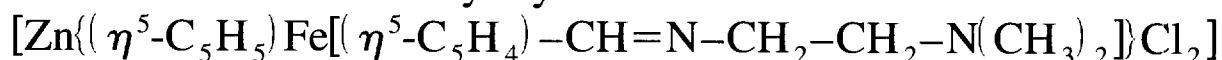


Syntheses, characterization and study of the properties of heterobimetallic compounds containing ferrocenyl units

X-ray crystal structure of:



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Abstract

The synthesis, characterization and study of the new ferrocenyl Schiff base: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]]$ (1) is reported. This substrate reacts with $\text{Na}_2[\text{PdCl}_4]$ or with transition metal dichlorides $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ {with $\text{M} = \text{Zn, Ni, Co}$ or Cu } giving the corresponding coordination compounds: $[\text{M}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]\}\text{Cl}_2]$ {with $\text{M} = \text{Pd}$ (2), Zn (3), Ni (4), Co (5), and Cu (6)}. These heterobimetallic compounds have been characterized by infrared and UV-visible spectroscopies. NMR-spectroscopic studies on the diamagnetic derivatives (1–3) together with magnetochemical studies on the paramagnetic species (4–6) are also reported. Crystals of complex 3 have also been characterized by X-ray diffraction: orthorhombic, space group Pcab , with $a = 12.225(1) \text{ \AA}$; $b = 14.685(1) \text{ \AA}$; $c = 19.474(1) \text{ \AA}$, and $V = 3498.4(4) \text{ \AA}^3$. Electrochemical studies, based on cyclic voltammetry, for all the compounds have allowed us to establish the influence of the central atom M(II) upon the redox ability of the Fe(II) . © 1997 Elsevier Science S.A.

1. Introduction

Since 1951, when Pauson and Miller isolated ferrocene [1], the interest in its derivatives and their properties has increased exponentially, mainly due to their applications in a wide variety of areas, among which those concerning the use of ferrocene derivatives in catalysis, organic synthesis or in the design of new materials such liquid crystals or polymers are specially important [2]. Of all the ferrocene derivatives described so far, those containing atoms with donor abilities have attracted great interest, since the coordination of a metal to these heteroatoms produces multicentre molecules [3]. In compounds of this kind, the presence of proximal metals with different environments and oxidation or spin states may influence the mutual cooperation of these metals in a wide variety of processes [4], and most of the articles reported so far reveal that the properties of these polymetallic species depend not only on the

structure of the ferrocenyl fragment, but also on the metal which binds to it. For instance, it has been reported that the proclivity of iron(II) to be oxidized in the free ferrocenylamine: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-N-CH}_2\text{-}]]_2$ is lower than in its copper(II) derivative [5]. However, as far as we know, none of the studies reported so far on ferrocenylimines and their coordination compounds has clarified the influence of the binding of different metal ions on the properties of the coordination complexes containing N-donor ferrocenyl ligands.

As a first approach to this problem, we attempted to prepare and characterize the novel ferrocenylimine: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]]$ (1) (Fig. 1) and to study its reactivity versus $\text{Na}_2[\text{PdCl}_4]$ or the transition metal dichlorides: $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ {with $\text{M} = \text{Zn, Ni, Co}$ or Cu } in order to obtain the heterobimetallic species: $[\text{M}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]\}\text{Cl}_2]$ in which the ferrocenyl substrate acts as an {NN} bidentate ligand. In addition, the comparison of the properties of the free imine and those of the coordination compounds

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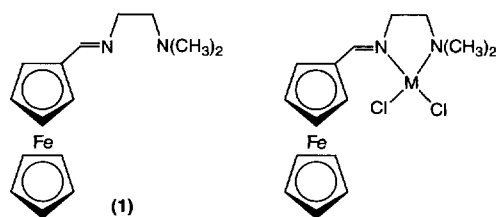


Fig. 1. Schematic view of the ferrocenyl Schiff base under study: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2]$ (1) and of the heterobimetallic complexes of general formula: $[\text{M}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2]\text{Cl}_2]$ with $\text{M} = \text{Pd}$ (2), Zn (3), Ni (4), Co (5) or Cu (6).

may clarify the influence of the nature of the transition metal upon the ferrocenyl moiety, in particular the proclivity of the iron(II) to undergo oxidation.

2. Results and discussion

2.1. Syntheses

The new ferrocenyl Schiff base: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2]$ (1) was prepared by reaction of formylferrocene and *N,N*-dimethylethylenediamine $\{\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2\}$ in a 1:1 molar ratio and benzene as solvent (Scheme 1). The condensation was achieved under reflux using a Dean-Stark apparatus to remove the benzene/water azeotrope formed in the process.

This substrate reacts in methanol at room temperature with $\text{Na}_2[\text{PdCl}_4]$ or the transition metal dichlorides $\{\text{MCl}_2 \cdot n\text{H}_2\text{O}$, with $\text{M} = \text{Zn}$, Ni , Co or Cu in a 1:1 molar ratio giving the corresponding coordination compounds: $[\text{M}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2]\text{Cl}_2]$ (with $\text{M} = \text{Pd}$ (2), Zn (3), Ni (4), Co (5) or Cu (6)) (Scheme 1). Among all these compounds, the formation of compound 4 is specially interesting since previous studies on Ni(II) complexes containing related Schiff bases of general formula: $(\text{CH}_3\text{-C}_6\text{H}_4)\text{CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{R}')_2$ (7) (with $\text{R}' = \text{CH}_3$ or CH_2CH_3) have demonstrated that the formation of $[\text{Ni}\{(\text{CH}_3\text{-C}_6\text{H}_4)\text{CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{R}')_2\}\text{X}_2]$ (with $\text{X} = \text{Cl}$, Br or I) could be achieved exclusively working

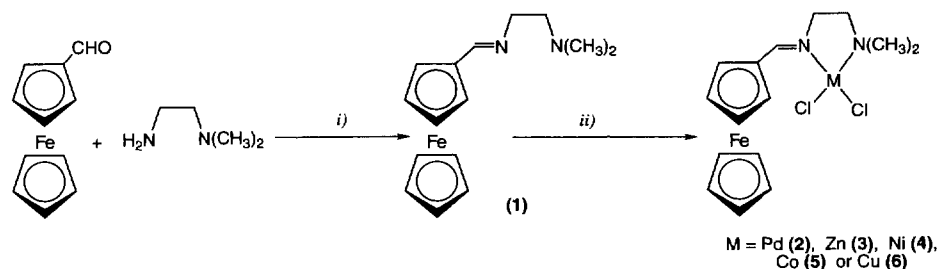
under anhydrous conditions [6]. In contrast, when the ferrocenylimine 1 (which could be visualized as derived from (7) by the replacement of the aryl ring by a ferrocenyl fragment) is treated with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in methanol, the isolation of complex 4 can be achieved.

2.2. Characterization

Except ligand 1, which is an oily material, the remaining compounds are stable solids at room temperature and their colours vary from brown to red. Compounds 1–6 are soluble in CH_2Cl_2 and CHCl_3 . These compounds are also soluble in acetonitrile, but when 10^{-3} M solutions of compound 4 in acetonitrile was stored at room temperature for several hours, a change of colour from pale yellow to reddish was detected, while for derivatives 1–3, 5 and 6 the solutions remained unchanged. Thus suggesting the lower stability of 4 in acetonitrile. This finding is not surprising since it is well known that the closely related complexes: $[\text{Ni}\{(\text{CH}_3\text{-C}_6\text{H}_4)\text{CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{R}')_2\}\text{X}_2]$ undergo dissociation in donor solvents [6].

Elemental analyses of all the compounds used in this study are consistent with the proposed formulae (see Section 3). The infrared spectrum of the ligand shows a sharp and intense band at 1644 cm^{-1} , which is assigned to the asymmetric stretching of the functional group $>\text{C}=\text{N}-$. For the coordination compounds, the band appears at lower wavenumbers due to the coordination of the imine nitrogen.

Compounds 1–3 have also been characterized by proton NMR spectroscopy. The most relevant features observed in the spectrum of the free ligand is the presence of three signals (one singlet and two triplets of relative intensities 5:2:2) in the range 4.00–4.50 ppm which are due to the three types of proton nucleus in the ferrocenyl moiety (Table 1). The resonance of the imine proton appears as a singlet at 8.17 ppm. The multiplicities and positions of these signals are consistent with those reported for related ferrocenyl Schiff bases, for which a *trans* conformation of the imine has been confirmed by X-ray diffraction [7]. The resonances due to the methylenic protons appear as two triplets in the higher field region of the spectrum. Table 2.



Scheme 1.

Table 1

Proton-NMR data (in ppm)^a for the free ligand (1), [Pd(η^5 -C₅H₅)Fe(η^5 -C₅H₄)-CH=N-CH₂-CH₂-N(CH₃)₂)]Cl₂ (2), and [Zn(η^5 -C₅H₅)Fe(η^5 -C₅H₄)-CH=N-CH₂-CH₂-N(CH₃)₂)]Cl₂ (3)

	(1)	(2)	(3)
-HC = N-	8.17	8.70	8.37
Cp	4.18	4.37	4.34
H(2), H(5) ^b	6.63	4.70	5.05
H(3), H(4) ^b	4.36	4.60	4.69
N-CH ₂ - ^b	3.60	3.70	3.70
-CH ₂ - ^b	2.57	2.64	2.80
CH ₃	2.30	2.92	2.63

^a Labelling refers to the scheme shown on previous page.

¹H-NMR of the complexes 2–3 exhibited an identical pattern to that of the free ligand. However, slight differences in the position of the signals were detected. In all cases the binding of the ligand to a metallic centre produces a low field shift of the imine proton. This finding is consistent with those reported for related complexes of general formula: [Pd(η^5 -C₅H₅)Fe(η^5 -C₅H₄)-CH=N-CH(C₆H₃-R')]Cl(PPh₃)] which contain a bidentate {CN}⁻ ferrocenyl ligand and an *exo-cyclic* imine group [8,9].

¹³C-NMR data for the free ligand exhibit three singlets in the range 68–72 ppm, which are assigned to the carbon nuclei of the cyclopentadienyl ring {C₅H₅} and to the pairs {C(2), C(5)} and {C(3), C(4)}. The resonances of the quaternary carbon of the substituted ring {C(1)} and that of the imine group appear at 81.01 and 162.15 ppm, respectively and exhibit low intensity due to the Nuclear Overhauser Effect. The position of these signals and their multiplicities are in good agreement with those reported previously for related ferrocenylaldimines [7]. The resonances of the methylene and methyl carbons of the ligand were also observed in the higher field region of the spectrum.

In order to clarify the effect of chelation upon the ferrocenyl unit, the ¹³C-NMR spectrum of complex (3) was also recorded. In this case the number of signals and their multiplicities did not change appreciably from

Table 2

¹³C-NMR data (in ppm)^a for the ligand and [Zn(η^5 -C₅H₅)Fe(η^5 -C₅H₄)-CH=N-CH₂-CH₂-N(CH₃)₂)]Cl₂ (3)

	(1)	(3)
-HC = N-	162.15	171.71
Cp	69.60	70.64
C(1)	81.01	^b
C(2), C(5)	70.80	74.50
C(3), C(4)	68.91	71.75
-CH ₂	-60.68	54.91
-CH ₂	-60.57	59.41
CH ₃	46.40	47.22

^a Labelling refers to the scheme shown in Table 1.

^b Not observed.

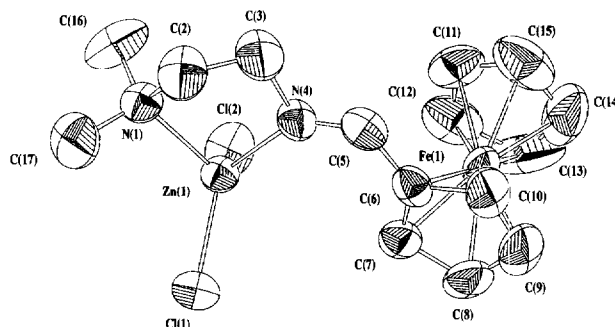


Fig. 2. Molecular structure and atom labelling scheme for complex: [Zn(η^5 -C₅H₅)Fe(η^5 -C₅H₄)-CH=N-CH₂-CH₂-N(CH₃)₂)]Cl₂ (3).

those of the parent ligand. However, it is worth noting that the binding of the Zn(II) cation produces a downfield shift of all the signals due to the carbon atoms of the ferrocenyl unit, and the shift is greater for the carbon atoms which are closer to the imine nitrogen, such as the methinic carbon, thus suggesting that the formation of the complex decreases of the electronic density of this group.

2.3. Description of the crystal structure of compound: [Zn(η^5 -C₅H₅)Fe(η^5 -C₅H₄)-CH=N-CH₂-CH₂-N(CH₃)₂)]Cl₂ (3)

The molecular structure of compound 3 together with the atom labelling scheme is presented in Fig. 2. Selected bond lengths and angles are summarized in Table 3.

Table 3

Selected bond lengths (in Å) and angles (in deg.) for compound: [Zn(η^5 -C₅H₅)Fe(η^5 -C₅H₄)-CH=N-CH₂-CH₂-N(CH₃)₂)]Cl₂ (3)

Bond lengths			
Zn(1)-Cl(1)	2.2106(14)	Zn(1)-Cl(2)	2.133(13)
Zn(1)-N(1)	2.117(4)	Zn(1)-N(4)	2.040(4)
N(1)-C(2)	1.471(6)	C(2)-C(3)	1.485(8)
C(3)-C(4)	1.471(6)	N(4)-C(5)	1.269(6)
C(5)-C(6)	1.437(7)	C(6)-C(7)	1.430(7)
C(7)-C(8)	1.437(7)	C(8)-C(9)	1.410(9)
C(9)-C(10)	1.416(9)	C(10)-C(6)	1.438(7)
C(11)-C(12)	1.371(7)	C(12)-C(13)	1.427(7)
C(13)-C(14)	1.423(8)	C(14)-C(15)	1.358(7)
Fe-C _{average value}	2.031(6)	C-C _{average value}	1.405(7)
Bond angles			
Cl(1)-Zn-Cl(2)	118.83(6)	N(1)-Zn-N(4)	86.0(2)
N(1)-Zn-Cl(1)	109.22(11)	N(4)-Zn-Cl(2)	112.29(12)
N(1)-Zn-Cl(2)	110.11(11)	N(4)-Zn-Cl(1)	115.40(12)
N(1)-C(2)-C(3)	111.2(5)	N(4)-C(5)-C(6)	126.9(4)
C(17)-N(1)-C(16)	108.9(5)	C(3)-N(4)-C(5)	117.1(4)
C(5)-C(6)-C(7)	129.5(4)	C(5)-C(6)-C(10)	121.7(5)
C(2)-N(1)-Zn	102.6(3)	C(5)-N(4)-Zn	136.2(2)
Zn-N(1)-C(16)	113.2(3)	Zn-N(1)-C(17)	113.8(3)
C(16)-N(1)-C(2)	112.1(5)	C(17)-N(1)-C(2)	107.0(4)

Table 4

Visible-ultraviolet data (wavelengths, λ (in nm)) and logarithms of the molar extinction coefficients ($\log \epsilon$) for compounds under study

	$\lambda_1(\log \epsilon_1)$	$\lambda_2(\log \epsilon_2)$
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]$ (1)	322 (sh)	450 (2.8)
$[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2\}]\text{Cl}_2$ (2)	356 (3.3)	479 (3.2)
$[\text{Zn}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2\}]\text{Cl}_2$ (3)	355 (3.2)	475 (3.0)
$[\text{Ni}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2\}]\text{Cl}_2$ ^a (4)	344 (3.4)	471 (3.1)
$[\text{Co}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2\}]\text{Cl}_2$ ^b (5)	356 (3.1)	494 (3.1)
$[\text{Cu}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2\}]\text{Cl}_2$ (6)	346 (sh)	472 (2.9)

^a The spectrum of this complex exhibits an additional shoulder at ca. 526 nm, which is partially overlapped by the intense absorption at 471 nm.^b Additional absorptions at: 577 nm and 654 nm.

The structure consists of discrete molecules of $[\text{Zn}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2\}]\text{Cl}_2$ separated by van der Waals contacts. The zinc atom is tetracoordinated, bound to two chlorines {Cl(1) and Cl(2)} and the two nitrogens {N(1) and N(4)} of the ferrocenyl moiety in a slightly distorted tetrahedral environment.

The *endocyclic* N(1)–Zn–N(4) angle of 86.0(1)° is drastically reduced from the ideal tetrahedral value and the opposite Cl(1)–Zn–Cl(2) angle is 118.83(6)° which reflects a strong σ -donating contribution of the Zn–Cl bonds.

The five-membered metallacycle has an envelope-like conformation with the C(2) atoms above the plane defined by the atoms Zn, N(1), C(3) and N(4), just on the opposite site of the iron(II). These four atoms and the fragment containing Zn, N(4), C(5), C(6) are nearly coplanar with the C₅H₄ ring of the ferrocenyl units as reflected in the values of the angles between the normals to their planes: 172.6(3)° and 12.1(4)°, respectively. Such arrangement produces a displacement of the Zn atom versus the C₅H₄ ring of 0.168 Å towards the opposite side of the iron(II).

The C=N bond length [1.269(6) Å] is similar to the values reported for related Schiff bases of general formula: $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-C(R)=N-R}']$ derived from formyl-, acetyl- or benzoylferrocene [7] and clearly larger than in $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-(CH}_2)_n\text{-N=C(H)R}']$ {with $n = 0$, R' = C₆H₅-2-OH or $n = 1$ and R' = C₆H₃-2,6-Cl₂} [9,10].

The substituents at the imine group: C₅H₄ and $\text{-(CH}_2)_2\text{-N(CH}_3)_2$, have a *trans*-arrangement [the torsion angle defined by C(3), N(4), C(5) and C(6) is $-177.3(3)^\circ$] thus confirming the *anti*-conformation of the ligand. This arrangement is consistent with the results obtained from X-ray studies for a wide variety of Schiff bases containing ferrocenyl units and for their palladium(II) compounds, where the imine acts as a (NC)⁻ bidentate ligand.

Fe–C and C–C bond lengths and angles in the ferrocenyl- substituent are similar to those reported in the literature for related complexes [11]. The two pentagonal rings are planar, nearly parallel [*tilt angle*:

1.0(2)°] and their conformation is eclipsed as reflected in the value of the *twist angle* [average value: 8.4(2)°] [12]. The separation between the two metals is 4.792(2) Å, which implies that there is no direct interaction. The remaining distortions observed in the ferrocenyl unit are similar to those reported previously [13].

2.4. UV-visible spectra

The compounds under study are all strongly coloured dark reddish or brownish as is normal for ferrocenyl containing complexes. Spectral data for compounds 1–6 are summarized in Table 5. These compounds have highly intense absorptions at wavelengths lower than 400 nm. The most outstanding feature is that the two bands observed for the ligand at ca. 322 and 450 nm shift to lower energy regions for the metal complexes, and the magnitude of the shift seems, moreover, to be dependent on the nature of the metal ion of the 'MCl₂' moiety. The additional shoulder (at ca. 526 nm) observed in the spectrum of 4 is in good agreement with data reported for tetrahedral compounds [6], such as $[\text{Ni}\{(\text{CH}_3\text{-C}_6\text{H}_4)\text{CH=N-CH}_2\text{-CH}_2\text{-N(R}')_2\}]\text{X}_2$ (with X = Cl, Br or I) [6], while for compound 5 the two additional bands (at ca. 577 and 654 nm) observed in the spectrum suggest a pseudotetrahedral geometry. In general, when acetonitrile (HPLC-grade) was used as solvent not significant variation was detected, except for the position of the bands which shifted (ca. 10 nm) to lower energies. However, for complex 4, the band at ca. 526 nm (which is indicative of a tetrahedral geometry) was not detected thus suggesting a change in the geometry. In addition, when the solution was stored for 4 h at room temperature, a change of colour from yellow to reddish was detected and the position of the bands due to the ferrocenyl fragment became closer to those of the free ligand, thus suggesting that a dissociation process was taking place. In contrast, for compounds 1–3, 5 and 6 no significant change was detected when their acetonitrile solutions were stored for 3 days at room temperature, thus suggesting the higher stability of these compounds in this solvent (Table 4).

Table 5
Half-wave potentials, referred to ferrocene, $E_{1/2}(Fc)$, (in V) for the ferrocenylimines: $[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2]$ (1) and $[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-N=CH(C_6H_4-2-OH)]$ (1'), as well as for their coordination compounds of general formulae: $[M((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2)]Cl_2$ [with M = Zn (3), Ni (4) or Cu (6)] and $[M((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-N=CH(C_6H_4-2-O))]_2$ [with M = Zn (3'), Ni (4') or Cu (6')]

Compound	$E_{1/2}(Fc)$	Compound	$E_{1/2}(Fc)$ ^a
$[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2]$ (1)	0.08	$[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-N=CH(C_6H_4-2-OH)]$ (1')	0.06
$[Pd((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2)]Cl_2$ (2)	0.30	$[Zn((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-N=CH(C_6H_4-2-O))]_2$ (3')	0.24
$[Zn((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2)]Cl_2$ (3)	0.31	$[Ni((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-N=CH(C_6H_4-2-O))]_2$ (4')	0.13
$[Ni((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2)]Cl_2$ (4)	0.26	$[Cu((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-N=CH(C_6H_4-2-O))]_2$ (6')	0.08
$[Cu((\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2)]Cl_2$ (6)	0.24		

^a Data from Ref. [10].

2.5. Electrochemical studies

Electrochemical data for compounds under study were obtained from cyclic voltammetric studies of freshly prepared solutions (10^{-3} M) in acetonitrile using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. Cyclic voltammograms of **1–5** exhibit an anodic peak with a directly associated reduction in the reverse scan. The half-wave potentials, referred to ferrocene [$E_{1/2}(Fc)$], for complexes under study are summarized in Table 5.

The half-wave potential for ligand **1** is in good agreement with those reported for related Schiff bases of general formula: $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-C(R)=N-R'\}]$ {where $R = H, CH_3$ or C_6H_5 and $R' =$ aryl, benzyl or naphthyl groups} [14]. The heterobimetallic derivatives: $[M\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2]\}Cl_2]$ {with $M = Pd$ (**2**), Zn (**3**), Ni (**4**) or Cu (**6**)} exhibit higher half-wave potentials than the free ligand, and the values shown in Table 5 indicate that the binding of the imine nitrogen to the 'MCl₂' units hinders the oxidation of the iron(II). This result is in good agreement with those reported by Bracci et al. [10] for the imine $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-N=C(H)(C_6H_4-2-OH)\}]$ (**1'**) and the coordination compounds: $[M\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-N=C(H)(C_6H_4-2-O)]_2\}]$ { $M = Zn$ (**3'**), Ni (**4'**) or Cu (**6'**)}, in which the imine acts as a monoanionic (NO)⁻ bidentate ligand.

From electrochemical studies on ferrocene derivatives it is accepted that the $E_{1/2}$ values are clearly dependent on the nature of the substituent [14]. In general, higher values are found for derivatives containing electron-withdrawing substituents, while electron donor groups facilitate the oxidation of the iron centre (as reflected in their $E_{1/2}(Fc)$ values which are more cathodic than that of ferrocene)[14]. On this basis in compounds **2–5** the substituents in the ferrocenyl moiety, appear at first sight to have a stronger electron withdrawing effect than the aldehyde or ketone groups in ferrocenecarbaldehyde { $E_{1/2}(Fc) = 0.24$ V} or acetylferrocene { $E_{1/2}(Fc) = 0.22$ V} [15].

In addition the $E_{1/2}(Fc)$ values reported in Table 5 indicate that the oxidation of the Fe(II) depends markedly on the nature of the central metal ion, M(II). The proclivity to oxidize increases in the order: (**2**) < (**3**) < (**4**) < (**6**) < (**1**), which reflects the electron withdrawing effect of the 'MCl₂' moieties upon the ferrocenyl fragment. It is interesting to mention, moreover, that this trend is in excellent agreement with that obtained from the electrochemical studies of the ferrocenylimine: $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-N=C(H)(C_6H_4-2-OH)\}]_2$ (**1'**) and of the complexes: $[M\{(\eta^5-C_5H_5)Fe[(\eta^5-C_5H_4)-N=C(H)(C_6H_4-2-O)]_2\}]$ { $M = Zn$ (**3'**), Ni (**4'**) or Cu (**6'**)} {for which the $E_{1/2}(Fc)$ decreases in the order: (**3'**) < (**4'**) < (**6'**) < (**1'**), thus

suggesting that for the two families of complexes the influence of a given 'MCl₂' fragment on the imine has the same origin. It is also interesting to mention that this trend is similar to that detected in the UV-visible spectra, which show that the band appears at higher energies for the free ligand than for the metal complexes. This finding suggests that the properties of the iron(II) in these complexes may be modulated by an accurate selection of the 'MCl₂' moiety which modifies the electronic environment of the Fe(II).

Furthermore, the half-wave potential of compound **2** (which is quite close to those reported for the nine-membered palladacyclic compounds: $[Pd\{[(RC=CR)_2(\eta^5-C_5H_3)-C(H)=N-(CH_2)-(C_6H_5)]-Fe(\eta^5-C_5H_5)Cl\}]$ [16]) falls in the higher range of potentials obtained for palladium(II) compounds containing bidentate ferrocenylimines [17]. In particular, derivatives where the imine acts as a (CN)⁻ ligand are more prone to oxidize. Consequently, the electronic effect of the palladium(II) bound to these ferrocenylimines upon the redox ability of the Fe(II) is highly dependent not only on the nature of the imine, but also on the mode of coordination of the ligand to the palladium(II).

2.6. Magnetic measurements

Magnetic measurements for compounds **4–6** were also undertaken {the magnetic moments: μ_{eff} at room temperature are 3.76, 4.97 and 2.24 MB, respectively}, and in all cases the plots of the inverse magnetic susceptibility ($1/\chi_M$) versus temperature are fairly linear (Fig. 3) and thus being consistent with the simple Curie-Weiss law. The low Curie-Weiss' temperatures for these compounds ($\Theta = 0.81, -1.42$ and -9.28 K

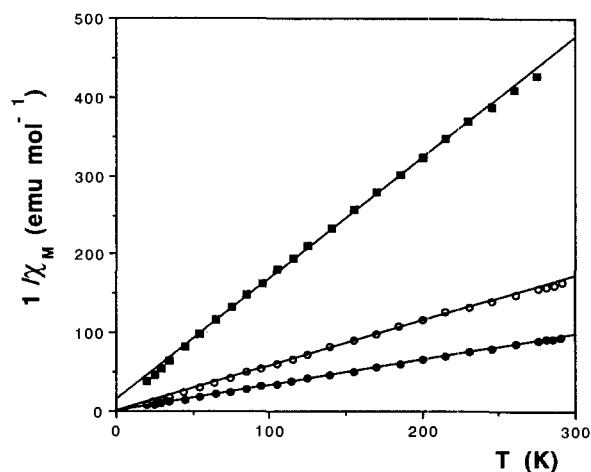


Fig. 3. Plots of inverse molar susceptibility ($1/\chi_M$, in mol cm³) versus temperature (T in K) for compounds: $[M(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-CH_2-CH_2-N(CH_3)_2\}]Cl_2$ with $M = Ni$ (**4**) Co (**5**) or Cu (**6**). Experimental data are shown as open circles for (**4**), squares for (**5**) or filled circles for (**6**). The solid lines through the points are the best fits of the data to the Curie-Weiss law.

for **4**, **5** and **6**, respectively) are in good agreement with the expected values for non-interacting monomeric units, which result in the absence of significant magnetic exchange.

2.7. Final remarks

The results reported in this work have allowed us to prepare and characterize the novel ferrocenyl Schiff base: $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]]$ (**1**) and to study the reactivity of this substrate versus $\text{Na}_2[\text{PdCl}_4]$ or divalent transition ions such as Pd, Zn, Ni, Co or Cu. In all cases the reactions produce heterobimetallic coordination compounds of general formula: $[\text{M}\{(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]\}\text{Cl}_2]$ (**2–6**), in which the ferrocenylimine acts as a neutral (NN) bidentate ligand. Proton NMR-spectra of the diamagnetic compounds (**1–3**) have revealed the influence of the metallic atom upon the ferrocenyl moiety.

Electrochemical studies, based on cyclic voltammeteries, have shown not only, that the coordination of a 'MCl₂' unit to the ferrocenylimine produces an increase in the first oxidation potential {Fe(II) → Fe(III)}, but also that the magnitude of the shift depends on the nature of the central metal ion. Consequently, these findings provide a method of fine tuning of the oxidation potential of the iron(II) from 0.08 V to ca. 0.31 V, by modifying the nature of the central atom. In addition, the comparison of the half-wave potential for complex **2** with those of related palladium(II) compounds that also contain bidentate Schiff bases reveals that in these cases a wider range of oxidation potentials of the iron(II) can be obtained depending on the nature of the donor atoms of the ligand: (NN) or (NC)⁻.

3. Experimental

Elemental analyses (C, H and N) were carried out at the Serveis Científico-Tècnics de la Universitat de Barcelona. Infrared spectra were obtained with a NICOLET 520-FTIR spectrophotometer using NaCl discs (for the ligand) and KBr pellets for the metal complexes. Decomposition points were determined with a Galenkamp melting point instrument. Visible–Ultraviolet spectra were recorded using 10⁻³ M solutions of the compounds in CH₂Cl₂ and using a SHIMADZU-spectrophotometer. Routine ¹H and ¹³C{¹H}-NMR spectra were recorded at ca. 20°C on a GEMINI-200MHz spectrophotometer using CDCl₃ (99.8%) and Si(CH₃)₄ as solvent and internal standard, respectively.

3.1. Materials and syntheses

Formylferrocene, N,N-dimethylethylenediamine and the metallic salts were obtained from standard sources

and used as received. Some of the preparations described below involve the use of benzene, which should be handled with CAUTION. All the solvents were distilled before use.

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

Formylferrocene (1.0 g, 4.57 mmol) was dissolved in benzene (30 cm³) at 20°C and then N,N-dimethylethylenediamine (4.57 mmol) was added. The reaction flask was connected to a condenser equipped with a Dean–Stark apparatus (ca. 20 cm³). The wine red solution was refluxed on an ethyleneglycol bath until 10 cm³ of the azeotrope (benzene/water) had been collected in the Dean–Stark. The hot solution was then filtered and concentrated in a rotary evaporator. The ferrocenyl Schiff base was obtained as an oily material. (Yield: 80%.)

3.1.2. Preparation of $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]\}\text{Cl}_2]$ (**2**)

$\text{Na}_2[\text{PdCl}_4]$ (0.412 g, 1.4 mmol) and the ferrocenyl Schiff base (**1**) (0.402 g, 1.4 mmol) were dissolved in 10 cm³ of methanol. The reaction mixture was stirred at room temperature (ca. 20°C) for 3 h. The solid formed was filtered off, washed with 3 (5 cm³) portions of methanol, and air-dried. (Yield: 82%.) Characterization data: Anal. (%), Calc. for: C₁₅H₂₀N₂FePdCl₂ (found): C, 38.28 (38.1); H, 4.47 (4.45) and N, 5.95 (6.05). Decomp. point (°C): 183–189. IR (KBr-pellets), $\nu(\text{C=N})$: 1626 cm⁻¹.

3.1.3. Preparation of $[\text{Zn}\{(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]\}\text{Cl}_2]$ (**3**)

The ferrocenylimine (0.208 g, 0.7 mmol) and ZnCl₂ (0.100 g, 0.7 mmol) were dissolved in 5 cm³ of methanol. The reaction mixture was stirred at room temperature (ca. 20°C) for 2 h and the bright orange solid formed during the reaction was then filtered off and washed with methanol (until colourless washings were obtained), and air-dried. (Yield: 86%.) Characterization data: Anal. (%), Calc. for: C₁₅H₂₀N₂FeZnCl₂ (found): C, 42.72 (42.8); H, 4.76 (4.8) and N, 6.66 (6.6). Decomp. point (°C): 236–240. IR (KBr-pellets): $\nu(\text{C=N})$ = 1637 cm⁻¹.

3.1.4. Preparation of $[\text{M}\{(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-CH}_2\text{-CH}_2\text{-N(CH}_3)_2]\}\text{Cl}_2]$ (M = Ni (**4**), Co (**5**), or Cu (**6**))

These compounds were prepared according to the procedure described above for (**3**) but using the stoichiometric amounts of NiCl₂ · 6H₂O, CoCl₂ · 6H₂O or CuCl₂ · 5H₂O as starting materials. (Yields: 72, 62 and 15% for **4**, **5** and **6**, respectively.) Characterization data: for (**4**) Anal. (%), Calc. for: C₁₅H₂₀N₂FeNiCl₂ (found): C, 41.71 (41.5); H, 5.1 (5.0) and N, 6.50 (6.4). Decomp. point (°C): 180–186. IR (KBr-pellets),

$\nu(\text{C}=\text{N})$: 1640 cm^{-1} . (5) Anal. (%), Calc. for: $\text{C}_{15}\text{H}_{20}\text{N}_2\text{FeCoCl}_2$ (found): C, 41.69 (41.5); H, 5.10 (4.8) and N, 6.49(6.4). Decomp. point ($^{\circ}\text{C}$): 179–183. IR (KBr-pellets), $\nu(\text{C}=\text{N})$: 1621 cm^{-1} . (6) Anal. (%), Calc. for: $\text{C}_{15}\text{H}_{20}\text{N}_2\text{FeCuCl}_2 \cdot 1/2\text{H}_2\text{O}$ (found): C, 42.10 (42.1); H, 4.91 (4.8) and N, 6.54 (6.4). Decomp. point ($^{\circ}\text{C}$): 192–196. IR (KBr-pellets), $\nu(\text{C}=\text{N})$: 1637 cm^{-1} .

3.1.5. Crystal structure determination and refinement

A prismatic red crystal of compound **3** was selected and mounted on an Enraf–Nonius CAD4 diffractometer. Unit cell parameters (Table 6) were determined from automatic centring of 25 reflections ($12^{\circ} \leq \theta \leq 21^{\circ}$) and refined by least-squares method. Intensities were collected with graphite-monochromated Mo-K α radiation using the $\omega - 2\theta$ scan technique. Three reflections were collected every hour as orientation and intensity control, and no significant intensity decay was observed. Lorentz polarization corrections as well as the empirical psi-scan absorption corrections were applied (maximum and minimum transmission factors were 0.997 and 0.787).

The structure was solved by Patterson synthesis using the SHELXS computer program [18] and refined by full-matrix least squares on F^2 using the SHELXL93 computer program [19]. The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(F_o)^2 + 0.0469 P^1 + 4.58 P]^2$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f , f' and f''

were taken from the literature [20]. The positions of the hydrogen atoms were computed and refined with an overall isotropic thermal parameter, using a riding model. The final R_1 and wR_2 values as well as the number of parameters refined and other details concerning the refinement of the crystal structure are presented in Table 6.

3.2. Physical measurements

Electrochemical data for compounds under study were obtained by cyclic voltammetry under argon at 20°C using acetonitrile (HPLC-grade) as solvent, tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte and a VERSSTAT potentiostat. The redox half-wave potentials $E_{1/2}$ were referred to an Ag–AgNO₃ (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 ferrocene were recorded before and after each sample to ensure the repeatability of the results, in particular to test and monitor the stability of the Ag–AgNO₃ electrode. Cyclic voltammograms of freshly prepared solutions (10^{-3} M) of the samples in acetonitrile were run and the average values of the $E_{1/2}$ measured were then referred to ferrocene ($E_{1/2}(\text{Fc})$). In these experimental conditions the standard error of the oxidation potentials is ± 5 mV.

Magnetic measurements were carried out in the 294–19 K temperature range on polycrystalline samples with a pendulum type magnetometer (Manics-DSM8) equipped with a helium continuous flow cryostat and a Drusch-EAF-16UE electromagnet. The magnetic field was approximately 1.5 T. Diamagnetic corrections were estimated as $\{- (\text{MW})/2 \times 10^{-6} \text{ emu mol}^{-1}\}$.

Table 6
Crystal data and details of the refinement for compound:

Empirical formula	$\text{C}_{15}\text{H}_{20}\text{N}_2\text{Cl}_2\text{FeZn}$
Molecular weight/ $\text{g} \times \text{mol}^{-1}$	420.45
Crystal system	Orthorhombic
Space group	Pcab
Crystal size/ $\text{mm} \times \text{mm} \times \text{mm}$	$0.50 \times 0.36 \times 0.38$
Unit cell parameters/ \AA	$a = 12.225(1)$, $b = 14.695(1)$, $c = 19.474(1)$
Volume/ \AA^3	3498.4(4)
Z	8
$D_x / \text{g cm}^{-3}$	1.597
$\lambda(\text{Mo, K}\alpha) / \text{\AA}$	0.71069
Absorption coefficient/ mm^{-1}	2.499
$F(000)$	1712
θ range for data collection/ $^{\circ}$	from 2.41 to 30.40
Index ranges	$-17 \leq h \leq 0$, $0 \leq k \leq 20$, $-27 \leq l \leq 0$
No. of reflections collected	5288
No. of independent reflections	5288
Method of refinement	Full-matrix least squares on F^2
No. of data and parameters	5287 and 191
Goodness of fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$] (all data)	$R_1 = 0.0452$, $wR_2 = 0.1049$ $R_1 = 0.1541$, $wR_2 = 0.1400$
Largest difference peak and hole/ $\text{e} \times \text{\AA}^{-3}$	0.539 and -0.521
Temperature/K	293(2)

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