

## New dimeric phosphine ylide copper (I) complexes: Synthesis, coordination behavior, and application in Suzuki cross-coupling reactions

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### ABSTRACT

The reaction of the non-symmetric phosphorus ylides,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{PhR}$  with  $\text{CuCl}$  in equimolar ratios using dry methanol as solvent give binuclear complexes of the type  $[\text{Cu}(\mu\text{-Cl})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{PhR}\}]_2$  ( $n = 1$ :  $\text{R} = \text{Br}$  (**1**),  $\text{OCH}_3$  (**2**);  $n = 2$ :  $\text{R} = \text{Br}$  (**3**),  $\text{OCH}_3$  (**4**)). X-ray analyses of **1** demonstrate the Cl bridged dimeric structures with P,C-chelated ligands. Characterizations of these compounds were carried out by FT-IR and multinuclear NMR technique. Elemental analysis indicate a 1:1 stoichiometry between the ylides and the Cu(I) chloride in the four complexes. The precursor complexes **1** and **3** are found to exhibit high catalytic activity in the Cu-catalyzed Suzuki cross-coupling reactions in an air atmosphere at medium catalyst loading in DMF as a solvent. The use of 5 mol% catalyst in the presence of  $\text{Cs}_2\text{CO}_3$  allows the coupling reaction to proceed with moderate to excellent yields.

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Phosphorus ylides are a group of very interesting ligands in organo-metallic chemistry; these compounds are also useful intermediates in organic synthesis and have been used as reducing agents in coordination chemistry [1–4]. The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [5–7]. The  $\alpha$ -ketostabilized ylides derived from bisphosphines, viz.,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2 = \text{C}(\text{H})\text{C}(\text{O})\text{R}$  and  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 = \text{C}(\text{H})\text{C}(\text{O})\text{R}$  ( $\text{R} = \text{Me}$ ,  $\text{Ph}$  or  $\text{OMe}$ ) [8], constitute an important class of hybrid ligands containing both phosphine and ylide functionalities and can exist in ylidic and enolate forms. These ligands can therefore engage in different kinds of bonding with metal ions [8–19]. P,C-coordination mode of stabilized phosphorus ylides have been previously observed for Pd(II), Pt(II), Rh(I), Hg(II) species [8–18]. In 1975, Yamamoto et al. [20] reported Cu(I) complexes of phosphorus ylides of the type  $(\text{C}_6\text{H}_5)_3\text{PCHR}$  ( $\text{R} = \text{H}$ ,  $\text{CH}_3$ ,  $\text{CH}(\text{CH}_3)_2$ ). The use of copper complexes in the Suzuki coupling has been studied in recent years. Suzuki cross-coupling reactions have proven to be important transformations, as the resulting biaryl products are extremely valuable intermediates in organic synthesis, natural products, and biological molecules [21–27]. The general Suzuki coupling procedures involves the use of palladium phosphine complexes as catalysts [21–23]. Nevertheless, the high price of Pd renders commercial processes based on Pd less attractive unless extremely active and/or recyclable catalysts are available. For these reasons, much recent attention has been attracted on employing less expensive transition metal catalyst complexes, [23–33] in particular, copper, to replace the palladium. However, only a few copper-catalyzed Suzuki cross-coupling procedures exist [21–23,28,29,34,35]. Phosphorus

ylides as a particular ligand has been specially used in C–C coupling reactions. Our previous research showed that symmetrical and non-symmetrical phosphorus ylides are versatile ligands and their palladium complexes are quite efficient cross-coupling catalysts [36–39]. Excellent activities observed with Pd (II) complexes of phosphine ylide ligands encouraged us to explore the chemistry of copper compounds. In the first, we have now focused our attention in the study of the coordination modes adopted by the resonance stabilized ylides when ligated to Cu(I). Second, we have worked on catalytic activity of the new copper (I) phosphine mono-ylide Complexes **1** and **3** in Suzuki cross-coupling reactions.

Reaction of the ligands with  $\text{CuCl}$  in methanol (1:1) yielded the binuclear complexes [40]. The X-ray structure of complex **1** demonstrates the five-membered chelate ring in which the ligands were chelated to the metals through the free phosphine group and the ylidic carbon atom. The  $^{31}\text{P}$  NMR spectra of complexes **1** and **2** show two doublets that indicate the presence of the PCH and  $\text{PPh}_2$  groups in these molecules (see Supplementary material). The significant downfield shift of the signals due to PCH groups indicates C-coordination of the ligand to Cu center [15]. The strong downfield shifting and broadening of doublets of  $\text{PPh}_2$  groups due to rapid equilibrium with non-coordinated forms is other clear evidence for P-coordinating of the ligands [15]. The identical pattern in chemical shift values in the  $^{31}\text{P}$  NMR spectra of complexes **3** and **4** suggest similar structures with complexes **1** and **2**. The P, C-chelation of ligands has been previously observed for mercury halide and palladium complexes [41–43]. The downfield shift and broadening of the doublet signal was observed due to methinic (PCH) group in the  $^1\text{H}$  NMR spectra of complexes **1** and **2** [41]. Similar behavior was observed earlier in the case of ylide complexes of platinum(II) chloride

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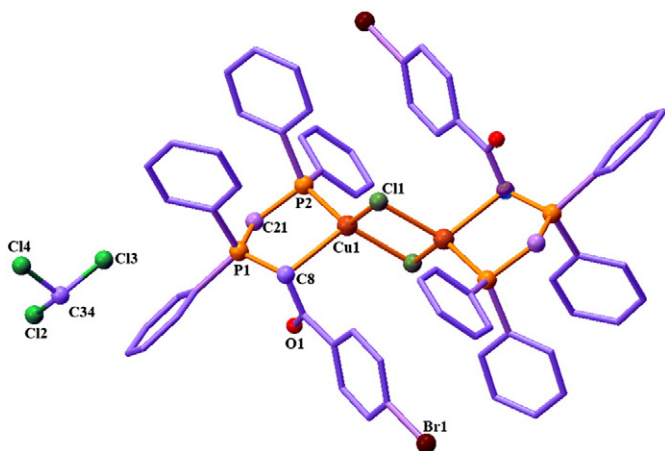


Fig. 1. X-ray crystal structure of **1**. Hydrogen atoms are omitted for clarity.

[44]. In the case of complexes **3** and **4**, these signals are weak and broad due to low solubility in common solvents. The up-field shift of the signals due to ylidic carbons in the  $^{13}\text{C}$  NMR spectra of complexes **1** and **2** also are an evidence for C-coordination [45,46]. The  $^{13}\text{C}$  NMR shift of the CO signal (180 to 187 ppm) with reference to the parent ylides indicates a much lower shielding of the carbon of the CO group in these complexes. Neither H-Cu nor P-Cu coupling was observed at room temperature in the spectra; possibly a fast equilibrium between the complexes and the free ylides is responsible for the failure to observe NMR coupling or two diastereoisomers. The  $\nu_{\text{CO}}$  for ylides are observed in lower frequencies than those of the related phosphonium salts as in the case of other resonance stabilized ylides [47], suggesting some removal of electron density in the C = O bond. As noted previously [48–50], the coordination of the ylide through carbon or oxygen causes a significant increase or decrease, respectively, in the  $\nu_{\text{CO}}$  frequency. The infrared absorption bands observed for these complexes around  $1540\text{ cm}^{-1}$  indicate coordination of the ylide through ylidic carbon atom [15].

The crystals of complex **1** were grown by the slow evaporation of the chloroform solution. An ORTEP diagram of the complex with atomic numbering scheme is shown in Fig. 1. Relevant parameters concerning data collection and refinement are given in supplementary material and selected bond distances, and angles are collected in Table S1 and Table S2, respectively.

The complex consists of centrosymmetrical dimeric units with the two chlorine atoms bridging the two copper atoms. The tetrahedral coordination of the copper atoms is achieved by P,C-chelating the ylide.

Two ylidic ligands are, respectively, located on the opposite sides to minimize the repulsion between them. The angles subtended by the ligand at the Cu(I) center in **1** vary from 93.48 to 126.11, indicating a distorted tetrahedral environment. The Cu–P bond lengths ( $\sim 2.19\text{ \AA}$ ) are in the usual range for Cu(I) complexes. The Cu  $\cdots$  Cu distance of  $3.115\text{ \AA}$  (**1**) is longer than two van der Waals radii for copper ( $2.8\text{ \AA}$ ) [51], indicating the absence of significant bonding interactions between the Cu atoms in the molecular structures (see Fig. 2). The non-classical C–H $\cdots$ Cl and C = O $\cdots$ H–C hydrogen bonds determine the structural assembly in this compounds and are shown in supplementary material (Fig. S1).

It is well established that palladium complexes containing phosphine ligands, which combines both good donor strength and  $\pi$ -accepting capacity, always have a high catalytic activity in Suzuki cross-coupling reactions [52–55]. The copper-catalyzed Suzuki cross-coupling reaction has received a lot of attention in the past few years and has already been reviewed [28,34,56–60]. Based on these prior examples, our group began a study of using phosphine mono-ylide copper (I) complexes **1** and **3** for Suzuki cross-coupling reactions in the first time. These copper complexes are soluble in a variety of organic solvents that have been shown to be effective as additives in the modern copper-catalyzed cross-coupling reactions. These reactions are general, tolerate a variety of functional groups and substrates, avoid the use of expensive and/or air-sensitive additives and overcome some of the limitations of the palladium-catalyzed analogues. The model reaction of iodobenzene with phenylboronic acid achieved maximum yields when  $\text{Cs}_2\text{CO}_3$  was used as a base, DMF as a solvent, and the reaction occurred at  $130\text{ }^\circ\text{C}$  under aerobic conditions (see Ref. [36,37,39]).

Catalyst loading tests were performed to determine the catalytic efficiency of the catalyst in the presence of DMF and  $\text{Cs}_2\text{CO}_3$ . In order to optimize the reaction condition for the coupling reactions, different amounts of catalyst (mol%) were taken and the results are summarized in Table S3 (see supplementary material). Various catalyst concentrations were also tested and 5 mol% gave the best result. These are the indications of an effective catalytic system that merits more downstream explorations.

In the first, the four copper(I) complexes has been observed to catalyze the targeted coupling reactions, but because of their similar structural and catalytic efficiency, we have investigated the catalytic activity of complex **1** and **3** in this work. These Cu(I) complexes were used for the first time in Suzuki cross-coupling reactions.

Under above conditions (base:  $\text{Cs}_2\text{CO}_3$ ; solvent: DMF; temperature:  $130\text{ }^\circ\text{C}$ ), we examined the scope of the reaction of phenylboronic acid with various aryl halides bearing electron-donating and electron-withdrawing groups in the presence of 5 mol% of catalyst **1** and the results are shown in Table 1. A number of aryl iodides, bromides, and

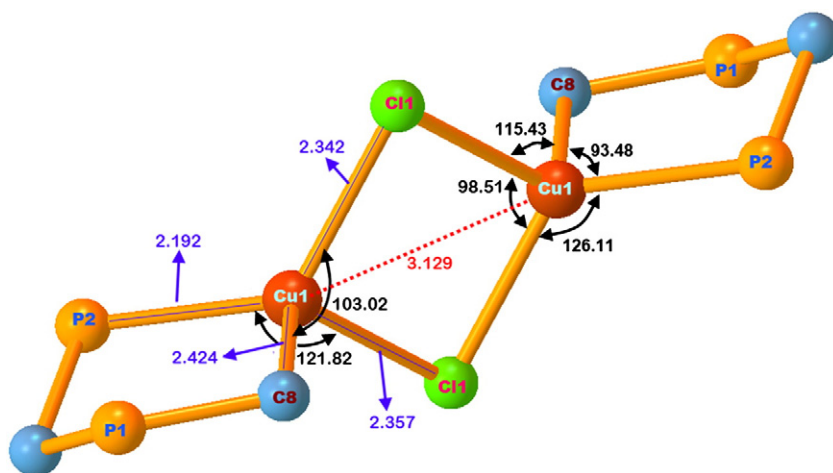


Fig. 2. Selected bond lengths and bond angles for **1**.

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