Journal of Organometallic Chemistry 762 (2014) 40–47

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

The ionic mononuclear and trinuclear Au(I)-complexes ligated by phosphine-functionalized ionic liquids: Synthesis, characterization, and catalysis to hydration of phenylacetylene

Xuezhu Wang, Yongyong Wang, Jing Zhang, Xiaoli Zhao, Ye Liu*

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

ARTICLE INFO

Article history:
Received 22 January 2014
Received in revised form
17 March 2014
Accepted 3 April 2014

Keywords:
Gold complexes
Phosphine ligands
Hydration of phenylacetylene
Functionalized ionic liquids

ABSTRACT

A series of ionic Au(I)-complexes ligated by the phosphine-functionalized ionic liquids were synthesized and characterized, which are composed of the Au(I)-complex cation and the counteranion of OTf^-, $AuCl_4^-$, or PF_6^-, respectively. The single crystal X-ray diffraction analyses show that the Au(I)-centered vector in **1A**, **1B**, **2A**, **3A**, and **4A** all possess the slightly twisted linear geometry, and in each individual the Au(I)-center is coordinated by one chlorine and one imidazolium-based phosphine. The aggregation of **1B** in acetone can lead to the formation of the trinuclear Au(I)-complex of **1C** due to the aurophilic Au(I)–Au(I) interaction, the electrostatic attraction, and the steric preference. When these ionic Au-complexes were employed as precatalysts for hydration of phenylacetylene in aqueous-methanol media, the reaction proceeded selectively according to Markovnikov's rule with moderate to high yields of acetophenone. The highest activities were achieved over **2A** with hydrophobic PF_6^- as the counteranion and the trinuclear **1C** under mild conditions (75 °C, 2 h), in conjunction with the additive of proton acid H_2SO_4. The ion-pair effect on the catalytic performance of the corresponding Au(I)-complexes, coming from the phosphine-ligated cations and the counteranions, were investigated.

Introduction

The application of Au-complexes has been undervalued for many years due to the preconceived opinion that gold was an expensive and extremely inert metal [1]. Only in recent decade, homogeneous catalysis promoted by Au-complexes containing phosphines or *N*-heterocyclic carbene (NHC) has emerged as a powerful tool for organic synthesis [2,3]. The cationic Au(I)-complexes are featured with the strong Lewis acidity due to the relativistic effect coming from the extent of contraction of 6s orbital and the expansion of 5d orbital [4], which is of great interest to catalyze the nucleophilic addition of water to alkynes following Markovnikov's rule for the generation of the ketones [1,5]. Benefiting from the clean water as the nucleophile, the synthesis of carbonyl compounds by Au-catalyzed hydration of alkynes was extensively attractive and potentially interested in industrial processes because of the replacement of the uses of highly toxic mercury salts and strong Brönsted or Lewis acids, like $HgO-H_2SO_4$ (Kucherov catalyst) [6,7] and $HgO-BF_3$ (Hennion–Nieuwland catalyst) [8].

In order to develop the efficient catalytic systems for hydration of alkynes, much effort has been devoted to modulate the structures and compositions of the Au(I) complexes ligated by the phosphines or NHCs [2f,9], the reaction condition (microwave irradiation) [10], and the reaction media (such as ionic liquids) [11,12]. More recently, Nolan and Corma respectively reported the use of cationic $[(IPr)Au]^+[X]^-$ ($X^- = BF_4^-, SbF_6^-, OTf^-, PF_6^-, NTf_2^-$) generated in situ to be a versatile and selective catalyst for hydration of alkynes [13,14]. Comparatively, the examples of using the multi-nuclear Au(I)-complexes to catalyze hydration of alkynes have not been exploited yet, although many of them have been synthesized [15].

It has been known that ionic liquids (ILs) can be functionalized flexibly by incorporating functional moieties into the IL structure to develop different functionalized ILs (FILs), which dually possess the characters of the incorporated functionalities as well as those of the ILs [16]. The phosphine-FILs have long been investigated for the design of the ionic organometallic compounds and application to homogeneous catalysis [17–19]. It has been found in our previous work that, while the coordinating P(III) atom is vicinal to the

---

* Corresponding author.
E-mail address: yliu@chem.ecnu.edu.cn (Y. Liu).

http://dx.doi.org/10.1016/j.jorganchem.2014.04.005

positive charged imidazolium ring, the corresponding phosphine-FILs are featured with π-acceptor character as well as σ-donor [20]. Hence, the varied coordination behaviors of such phosphine-FILs are in great concerns in the coordinating chemistry and homogeneous catalysis, leading to the significant changes of the complex configurations and catalytic performance.

Continuous efforts to utilize the phosphine-FILs (which can be defined as the phosphino-imidazolium salts due to their solid state at room temperature) with the positive charge vicinal to the P(III) atom evoked us to prepare the corresponding ionic gold(I) complexes of the types of $[Au^{I}(\mathbf{L})Cl]^{+}Y^{-}$ (**1A**, **1B**, **2A**, **3A**, and **4A**) (**L** = imidazolium-based phosphine, Scheme 1). Unexpectedly, the trinuclear complex of the type of $[Au^{I}(\mathbf{L})Cl{-}AuCl_2{-}Au(\mathbf{L})Cl]^{+}[AuCl_4]^{-}$ (**1C**) was formed in good yield due to the aggregation of **1B** with its derivative [4]. The obtained ionic complexes (**1A**–**1C** and **2A**–**4A**) were investigated comparatively herein as the homogeneous precatalysts for hydration of phenylacetylene in conjunction with Brönsted acid of H_2SO_4. The ligand effect and the ion-pair effect on the catalytic performance of these Au(I)-complexes were discussed.

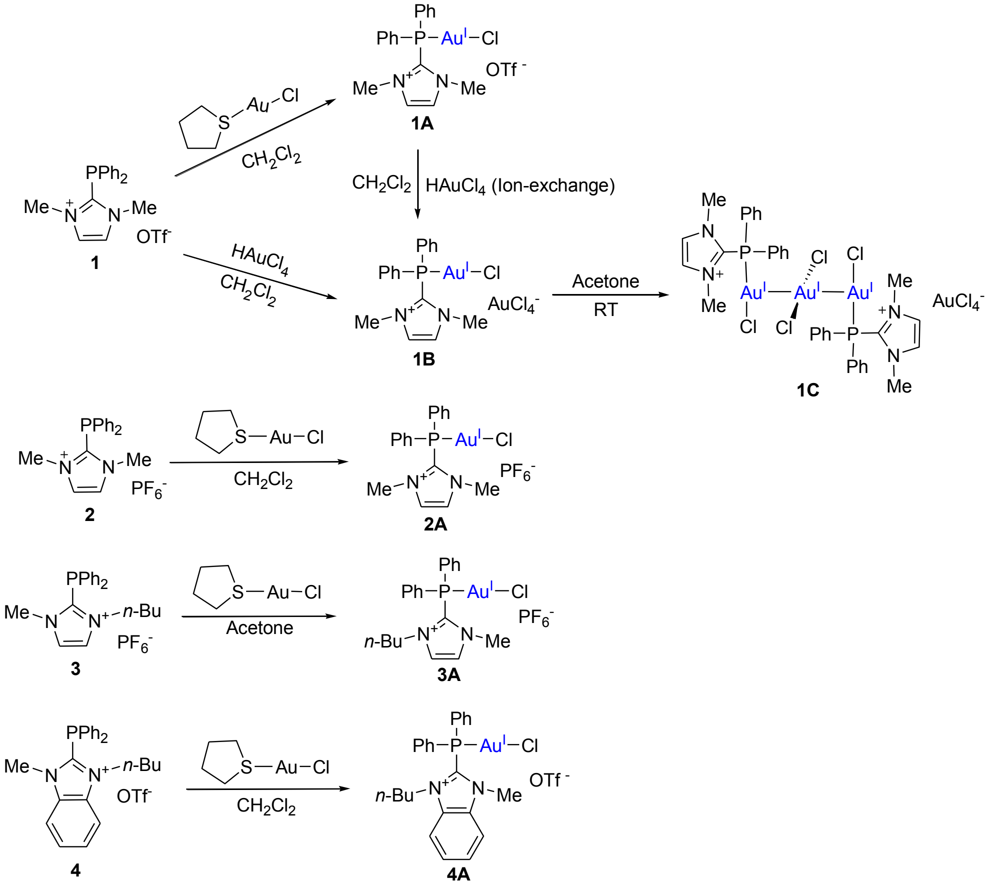
Results and discussion

Synthesis and characterization of the ionic Au(I)-complexes

When the phosphine-FIL of **1** was coordinated to the different Au-precursors under the applied reactions conditions, the ionic complexes of **1A**–**1C** were obtained respectively with good to excellent yields (78–98 wt%). The use of equivalent of tetrahydrothiophene–gold(I) chloride $[Au^{I}(tht)Cl]$ led to the formation of **1A** with OTf^{-} as the counteranion, while the use of equivalent of $HAu^{III}Cl_4\cdot4H_2O$ led to the formation of **1B** with $AuCl_4^{-}$ as the counteranion. It was found that the high valence state Au^{III} ion was partially reduced to Au^{I} by **1** before the coordination, subsequently leading to the formation of the monovalent Au(I)-complex of **1B** with the left $AuCl_4^{-}$ as the counteranion. **1B** could also be obtained through the ion-exchange of **1A** with equivalent of $HAu^{III}Cl_4\cdot4H_2O$. When the collected yellow crystal solids of **1B** was dissolved in acetone and stood-by up to 72 h at ambient condition, the red–orange solids were obtained unexpectedly after the solvent removal and recrystallization in acetone–hexane, which proved to be a trinuclear Au(I)-complex of **1C**; Whereas under the similar conditions, the transformation of **1A** with OTf^{-} as the counteranion, or the others (**2A**–**4A**), to the trinuclear Au(I)-complexes like **1C** was unsuccessful.

Following the similar procedures for preparation of **1A**, the ionic complexes of **2A**–**4A** ligated by the phosphine-FILs of **2**–**4** were obtained respectively.

All of the obtained ionic Au(I)-complexes, with insensitivity to moisture and oxygen both in the solid state and in organic solvent at room temperature, were characterized by $^{1}H/^{31}P$ NMR spectroscopy and single-crystal X-ray diffraction analysis. The molecular structures in Fig. 1 show that, except for **1C**, the others are composed of the mononuclear Au(I)-complex cations with structural similarity to that of the neutral complex of $Au^{I}(PPh_3)Cl$ [21], and the corresponding counteranions. **1A**, **1B**, and **2A** possess the same Au(I)-complex cation, but are counteracted by the different anions of OTf^{-}, $AuCl_4^{-}$, and PF_6^{-} respectively; While **1A** and **4A** possess the different phosphine-ligated Au(I)-complex cation along with the same counteranion of OTf^{-}. The Au(I)-centered vectors in **1A**, **1B**, **2A**, **3A**, and **4A** are all in a slightly distorted linear



Scheme 1. Synthesis of the ionic Au(I) complexes ligated by the phosphine-FILs of **1**–**4**.