

Imidazolio-substituted secondary phosphine oxides as potential carbene reagents



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ABSTRACT

New pre-ligands of 1-aryl-1*H*-imidazol-2-yl substituted secondary phosphine oxides (HRP(=O)-Im:SPO-Im) were prepared and characterized by spectroscopic means. The SPO-Im pre-ligands are able to tautomerize to their corresponding genuine ligands, the 1-aryl-1*H*-imidazol-2-yl substituted phosphinous acids ((HO)RP-Im:PA-Im) while the condition permitted. Further reactions of selected SPO-Im pre-ligands toward Pd(COD)Cl₂ or PdBr yielded *bis*-(PA-Im)-coordinated *cis*-palladium dichloride or dibromide complexes, respectively. These *cis*-palladium dihalide complexes are all having an intramolecular hydrogen bond between two coordinated PA-Im ligands (R(Im(H)⁺)P-O⁻...HO-PRIm) by transferring a proton from one of the two P-OH groups to its free nitrogen site of imidazolyl substituents; and, therefore, imposes the formation of zwitterionic *cis*-form palladium complexes. Three crystal structures of these square-planar zwitterionic palladium complexes were determined by the X-ray diffraction methods. Additionally, two novel NHC carbene coordinated palladium complexes were obtained from the crystal-growing process of the above-mentioned zwitterionic *cis*-palladium dihalide complexes. The crystal structures of two NHC carbene coordinated palladium complexes were also successfully determined. Density-functional theory (DFT) calculations were carried out to substantiate the feasibility of the proposed reaction pathways for the formation of NHC carbene coordinated palladium complexes. Finally, applying selected SPO-Im pre-ligands to Heck reactions with pre-optimized reaction conditions exhibited satisfactory performances.

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1. Introduction

Various types and functions of organophosphines have probably been the most employed ligands in transition-metal complexes catalyzed reactions, particularly in cross-coupling reactions [1]. Nevertheless, these tri-substituted organophosphine ligands often create practical problems of being sensitive towards air and moisture and eventually loss their coordinating capacities [2]. Thereby, other air-stable heterocyclic ligands such as pyridines [3], quinolines [4], imidazoles [5], tetrazoles [6], oxazolines [7], Schiff bases and hydrazones [8], were introduced as alternative solutions. Particularly, N-heterocyclic carbenes (NHCs) have merged recently as one of the most prestigious competitors among non-phosphine ligands. Moreover, methods for the preparation of phosphines [9], NHCs [10] and the hybrid of these two types of ligands [11]

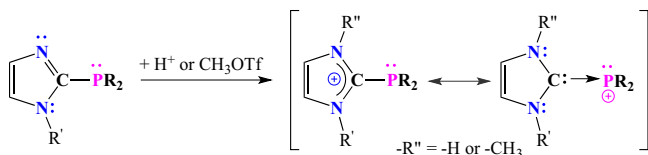
have been reported and their catalytic performances were examined.

Recently, a fascinating category of phosphine ligands having the general form of PR₂-Im (Im: imidazolyl) has been developed (Scheme 1). For PR₂-Im, protonation or alkylation on lone pair of nitrogen atom of imidazolyl ring can give rise to cationic and dative-bond featured phosphonium-NHC species (PR₂⁺ ← NHC, NHC: N-heterocyclic carbene) [12] capable of acting as potential carbene-transfer reagent [13]. For instance; an NCH-coordinated gold complex was obtained from the reaction of AuCl ← (PR₂-Im) complex with methanol (proton and weak nucleophile source) [14]. Note that the PR₂(OMe) byproduct is still a potential ligand for metal coordination. Thus, protonated or alkylated phosphonium-NHC can be regarded as a two-in-one compound ligating system.

In ligand-assisted transition-metal catalyzed reactions, the application of secondary phosphine oxides as pre-ligands (SPOs, RR'P(O)H) has attracted much attention due both to their thermal- and air-stability [15]. As demonstrated repeatedly, the coordinating capacity of SPO towards transition metal is acquired through

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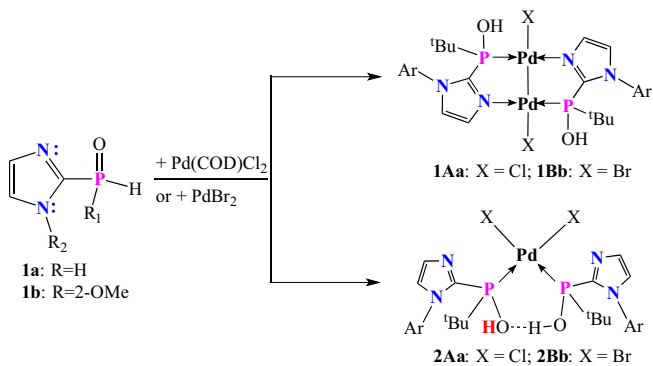
Scheme 1. Illustration of chemical transformation for $\text{PR}_2\text{-Im}$ to $\text{PR}_2^+\text{-NHC}$ adduct.

tautomerization, in which the P(V) in $\text{RR}'\text{P}(\text{O})\text{H}$ is converted to P(III) in phosphinous acid (PA, $\text{RR}'\text{POH}$) in solution [16]. The PA tautomer is having a lone pair of electrons and functioning as authentic phosphine-like ligand in coordination chemistry.

Previously, we had demonstrated that SPO-imidazolios **1a** and **1b** are active SPO pre-ligands for Suzuki–Miyaura cross-coupling reactions (Scheme 2) [17]. These SPO-based pre-ligands **1a** and **1b** are symbolized as SPO-Im, which is analogous to the neutral $\text{PR}_2\text{-Im}$ [17]. Herein, we show that palladium complex **2Aa** can be obtained by treating **1a** with $\text{Pd}(\text{COD})\text{Cl}_2$; while **2Bb** was synthesized from the reaction of **1b** with PdBr_2 (Scheme 2). Their crystal structures were determined by X-ray diffraction methods. More interestingly, two unconventional dinuclear Pd(I)–Pd(I) complexes, **1Aa** and **1Bb**, were also obtained from these two reactions of **1a** and **1b**, respectively [17]. In the literature, only few palladium complexes Pd(I)–Pd(I) were reported [18]. Therefore, as shown in Scheme 2 and referenced from literature, the resulted palladium complexes in our studies were classified into two categories: (i) dinuclear Pd(I)–Pd(I) complexes **1Aa** and **1Bb**; [17,18] and (ii) *cis*-form Pd(II) complexes **2Aa** and **2Bb** [19].

On the other hand, palladium-catalyzed coupling of olefins with aryl and vinyl halides, known as Heck reaction [20], is one of the most important methods to the formation of substituted double bond in organic synthesis [20j,21]. Heck reaction has been proven to be a rather versatile method in the syntheses of important building blocks in pharmaceuticals and bioactive compounds, natural products, monomers, herbicides and high performance materials [1i,5a,20f,20j,21b,22].

Herein, we wish to report the preparations of a number of new pre-ligands of SPO-Im **1c–1l** and the related palladium complexes (zwitterionic complex **2'** and neutral complexes **3** and **4** shown in Scheme 3). In comparison with the stable carbene-transfer analogue of NHC-phosphenium oxide or sulfide with non-coordinating pentavalent phosphorus [23], $[\text{P}(=\text{Y})\text{R}_2\text{-NHC}]^+$ ($\text{Y} = \text{O}$ or S), SPO-Im **1s** are potential pre-ligands for metal-coordination (complex **2'** in Scheme 3) and catalysis. It is closely related to the SPO-to-PA ($\text{RR}'\text{P}(\text{O})\text{H}$ to $\text{RR}'\text{POH}$) tautomerization that creating a trivalent phosphorus atom in phosphine-like PA ligand. Upon nucleophilic attack on P(III) atom of zwitterionic PA ligand in complex **2'**, the



Scheme 2. Reactions of pre-ligand SPO-Im **1a** with $\text{Pd}(\text{COD})\text{Cl}_2$ and **1b** with PdBr_2 [17]. The abbreviations of the species are as follows: **Aa** indicates products obtained from the reaction of **1a** + $\text{Pd}(\text{COD})\text{Cl}_2$, while **Bb** denotes products from **1b** + PdBr_2 .

NHC and phosphite-coordinated complex **3** could be obtained. Thus, we are demonstrating here that SPO-Im **1** could act as two-in-one pre-ligands (PA and NHC). If the substituent on nitrogen atom of imidazolyl ring is equipped with an extra coordinating site, complex **3** could dissociate a phosphite ligand to yield complex **4** (Scheme 3). In addition, DFT methods were employed to probe the probable reaction pathways for the formation of unexpected carbene-coordinated palladium complex (**3Aa**) from the reaction of SPO-Im **1a** with $\text{Pd}(\text{COD})\text{Cl}_2$. Selected SPOs as efficient mono- or bi-dentate pre-ligands in palladium-catalyzed Heck reactions were also investigated.

2. Results and discussion

2.1. Preparation of SPO-Im **1c–1l** and the unexpected observations from the reactions with palladium salts

Several new SPO-Im **1c–1l** were prepared according to the procedures modified from our previous work [17]. Firstly, 1-aryl-1*H*-imidazole was prepared by Cu(I)-catalyzed coupling reaction between imidazole and the matching substituted bromobenzene. The first resultant intermediate was then treated with BuLi and P(^{*t*}Bu)Cl₂. Finally, the second intermediate containing one P–Cl bond was followed by hydrolysis work-up in acidic media. Notably, *cis*-form of *bis*-PA coordinated palladium complexes **2Af'**, **2Ag'**, **2Ah'** and **4Ah** can be successfully obtained from the reactions of corresponding pre-ligands of SPO-Im **1f**, **1g**, and **1h** with $\text{Pd}(\text{COD})\text{Cl}_2$ (Scheme 4). Another palladium complexes **3Bb** that bearing NHC and phosphite ligands was yielded from the reaction of SPO-Im **1b** with PdBr_2 (Scheme 4). These palladium complexes were all synthesized with half molar equivalent of PdX_2 ($\text{X} = \text{Cl}$ or Br) at 25 °C for two hours. It is believed that the formations of **2Ax'** and **2Bx'** were from the tautomerization of their corresponding tautomers **2Ax** and **2Bx**, respectively [17].

The structures of three *cis*-form complexes, **2Af'**, **2Ag'** and **2Ah'**, were determined by X-ray diffraction methods. As shown in Fig. 1, a hydrogen bonding between O(1)–H(1)···O(2) is present in each case. Compared with the bonding modes of conventional tri-substituted phosphines toward metals, this manner is quite unique for these *cis*-form of *bis*-phosphine ligands coordinated palladium complexes [5]. Interestingly, the released H⁺ dissociated from one of the SPOs is relocated to the nitrogen atom of imidazole, forming zwitterionic type complexes **2Af'**, **2Ag'** and **2Ah'** [24]. Thereby, it is believed that the conversion of **2Ax** to its more stable tautomer **2Ax'** shall take place in solution [25].

For comparison, the selected structural data of several related compounds are listed in Table 1. Except for **2Ah'**, the distances between the protonated N and the closest X ($\text{X} = \text{Cl}$, Br) range from 3.047 Å to 3.197 Å, those are shorter than the sums of their van der Waals radius. An intra-molecular hydrogen bond is present in either **2Af'** or **2Ag'** where the protonated imidazole ring tilts away from chloride. Generally speaking, *trans*-form of *bis*-phosphine coordinated palladium complexes are presumably more stable than that of *cis*-form complexes in terms of less steric hindrance between two bulky ligands. Nevertheless, the fact that the *cis*-conformations are dominated here is most likely due to the existence of an intra-molecular hydrogen bond between two ligands. Moreover, the environments of the two coordinated phosphine ligands are not the same. The differences in the P–C(im) bond lengths range from 0.019 Å to 0.052 Å. The reason could be that the bonding between C(im) and P(2) can be regarded as a carbon-to-phosphorus dative bond after the imidazolophosphine is converted to a NHC-phosphenium in **2Ax'** [12,26a–e].

Unexpectedly, a unique palladium complex, **3Bb** was obtained from the reaction of **1b** with PdBr_2 . This square planar palladium

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