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P,C-palladacycle complexes of triphenylphosphite: Synthesis, characterization and catalytic activity in the Suzuki cross-coupling reaction

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ABSTRACT

Five-membered P,C-palladacycles were synthesized through the reaction of the binuclear triphenylphosphite complex $[Pd(\mu\text{-}Cl)P(OPh)_2(OC_6H_4)]_2$ (**1**) with different monodentate ligands [L = triphenylphosphine (PPh_3), thiourea (tu), 2,4,6-trimethylpyridine (Me_3Py), pyridine (Py)] and bidentate ligands [N^N = 1,10-phenanthroline (Phen), 4-methyl-1,10-phenanthroline (MePhen)], giving mononuclear P,C-palladacycles $[Pd(L)(Cl)\{P(OPh)_2(OC_6H_4)\}]$ [L = PPh_3 (**2a**), tu (**2b**), Me_3Py (**2c**)], $[PyH]^+[Pd(Cl)_2\{P(OPh)_2(OC_6H_4)\}]^-$ (**3d**) and $[Pd(N^N)\{P(OPh)_2(OC_6H_4)\}]^+ NO_3^-$ [N^N = Phen (**4a**), MePhen (**4b**)]. The synthesized complexes were characterized by ^1H, $^{13}C\text{–}\{^1H\}$ and $^{31}P\text{–}\{^1H\}$ NMR spectroscopy, elemental analysis and FT-IR techniques. Structural details of complexes **2a**, **2c** and **3d** were determined by X-ray crystallography, which showed these complexes crystallize in the triclinic (**2a**) and monoclinic (**2c** and **3d**) crystalline systems. According to the structural data, the orthopalladated complex **3c** has two different conformers (R,S) in the solid state, although it appeared as one isomer in the solution state, as confirmed by the NMR spectroscopy. Complex **2a**, containing PPh_3, was evaluated as a homogeneous catalyst for a variety of substrates, affording coupled products in good to excellent yields, importantly at room temperature. Furthermore, the use of the lesser reactive aryl chloride as a substrate in the Suzuki reaction under mild conditions, has received much attention.

1. Introduction

Organopalladium complexes have found many valuable uses in different areas such as organic synthesis [1–4], homogeneous catalysis [5–11], photochemistry [12–15], design of new metallomesogenes [16–18], antitumor drugs [19,20], etc [21,22]. The Suzuki–Miyaura cross-coupling of aryl halides with aryl boronic acids is one of the most powerful methods for the preparation of unsymmetrical biaryls [23–27]. Palladium derivatives potentially have catalytic activities along with special advantages like versatility, compatibility with most functional groups and relatively low toxicity [28–34]. Furthermore, a great deal of interest has been recently devoted to the synthesis of orthopalladated triarylphosphite complexes which have extensive applications in many organic reactions [35–38]. In these complexes, orthometallation of triarylphosphite to the Pd center occurred via C–H activation of the phenyl ring. In our previous work, the application of a binuclear P,C-palladacycle of triphenylphosphite as a catalyst precursor was investigated for the Heck and Suzuki reactions [39].

Our continuing interest in the synthesis of new palladacycles [40–42] encouraged us to synthesize mononuclear orthopalladated triphenylphosphite complexes with mono- and bidentate ligands. Furthermore, due to the efficient characteristics of palladium compounds containing phosphorous ligands [43,44], the catalytic activity of the orthopalladated complex **2a**, containing PPh_3, was evaluated in the Suzuki cross-coupling reaction, applying a representative range of aryl halides.

2. Experimental

2.1. General

Starting materials were purchased from the Merck, Sigma–Aldrich or Alfa Aesar companies and solvents were used as commercially available chemicals without any purification. The binuclear palladacycle **1** was obtained using the procedure described earlier [45]. ^1H NMR (400.13 MHz), $^{13}C\text{–}\{^1H\}$ NMR (100.61 MHz) and $^{31}P\text{–}\{^1H\}$ NMR (161.97 MHz) spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions at room temperature on a 400 MHz Bruker spectrometer. Chemical shifts (δ) are reported relative to internal TMS and external 85% phosphoric acid. FT-IR spectra were recorded on a spectrophotometer (JASCO-680, Japan) in the

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spectral range 4000–400 cm^{-1} using the KBr pellet technique. Elemental analysis was performed on Leco, CHNS-932 apparatus. Gas chromatography was carried out with a Shimatzo GC 14-A gas chromatograph and was used for monitoring the progress of reactions.

2.2. General synthesis procedure for cyclopalladated complexes **2a**, **2b**, **2c** and **3d**

To a solution of complex **1** (0.1 mmol, 0.140 g) in CH_2Cl_2 (10 ml), 0.2 mmol of the desired nucleophile [triphenylphosphine (**2a**), thiourea (**2b**), 2,4,6-trimethylpyridine (**2c**) or pyridine (**3d**)] was added. The resulting mixture was stirred for 5 h at room temperature. The solvent was removed the obtained product was then recrystallized with CH_2Cl_2/*n*-hexane (1:3).

2.2.1. [Pd(PPh$_3$)(Cl){P(OPh)$_2$(OC$_6$H$_4$)}] (**2a**)

Yield: 70%. *Anal.* Calc. for $C_{36}H_{29}ClO_3P_2Pd$: C, 60.60; H, 4.06. Found: C, 60.60; H, 4.30%. IR (cm^{-1}, KBr) ν: 1586 (aromatic C=C), 3025 (aromatic C–H). ^{1}H NMR (DMSO-d_6, ppm) δ: 6.87 (d, 3H, H*p* of PPh_3, $^3J_{HH}$ = 8.0 Hz), 7.02 (dd, 1H, H^5, $^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 7.2 Hz), 7.03 (d, 1H, H^6, $^3J_{HH}$ = 3.2 Hz), Aromatic region {7.27–7.56}, 8.18 (dd, 1H, H^3, $^3J_{HH}$ = 12.4 Hz, $^4J_{HP}$ = 7.0 Hz). ^{13}C–{^{1}H} NMR (DMSO-d_6, ppm) δ: Aromatic region {119.77, 1119.83, 122.98, 123.06, 126.76, 130.22, 131.11, 133.98, 134.10, 134.47}, 136.94 (d, 1C, C^1, $^2J_{CP}$ = 3.0 Hz), 142.53 (s, 2C, C–O in free phenyls of phosphite), 149.11 (d, 1C, C^2, $^2J_{CP}$ = 5.9 Hz), ^{31}P–{^{1}H} NMR (DMSO-d_6, ppm) δ: 17.92 (s, 1P, phosphine), 131.10 (s, 1P, phosphite) [45].

2.2.2. [Pd(tu)(Cl){P(OPh)$_2$(OC$_6$H$_4$)}] (**2b**)

Yield: 51%. *Anal.* Calc. for $C_{19}H_{18}ClN_2O_3SPPd$: C, 43.27; H, 3.41; N, 5.31; S, 6.47. Found: C, 41.13; H, 3.50; N, 6.03; S, 6.07%. IR (cm^{-1}, KBr) ν: 687 (C=S), 1586 (aromatic C=C), 1617 (NH_2-bending), 3173, 3283 (NH_2-streching). ^{1}H NMR (DMSO-d_6, ppm) δ: Aromatic region {6.80–7.21}, 7.28 (s, 4H, H_m), 7.43(s, 6H, H_o and H_p), 7.85 (s, 2H, NH_2), 8.38 (s, 2H, NH_2). ^{13}C–{^{1}H} NMR (DMSO-d_6, ppm) δ: Aromatic region {110.82, 110.97, 120.91, 121.43, 124.87, 126.23, 127.40, 129.76, 130.12, 130.26}, 136.62 (d, 1C, C^1, $^2J_{CP}$ = 6.0 Hz), 140.44 (s, 2C, C–O in free phenyls of phosphite), 144.09 (s, 1C, C^2), 191.55 (s, 1C, C=S). ^{31}P–{^{1}H} NMR (DMSO-d_6, ppm) δ: 129.48, 130.23 (s, 1P, R,S isomers).

2.2.3. [Pd(Me$_3$Py)(Cl){P(OPh)$_2$(OC$_6$H$_4$)}] (**2c**)

Yield: 62%. *Anal.* Calc. for $C_{26}H_{25}ClNO_3PPd$: C, 54.55; H, 4.37; N, 2.44. Found: C, 53.90; H, 4.50; N, 2.54%. IR (cm^{-1}, KBr) ν: 1485 (C–N), 1587 (C=C), 1622 (C=N), 2921 (aliphatic C–H), 3050 (aromatic C–H). ^{1}H NMR ($CDCl_3$, ppm) δ: 2.35 (s, 3H, Me_p), 2.49 (s, 6H, Me_o), 5.92 (ddd, 1H, H_6, $^4J_{HH}$ = 1.2 Hz, $^3J_{HP}$ = 6.6 Hz, $^3J_{HH}$ = 9.9 Hz), 6.61 (td, 1H, H^5, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.6 Hz), 6.94 (s, 2H, H_m of Me_3Py), Aromatic region {7.00–7.57}. ^{13}C–{^{1}H} NMR ($CDCl_3$, ppm) δ: 20.91 (s, 1C, Me_P), 25.74 (s, 2C, Me_o), Aromatic region {111.33, 111.54, 121.18, 122.54, 122.97, 123.87, 125.88, 127.04, 129.67} 134.18 (d, 1C, C^1, $^2J_{CP}$ = 4.0 Hz), 150.48 (s, 2C, C–O in free phenyls of phosphite), 157.83 (s, 1C, C^2), ^{31}P–{^{1}H} NMR ($CDCl_3$, ppm) δ: 134.78 (s, 1P).

2.2.4. [PyH]$^+$[Pd(Cl)$_2${P(OPh)$_2$(OC$_6$H$_4$)}]$^-$ (**3d**)

Yield: 50%. IR (cm^{-1}, KBr) ν: 1585 (aromatic C=C), 1635 (C=N), 3058 (aromatic C–H). ^{1}H NMR ($CDCl_3$, ppm) δ: Aromatic region {6.80–7.50}. ^{31}P–{^{1}H} NMR ($CDCl_3$, ppm) δ: 130.11 (s, 1P).

2.3. General synthesis procedure for cyclopalladated complexes **4a** and **4b**

Complex **1** (0.35 mmol, 0.030 g) was dissolved in THF (8 ml) and treated with $AgNO_3$ (0.071 mmol, 0.012 g). The resulting mixture was stirred for 45 min at room temperature and then filtered over $MgSO_4$. Afterwards, 0.071 mmol of the ligand [N^N = 1,10-phenanthroline (**4a**) or 4-methyl-1,10-phenanthroline (**4b**)] was added and the solution was stirred for 40 min, then the solvent was evaporated to dryness and the residue treated with Et_2O (2 ml).

2.3.1. [Pd(Phen){P(OPh)$_2$(OC$_6$H$_4$)}]$^+$NO$_3^-$ (**4a**)

Yield: 23%. *Anal.* Calc. for $C_{30}H_{22}N_2O_3PPd$: C, 54.27; H, 3.20; N, 4.08. Found: C, 54.20; H, 3.50; N, 6.97%. IR (cm^{-1}, KBr) ν: 1586 (aromatic C=C), 1625 (C=N), 3053 (aromatic C–H). ^{1}H NMR ($CDCl_3$, ppm) δ: 7.16 (dd, 1H, H^6 phosphite, $^3J_{HH}$ = 8.0 Hz, $^4J_{HP}$ = 1.2 Hz), Aromatic region {7.21-7.50}, 8.18 (bd, 1H, H^8 Phen, $^3J_{HH}$ = 8.2 Hz), 8.19 (bd, 1H, H^3 Phen, $^3J_{HH}$ = 8.2 Hz), 8.23 (s, 2H, $H^{5,6}$ Phen), 8.93 (d, 1H, H^7 Phen, $^3J_{HH}$ = 8.4 Hz), 8.94 (d, 1H, H^4 Phen, $^3J_{HH}$ = 8.4 Hz), 9.11 (m, 2H, $H^{2,9}$ Phen). ^{13}C–{^{1}H} NMR ($CDCl_3$, ppm) δ: Aromatic region {112.60, 120.86, 125.38, 126.68, 128.42, 129.25, 130.52}, 135.00 (d, 1C, C_1 coordinated C, $^2J_{CP}$ = 5.0 Hz), 141.30 (s, 2C, C–O in free phenyls of phosphite), 151.59 (s, 1C, C_2 phosphite). ^{31}P–{^{1}H} NMR ($CDCl_3$, ppm); 122.57 (s, 1P).

2.3.2. [Pd(MePhen){P(OPh)$_2$(OC$_6$H$_4$)}]$^+$NO$_3^-$ (**4b**)

Yield: 51%. *Anal.* Calc. for $C_{31}H_{24}N_2O_3PPd$: C, 54.88; H, 3.43; N, 4.00. Found: C, 54.40; H, 3.98; N, 6.54%. IR (cm^{-1}, KBr) ν: 1586 (aromatic C=C), 1625 (C=N), 2860 (aliphatic C–H), 3058 (aromatic C–H). ^{1}H NMR ($CDCl_3$, ppm) δ: 3.00 (s, 3H, Me), 7.16 (dd, 1H, H^6 phosphite, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 1.2 Hz), Aromatic region {7.21–7.49}, 7.95 (d, 1H, H^3 Phen, $^3J_{HH}$ = 8.0 Hz), 8.18 (dd, 1H, H^8 Phen, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 8.40 Hz), 8.32 (q, 2H, H^5 and H^6 Phen, $^3J_{HH}$ = 8.8 Hz), 9.04 (m, 2H, H^2 and H^7 Phen), 9.11 (m, 1H, H^9 Phen). ^{13}C–{^{1}H} NMR ($CDCl_3$, ppm) δ: 19.63 (s, 1C, Me), Aromatic region {112.63, 120.85, 124.40, 125.34, 126.54, 126.81, 127.01, 128.44, 129.17, 130.49}, 135.04 (d, 1C, C^1 phosphite, $^2J_{CP}$ = 4.0 Hz), 141.48 (s, 2C, C–O in free phenyls of phosphite), 150.92 (s, 1C, C^2 phosphite). ^{31}P–{^{1}H} NMR ($CDCl_3$, ppm) δ: 122.84 (s, 1P).

2.4. X-ray structure determinations

X-ray diffraction experiments were done at 100 K with the use of an Agilent SuperNova single crystal diffractometer (Mo Kα radiation). An analytical numeric absorption correction using a multi-faceted crystal model based on expressions derived by R.C. Clark and J.S. Reid was made [46]. The structures were solved by direct methods using the SHELXS97 program and refined with the use of SHELXL (Sheldrick 2008) program. Hydrogen atoms were added in the calculated positions and were riding on their respective carbon atoms during the refinement.

2.5. General experimental procedure for the Suzuki cross-coupling reaction

In this context complex **2a** was used as a catalyst for the Suzuki cross-coupling reaction. A 25 ml round-bottom flask was charged with the appropriate aryl halide (0.50 mmol), phenylboronic acid (0.55 mmol), base (1.00 mmol), and THF/H_2O (6 ml of a 2:1 v/v mixture). The catalyst (0.005 mmol) was then added to the solution and the mixture was stirred at room temperature for 1 h. Different aryl halides were employed in the Suzuki cross-coupling reaction with phenylboronic acid and the coupling products are listed in Table 4. Gas chromatographic (GC) analyses were performed using an Agilent Technologies 6890 N chromatograph equipped with a flame ionization detector (FID) and an HB-50$^+$ column (length = 30 m, inner diameter = 320 μm, and film thickness = 0.25 μm). The temperature program for the GC analysis was from 70 to 200 °C at 20 °C/min, held at 200 °C for 0 min, heated from 200 to 280 °C at 10 °C/min and held at 280 °C for 1 min. The inlet and detector temperatures were set at 260 and

280 °C, respectively. Products were identified by comparison with authentic samples.

3. Result and discussion

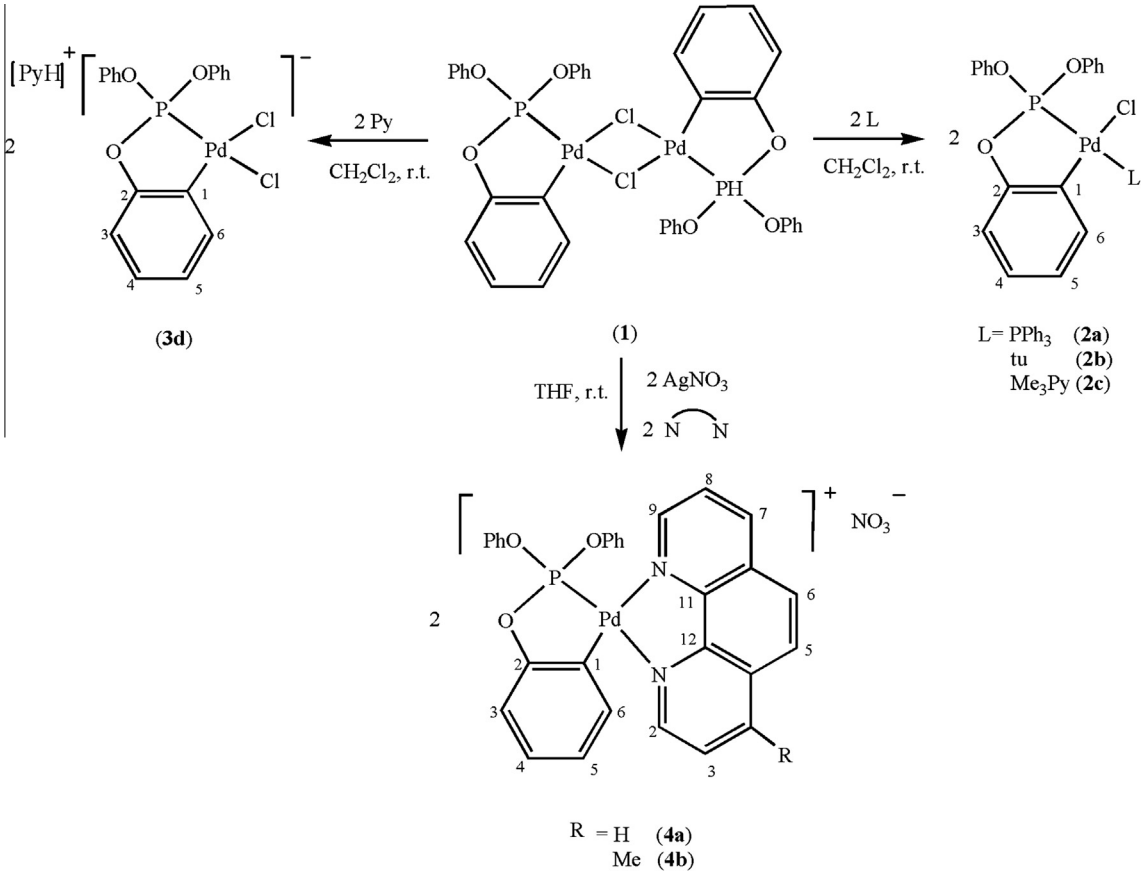
3.1. Synthesis

Treatment of the chloro-bridged complex [Pd(μ-Cl)P(OPh)$_2$(OC$_6$H$_4$)]$_2$ (**1**) with two equivalents of monodentate ligand [triphenylphosphine(PPh$_3$), thiourea(tu), 2,4,6-trimethylpyridine (Me$_3$Py) or pyridine (Py)] in CH_2Cl_2 afforded the corresponding mononuclear orthopalladated complexes **2a**, **2b**, **2c** and **3d**. Moreover, a solution of complex **1** in THF was reacted with $AgNO_3$ in the dark. After filteration over $MgSO_4$, an equimolar amount of the corresponding N^N bidentate ligand [1,10-phenanthroline (Phen) or 4-methyl-1,10-phenanthroline (MePhen)] was then added. The solution was stirred for 40 minutes to produce cyclometallated complexes of the general formula [Pd(N^N)(P^C)]$^+$ (**4a** and **4b**). For all the synthesized compounds, the results of the elemental analysis are in the good agreement with the calculated values.

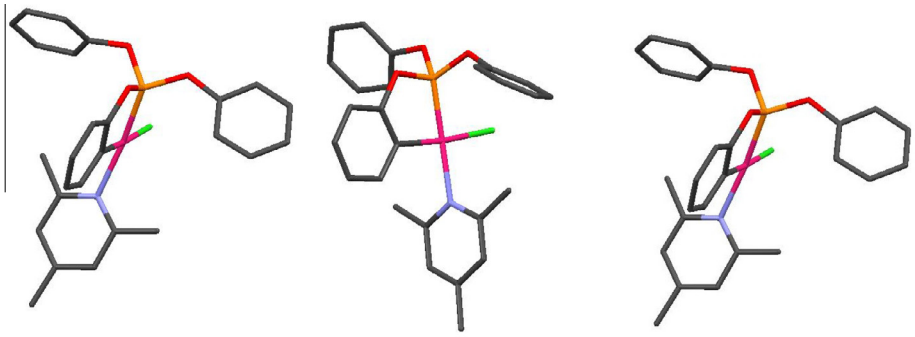
3.2. Characterization

The IR spectra of the synthesized complexes show characteristic bands for aromatic C=C and C–H at 1586 and 3050 cm^{-1}, respectively. In the IR spectrum of **2b**, the ν(C=S) band (that is sensitive to complexation) appeared at 687 cm^{-1}, whereas for the free thiourea, it should be at 725 cm^{-1} [46,47]. The complexation of thiourea is clearly confirmed by the appearance of additional ν(N–H) bands at 3173, 3283 (stretching) and 1617 cm^{-1} (bending). Moreover, the characteristic ν(C–N) band in the IR spectrum of **2b** was found at 1485 cm^{-1}, in comparison with 1465 cm^{-1} for the free ligand [46,47], indicating coordination to Pd. The vibrational frequencies of C=N in **2c**, **3d**, **4a** and **4b** appeared at about 1625 cm^{-1}. The FT-IR spectra of **2c** and **4b** show the typical bands at 2921 and 2860 cm^{-1}, respectively, related to their aliphatic C–H groups.

In the ^{31}P–{^{1}H} NMR spectrum of **2a**, two signals at 17.92 and 131.10 ppm are related to the P atoms of PPh$_3$ and P(OPh)$_3$, respectively. Concerning the ^{1}H NMR spectrum of **2b**, two broad signals at 7.85 and 8.38 ppm are clearly attribiuted to the two NH$_2$ groups of the coordinated thiourea. The downfield shifting of the NH$_2$ signals when compared with the free ligand (7.06 ppm) [48] suggest Pd–S bond formation. The NH$_2$ protons are diastereotopic, resulting in the formation of two separate signals in the ^{31}P–{^{1}H} NMR spectrum at 129.48 and 130.23 ppm. The ^{13}C–^{1}H} NMR spectrum of complex **2b** showed the typical signals of the quaternary carbon in the thiourea at 191.55 ppm, which is shifted downfield when compared with the free ligand (183.9 ppm). It is suggested that the downfield shift is attributed to a lowering of the C=S bond order due to the coordination to Pd. The ^{13}C–{^{1}H} NMR spectra of all the synthesized complexes have the signal of C^1 in P(OPh)$_3$ at about 135.00 ppm. The H^6 aromatic proton of the palladacycle ring in **2c** (Scheme 1) is shifted to a lower frequency at 5.92 ppm because of the anisotropic shielding from the phenyl or pyridine ring [49]. The ^{13}C–{^{1}H} NMR spectrum of **2c** shows signals for the *para* and *ortho* methyl groups at 20.91 and 25.74 ppm, respectively. It is worth noting that the orthopalladated complex **2c** has two different conformers in the solid state, fully confirmed by X-ray crystallography, but the multinuclear NMR spectra display the presence of only one set of signals which indicate that complex **2c** consists of only one isomer in the solution state (Scheme 2). It is



Scheme 1. Representation of the cleavage reaction of the dimeric cyclopalladated complex **1** by mono- and bidentate ligands.



Scheme 2. Conformational isomerism of complex **2c** in the solid state versus the solution state.

significantly clear by the $^{31}P–\{^{1}H\}$ NMR spectrum which shows a signal at 134.78 ppm.

In relation to the structures, monodentate nucleophiles (L) have two possible positions to attack. Although PPh_3 is a bulky group, it is located in the *cis* position to the coordinated P atom of $P(OPh)_3$ (**A**) in **2a** and Me_3Py is mutually *trans* to the P atom of $P(OPh)_3$ (**B**) in **2c**. Therefore, the electronic effects are determinant and control the site of the nucleophile with respect to the steric effects. According to the HSAB effect, the soft P atom of PPh_3 is *trans* to the hard sp^2 carbon in **2a**. However, in **2c** the hard N of Me_3Py is *trans* to the soft P atom of $P(OPh)_3$.

The $^{31}P–\{^{1}H\}$ NMR spectra of complexes **2a**, **2b**, **2c** and **3d** show a characteristic signal at about 130 ppm attributed to the P atom of $P(OPh)_3$. In **3d**, our purpose was to reach an orthopalladated complex in which the pyridine is coordinated to the palladium center through the N atom. Concerning the FT-IR, NMR, CHN and especially crystallographic data, we fully characterized a 5-membered palladacycle with two coordinated chloride anions in addition to pyridinium as a counter ion. A trace of HCl in CH_2Cl_2 as the reaction solvents may be a reasonable explanation for this event. The H^2 and H^9 aromatic protons in the 1,10-phenanthroline ligand are shifted downfield at 9.11 ppm because they are near the nitrogen atoms. In the $^{31}P–\{^{1}H\}$ NMR spectra of complexes **4a** and **4b** one signal was observed at about 122.60 ppm, corresponding to the P atom of $P(OPh)_3$. The methyl protons of 4-methyl-1,10-phenanthroline are shown as a singlet at 3.00 ppm in the ^{1}H NMR spectrum of complex **4b**. The H^2 and H^9 aromatic protons in the coordinated 4-methyl-1,10-phenanthroline are in the vicinity of the nitrogen atoms, so their signals in the ^{1}H NMR spectrum appeared at higher frequencies, 9.04 and 9.11 ppm, respectively. The $^{13}C–\{^{1}H\}$ NMR spectrum showed one signal at 19.63 ppm related to the methyl carbon.

3.3. Crystal structures

To further clarify the coordination environment around the Pd(II) center, molecular structures of **2a**, **2c** and **3d** were determined by X-ray crystallography. Crystals were obtained by

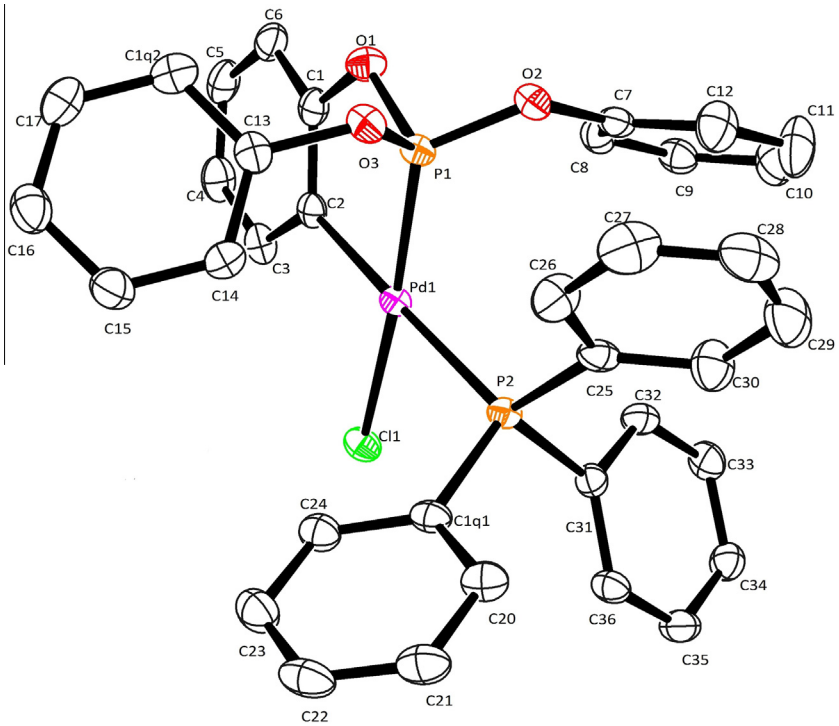


Fig. 1. ORTEP view of the X-ray crystal structure of complex **2a**. The disordered solvent molecule and all hydrogen atoms have been omitted for clarity.

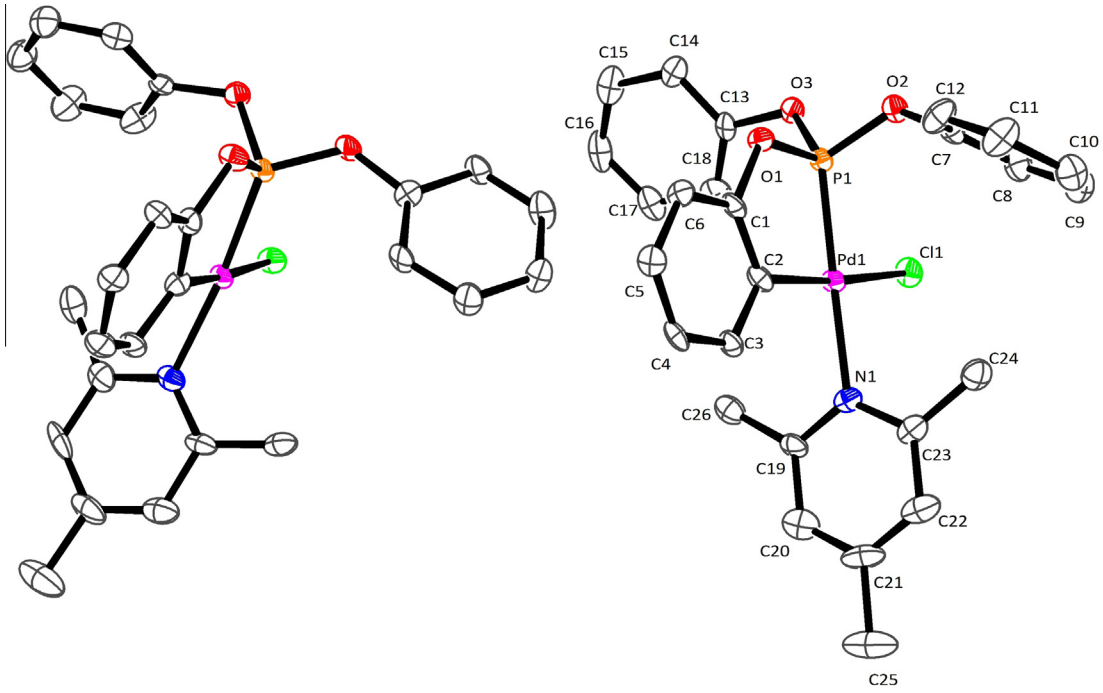


Fig. 2. ORTEP view of the X-ray crystal structure of complex **2c** including two independent molecules. Hydrogen atoms have been omitted for clarity.

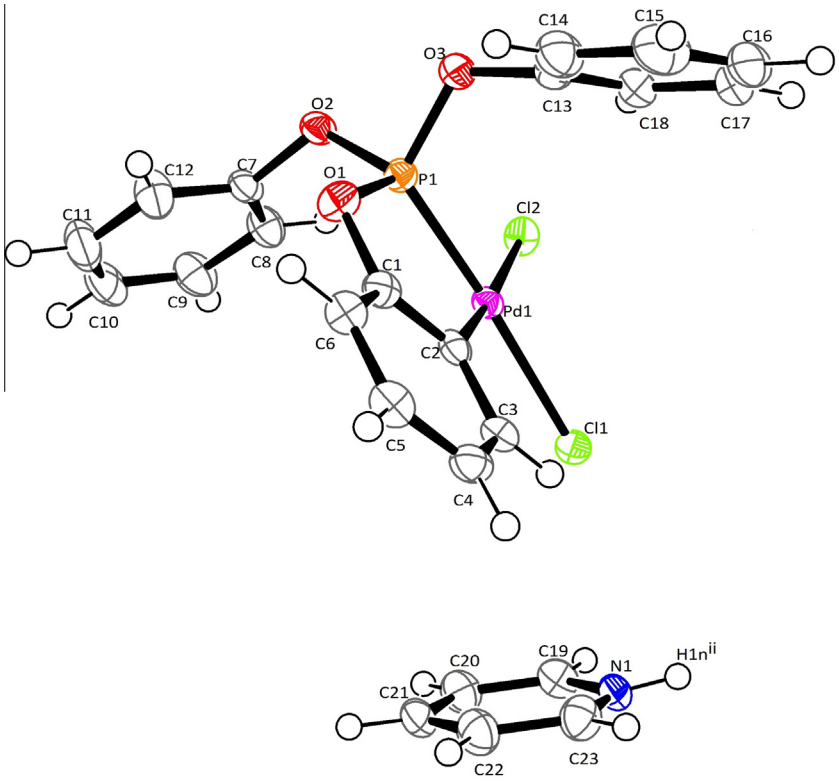


Fig. 3. ORTEP view of the X-ray crystal structure of complex **3d**.

diffusion of *n*-hexane into a THF solution of complex **2a** and CH_2Cl_2 solutions of complexes **2c** and **3d**. Figs. 1–3 show the ORTEP diagrams of **2a**, **2c** and **3d**. Crystallographic data and parameters concerning data collection and structure solution and refinements are summarized in Table 1 and some selected bond lengths (Å) and angles (°) are collected in Table 2.

Palladacycles **2a**, **2c** and **3d** crystallize in the triclinic $P\bar{1}$, monoclinic $P2_1$ and monoclinic $P2_1/n$ space groups, respectively. The X-ray crystal data demonstrate that each palladium metal is located in a distorted square-planar geometry surrounded by a chelating triphenylphosphite-C,P moiety (C2 and P1), chloride anion (Cl1) and phosphorus of PPh_3 (P2) in **2a** or nitrogen of Me_3Py

Table 1
Crystallographic data and structure refinement details for **2a**, **2c** and **3d**.

Empirical formula	$C_{39}H_{37}ClO_4P_2Pd$, **2a**	$C_{26}H_{25}ClNO_3PPd$, **2c**	$C_{23}H_{20}Cl_2NO_3PPd$, **3d**
Formula weight	773.48	572.29	566.67
T (K)	100(1)	100(1)	100(1)
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1$	$P2_1/n$
Z	2	4	4
a (Å)	10.4680(3)	9.1490(2)	16.4210(8)
b (Å)	13.5250(4)	16.6420(5)	9.1650(5)
c (Å)	14.5440(4)	16.1460(4)	16.7780(7)
α (°)	103.187(2)	90.00	90.00
β (°)	92.717(2)	90.311(2)	113.407(4)
γ (°)	111.543(3)	90.00	90.00
V (Å^3)	1845.12(9)	2458.32(11)	2317.3(2)
F_{000}	792	1160	1136
D_{cal} (Mg/m^3)	1.392	1.546	1.624
μ (mm^{-1})	0.70	0.96	9.45
No. of measured reflections	23233	25188	27350
No. of independent reflections	6266	7033	4357
No. of parameters	493	596	279
$R[F^2 > 2\sigma(F^2)]$	0.036	0.042	0.036
$wR(F^2)$	0.104	0.108	0.098
R_{int}	0.027	0.064	0.066
S	0.83	0.94	1.04

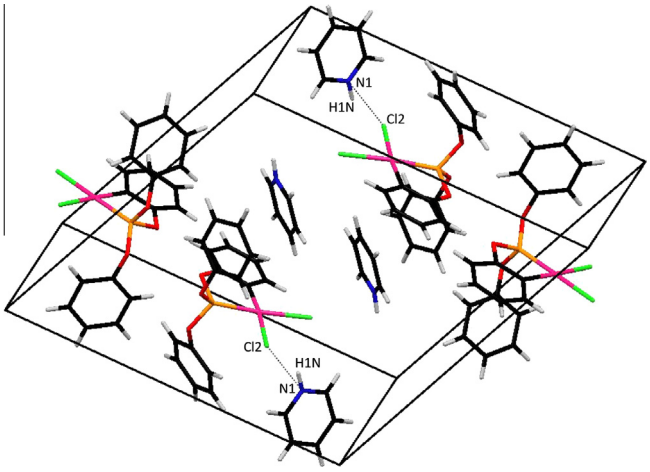


Fig. 4. The crystal packing of complex **3d**. Dotted lines represent the intermolecular hydrogen bonding interactions.

(N1) in **2c** or chloride anion (Cl2) in **3d**, confirming the presence of a five-membered palladacycle with a Pd-C2 bond. The angles around each palladium center deviate from the ideal value due to the small bite angle of the coordinated $P(OPh)_3$. In complex **2a**, the C2–Pd1–P1 bite angle is 80.00(9)°, while the opposite angle, Cl1–Pd1–P2, of 86.26(3)° deviates from the ideal value of 90°.

Table 3
Optimization of the reaction conditions for the Suzuki reaction of bromobenzene with phenyl boronic acid at room temperature[a].

Entry	Solvent	Base	Time (h)	Yield (%)[b]
1	THF/H_2O (2:1)	$K_3PO_4.3H_2O$	1	33
2	THF/H_2O (2:1)	K_2CO_3	1	64
3	THF/H_2O (2:1)	Na_2CO_3	1	65
4	THF/H_2O (2:1)	KOH	1	94
5	MeOH	KOH	1	54
6	acetone	KOH	1	10
7	THF	KOH	1	32
8	toluene	KOH	1	27
9	THF/H_2O (2:1)	KOH	2	68
10	THF/H_2O (2:1)	KOH	0.5	85

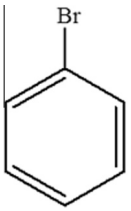
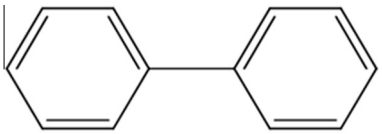
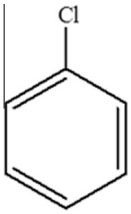
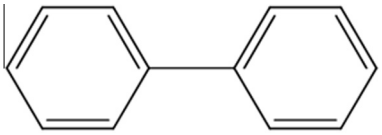
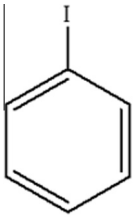
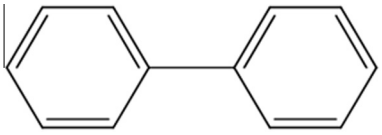
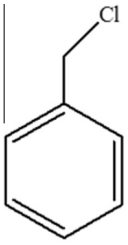
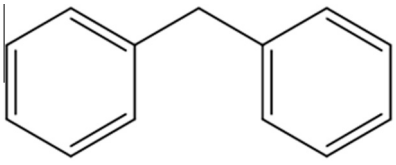
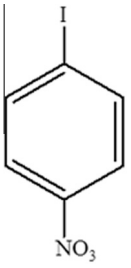
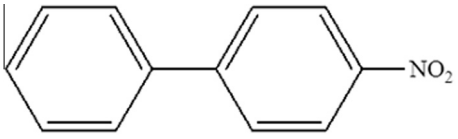
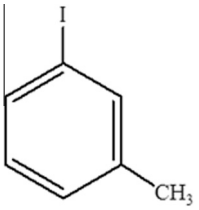
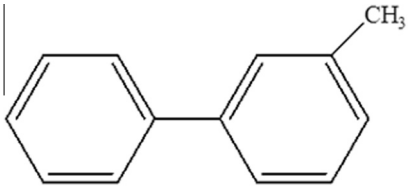
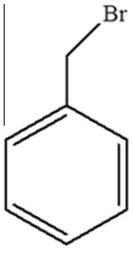
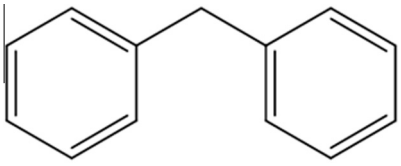
[a] Reaction conditions: bromobenzene (0.50 mmol), phenylboronic acid (0.55 mmol), base (1.00 mmol), solvent (6 ml), $[Pd(PPh_3)(Cl)\{P(OPh)_2(OC_6H_4)\}]$ (0.005 mmol).
[b] Determined by GC.

Due to these steric constraints, the other two angles around the Pd center are opened up and are significantly larger than 90°; P1–Pd1–P2 = 100.44(3)° and Cl1–Pd1–C2 = 93.28(9)°. The angles subtended by the cyclometallated $P(OPh)_3$ ligand at the Pd(II) center in **2c** and **3d**, are 81.48(17) and 80.40(9)°, respectively, for C2–Pd1–P1, indicating the distorted square-planar structures. The Pd1-C2 bond distances of 2.067(3), 2.027(6) and 2.013(3) Å, respectively for **2a**, **2c** and **3d** are identical to those found in other orthopalladated complexes [45].

Table 2
Selected bond distances (Å) and angles (°) for **2a**, **2c** and **3d**.

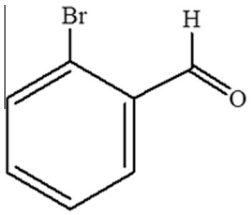
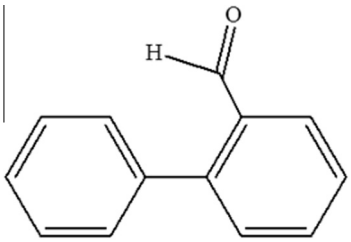
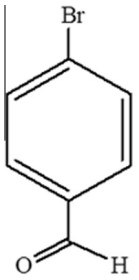
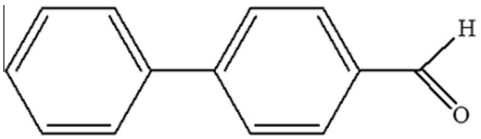
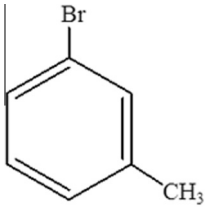
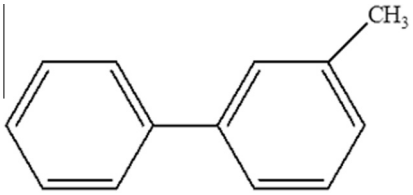
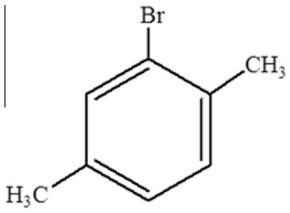
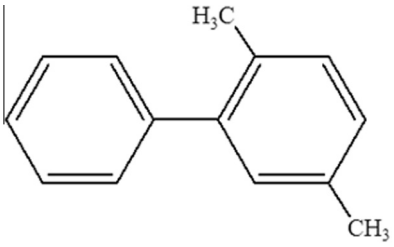
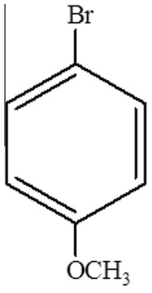
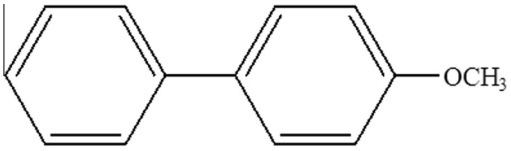
2a		**2c**		**3d**	
Pd1–C2	2.067(3)	Pd1–C2	2.027(6)	Pd1–C2	2.013(3)
Pd1–P1	2.1686(8)	Pd1–N1	2.115(5)	Pd1–P1	2.1542(8)
Pd1–Cl1	2.3473(8)	Pd1–P1	2.1576(15)	Pd1–Cl1	2.3694(8)
Pd1–P2	2.3737(8)	Pd1–Cl1	2.3864(14)	Pd1–Cl2	2.4205(8)
C2–Pd1–P1	80.00(9)	C2–Pd1–P1	81.48(17)	C2–Pd1–P1	80.40(9)
C2–Pd1–Cl1	93.28(9)	C2–Pd1–N1	93.5(2)	C2–Pd1–Cl1	94.68(9)
P1–Pd1–Cl1	173.26(3)	N1–Pd1–P1	172.77(13)	P1–Pd1–Cl1	174.61(3)
C2–Pd1–P2	177.61(8)	C2–Pd1–Cl1	174.07(18)	C2–Pd1–Cl2	173.81(9)
P1–Pd1–P2	100.44(3)	N1–Pd1–Cl1	91.88(13)	P1–Pd1–Cl2	94.05(3)
Cl1–Pd1–P2	86.26(3)	P1–Pd1–Cl1	93.34(5)	Cl1–Pd1–Cl2	90.96(3)

Table 4
Suzuki reaction of various aryl halides with phenylboronic acid using 0.005 mmol complex **2a.**[a]

Entry	Ar-X	Product	Yield (%)[b]
1			94
2			80
3			96
4			72
5			100
6			83
7			76

(*continued on next page*)

Table 4 (*continued*)

Entry	Ar-X	Product	Yield (%)[b]
8			80
9			83
10			70
11			66
12			73

[a] Reaction conditions: Derivatives of aryl halides (0.5 mmol), phenylboronic acid (0.55 mmol), KOH (1 mmol), THF:H_2O (2:1), (6 ml), Pd catalyst (0.005 mmol), r.t., 1 h.
[b] Determined by GC.

According to Figs. 1 and 2, the P-donor incoming ligand PPh_3 is mutually *trans* to the orthometallated carbon of $P(OPh)_3$ in **2a**, while in **2c**, the N-donor incoming ligand Me_3Py is located *trans* to the P atom of $P(OPh)_3$. The greater *trans* influence of the sp^2 carbon (C2) in each of the crystal structures **2a**, **2c** and **3d** leads to the elongation of the mutually *trans* bond with respect to similar complexes [50]. For instance, the Pd1–P2 bond distance (2.3737(8) Å) is significantly longer than the Pd1–P1 bond (1.1686(8) Å) in **2a**. The Pd1–Cl1 bond distances are elongated to (2.3864(14) Å) in **2c** [24] and the Pd1–Cl2 bond distance (2.4205(8) Å) is longer in comparison with the Pd1–Cl1 bond (2.3694(8) Å) in **3d**. The Pd1–N1 distance (2.115(5) Å) is similar to those found for related orthopalladated complexes (2.0599(15) Å) [51].

The mononuclear complex **2c** crystallizes with two independent molecules in the asymmetric unit. One structure has the palladated aromatic ring more or less perpendicular to the heterocycle of the auxiliary ligand; in the second structure, the angle between the planes formed by these two rings is smaller. So, these two structures are a result of a slightly restricted rotation around the single Pd–N bond due to the steric bulk of the auxiliary ligand.

Concerning the X-ray crystal structure of **3d**, the pyridinum molecule is located near the Pd(II) center as a counter ion. The adjacent molecules are linked by an intermolecular hydrogen bond between the coordinated chlorides and pyridinium cation (Fig. 4).

3.4. Suzuki cross-coupling reactions of aryl halides

Concerning the efficient characteristics of palladium compounds containing phosphorus ligands [43,44], the catalytic applicability of Pd(II) complex **2a**, containing PPh_3, was evaluated for

the Suzuki reaction. The cross-coupling of aryl halides with phenyl boronic acid was carried out according to the optimized conditions, in the presence of 0.005 mmol catalyst at room temperature for 1 h using THF/H_2O (2:1) as the solvent (Table 3).

The coupling reactions were studied in the presence of various bases (Table 3, entries 1-4), and KOH was found to be the most effective base. Thus, the other substrates were examined using KOH as the base (Table 3, entries 4–8). After optimization of the base, different solvents, such as MeOH, acetone and toluene, were tested in the Suzuki reaction for aryl bromides, which were not effective (Table 3, entries 5, 6 and 8). Moreover, the conversion of bromobenzene was low when THF was used as the solvent (Table 3, entry 7). Finally, THF/H_2O in a ratio of 2:1 was found to be the best solvent condition for this reaction. The data (Table 3, entries 9 and 10) clearly show that increasing the reaction time did not lead to a higher conversion of bromobenzene, and changing from 1 hour decreased the yield. All the cross-coupling reactions were performed importantly at room temperature and yield the data presented in Tables 3 and 4, which correspond to the average values obtained in two or three identical catalytic experiments.

To demonstrate the versatility of the catalytic system, we investigated the reaction using a variety of aryl halides with phenyl boronic acid under the optimized conditions. Table 4 summarizes the results for the Suzuki reactions. Concerning Table 4, aryl halides with electron-withdrawing substituents in *para* positions reacted smoothly, but the efficiencies were lower for the substrates with electron-donating groups (Table 4, entries 5, 9 and 12). Also aryl halides with an *ortho* substituent were poor substrates due to their sterically hindered conditions (Table 4, entry 8). In our catalytic system, the more easily accessible and cheaper aryl chloride also participated in these reactions (Table 4, entry 2).

4. Conclusion

In this study we have successfully synthesized five-membered P,C-orthopalladated complexes with different monodentate ligands. The N^N bidentate ligands also reacted with the precursor dimeric P,C-orthopalladated complex to yield new cationic orthopalladated complexes. These complexes were fully characterized by NMR spectroscopy, elemental analysis and FT-IR techniques. The identification of complexes **2a**, **2c** and **3d** have also been confirmed by X-ray structure analysis. According to the crystallographic data, the orthopalladated complex **2c** has two different conformational isomers in the solid state, although it appeared as one isomer in solution, as confirmed by NMR spectroscopy. The X-ray structure of the orthopalladated complex **3d** revealed that the pyridine molecule is located near to the anionic complex as a pyridinium counter ion. Due to the promising effects of palladium compounds containing phosphorus ligands in C–C cross-coupling reactions, complex **2a** has been evaluated as an efficient catalyst for the Suzuki cross-coupling reaction. Importantly, all of the reactions were performed at room temperature and the corresponding products were obtained in good to excellent yields. Also, in addition to diverse aryl bromides, the more easily accessible and cheaper aryl chloride was employed under mild reaction conditions. At present, further efforts to expand the catalytic applications of these palladacycles in other catalyzed reactions are in progress in our group.

Acknowledgements

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Appendix A. Supplementary data

CCDC 921982, 921983 and 921984 contain the supplementary crystallographic data for **2a**, **2c** and **3d**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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