

Versatility in the mode of coordination $\{(N), (N,O)^-, (C,N)^-$ or $(C,N,O)^{2-}\}$ of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}\}]$ to palladium(II)

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Abstract

The study of the reactivity of the ferrocenyliminoalcohol $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}\}]$ (**1b**) with $\text{Na}_2[\text{PdCl}_4]$ or $\text{Pd}(\text{OAc})_2$ has allowed the isolation and characterization of the heterotrimetallic complexes: *trans*- $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}\}\}_2\text{Cl}_2]$ (**2b**), $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2O)}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}\}\}]$ (**3b**) and *trans*- $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2O)}\}\}_2]$ (**4b**). Ligand **1b** acts as a (N) (in **2b**) or a (N,O)⁻ (in **4b**) ligand; while in **3b** the two units of the iminoalcohol exhibit simultaneously different modes of binding $\{(N)$ and $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{O}]^{2-}\}$. The crystal structures of **2b** · 3H₂O and **3b** · 1/2CHCl₃ are also reported and confirm the mode of binding of the ligand in these compounds. The relative importance of the factors affecting the preferential formation of products (**2b–4b**) is also discussed. The study of the reactivity of **3b** with PPh₃ has enabled the obtention of the cyclopalladated complexes $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2O)}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\{\text{PPh}_3\}]$ (**6b**) and $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}\{\text{PPh}_3\}]$ (**7b**), in which **1b** behaves as a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{O}]^{2-}$ (in **6b**) or $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$ (in **7b**) ligand. Treatment of **3b** with $\text{MeO}_2\text{C-C}\equiv\text{C-CO}_2\text{Me}$ produces $[\text{Pd}\{[(\text{MeO}_2\text{C-C}\equiv\text{C-CO}_2\text{Me})_2(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2O)}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ (**8b**), that arises from the bis(insertion) of the alkyne into the $\sigma[\text{Pd-C}(\text{sp}^2, \text{ferrocene})]$ bond. The comparison of the results obtained for **1b** and $[\text{C}_6\text{H}_5\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}]$ (**1a**) has allowed to establish the influence of the substituents on the imine carbon on their reactivity in front of palladium(II) as well as on the lability of the Pd-ligands bond. ⁵⁷Fe Mössbauer studies of **2b–4b** and **6b** provide conclusive evidence of the effect induced by the mode of binding of **1b** on the environment of the iron(II).

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1. Introduction

Organometallic palladium(II) complexes derived from polydentate ligands containing two or more donor atoms with different hardness [1] have attracted great interest

due to their potential hemilability [2], which may be particularly important in different areas including homogeneous catalysis [3]. A wide variety of palladacycles having $[\text{C}, \text{N}, \text{X}]$ (X = N, S, P) ligands and a $\sigma[\text{Pd-C}(\text{sp}^2, \text{aryl})]$ or to a lesser extent $\sigma[\text{Pd-C}(\text{sp}^3)]$ bonds have been described in the literature during the last decade [4]. Although the incorporation of a harder donor atom such as the oxygen in the “C,N,X” backbone is expected to

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introduce significant differences in the physical and chemical properties of the complexes, palladacycles with terdentate [C,N,O] ligands are not common [5–9], although they are especially attractive from different points of view. For instance, some compounds of this kind exhibit unusual structural features, such as $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2O)}\}]_4$, which arises from the iminoalcohol $[\text{C}_6\text{H}_5\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}]$ (**1a**) (Fig. 1) by the self-assembly of four cyclopalladated units containing a terdentate (C,N,O)²⁻ ligand [5]. Besides that, the coexistence of a $\sigma(\text{Pd-C})$ and a $\sigma(\text{Pd-O})$ bond make them especially interesting in view of their potential utility as precursors in organic or organometallic synthesis [3,6,10]. For instance, the two palladacycles depicted in Fig. 2 were used in the total synthesis of the central core of *Teleocidin B4* [9].

In recent years these studies have been extended to ligands derived from ferrocene and several palladacycles with $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{X}]^-$ (X = N', S) ligands have also been described [11,12]. However, their analogues with X = oxygen are extremely scarce [13,14]. Mak et al. [13] reported the first palladacycles containing a *mer*-terdentate $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{O}]^-$ ligand. More recently, the study of the reaction between 2-ferrocenyl-2,4-dihydro-1*H*-3,1-benzoxazine [15] and $\text{Na}_2[\text{PdCl}_4]$ has led to $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2CH}_2\text{OH)}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}]$ [14], which is a useful precursor for the synthesis of 1,2-disubstituted ferrocenyl products containing two unsaturated groups in adjacent positions [14].

In view of these facts and due to the potential utility of heterodimetallic complexes with ferrocenyl units we were prompted to study the reactivity of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}\}]$ (**1b**) [16] towards palladium(II). Since this product can be easily visualized as derived from **1a** by replacement of the phenyl group by a ferrocenyl unit, the comparison of the results obtained for **1b** with those reported for **1a** will

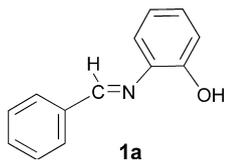


Fig. 1. Schiff base $[(\text{C}_6\text{H}_5)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}]$ (**1a**).

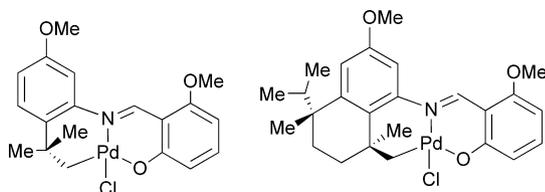


Fig. 2. Palladacycles containing (C,N,O)²⁻ ligands used in the total synthesis of the central core of *Teleocidin B4*.

enable us to elucidate the importance of the substituents on the imine carbon {a phenyl (in **1a**) or a ferrocenyl unit (in **1b**)} on the nature and nuclearity of the final product as well as on the versatility of the modes of bindings of **1a** and **1b**.

2. Results and discussion

The reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}\}]$ (**1b**) [16] with an equimolar amount of $\text{Na}_2[\text{PdCl}_4]$ in methanol at 298 K for 24 h produced a red solid. Its characterization data (see Section 4) agreed with those expected for *trans*- $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}\}\}_2\text{Cl}_2]$ (**2b**) (Table 1, entry I and Scheme 1, step (A)) in which two units of the iminoalcohol are bound to the palladium(II) through the imine nitrogen exclusively. Complex **2b** was isolated in a 74% yield.

The crystal structure of **2b**·3H₂O¹ (Fig. 3) contains molecules of *trans*- $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)}\}\}_2\text{Cl}_2]$ and water in a 1:3 molar ratio. In each one of the heterotrimetallic molecules, the palladium(II) atom is in a square-planar environment, where it is bound to two chlorides {Cl and Cl(A)} in a *trans* arrangement. The remaining coordination sites are occupied by the imine nitrogen of two iminoalcohols. The Pd–N and Pd–Cl bond lengths fall in the range reported for other palladium(II) complexes of the type *trans*- $[\text{Pd}(\text{L})_2\text{Cl}_2]$ where L represents an N-donor ferrocenyl ligand [17,18].

The >C=N- bond length {1.28(4) Å} is similar to those found for **1b** {average value for the two non-equivalent molecules: 1.26(2) Å [16]} and related ferrocenyl Schiff bases [18,19]. The values of the torsion angles C(10)–C(11)–N–C(12) and C(10A)–C(11A)–N(A)–C(12A) {179.4(3)°} agree with an *anti*-(*E*) conformation of the ligand.

The imine group is practically orthogonal to the “PdCl₂” moiety and forms an angle of 8.7° with the C₅H₄ ring. As a consequence of this arrangement, the separation between the palladium(II) atom and the hydrogen atoms H(9) and H(9A) is 2.63 Å. This finding, together with the values of the angles involving the H(9) or H(9A), the palladium(II) and the nitrogen or the chloride atoms, suggests the existence of transannular Pd···H(9) and Pd···H(9A) contacts, similar to those reported for *trans*- $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-NMe}_2\}\}_2\text{Cl}_2]$ [17] and other mono- and dinuclear complexes with “PdN₂Cl₂” cores [18–20].

¹ Crystallographic data: C₃₄H₃₀Cl₂Fe₂N₂O₂Pd (**2b**)·3H₂O, MAR345 diffractometer (Mo K α radiation), monoclinic, $a = 14.803(1)$ Å, $b = 13.968(1)$ Å, $c = 17.702(1)$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 112.190(1)^\circ$, space group: $C2/c$, $V = 3389.1(4)$ Å³, $Z = 4$, $T = 273(2)$ K, $\lambda = 0.71069$ Å, $D_{\text{calc}} = 1.639$ g cm⁻³, $\mu = 1.572$ mm⁻¹, $F(000) = 1768$, 2607 reflections collected of which 2207 were assumed as independent ($R_{\text{int}} = 0.0249$), R indices: $R_1 = 0.0529$ and $wR_2 = 0.1505$ {for $I > 2\sigma(I)$ } and $R_1 = 0.0618$ and $wR_2 = 0.1590$ (for all data).

Table 1
Summary of the experimental conditions {reagents, solvents, temperature (*T*) and reaction periods (*t*)} used to prepare the palladium(II) complexes containing the iminoalcohol **1b** acting as a (N), (N,O)⁻ or [C(sp², ferrocene),N,O]²⁻ donor ligand

Entry	Reagents (molar ratios)	Solvent	<i>T</i> (K)	<i>t</i>	Products	Yields ^a
I	1b and Na ₂ [PdCl ₄] (1:1)	MeOH	298	24 h	2b	74
II	1b , Na ₂ [PdCl ₄] and NaOAc · 3H ₂ O (1:1:1)	MeOH	298	24 h	3b	51
III	1b and Pd(OAc) ₂ (1:1)	Toluene	Reflux	2.5 h	3b	55
IV	1b and Pd(OAc) ₂ (1:1)	MeOH	Reflux	2.5 h	3b , 4b , 5b ^b	^c
V	1b and Pd(OAc) ₂ (2:1)	MeOH	298	20 min	3b and 4b ^d	^c
VI	2b and NaOAc (1:1) or (1:2)	MeOH	Reflux	24 h	3b	31 and 45 ^e

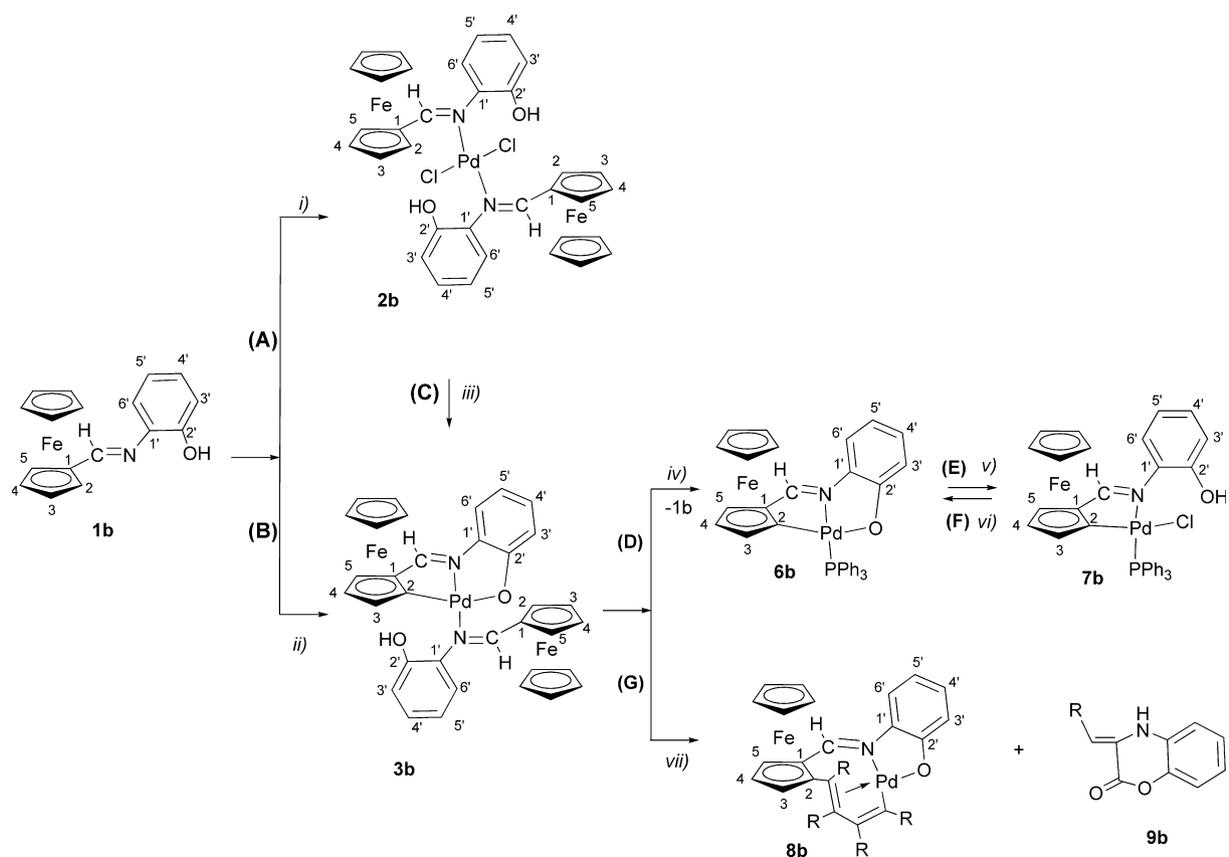
^a In %.

^b Compounds **3b** and **4b** were isolated in a molar ratio **3b**:**4b** = 1.00:0.65 and only traces (~5 mg) of **5b** were isolated (see text).

^c In this case competitive chemical reactions take place.

^d The molar ratio **3b**:**4b** was 1:4.

^e For molar ratios NaOAc:**2b** = 1.0 or 2.0, respectively.



Scheme 1. Reagents and conditions: R = CO₂Me. (i) Equimolar amount of Na₂[PdCl₄] in methanol at 298 K for 24 h. (ii) Treatment with Na₂[PdCl₄] and NaOAc · 3H₂O (in a molar ratio **1b**:Pd(II):OAc⁻ = 1:1:1) at 298 K for 24 h or addition of Pd(OAc)₂ in refluxing toluene for 2.5 h. (iii) NaOAc (in a molar ratio OAc⁻:**2b** of 2) in refluxing methanol for 24 h. (iv) Addition of the equimolar amount of PPh₃ in CH₂Cl₂ at 298 K followed by SiO₂ column chromatography. (v) In CDCl₃ followed by the addition of DCl (in a proportion DCl:**6b** = 0.8) in methanol-*d*₄ at 298 K. (vi) In NaOD (molar ratio OD⁻:**7b** = 0.5) in methanol-*d*₄. (vii) Addition of R-C≡C-R (in a molar ratio alkyne:**3b** = 4) in CH₂Cl₂ under reflux for 8 h followed by SiO₂ column chromatography.

The phenyl ring is planar and its main plane forms an angle of 104.9° with the imine group, as a result of this arrangement and of the relative orientation between the C₆H₄-2OH group of one of the ligands and the ferrocenyl moiety of the other one, the separation between the C(8)–H(8) bond {or the C(8A)–H(8A)} and the phenyl group defined by the set of atoms [C(12)–C(17)] {or

[C(12A)–C(17A)]} suggest the existence of a weak C–H···π interaction [21].

Bond lengths and angles of the ferrocenyl moieties agree with data reported for most ferrocene derivatives [18], the pentagonal rings are practically parallel (*tilt angle* = 2.9°) and they deviate by 15.6° from the ideal eclipsed conformation.

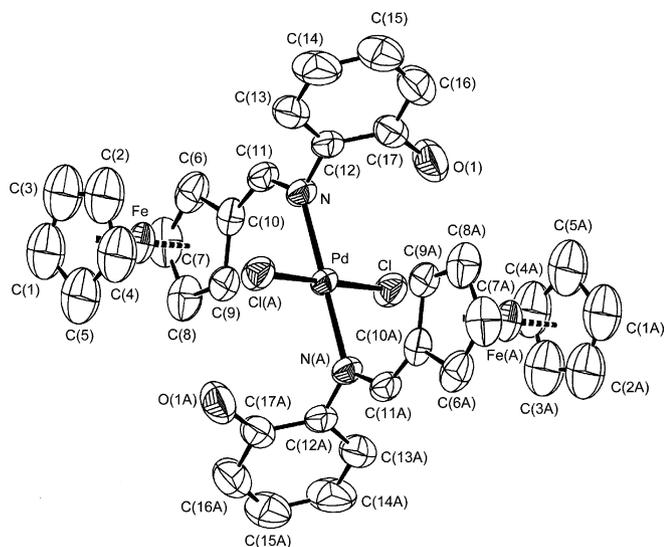


Fig. 3. ORTEP plot of *trans*-[Pd{(η⁵-C₅H₅)Fe(η⁵-C₅H₄)-CH=N-(C₆H₄-2OH)}₂Cl₂]·3H₂O (**2b**·3H₂O). The water molecules as well as hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–N, 2.016(2); Pd–Cl, 2.305(5); C(10)–C(11), 1.43(3); C(11)–N, 1.28(4); N–C(12), 1.44(4); C(12)–C(13), 1.38(3); C(13)–C(14), 1.39(3); C(14)–C(15), 1.33(4); C(15)–C(16), 1.37(4); C(16)–C(17), 1.36(3); C(17)–O(1), 1.35(3); C(12)–C(17), 1.39(3); N–Pd–Cl, 90.0(5); C(10)–C(11)–N, 128.4(18); C(11)–N–C(12), 118.7(16); N–C(12)–C(13), 121.0(18); O(1)–C(17)–C(12), 123.4(19) and O(1)–C(17)–C(16), 117(2).

The separation between the Pd(II) and the Fe(II) atoms (4.541 Å) clearly exceeds the sum of their van der Waals radii [22] thus suggesting that there is no direct interaction between them.

When the reaction was carried out in the presence of an equimolar amount of NaOAc·3H₂O (Table 1, entry II and Scheme 1, step (B)) a deep red solid (hereafter referred to as **3b**) was isolated. The ¹H NMR spectrum of **3b** (Fig. 4a) showed two sets of superimposed signals of identical intensity suggesting the presence of two non-equivalent units of the ligand.

One of the two sets of signals detected in the ¹H and ¹³C{¹H} NMR spectra of **3b** (in the ranges 3.50–5.50 ppm and 65.0–80.0 ppm, respectively) (Fig. 4a–c) was consistent with the typical pattern of monosubstituted ferrocene derivatives. For the other set, the number of resonances due to the ferrocenyl moiety, the low field shift of the signals due to the C¹ and C² nuclei of the ferrocenyl moiety (when compared with those of **1b**) and the absence of a cross-peak between signals due to C² and to any proton in the {¹H–¹³C} HSQC spectrum, suggested that the metallation of the ferrocenyl unit had taken place. In addition, the differences detected in the chemical shifts of the C¹, C² and C⁶ nuclei of **3b** and **1b** were very similar to those reported for [Pd{C₆H₄-CH=N-(C₆H₄-2O)}₂] (3a) {with a [C(sp², phenyl),N,O]²⁻ terdentate ligand} and its parent ligand **1a** [5]. All these findings suggested that **3b** contained two units of the iminoalcohol exhibiting different modes of binding {(N) and [C(sp², ferrocene),N,O]²⁻}.

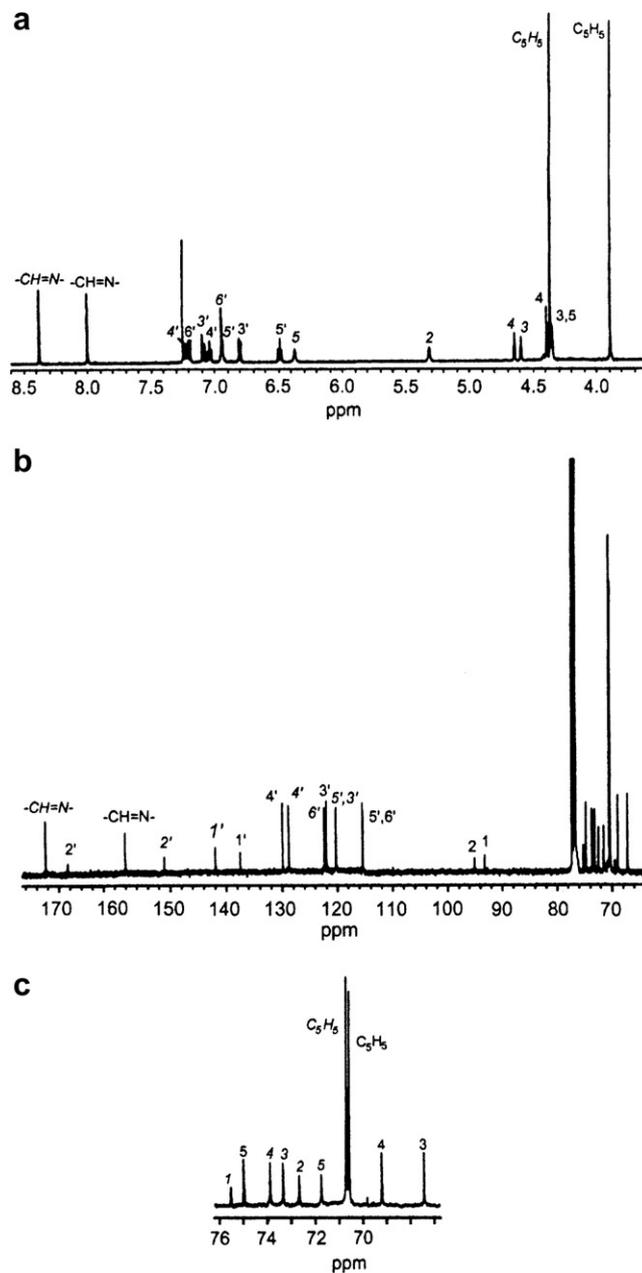


Fig. 4. Partial views of the ¹H NMR and ¹³C{¹H} NMR spectra (a and b, respectively) of **3b** in CDCl₃ at 298 K. An expansion of the ¹³C{¹H} NMR spectrum in the range 66.8 ppm < δ < 76.2 ppm is shown in (c). In all cases, characters in italics correspond to the non-cyclopalladated ligand (see text and Scheme 1).

In order to confirm the nuclearity of the complex and the mode of binding of **1b**, crystals suitable for X-ray analysis were grown. The crystal structure of **3b**² contains mol-

² Crystallographic data: C₃₄H₂₈Fe₂N₂O₂Pd (**3b**)·1/2CHCl₃, Mar 345 diffractometer (Mo Kα radiation), monoclinic, *a* = 19.4190(5) Å, *b* = 10.349(1) Å, *c* = 17.003(1) Å, α = γ = 90° and β = 101.47(1)°, space group: P2₁/c, *V* = 3348.8(4) Å³, *Z* = 4, *T* = 293(2) K, λ = 0.71069 Å, *D*_{calc} = 1.536 g cm⁻³, μ = 1.538 mm⁻¹, *F*(000) = 1566, 49 529 reflections collected of which 8455 were assumed as independent (*R*_{int} = 0.0294), *R* indices: *R*₁ = 0.0373 and *wR*₂ = 0.1175 {for *I* > 2σ(*I*)} and *R*₁ = 0.0441 and *wR*₂ = 0.1239 (for all data).

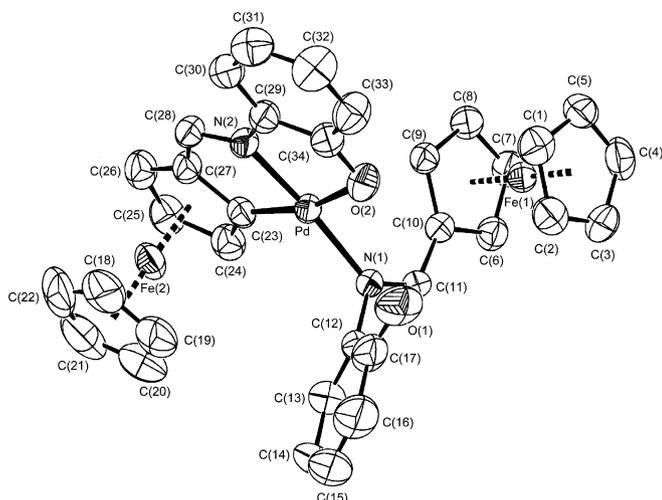


Fig. 5. ORTEP diagram of the heterotrimetallic complex **3b**. The CHCl_3 molecule as well as hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Pd–N(1), 2.028(2); Pd–N(2), 1.973(2); Pd–O(2), 2.094(2); Pd–C(23), 1.970(3); C(10)–C(11), 1.450(3); C(11)–N(1), 1.268(3); N(1)–C(12), 1.433(3); C(17)–O(1), 1.368(5); C(27)–C(28), 1.447(4); C(28)–N(2), 1.290(3); N(2)–C(29), 1.414(4); C(34)–O(2), 1.324(4); O(1)–C(17), 1.368(5); N(1)–Pd–C(23), 99.02(10); C(23)–Pd–N(2), 81.95(10); C(23)–Pd–O(2), 164.51(10); O(2)–Pd–N(1), 96.4(8); C(10)–C(11)–N(1), 126.4(2); C(11)–N(1)–C(12), 116.7(2); C(16)–C(17)–O(1), 117.7(4); C(12)–C(17)–O(1), 124.8(3); C(28)–N(2)–C(29), 129.0(2); N(2)–C(29)–C(30), 123.7(2); C(29)–C(34)–O(2), 122.0(3) and C(33)–C(34)–O(2), 121.1(3).

ecules of **3b** and CHCl_3 (in a 2:1 molar ratio). In each one of the heterotrimetallic molecules (Fig. 5), the palladium is in a slightly distorted square-planar environment, where it is bound to the deprotonated oxygen {O(2)}, the imine nitrogen {N(2)} and the C(23) atom of the ferrocenyl unit of one molecule of the iminoalcohol, thus confirming the $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{O}]^{2-}$ mode of binding. The remaining coordination site is occupied by the nitrogen {N(1)} of the other molecule of ligand **1b**. Thus confirming the conclusions reached by NMR.

The Pd–N(1) bond length {2.028(2) Å} is larger than the values obtained for **2b** {2.016(2) Å}, where the ligand also acts as a N-donor group, and for the Pd–N(2) bond. The values of the bond angles C(23)–Pd–N(2) and N(2)–Pd–O(2) agree with those reported for **3a** where the iminoalcohol **1a** exhibits a similar mode of binding. In the non-metallated unit of the ligand the bond length of the imine group {1.268(3) Å} is smaller than for the other unit of the ligand {1.290(3) Å} but the N–C(phenyl) and O–C(phenyl) bond distances are larger than those of the ligand acting as a $(\text{C}, \text{N}, \text{O})^{2-}$ donor group.

The complex contains a [5.5.5.6] tetracyclic system which is formed by the 1,2-disubstituted C_5H_3 ring, a five-membered palladacycle, the pentagonal chelate, formed by the binding of the N(2) and O(2) atoms and the phenyl ring. Bond lengths and angles of metallacycles are similar to those found for palladacycles derived from ferrocenylimines and palladium(II) complexes holding (N,O) bidentate ligands, respectively [17,18].

The distances between the palladium and the iron(II) atoms Fe(1) and Fe(2) (3.611 and 4.617 Å, respectively) clearly exceed the sum of the van der Waals radii of these atoms [22], this precludes the existence of any direct interaction. As expected bond lengths and angles of the two ferrocenyl units are consistent with the values reported for most ferrocene derivatives [17–19]. In both cases the pentagonal rings are planar, practically parallel {tilt angles of 1.3° and 1.5° for the moieties containing Fe(1) and Fe(2), respectively} and they deviate from the ideal eclipsed conformation by 1.5° (in the cyclometallated unit) and 0.9° (for the other unit).

The existence of two bands at ca. 1591 and 1616 cm^{-1} in the IR spectrum of **3b** is consistent with the results obtained from X-ray studies. Previous works on IR spectroscopy of cyclopallada- and cycloplatinated complexes derived from imines have shown the shift of the band due to the stretching of the $>\text{C}=\text{N}-$ group to lower frequencies is greater for the metallated derivatives than for the complexes where the same ligand acts as a N-donor group [23]. On this basis, we tentatively assign the absorption at 1591 cm^{-1} to the imine group of the terdentate ligand and that at 1616 cm^{-1} to the N-bonded iminoalcohol. The remaining characterization data of **3b** (see Section 4) are consistent with the results presented above and with the chemical formulae presented in Scheme 1. As far as we know organometallic palladium(II) complexes containing two units of the same ligand adopting simultaneously a (N) and a $(\text{C}, \text{N}, \text{O})^{2-}$ mode of binding have not been described so far, and consequently **3b** is particularly interesting from this point of view.

It should be noted that **3b** was also obtained when **1b** was reacted with $\text{Pd}(\text{OAc})_2$ (in a 1:1 molar ratio) in refluxing toluene for 2.5 h (Table 1, entry III) and evidence of the formation of any other by-product was not detected. This procedure has greater advantages than that described above (entry II of Table 1) since it allows the isolation of **3b** in slightly higher yield (55% versus 51% in entry II) and in less than one day. More interesting were the results obtained when equimolar amounts of the ligand and $\text{Pd}(\text{OAc})_2$ were refluxed in methanol for 2.5 h (Table 1, entry IV). This reaction gave **3b**, a red solid (here after referred to as **4b**) (in a molar ratio **3b**:**4b** = 1.00:0.65) and traces (≈ 5 mg) of a minor component (**5b**).

The IR spectra of **4b** did not show the typical band due to the stretching of the –OH group [24], thus suggesting that deprotonation of the alcohol group had taken place. In addition, no evidence of the presence of OAc^- groups was detected by IR or NMR spectroscopy [25,26]. Characterization data of **4b** were consistent with those expected for the trimetallic complex $[\text{Pd}\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}=\text{N}(\text{C}_6\text{H}_4\text{-2O})]\}_2]$ (Fig. 6a), where two deprotonated units of the ligand are bound to the palladium in a *trans*-arrangement.

It should be noted that the synthesis of **4b** can be improved if the reaction is performed in methanol at 298 K using palladium(II) acetate {in a molar ratio

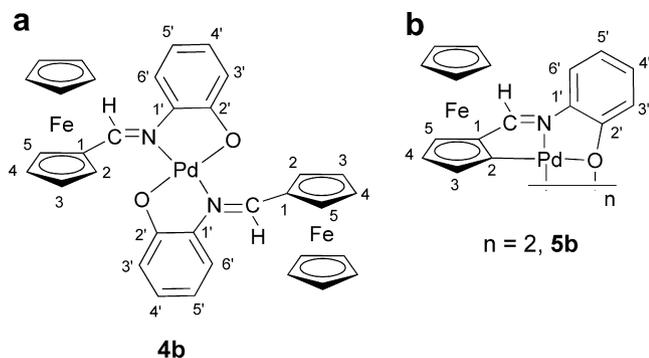


Fig. 6. Chemical formulae of the trimetallic complex **4b** (a) and of the polymeric compound holding a “Pd_nO_n” central core (b) (see text).

1b:Pd(II) = 2} (Table 1, entry V). Besides that, the treatment of a CDCl₃ solution of **4b** with DCl (dissolved in methanol-*d*₄) in a molar ratio **4b**:DCl = 0.5 showed the presence of FcCHO and the presence of compound **2b** was not detected by ¹H NMR. These results indicate that **4b** is unstable under acidic conditions.

The ¹H NMR spectrum of the minor component **5b** as well as its reactivity with PPh₃ (see below) suggested the existence of cyclopalladated units containing a terdentate [C(sp², ferrocene),N,O]²⁻ ligand. Besides that, the differences detected in the ¹H chemical shifts of the 1,2-disubstituted phenyl ring for **1b** and **5b** were very similar to those reported for **1a** and [Pd{C₆H₄-CH=N-(C₆H₄-2O)}₄ (**3a**) [5]. These findings suggested that **5b** could arise from the self-assembly of the cyclopalladated units “[Pd{[(η⁵-C₅H₃)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}]” forming a central “Pd_nO_n” ring (Fig. 6b). A few palladacycles with central “Pd_nO_n” cores have been reported [5,6a,6b,6c,20,27,28], among them those with a 4-membered central ring ($n = 2$) are more common than the tri- or tetrameric derivatives [27,28].

Due to: (a) the formal similarity between the ligands **1a** and **1b**, (b) the tetranuclear nature of the product obtained in the reaction of **1a** with Pd(OAc)₂ under identical experimental conditions as for **1b**, and (c) presence of a peak at $m/z = 1638.5$ in the mass spectrum, we tentatively postulated a tetrameric structure for **5b**. However, the use of molecular models for [Pd{[(η⁵-C₅H₃)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}₄ revealed that the self-assembly of the four cyclopalladated units is unlikely to occur due to the steric effects arising from the proximity between the “Fe(η⁵-C₅H₅)” moiety of one of the units and the protons of the phenyl ring of a neighbouring fragment. This would reduce significantly the stability of the [Pd{[(η⁵-C₅H₃)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}₄ in comparison with that of [Pd{C₆H₄-CH=N-(C₆H₄-2O)}₄ (**3a**), where the substituent on the imine carbon (a phenyl) is smaller than the ferrocenyl group [29].

Molecular models also show that this type of steric hindrance vanishes for the dimeric molecule [Pd{[(η⁵-C₅H₃)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}₂. It should be noted that the yield of **5b** did not improve significantly when

the refluxing periods were varied in the range (30 min < t < 3.5 h).

On this basis and with the results obtained in the reaction of **5b** with PPh₃ (vide infra), we tentatively postulate for **5b** the chemical formula (b) depicted in Fig. 6 with $n = 2$. Unfortunately, attempts to obtain crystals of **5b** suitable for X-ray diffraction failed.

The comparison of the chemical formula of **2b** and those of **3b**, **4b** and **5b** suggests that in principal **4b** could be easily visualized as derived from **2b** by deprotonation of the -OH groups and the subsequent replacement of the Cl⁻ ligands by the oxygen; while **3b** could arise from **2b** by activation of the σ[C(sp², ferrocene)-H], deprotonation of the O-H group and coordination of the oxygen of one of the two ligands of **2b**. The formation of **5b** could involve the dissociation of the N-donor ligand in **3b**, followed by the assembling of the “[Pd{[(η⁵-C₅H₃)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}]” units. Previous work on cyclopallada- and cycloplatination reactions have shown that some [M(N-donor imine ligand)₂Cl₂] and [M(N,X-donor ligand)Cl₂] complexes (M = Pd or Pt and X = N' or S) may undergo the cyclometallation in the presence of a base [4a,4b,11c,30,31]. In view of this, several additional experiments were performed in order to elucidate: (a) if **2b** could be an intermediate product in the formation of **3b**–**5b**, and (b) the potential ability of **2b** to undergo the activation of the σ(C-H) bond and/or the deprotonation of the -OH moiety.

Treatment of **2b** with NaOAc in methanol under reflux for 24 h (Table 1, entry VI and Scheme 1, step (C)) gave **3b** and the presence of either **4b** or **5b** was not detected by NMR studies of the crude of the reactions. In addition the relative abundance of **3b** was greater when the molar ratio AcO⁻:Pd(II) increases from 1 to 2. These findings confirm that **2b** is an intermediate product in the formation of **3b**. In addition, when the NaOAc was replaced by a stronger base (NaOH) the ¹H NMR spectra of the crude reaction mixtures indicated the existence of FcCHO (due to partial hydrolysis of the ligand), but **4b** or **5b** were not detected. Thus suggesting that the formation of **4b** and **5b** possibly takes place directly from the free ligand **1b** by a different pathway. All these studies suggest that the final products isolated in entries IV and V are produced in different chemical reactions that take place simultaneously.

Treatment of **3b** with an equimolar amount of PPh₃ in CH₂Cl₂ at 298 K involved the replacement of the N-bonded unit of **1b** by the phosphine giving [Pd{[(η⁵-C₅H₃)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}(PPh₃)] (**6b**) (Scheme 1, step (D)). The position of the signal detected in the ³¹P{¹H} NMR spectrum of **6b** is very similar to that of [Pd{[(η⁵-C₅H₃)-CH=N-(C₆H₄-2CH₂O)]Fe(η⁵-C₅H₅)}-(PPh₃)] [14] where the ferrocenyl ligand also acts as a [C(sp², ferrocene),N,O]²⁻ group. It should be noted that evidence of the formation of any other palladium(II) complex was not detected even when the molar ratio PPh₃:**3b** increased. All these findings indicate that the σ(Pd-O)

bond exhibits low lability and this agrees with the results obtained for $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2O)}\}_4]$ (**3a**) [5] and $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2-CH}_2\text{O})]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**5c**) [14], that contain terdentate $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}, \text{O}]^{2-}$ and $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{O}]^{2-}$ ligands, respectively.

When **5b** was treated with PPh_3 {in a molar ratio Pd(II):phosphine of 1}, a red solid was isolated. Its characterization data based on NMR, IR and mass spectra were identical to those of **6b**. This results supports the existence of cyclopalladated “Pd{[($\eta^5\text{-C}_5\text{H}_3$)–CH=N–(C₆H₄-2O)]–Fe($\eta^5\text{-C}_5\text{H}_5$)}” units in **5b**. The comparison of the reactivity of the palladacycles holding a $[\text{C}, \text{N}, \text{O}]^{2-}$ terdentate ligand (**3a**, **3b**, **5b** and **5c**), shows that in **5c** the lability of the Pd–O bond is greater than for **3a**, **3b** and **5b**. This could be related to the steric effects arising from the different size of the chelate a five- (in **3a**, **3b** and **5b**) or a six- (in **5c**) membered ring.

In a first attempt to induce the cleavage of the Pd–O bond of **6b** and the subsequent modification of the mode of binding of the ligand, the reactivity of this product with HCl was also studied on a NMR scale. As shown in Fig. 7, the ^1H NMR spectrum of a CDCl_3 solution of **6b** changed substantially upon the addition of a DCl solution (in methanol-*d*₄) in a molar ratio DCl: **6b** = 0.8 (Scheme 1, step (E)) thus sug-

gesting the formation of a new product. Its characterization data were consistent with those expected for $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2OH)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ (**7b**). The formation of **7b** requires the protonation of the oxygen atom of the terdentate ligand, the cleavage of the Pd–O bond and the incorporation of the Cl^- ligand in the coordination sphere of the palladium in a *cis*-arrangement to the phosphorus, in good agreement with the *transphobia effect* [32].

It has been recently reported that freshly prepared solutions of the cyclopalladated complex $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2-CH}_2\text{O)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{PPh}_3)]$ (**6c**) [14] (which can be easily visualized as derived from **6b** by incorporation of a $-\text{CH}_2-$ unit between the oxygen and the phenyl ring), in CDCl_3 changed with time giving a mixture of **6c** and $[\text{Pd}\{[(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2-CH}_2\text{OH)]Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ (**7c**) where the ligand acts as a $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$ group and the molar ratio **6c**:**7c** decreased to 0.9 after 5 days. The comparison of the results obtained for **6c** and those of **6b** indicate that the five-membered chelate ring of **6b** is less prone to undergo the opening of the five-membered chelate ring than **6c** where the chelate is hexagonal.

An interesting feature of **7b** is that it reacts with NaOD (molar ratio NaOD:**7b** = 0.5) giving **6b** (Scheme 1, step (F))

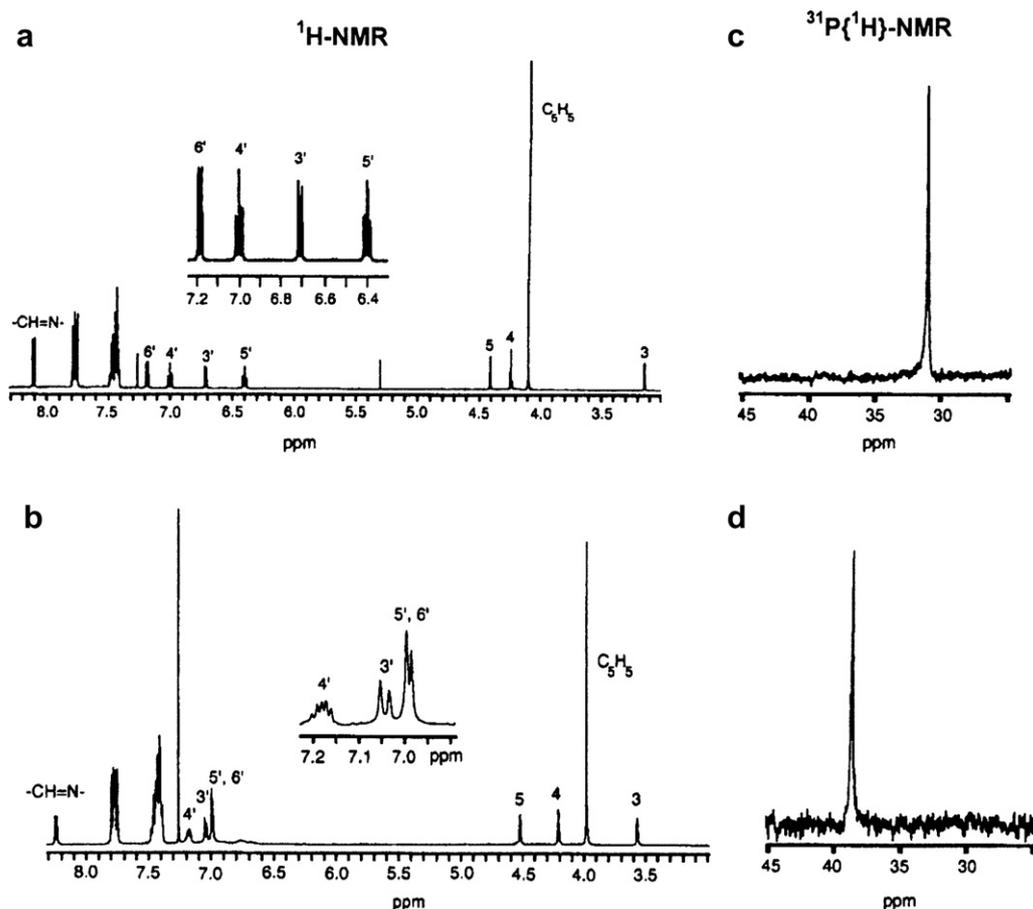


Fig. 7. Partial views of the ^1H NMR spectra (at 298 K) of a freshly prepared solution of **6b** (in CDCl_3) (a) and after the addition of DCl (in methanol-*d*₄) (b), together with their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (c and d, respectively).

and subsequent cycles exposing **6b** (or **7b**) to acidic (or basic) conditions showed that the transformations **6b** \leftrightarrow **7b** (Scheme 1, steps (E) and (F)) are reproducible and robust. Therefore, the mode of binding of **1b** to the palladium(II) in **6b** and **7b** can be easily tuned by manipulating the acidity/basicity of the media. Examples of palladacycles exhibiting this behaviour are not known. Previous studies on the coordinating ability of the pendant –OH group in palladacycles containing bidentate [C(sp², phenyl),N][–] ligands derived from organic iminoalcohols {i.e. 4,5-(MeO)₂-C₆H₃-CH=N-(CH₂)₂-OH} [8] have shown that the formation of the complexes where these ligands behave as a terdentate group requires the use of Ag⁺ salts. In none of these cases the change of the denticity of the ligand (from bidentate to terdentate or vice versa) could be so easily achieved as for the pair of compounds **6b** and **7b** reported here.

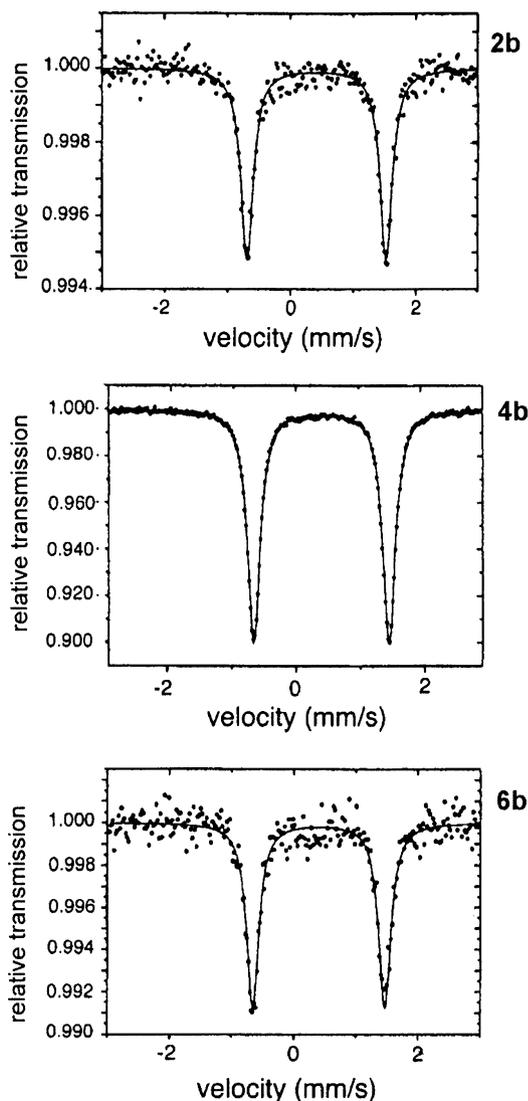


Fig. 8. ⁵⁷Fe Mössbauer spectra of solid samples of compounds **2b**, **4b** and **6b** at 80 K.

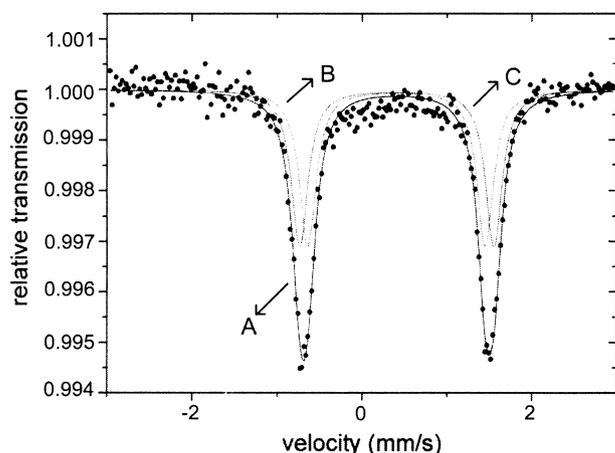


Fig. 9. ⁵⁷Fe Mössbauer spectra of a solid sample of compound **3b** at 80 K (see text). Experimental data (dots), fitting of the experimental data (solid line, A) and the results obtained from the fitting assuming the presence of two iron(II) centres in different environments (lines B and C, respectively).

To elucidate the influence of the mode of binding of the ligand in compounds **2b–4b** and **6b** upon the environment of the iron(II) centre, ⁵⁷Fe Mössbauer studies of solid samples at 80 K were carried out. The spectra of **2b**, **4b** and **6b** consisted of a single quadrupole doublet indicating a unique iron site (Fig. 8).³

Previous studies have shown that the quadrupole splitting parameter (ΔE_q) is very sensitive to the nature of the substituents [33]. In general electron-withdrawing groups produce a decrease of the ΔE_q value relative to ferrocene (hereafter referred to as FcH), while for electron-donating substituents the effect is opposite. The comparison of the data for **1b** [16], **2b**, **4b** and **6b**³ and FcH [34] reveals that the ΔE_q parameter decreases according to the sequence FcH > **1b** > **2b** > **4b** > **6b**, which reflects an increase of the electron-pulling nature of the substituent on the “(η^5 -C₅H₅)Fe(η^5 -C₅H₄)” moiety. Additionally the differences detected in the ΔE_q values for **2b** and **4b** indicate that the binding of the palladium(II) to the imine nitrogen exclusively has a weaker electron-withdrawing effect than in **4b** that contains two bidentate (N,O)[–] units of the iminoalcohol; while in **6b**,³ where the palladium(II) is directly attached to the ferrocenyl moiety, this effect is stronger.

In the ⁵⁷Fe-Mössbauer spectrum of **3b**, that contains two molecules of the ligand adopting different hapticities and modes of binding, a single quadrupole doublet (Fig. 9) was also observed, but the full-width at half-height

³ Summary of ⁵⁷Fe Mössbauer hyperfine parameters {isomer shift (*i.s.*), quadrupole splitting (ΔE_q) and full-width at half-height (*I*) in mm/s} at 80 K for compounds **2b**, **4b** and **6b**. For **2b**: *i.s.* = 0.520(3), ΔE_q = 2.218(6) and *I* = 0.235(9); for **4b**: *i.s.* = 0.5063(1), ΔE_q = 2.1646(2) and *I* = 0.2444(4) and for **6b**: *i.s.* = 0.5049(9), ΔE_q = 2.126(3) and *I* = 0.236(5).

(Γ)^{4(a)} was slightly greater than those obtained for **2b**, **4b** or **6b**.³ In addition, the ΔE_q obtained for **3b** is intermediate between those of **6b** and **2b**, where the iminophenol acts as a terdentate [C(sp², ferrocene),N,O]²⁻ (in **6b**) or a monodentate N-donor ligand (in **2b**). These findings suggested that the observed signal could be the result of the existence of two superimposed doublets due to the presence of two iron(II) centres with slightly different environments. Thus, we fitted the experimental data^{4(b)} according to this hypothesis and the sets of values obtained for the *i.s.*, ΔE_q and Γ for each one of the two iron(II) centres of **3b** agreed with those of compounds **6b** and **2b**, respectively.

As mentioned above, one of the main interest in palladacycles containing terdentate ligands arises from their potential utility as precursors in organic or organometallic synthesis [3,6,9,10]. Commonly these processes are based on the insertions of small molecules (i.e. alkynes, alkenes, CO, etc.) into the σ (Pd–C) bond. As a first attempt to evaluate the ability of **3b** to undergo this sort of reactions, we studied its reactivity toward MeO₂C–C≡C–CO₂Me. Treatment of **3b** with this alkyne in a 1:4 molar ratio under reflux for 8h gave, after work up, [Pd{[(Me₂OC–C≡C–CO₂Me)₂(η^5 -C₅H₅)–CH=N–(C₆H₄-2O)]Fe(η^5 -C₅H₅)}] (**8b**) (Scheme 1, step (G)) as the major product. Complex **8b** arises from the bis(insertion) of the alkyne into the σ (C–H) bond. NMR studies of **8b** suggested that the four substituents on the η^3 -butadienyl unit are in a *trans*-, *cis*-arrangement.

In this reaction small amounts of **3b**, ferrocenecarboxaldehyde and yellow needles of (*Z*)-methyl-2(2-oxo-2H-benzo[*b*][1,4]oxazin-3(4*H*)-ylidene) acetate (**9b**) were also isolated as by-products. Compound **9b**⁵ and the aldehyde were also obtained when the Schiff base **1b** was treated with the alkyne (in a 1:1 molar ratio) in refluxing CH₂Cl₂.

According to the mechanistic studies reported by Ryabov et al. [35] on the bis(insertion) of alkynes into the σ [Pd–C(sp², aryl)] bond of cyclopalladated complexes, in these reactions the first step of the process consists of the

coordination of the alkyne to the Pd(II) in a *cis*-arrangement to the metallated carbon. For **3b** this would require the release of the Schiff base **1b**, which could later on react with the alkyne and undergo an hydrolysis process to give **9b** and ferrocenecarboxaldehyde.

Additionally, the greater proclivity of **3b** to react with MeO₂C–C≡C–CO₂Me, when compared with that of **3a**⁶ could be related to several factors arising from: (a) the greater lability of the bond between the palladium and the donor atom in a *cis*-arrangement to the metallated carbon {a N (in **3b**) or a O_{alcoxo} (in **3a**)} or (b) steric effects affecting different accesibility of the alkyne to the palladium(II), this may be particularly important for the complexes containing central “Pd_{*n*}O_{*n*}” cores.

On the other hand, it should be noted that **3b** is more prone to react with this alkyne than the palladacycle [Pd{[(η^5 -C₅H₅)–CH=N–(C₆H₄-2SMe)]Fe(η^5 -C₅H₅)}Cl] (**3d**) that contains a [C(sp², ferrocene),N,S]⁻ ligand [12b]. For **3d**, the formation of the bis(insertion) product [Pd{[(Me₂OC–C≡C–CO₂Me)₂(η^5 -C₅H₅)–CH=N–(C₆H₄-2SMe)]Fe(η^5 -C₅H₅)}][BF₄] (**8d**) required the presence of thallium(I) salts to induce the cleavage of the Pd–Cl bond; while for **3b** the reaction proceeds without this requirement.

3. Conclusions

The results presented here show that **1b** exhibits an interesting coordination ability. These studies have allowed us to establish the best experimental conditions to selectively control the mode of binding [(N) (in **2b** and **3b**); (N,O)⁻ (in **4b**); {C(sp², ferrocene),N}⁻ (in **7b**) or {C(sp², ferrocene),N,O}²⁻ (in **3b** and **6b**)] of ligand **1b** to palladium(II). The versatility of the modes of binding of **1b** is greater than that of the iminoalcohol **1a** which differs from **1b** in the nature of the substituent on the imine carbon {a phenyl in **1a** or a ferrocenyl unit in **1b**}. These differences are important as to affect the number and the nature of the palladium(II) complexes formed, their nuclearity, the modes of binding of the ligand in the complexes as well as their reactivity. The results obtained from the reaction between the alkyne MeO₂C–C≡C–CO₂Me and **3b** indicated that **3b** is more prone to undergo the bis(insertion) of the alkyne than **3d** where the Schiff base behaves as a [C(sp², ferrocene),N,S]⁻ group. All these findings together with the recent interest generated by the potential utility of palladacycles holding terdentate (C,N,O)^{*q*-} (*q* = 1 or 2) ligands as precursors in organometallic and organic synthesis, indicate that **3b** is particularly relevant from these points of

⁴ Iron-57 Mössbauer hyperfine parameters {isomer shift (*i.s.*), quadrupole splitting (ΔE_q) and full-width at half-height (Γ) in mm/s} at 80 K for **3b**. (a) Parameters obtained from the fitting of the experimental data: *i.s.* = 0.510(2), ΔE_q = 2.191(4) and Γ = 0.287(7); (b) results of the fitting assuming the existence of two superimposed doublets due to the two iron(II) centres in different environments: for the Fe(II) of the ferrocenyl moiety that is linked to the palladium(II) through the nitrogen atom exclusively: *i.s.* = 0.512(3), ΔE_q = 2.289(7) and Γ = 0.235 and for the other Fe(II) centre: *i.s.* = 0.507(3), ΔE_q = 2.092(7) and Γ = 0.236. The areas of the two doublets have been imposed to be equal and full-width at half-height has been fixed to the values obtained for **2b** and **4b**, respectively, in order to avoid correlation between the fitting parameters.

⁵ Compound **9b** was previously prepared by treatment of the H₂N–(C₆H₄-2OH) and the alkyne in absolute ethanol at 273 K (G.W. Danswan, P.W. Hairsine, D.A. Rowlands, J.B. Taylor, R. Westwood, J. Chem. Soc., Perkin Trans. I 4 (1982) 1049–1058). In order to confirm that this product could also be formed under the experimental conditions used to isolate **8b**, we also studied the reaction between the aminoalcohol and MeO₂C–C≡C–CO₂Me in refluxing CH₂Cl₂. In this case **9b** was also isolated, but the yield was smaller than that reported.

⁶ No evidence of the formation of any product arising from the mono- or bis(insertion) of MeO₂C–C≡C–CO₂Me was detected when the tetrameric complex **3a** and this alkyne (in a alkyne: Pd(II) molar ratio of 4) were refluxed in CH₂Cl₂ for 8h. After this period the ¹H NMR spectrum of the solid isolated by after concentration to dryness of the reaction mixture revealed the presence of the starting materials exclusively.

view. Further studies on this field are currently under study.

4. Experimental

4.1. Materials and methods

Compound **1b** was synthesized as reported before [16] and the remaining reagents used in this work were obtained from commercial sources and used as received. The solvents were dried and distilled before use [36]. Some of the preparations described below require the use of HIGHLY HAZARDOUS materials such toluene which should be handled with CAUTION!

Elemental analyses (C, H and N) were carried out at the *Serveis de Recursos Científics i Tècnics* (Univ. Rovira i Virgili, Tarragona). Mass spectra {MALDI-TOF⁺ (for **5b**), ESI⁺ (for **8b**) and FAB⁺ (for the remaining compounds)} were performed at the *Servei d'Espectrometria de Masses* (Univ. Barcelona) with a VOYAGER-DE-RP, Waters Micromass and VG-Quattro instruments, respectively, using 2,5-dihydroxybenzoic acid {(DHB), for MALDI-TOF⁺} and 3-nitrobenzylalcohol {(NBA), for FAB⁺} as matrix. IR spectra were recorded with a Nicolet-400FTIR instrument using KBr pellets. Routine ¹H and ¹³C{¹H} NMR spectra were obtained with a Gemini 200 MHz, a Bruker 250-DXR or a Mercury 400 MHz instrument. High resolution mono- and two-dimensional [{¹H-¹H}-NOESY and COSY and {¹H-¹³C}-HSQC and HMBC] NMR experiments were recorded with either a Varian VRX-500 or with a Bruker Avance DMX 500 instruments at 298 K. The solvent used for the NMR studies was CDCl₃ (99.8%) and SiMe₄ was used as internal reference. ³¹P{¹H} NMR spectra of **6b** and **7b** were obtained with a Bruker 250-DXR instrument in CDCl₃ (99.9%) and using trimethylphosphite as reference [$\delta^{31}\text{P}\{\text{P}(\text{OMe})_3\} = 140.17 \text{ ppm}$]. The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz.

4.2. Preparation of the compounds

4.2.1. *trans*-[Pd{(η^5 -C₅H₅)Fe[(η^5 -C₅H₄)-CH=N-(C₆H₄-2OH)]₂Cl₂] (**2b**)

To a suspension formed by **1b** (202 mg, 6.62×10^{-4} mol) and 20 mL of methanol, Na₂[PdCl₄] (195 mg, 6.63×10^{-4} mol) was added. The reaction flask was protected from the light with aluminium foil and the mixture was stirred at 298 K for 24 h. The red solid that formed was isolated by filtration and air-dried (yield: 190 mg, 74%). Anal. Calc. for C₃₄H₃₀Cl₂Fe₂N₂O₂Pd: C, 51.84; H, 3.84; N, 3.56. Found: C, 51.7; H, 3.7; N, 3.5%. MS(FAB⁺): $m/z = 788\{[M]^+\}$ and $751\{[M-Cl]^+\}$. IR: 1609 cm⁻¹ $\nu(\text{C}=\text{N}-)$. ¹H NMR data:⁷ $\delta = 7.73(\text{s}, 1\text{H}, -\text{CH}=\text{N}-)$,

7.51(s, 1H, -CH=N-), 4.40(s, 10H, C₅H₅), 5.76(s, 4H, H² and H⁵), 4.67(s, 4H, H³ and H⁴), 7.14(dd, 2H, ³J = 7.5 and ⁴J = 1.5, H^{3'}), 7.33(td, 2H, ³J = 7.5 and ⁴J = 1.5, H^{4'}), 6.99(td, 2H, ³J = 7.5 and ⁴J = 1.5, H^{5'}) and 7.25(s, 2H, H^{6'}). ¹³C{¹H} NMR data:⁷ $\delta = 175.6(-\text{CH}=\text{N}-)$, 70.7(C₅H₅), 73.9(C^{1'}), 72.9(C² and C⁵), 74.6(C³ and C⁴), 139.2(C¹), 149.9(C^{2'}), 118.6(C^{3'}), 129.2(C^{4'}), 120.9(C^{5'}) and 125.7(C^{6'}).

4.2.2. [Pd{(η^5 -C₅H₅)-CH=N-(C₆H₄-2O)]Fe-(η^5 -C₅H₅)}{(η^5 -C₅H₅)Fe[(η^5 -C₅H₄)-CH=N-(C₆H₄-2OH)]}] (**3b**) · 1/2CHCl₃

Although this compound can be isolated by treatment of equimolar amounts of **1b**, Na₂[PdCl₄] and NaOAc · 3H₂O and following the same procedure as described for **2b**, or as a by-product during the synthesis of **4b**. The method described here allowed its obtention in higher yield.

Ligand **1b** (295 mg, 9.67×10^{-4} mol) was treated with 25 mL of toluene, then a solution of Pd(OAc)₂ (215 mg, 9.67×10^{-4} mol) in toluene (5 mL) was added. The reaction mixture was protected from the light and refluxed for 2.5 h. After this period the hot solution was carefully filtered and the filtrate was concentrated on a rotary evaporator to ca. 5 mL. The red solid formed upon cooling was collected by filtration and air-dried (yield: 396 mg, 55%). Anal. Calc. for C₃₄H₂₈Fe₂N₂O₂Pd: C, 57.14; H, 3.95; N, 3.92. Found: C, 57.4; H, 4.2; N, 4.0%. MS(FAB⁺): $m/z = 714\{[M]^+\}$. IR: 1591 and 1616 cm⁻¹ $\nu(\text{C}=\text{N}-)$. ¹H NMR data:⁷ for the metallated fragment $\delta = 7.98(\text{s}, 1\text{H}, -\text{CH}=\text{N}-)$, 3.89(s, 5 H, C₅H₅), 4.34(br, 2H, H³ and H⁵), 4.39(s, 1H, H⁴), 6.80(dd, 1H, ³J = 8.0 and ⁴J = 1.5, H^{3'}), 7.05(td, 1H, ³J = 8.0 and ⁴J = 1.5, H^{4'}), 6.48(td, 1H, ³J = 8.0 and ⁴J = 1.5, H^{5'}) and 7.11(dd, 1H, ³J = 8.0 and ⁴J = 1.5, H^{6'}) and for the non-cyclometallated moiety $\delta = 8.36(\text{s}, 1\text{H}, -\text{CH}=\text{N}-)$, 4.36(s, 5 H, C₅H₅), 5.31(s, 1H, H²), 4.59(br.s, 1H, H³), 4.65(s, 1H, H⁴), 6.37(s, 1H, H⁵), 7.09(dd, 1H, ³J = 8.0 and ⁴J = 1.5, H^{3'}), 7.21(br, 1H, H^{4'}), 6.94(m, 1H, ³J = 8.0 and ⁴J = 1.5, H^{5'}) and 6.95(m, 1H, H^{6'}). ¹³C{¹H} NMR data:⁷ for the cyclometallated unit $\delta = 157.9(-\text{CH}=\text{N}-)$, 70.6(C₅H₅), 93.5(C¹), 95.1(C²), 67.5(C³), 69.3(C⁴), 75.0(C⁵), 137.4(C^{1'}), 168.3(C^{2'}), 122.0(C^{3'}), 129.9(C^{4'}), 115.4(C^{5'}) and 115.3(C^{6'}) and for the non-cyclometallated unit $\delta = 172.3(-\text{CH}=\text{N}-)$, 70.7(C₅H₅), 75.6(C¹), 72.7(C²), 73.4(C³), 73.9(C⁴), 71.8(C⁵), 141.9(C^{1'}), 151.0(C^{2'}), 120.3(C^{3'}), 128.8(C^{4'}), 120.2(C^{5'}) and 122.4(C^{6'}).

4.2.3. *trans*-[Pd{(η^5 -C₅H₅)Fe[(η^5 -C₅H₄)-CH=N-(C₆H₄-2O)]₂] (**4b**)

Compound **1b** (272 mg, 8.91×10^{-4} mol) was dissolved in 10 mL of methanol, then a solution formed by Pd(OAc)₂ (100 mg, 4.45×10^{-4} mol) and 5 mL of methanol was added. The reaction mixture was protected from the light and stirred at 298 K for 20 min. The red solid formed (**4b**) was isolated by filtration and air-dried (yield: 120 mg). Slow evaporation of the filtrate gave small amounts (30 mg) of **3b**. Anal. Calc. for C₃₄H₂₈Fe₂N₂O₂Pd:

⁷ Labelling of the atoms corresponds to those presented in Scheme 1 (for **1b-3b** and **6b-8b**) and Fig. 6 (for **4b** and **5b**).

C, 57.13; H, 3.95; N, 3.92. Found: C, 57.0; H, 4.3; N, 3.9%. MS(FAB⁺): $m/z = 714\{[M]^+\}$. IR: 1616 cm⁻¹ $\nu(\text{>C=N-})$. ¹H NMR data:⁷ $\delta = 7.95(\text{s}, 2\text{H}, -\text{CH=N-})$, 4.38(s, 10H, C₅H₅), 4.76(t, 2H, ³J = 2.0, H² and H⁵), 4.61(t, 2H, ³J = 2.0, H³ and H⁴), 6.84(dd, 2H, ³J = 7.5 and ⁴J = 1.5, H^{3'}), 6.95(td, 2H, ³J = 7.5 and ⁴J = 1.5, H^{4'}), 6.30(td, 2H, ³J = 7.5 and ⁴J = 1.5, H^{5'}) and 7.44(dd, 2H, ¹J = 7.5 and ⁴J = 1.5, H^{6'}). ¹³C{¹H} NMR data:⁷ $\delta = 159.4(-\text{CH=N-})$, 71.2(C₅H₅), 76.0(C¹), 71.9(C² and C⁵), 72.7(C³ and C⁴), 139.2(C^{1'}), 168.9(C^{2'}), 118.4(C^{3'}), 129.6(C^{4'}), 113.4(C^{5'}) and 121.5(C^{6'}).

4.2.4. [Pd{[(η⁵-C₅H₅)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}] (5b)

This complex was obtained as a by-product using the following procedure: a mixture containing Pd(OAc)₂ (100 mg, 4.45 × 10⁻⁴ mol), **1b** (136 mg, 4.45 × 10⁻⁴ mol) and 50 mL of methanol was refluxed for 2.5 h. After this period the reaction mixture was allowed to cool to 298 K. The nearly black solid that formed (contained metallic palladium, compounds **4b** and **5b**) was collected by filtration and air-dried. Then it was dissolved in the minimum amount of CH₂Cl₂ and passed through a SiO₂ column. The elution with CH₂Cl₂ produced a narrow brown band that gave after concentration to dryness complex **5b** (5 mg). The major component **4b** was isolated after work up of the second band released. Slow evaporation of the filtrate obtained after the separation of the blackish solid at 298 K gave **3b** (40 mg). MS(MALDI-TOF⁺): $m/z = 1638.5\{[M_4]^+\}$ and 819.8 $\{[M_2]^+\}$. ¹H NMR data:⁷ $\delta = 7.33(\text{s}, 1\text{H}, -\text{CH=N-})$, 4.25(s, 5H, C₅H₅), 4.15(s, 2H, H⁴ and H⁵), 3.79(s, 1H, H³), 7.83(d, 1H, ³J = 7.8, H^{3'}), 7.04(t, 1H, ³J = 7.8, H^{4'}), 6.41(t, 1H, ³J = 7.8, H^{5'}) and 6.69(d, 1H, ³J = 7.8, H^{6'}).

4.2.5. [Pd{[(η⁵-C₅H₅)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}(PPh₃)] (6b)

Complex **3b** (155 mg, 2.17 × 10⁻⁴ mol) was dissolved in 15 mL of CH₂Cl₂, then PPh₃ (57 mg, 2.17 × 10⁻⁴ mol) was added. After stirring of the mixture at 298 K for 1 h, the undissolved materials were removed by filtration and discarded and the filtrate was concentrated to dryness on a rotary evaporator. The residue was treated with 5 mL of CH₂Cl₂ and passed through a short (4.5 cm × 2.5 cm) SiO₂ column. The orange-red band collected after the elution with a CH₂Cl₂:MeOH (100:0.3) solution was concentrated to dryness on a rotary evaporator, air-dried and then dried in vacuum (yield: 84 mg, 58%). Anal. Calc. for C₃₅H₂₈FeNOPPd: C, 62.57; H, 4.20; N, 2.08. Found: C, 62.3; H, 4.5; N, 2.1%. MS(FAB⁺): $m/z = 673\{[M+1]^+\}$. IR: 1582 cm⁻¹ $\nu(\text{>C=N-})$. ¹H NMR data:⁷ $\delta = 8.12(\text{d}, 1\text{H}, {}^4J_{\text{P-H}} = 9, -\text{CH=N-})$, 4.08(s, 5H, C₅H₅), 3.19(d, 1H, ³J = 2.2, H³), 4.24(t, 1H, ³J = 2.2, H⁴), 4.67(d, 1H, ³J = 2.2, H²), 6.73(dd, 1H, ³J = 7.5 and ⁴J = 1.5, H^{3'}), 7.00(td, 1H, ³J = 7.5 and ⁴J = 1.5, H^{4'}), 6.39(td, 1H, ³J = 7.5 and ⁴J = 1.5, H^{5'}) and 7.19(dd, 1H, J = 7.5 and

1.5, H^{6'}) and 7.30-7.80(m, 15H, PPh₃). ¹³C{¹H} NMR:^{7,8} $\delta = 155.8(-\text{CH=N-})$, 70.7(C₅H₅), 97.9(C²), 75.7(C³), 69.3(C⁴), 67.9(C⁵), 137.6(C^{4'}), 171.7(C^{2'}), 121.6(C^{3'}), 129.8(C^{4'}), 113.8(C^{5'}), 115.2(C^{6'}) and four additional doublets centred at ca. 128, 129, 131 and 135 due to the four types of non-equivalent ¹³C nuclei of the PPh₃ ligand. ³¹P{¹H} NMR: $\delta = 31.0$.

4.2.6. [Pd{[(η⁵-C₅H₅)-CH=N-(C₆H₄-2OH)]Fe(η⁵-C₅H₅)}Cl(PPh₃)] (7b)

This product was prepared on a NMR scale as follows: Complex **6b** (10 mg, 1.49 × 10⁻⁵ mol) was dissolved in 0.7 mL of CDCl₃. Then 0.25 μL of a 0.465 M solution of HCl in methanol-*d*₄ were added. The reaction mixture was stirred at 298 K for 30 min and then filtered. The filtrate was concentrated to dryness on a rotary evaporator giving a red solid, which was collected and air-dried (yield: 9 mg, 85%). MS(FAB⁺): $m/z = 673\{[M-Cl]^+\}$. IR: 1569 cm⁻¹ $\nu(\text{>C=N-})$ and 3420 cm⁻¹ $\nu(-\text{OH})$. ¹H NMR data:⁷ $\delta = 8.24(\text{d}, 1\text{H}, {}^4J_{\text{P-H}} = 6.8, -\text{CH=N-})$, 3.97(s, 5H, C₅H₅), 3.56(s, 1H, H³), 4.21(t, 1H, ³J = 2.0, H⁴), 4.52(d, 1H, ³J = 2.0, H⁵), 7.04(d, 1H, ³J = 8.4, H^{3'}), 7.18(t, 1H, ³J = 7.4, H^{4'}), 6.99(m, 2H, H^{5'} and H^{6'}) and 7.30-7.80(m, 15H, PPh₃). ¹³C{¹H} NMR:⁷ $\delta = 175.1(-\text{CH=N-})$, 70.8(C₅H₅), 86.9(C¹), 104.2(C²), 77.7(C³), 71.1(C⁴), 67.8(C⁵), 142.1(C^{1'}), 149.5(C^{2'}), 121.2(C^{3'}), 128.0(C^{4'}), 122.5(C^{5'}), 122.8(C^{6'}) and four additional doublets centred at ca. 128, 129, 131 and 135 due to the four types of non-equivalent ¹³C nuclei of the PPh₃ ligand. ³¹P{¹H} NMR: $\delta = 38.8$.

4.2.7. [Pd{[(MeO₂C-C≡C-CO₂Me)₂(η⁵-C₅H₅)-CH=N-(C₆H₄-2O)]Fe(η⁵-C₅H₅)}] (8b)

Compound **3b** (145 mg, 2.03 × 10⁻⁴ mol) was dissolved in CH₂Cl₂ (7 mL), then 0.1 mL of MeO₂C-C≡C-CO₂Me (8.12 × 10⁻⁴ mol) was added. The reaction mixture was refluxed for 8 h and then filtered. The undissolved materials were discarded and the filtrate was concentrated to dryness on a rotary evaporator. The residue was dissolved in the minimum amount of CH₂Cl₂ and passed through a SiO₂ column (4.5 cm × 2.0 cm). Elution with CH₂Cl₂ produced the release of three bands. The first one was yellow and gave after concentration to dryness small amounts of **9b**. Small amounts of ferrocenecarboxaldehyde (15 mg) and traces of **3b** (≈3 mg) were isolated from the second and third band, respectively. Once these bands had been collected a CH₂Cl₂:MeOH (100:0.4) mixture was used as eluant this produced a deep red band, which after concentration produced **8b** (49 mg, 35%). Anal. Calc. for C₂₉H₂₅NO₅FePd: C, 50.21; H, 3.63; N, 2.02. Found: C, 49.7; H, 3.5; N, 2.0%. MS(ESI⁺): $m/z = 694\{[M]^+\}$. IR: 1733 cm⁻¹ $\nu(\text{>COO})$ and 1597 cm⁻¹ $\nu(\text{>C=N-})$. ¹H NMR data:⁷ $\delta = 8.35(\text{s}, 1\text{H}, -\text{CH=N-})$, 4.35(s, 5H, C₅H₅),

⁸ The signal due to the C¹ carbon was not detected in the ¹³C{¹H} NMR spectrum.

4.77(s, 1H, H³), 4.91(t, 1H, ³J = 2.4, H⁴), 5.28(s, 1H, H⁵), 6.92(d, 1H, ³J = 8.4, H^{3'}), 7.11(t, 1H, ³J = 8.4, H^{4'}), 6.59(d, 1H, ³J = 8.4, H^{5'}), 7.33(d, 1H, ³J = 8.4, H^{6'}), four singlets at 3.95, 3.94, 3.74 and 3.58 (12H, 4OMe). ¹³C{¹H} NMR: δ = 152.6(–CH=N–), 72.0(C₅H₅), 78.0(C¹), 77.9(C²), 73.1(C³), 74.1(C⁴), 75.8(C⁵), 136.7(C^{1'}), 168.6(C^{2'}), 120.3(C^{3'}), 130.7(C^{4'}), 116.5(C^{5'}), 114.6(C^{6'}), four singlets at 53.3, 52.6, 52.3 and 53.1(4OMe) and 159.2, 164.1, 166.6 and 167.2 (4 >COO) and four additional singlets at 149.5, 136.3, 119.8 and 119.5 due to the C ^{α} , C ^{β} , C ^{δ} and C ^{γ} carbon nuclei of the inserted η^3 -butadienyl unit, respectively.

4.3. Mössbauer spectra

⁵⁷Fe Mössbauer spectra were recorded using powdered solid samples. The samples were placed inside an Oxford Instrument cryostat and the spectra were collected at 80 K using a constant acceleration Mössbauer spectrometer with a ⁵⁷Co/Rh source. The source was moved via triangular velocity wave and the γ -counts were collected in a 512 multi-channel analyser. The data were folded, plotted and fitted by a computer procedure. Velocity calibration was done using a 25 μ m thick metallic iron foil and the Mössbauer spectral parameters are given to this standard.

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Appendix A. Supplementary material

CCDC 622635 and 622636 contain the supplementary crystallographic data for **2b** · 3H₂O and **3b** · 1/2CHCl₃. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.01.054](https://doi.org/10.1016/j.jorganchem.2007.01.054).

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