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Novel Palladacycles Containing [C(sp^2, ferrocene), N, O]$^-$ or [C(sp^2, ferrocene), N, O]$^{2-}$ Terdentate Ligands

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The synthesis, characterization, and study of the reactivity of the novel cyclopalladated complexes [Pd{[(η^5-C$_5$H$_3$)CH=N(C$_6$H$_4$-2-CH$_2$OH)]Fe(η^5-C$_5$H$_5$)}Cl] (**2**) and [Pd{[(η^5-C$_5$H$_3$)CH=N(C$_6$H$_4$-2-CH$_2$O)]-Fe(η^5-C$_5$H$_5$)}]$_2$ (**3**) with PPh$_3$ or MeO$_2$CC≡CCO$_2$Me are described. Electrochemical and ^{57}Fe Mössbauer spectroscopic studies of the new palladacycles are also reported.

Palladium(II) compounds derived from ligands containing three donor atoms with different hardnesses[1] have attracted great interest due to their potential hemilability,[2] which is especially relevant in view of their use in homogeneous catalysis.[3] Despite of this and the prochiral nature of ferrocenyl ligands in the cyclopalladation processes,[4,5] palladium(II) compounds containing terdentate [C(sp^2, ferrocene), N, X]$^{q-}$ (X = N, S, O; q = 1, 2) ligands are scarce.[6−10] It is well-known that organometallic complexes with a σ(Pd−O) bond are particularly interesting, due to their applications in organic and/or organometallic synthesis and in homogeneous catalysis.[11,12] However, only two palladacycles with a [C(sp^2, ferrocene), N, O]$^{q-}$ ligand are known,[13] and in both cases, the palladium(II) is bound to the oxygen of an ether group. Recent contributions have shown that imino alcohols may exhibit greater versatility in the coordination modes than their analogues with an OR substituent.[11b,14−17] Palladium(II) or platinum(II) complexes derived from organic imino alcohols have been reported,[14−17] and some of them (i.e. [Pd{C$_6$H$_4$CH=N(C$_6$H$_4$-2-O)}]$_4$) exhibit unusual structural features.[16]

On the other hand, ring−chain tautomeric equilibria involving 1,3-O,N-heterocyclic systems have generated great interest in the last few years,[18−20] since this process may affect the reactivity of the species involved. However, none of the articles published so far have focused on the study of the effect produced by transition metals upon the reactivity of the two tautomers. We have recently reported the synthesis of 2-ferrocenyl-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine (**1a**) and the tautomeric equilibrium between **1a** and the imino alcohol [(η^5-C$_5$H$_5$)Fe{(η^5-C$_5$H$_4$)CH=N(C$_6$H$_4$-2-CH$_2$OH)}] (**1b**).[20] In view of this, **1b** appeared to be a good candidate to attempt the preparation of palladacycles with terdentate [C(sp^2, ferrocene), N, O]$^-$ or [C(sp^2, ferrocene), N, O]$^{2-}$ ligands. Here we describe the study of the reactivity of **1a** with palladium(II).

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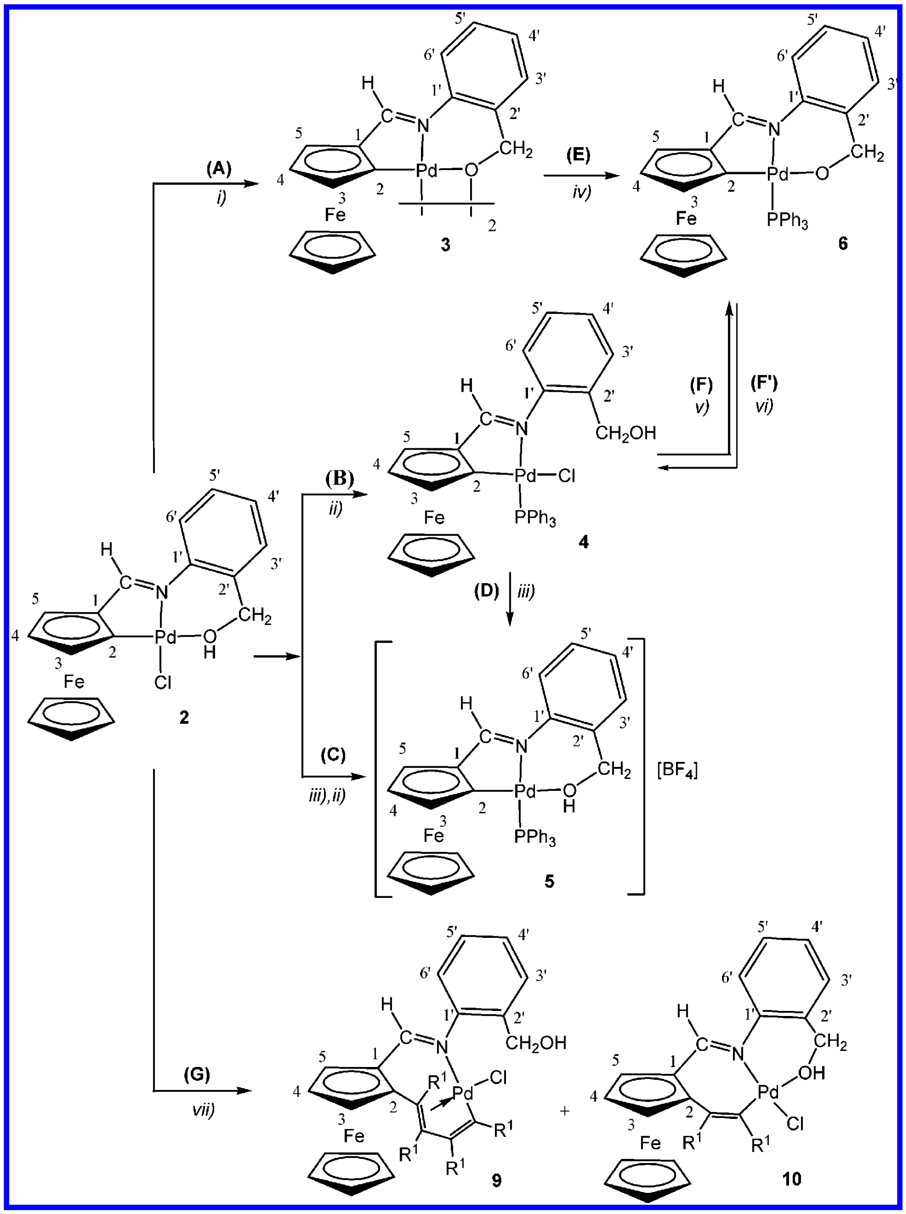
Scheme 1[a]



[a] $R^1 = CO_2Me$. Legend: (i) in MeOH followed by the addition of NaOH (in the molar ratio Pd(II):NaOH = 1:1) dissolved in MeOH at room temperature; (ii) PPh_3 (in the molar ratio Pd:PPh_3 = 1) in CH_2Cl_2 at 298 K; (iii) addition of Tl[BF_4] in acetone followed by the removal of the TlCl formed; (iv) PPh_3 in $CDCl_3$; (v) NaOH in methanol; (vi) in $CDCl_3$; (vii) addition of $MeO_2CC{\equiv}CCO_2Me$ (in the molar ratio alkyne:**2** = 2) in refluxing CH_2Cl_2 for 2 h, followed by SiO_2 column chromatography (see text).

The treatment of **1a**[20] with equimolar amounts of $Na_2[PdCl_4]$ and $NaOAc{\cdot}3H_2O$ in methanol at 298 K for 24 h produced a deep purple crystalline solid. Its characterization data agreed with those expected for $[Pd\{[(\eta^5\text{-}C_5H_3)CH{=}N(C_6H_4\text{-}2\text{-}CH_2OH)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**2**) (Scheme 1), in which the imine form **1b** acts as a $[C(sp^2$, ferrocene), N, O$]^-$ terdentate ligand.

The crystal structure of **2**[21] consists of two nonequivalent molecules of $[Pd\{[(\eta^5\text{-}C_5H_3)CH{=}N(C_6H_4\text{-}2\text{-}CH_2OH)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (hereafter referred to as **I** and **II**). In each one of the molecules (Figure 1) the palladium(II) atom is in a slightly distorted square-planar environment, where it is bound to a chloride (Cl(1) or Cl(2)), a carbon atom of the C_5H_3 ring of the ferrocenyl moiety (C(6) (in **I**) or C(6A) (in **II**)), the imine nitrogen (N(1) or N(2)), and the oxygen atom of the alcohol group (O(1) (in **I**) or O(2) (in **II**)). This confirms that, in **2**, ligand **1b** behaves as a $[C(sp^2$, ferrocene), N, O$]^-$ terdentate group. The palladium−donor atom bond lengths are similar to those reported for related palladacycles with $[C(sp^2$, phenyl), N, O$]^-$ groups,[14,16,17] and the bond angles around the palladium(II) vary from 83.3(4) to 96.2(2)° (in **I**) or from 82.5(4) to 94.46(17)° (in **II**).

Molecules **I** and **II** contain a [5.5.6.6] tetracyclic system formed by the C_5H_3 ring of the ferrocenyl moiety, a practically planar five-membered palladacycle, a six-membered chelate ring (with *half-chair* conformation), and the phenyl group. The phenyl rings are planar and form angles of 34.3, 33.1, and 33.0° (in **I**) or 32.3, 29.1, and 33.9° (in **II**) with the corresponding coordination plane, the metallacycle, and the mean plane of the C_5H_3 unit. The main difference between molecules **I** and **II**

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[21] Crystallographic data: $C_{18}H_{16}ClFeNOPd$, monoclinic, $a = 10.878(1)$ Å, $b = 20.934(1)$ Å, $c = 14.569(1)$ Å, $\alpha = \gamma = 90.0°$, $\beta = 90.560(1)°$, space group $P2_1/n$, $V = 3308.6(4)$ Å^3, $Z = 8$, $T = 293(2)$ K, $\lambda = 0.710\,69$ Å, $D_{calcd} = 1.847$ g cm^{-3}, $\mu = 2.217$ mm^{-1}, $F(000) = 1824$, 10 297 reflections collected, of which 7667 were assumed as independent ($R_{int} = 0.0543$). R indices: R1 = 0.0721 and wR2 = 0.2345 ($I > 2\sigma(I)$); R1 = 0.0994 and wR2 = 0.2556 (all data).

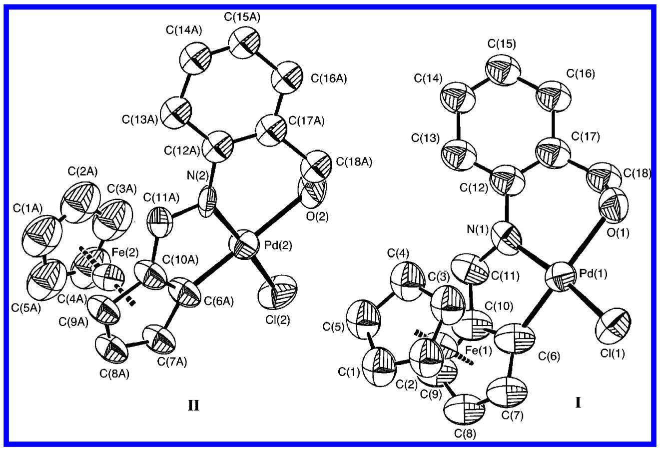

Figure 1. ORTEP diagrams of the two nonequivalent molecules (**I** and **II**) present in the crystal structure of [Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2OH)]Fe(η^5-C_5H_5)}Cl] (**2**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Pd(1)−C(6), 1.940(11); Pd(1)−N(1), 2.059(9); Pd(1)−O(1), 2.190(8); Pd(1)−Cl(1), 2.289(3); Pd(2)−C(6A), 1.914(10); Pd(2)−N(2), 1.033(8); Pd(2)−O(2), 2.191(8); Pd(2)−Cl(2), 2.292(2); C(6)−Pd(1)−N(1), 83.2(4); N(1)−Pd(1)−O(1), 90.0(3); O(1)−Pd(1)−Cl(1), 96.5(2); C(6)−Pd(1)−Cl(1), 90.7(4); C(6A)−Pd(2)−N(2), 82.5(4); N(2)−Pd(2)−O(2), 89.2(3); O(2)−Pd(2)−Cl(2), 94.52(18); C(6A)−Pd(2)−Cl(2), 94.3(3).

arises from the planar chirality of the "(η^5-C_5H_5)Fe(η^5-C_5H_3)" moieties (S_p in **I** and R_p in **II**).

The intramolecular and the minimum intermolecular separations between the iron(II) and palladium(II) atoms are clearly greater than the sum of their van der Waals radii.[22]

Bond lengths and angles of the ferrocenyl moieties agree with data reported for most ferrocene derivatives;[14] the pentagonal rings are practically parallel (*tilt angles* 1.3 and 2.6° in **I** and **II**) and they deviate by 13.3° (in **I**) or 2.6° (in **II**) from the ideal eclipsed conformation.

Since the molar ratio **1a**:**1b** is dependent on the solvent,[20] we also studied the reactivity of **1a** with *cis*-[$PdCl_2(PhCN)_2$] under different experimental conditions (reaction periods in the range 3 h to 1 day) using equimolar amounts of **1a** and *cis*-[$PdCl_2(PhCN)_2$] (or this reagent and NaAcO) as reactants and in refluxing toluene or toluene/methanol (5:1) mixtures. Unfortunately, in all these reactions the formation of metallic palladium was detected, even for the shortest reaction periods.[23] This suggests that the reduction of the palladium(II) could be promoted by the ferrocenyl substrate. In fact, electrochemical studies[20] have demonstrated that **1a** is more prone to oxidation than the ferrocenylimines [(η^5-C_5H_5)Fe{(η^5-C_5H_4)CH=N(R^1)}]-(R^1 = substituted phenyl ring).[9a,24]

To attempt the synthesis of palladacycles having a dianionic [C(sp^2, ferrocene), N, O]$^{2-}$ ligand, **2** was treated with NaOH in methanol at 298 K. This led to a deep purple solid (**3**; Scheme 1, step **A**). Its IR spectrum did not show the typical band due to the stretching of the −OH group,[25] thus suggesting that deprotonation of the alcohol group had taken place. In the ^{1}H and ^{13}C{^{1}H} NMR spectra most of the signals appeared in duplicate and none of them were coincident with those of **1a** or **1b**. The analysis of the cross-peaks detected in the {^{1}H−^{1}H} NOESY spectra of **3** suggested the existence of at least two nonequivalent units of the ligand. In one of them, one of the protons of the −CH_2− moiety was close to the C_5H_3 ring of the other ligand, while in the other nonequivalent unit it was proximal to the H^3 proton of the C_5H_5 ring. All of these findings suggested that **3** could have higher nuclearity. Elemental analyses of **3** did not differ significantly from those expected for [Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2O)]Fe(η^5-C_5H_5)}]$_n$, and the mass spectra showed an intense peak at *m*/*z* 848, which agreed with the value expected for a dimer. In the view of the characterization data available, we postulate for **3** the dimeric structure presented in Scheme 1. The complexity of the ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** could be ascribed to several factors, such as conformational differences of the nonplanar rings of **3** between the halves and/or the presence of isomeric forms of **3** in solution. Since the cyclopalladation produces 1,2-disubstituted ferrocenyl moieties with planar chirality, the formation of diastereomers of **3** could also be expected on principle.

Examples of palladium(II) compounds with central "Pd_2O_2" cores have been described,[11c,12,14,26] and the X-ray crystal structures reported so far show that when these sorts of compounds contain (L,L′) bidentate ligands, the two identical donor atoms of the two (L,L′) ligands are in a trans arrangement.[11c,12,14,26] The self-assembly of the two "[Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2O)]Fe(η^5-C_5H_5)}]" units forming the central "Pd_2O_2" ring of **3** is only possible if the metalated carbons of each one of the moieties are in a trans arrangement. VT-NMR sudies of **3** (in $CDCl_3$) showed that the relative intensities of the two sets of signals decreased upon cooling (from 1.0:1.0 (at 298 K) to 1.0:0.7 (at 223 K)) and the formation of small amounts of insoluble materials was detected. These findings could be rationalized by assuming the coexistence of isomeric forms (in a nearly 1:1 molar ratio at 298 K) with different solubilities at low temperatures.

In **3** the planar chiralities of the ferrocenyl moieties could be different ((R_p and S_p)) or identical ((R_p,R_p) or (S_p,S_p)). The coexistence of these species in solution would produce two sets of signals in the NMR spectra, one due to the centrosymmetric form and the other to the noncentrosymmetric species, respectively. The use of molecular models for these forms revealed that in both cases the environment of the palladium(II) atoms is rather crowded. In the centrosymmetric form one of the −CH_2− protons is close to the C_5H_5 group of the other half of the molecule (this is reflected in a high-field shift of the resonance), while for the non-centrosymmetric form it is near the H^3 proton. This arrangement of the groups introduces severe restrictions on the conformational changes of the six-membered chelate rings.

Treatment of **2** with PPh_3 in CH_2Cl_2 gave [Pd{[(η^5-C_5H_3)-CH=N(C_6H_4-2-CH_2OH)]Fe(η^5-C_5H_5)}Cl (PPh_3)] (**4**; Scheme 1, step **B**), where the ligand acts as a [C(sp^2, ferrocene), N]$^-$ group and the PPh_3 is in a cis arrangement to the metalated carbon atom, in good agreement with the *transphobia effect*.[27]Complex **4** results from the cleavage of the σ(Pd−OH) bond and the

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binding of the PPh_3. This process is fast at ca. 293 K and involves a change of the coordination mode of the ligand from [C(sp^2, ferrocene), N, O]$^-$ (in **2**) to [C(sp^2, ferrocene), N]$^-$ (in **4**).

As a first approach to achieve palladacycles containing simultaneously a [C(sp^2, ferrocene), N, O]$^-$ ligand and a PPh_3 group, the reactions shown in steps **C** and **D** of Scheme 1 were studied. In both cases, [Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2OH)]-Fe(η^5-C_5H_5)}(PPh_3)][BF_4] (**5**) was isolated. The differences detected in the ^{31}P{^{1}H} NMR spectra of **5** and **4** are similar to those reported for [Pd{(4,5-MeO)$_2C_6H_2$CH=N(CH_2CH_2OH)}-Cl(PPh_3)] and [Pd{(4,5-MeO)$_2C_6H_2$CH=N(CH_2CH_2OH)}(PPh_3)]-ClO_4, which contain a [C(sp^2, phenyl), N]$^-$ and a [C(sp^2, phenyl), N, O]$^-$ ligand, respectively.[17a]

The addition of PPh_3 to a solution of **3** (molar ratio PPh_3:Pd = 1) in $CDCl_3$ gave [Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2O)]Fe-(η^5-C_5H_5)}(PPh_3)] (**6**; Scheme 1, step **E**). The reactivity of **3** with PPh_3 is similar to that of [Pd{C_6H_4CH=N(C_6H_4-2-O)}]$_4$, which, under identical experimental conditions, gave [Pd{C_6H_4-CH=N(C_6H_4-2-O)}(PPh_3)], also containing a terdentate [C(sp^2, phenyl), N, O]$^{2-}$ ligand.[16] Comparison of the results obtained in the reactions of **2** and **3** with PPh_3 reveal that the Pd−OH bond (in **2**) is more labile than the Pd−O$_{alkoxo}$ bond (in **3**).

When a $CDCl_3$ solution of **4** was treated with the stoichiometric amount of NaOD dissolved in methanol (Scheme 2, step **F**), the ^{1}H NMR spectrum of the crude reaction mixture revealed the coexistence of **6** and **4** in the molar ratio **6**:**4** = 0.4. Furthermore, the ^{1}H NMR spectrum of a freshly prepared solution of **6** (in $CDCl_3$) changed with time. After several hours of storage the presence of **4** was also detected (Scheme 2, step **F′**) and the molar ratio **6**:**4** decreased slowly with time,[28] thus indicating that **6** was less stable than **4** in $CDCl_3$ at 298 K.

^{57}Fe Mössbauer spectra of **2**−**4**[29] consisted of a single quadrupole doublet, indicating a unique iron site. For **3**, the value of the Γ parameter is similar to those of **2** and **4**, thus suggesting that in the solid state the environments of the two iron(II) centers of **3** should be very similar at 80 K. Previous studies on ^{57}Fe Mössbauer spectroscopy of ferrocene derivatives have shown that the quadrupole splitting parameter (ΔE_q) is strongly sensitive to the nature of the substituents.[30] In particular, it is widely accepted that electron-withdrawing substituents produce a decrease of the ΔE_q value, relative to ferrocene, while for electron-donating groups the effect is opposite.[30] The ΔE_q values obtained for **2**−**4**[29] are smaller than that of ferrocene (ΔE_q = 2.37 mm/s (at 298 K) and 2.41 mm/s (at 80 K)).[31] This suggests that the formation of the palladacycles has an electron-withdrawing effect upon the iron(II). A comparison of the ΔE_q parameters for **2**[29] and [Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-SMe)]Fe-(η^5-C_5H_5)}Cl][9a] reveals that in these cyclopalladated complexes the replacement of the $-CH_2OH$ substituent (in **2**) by an −SMe group produces an increase of the electron-pulling character of the substituents on the "(η^5-C_5H_5)Fe(η^5-C_5H_3)" moiety. Additionally, the differences detected in the ΔE_q values of **2**−**4** confirm that the intensity of this effect is dependent on small changes on the heteroatoms bound to the palladium(II) that are at a distance of three bonds from the iron(II).

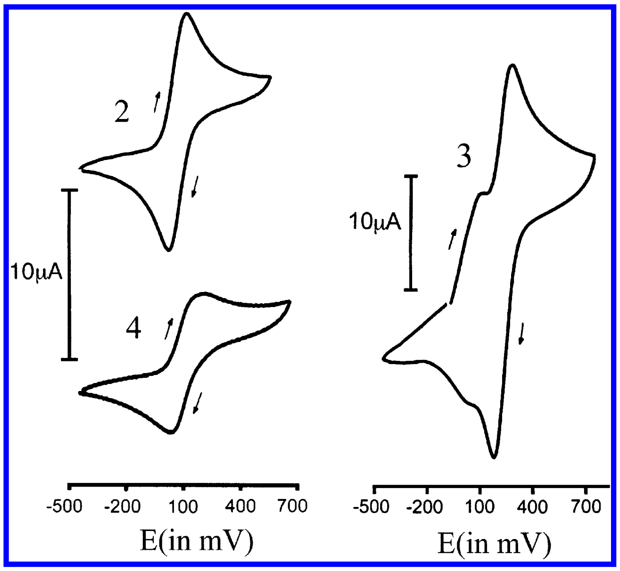

Figure 2. Cyclic voltammograms of the monomeric compounds [Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2OH)]Fe(η^5-C_5H_5)}Cl] (**2**) and [Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2OH)]Fe(η^5-C_5H_5)}Cl(PPh_3)] (**4**) and of the dinuclear product [Pd{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2O)]-Fe(η^5-C_5H_5)}]$_2$ (**3**) in CH_3CN at 293 K (the potentials are referred to the ferrocene/ferrocenium couple).

To elucidate the influence of the mode of binding of the ligand in **2**−**4** upon the proclivity of the iron(II) toward oxidation, electrochemical studies of **2**−**4**, based on cyclic voltammetry, were also performed.[32] The cyclic voltammogram of **2** (Figure 2) showed an anodic peak directly associated with a cathodic one in the reverse scan. The wave is shifted to a more anodic area than for ligand **1a**. This indicates, according to the literature,[33] that the substituents bound to the ferrocenyl moiety in **2** have a greater electron-withdrawing character than in **1a**. For **2**, the values of the cathodic and anodic potentials are similar to those of [Pd{[(η^5-C_5H_3)CH=N(R^1)]Fe(η^5-C_5H_5)}Cl(L)] (with R^1 = phenyl group and L = neutral ligand), in which the imine acts as a bidentate [C(sp^2, ferrocene), N]$^-$ group.[24a] The ^{1}H NMR spectrum of **2** (in acetonitrile-d_3) suggested that this solvent induced the cleavage of the Pd−OH bond, giving [Pd-{[(η^5-C_5H_3)CH=N(C_6H_4-2-CH_2OH)]Fe(η^5-C_5H_5)}Cl(acetonitrile-d_3)] (**7**). This confirms the lability of the terminal σ(Pd−OH) bond in **2**. The cyclic voltammogram of **4** (Figure 2) shifted to more anodic potentials than for **2**, and in this case, the shape of the wave, together with the larger ΔE value and the lack of a linear relationship between the $E_{p,a}$ values and the square-root of the scan rates ($\upsilon^{1/2}$), suggested a quasi-reversible electro-

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[28] The progress of the transformation of **6** (in $CDCl_3$) into **4** was monitored by ^{1}H NMR. The molar ratio **6**:**4** after different periods of storage at 298 K was 4.2 (24 h), 2.3 (48 h), 1.3 (96 h), and 0.9 (5 days; in this case the presence of traces of ferrocenecarboxaldehyde and other byproducts was also detected).

[29] Summary of ^{57}Fe Mössbauer hyperfine parameters (isomer shift (IS)-, quadrupole splitting (ΔE_q), and full-width at half-height (Γ, in mm/s) at 80 K): for **2**, IS = 0.475(4), ΔE_q = 2.122(4), and Γ = 0.25(1); for **3**, IS = 0.527(2), ΔE_q = 2.146(3), and Γ = 0.24(1); for **4**, IS = 0.492(4), ΔE_q = 2.164(6), and Γ = 0.233(8).

[30] (a) Houlton, A.; Miller, J. R.; Silver, J.; Jassim, N.; Ahmet, M. J.; Axon, T. L.; Bloor, D.; Cross, G. H. *Inorg. Chim. Acta* **1993**, *205*, 65. (b) Houlton, A.; Miller, J. R.; Roberts, R. M. G.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1991**, 467.

[31] Houlton, A., Bishop, P. T.; Roberts, R. M. G.; Silver, J.; Herberhold, M. *J. Organomet. Chem.* **1989**, *364*, 381.

[32] Summary of electrochemical data (in mV), with anodic ($E_{p,a}$) and cathodic ($E_{p,c}$) potentials and the separation between peaks (ΔE) for **2**−**4**: for **2**, $E_{p,a}$ = 118, $E_{p,c}$ = 27, and ΔE = 91; for **3**. $E_{p,a}(1)$ = 99, $E_{p,a}(2)$ = 291, $E_{p,c}(1)$ = 168, and $E_{p,c}(2)$ = 12 (see Figure 2), and ΔE = 123 and ca. 87; for **4**, $E_{p,a}$ = 214, $E_{p,c}$ = 37, and ΔE = 177.

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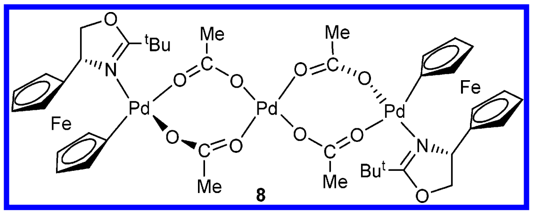
Chart 1



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chemical process.[34] The differences between the $E_{p,a}$ values of **7** and **4** suggest that **7** is more prone to oxidation than **4**.

The cyclic voltammogram of **3** (Figure 2) was more complex than those of **2** and **4** and showed two anodic peaks, in contrast with the results reported for the polynuclear cyclopalladated complex **8**, depicted in Chart 1, for which only one wave was detectable in the cyclic voltammogram under identical experimental conditions.[35] The differences detected in the electrochemical behaviors of **3** and **8** suggest that the replacement of the acetato bridges (in **8**) by the alkoxo oxygen (in **3**) is important in allowing communication between the two iron (II) centers.

It is well-known that palladacycles are useful precursors in the synthesis of organic or organometallic compounds.[35−41] Most of these reactions involve the insertion of small molecules, i.e. alkynes, alkenes, CO, or isonitriles, into the σ(Pd−C) bond of complexes containing bidentate [C, N]$^-$ ligands.[36−38] Previous studies on the alkyne insertion processes have shown that the nature of the final product formed depends on a wide variety of factors, including the nature of the metalated carbon, the electron-withdrawing/electron-donor nature of the substituents on the alkyne, the stoichiometry of the reaction, the remaining ligands bound to the palladium(II), etc. However, parallel studies on palladacycles with terdentate [C(sp^2, ferrocene), N, X]$^{q-}$ chelating groups are not common.[9b,40] To the best of our knowledge, only the reactions of [Pd{[(η^5-C_5H_3)CH═NCH_2(CH_2)$_n$$NMe_2$]Fe($\eta^5$-$C_5H_5$)Cl] and [Pd{[($\eta^5$-$C_5H_3$)CH═N($C_6H_4$-2-SMe)]Fe($\eta^5$-$C_5H_5$)}Cl] with the alkynes $R^1C{\equiv}CR^1$ (R^1 = CO_2Me, Et, Ph) have been described so far.[9b,40] In view of this and in order to elucidate if the nature of the heteroatom X could affect the reactivity of the σ(Pd−C(sp^2, ferrocene)) bond of complexes with a terdentate [C(sp^2, ferrocene), N, X]$^{q-}$ ligand, we also studied the reactions of **2** and **3** with $MeO_2CC{\equiv}CCO_2Me$. Treatment of **2** with this alkyne (molar ratio alkyne:Pd = 2) under reflux for 2 h allowed us to isolate two products (**9** and **10**, in the molar ratio **9**:**10** = 3.2) (Scheme 1, step **G**) which were identified as [Pd{[($MeO_2CC{=}CCO_2Me$)$_2$(η^5-C_5H_3)CH═N(C_6H_4-2-CH_2OH)]Fe(η^5-C_5H_5)Cl] and [Pd{[($MeO_2CC{=}CCO_2Me$)(η^5-C_5H_3)CH═N(C_6H_4-2-CH_2OH)]Fe(η^5-C_5H_5)}Cl], respectively. Compound **10**, which is formed by insertion of one molecule of the alkyne into the σ(Pd−C(sp^2, ferrocene)) bond of **2**, was isolated in higher yield when the reaction was performed using equimolar amounts of the palladium(II) complex and the alkyne and shorter refluxing periods (30 min). The relative arrangements of the −CO_2Me substituents on the alkene, presented in Scheme 1 for **9** and **10**, are the common ones described for all the palladacycles arising from mono or bis insertion of alkynes that have been characterized by X-ray diffraction.[14,38−40] A comparison of these results and those obtained for [Pd{[(η^5-C_5H_3)CH═NCH_2(CH_2)$_n$$NMe_2$]Fe($\eta^5$-$C_5H_5$)}Cl][39] and [Pd{[($\eta^5$-$C_5H_3$)CH═N($C_6H_4$-2-SMe)]Fe($\eta^5$-$C_5H_5$)}Cl][9b] suggests that for complexes with a terdentate [C(sp^2, ferrocene), N, X]$^-$ (X = O, S, N) the reactivity of the Pd−C(sp^2, ferrocene) bond increases according to the sequence $N_{amine} < S_{thioether} < O_{alcohol}$.

Furthermore, the results obtained for **2** differ from those reported for [Pd{[(η^5-C_5H_3)CH═N(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}Cl], for which the reaction with $MeO_2CC{\equiv}CCO_2Me$ (in the molar ratios Pd(II):alkyne = 1:1 and 1:2) gave [Pd{[($MeO_2CC{=}CCO_2Me$)(η^5-C_5H_3)CH═N(C_6H_4-2-SMe)]Fe(η^5-C_5H_5)}Cl] (**11**) exclusively.[9b] Since **10** and **11** contain a [C(sp^2, alkene), N, X]$^-$ (X = O (in **10**), S (in **11**)) ligand, these findings indicate that the σ(Pd−C(sp^2, alkene)) bond of **10** is more likely to undergo the insertion of $MeO_2CC{\equiv}CCO_2Me$ than when X is sulfur.

When **3** was treated with $MeO_2CC{\equiv}CCO_2Me$ (in the molar ratio alkyne:Pd = 1 or 2) and refluxed for periods varying between 1 h and 1 day, the starting materials were recovered unchanged and evidence of the formation of any product arising from the insertion of the alkyne into the σ(Pd−C(sp^2, ferrocene)) bond of **3** was not detected by NMR analyses of the crude mixture of these reactions. This suggests that **2** is more prone to react with the alkyne than **3**.

To sum up, the results presented here provide conclusive proof of the relevancy of the tautomeric equilibrium between **1a** and **1b** upon their reactivity with palladium(II). In solvents such as benzene, where the heterocyclic form is the major component,[20] the reduction of the palladium(II) takes place. This process may be induced by heterocyclic form **1a**, which is more prone to oxidation than **1b**.[20] In contrast with these findings, when **1a** reacted with $Na_2[PdCl_4]$ and NaOAc·$3H_2O$ in methanol (in which the molar ratio **1a**:**1b** = 0.5), the complex [Pd{[(η^5-C_5H_3)CH═N(C_6H_4-2-CH_2OH)]Fe(η^5-C_5H_5)}Cl] (**2**, with a [C(sp^2, ferrocene), N, O]$^-$ ligand) was isolated. Complex **2** is additionally of interest, due to its high reactivity with NaOH, PPh_3, and the alkyne that allows its use as a precursor in the synthesis of other organometallic palladium(II) compounds having ferrocenyl units. In particular, the reaction of **2** with NaOH revealed that the OH group could be easily deprotonated, giving [Pd{[(η^5-C_5H_3)CH═N(C_6H_4-2-CH_2O)]Fe(η^5-C_5H_5)}]$_2$ (**3**), which forms by the self-assembly of two cyclopalladated units in which the imino alcohol (**1b**) behaves as a [C(sp^2, ferrocene), N, O]$^{2-}$ terdentate ligand.

On the other hand, the studies presented show that the binding of the oxygen of the −OH group (in **2**) or of its deprotonated form (in **3**) clearly affects the reactivity of this sort of compound. The reactions of **2** and **3** with PPh_3 allow a fine tuning of the

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hapticity and mode of binding of **1b** ([C(sp^2, ferrocene), N]$^-$ (in **4**), [C(sp^2, ferrocene), N, O]$^-$ (in **5**), or [C(sp^2, ferrocene), N, O]$^{2-}$ (in **6**)) in the final products by the proper selection of the starting palladium(II) complex (**2** or **3**) and the experimental conditions. Additionally, a comparison of the results obtained indicated that the Pd−OH bond of **2** is more labile than the Pd−O$_{\text{alkoxo}}$ bond of **3**. A comparative study of the reactivity of the three types of palladacycles containing a [C(sp^2, ferrocene), N, X]$^-$ ligand revealed that the ease with which the insertion of the alkyne takes place depends on the nature of the heteroatom X (X = N, S, O).

It is well-known that palladium(II) compounds with a σ(Pd−O) bond, cyclopalladated complexes, and products formed by insertion of alkynes into the σ(Pd−C) bond have a variety of applications in several fields,[11,12,36−42] including organic and organometallic synthesis[36−41] and homogeneous catalysis;[11,12] the new products presented here appear to be excellent candidates to be studied in these fields.

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Supporting Information Available: Text giving experimental and spectroscopic details for all the compounds, ^{1}H NMR spectra of **3** (Figure S1), ^{57}Fe Mössbauer spectra of **2**−**4** (Figure S2), and full details of crystallographic analyses of **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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