Chinese Journal of Catalysis 37 (2016) 405–411

available at www.sciencedirect.com

ScienceDirect

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

Article

Ionic palladium complex as an efficient and recyclable catalyst for the carbonylative Sonogashira reaction

Da Yang, Dongliang Wang, Huan Liu, Xiaoli Zhao, Yong Lu, Shijun Lai #, Ye Liu *

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:
Received 2 November 2015
Accepted 23 November 2015
Published 5 March 2016

Keywords:
Ionic phosphine ligand
Palladium complex
Carbonylative Sonogashira reaction
Ionic liquid

ABSTRACT

The neutral palladium(II) complex bis-[1-(5'-diphenylphosphinothiazol-2'-yl)-imidazolyl] dichloropalladium(II) (**1A**) ligated by thiazolylimidazolyl-based phosphine (**L1**) in which thiazolylimidazolyl acted as an S- and N-donor provider with weak coordinating nature, and the ionic complex bis-[1-(5'-diphenylphosphinothiazol-2'-yl)-3-methylimidazolium] dichloropalladium(II) trifluoromethanesulfonate (**2A**) ligated by thiazolylimidazolium-based phosphine (**L2**) after quaternization of **L1** using methyl trifluoromethanesulphonate were synthesized. It was found that the introduced positive charges and strong electron-withdrawing effect in **2A** not only led to changes in the configuration and structural stability of the complex, but also lowered its catalytic performance in carbonylative Sonogashira reactions. These effects reveal the important role of the N-donor in **1A**. In addition, as an ionic palladium complex, **2A** combined with the room-temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate could be recycled eight times as the catalyst in carbonylative Sonogashira reactions without detectable metal leaching.

1. Introduction

Among aromatic carbonyl compounds, α,β-alkynones are important structural motifs in many bioactive molecules and intermediates for the synthesis of natural products and pharmaceuticals [1–4]. In general, α,β-alkynones have been prepared by the coupling of alkyne organometallic reagents with acid chlorides in the presence of transition metal reagents [5–9]. Unfortunately, this methodology is limited with respect to functional group tolerance, substrate stability, reaction conditions (dry solvent under an inert atmosphere), atom economy, and environmental friendliness. Since they were first reported by Tanaka's group [10] in 1981, palladium (Pd)-catalyzed carbonylative Sonogashira reactions have become an alternative approach to synthesize α,β-alkynones. In carbonylative Sonogashira reactions, CO acts as an important C1 building block to introduce carbonyl group into the parent molecules. Many researchers have modified and improved this methodology, including Wu et al. [11] for homogeneous carbonylative Sonogashira reactions and other groups [12–14] for heterogeneous ones. It is widely accepted that the involved ligands can greatly tailor the catalytic performance of homogenous Pd complex catalysts through electronic and steric effects [15–19]. However, these catalysts still suffer from the problems of difficult product separation, rapid activity loss, and non-recyclability [11,20,21].

Non-volatile ionic liquids (ILs) have been recognized as promising alternative solvents to immobilize homogenous pal-

---

* Corresponding author. Tel: +86-21-62232078; Fax: +86-21-62233424; E-mail: yliu@chem.ecnu.edu.cn

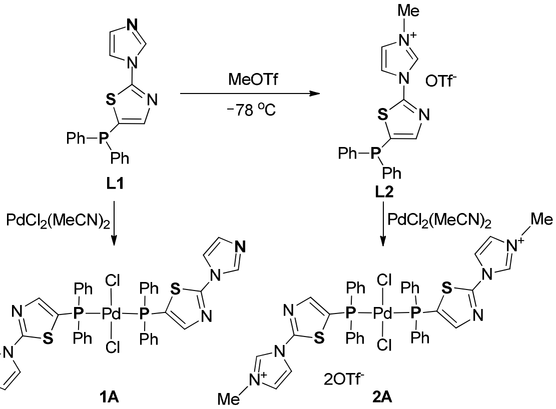
Corresponding author. Tel: +86-21-62232078; Fax: +86-21-62233424; E-mail: laishijun@126.com

This work was supported by the National Natural Science Foundation of China (21473058, 21273077).

DOI: 10.1016/S1872-2067(15)61022-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 3, March 2016

ladium catalysts, preventing their leaching and deactivation [22]. ILs can be functionalized with phosphine ligands, and the resulting phosphine-functionalized ILs have been investigated as ionic complexes (catalysts) and used in combination with room-temperature ionic liquids (RTILs) to immobilize homogenous catalysts [23–27]. Because the melting points of phosphine-functionalized ILs are usually higher than 100 °C, they are typically defined as ionic phosphines. It has also been found that when phosphines are introduced into ILs to obtain ionic phosphines, the positive charges of ILs with strong electron-withdrawing character dramatically influence the coordinating ability of the involved phosphines and in turn the properties of the corresponding transition metal complexes in terms of structure and catalytic activity [27,28].

Herein, the neutral monophosphine **L1** (1-(5'-diphenylphosphinothiazol-2'-yl)-imidazolyl) and its ionic counterpart **L2** (1-(5'-diphenylphosphinothiazol-2'-yl)-3-methylimidazolium trifluoromethanesulfonate) reported by us previously [29] were complexed with $PdCl_2(CH_3CN)_2$ to afford the neutral Pd(II) complex bis-[1-(5'-diphenylphosphinothiazol-2'-yl)-imidazolyl] dichloropalladium(II) (**1A**) and an ionic complex bis-[1-(5'-diphenylphosphinothiazol-2'-yl)-3-methylimidazolium] dichloropalladium(II) trifluoromethanesulfonate (**2A**) (Scheme 1). The effects of the positive charge in **L2** on the coordination ability of the involved phosphine, the structure of the corresponding Pd complex, and the catalytic performance of the complexes in the carbonylative Sonogashira reaction are discussed (Scheme 2). In addition, **2A** can be regarded as an ionic Pd complex that is compatible with RTILs, so its recyclability in 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) is investigated.



Scheme 1. Formation of complexes **1A** and **2A** from ligands **L1** and **L2**, respectively.

2. Experimental

2.1. Reagents and analysis

L1 and **L2** were first prepared according to our previously published method [29]. Other chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and Shanghai Alfa Aesar, China, and used as received. Diethyl ether was distilled from sodium. DMF was dried over $CaSO_4$ and distilled before use. Both diethyl ether and DMF were stored over 4Å molecular sieves under N_2. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer (400 MHz) at room temperature. ^{31}P NMR spectra were referenced to 85% H_3PO_4 sealed in a capillary tube as an internal standard. CHN elemental analysis was performed on a Vario EL III Elemental Analyzer. The amount of Pd in the organic phase was quantified by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). Gas chromatography (GC) was performed on a Shimadzu-2014 equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μm). GC-mass spectrometry (GC-MS) was recorded on an Agilent 6890 spectrometer equipped with an Agilent 5973 mass selective detector. Purification of the compounds was carried out by flash chromatography on silica gel.

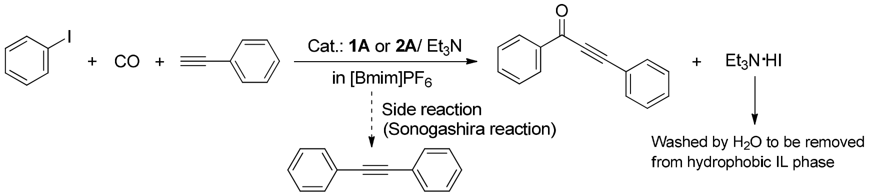
2.2. Synthesis of catalysts

2.2.1. Synthesis of complex *1A*

Under N_2 atmosphere, **L1** (0.13 g, 0.4 mmol) dissolved in dry CH_2Cl_2 (4 mL) was added to a solution of $PdCl_2(MeCN)_2$ (0.05 g, 0.2 mmol) in dry CH_2Cl_2 (8 mL). The mixture was stirred vigorously at room temperature for 3 h. The solvent was removed under vacuum using a rotary evaporator. The obtained yellow solid residue was washed with diethyl ether and dried under vacuum to give the product **1A** in 97% yield. A sample suitable for single-crystal X-ray diffraction (XRD) analysis was obtained by slow volatilization of a CH_2Cl_2 solution containing **1A**. ^1H NMR (δ, CD_2Cl_2): 8.23 (s, 2H, NCHN), 7.55–7.75 (m, 24H), 7.21 (s, 2H); ^{13}C NMR (δ, CD_2Cl_2): 164.43 (s, NCN), 151.17 (s), 135.69 (s), 134.25 (s), 131.70 (s), 131.05 (s), 128.67 (s), 128.23 (s), 121.70 (s), 117.62 (s); ^{31}P NMR (δ, CD_2Cl_2): 10.80 (s, PPh_2). CHN (%) elemental analysis for **1A** ($C_{36}H_{28}Cl_2N_6P_2Pd_1S_2$, 848.0): C 50.82, H 3.43, N 9.96 (Calcd. C 50.99, H 3.33, N 9.91).

2.2.2. Synthesis of complex *2A*

Under N_2 atmosphere, **L2** (0.250 g, 0.50 mmol) dissolved in dry CH_2Cl_2 (3 mL) was added to a solution of $PdCl_2(MeCN)_2$ (0.065 g, 0.25 mmol) in dry CH_2Cl_2 (7 mL). The mixture was



Scheme 2. Carbonylative Sonogashira reaction of iodobenzene with phenylacetylene catalyzed by **1A** and **2A**.