

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



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ABSTRACT

Binuclear orthopalladated complexes of phosphorus ylides containing electron-withdrawing fluoro (**Y1**), bromo (**Y2**) or phenyl (**Y3**) substituent, $[\text{Pd}\{\kappa^2(\text{C},\text{C})-[(\text{C}_6\text{H}_4-2)\text{PPh}_2]\text{CH}(\text{CO})\text{C}_6\text{H}_4\text{X}-4\}(\mu\text{-Cl})_2]$ (X = F (**1**), Br (**2**), Ph (**3**)) were obtained by two different methods from the reaction of corresponding ylides and PdCl_2 or $\text{Pd}(\text{OAc})_2$. The synthesized orthopalladated complexes **1** and **2** reacted with the monodentate ligands with various donor abilities affording the mononuclear complexes $[\text{PdCl}\{\text{C},\text{C}-\{\text{CH}[\text{P}(\text{C}_6\text{H}_4-2)\text{Ph}_2]\text{C}(\text{O})\text{C}_6\text{H}_4\text{X}-4\}\}\text{L}]$ [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 $[\text{Pd}_2\text{Cl}_2\{\text{C},\text{C}-\{\text{CH}[\text{P}(\text{C}_6\text{H}_4-2)\text{Ph}_2]\text{C}(\text{O})\text{C}_6\text{H}_4\text{X}-4\}\}_2](\mu\text{-P}^*\text{P}^*)]$ (P*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.

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Introduction

Cyclopalladated complexes has attracted considerable attention due to their potential applications in organic synthesis, homogeneous 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 $\text{Ph}_3\text{PCH}(\text{CO})\text{C}_6\text{H}_5$, can be

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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

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

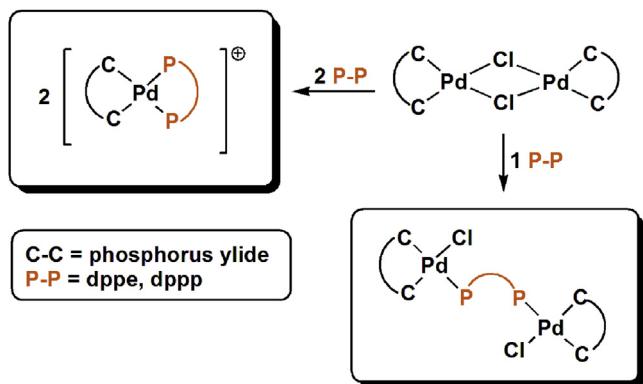
Each FT-IR spectra of ylides show the strong peak at 1505 – 1512 cm^{-1} due to the carbonyl stretching vibrations. This band appears at the lower energies comparing with the phosphonium salts, due to the charge delocalization present in such compounds. The C-coordination of the ylides leads to the increase 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 1. The reaction of cyclometallated complexes of phosphorus ylides with diphosphine ligands.

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