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Versatility in the mode of coordination $\{(\mathrm{N}), (\mathrm{N,O})^{-}, (\mathrm{C,N})^{-}$ or $(\mathrm{C,N,O})^{2-}\}$ of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2OH)\}]$ to palladium(II)

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Abstract

The study of the reactivity of the ferrocenyliminoalcohol $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2OH)\}]$ (**1b**) with $Na_2[PdCl_4]$ or $Pd(OAc)_2$ has allowed the isolation and characterization of the heterotrimetallic complexes: *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2OH)]\}_2Cl_2]$ (**2b**), $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2O)]Fe(\eta^5\text{-}C_5H_5)\}\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2OH)]\}]$ (**3b**) and *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2O)]\}_2]$ (**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 $[C(sp^2, \text{ferrocene}),N,O]^{2-}\}$. The crystal structures of $\mathbf{2b}\cdot 3H_2O$ and $\mathbf{3b}\cdot 1/2CHCl_3$ 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 PPh_3 has enabled the obtention of the cyclopalladated complexes $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2O)]Fe(\eta^5\text{-}C_5H_5)\}(PPh_3)]$ (**6b**) and $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2OH)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ (**7b**), in which **1b** behaves as a $[C(sp^2, \text{ferrocene}),N,O]^{2-}$ (in **6b**) or $[C(sp^2, \text{ferrocene}),N]^-$ (in **7b**) ligand. Treatment of **3b** with $MeO_2C\text{–}C{\equiv}C\text{–}CO_2Me$ produces $[Pd\{[(MeO_2C\text{–}C{=}C\text{–}CO_2Me)_2(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}(C_6H_4\text{-}2O)]Fe(\eta^5\text{-}C_5H_5)\}]$ (**8b**), that arises from the bis(insertion) of the alkyne into the $\sigma[Pd\text{–}C(sp^2, \text{ferrocene})]$ bond. The comparison of the results obtained for **1b** and $[C_6H_5\text{–}CH{=}N\text{–}(C_6H_4\text{-}2OH)]$ (**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. ^{57}Fe 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).

Keywords: Ferrocene derivatives; Iminoalcohols; Cyclopalladation; 57-Fe Mössbauer spectra; Alkyne insertions

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 [C,N,X] (X = N, S, P) ligands and a $\sigma[Pd\text{–}C(sp^2, \text{aryl})]$ or to a lesser extent $\sigma[Pd\text{–}C(sp^3)]$ 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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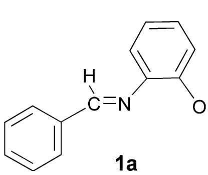
introduce significant differences in the physical and chemical properties of the complexes, palladacycles with terdentate [C,N,O] ligands are not common [5–9], although they are especially attractive from different points of view. For instance, some compounds of this kind exhibit unusual structural features, such as $[Pd\{C_6H_4–CH{=}N–(C_6H_4\text{-}2O)\}]_4$, which arises from the iminoalcohol $[C_6H_5–CH{=}N–(C_6H_4\text{-}2OH)]$ (**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 σ(Pd–C) and a σ(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 *Teleodicin B4* [9].

In recent years these studies have been extended to ligands derived from ferrocene and several palladacycles with $[C(sp^2, \text{ferrocene}),N,X]^-$ (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 $[C(sp^2, \text{ferrocene}),N,O]^-$ ligand. More recently, the study of the reaction between 2-ferrocenyl-2,4-dihydro-1*H*-3,1-benzoxazine [15] and $Na_2[PdCl_4]$ has lead to $[Pd\{[(\eta^5\text{-}C_5H_3)–CH{=}N–(C_6H_4\text{-}2CH_2OH)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ [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 $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)–CH{=}N–(C_6H_4\text{-}2OH)\}]$ (**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 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**.



1a

Fig. 1. Schiff base $[(C_6H_5)–CH{=}N–(C_6H_4\text{-}2OH)]$ (**1a**).

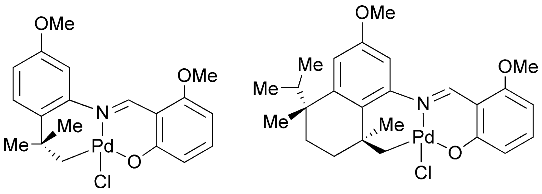


Fig. 2. Palladacycles containing $(C,N,O)^{2-}$ ligands used in the total synthesis of the central core of *Teleocidin B4*.

2. Results and discussion

The reaction of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)–CH{=}N–(C_6H_4\text{-}2OH)\}]$ (**1b**) [16] with an equimolar amount of $Na_2[PdCl_4]$ in methanol at 298 K for 24 h produced a red solid. Its characterization data (see Section 4) agreed with those expected for *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)–CH{=}N–(C_6H_4\text{-}2OH)\}]_2Cl_2]$ (**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 $\mathbf{2b}\cdot 3H_2O$[1] (Fig. 3) contains molecules of *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)–CH{=}N–(C_6H_4\text{-}2OH)]\}_2Cl_2]$ 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*-$[Pd(L)_2Cl_2]$ where L represents an N-donor ferrocenyl ligand [17,18].

The $\rangle C{=}N–$ 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 "$PdCl_2$" moiety and forms an angle of 8.7° with the C_5H_4 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 transanular Pd···H(9) and Pd···H(9A) contacts, similar to those reported for *trans*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)–CH{=}N–NMe_2]\}_2Cl_2]$ [17] and other mono- and dinuclear complexes with "PdN_2Cl_2" cores [18–20].

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[1] *Crystallographic data*: $C_{34}H_{30}Cl_2Fe_2N_2O_2Pd$ (**2b**) · $3H_2O$, MAR345 diffractometer (Mo Kα radiation), monoclinic, $a = 14.803(1)$ Å, $b = 13.968(1)$ Å, $c = 17.702(1)$ Å, $\alpha = \gamma = 90°$ and $\beta = 112.190(1)°$, space group: $C2/c$, $V = 3389.1(4)$ Å^3, $Z = 4$, $T = 273(2)$ K, $\lambda = 0.71069$ Å, $D_{calc} = 1.639$ g cm^{-3}, $\mu = 1.572$ mm^{-1}, $F(000) = 1768$, 2607 reflections collected of which 2207 were assumed as independent ($R_{int} = 0.0249$), 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).