Journal of Organometallic Chemistry 724 (2013) 235–243

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

Pd(II) complexes with mono- and bis-chelate carbene ligands tagged with pyridinium cation: Synthesis, structures, and their catalytic activities toward Heck reaction

Chen-Shiang Lee, Yong-Bin Lai, Wan-Jung Lin, Rui Rui Zhuang, Wen-Shu Hwang*

Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan, ROC

ARTICLE INFO

Article history:
Received 10 August 2012
Received in revised form
9 November 2012
Accepted 13 November 2012

Keywords:
Chelate
N-heterocyclic carbene
Palladium
Heck reaction

ABSTRACT

Homoleptic Pd(II) complexes with one and two chelating di-*N*-heterocyclic carbene (NHC) ligands tagged with pyridinium cation, $[\mathrm{Pd_2(^{PyBu}CC^{me})_2Cl_2}](\mathrm{PF_6})_6$ and $[\mathrm{Pd\ (^{PyBu}CC^{me})_2}](\mathrm{PF_6})_6$ ($^{\mathrm{PyBu}}\mathrm{CC}^{\mathrm{me}}$ = 1,1′-di-*N*-(2-pyridinium)butyl-3,3′-methylenediimidazol-2,2′-diylidene), were synthesized and their square planar molecular geometry were determined by X-ray diffraction analysis. These complexes exhibited high catalytic activity toward Heck reaction in both DMF and water.

1. Introduction

In the past decays, the Pd-catalyzed Heck reaction has become one of the most important tools for the preparation of aryl-substituted olefins [1]. Despite the ligandless systems in this field are aware, efficient catalysts systems with various types of ligands are widely studied [2]. Among those developments, the incorporation of bulky monophosphines and diphosphines received considerable attention [3]. So far, *N*-heterocyclic carbenes (NHCs) are recognized as the only class of ligands that can compete with tertiary phosphine. The strong σ-donating property of the NHC increases the strength of metal–NHC bond and enhances the thermo stability of the resulting complex. The functionality and the steric of the NHC ligand can be easily tuned by adapting different substituent to the *N* atoms depending on the requirement of the design for the catalyst. Hence, the metal–NHCs have been widely used in a number of industrially important organic processes [4].

While numerous monodentate Pd(II)–NHC complexes displayed good efficiency in catalytic reactions, using chelating NHC as ligand to improve the thermal stability of Pd–NHC complexes had been developed. However, the efficiency of most catalysts in Heck reactions using heteroleptic and homoleptic Pd(II)–NHC complexes consisting of only one chelating NHC unit remained unsatisfactory was noticed [5]. Recently, we reported the catalytic activity of a homoleptic bischelate tetracarbene Pd(II) complex [6]. Contrary to the assumption that the catalytic activity of a biscarbene system might be inhibited by the formation of a bischelate Pd–tetracarbene species [7], we proved that this complex is an excellent catalyst for the Heck reaction with potential recyclability.

Introducing charged groups in catalysts had recently been examined [8]. Focus of the published works mostly lie on enhancing the solubility of catalysts in polar or nonconventional media, enabling their recycling ability. The presence of ionic substituent can significantly influence their structural features [9]. Contrary to vast examples of phosphine, pyridine or cyclopentadienyl ligands bearing ionic substituent [10], few efforts for Heck reactions using NHC ligand functionalized by the ionic appendage had been devoted [8f], where the ionic portion is either cationic ammonium or anionic carboxylate/sulfonate moiety. In continuation of our studies on the catalytic activity of homoleptic bischelate Pd(II)–carbene complex, we anticipated that Pd(II) complex with chelating carbene ligand tagged with pyridinium cation might exhibit interesting properties when applied in Heck reaction.

Water is economic and provides potential for recyclable techniques. Theoretically, water molecule serves as placeholder on Pd center that can strongly coordinate but kinetically labile. Therefore, it can sometimes benefit the Pd-catalyzed transformation. However, water may displace some helpful ligand, giving a negative effect on the reaction. Moreover, the influence of water on the

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* Corresponding author. Tel.: +886 3 8633570; fax: +886 3 8633577.
E-mail address: hws@mail.ndhu.edu.tw (W.-S. Hwang).

0022-328X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2012.11.015

oxidative addition remained unclear. Consequently, reports of Heck reactions under aqueous phase were relatively rare and mostly showed only the results of aryl iodide [2a,8f,11]. In this report the catalytic activity of our pyridinium cation tagged Pd(II)–NHCs catalyst toward Heck reaction in pure aqueous phase was examined.

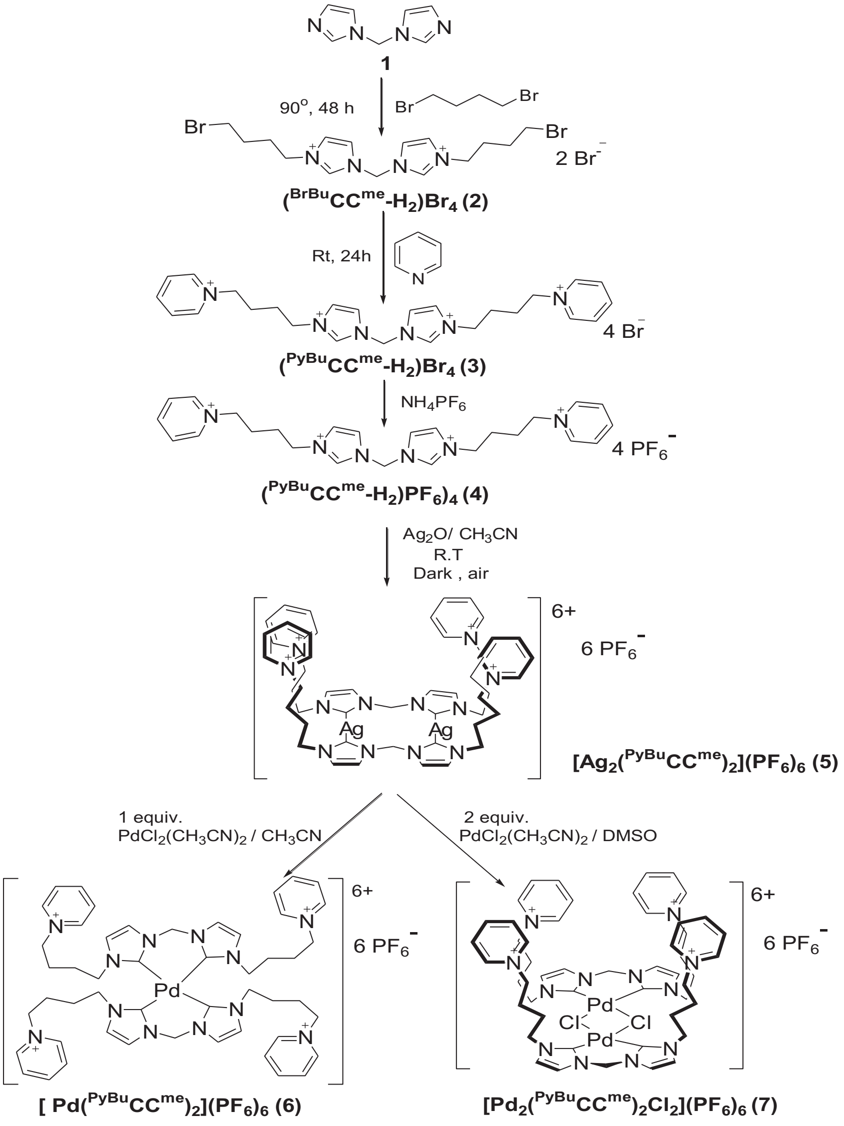
2. Results and discussion

2.1. Synthesis and characterization of $[Ag_2(^{PyBu}CC^{me})_2](PF_6)_6$ (**5**), $[Pd(^{PyBu}CC^{me})_2](PF_6)_6$ (**6**), and $[Pd_2(^{PyBu}CC^{me})_2Cl_2](PF_6)_6$ (**7**)

The pyridinium-tagged di-imidazolium salt $(^{PyBu}CC^{me}\text{-}H_2)Br_4$ (**3**) was prepared by treating the corresponding di-imidazolium bromide salt $(^{Bu}CC^{me}\text{-}H_2)Br_2$ (**2**) with 2 equiv. of pyridine in H_2O for 1 day (Scheme 1). Pure product could be obtained through recrystallization from H_2O/acetone. The subsequent anion exchange reaction was carried out in water to give the PF_6 salt $(^{PyBu}CC^{me}\text{-}H_2)(PF_6)_4$ (**4**). The Br and PF_6 salts were all characterized spectrally. Compared with the "un-tagged" di-imidazolium salt [6], the ^1H and ^{13}C NMR spectra of these pyridinium tagged salts showed additional resonances due to the pyridinium rings.

Reaction of **4** with Ag_2O in CH_3CN at room temperature for 24 h in dark gave $[Ag_2(^{PyBu}CC^{me})_2](PF_6)_6$ (**5**). The absence of the C_2–H at 8.77 ppm in the ^1H NMR spectrum confirmed the deprotonation of the imidazolium salt and the formation of the Ag–NHCs complex **5**. No related signal of carbenoic carbon for Ag–NHC was observed in its ^{13}C NMR spectrum, possibly due to the dynamic behavior of the NHC ligand [12]. Although the Br salt of the pyridinium-tagged di-imidazolium salt **3** can also be deprotonated by Ag_2O in H_2O, the resulting product was unstable for isolation and characterization. On the contrary, $[Ag_2(^{PyBu}CC^{me})_2](PF_6)_6$ shows high stability in CH_3CN solution. Similar anion effect had been reported [13].

Upon mixing with 1 equiv. and 2 equiv. of $PdCl_2(CH_3CN)_2$, $[Ag_2(^{PyBu}CC^{me})_2](PF_6)_6$ was readily converted into mononuclear $[Pd(^{PyBu}CC^{me})_2](PF_6)_6$ (**6**) and binuclear $[Pd_2(^{PyBu}CC^{me})_2Cl_2](PF_6)_6$ (**7**), respectively, via transmetallation (Scheme 1). It is worth to note that $[Ag_2(^{PyBu}CC^{me})_2](PF_6)_6$ has to be pre-treated with activated carbon for removing the trace impurity, which is found significantly influencing the transmetallation process. A chemical shift at 169.5 ppm in the ^{13}C NMR spectrum, which is characteristic for the resonance of carbenoic carbon C_2 in Pd–NHCs, supported the formation of **6**. The ^1H NMR spectrum of **6** shows two sets of doublet resonate at 6.45 and 6.28 ppm with a coupling constant of



Scheme 1. Synthesis of ligand precursors and complexes.