Catalysis Communications 40 (2013) 23–26

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Amphiphilic ionic palladium complexes for aqueous–organic biphasic Sonogashira reactions under aerobic and CuI-free conditions[☆]

Xuezhu Wang, Jing Zhang, Yongyong Wang, Ye Liu [*]

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, East China Normal University, Shanghai 200062, PR China

ARTICLE INFO

Article history:
Received 1 April 2013
Received in revised form 3 May 2013
Accepted 4 May 2013
Available online 10 May 2013

Keywords:
Sonogashira reaction
Water-soluble palladium complexes
Ionic complexes
Biphasic catalysis

ABSTRACT

The ionic Pd(II)-complexes of **2** (ammonium-[1-(2-hydroxyethyl)-3-methylimidazolium] bis[3-(diphenylphosphino)benzenesulfonate]-dichloropalladium(II) ([(NH_4)(Hemim)][$PdCl_2(TPPMS)_2$])) and **3** (bis[1-*n*-butyl-3-methylimidazolium] bis[3-(diphenylphosphino)benzenesulfonate]-dichloropalladium(II) ($[Bmim]_2[PdCl_2(TPPMS)_2]$)) were synthesized and fully characterized. The single crystal X-ray diffraction analyses show that **2** and **3** are composed of the imidazolium-based cations and $[PdCl_2(TPPMS)_2]^{2-}$ anions. The properties of such imidazolium-based Pd-complexes of **2** and **3**, in terms of the aqueous solubilities and the catalytic behaviors in water, could be dramatically varied. When **2** and **3** were applied as the precatalysts for the Sonogashira coupling of iodobenzene with phenylacetylene under aerobic and CuI-free conditions, the much higher yields of 1,2-diphenylethyne were obtained due to their amphiphilicity. The wide generality of **2** was available for aqueous–organic biphasic Sonogashira reactions.

1. Introduction

Palladium-catalyzed Sonogashira reaction is a powerful tool for the formation of Csp^2-Csp bond, and the most important method for the synthesis of internal acetylenes [1]. In a typical Sonogashira procedure, the reaction is conducted using a phosphine-ligated palladium complex with a catalytic amount of copper(I) iodide as a co-catalyst in the presence of base under inert atmosphere [1,2]. However, the in situ formed copper(I) acetylides with moisture- and air-sensitivity induce unwanted homocoupling products of terminal alkynes through Glaser reaction [2–4]. In the last few decades, a variety of efficient palladium catalysts containing hindered phosphines [5–9], palladacycles [10,11] and N-heterocylic carbene (NHC) [12–15] have been developed for the copper-free Sonogashira reactions, which allow the manipulation of the Sonogashira reaction with low catalyst loadings under copper-free conditions and without exclusion of air and moisture. The absence of copper also makes the Sonogashira reactions possibly be performed in water medium [14–16].

Aqueous organometallic catalysis (AOC) by water-soluble phosphine complexes has been developed into a most successful way for product isolation and/or catalyst recycling [17–19]. The solubility of the organometallic catalysts in water is determined by the solubility of the ligands, and the sulfonated phosphines are generally the most important ones in AOC [20–22]. Typically, under aqueous–organic biphasic condition in AOC, the addition of a phase-transfer catalyst, such as surfactant [23,24] or cyclodextrin [25,26], is required in order to eliminate the serious mass transfer limitation observed with hydrophobic substrates. The use of amphiphilic phosphines has recently been found to be a promising alternative to suppress the mass transfer factor because the amphiphilic phosphines incorporate the surface-active property and the coordinating ability to the metal into the same compound [27–29]. Unfortunately, the syntheses of amphiphilic phosphines are often time-consuming, laborious and expensive. The activities in the functionalization of ionic liquids in our group highlight us to replace the typical counter-cation of Na^+ or NH_4^+ in TPPMS by the imidazolium-based cation, which can provide amphiphilicity via incorporating lipophilic organic moieties. On the basis of this conception, herein, the amphiphilic TPPMS-ligated Pd complexes of **2** and **3** were synthesized (see Supplementary Information) and fully characterized (Scheme 1), which were further studied as the precatalysts for aqueous–organic biphasic Sonogashira reactions under aerobic and CuI-free conditions.

2. Results and discussion

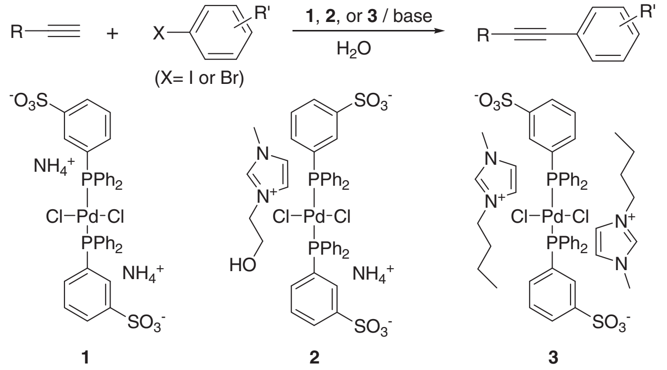
2.1. Synthesis and characterization of **1**, **2** and **3**

At room temperature, **2** and **3** were synthesized through exchanging the cation of NH_4^+ in **1** [30] by the imidazolium-based cations, which were fully characterized by ^1H NMR, ^{31}P NMR, CHN-elemental analysis, and single-crystal X-ray analysis. The molecular structures of **2** and **3**

[☆] This is an open-access article distributed under the terms of the Creative Commons Attribution-NonCommercial-No Derivative Works License, which permits non-commercial use, distribution, and reproduction in any medium, provided the original author and source are credited.

[*] Corresponding author. Tel.: +86 2162232078.
E-mail address: yliu@chem.ecnu.edu.cn (Y. Liu).

1566-7367/$ – see front matter © 2013 The Authors. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catcom.2013.05.005



Scheme 1. The ionic Pd-complexes of **1**, **2**, and **3** as the precatalysts for aqueous–organic biphasic Sonogashira reactions.

were depicted in Fig. 1, which were both composed of the imidazolium-based cations and the Pd-complex anions. The Pd-complex anion possesses the square-planar geometry which is similar to that in $PdCl_2(PPh_3)_2$ [31]. The Pd center, lying at the center of inversion, is coordinated by two chloride ions and two mono-sulfonated phosphine ligands. The Pd–P distances observed in **2** (2.33–2.34 Å) and **3** (2.32 Å) are in the classical range, compared to those observed in the reported phosphine-ligated Pd(II) complexes with structural similarity [31,32]. As for **2**, two benzenesulfonate groups located in the Pd-complex-anion ($[PdCl_2(TPPMS)_2]^{2-}$) are located in *cis*-position due to the strong hydrogen bond interactions between the sulfonate groups with NH_4^+. The presence of such strong hydrogen bond interaction led to the slightly distorted square-planar $[PdCl_2(TPPMS)_2]^{2-}$, which is counteracted by one NH_4^+ and one $[Hemim]^+$ (1-(2-hydroxyethyl)-3-methylimidazolium). Whereas in **3**, two benzenesulfonate groups are located in *trans*-position in the corresponding Pd-complex-anion with high symmetry, which is counteracted by two $[Bmim]^+$ (1-*n*-butyl-3-methylimidazolium). The ^1H NMR and ^{31}P NMR spectra further supported the assigned structures of **2** and **3**. The ^{31}P NMR spectra show the different resonances at 37.6 ppm for **2** and 25.1 ppm for **3**, due to the influence of the different cations on the chemical environment of $[PdCl_2(TPPMS)_2]^{2-}$ via the varied electrostatic interaction, and the additional hydrogen bond interaction in **2**.

The solubilities of **1**, **2**, and **3** in water were determined by the equilibrium method at 20 °C. It was found that, with the same Pd-complex anion, the different composition of the counter-cations could dramatically affect the solubility of the corresponding ionic compounds. When one of NH_4^+ in **1** was replaced by $[Hemim]^+$, the solubility of the resultant compound of **2** was increased from 36.9 g/L to 52.9 g/L, due to the presence of –OH in the cation which developed the strong hydrogen bond interaction with water. While two of NH_4^+ in **1** were replace by $[Bmim]^+$, the solubility of the resultant compound **3** was decreased to 3.4 g/L, due to the presence of the more lipophilic group of $[Bmim]^+$. On the other hand, besides hydrophilicity derived from $[PdCl_2(TPPMS)_2]^{2-}$, **2** and **3** were featured with lipophilicity because of the presence of the alkyl- and imidazolium-moieties. Hence, **2** and **3** are featured with more amphiphilic character in comparison to **1**, which is purely hydrophilic due to the present of NH_4^+ as the counter-cations.

2.2. Catalytic performance of **1**–**3** for aqueous–organic biphasic Sonogashira reaction

The coupling of phenylacetylene with iodobenzene was studied as a model reaction to investigate the catalytic performance of **1**–**3** in water under CuI-free conditions (Table 1). Through screening the bases, piperidine as a strong base and effective acid-scavenger could expedite the reaction rate more rapidly than the others such as K_2CO_3, Cs_2CO_3,

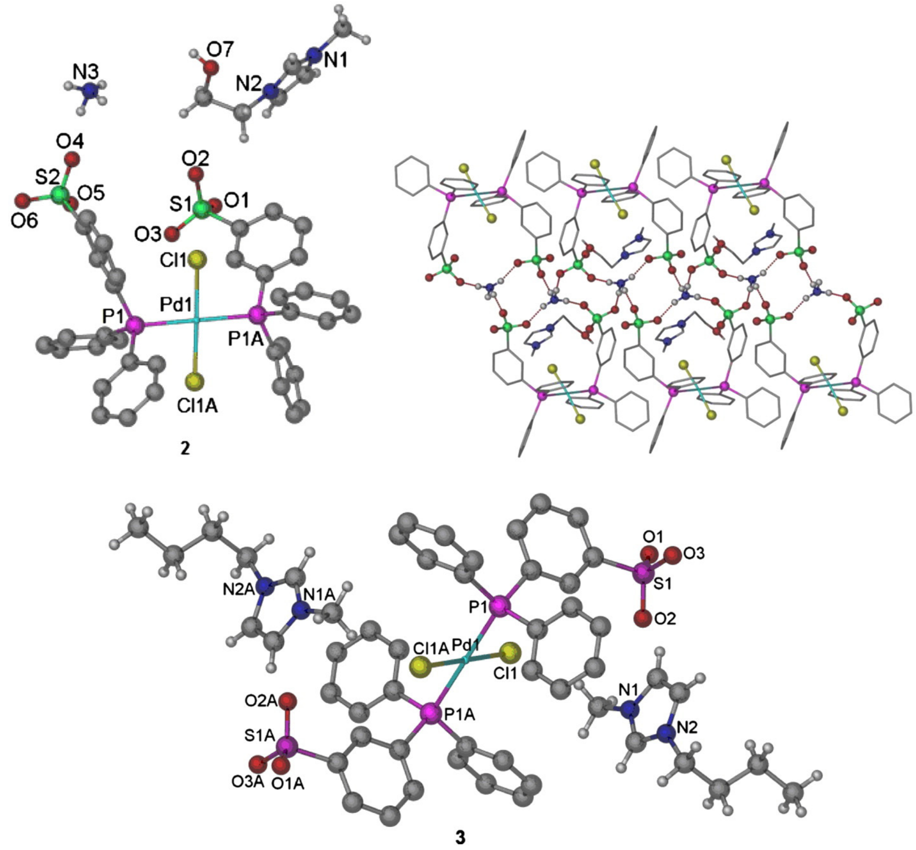


Fig. 1. The single crystal structures of **2** and **3** [the selected bond distances (Å) and bond angles (°): **2** Pd1-P1 2.3253(12), Pd1-P1A 2.3434(12), P1-Pd1-P1A 177.51(5), Cl1-Pd1-Cl1A 175.96(7), Cl1-Pd1-P1 91.06(5), Cl1-Pd1-P1A 89.86(4); **3** Pd1-P1 2.3326(18), Pd1-P1A 2.3326(17), P1-Pd1-P1A 180.0, Cl1-Pd1-Cl1A 180.0, Cl1-Pd1-P1 91.64(7) Cl1-Pd1-P1A 88.36(7)].