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Palladium (II) and platinum (II) compounds containing bi- and terdentate ferrocenyl ligands. X-ray crystal structure of *cis*-[Pd{(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH_2–CH_2–N$(CH_3)_2$]}Cl_2]

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Abstract

The synthesis, characterization and study of the three ferrocenyl Schiff bases: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH_2–CH_2–N$(CH_3)_2$}] (**1a**), [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH_2–CH_2–S–CH_2–CH_3}] (**1b**) and [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH($COOCH_3$)–CH_2–CH_2–S–CH_3}] (**1c**) are reported. Reactivity studies of these substrates *versus* palladium (II) and platinum (II) salts have allowed us to isolate and characterize different sorts of complex. The coordination complexes: *cis*-[M(ligand)Cl_2] {where M = Pd (**2a**–**2c**) or Pt (**3a**–**3c**)} were prepared by treatment of the corresponding ligand and $Na_2[PdCl_4]$ (for **2a**–**2c**) or *cis*-[$PtCl_2$(dmso)$_2$] (for **3a**–**3c**) in methanol. In compounds **2**, **3a**–**c** the ligand acts as a neutral bidentate group. The cyclopalladated complex: [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)–CH=N–CH_2–CH_2–N$(CH_3)_2$]}Cl] (**4a**) can be isolated by reaction of stoichiometric amounts of **1a**, $Na_2[PdCl_4]$ and Na(CH_3COO) · $3H_2O$ in methanol for 8 days. In complex **4a** the ligand acts as a monoanionic (C, N, N′)$^-$ terdentate group. The reaction of compound **4a** with an equimolar amount of PPh_3 produces [Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_3)–CH=N–CH_2–CH_2–N$(CH_3)_2$]}Cl(PPh_3)], in which the ligand acts as a monoanionic (C, N)$^-$ bidentate ligand. All the compounds included in this study have been characterized by infrared and NMR spectroscopy and complex **2a** has also been characterized structurally: monoclinic, $P2_1/m$, with $a = 6.034(2)$ Å, $b = 14.502(2)$ Å, $c = 10.236(2)$ Å and $\beta = 104.61(2)°$. The crystal structure of complex **2a** reveals that the imine adopts the Z-form.

Keywords: Ferrocenyl; Palladium; Platinum; Schiff bases

1. Introduction

The study of ferrocene derivatives has increased exponentially during the last decade due to their applications in a wide variety of areas, including catalysis, organic synthesis and the design of new materials such as liquid crystals or polymers [1]. Ferrocene derivatives containing atoms with good donor abilities have attracted additional interest, since the coordination of a metal to these heteroatoms produces multicentre molecules [2], in which the presence of proximal metals in different environments may influence the mutual cooperation of these metals in a variety of processes [3–17]. Besides that, some examples of antitumour materials containing ferrocenyl groups have also been reported [18,19].

On the other hand, the chemical structure of the tumour-inhibiting platinum (II) compounds have a *cis*-[PtX_2A_2] core, where A_2 represents either two primary amines or ammina groups or a bidentate amine ligand, and X is an easily replaceable group such as Cl^- or a

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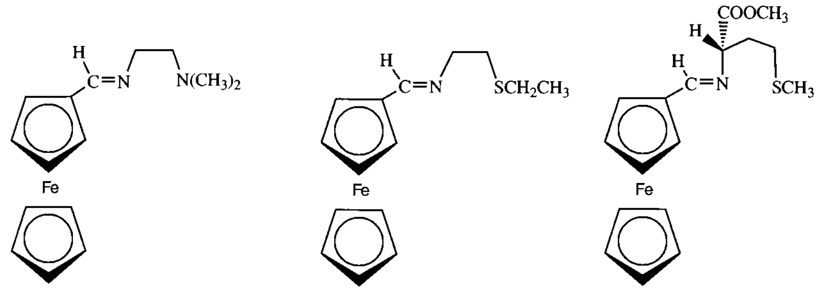


(1a) (1b) (1c)

Fig. 1. Schematic view of ferrocenyl ligands under study.

carboxylato [20]. In this sort of compound slight modifications of the ligands bound to the metal ion modify their activity and toxicity [21].

On this basis, we attempted to prepare and characterize some novel ferrocenyl ligands containing two heteroatoms with good donor abilities {such as nitrogen or sulfur} (Fig. 1) and to study their reactivity towards palladium (II) and platinum (II) salts.

These reactions could produce different sorts of complex depending on the mode of coordination of the ligand to the metal atom. For instance, the ferrocenyl substrate can act as a neutral bidentate group (Fig. 2A), or as a monoanionic mono-, bi- or terdentate group (Fig. 2B–D, respectively). Compounds of this kind are especially interesting due to their potential applications. The environment of the central atom in A is similar to that of *cisplatin*, which is used for cancer therapy [20]. On the other hand, palladium (II) and platinum (II) compounds containing σ(M–C) bonds are also useful as precursors for organic and organometallic synthesis. Thus, complexes of the type B–D (Fig. 2) are also interesting from this point of view [22,23]. In addition, some examples of cyclometallated derivatives (similar to those shown in Fig. 2C and D) as metallomesogens or as antitumoural drugs have also been reported [24,25].

2. Results and discussion

2.1. The ligands

The ferrocenyl ligands [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH_2–CH_2–N$(CH_3)_2$}] (**1a**), [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH_2–CH_2–S–CH_2CH_3}] (**1b**), or [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH($COOCH_3$)–CH_2–CH_2–SCH_3}] (**1c**) were prepared by condensation between equimolar amounts of ferrocenecarboxaldehyde and the corresponding amines in refluxing benzene, using a Dean-Stark apparatus to remove the benzene–water azeotrope formed during the process. Concentration of the resulting solutions to dryness on a rotary evaporator gave deep-red oils for **1a** and **1b** or a yellow solid for **1c**.

The three ligands were characterized by infrared and NMR spectroscopy and ligand **1c** was also characterized by elemental analyses. The infrared spectra of the free ligands showed a sharp, intense band in the range 1620–1650 cm^{-1}, which was assigned to the stretching of the >C=N– bond. The ^{1}H-NMR spectra of compounds **1a**–**1c** (Table 1) shows a singlet due to the imine proton in the range 8.15–8.25 ppm. The position of this signal is consistent with the results reported for a wide variety of ferrocenyl Schiff bases [26–30].

For compounds **1a** and **1b**, the signals due to the protons of the ferrocenyl fragment appear as a singlet and two triplets of relative intensities 5:2:2 in the area 4.10–4.70 ppm, in contrast the spectrum of the imine **1c** showed five singlets of relative intensities 5:1:1:1:1 in the same region, indicating that the four protons of the C_5H_4 ring are not equivalent. This finding may be

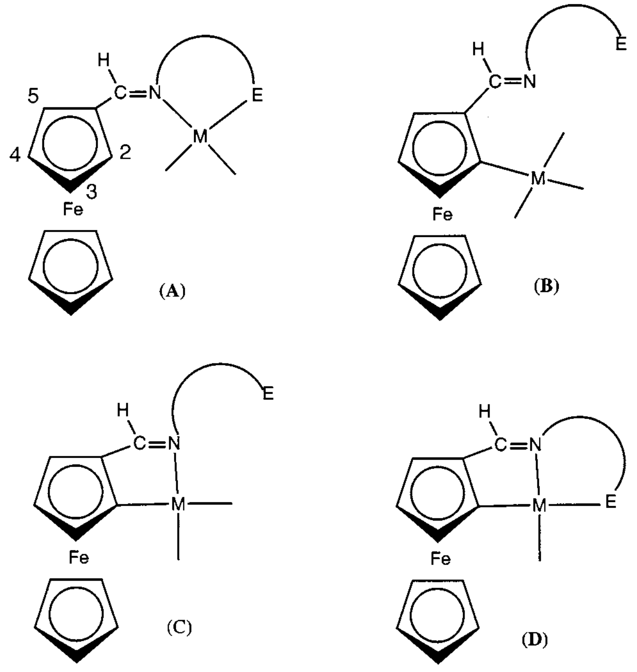


Fig. 2. Schematic view of the different sorts of palladium (II) and platinum (II) compounds containing ferrocenyl ligands **1a**–**1c** which can be formed.

Table 1
Proton NMR data (in ppm) for the free ligands (**1a**–**1c**) and for their palladium (II) and platinum (II) compounds[a]

	C_5H_5	Substituted ring	–CH=N–	>N–CH(R)–	$–CH_2–$	Others
1a	4.18, s	4.63, H^2 4.36, H^3 4.36, H^4 4.63, H^5	8.17, s	3.60, t	2.27, t	2.30, s, $N–CH_3$
1b	4.21, s	4.64, H^2 4.38, H^3 4.38, H^4 4.64, H^5	8.14, s	3.66, t	2.82, t	2.60, q, $–CH_2–S$ 1.29, t, $–CH_3$
1c	4.23, s	4.78, H^2 4.44, H^3 4.46, H^4 4.71, H^5	8.21, s	4.08, t	2.26, m	3.79, s, OCH_3 2.50, s, $S–CH_3$ 2.10, m, $–CH_2–S$
2a	4.37, s	4.70, H^2 4.60, H^3 4.60, H^4 4.70, H^5	8.72, s	3.70, t	2.64, t	2.92, s, $N–CH_3$
2b	4.43, s	4.68, H^2 4.29, H^3 4.29, H^4 4.68, H^5	9.20, s	3.82, m	3.05, m	3.56, m, $–CH_2–S$ 1.49, t, $–CH_3$
2c	4.40, s	5.96, H^2 4.80, H^3 4.80, H^4 6.00, H^5	8.29, s	4.25, m	3.30, m	3.83, s, OCH_3 2.70, s, $–CH_2–S$ 2.60, s, $S–CH_3$
3a	4.30, s	4.42, H^2 4.63, H^3 4.43, H^4 4.91, H^5	7.99, s	3.50, m	2.84	2.70, s, $N–CH_3$
3b[b]	4.31, s	4.65, H^2 4.64, H^3 4.76, H^4 4.76, H^5	9.07, s	3.80, m	3.50, m	3.46, m, $S–CH_3$ 1.37, t, CH_3
3c	4.20, s	5.19, H^2 4.64, H^3 4.68, H^4 4.63, H^5	8.44, s	4.25, m	3.50, m	4.20, s, OCH_3 2.30, t, $S–CH_3$ 2.80, m, $–CH_2–S$
4a	4.36, s	4.36, d, H^3 4.44, d, H^4 4.91, d, H^5	8.00, s	3.62, m[c]	2.85, m	2.70, s, $N–CH_3$[d] 2.67, s, $N–CH_3$[d]
5a	3.91, s	3.30, d, H^3 4.05, t, H^4 4.40, d, H^5	8.13, d[e]	4.10, m[c]	2.75, m	2.20, s, $N–CH_3$

[a] Labelling of the atoms refers to the schemes shown in Fig. 2(A).

[b] In this case the spectrum was recorded in dmso-d_6.

[c] These protons are diastereotopic.

[d] The protons of the two $–CH_3$ groups bound to the nitrogen are not equivalent.

[e] Doublet due to phosphorus coupling $\{^3J(P–H) = 7.2\ Hz\}$.

related to the presence of the bulky $–COOCH_3$ group in the vicinity of the imine nitrogen. The signals due to the protons bound to the terminal nitrogen in **1a** or sulfur in **1b**, **1c** were also present in the spectrum.

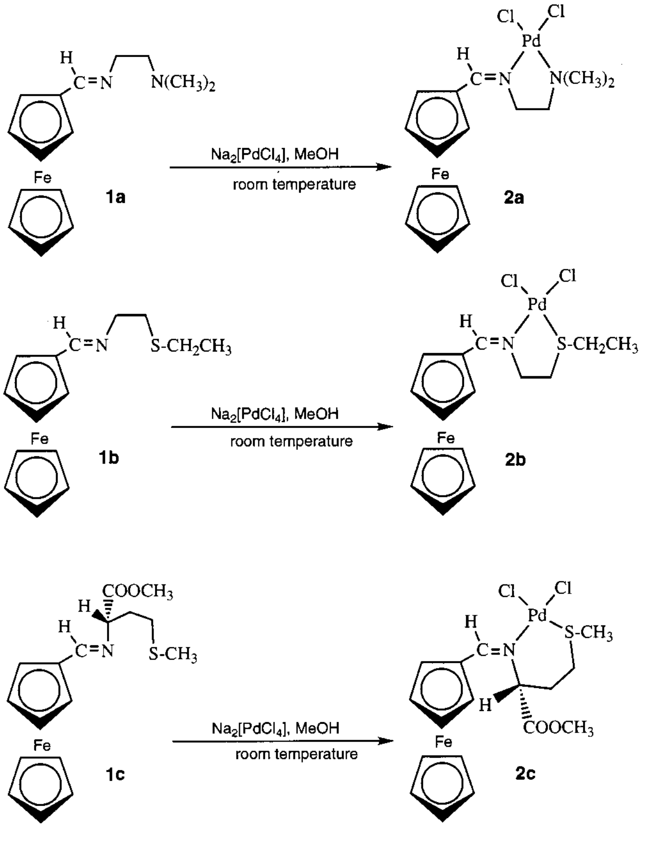
^{13}C-NMR spectra of the free ligands showed a singlet in the range 160–170 ppm (see Section 3), which was assigned to the >C=N– group. The position of all the signals observed in the ^1H- and ^{13}C-NMR spectra indicated that only one isomer (*E*-form) was present in solution.

2.2. Palladium (II) compounds

The reaction of the ferrocenylimines **1a**–**1c** with the stoichiometric amount of $Na_2[PdCl_4]$ in methanol at room temperature produced orange–red solids (Scheme 1). Their characterization data based on elemental analyses, infrared and NMR spectroscopy are consistent with those expected for *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)–CH{=}N–CH_2–CH_2–N(CH_3)_2]\}Cl_2]$ (**2a**), *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)–CH{=}N–CH_2–CH_2–S–$

$CH_2{-}CH_3]\}Cl_2]$ (**2b**), or *cis*-$[Pd\{(\eta^5{-}C_5H_5)Fe[(\eta^5{-}C_5H_4){-}CH{=}N{-}CH(COOCH_3){-}CH_2{-}CH_2{-}S{-}CH_3]\}Cl_2]$ (**2c**), respectively. In all cases these compounds were obtained in fairly good yields (60–80%).

Proton-NMR spectral data for compounds **2a**–**2c** are presented in Table 1. In all cases the spectra showed the typical pattern of monosubstituted ferrocenyl derivatives. The signal due to the imine proton in **2** is lowfield shifted compared with the free ligand **1a** $\{\delta^1H({-}CH{=}N{-}) = 8.17$ ppm$\}$ or with that of the complex: *cis*-$[Zn\{(\eta^5{-}C_5H_5)Fe[(\eta^5{-}C_5H_4){-}CH{=}N{-}CH_2{-}CH_2{-}N(CH_3)_2]\}Cl_2]$ $\{\delta^1H({-}CH = N{-}) = 8.37$ ppm$\}$, previously reported [31]. According to the literature [32], the variation of the chemical shifts of the imine proton in palladium (II) and platinum (II) compounds containing organic imine ligands can indicate the conformation of the ligand in the complex. It is generally accepted that if the ligand adopts the *E*-form, the chemical shift of the imine proton in the palladium (II) or platinum (II) complexes does not differ significantly from that of the free ligand, while in complexes containing the imine in the *Z*-form, the signal due to the –CH=N– proton appears at lower fields than in the free ligand, due to the proximity of this proton and the metal atom (Pd or Pt). This suggests that in **2a** the imine has a *Z*-conformation. As described above, NMR spectroscopic data of the free ligands agreed with a *trans*-arrangement of the ferrocenyl group and the substituent on the imine nitrogen (*E*-form). Thus, the results obtained from the NMR spectra of **2a** suggest that the $E \rightarrow Z$ isomerization of **1a** occurred in the course of reaction.



Scheme 1.

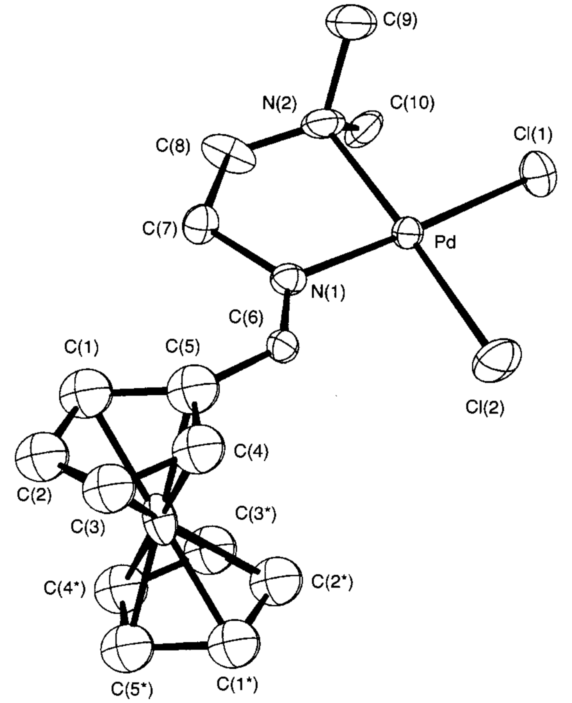


Fig. 3. Molecular structure and atom labelling scheme for complex *cis*-$[Pd\{\eta^5{-}C_5H_5)Fe[(\eta^5{-}C_5H_4){-}CH{=}N{-}CH_2{-}CH_2{-}N(CH_3)_2]\}Cl_2]$ (**2a**).

Complex **2a** was also characterized by X-ray diffraction. The molecular structure and the atom numbering scheme are presented in Fig. 3. Final atomic coordinates for non-hydrogen atoms and a selection of bond lengths and angles are presented in Tables 2 and 3, respectively.

The structure consists of discrete molecules of *cis*-$[Pd\{(\eta^5{-}C_5H_5)Fe[(\eta^5{-}C_5H_4){-}CH{=}N{-}CH_2{-}CH_2{-}N(CH_3)_2]\}Cl_2]$ separated by van der Waals contacts. The palladium atom is tetracoordinated, bound to two chlorines {Cl(1) and Cl(2), respectively} and the two nitrogens of the ferrocenyl ligand {N(1) and N(2)}, in a slightly distorted square-planar environment[1]. The five-membered metallacycle has an envelope-like conformation with the N(2) atom above the plane defined by the atoms: Pd, N(1), C(7) and C(8)[2]. These four atoms are

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[1] The least-squares equation of the plane defined by the atoms Pd, Cl(1), Cl(2), N(1) and N(2) is: $+(0.8213)XO + (-0.4532)YO + (0.3465)ZO = -1.6705$. The deviations from the plane are as follows: Pd, +0.035 Å; Cl(1), −0.009 Å; Cl(2), −0.009 Å; N(1), −0.010 Å; and N(2), −0.009 Å.

[2] The least-squares equation of the plane defined by the atoms Pd, N(1), C(7) and C(8) is: $+(0.7171)XO + (-0.4454)YO + (0.5351)ZO = -1.2432$. The deviations from the plane are as follows: Pd, +0.013 Å; N(1), −0.025 Å; C(7), −0.026 Å; C(8), −0.015 Å and N(2), +0.413 Å.

Table 2
Final atomic coordinates ($\times 10^4$) for non-hydrogen atoms in complex: *cis*-[Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–CH_2–CH_2–$N(CH_3)_2$]}Cl_2] (**2a**)[a]

	x	*y*	*z*
Pd	4587(1)	7500	3768(1)
Fe	0	500	0
Cl(1)	6061(3)	8934(1)	4526(2)
Cl(2)	6036(3)	7500	1899(1)
N(1)	3099(7)	6290(3)	3188(4)
N(2)	3138(6)	7500	5386(3)
C(1)	−243(10)	4555(3)	1776(5)
C(2)	−587(10)	3803(3)	908(5)
C(3)	1192(10)	3687(3)	363(5)
C(4)	2830(9)	4303(3)	822(5)
C(5)	2097(10)	4893(3)	1702(5)
C(6)	3348(8)	5766(3)	2238(4)
C(7)	1469(10)	6093(3)	4056(6)
C(8)	1309(12)	6934(5)	5061(9)
C(9)	4709(10)	7500	6729(4)
C(10)	2306(12)	8575(4)	5360(6)

[a] The estimated S.D. are given in parentheses.

not strictly coplanar with the C_5H_4 {the angle formed by the normals to their planes is 20.6(6)°}.

The >C=N– bond length [1.273(7) Å] is similar to those reported for related ferrocenyl imines which fall in the range: [1.25–1.31 Å] [27]. The substituents at the imine group: C_5H_4 and –CH_2–CH_2–$N(CH_3)_2$ are in *cis*-arrangement {the torsion angle defined by the atoms: C(5)–C(6)–N(1)–C(7) is 3.3(6)°}, thus confirming the *Z*-conformation of the imine in **2a**. This finding is in sharp contrast with the results obtained from X-ray studies for a wide variety of ferrocenylimines [27], for their palladium (II) compounds [26,28,33] and for [Zn{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–CH_2–CH_2–$N(CH_3)_2$]}Cl_2] [31], in which the ligand adopts the *E*-form.

Table 3
Selected bond lengths (Å) and angles (°) for *cis*-[Pd{η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–CH_2–CH_2–$N(CH_3)_2$]}Cl_2] (**2a**)[a]

Bond lengths (Å)			
Pd–N(1)	1.992(5)	Pd–N(2)	2.058(4)
Pd–Cl(1)	2.316(2)	Pd–Cl(2)	2.2956(13)
C(5)–C(6)	1.505(7)	N(1)–C(6)	1.273(7)
N(1)–C(7)	1.509(7)	C(7)–C(8)	1.615(9)
C(8)–N(2)	1.348(7)	N(2)–C(9)	1.460(6)
N(2)–C(10)	1.635(5)	Fe–C_{ring}[b]	2.031(6)
C–C_{ring}[b]	1.405(7)		
Bond angles (°)			
N(1)–Pd–N(2)	89.35(13)	Cl(1)–Pd–Cl(2)	94.82(5)
N(1)–Pd–Cl(2)	89.40(12)	N(2)–Pd–Cl(1)	86.33(7)
C(5)–C(6)–N(1)	129.5(5)	C(6)–N(1)–C(7)	123.8(5)
N(1)–C(7)–C(8)	122.6(5)	C(7)–C(8)–N(2)	116.1(7)
C(1)–C(5)–C(6)	130.0(5)	C(4)–C(5)–C(6)	122.7(5)

[a] The estimated S.D. is given in parentheses.

[b] Average value for the ferrocenyl unit.

NMR spectroscopic data of **1a** (described above) suggested that the free imine had an *E*-conformation in solution. However, in *cis*-[Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–CH_2–CH_2–$N(CH_3)_2$]}Cl_2] (**2a**) a *Z*-conformation of the ligand was found. This finding suggests that the isomerization of the imine **1a** is promoted by the palladium (II).

Bond lengths and angles of the (η^5-C_5H_5)Fe(η^5-C_5H_4) fragment are similar to those reported for most ferrocene derivatives [34]. Due to symmetry, the two C_5H_5 rings are parallel and the conformation of the ferrocenyl unit is eclipsed. The distance between the two metals, Fe and Pd (ca. 5.40 Å) is clearly greater than those detected for other palladium (II) complexes containing N-donor ferrocenyl ligands, which fall in the range: {3.4–4.5 Å} [26,28–30,33,35–38], thus suggesting that there is no direct interaction in **2a**.

As a first approach to determine the influence of the incorporation of the bulky ferrocenyl group on the structure of the complexes of general formulae: *cis*-[Pd{ligand}Cl_2], in which the palladium (II) is bound to a neutral bidentate N, N′ donor group, bond lengths and bond angles involving the palladium (II) atom in complex **2a** were compared with those reported in the literature for related compounds [39–44] (Table 4).

The Pd–N and Pd–Cl bond lengths do not differ significantly (the differences do not clearly exceed 3σ) for the compounds under study. However, changes of the (N, N′) group modify the N(1)–Pd–N(2) and the Cl(1)–Pd–Cl(2) bond angles. The differences in the N(1)–Pd–N(2) angles of these bidentate ligands correspond to small differences in their bites. The value found for **2a** is among the largest found for ligands forming five-membered rings. The typical bites for ethylenediamine, 2,2′-bipyridyl, tropolonato and oxalato are: 2.78, 2.56, 2.52 and 2.52, respectively [45]. The normalized bite, *b*, of ligand **1a** is slightly larger than those found for aliphatic diamine ligands forming five-membered rings [39–44,46].

2.3. Platinum (II) compounds

In an attempt to prepare the platinum (II) compounds, the ferrocenylimines **1a**–**1c** were treated with $Na_2[PtCl_4]$ in methanol at room temperature. In all cases dark violet solids were formed immediately after mixing the two solutions. However, their analytical data were not consistent with those expected for the platinum (II) compounds: *cis*-[Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–CH_2–CH_2–$N(CH_3)_2$]}Cl_2] (**3a**), *cis*-[Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–CH_2–CH_2–S–CH_2–CH_3]}Cl_2] (**3b**), or *cis*-[Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–CH($COOCH_3$)–CH_2–CH_2–S–CH_3]}-Cl_2] (**3c**). In addition, their proton-NMR spectra showed broad signals which could indicate the presence of metallic platinum. Attempts to separate the platinum

Table 4

Selected bond lengths (Å) and angles (°) for compounds of general formula: *cis*-[Pd(ligand)Cl_2], where ligand represents a neutral (N N) bidentate ligand, together with the bites {N(1)···N(2)} and the normalized bites[a], *b*, of the ligands in these complexes[b]

Ligand	Pd–N(1)	Pd–N(2)	Pd–Cl(1)	Pd–Cl(2)	Cl(1)–Pd–Cl(2)	N(1)–Pd–N(2)	N(1)···N(2)	*b*	Reference
1a	1.992(5)	2.058(4)	2.316(2)	2.2956(13)	94.82(5)	89.35(13)	2.849(6)	1.41	[c]
$H_2N–CH_2–CH_2–NH_2$	1.978(12)	1.978(12)	2.309(3)	2.309(3)	95.3(8)	83.1(1)	2.627(15)	1.33	[39]
$H_2N–CH(CH_3)–CH(CH_3)–NH_2$	2.029(5)	2.031(5)	2.318(3)	2.315(3)	95.31(4)	83.52(4)	2.704(7)	1.33	[40]
$H_2N–C(CH_3)_2–CH_2–NH\{C(CH_3)_2–COCH_3\}$	2.020(3)	2.096(3)	2.317(1)	2.276(1)	90.7(1)	83.2(1)	2.735(5)	1.33	[41]
$H_2N–CH_2–CH_2–NH(CH_2–CH_2OH)$	2.029(4)	2.062(4)	2.327(1)	2.318(1)	94.0(1)	84.6(2)	2.753(5)	1.35	[42]
(*S*)–$H_2N–CH(CH_3)–CH_2–N(CH_3)_2$[d]	2.05(2)	2.06(3)	2.31(1)	2.31(1)	92.7(1)	84.8(5)	2.77(3)	1.35	[43]
(*S*)–$H_2N–C(CH_3)–CH_2–N(CH_2–CH_3)_2$[e]	2.04(1)	2.08(3)	2.31(1)	2.31(1)	92.8(6)	83.8(5)	2.75(3)	1.34	[43]
$(HO_2C–CH_2)_2N–CH_2–CH_2–N(CH_2–CO_2H)_2$	2.09(2)	2.09(2)	2.30(1)	2.3(1)	90.7(3)	85.1(9)	2.83(4)	1.35	[44]

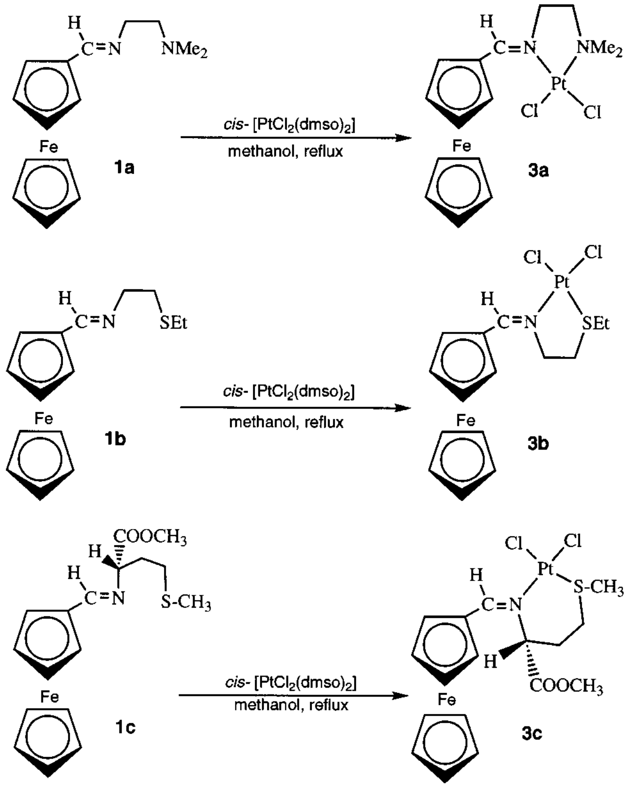
[a] The normalized bites were calculated according to the expression: $b=[N(1)\cdots N(2)]/[1/2\{Pd–N(1)+Pd–N(2)\}]$.

[b] For ligand **1a**, the labelling of the atoms corresponds to that shown in Fig. 3, and for the remaining complexes the N(1) atoms is that written on the left hand side of the first column. The two chlorines Cl(1) and Cl(2) are in a *trans*-arrangement to the N(1) and N(2) atoms, respectively. (The estimated S.D. is given in parentheses.)

[c] This work.

[d] Average values for the three non-equivalent molecules.

[e] Average values for the two non-equivalent molecules.



Scheme 2.

(0) by recrystallization or by column chromatography were unsuccessful.

In the view of these results, we decided to replace the $Na_2[PtCl_4]$ by the coordination complex: *cis*-$[PtCl_2(dmso)_2]$ [47], which has been found a useful reagent to isolate a wide variety of platinum (II) compounds of general formula: $[PtCl_2(L)]$ or $[PtCl(L')]$, where L and L′ represent a neutral bidentate or an anionic terdentate ligand [48]. Addition of the equimolar amount of the corresponding ligand to a hot solution of *cis*-$[PtCl_2(dmso)_2]$ [47] produced a deep red solution, which was refluxed for a further hours. During this period the formation of metallic platinum on the walls of the reaction flask was detected. The reaction mixtures were then filtered out and the filtrates were concentrated to dryness on a rotary evaporator, giving orange (for **1a**) or red (for **1b**, **1c**) solids, which were collected by filtration and dried in vacuum (Scheme 2).

Their characterization data based on elemental analyses and infrared and NMR spectroscopy are consistent with those expected for the coordination compounds: *cis*-$[Pt\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl_2]$ (**3a**), *cis*-$[Pt\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}S\text{–}CH_2\text{–}CH_3]\}Cl_2]$(**3b**), or *cis*-$[Pt\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH(COOCH_3)\text{–}CH_2\text{–}CH_2\text{–}S\text{–}CH_3]\}Cl_2]$ (**3c**), respectively. Compounds **3a**–**3c** were isolated in lower yield than their palladium (II) analogues. This can be ascribed to the partial reduction of platinum (II) in the course of the reaction.

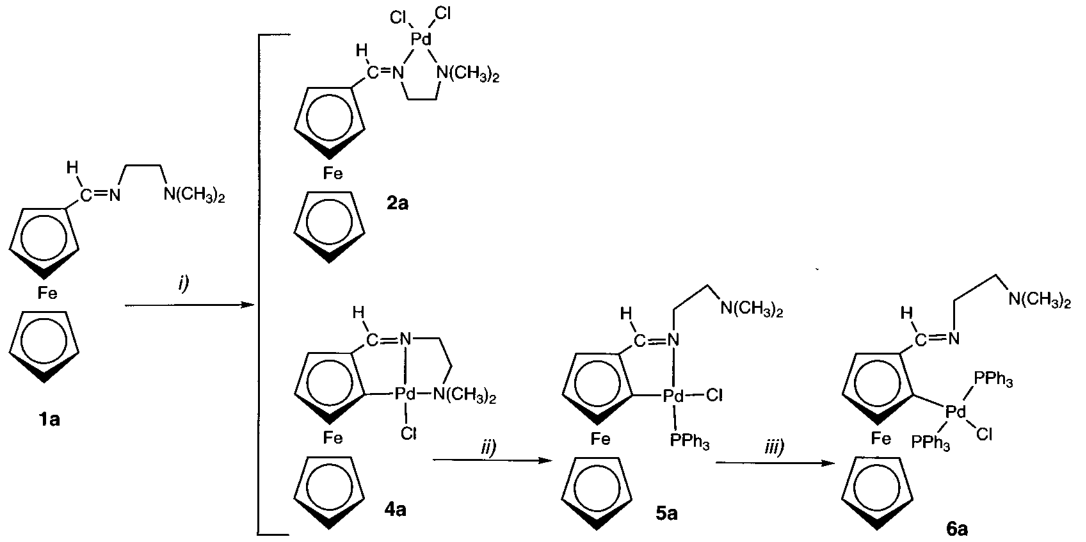
Proton-NMR spectroscopic data for **3** are summarized in Table 1. In compounds **3b** and **3c** the signal due to the imine proton is clearly lowfield shifted in respect to that of the free ligands, thus suggesting that in these compounds the ligands adopt the *Z*-conformation. In contrast, for complex **3a**, the signal is slightly shifted to higher fields than in **1a**, thus indicating an *E*-conformation of the ligand. The ^{13}C-NMR spectra of **3a**–**3c** were not recorded due to their low solubility.

Compounds **3** were also characterized by ^{195}Pt-NMR. In all cases a singlet was observed in the spectra but the position of the signal {−2262 ppm for **3a**, −2900 ppm for **3b** and −2890 ppm for **3c**} was strongly dependent on the nature of the two atoms bound to the platinum (two nitrogens in **3a** or a nitrogen and a sulfur in **3b** and **3c**), in good agreement with the values reported for related compounds of general formula: *cis*-$[Pd(N^\wedge N)Cl_2]$ and *cis*-$[Pt(N^\wedge S)Cl_2]$ [49].

2.4. Activation of the $\sigma(C_{sp^2,\ ferrocene}\text{–}H)$ bond

Ferrocenylimines 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, Me or Ph and R′ = phenyl or benzyl groups} undergo the activation of the $\sigma(C_{sp^2,\ ferrocene}\text{–}H)$ bond under mild experimental conditions [26–28,38]. This sort of reaction, which is produced by treatment of the ferrocenyl ligand, $Na_2[PdCl_4]$ and $Na(CH_3COO)\cdot 3H_2O$ (in a 1:1:1 molar ratio) in methanol at room temperature, gives $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}C(R){=}N\text{–}R']\}(\mu\text{-}Cl)]_2$. Thus, we decided to test whether the $\sigma(C_{sp^2,\ ferrocene}\text{–}H)$ bond in compounds **1** could be activated, and then isolate the corresponding palladacycles. When ligand **1a** was treated with $Na_2[PdCl_4]$ and $Na(CH_3COO)\cdot 3H_2O$ (in a 1:1:1 molar ratio) in methanol for 3 h, an orange solid formed (Scheme 3); its elemental analyses and IR and ^1H-NMR spectra were identical to those of complex **2a** (Fig. 4A). However, when the reaction time was increased to 3 days, the ^1H-NMR spectra of the solid showed two superimposed sets of signals. One was coincident with that of complex **2a**, while the other was consistent with that expected for $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl]$ (**4a**). The analyses of the integrals of the two signals due to the –CH=N– protons revealed that compounds **2a** and **4a** coexisted in a molar ratio of 2:3 (Fig. 4B).

For longer reaction periods (8 days) the precipitate formed was enriched in the cyclopalladated complex **4a** {the molar ratio **2a**:**4a** was ca. 1:7} (Fig. 4C). The two components of the mixture were separated by SiO_2 column chromatography using $CHCl_3$ as eluant.



Scheme 3. (i) $Na_2[PdCl_4]$, $Na(CH_3COO)\cdot 3H_2O$, MeOH, room temperature, see text. (ii) PPh_3, benzene, room temperature. (iii) PPh_3, $CDCl_3$, room temperature.

However, when ligands **1b** or **1c** were treated with $Na_2[PdCl_4]$ and $Na(CH_3COO)\cdot 3H_2O$ {in a 1:1.1 molar ratio} in methanol at room temperature using reaction periods up to 10 days, the ^{1}H-NMR spectra of the solids obtained in each experiment were identical to those of compounds **2b**–**2c** and no significant variation was detected in either the position of the signals or their multiplicities. This observation suggests that the activation of the $\sigma(C_{sp^2,\ ferrocene}–H)$ in **2a** is more favourable than in **2b** or **2c**. These results can be attributed to several causes, including the basicity of the ligand in **1a**–**1c**, the conformation of the imine ligand {*E*- or *Z*-} in the coordination compounds **2**, the relative orientation of the $\sigma(C_{sp^2,\ ferrocene}–H)$ bond *versus* the palladium (II) atom, the flexibility of the ring formed by the palladium and the chelating ligand, or even the presence of a bulky susbtituent in the neighbourhood of the imine nitrogen (in **2c**).

The three imines under study (**1a**–**1c**) differ in the nature of the terminal group {$–N(CH_3)_2$, $–S–CH_3$ or $–S–CH_2–CH_3$}, which affects the basicity of the ligand. This is important, since the cyclopalladation of N-donor ligands proceeds in two steps [50]: the coordination of the ligand to the palladium and the subsequent electrophilic attack of the palladium (II) on the C–H bond. Consequently, small variations in the basicity of the ligand may induce significant variations in the neat charge of the palladium (II) atom, which may hinder the formation of the metallacycle. Besides, the conformation of the ligand in the coordination complexes: *cis*-[Pd(ligand)Cl_2] (**2**) could also determine the proclivity of the σ(C–H) bond to be activated. If the imine has a *Z*-conformation (Fig. 5I), the orientation of the σ(C–H) bond to be activated is not appropriate to undergo metallation. In contrast the formation of the five-membered metallacycle can only be achieved if the imine has an *E*-conformation (Fig. 5II). The results summarized here reveal that: (1) the imine binds to the palladium (II) giving the coordination complex **2a**, where the ligand has a *Z*-conformation; and (2) in the presence of $NaCH_3COO$ complex **2a** evolves to the cyclopalladated derivative **4a**, in which the imine has an *E*-form. These findings suggest that the energy required for the $\{Z \rightarrow E\}$ isomerization of the ligand in **2a** should be small. In order to confirm this, the formation enthalpy ($\Delta H_{form.}$) for the two isomers of the complex **2a** (which differ in the conformation of the imine exclusively, Fig. 5), was calculated with the aid of the Spartan 4.0 program [51] (see Section 3) giving: $\Delta H_{form.} = -246.45$ kcal/mol (for *Z*-conformation of the ligand, Fig. 5I) and -242.13 kcal/mol {for the isomer in which the imine adopts the *E*-form, Fig. 5II}. This confirmed that the ΔH for the $Z \rightarrow E$ isomerization of **2a** is small (-4.32 kcal/mol).

When the cyclopalladated complex $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)–CH{=}N–CH_2–CH_2–N(CH_3)_2]\}Cl]$ (**4a**) is treated in benzene with the stoichiometric amount of PPh_3 the $Pd–N(CH_3)_2$ bond cleaves giving compound: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)–CH{=}N–CH_2–CH_2–N(CH_3)_2]\}Cl(PPh_3)]$ (**5a**), in which the palladium is linked to the ligand through the imine nitrogen and the *ortho*-carbon of the C_5H_3 ring (Scheme 3). The results of this reaction suggest that in **4a** the $Pd–N_{amine}$ bond is more labile than the $Pd–N_{imine}$. Further treatment of **5a**, with larger excesses of PPh_3 {up to six-fold the molar ratio} did not lead to the formation of $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)–CH{=}N–CH_2–CH_2–N(CH_3)_2]\}Cl(PPh_3)_2]$ (**6a**) (Scheme 3), thus suggesting the low lability of the $Pd–N_{imine}$ bond in **5a**. This finding agrees with the results obtained for cyclopalladated complexes

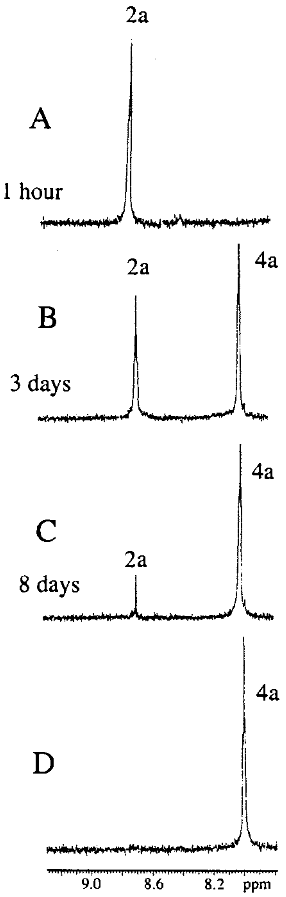
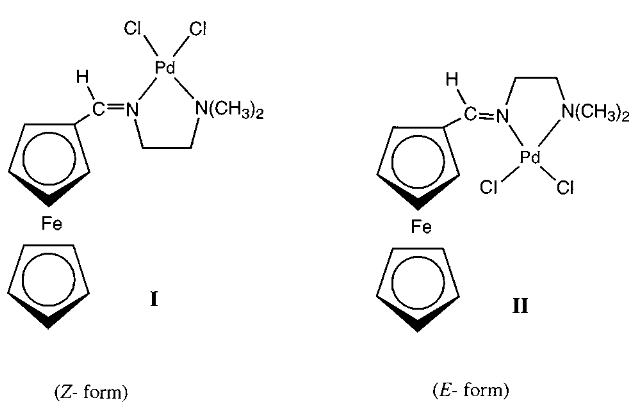


Fig. 4. Partial view of the ^{1}H-NMR spectra (in the ranges 7.3–10.0 ppm) of the solids obtained in the reaction of equimolar amounts of ligand **1a**, $Na_2[PdCl_4]$ and $Na(CH_3COO)\cdot 3H_2O$ in methanol, using reaction periods equal to: 1 h (A), 3 days (B), or 8 days (C), and that of pure complex **4a** (D).

of general formula: $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}C(R){=}N\text{–}R']\}Cl(PPh_3)]$ (with R = H, CH_3 or Ph and R′ = phenyl or benzyl groups), which do not undergo ring-opening processes in the presence of PPh_3 [26,29,38].



(*Z*- form) (*E*- form)

Fig. 5. Schematic view of the two isomers (I and II) of *cis*-$[Pd\{\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl_2]$ (**2a**). The ligand adopts the *E*-form in I and the *Z*-form in II.

Compounds **4a** and **5a** were characterized by elemental analyses, infrared and ^{1}H- and ^{13}C-NMR spectroscopy. In all cases the elemental analyses were consistent with the proposed formulae. In the ^{1}H-NMR spectra of **4a** and **5a** (Table 1) the resonances due to the protons of the ferrocenyl moiety appear as four signals of relative intensities 5:1:1:1 in the region 3.00–5.00 ppm, which are attributed to the four types of proton in the ferrocenyl moiety: C_5H_5, H^3, H^4 and H^5. Thus confirming the formation of a $\sigma(Pd\text{–}C_{sp^2,\ \mathrm{ferrocene}}\text{–}H)$ bond. Moreover, in **4a** the protons of the methyl groups are diastereotopic and consequently two singlets were observed in the spectrum of this complex. In contrast, for compound **5a**, in which there is no bond between the palladium and the $-N(CH_3)_2$ group, the resonance of the $-CH_3$ protons appears as one singlet. The signal due to the imine proton in the palladated complexes appear as a singlet (for **4a**) or as a doublet (due to phosphorus coupling for **5a**). ^{13}C-NMR spectroscopic data for **4a** and **5a** (Section 3) are consistent with the proposed formulae. The ^{31}P-NMR spectrum of **5a** showed a singlet in the range ca. 36–40 ppm. The position of this signal is consistent with those reported for a wide variety of palladium (II) compounds of general formula: $[Pd\{(C^\wedge N)\}Cl(PPh_3)]$, where $(C^\wedge N)$ represents a cyclopalladated N-donor ferrocenyl group, in which a *trans*-arrangement of the phosphine ligand and the imine nitrogen has been found [26–30,35–38].

2.5. Conclusions

The results summarized in this work have allowed us to isolate and characterize some heterobimetallic palladium (II) and platinum (II) compounds of general formula *cis*-$[MCl_2(\text{ligand})]$ {M = Pd (**2a**–**2c**) or Pt (**3a**–**3c**)}, $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl]$ (**4a**) or $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl(PPh_3)]$ (**5a**). We show the advantages of using of *cis*-$[PtCl_2(dmso)_2]$ [47] as starting materials for the preparation of the platinum (II) compounds (**3a**–**3c**), instead of the $Na_2[PtCl_4]$. The most relevant feature of complexes **2** and **3** is the presence of ferrocenyl ligands **1** acting as a neutral (N, N′) or (N, S) bidentate groups. In compounds **4a** and **5a** the ligand binds to the palladium (II) through a $C_{sp^2,\ \mathrm{ferrocene}}$ carbon and one {in **5a**} or both nitrogens {in **4a**}. Some examples of antitumour drugs containing similar cores have been described in the literature [21,25,52]. Besides that, the high solubility of compounds **3a**–**3c** in alcohols provides an additional interest since they might be useful as biomedical materials. Consequently, the palladium and platinum (II) compounds prepared in this work appear to be excellent candidates to study their interaction with DNA. Further work in this field is currently underway in order to elucidate the effect of the incorporation of the bulky ferrocenyl group.

3. Experimental

Elemental analyses (C, H, N and S) were carried out at the Serveis Cientifico-Tècnics (Universitat de Barcelona). Infrared spectra were obtained with a Nicolet-Impact-400-FTIR instrument using KBr pellets for the solid materials or NaCl discs for the oily products (**1a** or **3a**). Routine ^1H-NMR spectra were recorded at ca. 20°C on a Gemini-200 MHz instrument using $CDCl_3$ (99.5%) and $SiMe_4$ as internal standard, respectively. ^{13}C-NMR spectra were preformed ca. 20°C with a Varian-300 NMR instrument using $CDCl_3$ as solvent and $SiMe_4$ as internal standard. ^{31}P-NMR spectrum of **5a** was recorded at ca. 20°C with a Bruker-250-DXR instrument using $CDCl_3$ as solvent and $P(OMe)_3$ as standard, $\{\delta^{31}P\ [P(OMe)_3] = 140.17\ \text{ppm}\}$. ^{195}Pt-NMR spectra of compounds **3** were recorded with a Bruker-250-DXR instrument using $CDCl_3$ as solvent for **3a** and dmso-d_6 for **3b** and **3c**.

3.1. Materials and synthesis

Ferrocenecarboxaldehyde, *N*,*N*-dimethylethylendiamine, and the hydrochlorides of L-methionine methylester and 2-ethylthioethylamine were obtained from standard sources and used as received. The two hydrochlorides were converted into the corresponding amines before their use in the condensation reactions. *Cis*-$[PtCl_2(dmso)_2]$, the ligand $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2\}]$ (**1a**) and compound *cis*-$[Pd\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2]\}Cl_2]$ (**2a**) were prepared as described before [31,46]. Some of the preparations described below require the use of benzene which should be handled with caution.

3.1.1. *Preparation of* $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-S-CH_2-CH_3\}]$ *(**1b**) or* $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-CH(COOCH_3)-CH_2-CH_2-S-CH_3\}]$ *(**1c**)*

Ferrocenecarboxaldehyde (0.500 g, 2.28 mmol) was dissolved in 25 ml of benzene at 20°C. Then the stoichiometric amount (2.28 mmol) of $H_2N-CH_2-CH_2-S-CH_2-CH_3$ (for **1b**) or $H_2N-CH(COOCH_3)-CH_2-CH_2-S-CH_3$ (for **1c**) was added. The reaction flask was connected to a Dean–Stark apparatus (20 ml) and to a condenser. The wine-red reaction mixture was refluxed on an ethyleneglycol bath until ca. 15 ml had condensed on the Dean–Stark apparatus. The hot solution was carefully filtered out and the filtrate was concentrated to dryness on a rotary evaporator giving an oily residue. For ligand **1c** addition of *n*-hexane (ca. 20 ml) followed by vigorous stirring at room temperature for ca. 1 h produced a yellow solid, which was filtered out and air dried. (Yields: 79 and 75% for **1b** and **1c**, respectively). *Characterization data* for **1b**: IR(NaCl discs): $\nu(>C=N-) = 1641$ cm^{-1}. ^{13}C-NMR data (in ppm): 69.15 [C_5H_5], 73.15 [C^1], 69.62 [C^2], 68.45 [C^3 and C^4], 69.62 [C^5], 162.18 [$>C=N-$], 61.69 [$N-CH_2-$], 32.35 [$-CH_2-$], 26.31 [$-S-CH_2-$] and 14.94 [$-CH_3$]. For **1c**: Anal. Calc. (%) for: $C_{17}H_{21}NO_2SFe$ (found): C, 56.82 (57.0); H, 5.90 (5.9) and N, 3.90 (3.95). IR(KBr-pellets): $\nu(>CO) = 1728$ cm^{-1}, $\nu(>C = N-) = 1627$ cm^{-1} and $\nu_s(-COO) = 1434$ cm^{-1}.^{13}C-NMR data (in ppm): 69.98 [C_5H_5], 73.68 [C^1], 71.74 [C^2], 69.29 [C^3], 70.14 [C^4], 71.51 [C^5], 165.62 [$>C=N-$], 60.57 [$-N-CH<$], 57.76 [$-CH_2-$], 31.80 [$-OCH_3$], 30.83 [$-S-CH_2-$], 15.65 [$-CH_3$] and 172.79 [$-COO-$].

3.1.2. *Preparation of cis -* $[Pd\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-S-CH_2-CH_3]\}Cl_2]$ *(**2b**) and cis-*$[Pd\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-CH=N-CH(COOCH_3)-CH_2-CH_2-S-CH_2-CH_3]\}Cl_2]$ *(**2c**)*

A mixture containing 1.66 mmol of the corresponding ligand **1b** or **1c**, 0.489 g (1.66 mmol) of $Na_2[PdCl_4]$ and 50 ml of methanol was stirred at room temperature for 2 h. During this period the colour of the solution changed gradually from pale orange to red. The solid formed was collected by filtration and air dried. (Yields: 76 for **1b** and 70% for **1c**). *Characterization data* for **2b**: Anal. Calc. (%) for: $C_{15}H_{19}NSFePdCl_2 \cdot 1/2H_2O$ (found): C, 36.94 (37.0); H, 4.10 (3.95) and N, 2.87 (2.9). IR(KBr-pellets): $\nu(>C=N-) = 1625$ cm^{-1}. For **2c**: Anal. Calc. (%) for: $C_{17}H_{21}NO_2SFePdCl_2$ (found) C, 38.02 (37.8); H, 3.94 (3.9) and N, 2.62 (2.65). IR(KBr-pellets): $\nu(>CO) = 1744$ cm^{-1}, $\nu(>C=N-) = 1612$ cm^{-1} and $\nu_s(-COO) = 1436$ cm^{-1}.

3.1.3. *Preparation of cis-*$[Pt\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2]\}Cl_2]$ *(**3a**), cis-*$[Pt\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-S(CH_2-CH_3)\}Cl_2]$ *(**3b**) or cis-*$[Pt\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-CH=N-CH(COOCH_3)-CH_2-CH_2-SCH_3]\}Cl_2]$ *(**3c**)*

223 mg (0.528 mmol) of *cis*-$[PtCl_2(dmso)_2]$ [47] was suspended in 30 ml of methanol and refluxed until complete dissolution. Then a solution containing the corresponding ligand (0.528 mmol) and 2 ml of methanol was added. The resulting mixture was refluxed for 9 h. After this period the undissolved materials were removed by filtration and discarded. The deep-red filtrates were concentrated to ca. 15 ml on a rotary evaporator and the red solids formed were collected by filtration, washed with *n*-hexane and air-dried. (Yield: 35, 38 and 29% for **3a**, **3b** and **3c**, respectively). *Characterization data* for **3a**: Anal. Calc. (%) for: $C_{15}H_{20}N_2FePtCl_2H_2O$: C, 31.68 (31.7); H, 3.87 (3.7)

and N, 4.93 (4.9). IR(KBr-pellets): $\nu(C{=}N) = 1623$ cm^{-1}. ^{195}Pt-NMR (in ppm): $\delta = -2262$. For **3b**: Anal. Calc. (%) for: $C_{15}H_{19}NSFePtCl_2$ (found): C, 31.76 (31.7); H, 3.38 (3.4); N, 2.47 (2.46) and S, 5.65 (5.6). IR(KBr-pellets): $\nu(CO) = 1750$ cm^{-1} and $\nu(C{=}N) = 1607$ cm^{-1}. ^{195}Pt-NMR (in ppm): $\delta = -2900$. For **3c**: Anal. Calc. (%) for: $C_{17}H_{21}NSO_2FePtCl_2$ (found): C, 32.66 (32.5); H, 3.39 (3.5); N, 2.27 (2.25) and S, 5.13 (4.9). IR(KBr-pellets): $\nu(>C{=}N-) = 1627$ cm^{-1}. ^{195}Pt-NMR (in ppm): $\delta = -2989$.

3.1.4. *Preparation of* $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl]$ *(**4a**)*

A mixture containing 0.469 g (1.65 mmol) of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_5)-CH{=}N-CH_2-CH_2-N(CH_3)_2\}]$ (**1a**), 0.485 g (1.65 mmol) of $Na_2[PdCl_4]$ and 0.230 g (1.65 mmol) of $Na(CH_3COO)\cdot 3H_2O$ and 50 ml of methanol was stirred at room temperature for 8 days. During this period the colour of the solution changed gradually from pale orange–red. The solid formed was collected by filtration and air dried. This material consists of a mixture of *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl_2]$ (**2a**) and the cyclopalladated derivative $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2\}Cl]$ (**4a**) in a ca. 1:7 molar ratio. The solid was treated with 40 ml of $CHCl_3$, and the undissolved orange material was removed by filtration and discarded. The red filtrate was passed through an SiO_2 column (10 × 250 mm) using a $CHCl_3$:MeOH (400:1) as eluant. During the elution the separation of two bands became evident, a red one and an orange band. The first band was collected and concentrated to dryness on a rotary evaporator giving **4a** as dark-red solid (yield: 68%). Once the first band was collected a mixture of $CHCl_3$:MeOH (100:1) was used as eluant in order to collect the second band, which was afterwards concentrated to dryness on a rotary evaporator giving (**2a**) as a bright orange solid (yield: 10%). *Characterization data* for **4a**: Anal. Calc. (%) for: $C_{15}H_{19}N_2FePdCl$ (found): C, 42.38 (42.3); H, 4.47 (4.5) and N, 6.59 (6.6). IR(KBr-pellets): $\nu(C{=}N) = 1581$ cm^{-1}.^{13}C-NMR data (in ppm): 70.32 [C_5H_5], 100.27 [C^1], 85.62 [C^2], 69.32 [C^3], 69.45 [C^4], 76.55 [C^5], 170.21 [$>C{=}N-$], 63.48 [$N-CH_2-$], 52.85 [$-CH_2-$], 47.90 and 47.47 [$N-CH_3$].

3.1.5. *Preparation of* $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl(PPh_3)]$ *(**5a**)*

50 mg (0.12 mmol) of $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl]$ (**4a**) was suspended in 5 ml of benzene, then PPh_3 (31 mg, 0.12 mmol) was added. The resulting mixture was stirred vigorously at room temperature for 30 min. During this period the palladium (II) complex dissolved, giving a bright orange solution. The resulting solution was concentrated to dryness on a rotary evaporator. The red oil formed was dissolved in the minimum amount of CH_2Cl_2 (ca. 2 ml.) and filtered out. The undissolved materials were discarded and the filtrate was treated with *n*-hexane (ca. 10 ml) and stirred at room temperature (ca. 20°C) for 1 h, giving an orange solid which was collected by filtration and air-dried. (Yield: 79.1%). *Characterization data for **5a***: Anal. Calc. (%) for: $C_{33}H_{34}N_2ClFePPd$ (found): C, 56.91 (56.9); H, 4.99 (5.0) and N, 4.02 (4.2). IR(KBr-pellets): $\nu(>C{=}N-)$: 1598 cm^{-1}. ^{13}C-NMR data (in ppm): 70.41 [C_5H_5], 102.27 [C^1], 88.02 [C^2], 69.36 [C^3], 66.95 [C^4], 69.36 [C^5], 173.06 [$>C{=}N-$], 61.19 [$-N-CH_2-$], 53.97 [$-CH_2-$], 46.32 [$-N-CH_3$] and four additional doublets at ca. 134.90, 131.20, 130.70 and 128.30 ppm due to the carbon atoms of the PPh_3 ligand. ^{31}P-NMR: $\delta = 38.7$ ppm.

Table 5

Crystal data and details of the refinement of the crystal structure of *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}N(CH_3)_2]\}Cl_2]$ (**2a**)

Empirical formula	$C_{14}H_{16}Cl_2FeN_2Pd$
Formula weight	445.45
Temperature (K)	293(2)
Wavelength (Mo–K$_\alpha$) (Å)	0.71069
Crystal size (mm)	0.1 × 0.1 × 0.2
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell parameters	
a (Å)	6.034(2)
b (Å)	14.502(2)
c (Å)	10.236 (2)
α (°)	90
β (°)	104.61(2)
γ (°)	90
V (Å^3)	866.7(4)
Z	2
$D_{calc.}$ (Mg m^{-3})	1.571
Absorption coefficient (mm^{-1})	2.016
$F(000)$	406
Theta range for data collection (°)	2.06–29.97
Index ranges	$-8 \le h \le 8$, $0 \le k \le 20$, $0 \le l \le 14$
No. of reflections collected	2569
Independent reflections	2441 $\{R_{int} = 0.0372\}$
Method of refinement	Full-matrix least-squares on F^2
No. of data/No. of restrains/No. of parameters	2391/17/122
Goodness-of-fit on F^2	1.042
Final R indices $\{I > 2\sigma(I)\}$	$R_1 = 0.0325$, $wR_2 = 0.0863$
R indices (all data)	$R_1 = 0.0371$, $wR_2 = 0.1126$
Extinction coefficient	0.001(2)
Largest difference peak and hole (Å^{-3})	0.752 and −0.665

3.2. *Crystallographic studies*

A prismatic crystal (sizes in Table 5) was selected and mounted on a Enraf-Nonius CAD-4 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 graphite monochromated Mo–K_α radiation, using $\omega/2\Theta$ scan technique. A total of 2569 reflections were measured (in the range $2.06° < \Theta < 29.97°$) of which 2441 were non-equivalent by symmetry $\{R_{int}$ (on $I) = 0.037\}$ and 2329 reflections 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. Lorentz polarization corrections were made but absorption corrections were not.

The structure was solved by direct methods using the SHELXS computer program [53] and refined by full matrix least-squares method using the SHELX93 computer program [54] using 2391 reflections (very negative intensities were not assumed). The function minimized was $\Sigma\, w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0625P)^2 + 0.1701P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from the literature [55]. The crystal selected for the intensity measurement was a twin-crystal. The iron atom is on a symmetry centre and the palladium atom on a two fold axis which are not of molecular symmetry. N(1), C(8), C(10) and C(11) are disordered, and an occupancy factor of 0.5 was assigned to these atoms according to the height of the Fourier synthesis. The extinction coefficient was 0.032, wR (on $|F|^2) = 0.086$ and the goodness-of-fit was 1.053 for all observed reflections. The number of refined parameters, the final R-indices and further details concerning the crystal structure of compound **2a** are summarized in Table 5.

3.3. Computational details

The calculations were performed with the Spartan 4.0 suite of programs [50] using a silicon graphics {model: INDIGO-2 power XZ}.The PM3(tm) method was used with the default parameters provided by the program. geometrical restrictions were not imposed in any case. The geometry of the molecules was optimized before the calculation of the formation enthalpies. These calculations were undertaken with the option SCF = converge, and at least 500 cycles were necessary.

4. Supplementary material

Tables containing final atomic coordinates for non-hydrogen atoms and equivalent isotropic displacement parameters, complete listing of bond lengths and angles, anisotropic displacement parameters and observed and calculated structure factors for **2a** have been deposited as supplementary material.

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