. After this period the undissolved materials were removed by filtration and discarded. Then 1,1-dimethylhydrazine (0.31 ml, 4.1 mmol) was added to the red filtrate and the resulting mixture was stirred at room temperature (ca. 20 °C) for 1.5 h. Slow evaporation of the solvent (to ca. 4 ml) at room temperature produced the formation of a yellow microcrystalline material which was collected by filtration and air dried (yield 86%).

Characterization data. Anal. Found: C, 61.12; H, 5.76; N, 10.8. C$_{13}$H$_{16}$N$_2$Fe Calc.: C, 61.61; H, 5.92; N, 10.98%. IR: ν(>C=N–) = 1617 cm^{-1}.

3.1.2. Preparation of trans-[Pd{(η^5C$_5$H$_5$)Fe[(η^5-C$_5$H$_4$)–CH=N–N(CH$_3$)$_2$]}$_2$Cl$_2$] (2)

Na$_2$[PdCl$_4$] (0.294 g, 1.0 mmol) was added to a solution formed from 1.0 mmol (0.256 g) of the ferrocenylhydrazone [(η^5-C$_5$H$_5$)Fe{(η^5-C$_5$H$_4$)–CH=N–N(CH$_3$)$_2$}] (**1**) and 10 ml of methanol. The reaction mixture was stirred at room temparature (ca. 20 °C) for 2 h. The pale orange solid formed during this period was filtered out, washed with two 5 ml portions of methanol and air dried (yield 75%).

Table 5
Crystal data and details of the refinement of the crystal structure of **2** (standard deviations are given in parentheses)

Empirical formula	C$_{26}$H$_{32}$Cl$_2$Fe$_2$N$_4$Pd
Formula weight	689.56
Crystal size (mm^3)	0.1 × 0.1 × 0.2
Temperature	293(2) K
Wavelength (Å)	0.71069
Crystal system	orthorhombic
Space group	*Pcab*
Unit cell parameters	a = 9.353(2) Å b = 12.061(5) Å c = 23.487(4) Å
Volume (Å^3)	2649.5(13)
Z	4
D_{calc} (g cm^{-3})	1.729
Absorption coefficient	1.977 mm^{-1}
F(000)	1392
Θ range for data collection	from 2.42° to 29.96°
Index ranges h, k, l	$-1 \leq h < 13$, $0 < k \leq 16$, $0 \leq l \leq 33$
No. of reflections collected	3898
Independent reflections	3845 [R(int) = 0.0144]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3795/0/225
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0491, wR_2 = 0.1215
R indices (all data)	R_1 = 0.1054, wR_2 = 0.1949
Extinction coefficient	0.0001(2)
Largest difference peak and hole	0.697 and −0.645 e Å^{-3}

Characterization data. Anal. Found: C, 41.1; H, 4.3; N, 7.4. C$_{26}$H$_{32}$N$_4$Cl$_4$Fe$_2$Pd Calc.: C, 41.06; H, 4.24; N, 7.37%. IR: ν(>C=N–) = 1611 cm^{-1}.

3.2. X-ray structure analysis: data collection and refinement

A prismatic crystal (size in Table 5) was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters were obtained from automatic centring of 25 reflections in the range 12° < Θ < 21° and refined by least-squares methods. Intensities were collected with graphite monochromated Mo Kα radiation using the ω–2Θ scan technique. 3898 reflections were measured in the range 2.24° < Θ < 29.96°. Three reflections were measured every 2 h as orientation and intensity controls. Significant intensity decay was not observed. Lorentz polarization, but not absorption, corrections were made.

The structure was solved by direct methods, using the SHELXS computer program [22], and refined by the full-matrix least-squares method with the SHELXL-93 computer program [23], using 3795 reflections {highly negative intensities ($I < -10$) produced by asymmetric background were not assumed}. The function minimized was $\Sigma w||F_{o}|^2 - |F_{c}|^2|^2$, where $w = [\sigma^2(I) + (0.0866P)^2 + 0.3759P]^{-1}$, and $P = \{|F_{o}|^2 - 2|F_{c}|^2\}/3$. f, f' and f'' were taken from the *International Tables of X-ray Crystallography* [24]. The extinction coefficient was not significant [0.001(2)]. All the hydrogen atoms were located from a difference synthesis and refined isotropically. The final R (on F) factor was 0.105 {or 0.049 when computed using the 2267 reflections with $I > 2\sigma(I)$} {wR (on $|F|^2$) 0.195}. The goodness of fit, the number of refined parameters, and further details concerning the refinement of the structure are summarized in Table 5.

3.3. Electrochemical studies

Electrochemical data for compounds **1** and **2** were obtained from cyclic voltammetry under argon at 20 °C using acetonitrile (HPLC grade) as solvent and tetrabutylammonium hexafluorophosphate (0.1 M) as supporting 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 10^{-3} M solutions of the samples in acetonitrile were recorded with a VersaStat EG&G Princenton Applied Research potentiostat.

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