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Cyclopalladation of 3-methoxyimino-2-phenyl-3H-indoles

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ABSTRACT

The direct cyclopalladation of 3-methoxyimino-2-(4-chlorophenyl)-3H-indole (**1a**) and 3-methoxyimino-2-phenyl-3H-indole (**1b**) results in the regioselective activation of the ortho σ[C(sp^2, phenyl)-H] bond affording (μ-OAc)$_2$[Pd{κ^2-*C*,*N*-C$_6$H$_3$-4R-1-(C$_8$H$_4$N-3′-NOMe)}]$_2$ (**2**) {R = Cl (**2a**) or H (**2b**)} that contain a central "Pd(μ-OAc)$_2$Pd" core. Compounds **2a** and **2b** reacted with triphenylphosphine (in a molar ratio PPh$_3$:**2** = 2) giving [Pd{κ^2-*C*,*N*-C$_6$H$_3$-4R-1-(C$_8$H$_4$N-3′-NOMe)}(OAc)(PPh$_3$)] (**3**) {R = Cl (**3a**) or H (**3b**)}. Treatment of **2a** or **2b** with a slight excess of LiCl in acetone produced the metathesis of the bridging ligands and the formation of (μ-Cl)$_2$[Pd{κ^2-*C*,*N*-C$_6$H$_3$-4R-1-(C$_8$H$_4$N-3′-NOMe)}]$_2$ (**4**) {R = Cl (**4a**) or H (**4b**)} with a central "Pd(μ-Cl)$_2$Pd" moiety. The reactions of **4a** or **4b** with deuterated pyridine (py-*d*$_5$) or triphenylphosphine gave the monomeric derivatives [Pd{κ^2-*C*,*N*-C$_6$H$_3$-4R-1-(C$_8$H$_4$N-3′-NOMe)}Cl(L)] with R = Cl or H and L = py-*d*$_5$ (**5**) or PPh$_3$ (**6**). The crystal structure of **6b**·1/2CH$_2$Cl$_2$ confirmed the mode of binding of the ligand, the nature of the metallated carbon atom and a *trans*-arrangement of the phosphine ligand and the heterocyclic nitrogen. Theoretical calculations on the free ligands are also reported and have allowed the rationalization of the regioselectivity of the cyclopalladation process.

1. Introduction

The synthesis and study of the reactivity and applications of cyclopalladated compounds containing N-donor ligands is one of the most attractive areas of organometallic chemistry [1]. Most of the cyclopalladation reactions described so far involved the activation of a σ(C–H) bond of organic compounds containing a nitrogen atom of either a functional group (*i.e.* amines, imines, oximes, etc.) or a heterocyclic system. It has been reported that when this type of ligand has two or more σ(C–H) bonds susceptible to metallate, the reaction proceeds with a high degree of regioselectivity [2,3]. The preferential activation of one of the σ(C–H) bonds of the ligand is dependent on a wide variety of factors such as the nature and hybridization of the carbon atom, and the relative orientation between the nitrogen atom and the σ(C–H) bond in the precursor. Furthermore, for Schiff bases R-CH = N-R′ containing a σ(Csp^2–H) bond susceptible to metallation in the two substituents (R and R′), the formation of the palladacycles containing the >C=N– functional group in the new ring is strongly preferred (*endo effect*) [2].

Most of the work described so far is focused on monofunctional organic ligands or compounds bearing two identical functional groups. Examples of cyclopalladation of oximes, benzimidazole, benzothiazole and benzoxazole have been reported [4]. However, the study of the cyclometallation of more complex ligands with two different functional groups and a greater number of σ(C–H) bonds susceptible to be metallated is not common. It is also noteworthy that: (a) palladium chemistry of indole derivatives is of interest for catalysis, medicinal and synthetic chemistry [5], (b) oxime palladacycles are used in homogeneous catalysis [6] and (c) the regioselective palladation of oximes [1a,6b] is useful in the preparation of natural products [6b]. In this paper we present a new family of ligands, containing simultaneously the indole moiety and the oxime functional group, and a study of their reactivity towards palladium(II). The new ligands (**1**) (Fig. 1) can exhibit two different configurations (*E* and *Z*, Fig. 1) and may bind to the metal through two different nitrogen donor atoms.

2. Results and discussion

2.1. The ligands

The new indole derivatives **1a** (R = Cl) and **1b** (R = H) have been prepared using a two-step straightforward sequence of reactions (Scheme 1), which consisted of the synthesis of the 3-hydroxyiminoindole derivatives previously described [7,8] followed by alkylation of the oxime group.

The procedure used for the alkylation of the precursors (3-hydroxyiminoindole derivatives) is based on that described by

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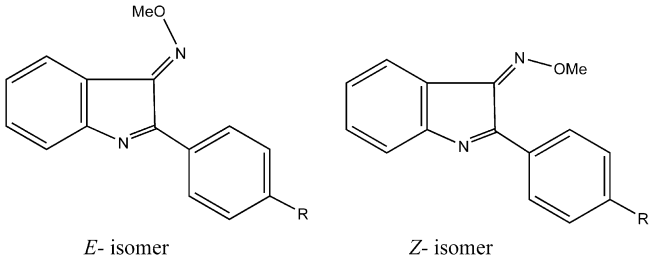


Fig. 1. Two possible isomers of the ligands C_6H_4-4R-1-[C_8H_4N-3′-NOMe] {R = Cl (**1a**) or H (**1b**)} selected for this study.

Pfeiffer and Bauer [9] for the alkylation of indigo in a two-phase system and it could be extended to the synthesis of related alkyl derivatives.

Elemental analyses of **1a** and **1b** were consistent with the proposed formulae and their mass spectra showed a peak at *m/z* = 271.1 (for **1a**) and at 237.1 (for **1b**) that agree with those expected for the corresponding $[M+H]^+$ cations.

As mentioned above, in compounds **1a** and **1b**, two different arrangements between the OMe group and the >C=N– bond of the heterocycle, could be expected {(*E*) and (*Z*) isomers, Fig. 1}. Their ^{1}H NMR spectra showed a singlet due to the OMe unit centered at δ = 4.34 ppm (for **1b**) or at δ = 4.32 ppm (for **1b**). This suggested that only one isomer was present in solution. For **1a**, a set of four doublets (of relative intensities 2:2:1:1) and two triplets (whose integration corresponded to one proton each) were detected in the range: 7.20–8.60 ppm. The most intense doublets were assigned to the pairs of protons (H^{11} and H^{15}) and (H^{12} and H^{14}). For **1b**, one of these signals was more complex due to the overlapping of the resonance of the H^{13} proton.

The unequivocal assignment of the signals due to the ^{1}H and ^{13}C nuclei of the bicyclic system [(H^5–H^8) and (C^2–C^9), respectively] required the use of two dimensional {^{1}H–^{13}C}-HSQC and HMBC experiments. In particular, in the {^{1}H–^{13}C}-HMBC spectra the existence of a cross-peak between the signal arising from the H^{11} proton and those of the C^{12} carbon nuclei and quaternary C^2 and C^{10} carbon atoms permitted the assignment of the chemical shift of C^2. The doublet at δ = 8.02 ppm showed cross-peaks with two quaternary carbons and none of them was coincident with C^2. This allowed us to assign this signal to the H^5 proton of indole unit and the resonances of the C^3 and C^4 carbon atoms. The identification of the remaining signals detected in the ^{1}H spectra of **1a** and **1b** was achieved with the aid of {^{1}H–^{1}H}-COSY and NOESY experiments.

{^{1}H–^{1}H}-NOESY and ROESY spectra did not allow us to clarify the configuration of the oxime. However, the use of molecular models for the *E* and *Z* isomers of **1a** and **1b**, revealed that in the *Z* isomer, the oxygen atom would be very close to the phenyl ring and consequently this would reduce the free rotation of the phenyl ring around the C^2–C^{10} bond and this suggested that the species present in solution is the *E* isomer. In order to confirm this hypothesis, we decided to undertake theoretical calculations for the *Z* and *E* isomers of **1a** and **1b** using the AM1 program [10] implemented in the SPARTAN 5.0 package [11]. The most relevant results obtained from this study are: (a) in optimized geometries of the *E* and *Z* isomers of **1a** and **1b**, the phenyl ring adopts different orientations (Fig. 2) and (b) the total energy of the *Z* isomer is {1.89 Kcal/mol (for **1a**) and 1.99 Kcal/mol (for **1b**)} greater than that of the *E* isomer. In view of these results we postulate that **1a** and **1b** adopt the *E* configuration in solution.

Once the ligands were completely characterized, we studied their reactivity towards palladium(II). It should be noted that despite compounds **1a** and **1b** have the *E*-configuration, examples of the *E/Z* isomerizations of Schiff bases during the reaction with transition metal salts or complexes have been reported [12] and consequently the isomerization of the ligand can not be excluded.

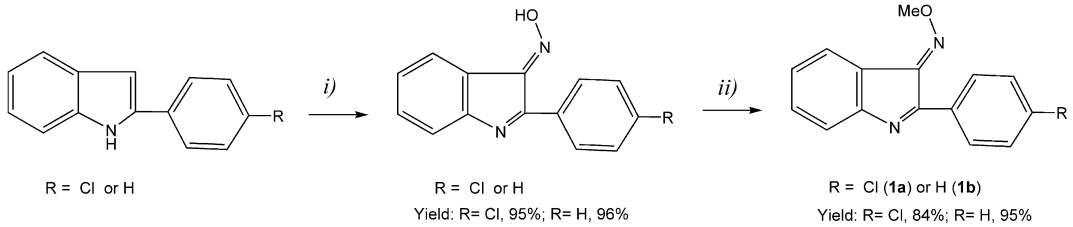
2.2. Palladium(II) complexes

When the corresponding ligand (**1a** or **1b**) was treated with the equimolar amount of $Pd(OAc)_2$ in a 10:1 mixture of acetic acid and acetic anhydride under reflux for 3.5 h, the formation of metallic palladium was observed. Filtration through *Celite* followed by concentration of the filtrate to dryness and the subsequent chromatography on SiO_2 column gave a deep-garnet solid in both cases (hereinafter referred to as **2a** and **2b**, respectively) (Scheme 2). Compounds **2a** and **2b** were characterized by elemental analyses, mass spectrometry, infrared spectroscopy and mono- [^{1}H and ^{13}C{^{1}H}] and two-dimensional [{^{1}H–^{13}C} heteronuclear correlations HSQC and HMBC and {^{1}H–^{1}H} NOESY] NMR experiments. The infrared spectra of **2a** and **2b** showed two bands at 1559 and 1410 cm^{-1} (for **2a**) or at 1572 and 1419 cm^{-1} (for **2b**) that were indicative of the presence of the OAc^- ligand. The separation between these two absorptions, suggests, according to the bibliography [13] that the OAc^- behaved as a (*O,O′*) bridging ligand.

Elemental analyses of **2a** and **2b** were consistent with those expected for the di-μ-acetato bridged cyclopalladated complexes: (μ-OAc)$_2$[Pd{κ^2-*C,N*-C_6H_3-4R-1-(C_8H_4N-3′-NOMe)}]$_2$ and the mass spectra showed a peak at *m/z* = 753.9 (for **2a**) or 684.0 (for **2b**), which correspond to the $[M\text{-}OAc]^+$ cations.

^{1}H and ^{13}C{^{1}H} NMR studies of **2a** and **2b** in $CDCl_3$ at room temperature showed two sets of superimposed signals of relative intensities 2.8:1.0 (for **2a**) and 2.7:1.0 (for **2b**), which could be indicative of the presence of two isomeric species [hereinafter referred to as $\mathbf{2a_I}$ and $\mathbf{2a_{II}}$ (for **2a**) and $\mathbf{2b_I}$ and $\mathbf{2b_{II}}$ (for **2b**)] in solution. Examples of the coexistence of two isomers of related dimeric compounds (μ-OAc)$_2$[Pd(κ^2-*C,N*-ligand)]$_2$ have been reported previously [14–16].

^{1}H NMR spectra of **2a** and **2b**, showed that the chemical shifts of the OMe protons were very similar to those of the corresponding



i) $NaNO_2$, CH_3COOH/DMF. *ii)* NaOH, CH_2Cl_2, CH_3I.

Scheme 1.

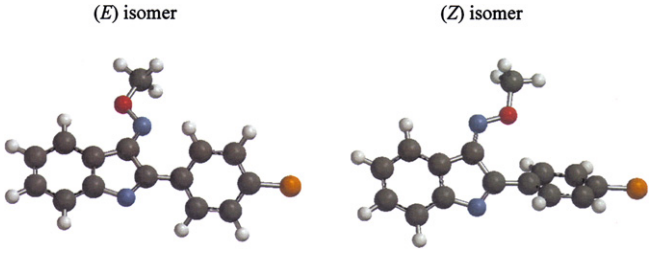


Fig. 2. Optimized geometries of the *E* and *Z* isomers of ligand **1a**.

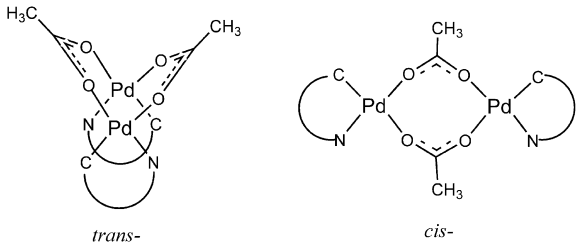


Fig. 3. Schematic view of the *trans*- isomers of cyclopalladated complexes $(\mu\text{-OAc})_2[Pd\{\kappa^2\text{-}C,N\text{-ligand}\}]_2$ with an *open-book* type structure and of the *cis*-isomers of these products.

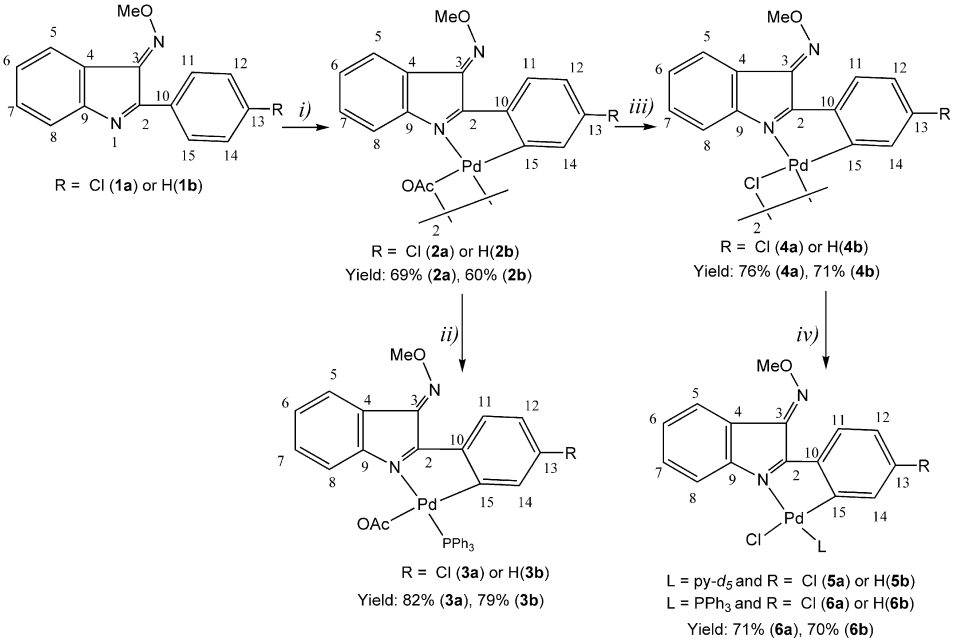
ligand for all the isomers. This finding suggested that none of the two donor atoms of oxime group was bound to the palladium(II) in the pairs (**2a$_I$**, **2a$_{II}$**) and (**2b$_I$**, **2b$_{II}$**). In the $^{13}C\{^1H\}$ NMR spectra of the major isomers (**2a$_I$**, **2b$_I$**) the intensity of the signal from the C^{15} atom decreased substantially and shifted towards low-field (ca. 21 ppm) in relation to the corresponding free ligand. In addition, no evidences of any cross-peak between the resonance of the C^{15} nuclei and those of the aromatic protons was detected in the $[^1H–^{13}C]$-HSQC spectra of any of the isomers. According to the literature [17], these findings suggested the existence of a $\sigma(Pd–C^{15})$ bond in the complexes. In view of the results obtained from the characterization data available, we concluded that in **2a$_I$** and **2b$_I$** the ligands behaved as a bidentate $[C(sp^2, \text{phenyl}), N_{indole}]^-$ group. The studies of the reactivity of **2** (*vide infra*) allowed us to confirm that in the minor isomers **2a$_{II}$** and **2b$_{II}$** the ligands exhibited the same hapticity and mode of binding than in **2a$_I$** and **2b$_I$**.

It is well-known that the dimeric cyclopalladated complexes $(\mu\text{-OAc})_2[Pd(\kappa^2\text{-}C,N\text{-ligand})]_2$ may exhibit different isomeric forms [14–16,18]. In these isomers, the two halves of the molecule could be in a *trans*- or *cis*-arrangement (Fig. 3). It has been reported that for the *trans*-isomers the resonance of the methyl groups of the bridging ligands appear as one singlet, but it splits into two singlets in the *cis*-isomers [14,15]. For **2a$_I$** and **2b$_I$**, one singlet [at 2.29 (for **2a$_I$**) or 2.26 ppm (for **2b$_I$**)] was observed in the ^1H NMR spectra; thus, we assumed that in these species the two halves were in a *trans*-arrangement.

Most of the acetato-bridged cyclopalladated dimers described before show a folded structure {commonly known as *open-book* structure (Fig. 3)} in solution as well as in the solid state [14–16,18]. On this basis, we assumed that in the major isomers (**2a$_I$** and **2b$_I$**) the relative orientation of the acetato ligands corresponds to the *open-book* type with a C_2 symmetry. $\{^1H–^1H\}$ NOESY and ROESY spectra of **2a** and **2b** did not provide evidences of the existence of any interconversion between **2a$_I$** or **2b$_I$** and the minor isomers (**2a$_{II}$** and **2b$_{II}$**, respectively). Moreover, the molar ratio between the two isomers did not vary substantially when the spectrum was recorded with a Bruker 250 MHz instrument {molar ratios **2a$_I$:2a$_{II}$** = 2.76 and **2b$_I$: 2b$_{II}$** = 2.70}.

For the minor isomers (**2a$_{II}$** and **2b$_{II}$**) most of the signals appeared duplicated in the ^1H NMR spectra and the chemical shifts of the resonances from the methyl protons of the OAc^- ligand were very similar to those reported previously for cyclopalladated complexes $(\mu\text{-OAc})_2[Pd(\kappa^2\text{-}C,N\text{-ligand})]_2$ with a *cis*-arrangement of the two halves of the molecule [14,15].

On the other hand, the $^{31}P\{^1H\}$ NMR spectra recorded after the addition of PPh_3 to a solution of **2a** or **2b** in $CDCl_3$ (in a PPh_3:Pd molar ratio = 2) showed only a singlet at δ = 42.5 and 43.7 ppm for **2a** and **2b**, respectively. Besides, only a single set of signals



i) $Pd(OAc)_2$, CH_3COOH, reflux 3.5h. *ii)* PPh_3, $CDCl_3$. *iii)* LiCl, acetone. *iv)* py-d_5, $CDCl_3$ or PPh_3, CH_2Cl_2

Scheme 2.

was observed in the ^{1}H NMR spectra and the resonance of the protons of the OAc^- ligand appeared as a singlet at higher fields than in **2a** and **2b**. This could be attributed to the proximity of the phenyl rings. All these findings indicate that the two isomeric species present in solution gave the same final products (**3a** or **3b**). These products were identified as [Pd{κ^2-*C*,*N*-C_6H_3-4R-1-(C_8H_4N-3′-NOMe)}(OAc)(PPh_3)] {R = Cl (**3a**) or H (**3b**)} (Scheme 2). These results confirmed that the nature of the metallated carbon is identical in the two pairs of isomers {(**2a$_I$**, **2a$_{II}$**) and (**2b$_I$**, **2b$_{II}$**)}.

Similar results were obtained when this reaction was performed using the crude of the reaction obtained (before the work-up of the column), but in this case it was necessary to filter the solution through *Celite*. In these cases, ^{1}H and ^{31}P{^{1}H} NMR spectra obtained were identical to of pure **2a** or **2b**. This is a proof of the inexistence of any other type of palladacycle in the crude of the reaction and indicates that the formation of **2** is regioselective.

Treatment of **2** with a slight excess of LiCl in acetone produced the formation of the di-μ-chloro-bridged cyclopalladated derivatives (μ-Cl)$_2$[Pd{κ^2-*C*,*N*-C_6H_3-4R-1-(C_8H_4N-3′-NOMe)}]$_2$ {R = Cl (**4a**) or H (**4b**)} (Scheme 2). Elemental analyses of **4a** and **4b** were consistent with the proposed formulae and the mass spectra showed the peak due to the corresponding cation [M-Cl]$^+$ (at *m*/*z* = 788.9 and 690.9 for **4a** and **4b**, respectively). Unfortunately, the low solubility of **4a** and **4b** in most of the common solvents used for NMR studies (*i.e.* acetone-d_6, $CDCl_3$, CD_2Cl_2) did not allow us to characterize them in solution. However, the addition of a few drops of deuterated pyridine (py-d_5) to a suspension of **4a** or **4b** in $CDCl_3$, produced the complete dissolution of the palladium(II) complex and the ^{1}H NMR spectra of the resulting deep-garnet solutions indicated the presence of the monomeric derivatives [Pd{κ^2-*C*,*N*-C_6H_3-4R-1-(C_8H_4N-3′-NOMe)}Cl(py-d_5)] {R = Cl (**5a**) or H (**5b**)} (Scheme 2).

Similarly, the addition of PPh_3 to suspensions of **4a** or **4b** (in a molar ratio PPh_3:**4** = 2) in CH_2Cl_2 produced the splitting of the "Pd(μ-Cl)$_2$Pd" bridges and the formation of [Pd{κ^2-*C*,*N*-C_6H_3-4R-1-(C_8H_4N-3′-NOMe)}Cl(PPh_3)] {R = Cl (**6a**) or H (**6b**)} (Scheme 2). Compounds **6a** and **6b** were characterized by elemental analyses, mass spectrometry, infrared spectroscopy and mono- and two-dimensional NMR spectra. The most relevant feature observed in the ^{1}H NMR spectra of **6a** (or **6b**) is the downfield shift of the signal arising from the H^8 proton when compared with that of **3a** (or **3b**). This variation could be attributed to the proximity between the C^8–H^8 bond and the chloride ligand (we will return to this point later on). The position of the signals observed in the ^{31}P{^{1}H} NMR spectra of **6a** and **6b** in $CDCl_3$ {δ = 44.2 (for **6a**) and 45.8 ppm (for **6b**)} is consistent with data reported for related palladacycles of general formula [Pd(κ^2-*C*,*N*-ligand)Cl(PPh_3)] [19] in which the phosphine is in a *cis*-arrangement to the metallated carbon atom and this is in good agreement with the so-called *transphobia effect* [20].

2.3. Crystal and molecular structure of 6b·1/2CH_2Cl_2

The structure features two non-equivalent molecules of [Pd{κ^2-*C*,*N*-C_6H_4-1-(C_8H_4N-3′-NOMe)}Cl(PPh_3)] **6b** (hereinafter referred to as **I** and **II**) and CH_2Cl_2. A selection of bond lengths and angles is presented in Table 1 and the ORTEP plot of molecule **I** is depicted in Fig. 4.

In molecules **I** and **II** the palladium atoms {Pd(1) and Pd(2), respectively} are located in a slightly distorted square-planar environment and they are bound to the heterocyclic nitrogen {N(11) (in **I**) and N(21) (in **II**)}, the *ortho* carbon atom {C(11) and C(21) in **I** and **II**, respectively} of the indole moiety, thus confirming that the mode of binding of **1b** is [C(sp^2,phenyl), N_{indole}]$^-$. One chloride {Cl(1) or Cl(2)} and a phosphorus atom {P(1) and P(2), respectively} fulfill the coordination sphere. Bond lengths and angles around the palladium(II) atoms are similar to those reported for most cyclopalladated complexes of the type [Pd(κ^2-*C*,*N*-ligand)Cl(PPh_3)] [2d,4b,16,19,20]. The values of the bond angles: P(1)–Pd(1)–C(11) and P(1)–Pd(1)–C(21) {93.63(12)° and 95.29(13)°, respectively}, indicate that the phosphine ligand is in a *cis*-arrangement to the metallated carbon which is in good agreement with the *transphobia effect* [20].

Table 1
Selected bond lengths (in Å) and angles (°) for the two non-equivalent molecules (**I** and **II**) found in the crystal structure of compound **6b**·1/2CH_2Cl_2 (standard deviations are given in parenthesis)

Molecule **I**		Molecule **II**	
Bond lengths			
Pd(1)–C(11)	2.008(4)	Pd(2)–C(21)	2.014(4)
Pd(1)–N(11)	2.105(3)	Pd(2)–N(21)	2.113(3)
Pd(1)–P(1)	2.2627(19)	Pd(2)–P(2)	2.2702(16)
Pd(1)–Cl(1)	2.3636(15)	Pd(1)–Cl(2)	2.363(3)
C(11)–C(16)	1.444(5)	C(21)–C(26)	1.432(5)
C(16)–C(17)	1.464(5)	C(26)–C(27)	1.445(5)
N(11)–C(17)	1.320(5)	N(21)–C(27)	1.332(5)
C(17)–C(18)	1.451(5)	C(27)–C(28)	1.487(5)
C(18)–C(19)	1.438(5)	C(28)–C(29)	1.447(6)
C(19)–C(110)	1.393(6)	C(29)–C(210)	1.406(6)
C(110)–C(111)	1.404(7)	C(210)–C(211)	1.342(7)
C(111)–C(112)	1.355(7)	C(211)–C(212)	1.396(7)
C(112)–C(113)	1.384(6)	C(212)–C(213)	1.395(7)
C(113)–C(114)	1.399(6)	C(213)–C(214)	1.373(6)
C(114)–N(11)	1.414(5)	C(214)–N(21)	1.434(5)
C(18)–N(12)	1.301(5)	C(28)–N(22)	1.277(5)
N(12)–O(11)	1.376(5)	N(22)–O(21)	1.388(4)
O(11)–C(115)	1.419(6)	O(21)–C(215)	1.404(6)
Bond angles			
Cl(1)–Pd(1)–P(1)	92.17(6)	Cl(2)–Pd(2)–P(2)	90.40(7)
P(1)–Pd(1)–C(11)	93.63(12)	P(2)–Pd(2)–C(21)	95.29(13)
C(11)–Pd(1)–N(11)	81.45(15)	C(21)–Pd(2)–N(21)	80.94(15)
N(1)–Pd(1)–Cl(1)	93.41(10)	N(21)–Pd(2)–Cl(2)	93.41(11)
Pd(1)–N(11)–C(17)	113.1(3)	Pd(2)–N(11)–C(27)	112.3(2)
Pd(1)–N(11)–C(114)	138.9(3)	Pd(2)–N(21)–C(214)	108.9(3)
Pd(1)–C(11)–C(16)	111.6(3)	Pd(2)–C(21)–C(26)	113.7(3)
C(11)–C(16)–C(17)	116.3(3)	C(21)–C(26)–C(27)	114.6(3)
C(16)–C(17)–N(11)	116.0(3)	C(26)–C(27)–N(21)	118.3(3)
N(11)–C(17)–C(18)	110.2(3)	N(21)–C(27)–C(28)	109.5(3)
C(17)–C(18)–C(19)	105.5(3)	C(27)–C(28)–C(29)	105.2(3)
C(18)–C(19)–C(114)	105.9(3)	C(28)–C(29)–C(214)	107.0(3)
C(18)–N(12)–O(11)	110.7(3)	C(28)–N(22)–O(21)	113.7(3)
N(12)–O(11)–C(115)	111.2(4)	N(22)–O(21)–C(215)	110.7(4)

Each one of the two molecules of **6b** contain a [6.5.5.6] tetracyclic system formed by the indole unit, a five-membered palladacycle and the phenyl ring. The indole and the phenyl rings of the 2-phenylindole unit are practically coplanar {angles between these planes are 1.0(3)° (in **I**) and 1.9(3)° (in **II**)}. The metallacycles are practically planar and form angles of 5.1(2)° (in **I**) and 2.6(2)° (in **II**) with the phenyl ring attached to them.

The values of the torsion angles O(11)–N(12)–C(18)–C(17) and O(21)–N(22)–C(28)–C(27) (178.10° and 179.17°, respectively) indicate that in **I** and **II** the oxime moiety adopts the *E* configuration. For this arrangement of substituents: (a) the nitrogen atoms {N(12) in **I** or N(22) in **II**} are close to the σ(C–H) bonds of the *ortho* site of phenyl unit and (b) the distance between the oxygen atom O(1) {or O(2)} and the C(110)–H(110) {or the C(210)–H(210)} bond (2.47 Å and 2.46 Å) suggests a weak C–H···O hydrogen bond.

On the other hand, the separation between the chloride ligand {Cl(1) or Cl(2)} and the C–H bond of the nearest site of the indole ring {C(113)–H(113) and C(213)–H(213) in molecules **I** and **II**} (2.63 and 2.51 Å in **I** and **II**, respectively) is smaller than the sum of their van der Waals radii {Cl (1.75 Å) and H (1.20 Å)} [21], thus indicating an intramolecular non-conventional weak hydrogen bond (C–H···Cl). This interaction could be the cause of the downfield shift detected for the H^8 proton of **6a** and **6b**, when compared with its position in **3a** and **3b**, respectively.

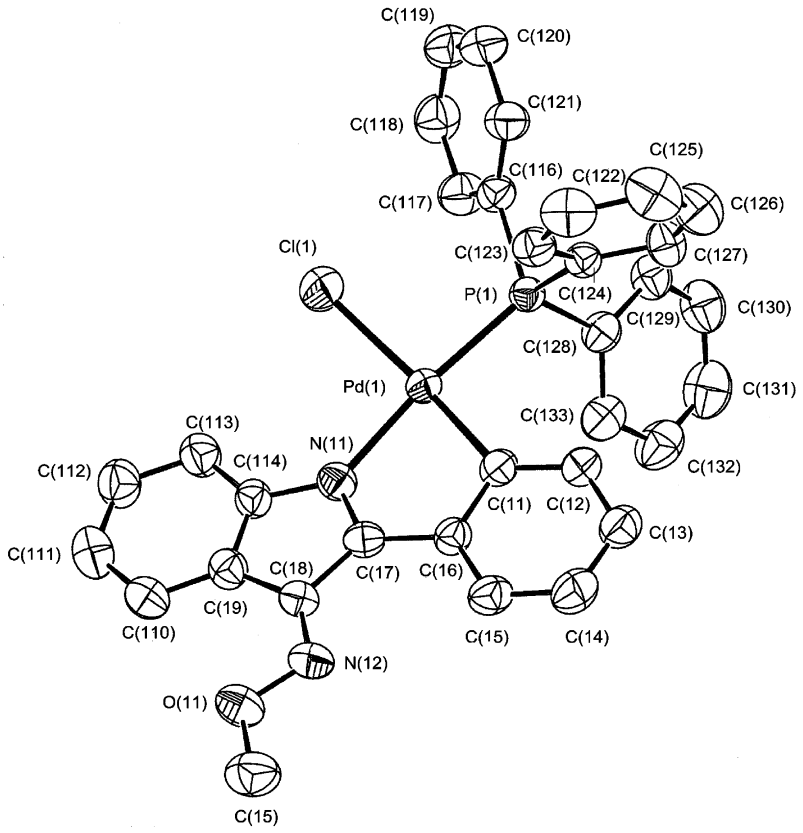


Fig. 4. ORTEP plot of molecule **I** found in the crystal structure of compound **6b**·1/2CH_2Cl_2. Hydrogen atoms as well as the molecule of CH_2Cl_2 have been omitted for clarity.

In the crystal, molecules **I** and **II** are associated in a *head to tail* arrangement (Fig. 5) in such a way that the C(232)–H(232) bond of the phosphine ligand of **II** is close to the π system of the indole unit of a neighbouring molecule **I** [22]. This distribution of molecules, connected by CH···π interactions [23], leads to a chain that stacks along the *b*-axis {[0 1 0] plane}.

Since: (a) it is well-known that in the cyclopalladation of N-donor ligands, the metallacycle formation requires the coordination of the nitrogen ligands followed by the electrophilic attack of the palladium(II) species formed to the carbon atom [12a,24] and (b) the ligands under study contain two different nitrogen atoms (N_{indole} and N_{oxime}), the first key point to rationalize the formation of the new palladacycles with a bidentate [C(sp^2,phenyl), N_{indole}]$^-$ ligand should be related to the coordination abilities of the two nitrogen atoms. The use of molecular models as well as the optimized geometries of the free ligands in the *E* and *Z* forms (Fig. 2) suggested that the accesibility of the palladium to the oxime nitrogen would be more hindered than for the heterocyclic nitrogen. In addition, molecular orbital calculations for **1a** and **1b** in the *E* and *Z* forms revealed that in both cases the HOMO orbital (Fig 6) is a combination of the atomic orbitals of the N_{indole} atom and π-bonding orbitals of the indole ring and the phenyl unit. Besides, the comparison of the Mulliken charges on the two nitrogen atoms indicates that the N_{indole} has higher electronic density than the N_{oxime} atom [25]. All these findings suggest that the binding of the ligand to the palladium would occur preferentially through the N_{indole} atom and this reduces to two the number of possible metallacycles.

After the coordination of the palladium to the N_{indole} atom of **1a** or **1b**, the activation of the σ[C(sp^2,phenyl)-H] bond gives palladacycles with a σ{Pd–Csp^2,phenyl)} bond, which are more stable than those arising from the metallation of the indole unit due to the smaller ring strain of the five-membered palladacycles compared to that of the four-membered metallacycles.

2.4. Conclusions

The results presented here show that the cyclopalladation of the two 3-methoxyimino-2-phenyl-3H-indole compounds (**1a** and **1b**) is regioselective and gives five-membered metallacycles containing simultaneously a σ(Pd–N_{indole}) and a σ[Pd–C(sp^2,phenyl)] bond in which the oxime unit exhibits the *E* form. Furthermore, theoretical calculations have allowed us to rationalize the preferential formation of these five-membered palladacycles and the optimized geometries of the two forms of the ligands reveal that in the *E* form of **1a** and **1b**: (a) the oxygen of the =NOMe moiety is close to one of hydrogen atoms of the indole ring and (b) the nitrogen is proximal to a hydrogen of the phenyl ring. The crystal structure of **6b**·1/2CH_2Cl_2 showed that this arrangement of groups prevails in the palladacycles allowing the existence of weak C–H···X (X = O and N) interactions.

Finally, due to the ongoing interest of oxime ligands, their palladium(II) derivatives or their analogues with indole units in homogeneous catalysis and organic synthesis [5,6], the new compounds presented in this work appear to be excellent candidates for further studies in these fields.

3. Experimental

3.1. Materials and methods

2-(4-Chlorophenyl)indole and 2-phenylindole, tricaprylmethylammonium chloride (*Aliquat336*), $Pd(OAc)_2$, LiCl and PPh_3, glacial acetic acid and acetic anhydride were obtained from commercial

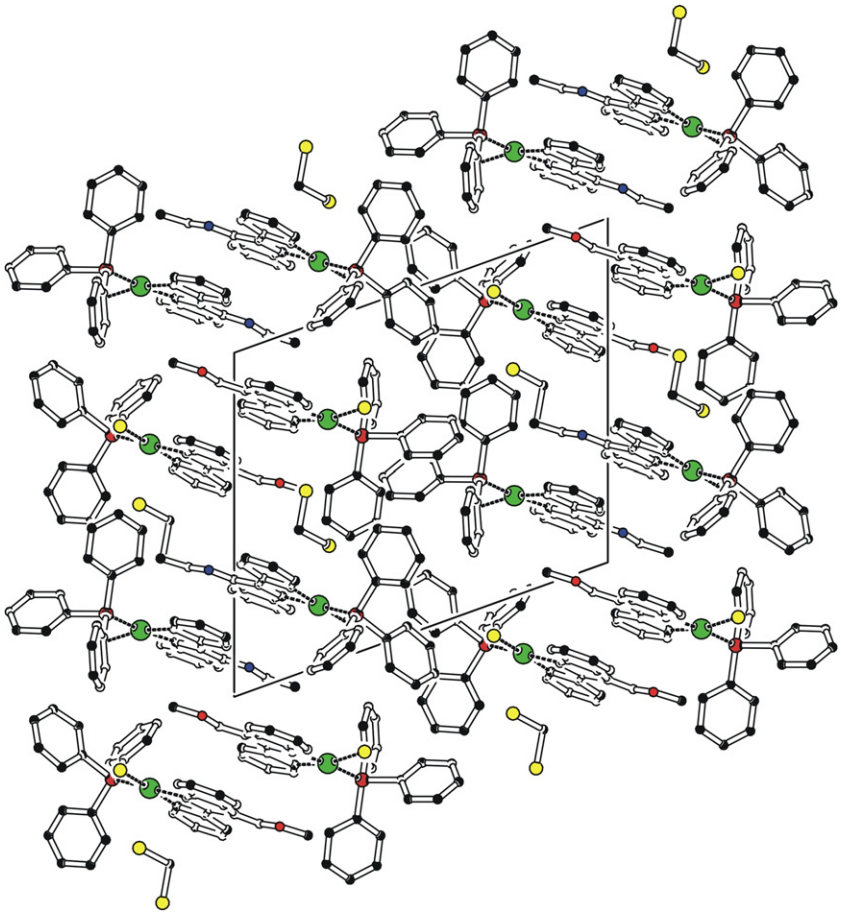


Fig. 5. Schematic view of the relative arrangement of the two non-equivalent molecules of **6b** in the crystal. The molecules of CH_2Cl_2 are shown but hydrogen atoms have been omitted for clarity.

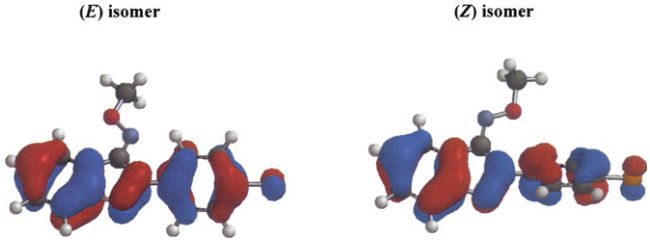


Fig. 6. HOMO orbitals of the *E* and *Z* isomers of ligand **1a.**

sources and used as received. Solvents were dried and distilled before use [26]. Elemental analyses were carried out at the Serveis de Recursos Cientifics i Tècnics (*Universitat Rovira i Virgili*). Mass spectra (ESI^+) were performed at the Servei d'Espectrometria de Masses (*Universitat de Barcelona*). Infrared spectra were obtained with a Nicolet 400FTIR instrument using KBr pellets. Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Mercury-400 MHz instrument. $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian-Unity-300 instrument using $P(OMe)_3$ as reference [$\delta(^{31}P) = 140.17$ ppm]. High resolution ^1H NMR spectra and the two-dimensional [$\{^1H–^1H\}$-NOESY, ROESY and COSY and $\{^1H–^{13}C\}$-HSQC and HMBC] experiments were registered with a Varian VRX-500 or a Bruker Avance DMX-500 MHz instruments at 298 K. The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz. Except where quoted, the solvent for the NMR experiments was $CDCl_3$ (99.9%) and $SiMe_4$ was used as reference.

3.2. Preparation of the compounds

3.2.1. Synthesis of C_6H_4-4R-1-(C_8H_4N-3′-NOH) {R = Cl or H)}

The synthesis of these products was previously described but the procedure used in this work is not identical to that reported before [7]. 3-Hydroxyimino-2-(4-chlorophenyl)-3H-indole was prepared as follows: 0.81 g (1.2×10^{-2} mol) of $NaNO_2$ was added under continuous stirring to a solution containing 2-(4-chlorophenyl)indole (2.50 g, 1.1×10^{-2} mol), acetic acid (20 mL) and dimethylformamide (8 mL). The resulting solution was stirred at room temperature for 3 h and then poured onto 100 mL of H_2O. The solid formed was collected by filtration, washed with water and dried in vacuum. Yield: 2.68 g (95%).

3-Hydroxyimino-2-phenyl-3H-indole was prepared similarly, but in this case starting material was 2-phenylindole. Yield: 2.26 g (96%). These precursors were used in the next step without any further purification.

3.2.2. Synthesis of C_6H_4-4R-1-(C_8H_4N-3′-NOMe) {R = Cl (**1a**) or H (**1b**)}

Compound **1a** was prepared as follows: to a solution containing 3-hydroxyimino-2-(4-chlorophenyl)-3H-indole (1.10 g, 4.28×10^{-3} mol), Aliquat 336 (800 mg, 1.9×10^{-3} mol) and NaOH (12 mL of a 40% solution) in CH_2Cl_2 (125 mL), methyl iodide (2.28 g, 1 mL, 16×10^{-3} mol) was added. The reaction mixture was stirred at room temperature for 24 h. After this period water (75 mL) was added and the resulting solution was transferred to a separating funnel. The organic layer was separated and the aqueous one was afterwards extracted with 20 mL of CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered and

concentrated. Further purification by flash chromatography on neutral alumina using diethylether as eluant produced the release of an orange band that was collected and concentrated to dryness on a rotary evaporator giving **1a**. This product was collected and dried in vacuum for one day. Yield: 0.97 g (84%)}.

Ligand **1b** was isolated as a deep-orange solid with the same procedure as that described for **1a** but using 3-hydroxyimino-2-phenyl-3H-indole (0.89 g, 4×10^{-3} mol) as starting material. Yield: 0.90 g (95%). *Characterization data* for **1a**: Elemental analyses calc. for $C_{15}H_{11}ClN_2O$: C, 66.55; H, 4.10; N, 10.35. Found: C, 66.47; H, 4.15; N, 10.12%. MS (ESI$^+$): m/z = 271.1 [M+H]$^+$. IR data: 2937(m), 1592(s), 1479(m), 1442(m), 1402(s), 1270(w), 1094(s), 1027(s), 951(m), 835(m) and 755(s). ^{1}H NMR data [27]: δ = 4.34[s, 3H, OMe], 8.02[d, 1H, J = 7.5, H^5], 7.24[td, J = 7.5 and 1.0, H^6], 7.40[td, 1H, J = 7.5 and 1.0, H^7], 7.53[d, 1H, J = 7.5, H^8], 8.26[dd, 2H, J = 9.2 and 2.0, H^{11} and H^{15}], 7.44[dd, 2H, J = 9.2 and 2.0, H^{12} and H^{14}]. ^{13}C{^{1}H} NMR data [27]: δ = 65.1(OMe), 165.2(C^2), 157.4(C^3), 138.4(C^4), 127.6(C^5), 132.2(C^6), 126.3(C^7), 121.2(C^8), 122.8(C^9), 155.1(C^{10}), 131.7(C^{11} and C^{15}), 132.4(C^{12} and C^{14}) and 123.3(C^{13}). For **1b**: Elemental analyses calc. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.12; H, 5.055; N, 11.72%. MS (ESI$^+$): m/z = 237.10[M+H]$^+$. IR data: 2940(m), 1602(s), 1512(m), 1436(m), 1349(s), 1270(w), 1107(s), 1028(s), 954(m), and 755(s). ^{1}H-NMR data [27]: δ = 4.32[s, 3H, OMe], 8.02[d, 1H, J = 7.7, H^5], 7.23[td, J = 7.7 and 1.5, H^6], 7.44[td, 1H, J = 7.7 and 1.5, H^7] [28], 7.55[d,1H, J = 7.7, H^8] [28], 8.23[dd, 2H, J = 9.2 and 2.0, H^{11} and H^{15}], 7.48–7.60[br.m, 3H, H^{12}, H^{13} and H^{14}]. ^{13}C{^{1}H} NMR data [27]: δ = 65.2(OMe), 166.1(C^2), 154.5(C^3), 139.2(C^4), 127.6(C^5), 132.6(C^6), 131.3(C^7), 121.4(C^8), 122.6(C^9), 155.6(C^{10}), 130.2(C^{11} and C^{15}), 128.8(C^{12} and C^{14}) and 127.9(C^{13}).

3.2.3. Synthesis of (μ-OAc)$_2$[Pd{κ^2-C,N-C$_6$H$_3$-4R-1-(C$_8$H$_4$N-3′-NOMe)}]$_2$ {R = Cl (**2a**) or H (**2b**)}

Compound **1a** (294 mg, 1.09×10^{-3} mol) or **1b** (257 mg, 1.09×10^{-3} mol) was dissolved in a mixture of glacial acetic acid and acetic anhydride (10:1), then 245 mg (1.09×10^{-3} mol) of Pd(OAc)$_2$ was added. The reaction mixture was heated at 90 °C for 3.5 h and then allowed to cool at room temperature. The resulting deep-brown mixture was filtered through Celite and the filtrate was concentrated to dryness on a rotary evaporator. Afterwards the nearly black solution was dissolved in the minimum amount of CH_2Cl_2 and passed through a SiO_2 column (2.0 cm × 6.5 cm). The column was first eluted with CH_2Cl_2 to remove traces (8 mg) of a minor pale yellow by-product. The subsequent elution with a CH_2Cl_2:MeOH mixture (100:0.25) produced the release of a garnet band that was collected and concentrated to dryness on a rotary evaporator giving **2a** and **2b**, respectively. The deep-red solid formed was collected and dried in vacuum for one day. Yields: 302 mg (69%) for **2a** and 243 mg (60%) for **2b**. *Characterization data* for **2a**: Elemental analyses calc. for $C_{32}H_{23}Cl_2N_4O_4Pd_2$: C, 47.37; H, 2.86; N, 6.91. Found: C, 47.12; H, 3.00; N, 6.8%. MS (ESI$^+$): m/z = 753.9 [M-OAc]$^+$. IR data: 2933(m), 1573(s), 2559(s, OAc), 1465(m), 1426(s, OAc), 1080(m), 1017(s), 752(m). Solution studies: two different isomers (**2a$_I$** and **2a$_{II}$** coexisted in a 2.8:1.0 ratio) in $CDCl_3$ at room temperature. ^{1}H NMR data for **2a$_I$** [27]: δ = 2.29[s, 6H, 2CH$_3$(OAc)], 4.37[s, 6H, 2OMe], 7.65[d, 2H, J = 7.2, 2H^5], 7.13[td, 2H, J = 7.2 and 1.0, 2H^6], 7.32[td, 2H, J = 7.2 and 1.0, H^7], 7.30[d, 2H, J = 7.2, 2H^8], 7.43[dd, 2H, J = 8.0 and 1.0, 2H^{11}], 6.52[dd, 2H, J = 8.0 and 1.0, 2H^{12}], 6.60[d, 2H, J = 8.0, 2H^{14}]; for **2a$_{II}$**: (in this case most of the signals appeared duplicated suggesting that the two halves were not equivalent) δ = 2.13[s, 3H, OAc], 2.30[s, 3H, OAc], 4.36[br.s, 6H, OMe], 7.50 and 7.48[d, 2H, J = 7.2, 2H^5], 7.18[br., 2H, 2H^6], 7.08 and 7.20[br., 2H, J = 7.2 and 1.0, 2H^8], 6.77[br.d, 2H, J = 8.0 and 1.0, H^{12}], 6.89[br.s, 2H, 2H^{14}] [29], the resonances due to H^7 and H^{11} appeared partially masked by the signals due to the same protons of **2a$_I$**. ^{13}C{^{1}H} NMR data for **2a$_I$** [27]: δ = 65.3(OMe), 170.5(C^2), 156.1(C^3), 136.9(C^4), 127.3(C^5), 132.5(C^6), 128.6(C^7), 124.7(C^8), 119.0(C^9), 151.0(C^{10}), 131.9(C^{11}), 132.4(C^{12}), 124.7(C^{13}), 131.9(C^{14}), 150.9(C^{15}), 24.91[CH$_3$(OAc)] and 182.1(>CO$_2$(OAc)]; for **2a$_{II}$** (selected data): 65.3(OMe), 24.9 and 25.3[CH$_3$(OAc)], 181.3 and 183.0 [>CO$_2$(OAc)]. For **2b**: Elemental analyses calc. for $C_{32}H_{25}N_4O_4Pd_2$: C, 51.77; H, 3.39; N, 7.55. Found: C, 51.59; H, 3.45; N, 7.42%. MS (ESI$^+$): m/z = 684.0 [M-OAc]$^+$. IR data: 2963(m), 1608(s), 1572(s, OAc), 1502(m), 1442(m), 1422(s, OAc), 1409(s), 1260)s), 1140(s), 1031(s), 961(m), 805(m), 748(s). Solution studies: two isomers (**2b$_I$** and **2b$_{II}$** coexisted in a 2.7:1.0 ratio) in $CDCl_3$ at room temperature. ^{1}H-NMR data for **2b$_I$** [27]: δ = 2.20[s, 6H, CH$_3$(OAc)], 4.29[s, 6H, OMe], 7.56[d, 2H, J = 7.6, 2H^5], 7.16[td, 2H, J = 7.6 and 1.0, 2H^6], 7.02[td, 2H, J = 7.6 and 1.0, 2H^7], 7.29[d, 2H, J = 7.6, 2H^8], 7.49[dd, 2H, J = 8.0 and 1.0, 2H^{11}], 6.48[dd, 2H, J = 8.0 and 1.0, 2H^{12}], 6.22[d, 2H, J = 8.0, 2H^{13}] and 7.16[d, 2H, 2H^{14}]; for **2b$_{II}$** (in this case most of the signals appeared duplicated suggesting that the two halves were not equivalent) δ = 2.28[s, 3H, OAc], 2.14[s, 3H, OAc], 4.26[br.s, 6H, OMe], 7.68[d, 2H, J = 7.6, 2H^5], 6.82[br., 2H, 2H^6], 7.18 [br, 2H, J = 7.2 and 1.0, 2H^8], 7.45[br., 2H, J = 8.0 and 1.0, 2H^{11}], 6.31–6.41[2 br.d, 4H, J = 8.0 and 1.0, 2H^{12} and 2H^{13}] [30], 6.80[br.s, 2H, 2H^{14}], (the resonances due to H^7 were partially masked by the signals due to solvent and the major isomer, respectively) [30]. ^{13}C{^{1}H} NMR data for **2b$_I$** [27]: δ = 65.6(OMe), 171.4(C^2), 154.2(C^3), 138.0(C^4), 127.0(C^5), 134.2(C^6), 129.4(C^7), 125.7(C^8), 118.9(C^9), 153.1(C^{10}), 131.6(C^{11}), 138.3(C^{12}), 130.5(C^{13}), 125.8(C^{14}), 152.7(C^{15}), 25.0[CH$_3$(OAc)] and 181.9(>CO$_2$(OAc)]; for **2a$_{II}$** (selected data): 65.3(OMe), 24.7 and 25.2[CH$_3$(OAc)], 181.40 and 183.2 [>CO$_2$(OAc)].

3.2.4. Synthesis of [Pd{κ^2-C,N-C$_6$H$_3$-4R-1-(C$_8$H$_4$N-3′-NOMe)}(OAc)(PPh$_3$)] {R = Cl (**3a**) or H (**3b**)}

These compounds were prepared as follows: 2×10^{-5} mol of **2a** (16 mg) or **2b** (15 mg) was dissolved in 0.7 mL of $CDCl_3$ and then 11 mg of PPh_3 (4×10^{-5} mol) was added and the resulting solution was analyzed by ^{1}H and ^{31}P{^{1}H} NMR. Concentration to dryness lead a purple solid that was collected and dried in vacuum for 3 days. Yields: 23 mg (82%) for **3a** and 21 mg (79%) for **3b**. *Characterization data* for **3a**: Elemental analyses calc. for $C_{35}H_{28}ClN_2O_3PPd$: C, 60.27; H, 4.05; N, 4.02. Found: C, 60.05; H, 3.98; N, 3.93%. MS (ESI$^+$): m/z = 638.4 [M-OAc]$^+$. ^{1}H NMR data [27]: δ = 4.30[s, 3H, OMe], 7.90[d, 1H, J = 7.1, H^5], 7.13[td, 1H, J = 7.2, and 1.5 H^6], 7.80[d, 1H, J = 7.1 and 1.0, H^8], 8.12[dd, 1H, J = 8.0 and 1.0, H^{11}], 6.83[dd, 1H, J = 8.0 and 1.0, H^{12}], 6.41[d, 1H, H^{14}], 1.30 [s, 3H, CH$_3$(OAc)] and 7.20–7.60 (br.m. 16 H, H^7 and aromatic protons of the PPh_3 ligand). For **3b**: Elemental analyses calc. for $C_{35}H_{29}N_2O_2PPd$: C, 63.40; H, 4.41; N, 4.23. Found: C, 63.29; H, 4.32; N, 4.11%. MS (ESI$^+$): m/z = 603.1 [M-OAc]$^+$. ^{1}H NMR data [27]: δ = 4.34[s, 3H, OMe], 7.92[d, 1H, J = 7.1, H^5], 7.11[td, 1H, J = 7.1, and 1.0 H^6], 7.84[d, 1H, J = 7.1 and 1.0, H^8], 8.16[dd, 1H, J = 8.0 and 1.0, H^{11}], 6.80–6.84[br.m, 2H, H^{12} and H^{13}], 6.45[d, 1H, H^{14}], 1.32[s, 3H, CH$_3$(OAc)] and 7.20–7.60 (br.m. 16 H, H^7 and aromatic protons of the PPh_3 ligand). ^{31}P{^{1}H} NMR data δ = 42.5.

3.2.5. Synthesis of (μ-Cl)$_2$[Pd{κ^2-C,N-C$_6$H$_3$-4R-1-(C$_8$H$_4$N-3′-NOMe)}]$_2$ {R = Cl (**4a**) or H (**4b**)}

To a solution containing 2.46×10^{-4} mol of **2a** (200 mg) or **2b** (232 mg) in acetone (10 mL), LiCl (23 mg, 5.42×10^{-4} mol) was added. The reaction mixture was stirred at 25 °C. The solid formed was removed by filtration and air-dried. Yields: 153 mg (76%) and 132 mg (71%) for **4a** and **4b**, respectively. *Characterization data for* **4a**: Elemental analyses calc. for $C_{30}H_{20}Cl_4N_4O_2Pd_2$: C, 43.77; H, 2.45; N, 6.81. Found: C, 43.70; H, 2.37; N, 6.59%. MS (ESI$^+$): m/z = 788.9 [M-Cl]$^+$. IR data: 2974(m), 1599(m), 1567(s), 1497(m), 1448(m), 1439(s), 1387(w), 1285(w), 1117(w), 1082(m), 1043(m) 1021(s), 968(w), 767(m), 756(m) and 486(w). For **4b**: Elemental

analyses calc. for $C_{32}H_{22}Cl_2N_4O_2Pd_2$: C, 47.77; H, 2.94; N, 7.43. Found: C, 47.85; H, 3.05; N, 7.35%. MS (ESI$^+$): m/z = 690.9 [M-Cl]$^+$. IR data: 2970(m), 1588(m), 1492(m), 1402(s), 1250(m) 1138(m) 1028(m) 959(m), 792(w) and 740(m).

3.2.6. Synthesis of [Pd{κ^2-C,N-C_6H_3-4R-1-(C_8H_4N-3′-NOMe)}Cl(py-d_5)] {R = Cl (**5a**) or H (**5b**)}

These compounds were prepared in solution and characterized by ^{1}H NMR. 2×10^{-5} mol of the corresponding complex **4** [16 mg (for **4a**) or 15 mg (for **4b**)] was suspended in 0.7 mL of $CDCl_3$, then two drops of deuterated pyridine (py-d_5) were added and the mixture was shaken for two minutes. After this period a deep-garnet solution containing **5a** or **5b** was obtained. ^{1}H-NMR data for **5a** [27]: δ = 4.39[s, 3H, OMe], 7.95[d, 1H, J = 7.2, H^5], 7.38[td, J = 7.2 and 1.0, H^6], 7.20[td, 1H, J = 7.2 and 1.0, H^7], 7.28[d, 1H, J = 7.2, H^8], 8.11[dd, 1H, J = 8.0 and 1.0, H^{11}], 7.02[dd, 1H, J = 8.0 and 1.0, H^{12}], 7.21[d, 1H, H^{14}]. For **5b** [27]: δ = 4.40[s, 3H, OMe], 8.02[d, 1H, J = 7.4, H^5], 7.26[td, J = 7.4 and 1.0, H^6], 7.42[td, 1H, J = 7.4 and 1.0, H^7], 7.30[d,1H, J = 7.2, H^8], 8.21[dd, 1H, J = 8.0 and 1.0, H^{11}] and 6.90–7.20[m, 3H, H^{12}, H^{13} and H^{14}].

3.2.7. Synthesis of [Pd{κ^2-C,N-C_6H_3-4R-1-(C_8H_4N-3′-NOMe)}Cl(PPh_3)] {R = Cl (**6a**) or H (**6b**)}

A suspension of 1.00×10^{-4} mol of **4a** (83 mg) or **4b** (76 mg) in CH_2Cl_2 (20 mL) was treated with PPh_3 (53 mg, 2.0×10^{-4} mol). The reaction mixture was stirred at 25 °C for 1 h and then filtered out. The deep-red filtrate was concentrated to dryness on a rotary evaporator giving a deep-garnet solid that was later on dissolved in the minimum amount of CH_2Cl_2 and passed through a short SiO_2 column (2.5 cm × 5.0 cm). Elution with CH_2Cl_2 produced the release of a red band that was collected and concentrated to dryness on a rotary evaporator. The bright garnet solid formed was collected and dried in vacuum for 2 days. Yields: 98 mg (71%) for **6a** and 101 mg (70%) for **6b**·1/2CH_2Cl_2. *Characterization data* for **6a**: Elemental analyses calc. for $C_{34}H_{28}ClN_2OPPd$: C, 59.28; H, 4.10; N, 4.07. Found: C, 59.39; H, 4.15; N, 4.27%. MS (ESI$^+$): m/z = 687.0 [M-Cl]$^+$. IR-data: 3055 and 3040(w), 1602(w), 1564(m), 1496(m), 1478(m), 1221(s), 1435(s), 1101(m), 1093(m), 1016(s), 973(m), 740(s), 702(m), 692(s), 535(s), 512(s) and 493(s). ^{1}H NMR data for **6a** [27]: δ = 4.41[s, 3H, OMe], 7.98[d, 1H, J = 7.2, H^5], 7.22[td, J = 7.2 and 1.0, H^6], 7.39[td, 1H, J = 7.2 and 1.0, H^7], 9.15[d, 1H, J = 7.2, H^8], 8.26[dd, 1H, J = 8.0 and 1.0, H^{11}], 6.93[dd, 1H, J = 8.0 and 1.0, H^{12}], 6.47[d, 1H, H^{14}] and 7.40–7.50 and 7.60–7.75(2m, 15H, aromatic protons of the PPh_3 ligand). ^{13}C{^{1}H}-NMR data [27]: 65.6(OMe), 173.7(d, $^3J_{P-C}$ = 3.6, C^2), 159.1(C^3), 140.1(C^4), 123.4(C^5), 132.8(C^6), 126.9(C^7), 123.8(C^8), 121.9(d, $^3J_{P-C}$ = 4.2, C^9), 153.6(C^{10}), 130.6(C^{11}), 136.8(C^{12}), 130.2(C^{13}), 124.7(C^{14}), 151.7(d, $^2J_{P-C}$ = 9.3, C^{15}) and four additional doublets centered at 128.1, 130.8, 131.2 and 135.0 due to ^{13}C nuclei of the PPh_3 ligand. ^{31}P{^{1}H} NMR data δ = 44.2. For **6b**: Elemental analyses calc. for $C_{33}H_{26}ClN_2OPPd·1/2CH_2Cl_2$: C, 59.01; H, 3.99; N, 4.11. Found: C, 58.97; H, 4.02; N, 4.03%. MS (ESI$^+$): m/z = 687.0 [M-Cl]$^+$. IR data: 3053(w), 3040(w), 2930(w), 1602(w) 1564(m), 1544(w), 1441(s), 1435(s), 1101(m), 1093(m), 1120(s), 773(m), 740(s), 703(m), 692(s), 534(s), 512(s) and 493(s). ^{1}H NMR data for **6b** [27]: δ = 4.41[s, 3H, OMe], 8.01[d, 1H, J = 7.2, H^5], 7.20[td, J = 7.2 and 1.0, H^6], 7.49[td, 1H, J = 7.2 and 1.0, H^7], 9.17[d, 1H, J = 7.2, H^8], 8.35[dd, 1H, J = 8.0 and 1.0, H^{11}], 6.54[br., 2H, H^{13} and H^{14}], 5.12[s, 1H, CH_2Cl_2] and 7.50–7.80(m, 15H, aromatic protons of the PPh_3 ligand). ^{13}C{^{1}H}-NMR data [27]: 65.9(OMe), 173.6(d, $^3J_{P-C}$ = 3.2, C^2), 158.8(C^3), 141.9(C^4), 122.6(C^5), 135.4(C^6), 127.3(C^7), 123.1(C^8), 121.5((d, $^3J_{P-C}$ = 4.0, C^9), 152.2(C^{10}), 130.2(C^{11}), 139.8(C^{12}), 130.5(C^{13}), 124.6(C^{14}), 153.5(d, $^3J_{P-C}$ = 9.5, C^{15}) and four additional doublets centered at ca. 128.1, 130.8, 131.2 and 135.0 due to the ^{13}C nuclei of the PPh_3 ligand ^{31}P{^{1}H} NMR data δ = 45.8.

3.3. Crystallography

A prismatic crystal of **6b**·1/2CH_2Cl_2 (sizes in Table 2) was selected and mounted on a Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($12° < \theta < 21°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using $\omega/2\theta$ scan-technique. The number of reflections measured in the range $2.14° \leqslant \theta \leqslant 29.97°$ was 17813, out of which 14109 were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made.

The structure was solved by direct methods, using the SHELXS computer program [31] and refined by full-matrix least-squares method with the SHELX-97 computer program [32] using 17813 reflections, (very negative intensities were not assumed). The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0255P)^2 + 5.5920P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were taken from the bibliography [33]. All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked. The final R (on F) factor was 0.049, wR(on $|F|^2$) = 0.0794 and goodness-of-fit = 1.334 for all observed reflections. Number of refined parameters was 730. Max. shift/esd = 0.00, Mean shift/esd = 0.00. Maximum and minimum peaks in final difference synthesis was 0.801 and −0.918 eÅ^{-3}, respectively. Further details concerning the solution and refinement of this crystal structure are presented in Table 2.

3.4. Theoretical studies. Computational details

Calculations were carried out at the AM1 computational level [10] using the SPARTAN 5.0 package [11]. Geometry optimizations were performed without symmetry restrictions.

Table 2
Crystal data and details of the refinement of the crystal structure of compound **6b** · 1/2CH_2Cl_2

Crystal size (mm × mm × mm)	0.20 × 0.05 × 0.05
Empirical formula	$C_{67}H_{54}Cl_4N_4O_2P_2Pd_2$
Molecular weight	1363.68
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.790(8)
b (Å)	15.474(11)
c (Å)	18.681(9)
α (°)	108.32(5)
β (°)	107.13(3)
γ (°)	91.89(4)
T (K)	293(2)
λ (Å)	0.71073
V (Å^3)	3062(4)
Z	2
D_{calc} (Mg/m^3)	1.479
μ (mm^{-1})	0.862
F(000)	1380
Θ range for data collection (°)	from 2.14 to 29.97
Number of collected reflections	17813
Number of unique reflections [R_{int}]	17813 [0.0443]
Completeness to Θ = 25.00°	100.0%
Refinement method	Full-matrix least-squares on F^2
Number of data/restraints/parameters	17813
Number of parameters	730
Goodness-of-fit (GOF) on F^2	1.334
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0487, wR_2 = 0.1005
R indices (all data)	R_1 = 0.0794, wR_2 = 0.1269
Largest difference peak and hole (e Å^{-3})	0.801 and −0.918

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Appendix A. Supplementary data

CCDC 680983 contains the supplementary crystallographic data for **6b**·1/2CH_2Cl_2. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.05.043.

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