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Mono- and binuclear orthopalladated complexes of phosphorus ylides containing nitrogen, phosphorus or bridging diphosphine ligands: Self-assembly, theoretical calculations and comparative catalytic activity

Kazem Karami [a, *], Sedigheh Abedanzadeh [a], Firoozeh Yadollahi [a], Orhan Büyükgüngör [b], Hossein Farrokhpour [a], Corrado Rizzoli [c], Janusz Lipkowski [d]

[a] Department of Chemistry, Isfahan University of Technology, Isfahan 84156/83111, Islamic Republic of Iran
[b] Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey
[c] Department of Chemistry, University of Parma, I-43124 Parma, Italy
[d] Cardinal Stefan Wyszynski University in Warsaw, Faculty of Mathematical and Natural Sciences, Wojcickiego 1/3, 02-093 Warszawa, Poland

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ABSTRACT

Binuclear orthopalladated complexes of phosphorus ylides containing electron-withdrawing fluoro (**Y1**), bromo (**Y2**) or phenyl (**Y3**) substituent, $[Pd\{\kappa^2(C,C)\text{-}[(C_6H_4\text{-}2)PPh_2]CH(CO)C_6H_4X\text{-}4\}(\mu\text{-}Cl)]_2$ (X = F (**1**), Br (**2**), Ph (**3**)) were obtained by two different methods from the reaction of corresponding ylides and $PdCl_2$ or $Pd(OAc)_2$. The synthesized orthopalladated complexes **1** and **2** reacted with the monodentate ligands with various donor abilities affording the mononuclear complexes $[PdCl\{C,C\text{-}\{CH[P(C_6H_4\text{-}2)Ph_2]C(O)C_6H_4X\text{-}4\}\}L]$ [L = triphenylphosphine (X = Cl (**1a**), X = Br (**2a**)); 3-methylpyridine (X = Cl (**1b**), X = Br (**2b**)); 4-methylpyridine (X = Br (**2c**)); 2,4,6-trimethylpyridine (X = Cl (**1c**)); pyridine (X = Cl (**1d**)); piperidine (X = Cl (**1e**)). The reaction of chloro-bridged complex **3** with bis(diphenylphosphino)ethane, dppe, and bis(diphenylphosphino)propane, dppp, in the 1:1 ratio occurred to give the symmetrical bridged complexes of general formula $[Pd_2Cl_2\{C,C\text{-}\{CH[P(C_6H_4\text{-}2)Ph_2]C(O)C_6H_4X\text{-}4\}\}_2](\mu\text{-}P^{\wedge}P)$ ($P^{\wedge}P$ = dppe (**3a**) and dppp (**3b**)). New complexes were fully characterized by elemental analysis, IR and NMR spectroscopies. The crystal structures of **1**, **1a**, **2a**, **3** and **3a** were determined by single-crystal X-ray diffraction analysis that revealed the self-assembly of complexes via the short contacts between donor and acceptor groups to form polymer, sheet or network supramolecular structures. Density functional theory (DFT) calculations for complexes **1**, **1a** and **2a** indicated the good agreement with the experimental value reported in this work. The catalytic activity of **1**, **1a** and **2a** were comparatively studied in the Suzuki cross-coupling reactions which showed the more efficiency of mononuclear complex **1a** with fluoro substituent.

Introduction

Cyclopalladated complexes has attracted considerable attention due to their potential applications in organic synthesis, homogenous catalysis, photochemistry, optical resolution, design of new metallomesogenes, antitumor drugs, etc [1–8]. More recently, various examples of their uses as building blocks in macromolecular chemistry have also been published [9–13].

Phosphorus ylides can be used as the chiral auxiliary reagents, reaction intermediates or starting materials in a wide variety of processes due to their nucleophilic character, particular bonding properties and diverse coordination modes [14–16]. The α-stabilized phosphorus ylides can coordinate to the Pd (II) center as the bidentate ligands and undergo the orthopalladation that has already been reported [17,18]. Due to the nearly ubiquitous nature of the C–H bond, it is common to find two or more C–H bonds in the same compound to be activated. According to the previous investigations [2], the stabilized ylide $Ph_3PCH(CO)C_6H_5$, can be

* Corresponding author.
E-mail addresses: karami@cc.iut.ac.ir (K. Karami), orhanb@omu.edu.tr (O. Büyükgüngör), corrado.rizzoli@unipr.it (C. Rizzoli), janusz.lipkowski@wp.pl (J. Lipkowski).

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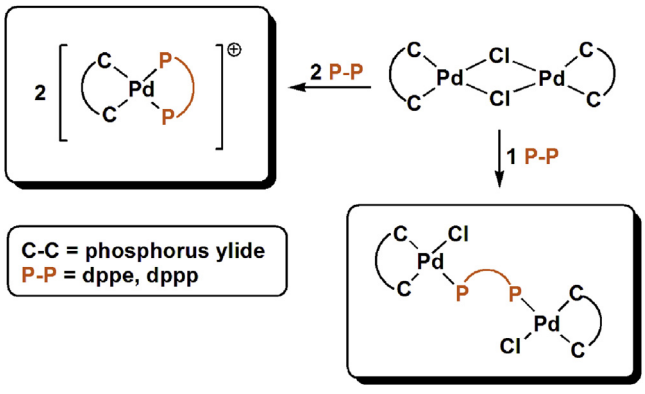
metallated at both aryl rings of phosphorus group and/or aryl ring of benzoyl fragment. In this paper, we report the orthometallated α-keto phosphorus ylides containing electron-withdrawing groups on the aromatic ring of C_6H_5CO, as well as the X-ray crystal structures of corresponding complexes **1**, **1a**, **2a**, **3** and **3a** revealing the proposed *C*,*C*-coordination of the orthometallated ylides. It is shown that some of these complexes undergo supramolecular self-assembly through the contacts between the specified atoms to form the supramolecular sheet or network structures. The structures of complexes **1a**, **2a** and **2b** were also theoretically studied that revealed good agreement between the calculated data and those obtained from the X-ray diffraction results. In continuation of our interest in the development of employing new palladium complexes in C–C bond forming reactions [19–21] and due to the high efficiency of Pd complexes containing phosphine ligands [22,23], we report the comparative evaluation of palladacycles **1**, **1a** and **2a** as the homogenous catalysts in the Suzuki C–C cross-coupling reactions.

In particular, this article also reports the reaction of binuclear chloro-bridged cyclopalladated complex of phosphorus ylide (**3**) with bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)propane (dppp) to prepare the square planar complexes with bridging dppe and dppp ligands. The reaction of the precursor complex with diphosphine ligands in a 1:2 molar ratio (Scheme 1) gives the mononuclear bischelate cyclopalladated complex, structurally determined in our previous studies [24,25] while the reaction in a 1:1 molar ratio gives the diphosphino-bridged binuclear complexes (Scheme 1). It is noteworthy that dppe and dppp are very strong chelating ligands in square planar complexes and there are few examples of d^8 metal complexes with bridging dppe and dppp due to their appropriate bite angles [26].

Result and discussion

Synthesis

The ylide ligands stabilized by carbonyl group were synthesized using published methods [27–31]. As shown in Scheme 2, the corresponding phosphorus ylides are refluxed with $Pd(OAc)_2$ (1:1) in CH_2Cl_2. The synthesized binuclear acetato-bridged intermediates react with excess NaCl in MeOH, affording complexes **1**, **2** or **3** (method **A**). These binuclear complexes can be produced directly from the refluxing reaction of $PdCl_2$ with phosphorus ylides in acetonitrile (method **B**). The second method (**B**) is preferred since it is a one step-reaction especially accomplishing in lower reaction time while it gives the higher yields. The elemental analysis results



Scheme 1. The reaction of cyclometallated complexes of phosphorus ylides with diphosphine ligands.

of the prepared compounds were in good agreement with the calculated values.

Ylides may undergo a C–H activation process at the two different positions namely, the aryl ring of the benzoyl fragment and the aryl ring of the phosphine group [32]. As we were increasing the electron-withdrawing nature of the *para* substituent of the benzoyl ring containing the strong deactivating carbonyl group and due to the presence of the electron-rich phenyl rings of PPh_3 fragment [33], the stabilized ylides containing deactivating fluoro, bromo or phenyl groups at the benzoyl ring, were metallated at the phenyl ring of the PPh_3 unit. This fact has been fully established through the spectroscopic characterization and the X-ray structure determination.

Characterization

FT-IR spectra

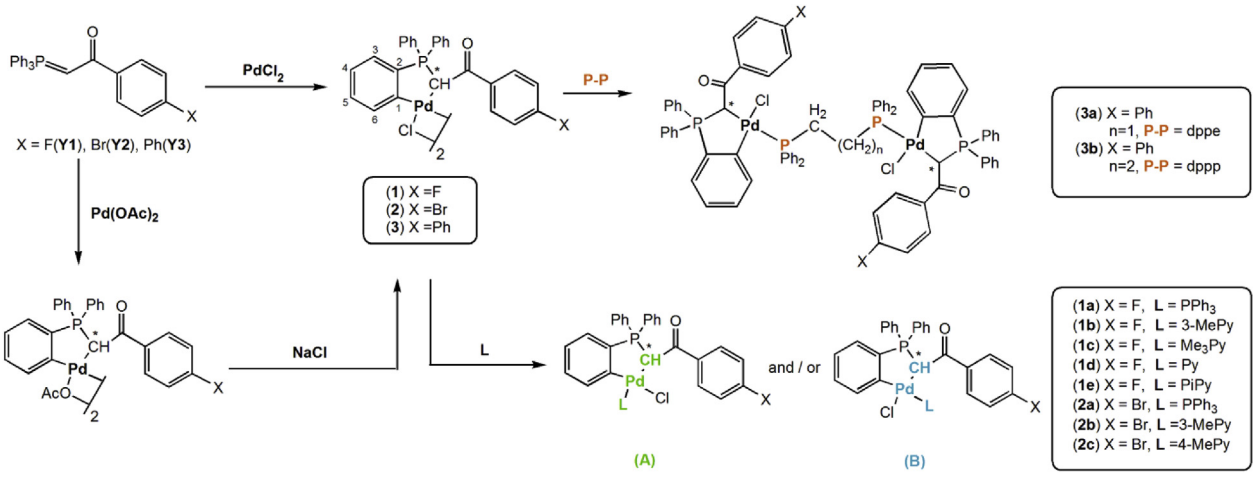
Each FT-IR spectra of ylides show the strong peak at 1505–1512 cm^{-1} due to the carbonyl stretching vibrations. This band appears at the lower energies comparing with the phosphonium salts, due to the charge delocalization present in such compounds. The *C*-coordination of the ylides leads to the increase in ν (CO) while for *O*-coordination; the lowering is expected relative to the free ylides [32]. The IR spectra of all complexes show the strong vibrations in the range of 1620–1630 cm^{-1}, which are shifted to a higher frequencies with respect to the starting ylides, confirming the *C*-coordination [32,34]. The ν (P^+–C^-) which is diagnostic of coordination, occurs at 837 cm^{-1} in $(C_6H_5)_3P^+-{}^-CH_2$ and at 878 cm^{-1} in $(C_6H_5)_3PCHCOC_6H_5$. In the present study, the ν (P^+–C^-) values are shifted to the lower frequencies in the synthesized complexes.

NMR spectra

In the ^1H NMR data of mononuclear complexes, the $^2J_{HP}$ values are in the range 2.0–4.0 Hz that are smaller than those in the free ylides and phosphonium salts [35–37]; a behavior that has already been observed in the other *C*-coordinated carbonyl-stabilized phosphorus ylide complexes due to the changes in the hybridization of the ylidic carbon (sp^2 to sp^3) in the *C*-coordination mode.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of complex **1**, is in agreement with the proposed structures. Theoretical calculations show the more stability of the trans-type isomer, confirming with NMR data. ^1H and $^{31}P\{^1H\}$ NMR signals for the CHP groups of all complexes are shifted to the lower field with respect to the parent ylides corresponding to the *C*-bonding of the ylides [24]. The signals related to the CHP groups of corresponding ylide appear as the broad singlet at 18.97 ppm (minor) and the broad doublets at 19.41 ppm (major). The presence of two lines of different intensities can be originated from the presence of two diastereoisomers (*RR*/*SS* and *RS*/*SR*). The metallation of a phenyl group of the PPh_3 unit is evident from the ^1H NMR spectrum which show the specified resonances assigned to the protons of the C_6H_4CO fragment while the expected 6:3:6 pattern of the H_o:H_p:H_m protons of the PPh_3 group is disappeared. A new pattern of signals with the relative intensities of 1:1:1:1:4:2:4 is observed and partially overlapped due to the presence of the two diastereoisomers [16,32]. The NMR spectra of complexes **2** and **3** have been already described [24].

The bridge-splitting reactions of **1** and **2** with the monodentate P or N-donor ligands (triphenylphosphine, pyridine derivatives and piperidine) afforded the corresponding mononuclear compounds **1a**–**e** and **2a**–**c**. According to the NMR data, X-ray determinations and based on our previous study [7], complexes **1a** and **2a** have been characterized as that containing the PPh_3 ligand trans with respect to the ylidic carbon. The $^{31}P\{^1H\}$ NMR spectra of **1a** and **2a** at room temperature show one singlet at about 15 ppm that is



Scheme 2. The cyclometallation reactions.

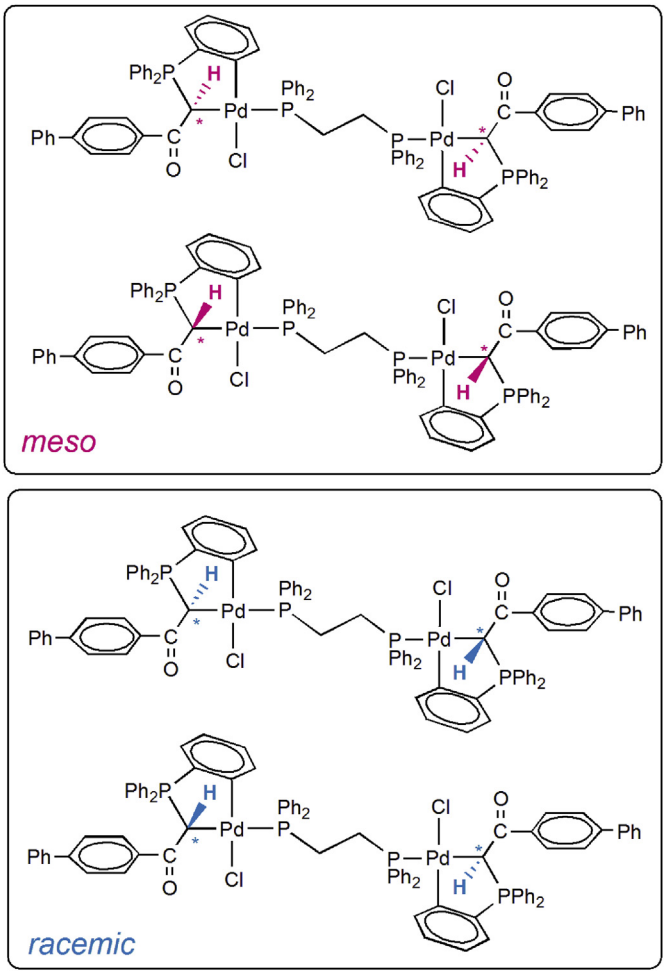
attributed to the phosphorous ylides and a singlet at about 32 ppm assigned to the phosphorus of PPh_3. Both ^1H and $^{31}P\{^1H\}$ NMR spectra show the presence of a single isomer. Accordingly, the complex containing Me_3Py ligand (**1c**), only the isomer with the nitrogen and yilidic carbon in trans position is obtained [1,35]. In accordance to the steric effects of the bulky PPh_3 and Me_3Py ligands, they are located in the trans position of the ylidic carbon. Our previous work structurally provide the location of the Me_3Py ligand trans to the yilidic carbon, according to the anti-symbiotic effect, whereas the 4-MePy ligand preferentially cis to the yilidic carbon [35]. The $^{31}P\{^1H\}$ NMR spectrum of **1c** shows a singlet at 18.95 ppm that is attributed to the CHP. The ^1H NMR data also show one doublet resonance at 5.14 ppm related to the phosphorous ylide (CHP). Also, in the $^{13}C\{^1H\}$ NMR spectrum of this complex, appearance of a doublet at 35 ppm with $^1J_{CP} = 59.5$ Hz, confirms the coordination of ylide to the Pd (II) center. Due to the changing in the hybridization (from sp^2 in the ylidic carbon to sp^3 in the *C*-coordination mode), the chemical shift value has been shifted to the downfield and the CP coupling constant ($^1J_{CP}$) would be smaller than those in the free ylides and phosphonium salts [36,37]. Both ^1H and $^{31}P\{^1H\}$ NMR spectra support the presence of a single isomer for the structure **1c**.

However, in the other complexes (**1b**, **1d**, **1e** and **2b**, **2c**), formation of two isomers **A** and **B** (Scheme 2), is suggested by NMR data. The presences of two signals for the P=C(H) group in the ^1H and $^{31}P\{^1H\}$ NMR spectra of these complexes show that two isomers have been produced.

The ^1H NMR spectrum of **2c** containing 4-MePy ligand, shows two signals for the P=C(H) group that are assigned to a fast equilibrium between the **A** and **B** isomers or a dynamic activity for exchange of 4-MePy and Cl groups in solution [1] (Scheme 1). This assignment of the structures **A** and **B** has been carried out by comparison of the chemical shifts of the H^6 proton of the C_6H_4 group (ortho to the metallated position) in the two isomers. Thus, the isomer **B** shows the signal corresponding to H^6 at $\delta = 6.93$ ppm, while the isomer **A** shows the corresponding signal at $\delta = 6.54$ ppm. This clear upfield shift can be due to the anisotropic shielding undergone by H^6, which is promoted by the cis pyridine ligand in isomer **A**.

The ^1H NMR spectra of **1b** and **2b**, **2c** show the presence of two different methyl groups of both isomers (**A** and **B**). Related to the complex **1e**, the ^1H NMR spectrum shows two sets of the aliphatic resonances for CH_2 groups in the piperidine ligand, suggesting the existence of two possible isomers.

The $^{13}C\{^1H\}$ NMR spectrum of complex **2c** shows one doublet resonance at 34.20 ppm with $^1J_{CP} = 58.5$ Hz. The chemical shift value is shifted to downfield with respect to the parent ylide [37], indicating that the coordination of ylide has been occurred.



Scheme 3. Possible isomers for $[Pd_2Cl_2\{\kappa^2(C,C)\text{-}[(C_6H_4\text{-}2)PPh_2]CH(CO)C_6H_4Ph\text{-}4\}_2(dppe)]$, **3a**.

The ^{1}H NMR spectra of complexes with pyridine derivatives (**1b**, **1c**, **1d** and **2b**, **2c**) show the resonances attributed to the H^6 of the C_6H_4, shifted strongly to upfield. This is also observed in the other complexes [34,38] according to the anisotropic shielding of this proton due to the vicinity to the cis pyridine ligand in the **A** type structures (Scheme 2) [40,41].

The dimeric palladacycle **3** reacted with one equivalent of diphosphinic ligands (dppe and dppp) to give the binuclear complexes in which the diphosphinic ligands would be bridging bidentate. The $^{31}P\{^1H\}$ NMR spectra show the appearance of broad and multiplet signals related to the CHP and diphosphinic ligands in **3a** and **3b**. The bridging diphosphine complexes **3a** and **3b** can exist as meso and racemic isomers as well as the presences of two chiral centers, which should give different $^{31}P\{^1H\}$ NMR spectra (Scheme 3). The structure of **3a**, which is isolated in pure form by recrystallization method, was confirmed by NMR spectroscopy and single crystal X-ray diffraction. The ORTEP view, crystal data and structural refinement parameters of complex **3a** are indicated in Supporting material. In each ^{1}H NMR spectrum of **3a** and **3b**, the observation of a broad signal at the yilidic CHP region (5.60 ppm for **3a** and 5.41 ppm for **3b**) probably indicates the presence of the geometric isomers (meso-rac).

X-ray crystallography study

Single crystals of **1**, **1a** and **2a**, suitable for X-ray, were obtained by diffusion of *n*-hexane into the CH_2Cl_2 solution of each complex. Crystallographic data and parameters including data collection, structure solution and refinement are summarized in Table 1. Moreover, the binuclear complexes **3** and **3a** were crystallized by slow evaporation of the concentrated CH_2Cl_2–hexane and $CHCl_3$–hexane solutions, respectively. The ORTEP view, crystal data and structural refinement parameters of complexes **3** and **3a** are listed in Supporting information.

In the structure of complex **1** (Fig. 1), each palladium atom is located in a slightly distorted square planar environment surrounded by the orthometallated carbon atom, the ylide carbon, and two bridging chloride ligands, confirming the metallation of the phosphorus ylide through the aryl ring of the phosphine group. The absolute configuration of the phosphorus atoms are depicted in the structures. The summation of the bond angles around each palladium is almost 360°. Although the orthometallated ligand is remarkably warped, the environment around each Pd is planar. In the X-ray crystal structure of **1**, there are two independent half-molecules in the asymmetric part of the unit cell, which are structurally analogous. Each independent molecule is a binuclear complex, in which two units [Pd{C_6H_4(PPh_2=CHC(O)C_6H_4–F)-2}] are bridged by two chloride atoms. The Pd1–C2 bond distance found in complex **1** (1.981(4) Å) is identical with those found in the other complexes (1.965(6) Å) [29]. The bond length of P1–C19 in the similar ylide is (1.706 Å) which shows that the bond has been considerably elongated to (1.784(4) Å) in complex **1** [27].

The self-assembly of organometallic complexes leads to creation of new polymer, sheet or network structures that have great potential as building blocks in the development of supramolecular organometallic chemistry [12,13]. The binuclear complex **1**, is self-assembled into supramolecular sheet structure by intermolecular interactions between fluoride and hydrogen groups (F1···H17 = 2.668 Å and F1···F1 = 2.768 Å), which leads to connect the layers (Supporting material). Phenyl groups take part in intermolecular π-stacking with mean interplanar separation 3.495 Å.

According to Figs. 2 and 3, the Pd atoms of complexes **1a** and **2a** are located in distorted square planar environments, surrounded by the ylidic carbon (C19 in **1a** and C37 in **2a**), the metallated carbon (C1 in **1a**, C18 in **2a**), one chloride (Cl1) and one phosphorus (P2) that forms a five-membered cycle. The angles subtended by the ligands at the Pd (II) center (C19–Pd1–P2 = 167.82(14), C1–Pd1–Cl1 = 174.63 (17) in **1a** and C37–Pd1–P2 = 170.92 (7), C18–Pd1–Cl1 = 176.06 (10) in **2a**) deviate from linearity, indicating the distorted square planar environments. The bond distance between each central Pd (II) and orthometallated carbon (1.996(6) Å in **1a** and 2.007(3) in **2a**) is statistically identical to those found in the other orthopalladated complexes (2.035(5) Å) [2,28]. The non-equivalent Pd–C distances in each complex is related to the different donating character of the carbon atoms, in addition to reflecting the different influence of the atoms in the trans position of carbons. The stabilized resonance structures of the parent ylides were disappeared due to the complex formation, thus the C19–C20 in **1a** (1.465(8) Å) and C37–C38 in **2a** (1.467(5) Å) bond lengths were longer than the corresponding distances found in similar free phosphoranes (1.407(8) Å [39] and 1.401(2) Å [36]). Likewise the bond lengths between ylidic carbon and phosphorus have considerably elongated to 1.766(6) Å in **1a** or 1.771(3) Å in **2a**, in comparison with the similar ylides (1.7194(17) Å) [29,30].

The complex network structure of **1a** is shown in the Supporting material. The supramolecular pattern is formed through the self-assembly of these molecules by the presence of contacts between the atoms which connect the layers in three dimensions. The complex has been crystallized with $Z = 8$, that means eight complex molecules locate in one unit cell. Due to the existence of large amount of interactions, only the final network structure is shown.

Table 1
Crystal data and structure refinements of complexes.

Chemical formula	$C_{52}H_{38}Cl_2F_2O_2P_2Pd_2$ (**1**)·$2CH_2Cl_2$	$C_{44}H_{34}ClFOP_2Pd$ (**1a**)·CH_2Cl_2·H_2O	$C_{44}H_{34}ClBrOP_2Pd$ (**2a**)
Formula mass	1248.32	904.44	862.41
Crystal system	Triclinic	Orthorhombic	Triclinic
a/Å	9.3556(4)	18.6397(9)	10.5507(5)
b/Å	10.5474(4)	20.9401(9)	13.2302(6)
c/Å	15.2145(6)	20.5403(9)	14.0429(6)
α/°	94.007(3)	90	79.614(3)
β/°	105.138(3)	90	87.006(4)
γ/°	113.026(3)	90	76.740(3)
Unit cell volume/Å^3	1308.52(9)	8017.2(6)	1876.58(15)
Temperature/K	296	296	296
Space group	$P\bar{1}$	*Pbca*	$P\bar{1}$
No. of formula units per unit cell, *Z*	1	8	2
No. of reflections measured	18,948	36,816	18,552
No. of independent reflections	5143	7883	7743
R_{int}	0.038	0.099	0.060
Final *R*1 values ($I > 2\sigma(I)$)	0.048	0.062	0.038
Final *wR*(F^2) values ($I > 2\sigma$(I))	0.146	0.159	0.096

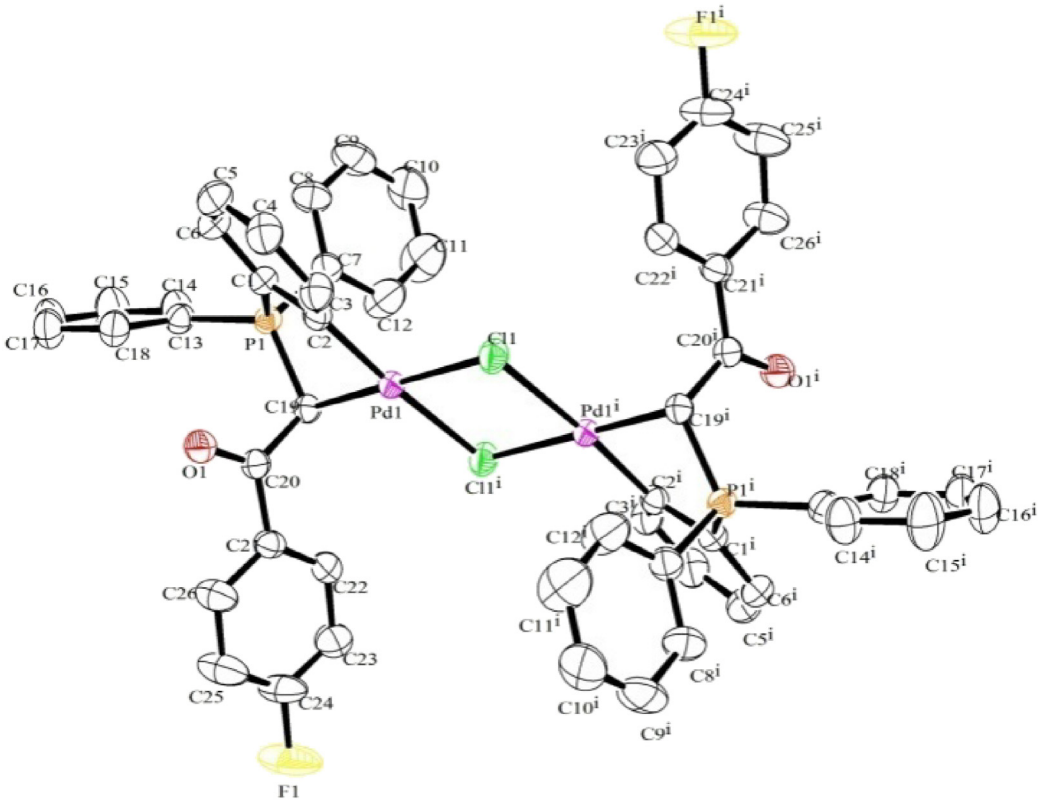


Fig. 1. ORTEP view of the X-ray crystal structure of **1**·$2CH_2Cl_2$. Solvent molecules are omitted for clarity.

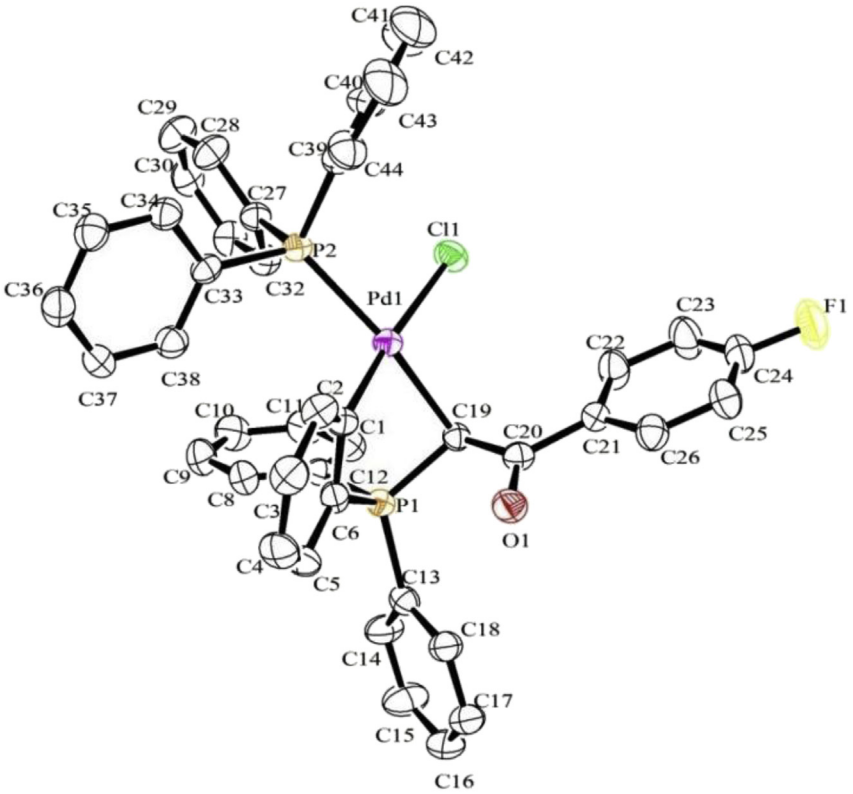


Fig. 2. ORTEP view of the X-ray crystal structure of **1a**·CH_2Cl_2·H_2O. Solvent molecules are omitted for clarity.

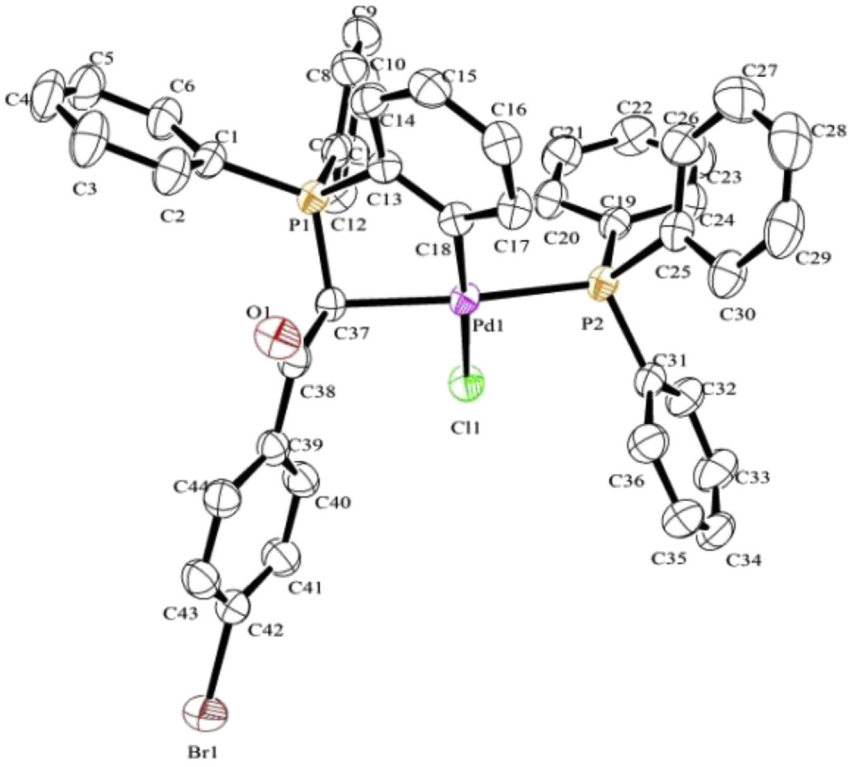


Fig. 3. ORTEP view of the X-ray crystal structure of **2a**.

The sheet supramolecular structure in Supporting material is related to the monomeric complex **2a**. In this organopalladium (II) complex, the coordinated chloride atom has intermolecular interactions with the hydrogen atom of phenyl ring in the neighboring complex leading to the supramolecular dimers (Cl···H = 2.848 Å). This conformation allows intermolecular π-stacking between phenyl groups to form polymeric supramolecular structure (C···C = 3.399 Å). All of the ylidic C═O and the aromatic hydrogens form C═O···H interactions (O···H = 2.550 Å) and bring the layers near to each other affording the stabilized sheet structure.

Theoretical calculations

The structures of the synthesized complexes including, **1**, **1a** and **2a** (only trans isomer) were fully optimized at the B3LYP level of theory. The standard relativistic effective core pseudo potential LAN2DZ basis set were used for Pd atom and the 6-31+G(d,p) basis set for C, H, P, O, Cl, F and Br atoms. Atomic coordinates for these optimizations were taken from the experimental X-ray data reported in this paper. To verify the properties of the obtained stationary points, the vibrational frequency calculations were done at the same levels of theory and there was no imaginary vibrational frequency which indicates that the optimized structures are at the stationary point corresponding to local minima. All of the calculations were performed using the Gaussian 09 computational package [42].

The optimized structures of the considered compounds have been shown in Fig. 4. Table 2 compares some of the bond length and bond angles obtained from the calculations with those obtained experimentally from X-ray data obtained from solid state crystallography for **1**, **1a** and **2a**, respectively.

There is a very good agreement between the calculated bond lengths and angles and those obtained from the experiment. The similarity between the bond angles confirms the presence of similar geometrical structures for the synthesized complexes in the solid and gas phase.

It should be mentioned that the cis isomer of **1**, was also optimized at the same level of theory but it was shown during the optimization that the distance between two palladium atoms increases and causes that the distance between the Cl atom, connected to one Pd atom, and the other Pd atom reaches to above 4 Å. This shows that there is no bond between the Cl and Pd atom and the dimer in the cis structure is not stable (Scheme 4).

To calculate the energy gap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO), the PM6 semi-empirical method was employed on the structures optimized at the B3LYP level of theory. The energy gap calculated at this level of theory for complexes **1a**, **2a** and **1**, are 169.358, 169.101 and 155.120 kcal/mol, respectively.

The energy gap of **1a** and **2a** are equal to each other. It is expected that the shape of the HOMO and LUMO for these two complexes should be the same. The shapes of the HOMO and LUMO for the considered complexes have been shown in Fig. 5. It is obvious from the figure that the HOMO of **1a**, and **2a**, complexes is mainly related to the overlap between the *p* molecular orbital of halogen atom with the dz^2 orbital of Pd atom. The LUMO of **1a** and **2a** are only due to the molecular orbitals of the benzene ring (π*). It should be mentioned that the HOMO and LUMO of **1a** and **2a** have the bonding and antibonding character, respectively. Again, the HOMO of **1**, is related to *p* atomic orbital of Cl and dz^2 orbital of Pd atom and its LUMO is related to the π* of one of the phenyl rings connected to phosphorus atom. The vibrational frequency for the stretching of C═O bond for three synthesized complexes is about 1670 cm^{-1} which is very close to the experimental value (1620–1630 cm^{-1}) reported in this work.

Suzuki cross-coupling reaction

Based on our previous studies [19,20] and the efficient characteristics of palladium compounds containing phosphorus ligands

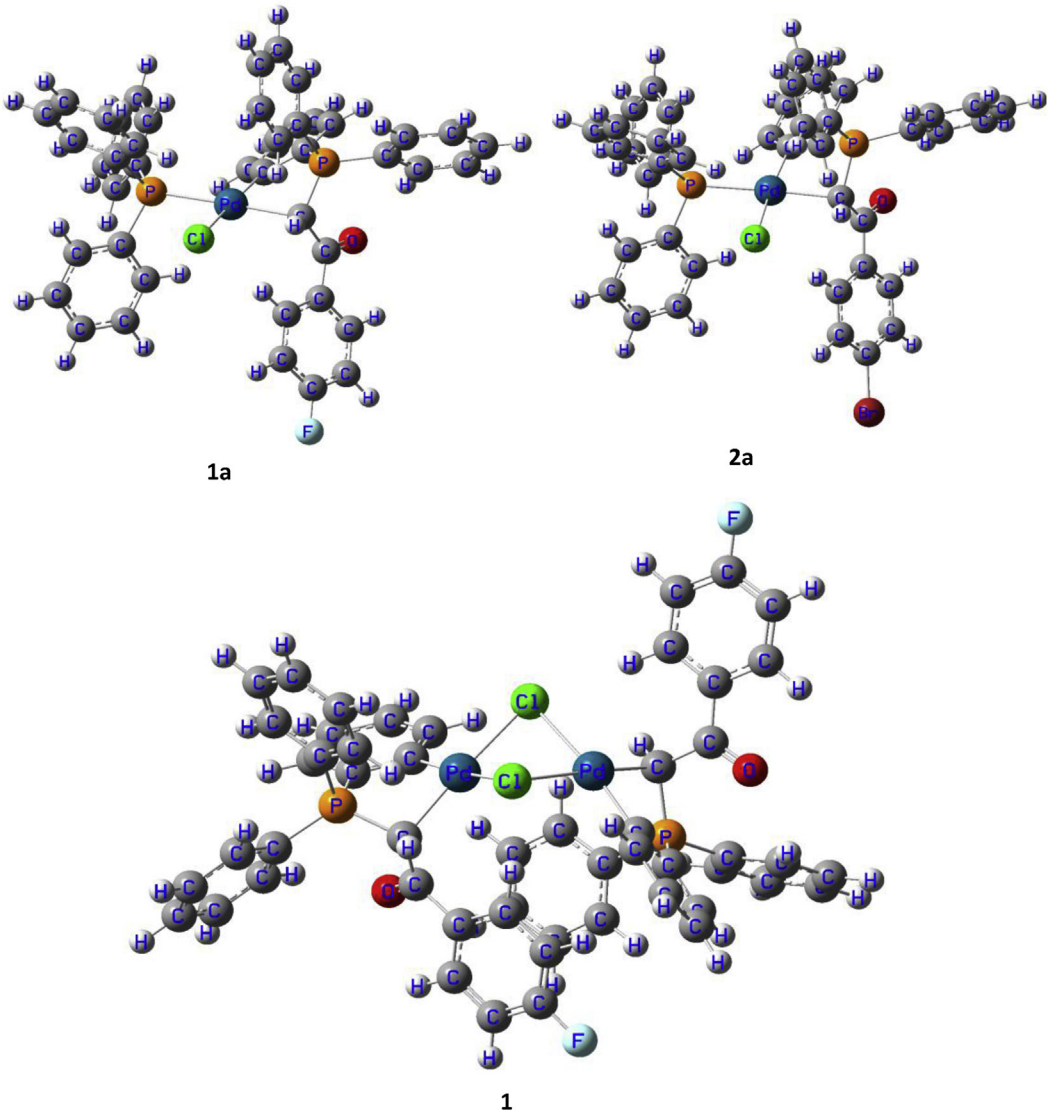


Fig. 4. Optimized structures of **1**, **1a** and **2a**, calculated at the B3LYP/6-31+G(d,p)/LANL2DZ level of theory.

[22,23], complexes **1**, **1a** and **2a** were studied comparatively as the homogenous catalysts in the Suzuki cross-coupling reactions.

Initially, phenyl boronic acid and bromobenzene were refluxed at 75 °C in the presence of catalyst and Na_2CO_3 in MeOH for 1 h. Although a binuclear complex **1** with two Pd active sites was expected to be more efficient in the catalytic systems, cross-coupling reactions yielded products almost quantitatively when complex **1a** and **2a** were used (Table 3). Comparing the catalytic performances between complex **1a** with fluoro-substituent and complex **2a** with bromo-substituent, the former was more active in the Suzuki cross-coupling reactions (Table 3, entries 6–10).

The data shown in Table 3 indicate that increasing the catalyst concentration leads to the higher conversion of bromobenzene; but higher loads were avoided due to the price of the catalyst. Therefore, cross-coupling reactions were evaluated with optimum 0.1 mol% catalyst **1a** (Fig. 6).

In our previous report [7], we studied the catalytic activity of similar orthopalladated complex of phosphorus ylide containing phenyl substituent and PPh_3. The catalyst promoted the Suzuki cross-coupling reaction of various aryl halides to produce the corresponding products by using 1 mol% of the Pd catalyst in MeOH as the solvent and Na_2CO_3 as the base at 60 °C in 40 min. It is noteworthy that in this study, the presence of more electron withdrawing substituent (fluoro) in complex **1a**, afforded the excellent yield of the biphenyl product by using 0.1 mol% of the Pd catalyst at 75 °C in 15 min.

To verify the base effect in the Suzuki reactions, we investigated a series of reactions by taking the model reaction with different bases. We tested the bases usually being used for Suzuki cross-coupling reactions mentioned in our previous studies (Table 4, entries 1–4) [19–21]. Although Cs_2CO_3 often reported as the best base for the Suzuki cross-coupling reactions (Table 4) [5,43–45], K_2CO_3 was found to be the most effective and specially preferred base for the reactions. Among several solvents, MeOH was selected as the best candidate in these reactions. Interestingly, high yield were obtained as well as decreasing the reaction time (Table 4, entries 10–13). So, the best reaction condition for the Suzuki cross-coupling of bromobenzene and phenyl boronic acid reaction was obtained by using 0.1 mol% of the Pd catalyst in MeOH as the solvent and K_2CO_3 as the base at 75 °C in 15 min, which worked efficiently in Suzuki cross-coupling reaction with excellent TOF (turn over frequency) of 3500 h^{-1}.

Table 2
Bond lengths (Å) and angles (°) obtained from the theoretical calculations and those obtained from solid state crystallography for $C_{52}H_{38}Cl_2F_2O_2P_2Pd_2$ (**1**)·$2CH_2Cl_2$, $C_{44}H_{34}ClFOP_2Pd$ (**1a**)·CH_2Cl_2·H_2O, $C_{44}H_{34}ClBrOP_2Pd$ (**2a**).

1			**1a**			**2a**		
	X-ray	Calculated		X-ray	Calculated		X-ray	Calculated
C2–Pd1	1.981(4)	2.102	C1–Pd1	1.996(6)	2.042	C18–Pd1	2.007(3)	2.045
C19–Pd1	2.092(4)	1.9946	C19–Pd1	2.185(5)	2.185	P2–Pd1	2.3189(9)	2.412
Cl1–Pd1	2.3812(12)	2.563	P2–Pd1	2.3070(16)	2.410	Cl1–Pd1	2.4008(8)	2.480
Cl1–Pd1i	2.4508(12)	2.454	Cl1–Pd1	2.3939(17)	2.47	C37–P1	1.772(3)	1.796
Pd1–Cl1i	2.4508(12)	2.447	C19–P1	1.767(6)	1.797	C19–P2	1.828(3)	1.851
Pd1–Cl1–Pd1i	94.53(4)	78.758	C1–Pd1–C19	85.2(2)	84.903	C18–Pd1–C37	86.01(13)	84.921
C2–Pd1–C19	86.71(8)	86.589	C1–Pd1–P2	95.96(19)	99.102	C18–Pd1–P2	97.31(10)	99.61
C2–Pd1–Cl1	93.85(14)	93.682	C19–Pd1–P2	167.82(14)	175.062	C37–Pd1–P2	170.9(7)	175.367
C19–Pd1–Cl1	179.26(13)	176.434	C1–Pd1–Cl1	174.63(17)	172.433	C18–Pd1–Cl1	176.07(10)	171.225
C19–Pd1–Cl1i	93.93(13)	93.682	C19–Pd1–Cl1	91.16(17)	89.099	P2–Pd1–Cl1	91.03(8)	86.674

Experimental

General

^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solutions at room temperature on a 400 and 500 MHz Bruker spectrometers. Chemical shifts (δ) are reported relative to internal TMS and external 85% phosphoric acid. C, H and N elemental analysis were performed using a PE 2400 series analyzer. IR spectra were recorded on a FT-IR JASCO 680 spectrophotometer using the KBr pellets. Analytical TLC was performed using Merck TLC Silica gel 60 F254 glass plates. Gas chromatography analyzes were performed with a FID detector and a 30 m column HP-5. $PdCl_2$, $Pd(OAc)_2$, 2-bromo-4′-fluoroacetophenone, 2,4′-dibromoacetophenone, 2-bromo-4′-phenylacetophenone, triphenylphosphine (PPh_3), 3-methylpyridine (3-MePy), 4-methylpyridine (4-MePy), 2,4,6-trimethylpyridine (Me_3Py), pyridine (Py), piperidine (PiPe) and solvents were used as commercially available chemicals without any purification. The phosphorus ylides were synthesized according to the procedure reported previously [27–31].

Synthesis procedure for cyclopalladated complexes

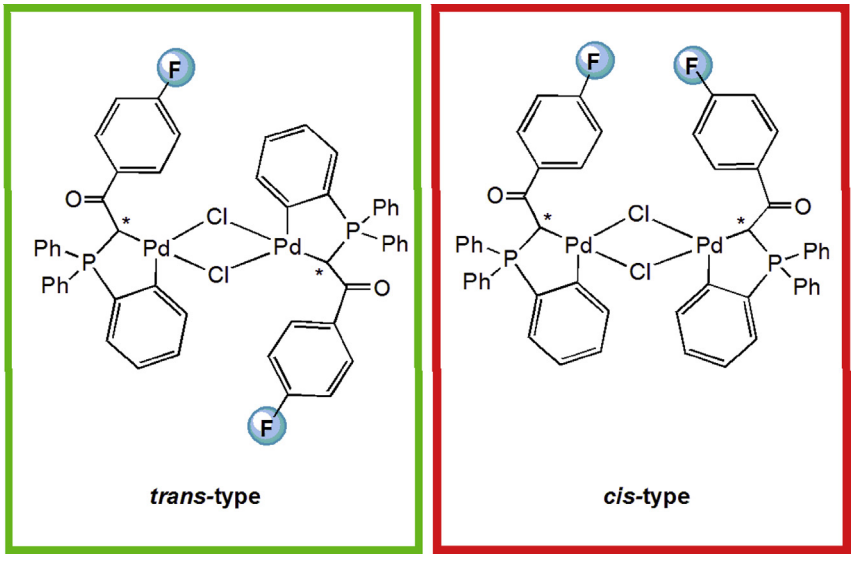
*[Pd{κ²(C,C)-[(C_6H_4-2)PPh_2]CH(CO)C_6H_4X-4}(μ-Cl)]₂, X = F (**1**), Br (**2**) and Ph (**3**)*

Method A: $Pd(OAc)_2$ (0.123 g, 0.5 mmol) was added to the solution of phosphorus ylide **Y1** (0.215 g, 0.5 mmol), phosphorus ylide **Y2** (0.248 g, 0.5 mmol) or phosphorus ylide **Y3** (0.116 g, 0.5 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was refluxed for 24 h. The solvent was then evaporated and the yellow solid residue was dissolved in MeOH (10 mL) and excess amount of anhydrous NaCl (0.111 g, 1.9 mmol) was added. The reaction mixture was stirred for 12 h at room temperature and the resulting suspension was filtered off. The yellow solid was washed with H_2O (5 mL), MeOH (10 mL) and Et_2O (15 mL) and dried to produce complexes **1**, **2** or **3**.

Method B: To the suspension of $PdCl_2$ (0.011 g, 0.1 mmol) in MeCN (15 mL), the phosphorus ylide **Y1** (0.049 g, 0.1 mmol), phosphorus ylide **Y2** (0.049 g, 0.1 mmol) or phosphorus ylide **Y3** (0.049 g, 0.1 mmol) was added and the mixture was refluxed for 12 h. After cooling, the suspension was filtered off and the solid was washed with Et_2O (10 mL) to give a yellow solid as the crude product. The residue was recrystallized with CH_2Cl_2 (5 mL) and *n*-hexane (30 mL), to precipitate the solid **1**, **2** or **3**.

1: Yield (87% – method **B**); M.p. 270–272 °C, Anal. Calc. for $C_{52}H_{38}Cl_2F_2O_2P_2Pd_2$: C, 57.91; H, 3.55; found. C, 57.85; H, 3.50; IR (KBr, cm^{-1}): ν (CO) = 1643; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 4.82 (s, CHP, minor), 4.91 (d, CHP, major, $^2J_{HP}$ = 2.7 Hz), 6.56 (t, 1H, H^6,C_6H_4, $^3J_{HH}$ = 7.9 Hz, major), 6.62 (t, 1H, H^6,C_6H_4, minor), 6.97, 7.03, 7.25, 7.39, 7.48, 7.59, 7.71, 7.91, 8.06, 8.15 (m, 3H–C_6H_4 + $2PPh_2$ + C_6H_4CO, both isomers); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, ppm): δ = 18.97 (major isomer), 19.42 (minor isomer).

2: Yield (97% – method **B**); M.p. 260–261 °C (258–260 °C [24]), Anal. Calc for $C_{52}H_{38}Cl_2Br_2O_2P_2Pd_2$: C, 52.03; H, 3.19; found. C,



Scheme 4. Cyclometallated complexes of phosphorus ylides with diphosphine ligands.

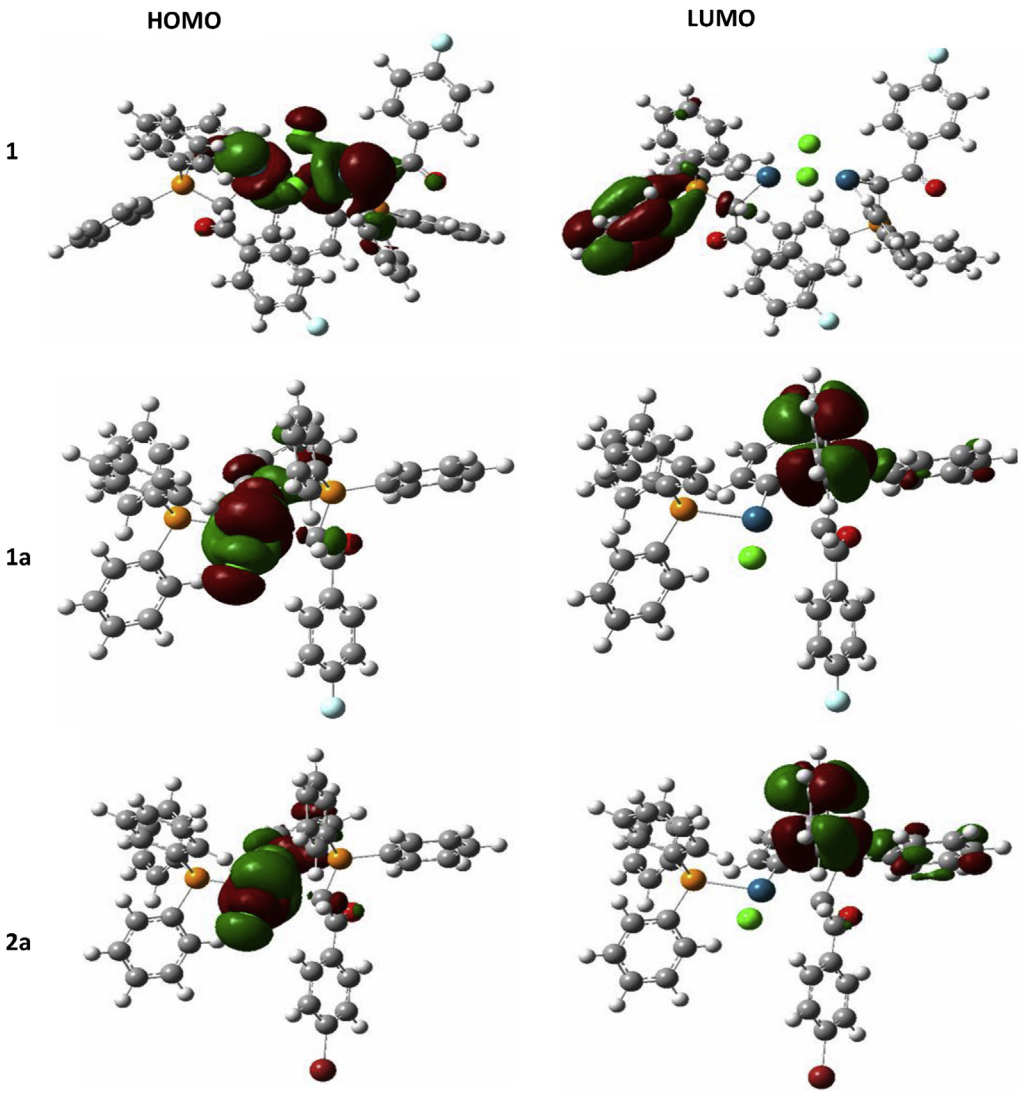


Fig. 5. The shapes of the HOMO and LUMO of **1**, **1a** and **2a**.

53.57; H, 3.40; IR, ^{1}H and ^{31}P{^{1}H} NMR spectra were identical to those reported previously [24].

3: Yield (82% – method **B**); M.p. 300–302 °C (298 °C [24]), Anal. Calc. for $C_{64}H_{48}Cl_2O_2P_2Pd_2$: C, 64.34; H, 4.05; found. C, 64.50; H, 4.11; IR, ^{1}H and ^{31}P{^{1}H} NMR spectra were identical to those reported previously [24].

*[PdCl{κ^2(C,C)-[(C$_6$H$_4$-2)PPh$_2$]CH(CO)C$_6$H$_4$X-4}(PPh$_3$)], X = F (**1a**) and Br (**2a**)*

To the suspension of 0.108 g (0.1 mmol) complex **1**, or 0.120 g (0.1 mmol) complex **2** in CH_2Cl_2 (10 mL), triphenylphosphine (PPh_3) (0.052 g, 0.2 mmol) was added. The initial yellow suspension gradually dissolved and after stirring for 30 min at room temperature (RT) the resulting solution was filtered over a Celite pad in order to remove any residual insoluble solids. The clear solution was evaporated. After the treatment of the residue with Et_2O, the yellow precipitate was formed and then air-dried to give **1a** or **2a**.

1a: Yield (79%); M.p. 146 °C, Anal. Calc for $C_{44}H_{34}ClFOP_2Pd$: C, 65.93; H, 4.28; found. C, 65.89; H, 4.20; IR (KBr, cm^{-1}): ν (CO) = 1618; ^{1}H NMR (500 MHz, $CDCl_3$, ppm); δ = 5.40 (s, 1H, CHP), 6.53 (s, 2H, C_6H_4), 6.90 (m, 1H, C_6H_4), 7.16–7.32 (m, 15H, PPh_3), 7.44–7.69 (m, 8H, H_m + H_o, PPh_2 and 1H, C_6H_4), 7.85 (m, 2H, H_p, PPh_2), 8.02 (m, 2H, C_6H_4CO), 8.30 (d, 2H, C_6H_4CO, $^{3}J_{HH}$ = 7.1 Hz); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, ppm): δ = 15.09 (s, 1P, CHP), 32.14 (s, 1P, Pd-PPh_3).

2a: Yield (58%); M.p. 203 °C, Anal. Calc for $C_{44}H_{34}ClBrOP_2Pd$: C, 61.28; H, 3.97; found. C, 61.35; H, 3.82; IR (KBr, cm^{-1}): ν (CO) = 1610; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 5.50 (br s, 1H, CHP), 6.52 (s, 2H, C_6H_4, $^{3}J_{HH}$ = 2.6 Hz), 6.90 (m, 1H, C_6H_4, $^{3}J_{HH}$ = 4.0 Hz), 7.02 (t, 2H, H_p, PPh_2, $^{3}J_{HH}$ = 8.7 Hz), 7.15–7.18 (m, 6H, H_m, PPh_3), 7.28–7.32 (m, 9H, H_o + H_p, PPh_3), 7.43–7.47 (m, 2H, H_m, PPh_2), 7.55–7.61 (m, 4H, H_o + H_m,PPh_2), 7.67 (m, 1H, C_6H_4), 7.85 (m, 2H, H_o, PPh_2), 8.03 (m, 2H, C_6H_4CO), 8.47 (m, 2H, C_6H_4CO); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, ppm): δ = 15.03(s, 1P, CHP), 31.98 (s, 1P, Pd-PPh_3).

*[PdCl{κ^2(C,C)-[(C$_6$H$_4$-2)PPh$_2$]CH(CO)C$_6$H$_4$X-4}(3-MePy)], X = F (**1b**) and Br (**2b**)*

To the solution of 0.108 g (0.1 mmol) complex **1** or 0.120 g (0.1 mmol) complex **2** in CH_2Cl_2 (10 mL), 3-methylpyridine (3-MePy) (19 μL, 0.2 mmol) was added, and the resulting yellow solution was stirred for 30 min at room temperature (RT). The solvent was evaporated and the residue was treated with cold *n*-hexane (15 mL) to give **1b** or **2b** as the yellow solid.

Table 3
Comparative catalyst efficiency in Suzuki cross-coupling reaction.[a]

Entry	Catalyst	mol% Pd	Conversion (%)
1	**1**	0.05	Trace
2	**1**	0.1	Trace
3	**1**	0.35	10
4	**1**	0.7	18
5	**1**	1	40
6	**1a**	0.05	91
7	**1a**	0.1	96
8	**1a**	0.35	100
9	**1a**	0.7	100
10	**1a**	1	100
11	**2a**	0.05	20
12	**2a**	0.1	32
13	**2a**	0.35	30
14	**2a**	0.7	57
15	**2a**	1	78

[a] Reaction conditions: bromobenzene (0.5 mmol), phenyl boronic acid (0.75 mmol), Na_2CO_3 (1.5 mmol), MeOH (6 mL), 75 °C, 1 h.

1b: Yield (92%); M.p. 189 °C, Anal. Calc for $C_{32}H_{26}NClFOPPd$: C, 60.78; H, 4.14; N, 2.21; found. C, 60.06; H, 3.98; N, 2.21; IR (KBr, cm^{-1}): ν (CO) = 1627; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.94 (s, 3H, 3-MePy, isomer A), 2.25 (s, 3H, 3-MePy, isomer B), 4.99 (s, 1H, CHP, isomer A), 5.09 (d, 1H, CHP, $^2J_{HP}$ = 4.1 Hz, isomer B), 6.51 (d, 1H, H^6, C_6H_4, $^3J_{HH}$ = 7.0 Hz, isomer A), 6.70 (m, 1H, H^5, C_6H_4, isomer A), 6.86 (m, 1H, H^5, isomer B), 7.00 (d, 1H, H^6, C_6H_4, $^3J_{HH}$ = 7.0 Hz, isomer B), 7.06 (m, 4H, $H^3 + H^4$, C_6H_4, both isomers), 7.40, 7.49, 7.57, 7.64, 8.21, 8.37 (m, 3-MePy + $2PPh_2$ + C_6H_4CO, both isomers); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, ppm): δ = 15.75 (s, 1P, CHP, isomer A), 20.30 (s, 1P, CHP, isomer B).

2b: Yield (63%); M.p. 152 °C, Anal. Calc for $C_{32}H_{26}NClBrOPPd$: C, 55.44; H, 3.78; N, 2.02; found. C, 55.58; H, 3.63; N, 1.98; IR (KBr, cm^{-1}): ν (CO) = 1625; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.95 (s, 3H, 3-MePy, isomer A), 2.24 (s, 3H, 3-MePy, isomer B), 4.96 (br s, 1H, CHP, isomer A), 5.08 (d, 1H, CHP, $^2J_{HP}$ = 4.0 Hz, isomer B), 6.49 (d, 1H, H^6, C_6H_4, $^3J_{HH}$ = 7.6 Hz, isomer A), 6.73 (dd, 1H, H^5, C_6H_4, $^3J_{HH}$ = 5.8 Hz, isomer A), 6.94 (dd, 1H, H^5, C_6H_4, $^3J_{HH}$ = 6.0 Hz, isomer B), 7.02 (t, 1H, H^3, C_6H_4, isomer A), 7.09 (m, 2H, $H^3 + H^4$, isomer B), 7.14 (d, 1H, H^6, isomer B), 7.32, 7.47, 7.52, 7.58, 7.65, 7.82, 8.19, 8.31, 8.35 (m, 3-MePy + $2PPh_2$ + C_6H_4CO, both isomers); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, ppm): δ = 16.03 (s, 1P, CHP, isomer A), 20.49 (s, 1P, CHP, isomer B).

[PdCl{κ²(C,C)-[(C_6H_4-2)PPh_2]CH(CO)C_6H_4F-4}(Me_3Py)], ***1c***

To the solution of 0.108 g (0.1 mmol) complex **1** in CH_2Cl_2 (10 mL), 2,4,6-trimethylpyridine (Me_3Py) (27 μL, 0.2 mmol) was added and the solution was stirred for 30 min at room temperature (RT). After 1 h, the solvent was evaporated and the residue was treated with cold *n*-hexane (15 mL) to give **1c** as the yellow solid.

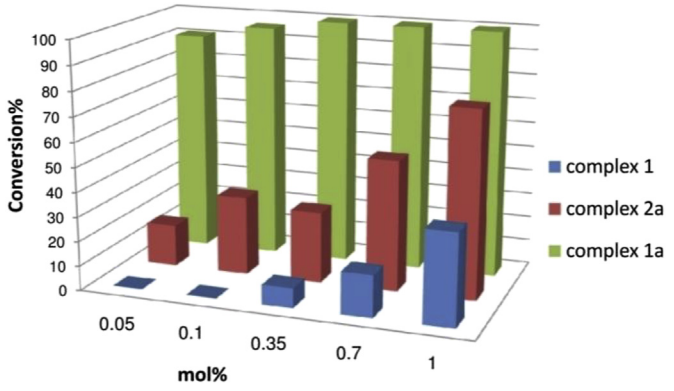
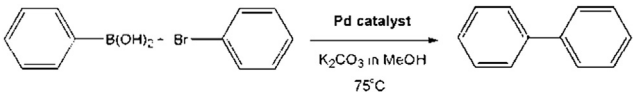


Fig. 6. Effects of catalyst amount on the Suzuki cross-coupling reaction. Reaction condition: bromobenzene (0.5 mmol), phenyl boronic acid (0.75 mmol), Na_2CO_3 (1.5 mmol), MeOH (6 mL), 75 °C, 1 h.

Table 4
Reaction condition in Suzuki cross-coupling of bromobenzene with phenyl boronic acid.[a]



Entry	Base	Solvent	Time (min.)	Yield (%)
1	NaOAc	MeOH	60	Trace
2	Et_3N	MeOH	60	51
3	Cs_2CO_3	MeOH	60	97
4	Na_2CO_3	MeOH	60	96
5	K_2CO_3	MeOH	60	100
6	K_2CO_3	THF	60	Trace
7	K_2CO_3	Toluene	60	Trace
8	K_2CO_3	DMF	60	46
9	K_2CO_3	MeCN	60	73
10	K_2CO_3	MeOH	30	100
11	K_2CO_3	MeOH	25	100
12	K_2CO_3	MeOH	20	100
13	K_2CO_3	MeOH	15	100
14	K_2CO_3	MeOH	10	96

[a] Reaction conditions: bromobenzene (0.5 mmol), phenyl boronic acid (0.75 mmol), base (1.5 mmol), complex **1a**, (0.1 mol%), solvent (6 mL), 75 °C.

Yield (69%), M.p. 210 °C, Anal. Calc for $C_{34}H_{30}NClFOPPd$: C, 61.83; H, 4.58; N, 2.12; found. C, 61.75; H, 4.48; N, 2.10; IR (KBr, cm^{-1}); ν (CO) = 1621; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 2.03 (s, 3H, Me), 2.23 (s, 3H, Me), 2.88 (s, 3H, Me), 5.14 (d, 1H, CHP, $^2J_{HP}$ = 4.9 Hz), 6.16 (d, 1H, H^6, C_6H_4, $^3J_{HH}$ = 7.0 Hz), 6.69 (s, 1H, C_6H_4), 6.91 (m, 2H, C_6H_4), 7.08 (t, 2H, H_p, PPh_2, $^3J_{HH}$ = 8.6 Hz), 7.10 (s, 1H, Me_3Py), 7.40 (s, 1H, Me_3Py), 7.48 (t, 1H, C_6H_4CO), 7.63 (t, 2H, H_m, PPh_2, $^3J_{HH}$ = 7.2 Hz), 7.86 (m, 3H, C_6H_4CO), 8.22 (dd, 2H, H_o, PPh_2, $^3J_{HH}$ = 6.0 Hz), 8.51 (dd, 2H, H_o, PPh_2, $^3J_{HH}$ = 5.8 Hz); $^{13}C\{^1H\}$ NMR (125.5 MHz, $CDCl_3$, ppm): δ = 21.14, 26.58, 27.19 (s, 3Me, Me_3Py), 35.00 (d, CHP, $^1J_{CP}$ = 59.5 Hz), 124.40 (d, C^2, C_6H_4, $^4J_{CP}$ = 13.2 Hz), 124.90 (s, C^1, C_6H_4), 129.63 (d, C_{ipso}, PPh_2, $^1J_{CP}$ = 68.0 Hz), 130.4 (d, C^4, C_6H_4, $^2J_{CP}$ = 13.2 Hz), 133.78 (d, C_m, PPh_2, $^3J_{CP}$ = 9.1 Hz), 134.96 (d, C_m, PPh_2, $^3J_{CP}$ = 9.1 Hz); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, ppm): δ = 18.95 (s, 1P, CHP).

[PdCl{κ²(C,C)-[(C_6H_4-2)PPh_2]CH(CO)C_6H_4Br-4}(4-MePy)], ***2c***

To the solution of 0.120 g (0.1 mmol) complex **2** in CH_2Cl_2 (10 mL), 4-methylpyridine (4-MePy) (19 μL, 0.2 mmol) was added, and the resulting yellow solution was stirred for 30 min at room temperature (RT). After that, the solvent was evaporated and the residue was treated with cold *n*-hexane (15 mL) to give **2c** as the yellow solid.

Yield (73%), M.p. 160 °C, Anal. Calc for $C_{32}H_{26}NClBrOPPd$: C, 55.44; H, 3.78; N, 2.02. Found. C, 55.42; H, 3.80; N, 1.98; IR (KBr, cm^{-1}); ν (CO) = 1620; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 2.13 (s, 3H, 4-Mepy, isomer A), 2.32 (s, 3H, 4-Mepy, isomer B), 4.97 (s, 1H, CHP, isomer A), 5.08 (d, 1H, CHP, $^2J_{HP}$ = 4.0 Hz, isomer B), 6.54 (d, 1H, H^6, C_6H_4, $^3J_{HP}$ = 7.2 Hz, isomer A), 6.56 (d, 1H, H^5, C_6H_4, $^3J_{HH}$ = 6.0 Hz, isomer A), 6.93 (dd, 1H, H^6, C_6H_4, $^3J_{HH}$ = 6.0 Hz, isomer B), 7.01 (m, 4H, C_6H_4, both isomers), 7.15 (m, 2H, $H^3 + H^4$, isomer B), 7.32–7.82 (m, 28H, PPh_2 + 4-MePy, both isomers), 8.19–8.35 (m, 8H, C_6H_4CO, both isomers); $^{13}C\{^1H\}$ NMR (125.5 MHz, $CDCl_3$, ppm): δ = 21.19 (s, Me, isomer A), 21.51 (s, Me, isomer B), 34.20 (d, CHP, $^1J_{CP}$ = 58.5 Hz), 124.75 (s, C^2, both isomers), 125.61 (s, C^1, C_6H_4, isomer A), 125.96 (s, C^1, C_6H_4, isomer B), 127.51 (s, C_{ipso}, PPh_2, isomer A), 128.98 (s, C_{ipso}, PPh_2, isomer B), 129.18 (s, C_m, PPh_2, isomer A), 129.26 (s, C_m, PPh_2, isomer B), 129.59 (s, C_6,

C_6H_4, both isomers), 129.77 (s, C_4, C_6H_4, both isomers), 129.85 (s, C_m, C_6H_4CO, isomer A), 129.94 (s, C_m, C_6H_4CO, isomer B), 130.22 (s, C^3, C_6H_4, both isomers), 130.75 (s, C_p, PPh_2, both isomers), 131.48 (s, C_o, C_6H_4CO, isomer B), 131.54 (s, C_o, C_6H_4CO, isomer A), 133.03 (s, C_p, C_6H_4CO, isomer A), 133.11 (s, C_p, C_6H_4CO, isomer A), 133.49 (s, C_o, PPh_2, isomer B), 133.57 (s, C_o, PPh_2, isomer A), 136.40 (s, C^1, C_6H_4, isomer A), 136.48 (s, C^1, C_6H_4, isomer B), 149.71 (s, C_o, 4-MePy, both isomers), 150.51 (s, C_p, 4-MePy, both isomers), 152.41 (s, C_m, 4-MePy, both isomers); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, ppm): δ = 15.89.03 (s, 1P, CHP, isomer A), 20.35 (s, 1P, CHP, isomer B).

[PdCl{κ²(C,C)-[(C₆H₄-2)PPh₂]CH(CO)C₆H₄F-4}(Py)], ***1d***

To the solution of 0.108 g (0.1 mmol) complex **1** in CH_2Cl_2 (10 mL), pyridine (Py) (16 μL, 0.2 mmol) was added and the solution was stirred for 30 min at room temperature (RT). After 1 h, the solvent was evaporated and the residue was treated with cold *n*-hexane (15 mL) to give **1d** as the yellow solid.

Yield (78%), M.p. 189 °C, Anal. Calc for $C_{31}H_{24}NClFOPPd$: C, 60.21; H, 3.91; N, 2.27. Found. C, 60.37; H, 3.86; N, 2.25; IR (KBr, cm^{-1}); ν (CO) = 1625, ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 5.02 (s, 1H, CHP, isomer A), 5.11 (d, 1H, CHP, $^2J_{HP}$ = 4.1 Hz, isomer B), 6.51 (d, 1H, H^6, C_6H_4, $^3J_{HP}$ = 7.0 Hz, isomer A), 6.81–6.87 (m, 4H, $H^4 + H^5$, C_6H_4, both isomers), 6.93 (m, 1H, H_p, py, isomer A), 7.01 (m, 1H, H_p, py, isomer B), 7.04 (m, 1H, H^6, C_6H_4, isomer B), 7.06 (m, 2H, H^3, both isomers), 7.16 (m, 2H, H_m, py, isomer A), 7.22 (m, 2H, H_m, Py, isomer B), 7.32 (m, 2H, H_o, py, isomer A), 7.40 (m, 2H, H_o, py, isomer B), 7.47–7.82 (20H, PPh_2, both isomers), 8.20 (m, 2H, C_6H_4CO, isomer A), 8.30–8.37 (m, 2H, C_6H_4CO, isomer B), 8.47 (m, 2H, C_6H_4CO, isomer A), 8.52 (m, 2H, C_6H_4CO, isomer B); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, ppm): δ = 15.86 (s, 1P, CHP, isomer A), 20.38(s, 1P, CHP, isomer B).

[PdCl{κ²(C,C)-[(C₆H₄-2)PPh₂]CH(CO)C₆H₄F-4}(PiPe)], ***1e***

To the solution of 0.108 g (0.1 mmol) complex **1** in CH_2Cl_2 (10 mL), piperidine (PiPe) (20 μL, 0.2 mmol) was added and the solution was stirred for 30 min at room temperature (RT). After 1 h, the solvent was evaporated and the residue was treated with cold *n*-hexane (15 mL) to give **1e** as the green solid.

Yield (84%), M.p. 189 °C, Anal. Calc for $C_{31}H_{30}NClFOPPd$: C, 59.63; H, 4.84; N, 2.24. Found. C, 59.59; H, 4.80; N, 2.25; IR (KBr, cm^{-1}); ν (CO) = 1620, ν (NH) = 3411; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.24–3.12 (m, 11H, PiPe, both isomers), 4.85 (s, 1H, CHP, isomer A), 4.96 (d, 1H, CHP, $^2J_{HP}$ = 4.4 Hz, isomer B), 6.82 (t, $H^3 + H^6$, C_6H_4, isomer A), 7.03 (t, 2H, $H^4 + H^5$, C_6H_4, $^3J_{HH}$ = 9.2 Hz, isomer B), 7.15 (t, 2H, $H^4 + H^5$, $^3J_{HH}$ = 9.2 Hz, isomer A), 7.21 (m, 2H, $H^3 + H^6$, C_6H_4, isomer B), 7.35–7.78 (10H, PPh_2, both isomers), 8.08 (dd, 2H, C_6H_4CO, isomer B), 8.15–8.28 (m, 4H, C_6H_4CO, isomer A), 8.44 (dd, 2H, C_6H_4CO, isomer B); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, ppm): δ = 13.86 (s, 1P, CHP, isomer A), 17.59 (s, 1P, CHP, isomer B).

[Pd₂Cl₂{κ²(C,C)-[(C₆H₄-2)PPh₂]CH(CO)C₆H₄Ph-4}₂(dppe)], ***3a***

To the solution of 0.124 g (0.1 mmol) complex **3** in $CHCl_3$ (10 mL), bis(diphenylphosphino)ethane (dppe) (0.040 g, 0.1 mmol) was added, and the resulting solution was stirred for 3 h at room temperature (RT). After that, the solvent was evaporated and the residue was treated with 15 mL CH_2Cl_2/*n*-hexane (1:3) to give **3a** as the yellow solid.

Yield (85%), M.p. 178 °C (dec.), IR (KBr, cm^{-1}); ν (CO) = 1621,^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.94–2.83 (m, CH_2 (dppe)), 5.00, 5.60 (m, CHP, meso-rac), 6.17, 6.46, 6.83, 7.19, 7.34, 7.45, 7.57, 7.61, 7.66, 7.73, 7.89, 7.92, 8.02, 8.04, 8.14, 8.59 (m, C_6H_4, C_6H_4CO, PPh_2, meso-rac); $^{31}P\{^1H\}$ NMR (161.97 MHz, $CDCl_3$, ppm): δ = 12.34, 17.89, 24.09, 30.60, 32.04, 43.43, 52.48, 63.84 (dppe and CHP, meso-rac isomers).

[Pd₂Cl₂{κ²(C,C)-[(C₆H₄-2)PPh₂]CH(CO)C₆H₄Ph-4}₂(dppp)], ***3b***

To the solution of 0.124 g (0.1 mmol) complex **3** in $CHCl_3$ (10 mL), bis(diphenylphosphino)propane (dppp) (0.041 g, 0.1 mmol) was added, and the resulting solution was stirred for 3 h at room temperature (RT). After that, the solvent was evaporated and the residue was treated with 15 mL CH_2Cl_2/*n*-hexane (1:3) to give **3b** as the yellow solid.

Yield (82%), M.p. 164 °C (dec.), IR (KBr, cm^{-1}); ν (CO) = 1621,^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.00–2.70 (m, CH_2 (dppp)), 4.54, 5.41 (m, CHP, meso-rac), 6.57, 6.91, 7.06, 7.20, 7.37, 7.45, 7.53, 7.63, 7.82, 7.92, 8.52 (m, C_6H_4, C_6H_4CO, PPh_2, meso-rac); $^{31}P\{^1H\}$ NMR (161.97 MHz, $CDCl_3$, ppm): δ = −2.76, −2.55, 11.22, 13.66, 24.09, 24.33, 25.02, 25.22 (dppp and CHP, meso-rac isomers).

DFT calculations

All of the theoretical calculations were performed using the Gaussian 09 computational package [42].

X-ray structure determinations

The data collection was performed at room temperature using the X-scan technique and the STOE X-AREA software package [46]. The crystal structures were solved by direct methods and refined by full-matrix least-squares on F^2 by SHELXL97 [47] and using the ORTEP-3 crystallographic software package [48]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2r$ (I). Hydrogen atoms were inserted at calculated positions using a riding model with fixed thermal parameters.

General experimental procedure for the Suzuki cross-coupling reaction

Typical experimental procedure was carried out for the Suzuki cross-coupling reaction under air atmosphere. A reaction tube was charged with Pd catalyst (0.1 mol%), aryl bromide (0.5 mmol), aryl boronic acid (0.75 mmol), Solvent (6 mL), bases (1.5 mmol). The mixture was refluxed for 1 h (75 °C). Then the mixture was filtered with silica gel and used for TLC. After the reaction was completed, if the reaction's conversion wasn't completed we used GC. The solvent was evaporated under reduced pressure to provide a white solid; the pure product was prepared via dissolving the white solid and again precipitating with dichloromethane and *n*-hexane and dried under reduced pressure.

Conclusion

In this work, the synthesis and characterization of cyclopalladated complexes of phosphorus ylides containing nitrogen, phosphorus or bridging diphosphine ligands have been investigated. The presence of intermolecular interactions in some new complexes which were structurally determined, lead to supramolecular structures. Overall, these organopalladated (II) complexes have considerable potential as building blocks through their polymer, sheet or network supramolecular structures.

According to the theoretical calculations for the synthesized complexes **1**, **1a** and **2a**, there are very good agreements between the calculated bond lengths and angles and those obtained from the experiment. The vibrational frequencies obtained theoretically for the stretching of C=O bond for each three synthesized complexes, are very close to the experimental value reported in this work. Theoretical data for structure **1** fully confirmed the more stability of the trans isomer.

The binuclear chloro-bridged cyclopalladated complex of phosphorus ylide (**1**) and two mononuclear phosphine palladium

(II) complexes (**1a** and **2a**) were comparatively evaluated as the homogenous catalysts in the Suzuki cross-coupling of phenyl boronic acid with bromobenzene which revealed the higher catalytic performance of complex **1a** with the fluoro substituent.

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Appendix A. Supplementary material

CCDC 749573, 693528 and 693527 contains 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 data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.01.003.

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