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The cyclopalladation reaction of 2-phenylaniline revisited

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Abstract

2-Phenylaniline reacted with $Pd(OAc)_2$ in toluene at room temperature for 24 h in a one-to-one molar ratio and with the system $PdCl_2$, NaCl and NaOAc in a 1 (2-phenylaniline):1 ($PdCl_2$):2 (NaCl):1 (NaOAc) molar ratio in methanol at room temperature for one week to give the dinuclear cyclopalladated compounds $(\mu\text{-X})_2[Pd\{\kappa^2\text{-}\boldsymbol{N2'},\boldsymbol{C1}\text{-2-}(2'\text{-}NH_2C_6H_4)C_6H_4\}]_2$ [**1a** (X = OAc) and **1b** (X = Cl)] in high yield. Moreover, the reaction between 2-phenylaniline and $Pd(OAc)_2$ in one-to-one molar ratio in acid acetic at 60 °C for 4 h, followed by a metathesis reaction with LiBr, allowed isolation of the dinuclear cyclopalladated compound $(\mu\text{-Br})_2[Pd\{\kappa^2\text{-}\boldsymbol{N2'},\boldsymbol{C1}\text{-2-}(2'\text{-}NH_2C_6H_4)C_6H_4\}]_2$ (**1c**) in moderate yield. A parallel treatment, but using monodeuterated acetic acid (DOAc) as solvent in the cyclopalladation reaction, allowed isolation of a mixture of compounds **1c**, $\mathbf{1c_{d1}}$ $[Pd\{\kappa^2\text{-}\boldsymbol{N2'},\boldsymbol{C1}\text{-2-}(2'\text{-}NH_2C_6H_4)C_6H_4\}(\mu\text{-Br})_2[Pd\{\kappa^2\text{-}\boldsymbol{N2'},\boldsymbol{C1}\text{-2-}(2'\text{-}NH_2C_6H_4)\text{-3-D-}C_6H_3\}]$ and $\mathbf{1c_{d2}}$ $(\mu\text{-Br})_2[Pd\{\kappa^2\text{-}\boldsymbol{N2'},\boldsymbol{C1}\text{-2-}(2'\text{-}NH_2C_6H_4)\text{-3-D-}C_6H_3\}]_2$ in moderate yield and with a deuterium content of ca. 60%. **1a** and **1b** reacted with pyridine and PPh_3 affording the mononuclear cyclopalladated compounds $[Pd\{\kappa^2\text{-}\boldsymbol{N2'},\boldsymbol{C1}\text{-2-}(2'\text{-}NH_2C_6H_4)C_6H_4\}(X)(L)]$ [**2a** (X = OAc, L = py), **2b** (X = Cl, L = py), **3a** (X = OAc, L = PPh_3) and **3b** (X = Cl, L = PPh_3)] in a yield from moderate to high. Furthermore, **1a** reacted with $Na(acac)\cdot H_2O$ to give the mononuclear cyclopalladated compound **4** $[Pd\{\kappa^2\text{-}\boldsymbol{N2'},\boldsymbol{C1}\text{-2-}(2'\text{-}NH_2C_6H_4)C_6H_4\}(acac)]$ in moderate yield. ^1H NMR studies in $CDCl_3$ solution of **2a**, **2b**, **3a**, **3b** and **4** showed that **2a** and **3a** presented an intramolecular hydrogen bond between the acetato ligand and the amino group, and were involved in a dynamic equilibrium with water present in the $CDCl_3$ solvent; and that the enantiomeric molecules of **2b** and **4** were in a fast exchange at room temperature, while they were in a slow exchange for **2a**, **3a** and **3b**. The X-ray crystal structures of **3b** and **4** were determined. **3b** crystallized in the triclinic space group $P\bar{1}$ with $a = 9.9170(10)$, $b = 10.4750(10)$, $c = 12.0890(10)$ Å, $\alpha = 98.610(10)°$, $\beta = 94.034(10)°$ and $\gamma = 99.000(10)°$ and **4** in the monoclinic space group $P2_1/a$ with $a = 11.5900(10)$, $b = 11.2730(10)$, $c = 12.2150(10)$ Å, $\alpha = 90°$, $\beta = 107.6560(10)°$ and $\gamma = 90°$.

Keywords: Cyclometallation; 2-Phenylaniline; Palladium

1. Introduction

Cyclopalladated compounds containing a biphenyl cyclopalladated unit have previously been used as starting materials in organic and organometallic synthesis [1–8], as precursors of catalytic species in C–C and C–N coupling reactions [9] and in cyclopalladation reactions to address questions such as the regioselectivity of the cyclopalladation reaction [10] and the $E \rightarrow Z$ isomerization of *exo*-cyclopalladated imines [11]. Furthermore, an intramolecular C–H bond activation of a biphenyl group in a palladium(II) centre has been proposed in a catalytic cycle that transforms a C–H bond in a C–C bond [12].

In spite of these precedents, little attention has been focused on the synthesis, structure, and dynamic behaviour of di- and mono-nuclear cyclopalladated compounds containing a biphenyl cyclopalladated unit. Furthermore, it is well known that cyclopalladation of

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primary amines in high yield is a challenging problem [13]. These precedents prompted us to reinvestigate the cyclopalladation reaction of 2-phenylaniline, which we reported previously in a moderate yield of ca. 50% [14].

2. Results and discussion

Scheme 1 shows the di- and mono-nuclear cyclopalladated compounds discussed in this paper, and Fig. 1 the letters assigned to the protons of their biphenyl cyclopalladated unit in regard to the discussion that follows.

Notably, compounds **1a** and **1b** were obtained in 85% and 75% yield, respectively, by treating 2-phenylaniline with palladium(II) acetate in toluene at room temperature for 24 h in a one to one–one molar ratio and by treating the system 2-phenylaniline/$PdCl_2$/NaCl/NaOAc in a molar ratio of 1/1/2/1 in methanol at room temperature for one week. In both cases, **1a** and **1b** precipitated in the reaction medium, were isolated by filtration and purified by washing with adequate solvents. It should be noted that **1a** was isolated as an addition compound of formula **1a** · 0.8 toluene and that the attempts to eliminate the toluene retained for **1a** were not successful. In addition, the reaction between 2-phenylaniline and palladium(II) acetate in one-to-one molar ratio in acetic acid at 60 °C for 4 h, followed by a metathesis reaction with LiBr, allowed the isolation of compound **1c** in a moderate yield of 39%. It should be noted that the cyclopalladation reaction (ii) of Scheme 1 is the first example of a cyclopalladation reaction of a primary amine, which proceeds in good yield, that uses as palladating agent the system $PdCl_2$/NaCl/NaOAc.

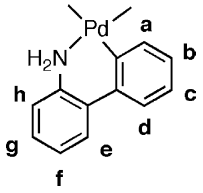
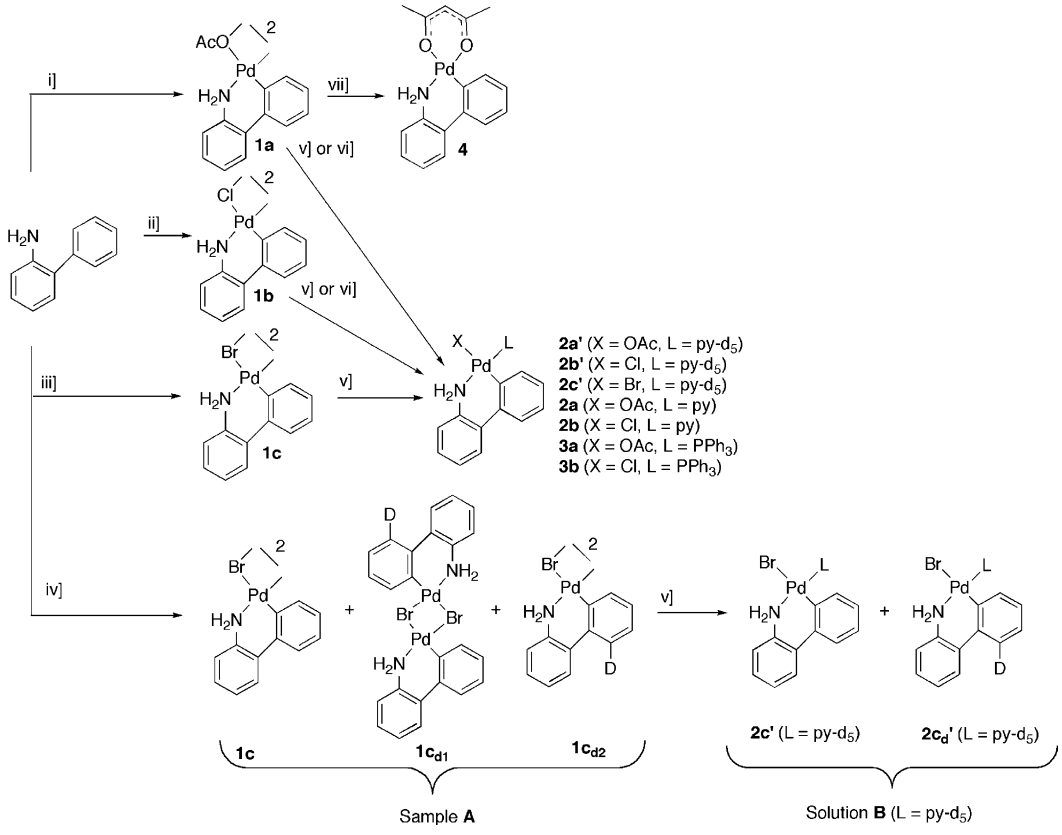


Fig. 1. Lettering of the protons of the biphenyl cyclopalladated unit.

Compounds **1** were only slightly soluble in common organic solvents, but compound **1c** was soluble in



Scheme 1. (i) 2-phenylaniline/ $Pd(OAc)_2$, molar ratio = 1:1, toluene, room temperature, 24 h. (ii) 2-phenylaniline/$PdCl_2$/NaCl/NaOAc, molar ratio = 1:1:2:1, MeOH, room temperature, 1 week. (iii) (a) 2-phenylaniline/ $Pd(OAc)_2$, molar ratio = 1:1, acetic acid, 60 °C, 4 h, (b) LiBr (excess), acetone, room temperature, 45 min, (c) Purification by column chromatography: stationary phase, SiO_2; mobile phase, $CHCl_3$/MeOH (100/6). (iv) (a) 2-phenylaniline/$Pd(OAc)_2$, molar ratio = 1:1, monodeuterated acetic acid (DOAc), 60 °C, 4 h, (b) LiBr (excess)/acetone, room temperature, 45 min, (c) purification by column chromatography: stationary phase, SiO_2; mobile phase, $CHCl_3$/MeOH (100/6). (v) py-d_5 (excess), $CDCl_3$, room temperature. (vi) L = py (excess) or PPh_3 (molar ratio **1**/PPh_3 = 1:2), acetone, room temperature, 3 h. (vii) Na(acac) · H_2O (excess), acetone, room temperature, 3 h.

acetone. Compounds **1a** and **1b** gave satisfactory elemental analyses, IR and FAB^+. In the IR of **1a**, the asymmetric and symmetric stretchings of the carboxylate groups appeared at 1581 and 1419 cm^{-1}, respectively, indicating that the acetato ligands presented a bidentate bridging coordination mode [15] and in the FAB^+ of compounds **1**, one of the most intense peaks was $[M_y + H^+ - HX]$, [y = **1a** (X = OAc), y = **1b** (X = Cl) or y = **1c** (X = Br)], according to their dinuclear structure [16]. In addition, suspensions of compounds **1** in $CDCl_3$ reacted with an excess of py-d_5 affording yellow solutions whose ^1H NMR spectra at 200 MHz showed the quantitative formation of the mononuclear cyclopalladated compounds **2′**. Thus, according to the *cis* arrangement between the py-d_5 ligand and the palladated phenyl ring and the structure of compounds **2′**, their **a** proton resonated at low frequencies (6.52, 6.48 and 6.47 ppm, respectively) and appeared as a doublet ($^3J_{HH}$ = 7–8 Hz) due to their coupling with the **b** proton [10,11,14]. Furthermore, ^1H–^1H COSY and NOESY experiments at 500 MHz allowed the assignment of the **a**–**e** protons in compound **2c′**.

In order to elucidate whether the C–H activation step of the cyclopalladation reaction was a reversible process, 2-phenylaniline was treated with palladium(II) acetate in a one-to-one molar ratio in monodeuterated acetic acid (DOAc) at 60 °C for 24 h, followed by a metathesis reaction with LiBr. This procedure allowed the isolation of sample **A** in a yield of 45%. Sample **A** was a mixture of compounds **1c**, $\mathbf{1c_{d1}}$ and $\mathbf{1c_{d2}}$. This was inferred from the ^1H NMR at 500 MHz of solution **B**, which presented the signals corresponding to compounds **2c′** and $\mathbf{2c'_d}$. Solution **B** was obtained by treating a suspension of **A** in $CDCl_3$ with py-d_5. It should be noted that the ^1H NMR in perdeuterated acetic acid of 2-phenylaniline demonstrated that 2-phenylaniline was in the form 2-$PhC_6H_4ND_2$ in this solvent, but the ^1H NMR of solution **B** showed that the amino groups of sample **A** did not present deuterium. Thisresult suggested that the amino groups of sample **A** exchanged D by H with water molecules present in the acetone solvent used in its preparation. In the ^1H NMR at 500 MHz of solution **B**, the decrease of the intensity of the signal of the **d** proton in relation to the intensity of the remaining aromatic protons, demonstrated that deuterium atoms were incorporated at the 3 position of the metallated phenyl ring. Thus, applying Eq. (1), in which $\chi(\mathbf{2c'_d})$ and r were the mole fraction of compound $\mathbf{2c'_d}$ and the ratio between the integrals of the **d** and **e** protons, it was found that the molar fraction of compound $\mathbf{2c'_d}$ in solution **B** was ca. 0.6. The mole fraction of $\mathbf{2c'_d}$ in solution **B** was thereafter assumed to be the deuterium content of samples **A** (ca. 60%); because the splitting reaction with py-d_5, which transforms sample **A** into solution **B**, should affect neither the Pd–C σ bonds nor the C–D σ bonds of sample **A**.

$$\chi(\mathbf{2c'_d}) = 1 - r \qquad (1)$$

It should be noted that the presence of deuterium atoms in the three position of the palladated phenyl ring of the molecules, which constitute sample **A**, showed that the C–H bond activation step of the cyclopalladation reaction of 2-phenylaniline was a reversible process. Furthermore, these findings were consistent with an intramolecular mode for the C–H bond activation, in accordance with the general mechanism accepted for the cyclometallation reaction [17]. It should be noted that studies on the cyclopalladation reaction of benzylamine in monodeuterated acetic acid using as metallating agent palladium(II) acetate also showed that the C–H bond activation step of this reaction is a reversible process and proceeds in an intramolecular mode [18].

In order to fully characterize compounds **1a** and **1b**, they were transformed by splitting reactions in the mononuclear cyclopalladated compounds **2a**, **2b**, **3a** and **3b**. Furthermore, **1a** was transformed into the mononuclear compound **4** by a reaction between **1a** and an excess of Na(acac) · H_2O. Compounds **2a**, **2b**, **3a**, **3b** and **4** were obtained in moderate to high yields, were soluble in $CHCl_3$ and acetone and gave satisfactory elemental analyses, IR, FAB^+ and ^1H NMR. In the IR of **2a** and **3a**, the difference in the wave numbers of the asymmetric and symmetric stretchings of their carboxylate group, indicated that the acetato ligand presented a monodentate coordination mode [15]. In the FAB^+ of **2a**, **2b**, **3a**, **3b** and **4**, the base peak was $[M_y + H^+ - HX]$, [y = **2a** or **3a** (X = OAc), y = **2b** or **3b** (X = Cl), and y = **4** (X = acac)], according to their mononuclear structure [16]. Furthermore, ^1H–^1H COSY and NOESY experiments at 500 MHz for compounds **2a**, **2b**, **3a** and **3b** allowed the assignment of the most informative aromatic protons. Thus, according to the *cis* arrangement between their pyridine or triphenylphosphine ligand and their palladated phenyl ring and to their structure [10,11,14,19], the **a** proton of compounds **2a**, **2b**, **3a** and **3b** resonated at low frequencies (6.54, 6.53, 6.41 and 6.50 ppm, respectively) and appeared as a doublet for **2a** and **2b**, due to the coupling of the **b** proton with the **a** proton, and as a triplet for **3a** and **3b**, due to the coupling of the **b** proton and the phosphorus nucleus with the **a** proton. Moreover, for compounds **3a** and **3b**, the coupling constant between the phosphorus nucleus and the **a** proton (7–8 Hz) was consistent with a *cis* arrangement between the triphenylphosphine ligand and the palladated phenyl ring. In addition, the chemical shift of the phosphorus nucleus of **3a** (34.25 ppm) and **3b** (35.12 ppm) was in the interval expected for a cyclopalladated compound of general formula *trans*-***N***,***P***-[Pd(C,N)X-(PPh_3)] (X = OAc, Cl or Br) with a six-membered palladacycle [10,11,14,20–22].

The X-ray crystal structure of compounds **3b** and **4** was determined. Figs. 2 and 3 show the X-ray molecular structures of **3b** and **4** and the labels of selected atoms

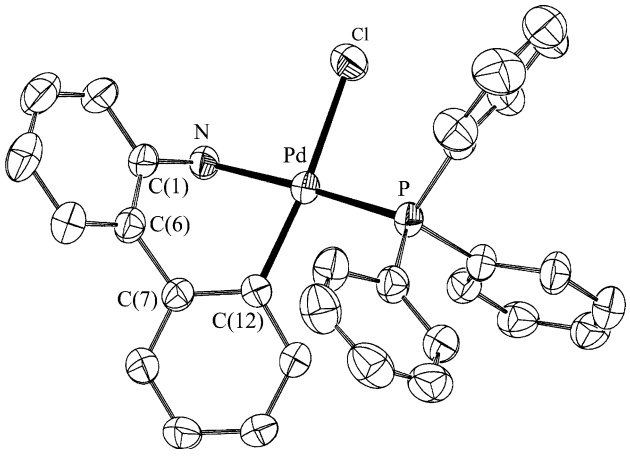


Fig. 2. X-ray molecular structure of compound **3b**.

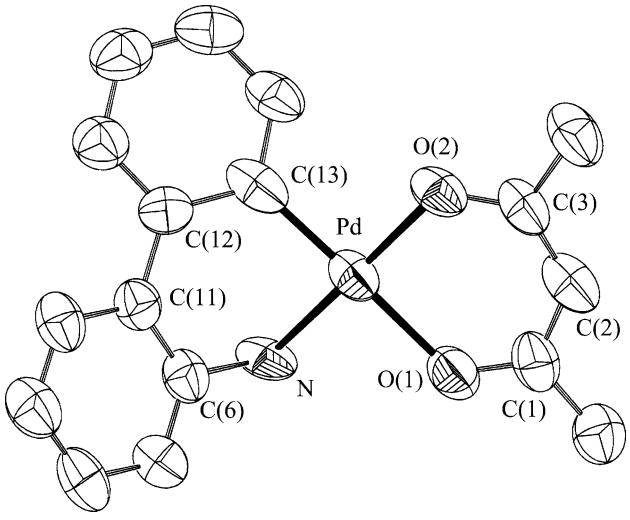


Fig. 3. X-ray molecular structure of compound **4**.

Table 1
Selected bond distances and angles for compounds **3b** and **4**

3b		**4**	
Pd–C(12)	2.021(4)	Pd–C(13)	1.969(6)
Pd–N	2.115(3)	Pd–N	1.995(4)
Pd–P	2.2490(9)	Pd–O(2)	1.993(3)
Pd–Cl	2.4056(11)	Pd–O(1)	2.093(4)
C(12)–Pd–N	84.38(13)	C(13)–Pd–N	86.4(2)
C(12)–Pd–P	92.52(11)	C(13)–Pd–O(2)	92.72(19)
N–Pd–P	176.62(8)	N–Pd–O(2)	178.52(12)
C(12)–Pd–Cl	171.40(11)	C(13)–Pd–O(1)	173.33(18)
N–Pd–Cl	87.35(9)	N–Pd–O(1)	89.38(16)
P–Pd–Cl	95.80(4)	O(2)–Pd–O(1)	91.62(15)
C(1)–N–Pd	107.5(2)	C(6)–N–Pd	114.9(3)

Distances in Å and angles in °.

for the following discussion, and Table 1 gives selected bond distances and angles. **3b** crystallized in the triclinic space group $P\bar{1}$ and **4** in the monoclinic space group $P2_1/a$. Thus, a pair of enantiomeric molecules was present in the unit cell of **3b** ($Z = 2$) and two pairs of enantiomeric molecules were present in the unit cell of **4** ($Z = 4$).

The structures consisted of discrete molecules separated by van der Waals distances and presented neither hydrogen bonds nor π–π stacking interactions between neighbouring molecules [23]. The distances and angles around the palladium atoms were in the usual intervals [21,24,25]. The palladium atoms presented a distorted square planar coordination. Thus, for **3b**, the deviation of C(12) from the plane formed by N, Pd, P and Cl was −0.108(4) Å and for **4**, the deviation of O(1) from the plane formed by N, Pd, O(2) and C(13) was −0.215(3) Å. In both cases, the six-membered palladacycle was nonplanar and the palladium atom and the metallated carbon atom were out of the plane formed by the other four atoms of the metallacycle. This was inferred for **3b** by the torsion angles N–C(1)–C(6)–C(7), C(12)–(C7)–C(6)–C(1) and Pd–C(12)–C(7)–C(6), which were 0.3(5)°, 38.0(5)° and −5.4(5)°, respectively; and for **4**, by the torsion angles N–C(6)–C(12)–C(11), C(6)–C(11)–C(12)–C(13) and C(11)–C(12)–C(13)–Pd; which were −1.6(7)°, −30.5(7)° and 5.2(7)°, respectively. It should be noted that the nonplanar structure of the six-membered palladacycle is the origin of the chirality in this kind of compounds. In addition, for compound **4**, the six-membered metallacycle formed by the acetylacetonate ligand and the palladium atom was planar since the torsion angles Pd–O(2)–C(3)–C(2), O(1)–Pd–O(2)–C(3) and O(2)–C(3)–C(2)–C(1) were −0.5(7)°, 5.3(4)° and −3.7(9)°, respectively. For compound **4**, and according to the *trans* influence of the coordinated ligands to the palladium atom, the Pd–O(1) distance [2.093(4) Å] was larger than the Pd–O(2) distance [1.993(3) Å]. Furthermore, comparing **3b** and **4**, the Pd–N distance [2.115(3) Å] and the Pd–C(12) distance [2.021(4) Å] for **3b** were larger than the Pd–N distance [1.995(4) Å] and the Pd–C(13) distance [1.969(6) Å] for **4**, due to the greater *trans* influence of the P and Cl atoms in relation to the O(2) and O(1) atoms, respectively [26].

In a previous paper [14], we reported the X-ray crystal structure of the mononuclear compound [Pd{κ^2-***N2′***,***C1***-2-(2′-$NH_2C_6H_4$)C_6H_4}Br(PPh_3)] (compound **3c**); which is identical to compound **3b**, but it presents as unidentate anionic ligand a bromo ligand. It should be noted that there were no significant differences between the crystal structures of compounds **3c** and **3b**, both crystallized in the triclinic space group $P\bar{1}$ and the distances and angles were quite similar for both compounds, but in **3c** the distance Pd–Br was 2.5399(7) Å and in **3b** the distance Pd–Cl was 2.4056(11) Å.

We note that in the room temperature ^{1}H NMR at 200 MHz of compounds **2b** and **4**, the protons of the amino group appeared as a broad A_2 spin system, centred at 5.77 ppm for **2b** and at 4.92 ppm for **4**. This

result indicated a fast exchange between their enantiomeric molecules. In contrast, in the same conditions, the protons of the amino group of **3b** produced a broad AB spin system, centred at 4.97 ppm, due to a slow exchange between their enantiomeric molecules. These results agreed with previous studies on the dynamic behaviour of nonplanar six-membered palladacyles, which related the rate of transformation between their enantiomeric conformations with the volume of the ancillary ligands coordinated to the metal centre [27]. It should be noted that at −60 °C, the conversion between the enantiomeric molecules of **2b** and **4** was still in a fast exchange. This result contrasted with the behaviour of mononuclear cyclopalladated compounds containing a six-membered palladacycle derived from 2-benzylpyridine and 2-benzylbenzothiazole for which the exchange between their enantiomeric molecules was in a slow exchange at low temperature [27,28].

It is noteworthy that in the room temperature ^{1}H NMR at 200 MHz of **2a** and **3a**, the protons of the amino group were not observed. Nevertheless, at 300 MHz and at −60 °C, they gave place to a broad AX spin system, with the branches centred at 10.41 and 4.35 ppm for **2a** and at 8.83 and 4.54 ppm for **3a**. In addition, the chemical shift of the water present in the $CDCl_3$ was 2.33 ppm for the $CDCl_3$ solution containing **2a** and 2.72 ppm for the $CDCl_3$ solution containing **3a**. Raising the temperature for the $CDCl_3$ solution containing **3a** until 10 °C, the signals of the amino protons broadened and were centred at 9.51 and 4.33 ppm and the chemical shift of the water present in the $CDCl_3$ moved to 1.71 ppm. Similar behaviour was observed when the temperature of the $CDCl_3$ solution containing **2a** was increased. These results were consistent with: (i) a slow conversion between the enantiomeric molecules of **2a** and **3a**; (ii) the existence of an intramolecular hydrogen bond between the amino group and the acetato ligand of compounds **2a** or **3a**, and; (iii) the establishment of the dynamic equilibrium shown in Fig. 4 between **2a** or **3a** and water present in the $CDCl_3$ solvent. In addition, the dependence of the chemical shift of the water present in the $CDCl_3$ solvent containing **2a** or **3a** with the temperature indicated that, for the dynamic equilibrium shown in Fig. 4, at low temperature the predominant species was the aqua complex **II** while at high temperature it was the acetato complex **I**. Note that for the consistency of the precedent discussion, the acetate anion should remain associated with the aqua complex **II** through hydrogen bonds. In support of the proposed behaviour of compounds **2a** and **3a** in $CDCl_3$ solution, it should be noted that: (i) an intramolecular hydrogen bond between an acetato ligand and a coordinated amino group to a palladium(II) centre has been determined by X-ray diffraction [22]; (ii) the chemical shift of the protons of the aqua ligand of neutral organoaquopalladium(II) complexes appears between 1.70 and 2.80 ppm, and; (iii) these latter compounds experience a fast exchange between coordinated water and free water [29].

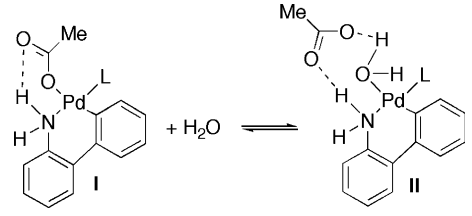


Fig. 4. Dynamic equilibrium between compounds **2a** (L = py) or **3a** (L = PPh_3) and water present in $CDCl_3$.

3. Experimental

3.1. Instruments and reagents

Elemental analyses of C, H and N were performed with an Eager 1108 microanalyzer. Infrared spectra were recorded on a Nicolet Impact-400 spectrophotometer using pressed discs of dispersed samples of the compounds in KBr. ^{1}H NMR spectra in $CDCl_3$ were recorded at 500 MHz on a Bruker DMX 500 instrument, at 300 MHz on a Varian 300 instrument and at 200 MHz on a Varian Gemini-200 instrument. The $^{31}P\{^1H\}$ NMR spectra in $CHCl_3$ were recorded at 101.26 MHz in a Bruker DRX 250 instrument. Chemical shifts are reported in δ values (ppm) [relative to $SiMe_4$ for ^{1}H and 85% H_3PO_4 for ^{31}P] and coupling constants in Hz. FAB^+ mass spectra were obtained with a VG-Quatro Fisions instrument, using 3-nitrobenzylalcohol as matrix. All chemicals and solvents were of commercial grade and used as received, except MeOH that was distilled over $CaCl_2$ and toluene that was distilled over sodium and benzophenone.

3.2. Synthesis of compounds *1* and sample *A*

1a: A suspension formed by 0.375 g (2.23×10^{-3} mol) of 2-phenylaniline, 0.500 g (2.23×10^{-3} mol) of $Pd(AcO)_2$ and 20 mL of toluene was stirred at room temperature for 24 h. The precipitate was filtered, washed with 5 mL of diethylether and dried under vacuum. Yield: 85% (in relation to the isolated **1a** · 0.8 toluene). *Characterization data*: Anal. Calc. for $C_{28}H_{26}N_2O_4Pd_2 \cdot 0.8$ toluene: C, 54.46; H, 4.41; N, 3.78. Found: C, 54.4; H, 4.6; N, 3.7%. EM-FAB^+ (Da/e) (selected data): $[M + H^+] = 667$, $[M + H^+ - HOAc] = 607$, $[M + H^+ - HOAc–OAc]^+ = 548$, $[M/2 - OAc^- + Pd] = 380$. IR (cm^{-1}): $\nu_a(COO) = 1581$, $\nu_s(COO) = 1419$, $\nu_a(NH_2) = 3318$, $\nu_s(NH_2) = 3269$. **1b**: A suspension formed by 0.239 g (1.41×10^{-3} mol) of 2-phenylaniline, 0.250 g (1.41×10^{-3} mol) of $PdCl_2$, 0.164 g (2.82×10^{-3} mol) of NaCl, 0.115 g (1.41×10^{-3} mol) of NaOAc and 20 mL of MeOH was stirred at room temperature for 1 week. The precipitate was filtered, washed with 5 mL of water

and 5 mL of diethylether and dried under vacuum. Yield: 75%. *Characterization data*: Anal. Calc. for $C_{24}H_{20}N_2Cl_2Pd_2$: C, 46.48; H, 3.25; N, 4.52. Found: C, 46.3; H, 3.4; N, 4.4%. EM-FAB$^+$ (Da/e) (selected data): $[M + H^+] = 619$, $[M + H^+ - HCl] = 583$, $[M/2 - Cl^-] = 274$. IR (cm^{-1}): $\nu_a(NH_2) = 3283$, $\nu_s(NH_2) = 3234$. **1c**: A suspension formed by 0.188 g (1.11×10^{-3} mol) of 2-phenylaniline, 0.250 g (1.11×10^{-3} mol) of $Pd(AcO)_2$ and 20 mL of acetic acid was stirred at 60 °C for 4 h. The solution was concentrated under vacuum and the residue was treated with 0.348 g (4.44×10^{-3} mol) of LiBr and 10 mL of acetone. The suspension formed was stirred at room temperature for 30 min. The resulting suspension was filtered, the solution concentrated under vacuum and the residue eluted through a SiO_2 column chromatography using as eluent $CHCl_3$/MeOH (100/6). The orange band was collected and concentrated under vacuum. Addition of 5 mL of diethylether to the residue produced the precipitation of **1c** that was filtered and dried under vacuum. Yield: 39%. *Characterization data*: IR and EM-FAB$^+$ were coincident with those previously reported [14]. Sample **A**: A suspension formed by 0.094 g (5.5×10^{-3} mol) of 2-phenylaniline, 0.125 g (5.5×10^{-3} mol) of $Pd(OAc)_2$and 10 mL of monodeuterated acetic acid was stirred at 60 °C for 24 h. The solution was concentrated under vacuum and the residue was treated with 0.174 g (2.0×10^{-3} mol) of LiBr and 5 mL of acetone. The suspension formed was stirred at room temperature for 30 min. The resulting suspension was filtered, the solution concentrated under vacuum and the residue eluted through a SiO_2 column chromatography using as eluent $CHCl_3$/MeOH (100/6). The orange band was collected and concentrated under vacuum. Addition of 5mL of diethylether to the residue produced the precipitation of sample **A** that was filtered and dried under vacuum. Yield: 45%.

3.3. Preparation of compounds 2′ and solution B

A suspension formed by 0.010 g of the corresponding compound **1** or of the sample **A** and 0.7 mL of $CDCl_3$ was treated with 2 drops of py-d_5 in a NMR tube and shacked until a pale yellow solution was formed. *Characterization data*: **2a′**: ^{1}H NMR (200 MHz): 7.52 dd, $^3J_{HH} = 6.9$ $^4J_{HH} = 1.9$ (1H, H_e); 7.39 d, $^3J_{HH} = 7.6$ (1H, H_d); 7.32 d, $^3J_{HH} = 7.6$ (1H, H_h); 7.25–7.08 (2H, H_g and H_f); 7.04 t, $^3J_{HH} = 7.4$ (1H, H_c); 6.83 t, $^3J_{H-H} = 7.4$ (1H, H_b); 6.52 d, $^3J_{HH} = 7.6$ (1H, H_a); 1.94 s (3H, OAc). **2b′**: ^{1}H NMR (200 MHz): 7.55 d, $^3J_{HH} = 6.8$ (1H, H_e); 7.40 dd, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.1$ (1H, H_d); 7.1–7.3 m (3H, H_f, H_g and H_h); 7.07 td, $^3J_{HH} = 7.2$, $^4J_{HH} = 1.0$ (1H, H_c); 6.83 td, $^3J_{H-H} = 7.4$, $^4J_{H-H} = 1.3$ (1H, H_b); 6.48 d, $^3J_{HH} = 7.6$ (1H, H_a); 6.03 br s (2H, NH_2). **2c′**: ^{1}H NMR (500 MHz): 7.60 d $^3J_{HH} = 7.0$ Hz (1H, H_e), 7.47 dd, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.5$ (1H, H_d); 7.23–7.27 m, (1H, H_f), 7.23–7.13 m (2H, H_g and H_h); 7.11 td, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.5$ (1H, H_c); 6.88 td, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.5$ (1H, H_b), 7.47, br d, $^3J_{HH} = 8$, (1H, H_a), 5.20 br s, (2H, NH_2). Solution **B**: Its ^{1}H NMR spectrum is the addition of the ^{1}H NMR of **2c′** to the ^{1}H NMR of $\mathbf{2c'_d}$. The ^{1}H NMR of $\mathbf{2c'_d}$ is identical to that of compound **2c′**, but the **d** proton is absent and the **c** proton is a doublet.

3.4. Preparation of compounds 2

2a: A suspension formed by 0.150 (0.225×10^{-3} mol) of **1a**, 0.036 (0.450×10^{-3} mol) of pyridine and 20 mL of acetone was stirred at room temperature for 3 h and the solution formed was concentrated under vacuum. Addition of 5 mL of diethylether to the residue produced the precipitation of **2a**, which was filtered and dried under vacuum. Yield: 59%. *Characterization data:* Anal. Calc. for $C_{19}H_{18}N_2O_2Pd$: C, 55.29; H, 4.40; N, 6.79. Found: C, 55.6; H, 4.2; N, 6.6%. EM-FAB$^+$ (Da/e) (selected data): $[M + H^+] = 413$, $[M + H^+ - HOAc\ ] = 353$, $[M + H^+ - HOAc–py] = 274$. IR ($cm^{-1}$): $\nu_a(NH_2) = 3248$, $\nu_s(NH_2) = 3100$, $\nu_a(COO) = 1581$, $\nu_s(COO) = 1384$. ^{1}H NMR (500 MHz): 8.55 dd, $^3J_{HH} = 6.5$ $^4J_{HH} = 1.5$ (2H, $H_o$py); 7.78 tt, $^3J_{HH} = 7.5$ $^4J_{HH} = 1.5$ (1H, $H_p$py); 7.57 dd, $^3J_{HH} = 7.3$, $^4J_{HH} = 1.3$ (1H, H_e); 7.44 dd, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.5$ (1H, H_d); 7.35 dd, $^3J_{HH} = 7.5$ $^4J_{HH} = 1.5$ (1H, H_h); 7.29 td, $^3J_{HH} = 6.5$ $^4J_{HH} = 1.0$ (2H, $H_m$py); 7.23 td, $^3J_{HH} = 7.5$ $^4J_{HH} = 1.0$ (1H, H_f); 7.19 td $^3J_{HH} = 7.5$ $^4J_{HH} = 1.5$ (1H, H_g); 7.09 td, $^3J_{HH} = 7.3$ $^4J_{HH} = 1.0$ (1H, H_c); 6.88 td, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.5$ (1H, H_b); 6.54 dd, $^3J_{HH} = 8.0$ $^4J_{HH} = 1.0$ (1H, H_a); 1.97 s (3H, OAc). **2b**: A suspension formed by 0.100 g (0.161×10^{-3} mol) of **1a**, 0.025 g (0.322×10^{-3} mol) of pyridine and 20 mL of acetone was stirred at room temperature for 3 h and the solution formed was concentrated under vacuum. Addition of 5 mL of diethylether to the residue produced the precipitation of **2b**, which was filtered and dried under vacuum. Yield: 85%. *Characterization data:* Anal. Calc. for $C_{17}H_{15}N_2ClPd$: C, 54.64; H, 3.89; N, 7.20. Found: C, 54.2; H, 4.0; N, 7.1%. EM-FAB$^+$ (Da/e) (selected data): $[M + H^+] = 389$, $[M + H^+ - HCl] = 353$, $[M + H^+ - HCl–py] = 274$. IR (cm^{-1}): $\nu_a(NH_2) = 3177$, $\nu_s(NH_2) = 3100$. ^{1}H NMR (500 MHz): 8.67 dd, $^3J_{HH} = 6.5$ $^4J_{HH} = 1.5$ (2H, $H_o$py); 7.76 tt, $^3J_{HH} = 7.5$ $^4J_{HH} = 1.5$ (1H, $H_p$py); 7.52 d, $^3J_{HH} = 7.0$ (1H, H_e); 7.48 dd, $^3J_{HH} = 8.0$ $^4J_{HH} = 1.5$ (1H, H_d); 7.2–7.4 m (5H, H_f, H_g, H_h and $H_m$py); 7.14 td, $^3J_{HH} = 7.5$ $^4J_{HH} = 1.0$ (1H, H_c); 6.91 td, $^3J_{HH} = 7.5$ $^4J_{HH} = 1.5$ (1H, H_b); 6.53 dd, $^3J_{HH} = 8.0$ $^4J_{HH} = 1.0$ (1H, H_a); 5.77 br s (2H, NH_2).

3.5. Preparation of compounds 3

3a: A suspension formed by 0.100 g (0.3×10^{-3} mol) of **1a**, 0.078 g (0.6×10^{-3} mol) of triphenylphosphine and 20 mL of acetone was stirred at room temperature

for 3 h and the solution formed was concentrated under vacuum. Addition of 5 mL of diethylether to the resulting residue produced the precipitation of **3a**, which was filtered and dried under vacuum. Yield = 74%. *Characterization data:* Anal. Calc. for $C_{32}H_{28}NO_2PPd$: C, 64.49; H, 4.74; N, 2.39. Found: C, 64.6; H, 4.8; N, 2.4%. EM-FAB$^+$ (Da/e) (selected data): [M + H$^+$ − HOAc] = 536, [M + H$^+$ − HOAc–phenylaniline] = 367. IR (cm^{-1}): IR (cm^{-1}): $\nu_a(NH_2)$ = 3290 $\nu_s(NH_2)$ = not observed; $\nu_a(COO)$ = 1581, $\nu_s(COO)$ = 1391, ν(q X-sensitive mode of coordinated PPh_3) = 1096. ^{1}H NMR (500 MHz): 7.4–7.5 m, (6H, H_oPPh_3); 7.3–7.4 m, (3H, H_pPPh_3); 7.2–7.3 m, (11H, H_d, H_e, H_f, H_g, H_h, H_mPPh_3); 6.86 t, $^3J_{HH}$ = 7.0 (1H, H_c); 6.45 t $^3J_{HH}$ = $^4J_{PH}$ = 7.0 (1H, H_a); 6.41 t, $^3J_{HH}$ = 7.5 (1H, H_b); 1.64 s (3H, OAc). RMN $^{31}P\{^1H\}$ (101.26 MHz) = 34.25 s. **3b**: A suspension formed by 0.100 g (0.16×10^{-3} mol) of **1b**, 0.084 g (0.32×10^{-3} mol) of triphenylphosphine and 20 mL of acetone was stirred at room temperature for 3 h. The solution was concentrated under vacuum and the residue was eluted through a SiO_2 column chromatography using as eluent $CHCl_3$/MeOH (100:6). The orange band was collected and concentrated under vacuum. Addition of 5 mL of diethylether to the residue produced the precipitation of **3b**, which was filtered and dried under vacuum. Yield = 60%. *Characterization data:* Anal. Calc. for $C_{30}H_{25}NClPPd$: C, 62.96; H, 4.40; N, 2.45. Found: C, 63.3; H, 4.5; N, 2.5%. EM-FAB$^+$ (Da/e) (selected data): [M + H$^+$ − HCl] = 536, [M + H$^+$ − HCl–phenylaniline] = 367. IR (cm^{-1}): $\nu_a(NH_2)$ = 3311, $\nu_s(NH_2)$ = 3241, ν(q X-sensitive mode of coordinated PPh_3) = 1097. ^{1}H NMR (500 MHz): 7.45 dd, $^3J_{H-H}$ = 7.5 $^3J_{H-P}$ = 12 (6H, H_oPPh_3); 7.34 td, $^3J_{HH}$ = 7.5 $^4J_{HH}$ = 2.0 (3H, H_pPPh_3); 7.27–7.22 m, (10H, H_e, H_f, H_g, H_h, H_mPPh_3); 7.21 dd, $^3J_{HH}$ = 7.5 $^4J_{HH}$ = 1.0 (1H, H_d); 6.86 t, $^3J_{HH}$ = 7.7 (1H, H_c); 6.50 t, $^3J_{HH}$ = $^4J_{HP}$ = 7.0 (1H, H_a); 6.44 t, $^3J_{H-H}$ = 7.5 (1H, H_b); 4.88 and 5.07 br signals, (2H, NH_2). RMN $^{31}P\{^1H\}$ = 35.12 s.

3.6. Preparation of compound *4*

A suspension formed by 0.300 g (0.450×10^{-3} mol) of compound **1a**, 0.252 g (1.8×10^{-3} mol) of Na(acac)·H_2O and 20 mL of acetone was stirred at room temperature for 1 h. The suspension was concentrated under vacuum and the residue was eluted through a SiO_2 column chromatography using as eluent $CHCl_3$/MeOH (100:10). The yellow band was collected and concentrated under vacuum. Addition of 5 mL of diethylether

Table 2
Crystallographic data for **3b** and **4**

Compound	**3b**	**4**
Empirical formula	$C_{30}H_{25}ClNPPd$	$C_{17}H_{17}NO_2Pd$
Formula weight	572.33	373.72
Temperature (K)	293 (2)	293 (2)
Wavelength (Å)	0.71069	0.71069
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/a$
Unit cell dimensions		
a (Å)	9.9170(10)	11.5900(10)
b (Å)	10.4750(10)	1.2730(10)
c (Å)	12.0890(10)	12.2150(10)
α (°)	98.610(10)	90
β (°)	94.034(10)	107.6560(10)
γ (°)	99.000(10)	90
Volume (Å^3)	1220.7(2)	1520.8(2)
Z	2	4
D_{Calc} (mg/m^3)	1.557	1.632
Absorption coefficient (mm^{-1})	0.995	1.223
F(000)	580	752
Crystal size (mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
Theta range for data collection	1.71–31.62°	3.42–31.84°
Index ranges	$0 \leqslant h \leqslant 14$	$-15 \leqslant h \leqslant 14$
	$-15 \leqslant k \leqslant 15$	$0 \leqslant k \leqslant 16$
	$-17 \leqslant l \leqslant 17$	$0 \leqslant l \leqslant 17$
Reflections collected/unique (R_{int})	11270/6458 (0.0284)	12664/3820 (0.0395)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6458/0/368	3820/0/191
Goodness-of-fit on F^2	1.142	1.095
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0532	R_1 = 0.0565
	wR_2 = 0.1444	wR_2 = 0.1657
R indices (all data)	R_1 = 0.0652	R_1 = 0.1070
	wR_2 = 0.1592	wR_2 = 0.1849
Extinction coefficient	0.072(4)	
Largest different peak and hole (e Å^3)	0.810 and −0.659	0.631 and −1.352

to the residue produced the precipitation of **4**, which was filtered and dried under vacuum. Yield = 46%. Characterization *data:* Anal. Calc. for $C_{17}H_{17}NO_2Pd$: C, 54.64; H, 4.58; N, 3.75. Found: C, 54.3; H, 4.7; N, 3.7%. EM-FAB$^+$ (Da/e) (selected data): $[M + H^+] = 374$, $[M + H^+ - Hacac] = 273$. IR (cm^{-1}): $\nu_a(NH) = 3283$, $\nu_s(NH) = 3191$, $\nu(C:::C + C:::O) = 1588$, $\nu(C:::O + C:::C) = 1511$, $\delta d(CH_3) = 1391$, $\nu(C–CH_3 + C:::C) = 1264$. ^1H NMR (500 MHz): 7.57 d, $^3J_{H–H} = 8.0$ (1H, H_e); 7.36–7.42 m, (2H, H_by H_d); 7.22–7.27 m, (1H, H_f); 7.1–7.2 m, (4H, H_a, H_c, H_g y H_h), 5,30 (1H, $H_{CH\ acac}$); 4.92 br s (NH_2), 1.99 and 1.94 s (6H, $H_{Me\ acac}$).

3.7. Crystal structures

Crystals for the X-ray molecular structure determination of **3b** and **4** were obtained by slow evaporation of the solvents of a solution of **3b** in methanol/dichloromethane (1/1) and of a solution of **4** in dichloromethane. In both cases a prismatic crystal was selected and mounted on a MAR345 diffractometer with an image plate detector. Intensities were collected with graphite-monochromatized Mo Kα radiation. The structures were solved by direct methods using the SHELXS [30] computer program and refined by the full-matrix least squares method, with the SHELXL 97 [31] computer program. A summary of crystallographic data and some details of the refinement are given in Table 2.

4. Supplementary material

Crystallographic data for the structural analyses of **3b** and **4** have been deposited at the Cambridge Crystallographic Data Centre, CCDC, Nos. 240805 for **3b** and 240804 for **4**. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1233-336033; e-mail: deposit@ccdc.ac.uk or www.ccdc.cam.ac.uk).

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