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Hemilabile and luminescent palladium(II) azo-2-phenylindole complexes

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ABSTRACT

The synthesis of three azoderivatives {R^1–N=N–R^2 with R^1 = 2-phenylindole and R^2 = 4-Me–C_6H_4– (**2a**), 4-Cl–C_6H_4– (**2b**) or 2-phenylindole (**2c**)} and the study of their reactivity in front of Pd(II) salts are described. Treatment of **2a** or **2b** with $PdCl_2$ in a CH_2Cl_2:CH_3OH mixture at 298 K followed by the action of PPh_3 produced the cyclopalladated complexes: [Pd(κ^2-*C*,*N*)Cl(PPh_3)] (**3a** and **3b**) with a σ{Pd–C(indole)} bond. For **2c**, metallation takes place on the same position but required stronger reaction conditions {$Pd(OAc)_2$ in acetic acid at 398 K}. A comparative study of the spectroscopic and photo-optical properties of ligands **2a**–**2c** and their palladium(II) derivatives (**3a**–**3c**) is also reported. Addition of PPh_3 to CH_2Cl_2 solutions of compounds **3a**–**3c** produced the opening of the six-membered metallacycle and the formation of the *trans*-[Pd(κ^1-*N*)Cl(PPh_3)$_2$] derivatives (**4a**–**4c**). The crystal structures of **3c**·CH_2Cl_2, **4a**, **4b** and **4c**·3/2CH_2Cl_2·1/2H_2O confirm the mode of binding and the *anti*-(*E*) configuration of **2a**–**2c** in the complexes as well as the relative disposition of the remaining ligands bound to the Pd(II) atom. Solution studies reveal that in $CDCl_3$, the Pd–N bond of **4a**–**4c** is hemilabile. Computational studies (at DFT or PM6 level) have also been performed in order to rationalize the high degree of regioselectivity of the cyclopalladation process and the solution behaviour of **4a**–**4c**.

1. Introduction

The chemistry of azobenzene derivatives has stimulated research efforts directed towards their use as materials for digital storage, as building blocks in supramolecular systems, switches in nanomolecular devices and polymer materials [1–3]. However, very few studies have been addressed specifically to the preparation of azoindole derivatives [4].

On the other hand, palladium coordination chemistry has undergone a fast development in recent years [5]. Special attention has been paid to complexes with nitrogen donors such as amines, imines, azo and heterocyclic compounds [6]. Examples of their utility in homogeneous catalysis or in macromolecular chemistry [6c,6d] have been reported. In addition, cyclopalladated complexes of *N*-donor ligands are particularly relevant in homogeneous catalysis, luminescence, liquid crystals, optical resolution and biological active materials [7–11].

A few 2-phenylindoles and their palladium(II) and platinum(II) complexes have been recently published [12]. Azoindoles are not common, only a few examples of palladium(II) complexes [13], have been reported, but products arising from cyclopalladation of azo-2-phenylindole derivatives are still unknown.

In this paper we present three azo derivatives R^1–N=N–R^2 {R^1 = 2-phenylindole and R^2 = 4-Me–C_6H_4– (**2a**), 4-Cl–C_6H_4– (**2b**) or 2-phenylindole (**2c**), shown in Scheme 1} and the study of their reactivity in front of palladium(II) salts. In addition, the presence of one (in **2a**, **2b**) or two (in **2c**) bulky 2-phenylindole units may also introduce significant steric effects that may affect the properties and reactivity of the ligands and their cyclopalladated derivatives. For instance, the hemilability [14] of the ligands, that is relevant in view of their utility in homogeneous catalysis [15,16].

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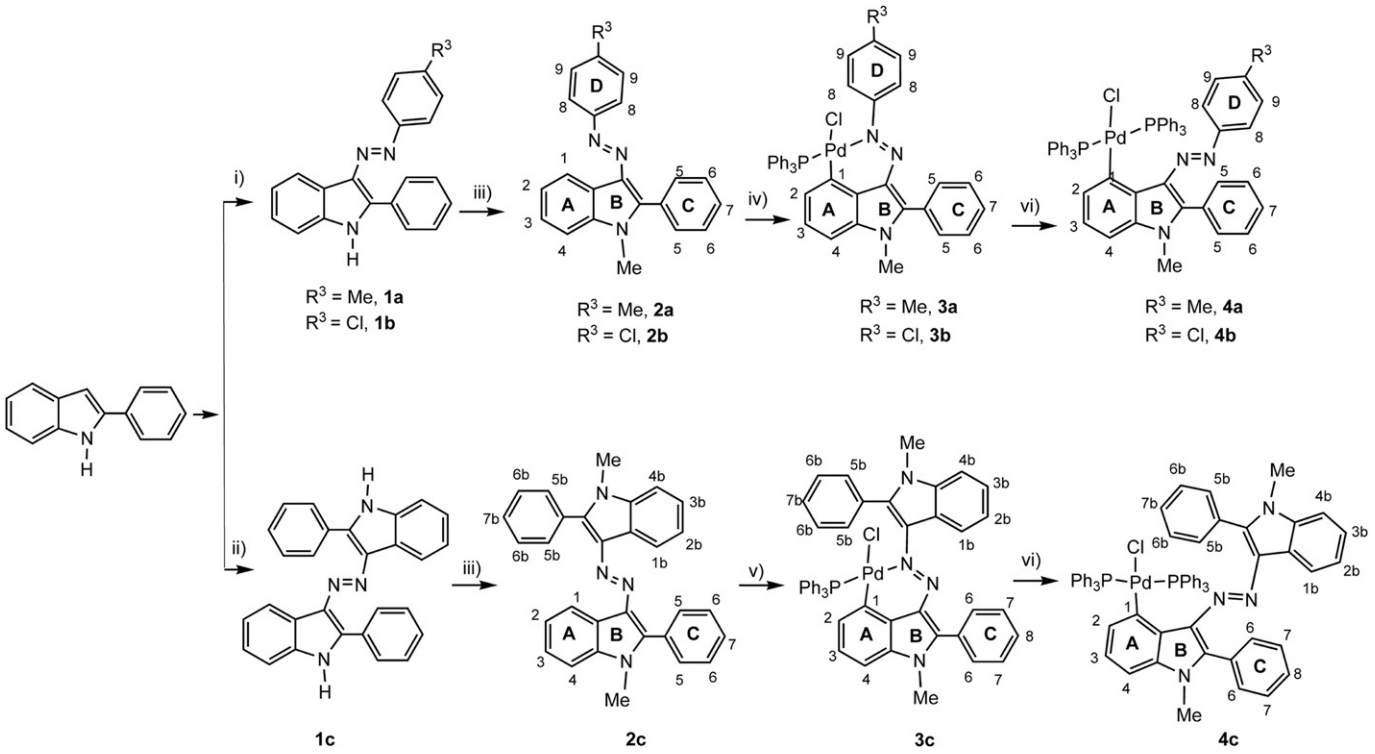

Scheme 1. Synthesis of the azocompounds and the palladium (II) complexes. Key reagents and conditions: i) (R^3–$C_6H_4N_2$)Cl, 0–20 °C, 30 min then NaOAc to 298 K ii) 3-diazo-2-phenylindole, HOAc, 80 °C 2 h, iii) MeI, 40% NaOH, CH_2Cl_2, 2 h. iv) $PdCl_2$, MeOH: CH_2Cl_2 (1:1), 24h, followed by treatment with PPh_3 in CH_2Cl_2; v) $Pd(OAc)_2$ in acetic acid 100 °C, 3h followed by treatment with LiCl first and PPh_3 later on and vi) PPh_3 in CH_2Cl_2.

2. Results and discusion

2.1. Synthesis

Compounds **2a**–**2b** were prepared from commercially available 2-phenylindole using a straightforward two-steps procedure [Scheme 1,i) and ii)], based on the electrophilic coupling on position 3 of the indole ring, using diazotized para-substituted anilines [17] to give the precursors **1a** and **1b**, and the subsequent treatment with methyl iodide in CH_2Cl_2 and NaOH (40%) under phase-transfer catalysis [18].

The azoindoles **1c** and **2c** have been described in the reaction of 1-methyl-2-phenylindole and 2-phenylindole respectively with nitrous acid [19]. The classical preparative method for azobis(indole) **1c** requires the coupling of 3-diazo-2-phenylindole (available through a three-steps protocol: nitrosation, reduction to amine and diazotization) with 2-phenylindole in acidic media [20]. Due to the easier availability of 3-diazo-2-phenylindole in one step [21] in this work we have used a slightly modified procedure based on the synthesis of the precursor **1c** [Scheme 1, iii)] followed by the subsequent methylation of the nitrogen using the same method as for **2a** and **2b** [Scheme 1, ii)].

Treatment of **2a** or **2b** with $PdCl_2$ in a CH_2Cl_2–methanol (1:1) mixture at 298 K for 48 h produced a solid that reacted with PPh_3 (in a 1/1 M ratio) giving the palladacycles **3a** and **3b**, respectively [Scheme 1, iv)]. In contrast with these results when the reaction was carried out using **2c** instead of **2a** or **2b**, no evidences of the formation of any cyclopalladated complex was observed. However, the treatment of **2c** with $Pd(OAc)_2$, that is a more potent metallating agent than $PdCl_2$, in acetic acid at 100 °C produced after treatment with PPh_3 complex **3c** [Scheme 1, v)]. It should be noted that the cyclometallation of **2a**–**2c** takes place with completely regioselectivity at the *peri*-position of the indole.

It is well-known that cyclopalladation of *N*-donor ligands proceeds in two steps: the binding of the ligand through the *N* atom to the palladium, followed by the activation of the C–H bond. The use of molecular models reveals that: a) in **2c** the environment of the donor atoms is more crowded than in **2a** and **2b**, and consequently, this reduces the accessibility of the Pd(II) atom. Moreover, for the intermediate formed in the first step, the C–H bond of the indole ring (**A**) has a better orientation towards Pd(II) than the C–H bonds on the ortho sites of the phenyl rings **C** or **D** and it is closer to the Pd(II) centre. These findings could explain why in all cases metallation occurs on ring **A**.

2.2. Structures

It is well-known that for azo-derivatives R^1–N=N–R^2 the relative disposition of the substituents (*E*- or *Z*-) affects their spectroscopic and photochemical properties as well as their reactivity [22]. NMR spectra of **1a**–**1c** and **2a**–**2c** in $CDCl_3$ at 298 K indicated the presence of only one isomer in solution [23]. Since all azo-2-phenylindole derivatives described so far adopt the *E*- form in solution as well as in the solid state [24–26], we assumed that **1a**–**1c** and **2a**–**2c** were the *E*- isomers. Computational studies at the DFT level [27] for **2a** confirmed this hypothesis, the existence of C–H···N contacts in the two conformers of **2a** (Fig. 1, forms **I** and **II**) and also that form **II** was (ca. 5.74 kcal/mol) more stable than form **I**. Due to the similarity between **2a** and **2b**, we assumed that for **2b**, form **II** would also be the most stable one.

The crystal structure of **3c**·CH_2Cl_2 (Fig. 2), reveals that the Pd(II) atom is bound to the azo nitrogen N(3) and the carbon atom C(1) on the *ortho* site of the phenylindole moiety, forming a six-membered palladacycle with a twisted boat conformation [28]. The Pd–C(1) and Pd–N(3) bond distances fall in the ranges reported for [Pd(κ^2-*C*,*N*)Cl(PPh_3)] and the C(1)–Pd–N(3) bond angle [89.94(9)°]

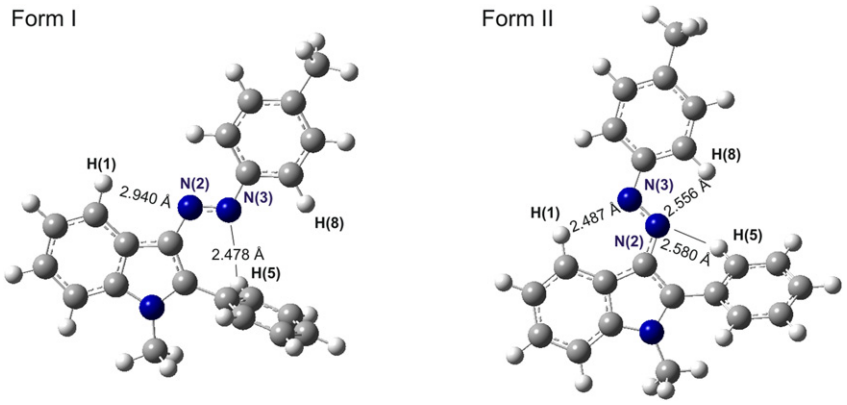

Fig. 1. Optimized geometries of the two forms (**I** and **II**) of ligand **2a**. Showing the most relevant C–H···N distances. In form **I** the shortest C–H···N contact takes place between the N(3) atom and the H(5) atom (2.478 Å), and the distance N(2)···H(1)$_{(indole)}$ is 2.940 Å. For form **II**: Distances N(3)···H(1) = 2.467 Å, N(2)···H(8) = 2.556 Å and N(2)···H(5) = 2.580 Å}.

is bigger than those found in the *Cambridge Crystallographic Data Base*, for analogous palladacycles [in the range 81.7°–86.3°] [24]. The remaining two coordination sites of the Pd(II) atom are occupied by the phosphorus atom of the PPh_3 ligand, in a *cis*-arrangement to the metallated carbon [bond angle C(1)–Pd–P(1) = 90.4(7)°], and the Cl^- ligand.

The N(2)–N(3) bond length [1.286(3) Å] is similar to the values found for most 2-phenylindole containing azoderivatives [24–26], and the ligand adopts the *E*- form [torsion angle C(7)–N(2)–N(3)–C(16) = 175.3(4)°]. The two indoles are nearly planar, form an angle of 30.1° and the phenyl rings are twisted in relation to the coordination plane of the palladium(II) [29]. For this arrangement of substituents, the distances N(2)···H(15) [2.78 Å] and N(2)···H(18) [2.72 Å], suggest weak intramolecular C–H···N contacts.

2.3. Photo-optical properties

One of the main interests of phenylindole derivatives arises from their potential luminescence [30,31] that makes them useful in fluorescence imaging microscopy and for the labelling of biomolecules such as DNA [31]. In addition, palladacycles derived from azobenzene with interesting photo-optical properties have also been described [7a–c,32,33]. In view of this and in order to examine the effects induced by: a) the nature of the substituent R^3 of the 4-R^3–C_6H_4– rings in **2a**–**2b** and **3a**–**3b** and b) the replacement of the phenyl rings of **2a**, **2b**, **3a** or **3b** by a 2-phenylindole unit on the potential luminescence of the ligands and their palladacycles, we also studied their absorption and emissive properties.

The UV–vis. spectra of ligands **2a**–**2c** in CH_2Cl_2 at 298 K (Table 1) showed the typical pattern of 2-phenylindole derivatives [30,33,34]. For the palladacycles **3a**–**3c** three bands were detected in the spectra, of which those at higher energies appears in the same range as those of the free ligands and are due to a metal perturbed intraligand transition (MPILT). The third and new band is affected by the polarity of the solvent [35] and is assigned to the metal to ligand charge transfer transition (MLCT): *4d*(Pd) → π* orbitals of the cyclometallated ligand [7a–c,32,33,36].

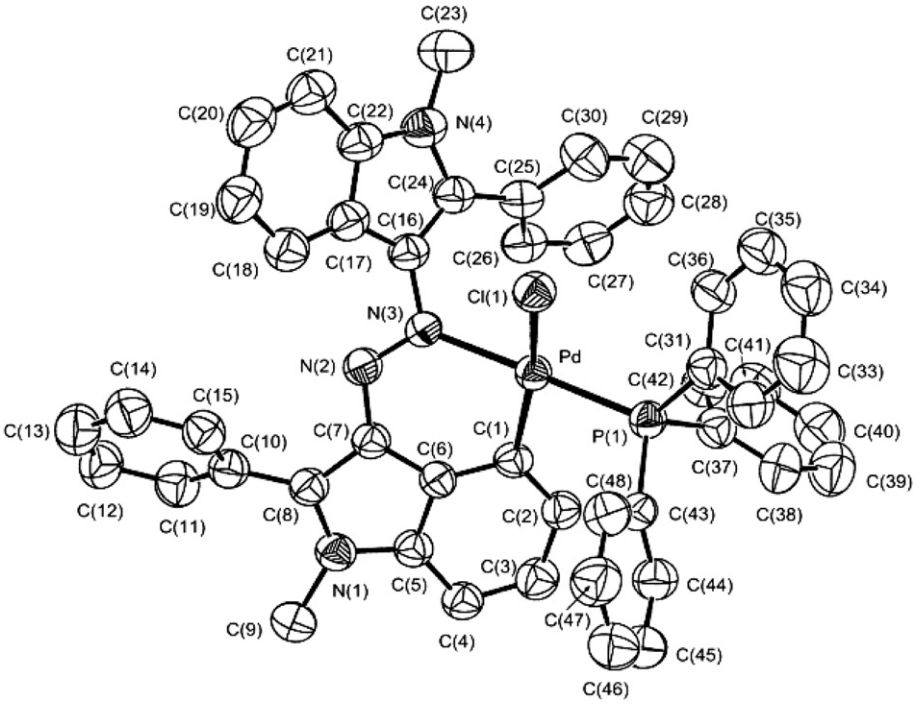

Fig. 2. ORTEP plot of **3c**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and bond angles (in deg.): Pd–Cl(1), 2.4180(9); Pd–N(3) 2.148(2); Pd–P(1), 2.2739(12); Pd–C(1), 2.032(2); C(1)–Pd–N(3), 89.94(9); P(1)–Pd–C(1), 90.40(7), P(1)–Pd–Cl(1), 92.09(3) and N(3)–Pd–Cl(1) 89.93(3).

Table 1
Absorption and emission properties of the free ligands **2a**–**2c** and the cyclopalladated complexes **3a**–**3c** in CH_2Cl_2 solution at 298 K {wavelengths, λ_i (i = 1,2 or 3) excitation wavelength $\lambda_{exc.}$ And λ_{max} in nm and extinction coefficients ε_i (in M^{-1} cm^{-1}) and quantum yields, Φ[a]}.

	Absorption spectroscopic data			Emission data, λ_{max}			
	λ_1 (ε_1)	λ_2 (ε_2)	λ_3 (ε_3)	$\lambda_{exc.}$	Solid state	In solution	Φ
Free ligands							
2a	381 (27.0×10^3)	275 (45.6×10^3)	–	280	–	430	0.0015
2b	386 (11.8×10^3)	273 ($101. \times 10^3$)	–	280	–	396	0.0012
2c	301 (6.9×10^3)	232 (10.8×10^3)	–	300	–	415, 379, 363 and 349	0.17
Cyclopalladated complexes:							
3a	468 (20.6×10^3)	326 (22.3×10^4)	269 (18.4×10^4)	480	594	[b]	–
				275	–	408	0.0018
3b	472 (16.6×10^3)	326 (62.7×10^3)	255 (49.1×10^3)	480	590	[b]	–
				275	–	395	0.0016
3c	518 (20.0×10^3)	326 (92.4×10^4)	234 (66.3×10^3)	520	630	610	0.0053

[a] Quantum yields referred to quinine sulphate in H_2SO_4 1 N (for **2a**–**2c** and **3a**–**3b**) and to $[Ru(bipy)_3]^{2+}$ in H_2O (for **3c**).
[b] No emission was observed.

We also explored the potential emissive properties of **2a**–**2c** and complexes **3a**–**3c** in the solid state and in CH_2Cl_2 solution at 298 K. The free ligands were not emissive in the solid state, but in solution they became luminescent upon excitation at $\lambda_{exc} = 280$ nm (for **2a** and **2b**) or 300 nm (for **2c**). It should be noted that the quantum yield of **2c** (Table 1) is significantly higher than those of **2a** and **2b**, in which the R^3 unit is a 4-methyl or 4-chlorophenyl group.

The emission spectra of solid samples of the palladacycles **3a** and **3b** (at $\lambda_{exc} = 480$ nm) at 298 K showed a broad emission band in the range 590–595 nm; while for **3c** a stronger emission (at $\lambda_{em} = 630$ nm) was observed ($\lambda_{exc} = 520$ nm) [37]. This reflects once more the relevancy of the presence of two phenylindole groups on the photo-optical properties of the azo-compounds (**2a**–**2c**) and their palladium(II) complexes (**3a**–**3c**). It should be noted that for (**3a**–**3c**), the emission wavelength was similar to those reported for related mononuclear cyclopalladated azobenzenes {500 nm $\leq \lambda_{max} \leq$ 650 nm} [7a,b,31,32].

The crystal structure of **3c** (described above) revealed that the metallated and non-metallated indole units are not coplanar and this can modify the aromaticity of the ligand. It is well known that photophysical properties of palladium(II) complexes are dependent

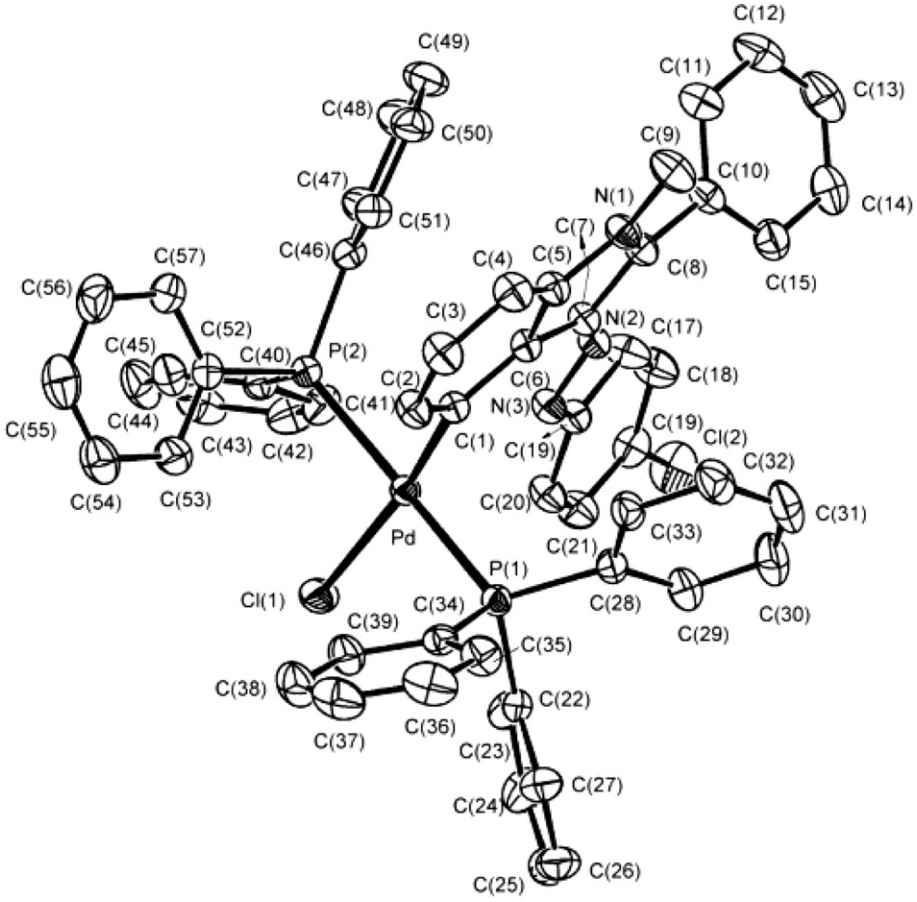

Fig. 3. ORTEP plot of **4a**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and bond angles (in deg.): Pd–Cl(1), 2.4187(17); Pd–P(1), 2.3389(13); Pd–P(2), 2.3422(12); Pd–C(1), 1.994(4); P(1)–Pd–P(2), 169.13(4); P(1)–Pd–C(1), 85.25(11); Pd(2)–Pd–C(1) 86.61(11) and P(2)–Pd–Cl(l), 91.43(5).

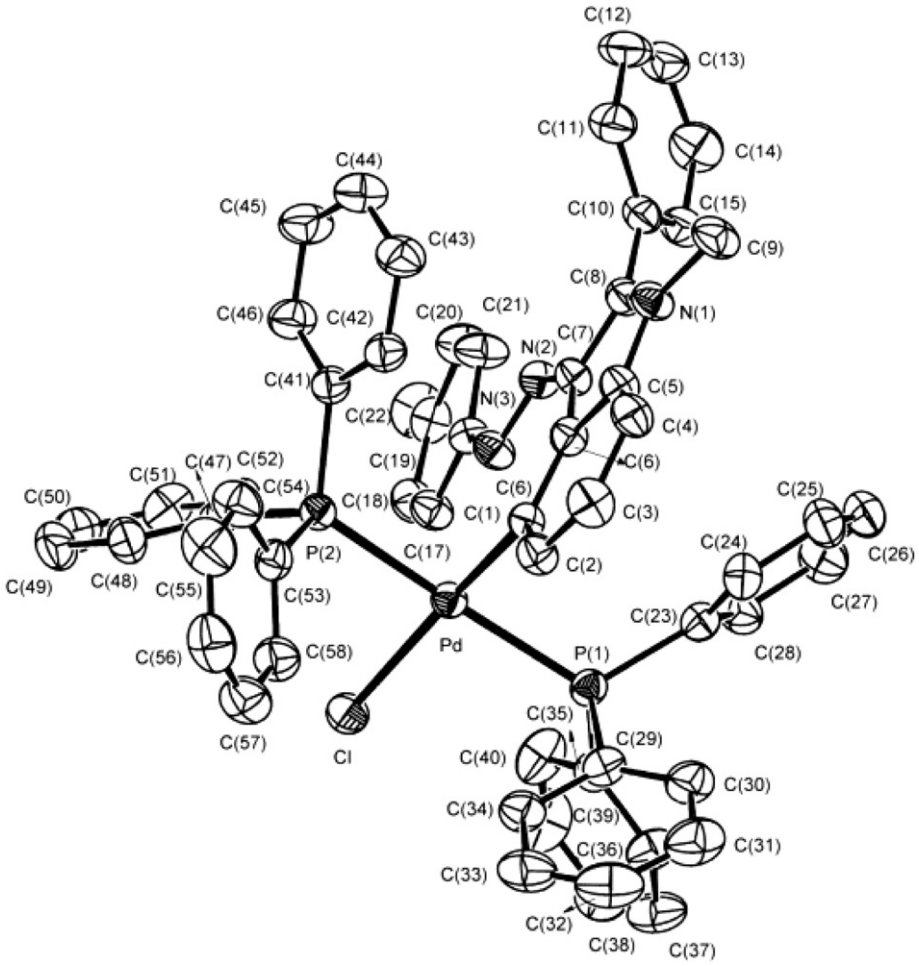

Fig. 4. ORTEP plot of **4b**. Hydrogen atoms have been omitted for clarity. Pd–Cl(1), 2.4188(19); Pd–P(1), 2.3329(10); Pd–P(2), 2.3389(11); Pd–C(1), 1.995(3); P(1)–Pd–P(2), 188.71(3); P(1)–Pd–C(1), 84.89(9); P(2)–Pd–C(1), 86.56(9) and P(2)–Pd–Cl(l), 91.18(4).

on a wide variety of factors including the nature of the ligands bound to the Pd(II) as well as the existence of Pd···Pd and/or π···π interactions between vicinal molecules. In the crystal structure of **3c**: a) the shortest Pd···Pd distance is 8.306 Å and allows us to discard the existence of any interaction between them and b) the molecules are assembled mainly by C–H···π and C–H···Cl intermolecular interactions.

.The excitation of CH_2Cl_2 solutions of **3a** and **3b** (at $\lambda_{exc} = 480$ nm) produced no significant emission (Table 1). According to the bibliography this is commonly due to the presence of low-lying metal centred excited states that deactivate the potentially emitting metal-to-ligand charge transfer [4*d*(Pd) → π (ligand)] and the ligand centred levels [38].

In contrast with the results obtained for **3a** and **3b**, complex **3c** was strongly luminescent under the same conditions and the emission spectra obtained when excited at 520 nm showed a band at low energies ($\lambda_{max} = 610$ nm). The red-shift emission of **3c** with respect with that of **2c** (and corresponding larger Stokes' shift) suggests a phosphorescence origin of this emission band.

2.4. Study of the reactivity and stability of *3a–3c*

We also evaluated the stability of the Pd–N bond in **3a–3c** using the typical procedure based on their reaction with nucleophiles [39,40]. Treatment of **3a**, **3b** or **3c** with an excess of PPh_3 produced **4a–4c** [Scheme 1, vi)]. IR spectra of **4a–4c** in the range (500–550 cm^{-1}) showed the typical pattern reported for complexes of the type *trans*-[Pd(κ^1-*C*)X(PPh_3)$_2$] [40].

The crystal structures of **4a**, **4b** and **4c**·3/2CH_2Cl_2·1/2H_2O (Figs. 3–5) revealed that existence of molecules of **4a–4c** in which the palladium(II) atom is bound to the C(1) atom of the 2-phenylindol, thus confirming that metallation occurred at the **A** ring. The three remaining coordination sites are occupied by a chloride and the phosphorous atoms of two different PPh_3 molecules in a *trans*- arrangement. In **4a** and **4b** the two Pd–P bond lengths are similar and fall in the range of other *trans*-[Pd(κ^1-*C*)Cl(PPh_3)$_2$] derivatives [24,40,41]. However, in **4c**, these two Pd–P distances are different and bigger than in **4a** and **4b** or in its precursor **3c**. This can be related to the stronger steric hindrance induced by the presence of two bulky 2-phenylindole units bound to each one of the nitrogen atoms of the azo group.

In the three cases the azo ligands are in the *E* configuration and they adopt form **II** shown in Fig. 1. As a consequence of the nearly coplanar arrangement of the 4-substituted phenyl ring and the azo functionality, the H atoms on the ortho sites of the 4-R^4–C_6H_4– unit are close to the nitrogen atoms of the –N=N– group [42]. In **4c**, there are also C–H···N contacts but the distances N···H are bigger [43] than in **4a** and **4b**. Comparison of the structures of **3c** and **4c** also reveals that the transformation of **3c** into **4c** requires a change of the relative orientation of the azo moiety in relation to the Pd–C bond [from form **I** (in **3c**) to form **II** (in **4c**)].

Finally, it should be noted that in the three complexes the separations between the palladium(II) atom and the nitrogen N(3)

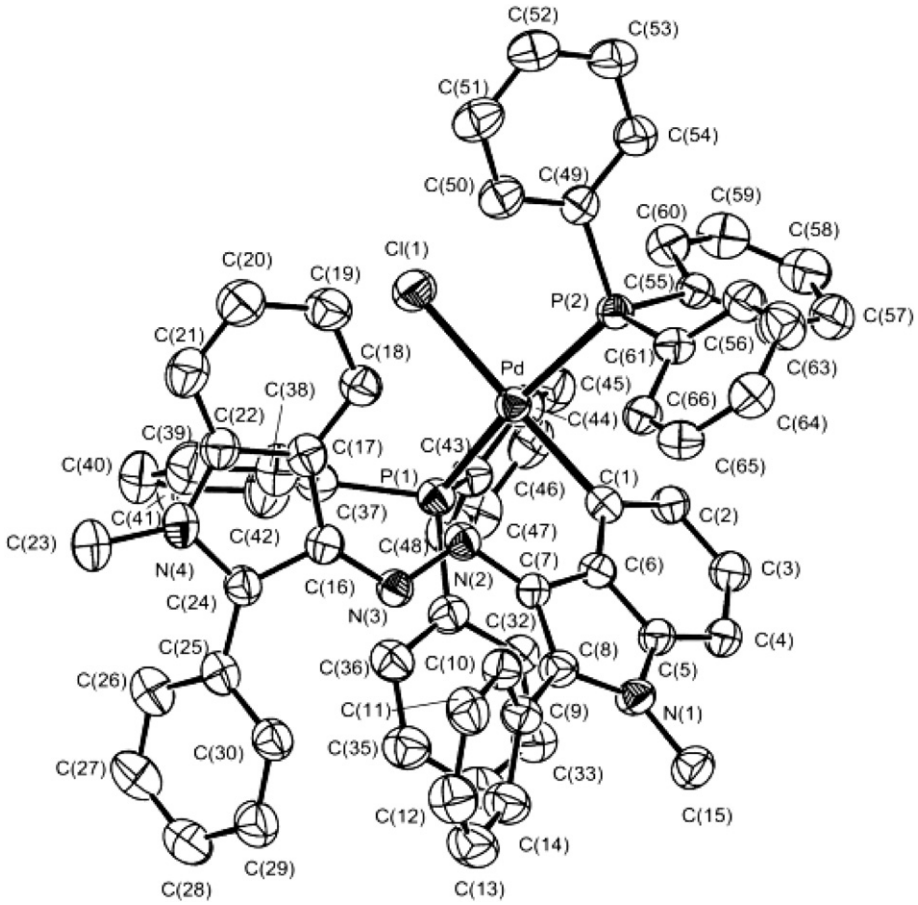

Fig. 5. ORTEP plot of **4c**. In both cases hydrogen atoms have been omitted for clarify. Pd–Cl(1), 2.438(2); Pd–P(1), 2.3549(17); Pd–P(2), 2.3710(17); Pd–C(1), 2.118(2); P(1)–Pd–P(2), 166.24(5); P(1)–Pd–C(1), 86.48(10); P(2)–Pd–C(1) 88.41(10) and P(2)–Pd–Cl(l), 94.27(5).

(in **3a** and **3b**) or the N(2) atom for **3c**, are small (2.961, 2.998 and 3.328 Å, for **4a**, **4b** and **4c**, respectively), they hardly exceed the sum of the van der Waals radii of the Pd and N atoms (1.63 and 1.55 Å, respectively) [44]. In addition, for compounds **4a** and **4b** the angles N(3)-Pd-ligands are close to 90° [45], thus suggesting that the N(3) atom lies on the axial direction. In **4c** the N(2) atom has a similar orientation.

Compounds **4a**–**4c** are stable in the solid state, but they exhibit an interesting behaviour in solution. First, their ESI mass spectra were essentially the same as those of their corresponding parent complex **3a**–**3c**. The $^{31}P\{^{1}H\}$ NMR spectra of **4a** and **4b** showed broad and poorly defined signals at 298 K; but at 240 K a narrow singlet [at $\delta = 17.26$ (for **4a**) and 17.30 ppm (for **4b**)] was observed exclusively and its position was similar to those of related *trans*-$[Pd(\kappa^1\text{-}C)X(PPh_3)_2]$ [39,40].

The $^{31}P\{^{1}H\}$ NMR spectrum of **4c** (in $CDCl_3$ at 298 K) showed three singlets of which that at $\delta = 20.3$ ppm is assigned to **4c**; while the other two singlets (at $\delta = 39.7$ and -6.0 ppm) correspond to **3c** and the free PPh_3. When this solution was cooled to 240 K, the intensity of the signal at $\delta \sim 20$ ppm increased while the other two nearly vanished (Fig. 6). These findings suggest that in $CDCl_3$ solution, a dynamic process involving the cleavage of one of the two Pd–P bonds of **4c**, the release of this ligand and the formation of **3c** takes place. These results are specially outstanding because they allow a fine tuning of the environment of the Pd(II) atom by a simple change of the temperature.

Secondly, when PPh_3 was added to diluted solutions of **4c** in $CDCl_3$ the signal due to the ^{31}P nuclei of **3c** decreased thus

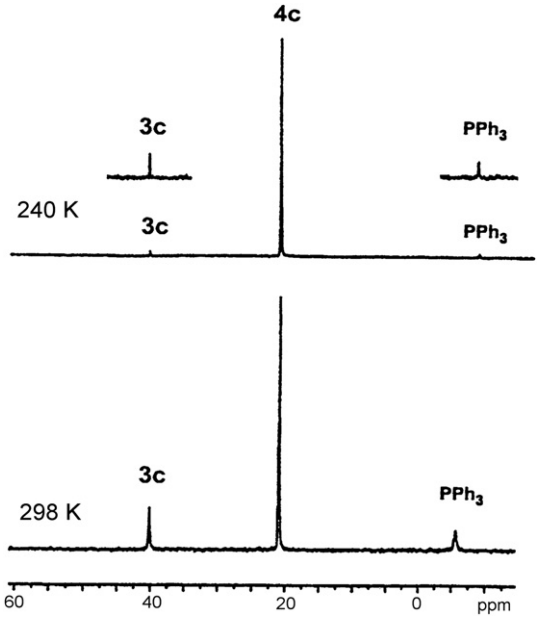

Fig. 6. $^{31}P\{^{1}H\}$ NMR spectra of a solution of **4c** in $CDCl_3$ at 298 K and at 240 K, showing (as insets) expansions of the two additional and low intense signals due to the minor components (**3c** and the free PPh_3).

Table 2
Values of the variation of the free energy (ΔG_T in kcal/mol), for the reaction **4c** → **3c** + PPh_3 determined with the PM6 computational method [in vaccum or in $CHCl_3$ at different temperatures (T)].

ΔG_T (in kcal/mol)		
T (in K)	In vacuum	In $CHCl_3$
300	−18.71	−16.91
240	−14.95	−13.53
100	−6.04	−5.51

indicating that the reaction **4c** → **3c** + PPh_3 is reversible. It should be noted that organometallic compounds showing this type of behaviour, that involves the decoordination/coordination of a ligand ("*base off/base on*" processes), are specially attractive in view of the potential utility in homogeneous catalysis where complexes with hemilabile ligands play a key role [14–16].

In a first attempt to rationalize the solution behaviour of compound **4c**, we decided to undertake DFT calculations [27] for the three products involved in the equilibrium: **4c** ⇆ **3c** + PPh_3. In the first stage, the optimization of the geometries of the three molecules involved in the reaction was carried out; later on their total energies (E_T) were determined. The results obtained revealed that the difference of ΔE_T {defined as $\Delta E_T = \{[E_T$ (for **3c**) + (E_T (for PPh_3)] − E_T(for **4c**)} in vacuum was 7.15 kcal/mol, but this value decreased by ca. 6.8 kcal/mol) when the effect induced by the $CHCl_3$ solvent was considered ($\Delta E_T = 0.34$ kcal/mol).

As described above, the behaviour of **4c** in $CDCl_3$ is temperature dependent. This prompted us to undertake a theoretical estimation of the variation of the free energy ΔG_T of the reaction **4c** → **3c** + PPh_3 at different temperatures. It should be noted that the bulky PPh_3 ligands are involved in this process and consequently simplified models (commonly based in the replacement of the PPh_3 by PH_3 or PMe_3) could not be used. In addition, molecules of **4c** ($C_{66}H_{53}ClN_4P_2Pd$) are complex and huge and this made the calculations at a DFT level extremely complex, difficult and slow. Thus, we decided to determine the ΔG_T for the reaction **4c** → **3c** + PPh_3 in vacuum and in $CHCl_3$ at three different temperatures (T = 300, 240 and 100 K) at a PM6 computational level [46]. As shown in Table 2 for a given constant temperature the ΔG_T (in solution) < ΔG_T (in vacuum) and higher temperatures produced a decrease of the calculated ΔG_T in both cases (vacuum and solution), thus from a thermodynamic point of view the proclivity of **4c** to undergo the cleavage of the Pd–N bond and the formation of **3c** and free PPh_3 is favoured at higher temperatures. In fact the calculation of the enthalpy of the process (ΔH), using the formation enthalpies of **3a**, **4a** and PPh_3 obtained from program, indicated that it was endothermic (ΔH = 4.3 kcal/mol) This is consistent with the results obtained from the variable temperature $^{31}P\{^1H\}$ NMR studies of compound **4c**.

3. Conclusions

The results presented here reveal that despite the azo derivatives **2a**–**2c** exhibit different C–H bonds susceptible to be activated in all cases the cyclopalladation occurs at the *peri* position of the indole ring yielding six-membered palladacycles (**3a**–**3c**).

The study of the photo-optical properties of **2a**–**2c** and **3a**–**3c**, not only reveals that they are luminescent in CH_2Cl_2 solutions at 298 K, but also provides conclusive evidence of the influence of the nature of substituent R^2 of the R^1–N=N–R^2 ligands. The symmetrically substituted ligand **2c** is a more powerful emitter than **2a** and **2b** where R^2 is the 4-methyl (or 4-chloro) phenyl. Palladacycles **3a**–**3c** are luminescent in the solid state and in solution, but in these cases the emission band is shifted to lower energies when compared with those of the free ligands.

The study of the reactivity of **3a**–**3c** with PPh_3 produced the cleavage of the Pd–N bond and the formation of *trans*-[Pd(κ^1-*C*)Cl(PPh_3)$_2$] (**4a**–**4c**). These compounds are stable in the solid state but in solution they undergo a "*base-off/base-on*" process that involves the dissociation of one of the two PPh_3 ligands and the formation of the corresponding palladacycle (**3a**–**3c**) in which the azo ligand behaves as a bidentate {*N*,*C*(indole)}$^-$ group.

The transformations **4** → **3** + PPh_3 are reversible (by cooling or by an addition of PPh_3 at 298 K) and these changes produced significant variations in the ^1H and $^{31}P\{^1H\}$ NMR spectra, thus allowing to tune the properties and/or reactivity of these products in view of their utility in synthesis, catalysis or the design of sensors, etc. It should be noted that palladated complexes showing a behaviour similar to those of **4a**–**4c** are extremely scarce.

Among the complexes presented here, compound **3c** is the best candidate to explore these fields due to its higher emissive efficiency both in solution and in the solid state. Further studies on these areas are currently under way.

4. Experimental section

4.1. Materials and methods

4-Chloro and 4-methyl anilines, 2-phenylindole, $PdCl_2$, $Pd(AcO)_2$, LiCl and PPh_3 were obtained from commercial sources and used as received and 3-diazo-2-phenylindole was prepared as reported [21]. Solvents were distilled and dried before use [47]. Elemental analyses were carried out at the Serveis de Científico-Tècnics (*Universitat Barcelona*). Mass spectra (MALDI-TOF for **2c** or ESI^+ in the remaining cases) were performed at the Servei d'Espectrometria de Masses (*Universitat de Barcelona*). Infrared spectra were obtained with a Nicolet 400FTIR instrument using KBr pellets and only the most relevant absorptions of the new products are presented in the following sections.

High resolution ^1H NMR spectra and the two-dimensional {^1H–^1H}-NOESY and COSY experiments were registered with a Varian VRX-500 or a Bruker Avance DMX-500MHz instruments. Except where quoted the solvent used for NMR experiments was $CDCl_3$ (99.9%) and the references were $SiMe_4$ [for ^1H NMR] and $P(OMe)_3$ [$\delta(^{31}P)$ = 140.17 ppm] for ^{31}P NMR and b) these NMR studies were performed at 298 K. The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz. In the characterization section of each product the assignment of signals detected in the ^1H NMR spectra refers to the labelling patterns presented in Scheme 1. UV–vis. spectra of CH_2Cl_2 solutions of the free ligands **2a**–**2c** and the palladacycles **3a**–**3c** and **4a**–**4c** were recorded at 298 K with a Cary 100 scan 388 Varian UV spectrometer and their emission and excitation spectra of **2a**–**2c** and **3a**–**3c** were obtained on a Horiba Jobin–Yvon SPEX Nanolog-TM spectrofluorimeter at 298 K. Total luminescence quantum yields were measured at 298 K relatively to quinine sulphate in 1 N H_2SO_4 (ϕ = 0.54) (for **2a**–**2c**, **3a** and **3b**) or to $[Ru(bipy)_3]Cl_2$ in water (ϕ = 0.042) (for **3c**) as standard references.

4.2. Preparation of the precursors (*1a*–*1c*)

4.2.1. 2-Phenylindole-3-azo-(4′-methylbenzene), *1a*

To a suspension of *p*-toluidine (2.30 g, 21.5 × 10^{-3} mol) in 6 M hydrochloric acid (90 mL) was added dropwise $NaNO_2$ (1.52 g, 22.0 × 10^{-3} mol) in water (8 mL) at 0 °C. The reaction mixture was stirred for 15 min and then a solution of sodium acetate (8 g) in water (50 mL) was added over 10 min at 0 °C. A solution of 2-phenylindole (3.5 g, 18.0 × 10^{-3} mol) in ethanol (50 mL)/DMF

(10 mL) was then added over 15 min under cooling and then allowed to warm slowly to room temperature and stirred overnight. Water (50 mL) was added; the brown-red solid formed was collected by filtration, washed with water (25 mL) and finally dried under vacuum (4.42 g, 14.2×10^{-3} mol, 79%). It was used in the next step without further purification. Anal. (%) Calc. for $C_{21}H_{17}N_3$: C 81.00, H 5.50 and N 13.49; found: C 80.86, H 5.71 and N 13.27; MS (ESI^+): 312.15 $\{[M] + H\}^+$. IR data: ν = 3418, ν (N–H); 1454 and 1233 cm^{-1} ν_a (–N=N–) and ν_s (–N=N–), respectively. ^1H NMR data: δ = 9.68 (br. s, 1H, >NH), 2.22 (s, 3H, –Me), 8.60 (d, 1H, $^3J_{H,H} = 7.8$, H^1), 6.92 (t, 1H, $^3J_{H,H} = 7.8$, H^2), 7.12 (t, 1H, $^3J_{H,H} = 7.8$, H^3) and 7.30–7.50 (m, 10H, H^4–H^9).

4.2.2. 2-Phenylindole-3-azo-(4′-chlorobenzene), **1b**

This product was obtained following the procedure described above for **1a**, but using 2.74 g of p-chloroaniline (21.5×10^{-3} mol), as starting material instead of the p-toluidine (yield 4.89 g, 14.7×10^{-3} mol, 82%). Anal. (%) Calc. for $C_{20}H_{14}ClN_3$: C 72.40, H 4.25 and N 12.66; found C 72.55, H 4.40 and N 12.50. MS (ESI^+): 332.09 $\{[M] + H\}^+$. IR data: ν = 3418, ν (N–H); 1455 and 1232 cm^{-1}, ν_a (–N=N–) and ν_s (–N=N–), respectively. ^1H NMR data: δ = 9.52 (br. s, 1H, >NH), 8.61 (d, 1H, $^3J_{H,H} = 7.7$, H^1), 7.01 (t, 1H, $^3J_{H,H} = 7.7$, H^2), 7.18 (t, 1H, $^3J_{H,H} = 7.7$, H^3) and 7.280–7.52 (m, 10H, H^4–H^9).

4.2.3. 2-Phenylindole-3-azo-(2-phenylindole), **1c**

A solution of 2-phenylindole (0.65 g, 3.37×10^{-3} mol) and 3-diazo-2-phenylindole (0.74 g, 3.37×10^{-3} mol) in CH_3COOH (25 mL) was heated under stirring at 80 °C for 2 h. The reaction mixture was cooled to 298 K, evaporated to dryness under reduced pressure and the crude solid washed with ether (2 × 4 mL). The brown solid was collected and dried to give the azo-bis-indole **1c** (1.18 g, 2.8×10^{-3} mol, 85%) that was used in the next step without further purification. *Characterization data*: Anal.(%) Calc. for $C_{28}H_{20}N_4$: C, 81.53, H, 4.89 and N, 13.58; found C 81.31, H 5.02 and N 13.43. MS (ESI^+): 413,18 $\{[M] + H\}^+$. IR data: ν = 3291, ν (N–H); 1447 and 1235 cm^{-1}): ν_a (–N=N–) and ν_s (–N=N–), respectively. ^1H NMR data: δ = 9.79 (br. s, 2H, >NH), 6.90 (t, 2H, $^3J_{H,H} = 7.7$, H^2 and H^{2b}), 7.00 (t, 2H, $^3J_{H,H} = 7.7$, H^3 and H^{3b}) and 7.15–7.50 (m, 14 H, $H^{4a,b}$–$H^{9a,b}$).

4.3. Preparation of the ligands (**2a**–**2c**)

4.3.1. 1-Methyl-2-phenylindole-3-azo-(4′-methylbenzene), **2a**

To a solution of 2-phenylindole-3-azo-(4′-methylbenzene) **1a** (1.24 g, 4.0×10^{-3} mol), Aliquat 336 (0.8 g, 1.9×10^{-3} mol) and 40% NaOH (12 mL) in CH_2Cl_2 (125 mL) was added methyl iodide (2.27 g, 1 mL, 16.0×10^{-3} mol) and stirred for 24 h at 298 K. After this period, water (75 mL) was added and the mixture was transferred to a separating funnel. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (20 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated. Further purification by flash chromatography (Silica gel, ether/CH_2Cl_2 5:5) gave **2a** (1.0 g, 3.1×10^{-3} mol, 77%) as an orange solid. Anal. (%) Calc. for $C_{22}H_{19}N_3$: C 81.20, H 5.89, N 12.91; found for $C_{22}H_{19}N_3$: C 81.0, H 6.0, N 12.7. MS (ESI^+): 326.16 $\{[M] + H\}^+$. IR data: ν = 1459 and 1252 cm^{-1} ν_a (–N=N–) and ν_s (–N=N–), respectively. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 3H, Me); 3.82 (s, 3H, NMe); 7.20 (d, 2H, $J_{HH} = 8.5$, H^9); 7.30–7.60 (m, 7H, aromatic); 7.70–7.80 (m, 3H, H^8, H^4); 8.70 (d, 1H, $J_{HH} = 8.2$, H^1).

4.3.2. 1-Methyl-2-phenylindole-3-azo-(4′-chlorobenzene), **2b**

This product was obtained following the procedure described above for **2a**, but using the 2-phenylindole-3-azo-(4′-chlorobenzene), **1b** (1.33 g, 4.0×10^{-3} mol), instead of **1a**. This product was isolated as an orange solid (yield: 1.2 g, 3.5×10^{-3} mol, 87%). Anal. (%) Calc. for $C_{21}H_{16}ClN_3$: C 72.93, H 4.66, N 12.15; found C 72.6, H 4.5, N 12.3. MS (ESI^+): 346.11 $\{[M] + H\}^+$. IR data: ν = 1468 and 1249 cm^{-1} ν_a (–N=N–) and ν_s (–N=N–), respectively. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3H, NMe); 7.36 (d, 2H, $J_{HH} = 8.6$, H^9); 7.30–7.60 (m, 8H, aromatic); 7.70 (d, 2H, $J_{HH} = 8.6$, H^8); 8.64 (d, 1H, $J_{HH} = 8.0$, H^1).

4.3.3. 1,1′-Dimethyl-2-phenylindole-3-azo-(2-phenylindole), **2c**

To a solution of 2-phenylindole-3-azo-(2-phenylindole), **1c** (1.18 g, 2.86×10^{-3} mol), Aliquat 336 (0.8 g, 1.9×10^{-3} mol) and 40% NaOH (12 mL) in CH_2Cl_2 (50 mL) was added, methyl iodide (2.27 g, 1 mL, 16×10^{-3} mol) and stirred for 24 h at room temperature. A yellow precipitate appeared which was filtered, washed with water (3 × 20 mL) and dried under vacuum to give **2c** (0.97 g, 2.2×10^{-3} mol, 77%). Anal. (%) Calc. for $C_{30}H_{24}N_4$: C 81.79, H 5.49, N 12.72; found: C 81.5, H 5.62, N 12.5. MS (Maldi-TOF^+) m/z = 440.2 $[M]^+$. IR data: ν = 3060, 3044, 2929 and 2856, ν (C–H); 1467 and 1254 in cm^{-1} ν_a (–N=N–) and ν_s (–N=N–), respectively. ^1H NMR data (in dmso-d_6, 400 MHz): δ = 3.78(s, 6H, 2-NMe); 7.05(td, $^3J_{H,H} = 8.0$, $^3J_{H,H} = 1.0$, H^{3a} and H^{3b}); 7.25 (td, $^3J_{H,H} = 8.1$ and $^4J_{H,H} = 1.1$, 2H, H^2 and H^{2b}); 7.54 (d, $^3J_{H,H} = 8.0$, 2H, H^4 and H^{4b}); 7.64 (m, 6H, $2H^6$, H^7, $2H^{6b}$ and H^{7b}); 7.79 (dt, $^3J_{H,H} = 8.2$ and $^4J_{H,H} = 1.8$, 4H, $2H^5$ and $2H^{5b}$) and 8.10 (d, 2H, H^1 and H^{1b}).

4.4. Preparation of the palladium(II) complexes

4.4.1. Compound **3a**

A mixture of azoindole **2a** (429 mg, 1.4×10^{-3} mol) and $PdCl_2$ (280 mg, 1.4×10^{-3} mol) in 50 mL of methanol-dichloromethane (in a 1:1 ratio) was stirred at 298 K for 48 h. The precipitate formed was filtered off, washed with methanol. Then, it was treated with PPh_3 (310 mg, 1.2×10^{-3} mol) in 50 mL of a MeOH: CH_2Cl_2 (a 1:1) mixture and stirred at 298 K for 24 h, After this period it was filtered and the filtrate was concentrated in vacuo. The red solid obtained, after addition of diethylether, was recrystallized from CH_2Cl_2–ether and dried in vacuo to obtain **3a** as a red solid (yield: 520 mg, 0.84×10^{-3} mol, 60%). Anal. (%) Calc. for $C_{40}H_{33}ClN_3PPd$: C 65.94, H 4.57 and N 5.77; found: C 65.9, H, 4.3 and N 5.8. MS-positive ESI: 692.13 $\{[M] - Cl\}^+$. IR data: ν = 3050, 2914 and 2844, ν (C–H); 1460 and 1295 ν_a (–N=N–) and ν_s (–N=N–), respectively; 529, 507 and 506 cm^{-1} (PPh_3). $^{31}P\{^1H\}$ NMR: δ = 40.16, s. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 3H, Me); 3.86 (s, 3H, NMe); 6.50 (t, 1H, $^3J_{HH} = 8.0$, H^3); 6.59 (t, 1H, $^3J_{H,H} = {}^3J_{H,P} = 8.1$, H^2); 6.89 (d, 1H, $^3J_{H,H} = 8.0$, H^4); 7.09 (d, 2H $^3J_{HH} = 8.2$, H^5); 7.29–7.78 (m, 22H, aromatic).

4.4.2. Compound **3b**

This complex was obtained using the same procedure as that described above for **3a**, but using 277 mg (0.8×10^{-3} mol) of **2b**, 142 mg (0.8×10^{-3} mol) of $PdCl_2$ and 183 mg (0.7×10^{-3} mol) of PPh_3 (yield: 262 mg, 4.0×10^{-4} mol, 50%). Anal. (%) Calc. for $C_{39}H_{30}Cl_2N_3PPd$: C 62.54, H 4.04, N 5.61; found: C 62.5, H 3.9, N 5.5. MS(ESI^+): 714.09 $\{[M] - Cl\}^+$. IR data: ν = 3046, 2923 and 2848, ν (C–H); 1461 and 1288 ν_a (–N=N–) and ν_s (–N=N–), respectively; 529, 511 and 498 cm^{-1} (PPh_3). $^{31}P\{^1H\}$ NMR: δ = 41.44, s. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.87 (s, 3H, NMe); 6.52 (t, 1H, $^3J_{H,H} = 7.8$, H^3); 6.61 (t, 1H, $^3J_{H,H} = {}^4J_{P,H} = 7.8$, H^2); 6.90 (d, 1H, $^3J_{H,H} = 7.9$, H^4); 7.29–7.80 (m, 24H, aromatic).

4.4.3. Compound **3c**

Ligand **2c** (0.44 g, 1.0×10^{-3} mol), $Pd(OAc)_2$ (0.246 g, 1.1×10^{-3} mol) and 50 mL of acetic acid were introduced in 100 mL flask and the mixture was stirred at 100 °C for 3 h. Then cooled to room temperature and evaporated under reduced pressure. The residue was treated with CH_2Cl_2 (250 mL), filtered through celite

and the solution was concentrated in vacuum. The deep-red solid formed was treated with 50 mL of acetone and 170 mg of LiCl (4.0×10^{-3} mol) and the reaction mixture was stirred for 24 h at 298 K. The solid formed was filtered through a short pad (ca. 1 cm) of silica using CH_2Cl_2 as solvent to yield 0.434 g of a red solid that was collected by filtration and air-dried. Afterwards it was suspended in 50 mL of CH_2Cl_2, treated with triphenylphosphine (524 mg, 2.0×10^{-3} mol) and the mixture was stirred for 24 h. The resulting solution was evaporated to dryness and purified by silica gel column chromatography with ether as eluant. The deep garnet band eluted was collected and concentrated to dryness. The solid formed was dissolved in the minimum amount of CH_2Cl_2 and slow evaporation of this solution at 278 K produced **3c** as a crystalline sample (yield: 0.75 g, 0.8×10^{-3} mol, 62%) of **3c** as a deep-red solid. Anal. (%) Calc. for $C_{48}H_{38}ClN_4PPd \cdot CH_2Cl_2$: C 63.38, H 4.34, N 6.03; found: C 63.15, H 4.30, N 5.98. MS (ESI^+): 807.2 $\{[M] - Cl{-}CH_2Cl_2\}^+$ and 545.1 $\{[M] - Cl - (PPh_3) - CH_2Cl_2\}^+$. IR data: ν = 3043, 2906 and 2843, ν (C–H); 1456 and 1274, ν_a (–N=N–) and ν_s (–N=N–), respectively; 530, 512 and 502 cm^{-1}:(PPh_3). ^1H NMR data: δ = 3.57 (s, 3 H, Me^b), 3.81(s, 3 H, Me), 6.38 (t, 1H, $^3J_{H,H}$ = 7.8, H^3), 6.42 (dd, 1H, $^3J_{H,H}$ = 7.8 and $^4J_{P,H}$ = 7.2, H^2) 6.80 (d, 1H, $^3J_{H,H}$ = 7.8, H^4) 7.05 (t, 1H, $^3J_{H,H}$ = 7.5, H^{2b}), 7.20 (t, 1H, $^3J_{H,H}$ = 7.5, H^{3b}), 8.40 (d, 1H, $^3J_{H,H}$ = 7.5, H^{1b}), 7.69 (d, 1H, $^3J_{H,H}$ = 7.3, H^5), 7.80 (d, 2H, $^3J_{H,H}$ = 7.3, H^{5b}) and 7.30–7.55 (m, 22H, H^{4b}, H^6, H^{6b}, H_7 and protons of the PPh_3). $^{31}P\{^1H\}$ NMR: δ = 39.7, s.

4.4.4. Compound *4a*

A mixture of **3a** (85 mg, 9×10^{-5} mol) and PPh_3 (144 mg, 3.6×10^{-4} mol) in 50 mL of CH_2Cl_2 was stirred for 2 h at 298 K and then filtered. The filtrate was concentrated in vacuum. Addition of diethylether gave a red solid obtained, that was later on recrystallized from CH_2Cl_2–ether and dried in vacuum to obtain **4a** as a red solid (yield: 85 mg, 8.5×10^{-5} mol, 95%). Anal. (%) Calc. for $C_{58}H_{48}ClN_3P_2Pd$: C 70.31, H 4.88, N 4.24; found: C 70.1, H 4.7, N 4.2 MS(ESI^+): 692.13 $\{[M] - Cl{-}PPh_3)\}^+$. IR data: ν = 3040, 2910 and 2844, ν (C–H); 1434 and 1189 ν_a (–N=N–) and ν_s (–N=N–), respectively; 521, 510 and 496 (in cm^{-1}) (PPh_3). $^{31}P\{^1H\}$ NMR (240 K): δ = 17.26, s. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.35 (s, 3H, Me); 3.50 (br s, 3H, NMe); 6.20–6.50 (br m, 2H, H^3 and H^2); 6.70 (d, 1H, J_{HH} = 7.7, H^4); 7.29–7.78 (m, 22H, aromatic); 7.85 (d, 2H, J_{HH} = 7.2H^5).

4.4.5. Compound *4b*

This product was obtained using the same procedure as that described above for **4a**, but using 82 mg (1.1×10^{-4} mol) of **3b** and 115 mg (4.4×10^{-4} mol) of triphenylphosphine (yield: 105 mg, 1.0×10^{-4} mol, 95%). Anal. (%) Calc. for $C_{57}H_{45}Cl_2N_3P_2Pd$: C 67.70, H 4.49, N 4.2; found: C 67.5; H 4.6, N 4.2. MS(ESI^+) 714.09 $\{[M] - Cl - PPh_3)\}^+$. IR data ν = 3045, 2929 and 2847, ν (C–H); 1437 and 1192 ν_a (–N=N–) and ν_s (–N=N–), respectively; 521, 511 and 508 cm^{-1} (PPh_3). $^{31}P\{^1H\}$ NMR (240 K): δ = 17.30, s. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.50 (br s, 3H, NMe); 6.20–6.50 (br m, 2H, H^3, H^2); 6.77 (d, 1H, $^3J_{HH}$ = 7.2, H^4); 7.29–7.78 (m, 22H, aromatic); 7.93 (d, 2H, $^3J_{HH}$ = 8.5 Hz, H^5).

4.4.6. Compound *4c*·3/2CH_2Cl_2·1/2H_2O

Compound **3c**·CH_2Cl_2 (30 mg, 3.2×10^{-5} mol) was dissolved in 15 mL of CH_2Cl_2, then PPh_3 (17 mg, 6.5×10^{-5} mol) was added and the reaction mixture was stirred at 298 K for 1 h. After this period the solution was concentrated in a rotary evaporator to ca. 1 mL, and transferred to a small vessel. The addition of diethylether (1.0 mL) and the slow diffusion of this solvent at 298 K produced monocrystals of **4c**·3/2CH_2Cl_2·1/2H_2O that were collected and air dried (yield: 34 mg, 2.7×10^{-5} mol, 85%). Anal. (%) Calc. for $C_{66}H_{53}ClN_4P_2Pd \cdot 3/2CH_2Cl_2 \cdot 1/2H_2O$: C 65.26, H 4.62, N 4.51; found: C 65.3, H 4.6, N 4.5. MS (ESI^+): 807.2 $\{[M] - (\text{solvation molecules}) - Cl\}^+$ and 545.1 $\{[M] - (\text{solvation molecules}) - Cl - (PPh_3)\}^+$. IR data: ν = 3050, 2919 and 2859, ν (C–H); 1430 and 1254 ν_a (–N=N–) and ν_s (–N=N–), respectively; 525, 512 and 507 cm^{-1} (PPh_3). ^1H NMR (250 MHz, at 240 K and $c = 4 \times 10^{-2}$ M): δ = 3.07 (s, 3 H, Me), 3.72 (s, 3 H, Me), 5.12 (s, 3H, CH_2Cl_2), 6.30 (br, 1H, H^2), 6.60 (d, 1H, $^3J_{H,H}$ = 7.4, H^3), 6.80 (d, 1H, $^3J_{H,H}$ = 7.6, H^4), 7.80 (d, 1H, $^3J_{H,H}$ = 7.4, H^{5b}), 7.93 (d, 2H, $^3J_{H,H}$ = 7.4, 1.0, H^{6b}), 6.90–7.70 (m, 37H, H^5, H^{1b}–H^{4b}, $H^{6a,b}$–$H^{7a,b}$ and protons of the PPh_3 ligands) $^{31}P\{^1H\}$ NMR (at 240 K and $c = 4 \times 10^{-2}$ M): δ = 20.3, s (see text and Fig. 6).

4.5. Crystallography

A prismatic crystal of **3c**·CH_2Cl_2, **4a**, **4b** or **4c**·3/2CH_2Cl_2·1/2H_2O (sizes in Table 3) was selected and mounted on a MAR345 diffractometer an image plate detector. Unit-cell parameters were determined from 3997 (for **3c**·CH_2Cl_2), 304 (for **4a**), 25 (for **4b**) and 205 (for **4c**·3/2CH_2Cl_2·1/2H_2O) reflections {in the ranges, $12° < \theta < 21°$, $3° < \theta < 31°$, $12° < \theta < 21°$, and $3° < \theta < 31°$, respectively) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo K_α radiation. The number of reflections collected were 43,288 (for **3c**), 23,851 (for **4a**), 14,018 (for **4b**) and 27,382 (for **4c**·3/2CH_2Cl_2·1/2H_2O), in the ranges $2.61° \le \theta \le 32.45°$, $2.57° < \theta < 30.00°$, $2.02° < \theta < 29.97°$ and $1.38° \le \theta \le 32.03°$, for **3c**, **4a**, **4b** and **4c**, respectively}, of which 12,745 (for **3a**), 12,264 (for **4a**) were non-equivalent by symmetry. The number of reflections assumed as observed applying the condition $I > 2\sigma(I)$. were 9598, 9003, 12,149 and 10,198 (for **3a**·CH_2Cl_2, **4a**, **4b** and **4c**·3/2CH_2Cl_2·1/2H_2O, respectively). Lorentz-polarization and absorption corrections were made.

These structures were solved by Direct methods, using SHELXS computer program [48] and refined by full-matrix least-squares method with SHELX97 computer program [49] using 43,288, 14,018, 23,851, and 27,382 reflections for **3c**·CH_2Cl_2, **4a**, **4b** and **4c**·3/2CH_2Cl_2·1/2H_2O, respectively, (very negative intensities were not assumed). The function minimized was $\Sigma w||Fo|^2 - |Fc|^2|^2$, where $w = [\sigma^2(I) + 0.0597P)^2 + 0.0901P]^{-1}$ (for **3c** CH_2Cl_2), $w = [\sigma^2(I) + (0.0401P)^2 + 3.9847P]^{-1}$ (for **4a**) and $w = [\sigma^2(I)+(0.0493P)^2 + 0.4243P]^{-1}$ (for **4b**), $w = [\sigma^2(I) + (0.1136P)^2 + 0.6964P]^{-1}$ (for **4c**·3/2CH_2Cl_2·1/2H_2O), and $P = (|Fo|^2 + 2|Fc|^2)/3$; f, f', and f'' were taken from the bibliography [50]. 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 0.0470, 0.060, 0.05 and 0.084 for **3c**·CH_2Cl_2, **4a**, **4b** and **4c**·3/2CH_2Cl_2·1/2H_2O, respectively and the wR(on $(|F|^2)$ values equal to 0.0710 (for **3c**·CH_2Cl_2), 0.0148 (for **4a**), 0.098 (for **4b**) and 0.248 (for **4c**·3/2CH_2Cl_2·1/2H_2O). Further details concerning the resolution and refinement of these crystal structures are given in Table 3.

4.6. Computational details

DFT calculations of **3c**, **4c** and the free PPh_3 have been performed at the B3LYP level [51] using the Gaussian 03 software [27]. The basis set has been chosen as follows: LANL2DZ [52] for Pd and Cl, including polarization functions for Cl [53], 6-31G [54], for hydrogen [55], and 6-31G(d) including polarization functions [56] for the remaining atoms. Solvent effects have been calculated using the C-PCM model.13Semiempirical calculations have been performed with the PM6 method, using the MOPAC2009 software [46b]. Solvent effects have been taken into account using the COSMO model [46].

Table 3
Crystal data and details of the refinement of the crystal structures of compounds **3a** CH_2Cl_2, **4a**, **4b** and **4c** $3/2CH_2Cl_2 \cdot 1/2H_2O$.

	3a CH_2Cl_2	**4a**	**4b**	**4c** $3/2CH_2Cl_2 \cdot 1/2H_2O$
Chemical formula	$C_{49}H_{40}Cl_3N_4PPd$	$C_{56}H_{48}ClN_3P_2Pd$	$C_{56}H_{48}Cl_2N_3P_2Pd$	$(C_{66}H_{53}ClN_4P_2Pd)_2$ $3CH_2Cl_2 \cdot H_2O$
Formula weight	928.57	990.78	1011.20	2484.62
Crystal size/mm × mm × mm	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	P-1	P-1
a/Å	14.216(6)	11.402(6)	11.344(8)	13.657(7)
b/Å	18.909(5)	12.106(4)	12.015(3)	15.905(7)
c/Å	16.536(6)	18.110(7)	18.111(11)	16.135(7)
α/deg.	90.0	99.12(2)	99.65(3)	90.98(3)
β/deg.	102.64(2)	97.44(2)	96.98(6)	90.98(3)
γ/deg.	90.0	92.78(3)	92.13(3)	111.81(2)
T/K	293(2)	293(2)	293(2)	293(2)
V/Å^3	4337(3)	2441.3(18)	2411(2)	3252(3)
Z	4	2	2	1
D_{calc}/Mg × m^{-3}	1.422	1.348	1.393	1.269
μ/mm^{-1}	0.689	0.542	0.604	0.541
F(000)	1896	1020	1036	1276
Θ range for data collection/deg.	From 2.61 to 32.45	From 2.57 to 32.44	From 2.02 to 29.97	From 1.38 to 32.03
N. of collected reflections	43,288	23,831	14,019	27,382
N. of unique reflections {R(int)}	12,745 {0.0416}	12,955 {0.0595}	14,019 {0.0119}	16,144 {0.0798}
N. of parameters	542	587	587	610
Goodness of fit on F^2	1.124	1.240	1.014	1.116
R indices {$I > 2\sigma(I)$}	$R_1 = 0.0470$, $wR_2 = 0.1165$	$R_1 = 0.0639$, $wR_2 = 0.1644$	$R_1 = 0.0496$, $wR_2 = 0.0986$	$R_1 = 0.0837$, $wR_2 = 0.2252$
R indices (all data)	$R_1 = 0.0710$, $wR_2 = 0.1261$	$R_1 = 0.0642$, $wR_2 = 0.1645$	$R_1 = 0.1174$, $wR_2 = 0.1171$	$R_1 = 0.1216$, $wR_2 = 0.248$

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Appendix A. Supplementary material

CCDC 857266–857269 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via: www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary information

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.11.036.

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