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

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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

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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.

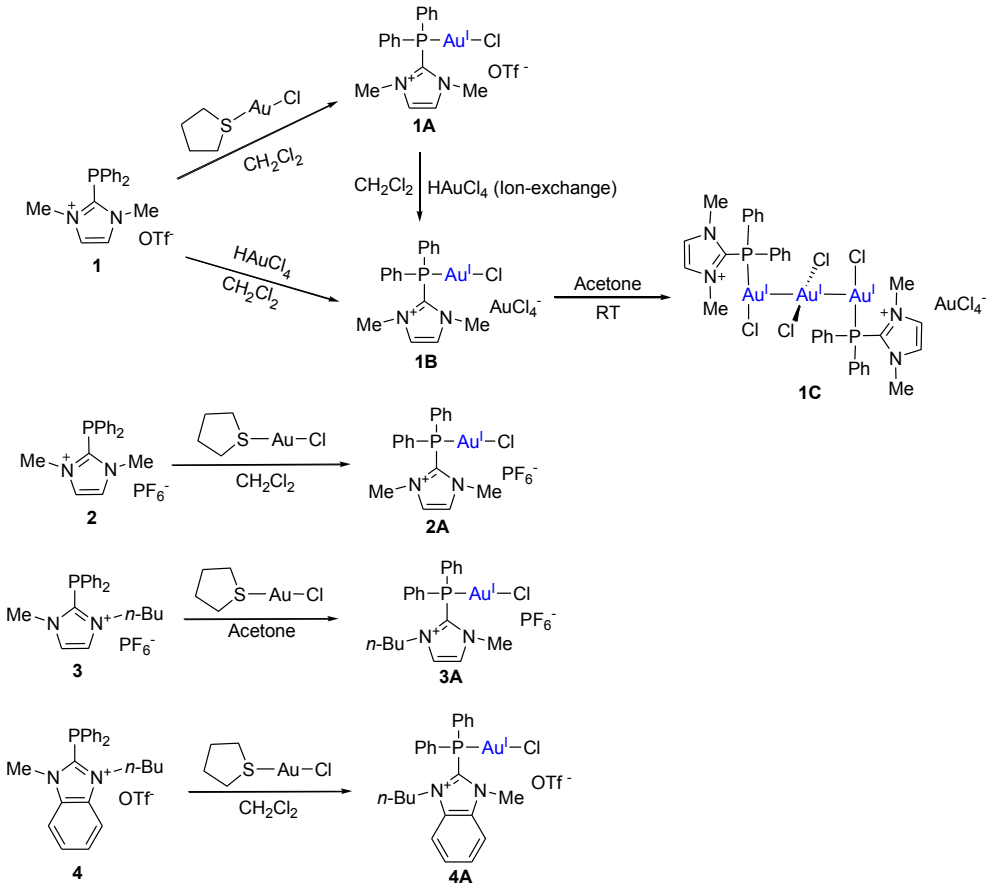
Results and discussion

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 $HAu^{III}Cl_4{\cdot}4H_2O$ 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 $HAu^{III}Cl_4{\cdot}4H_2O$. 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**.

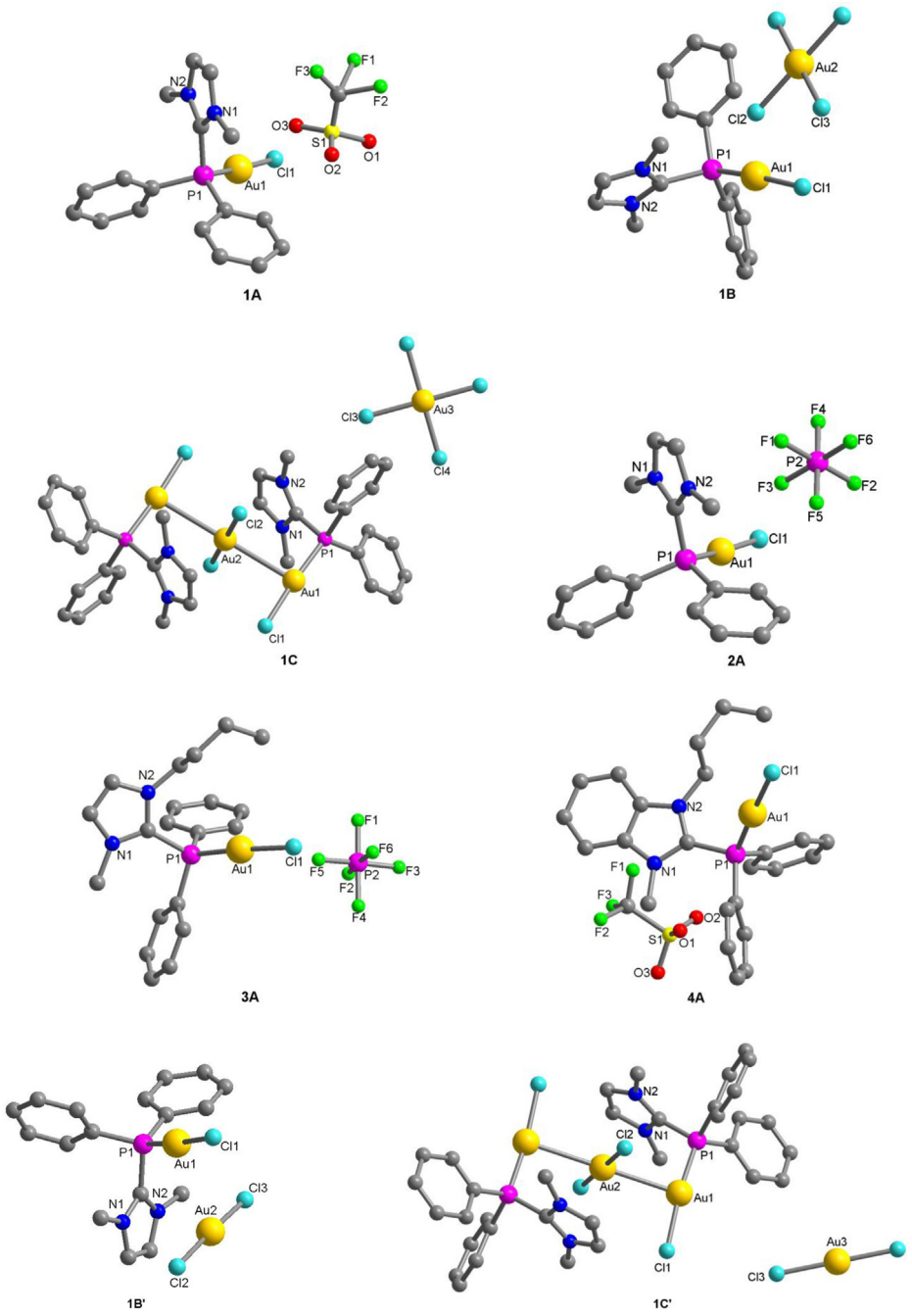


Fig. 1. The single crystal structure of the ionic Au(I)-complexes of **1A**, **1B**, **1C**, **2A**, **3A**, **4A**, **1B′**, and **1C′**.

configuration, which is the typical character for the mononuclear Au(I)-complexes. Au(I) center is diagonally coordinated by one Cl^- and one imidazolium-based phosphine. The bond angles of P(1)–Au(1)–Cl(1) are 175–178°. The bond distances of Au–P are in the range of 2.221–2.227 Å, which are comparative to that of $Au^I(PPh_3)Cl$ (2.235 Å, Table 1). The structure of **1C** shows that the trimetallic Au(I)-nucleus is arranged in an ideal linear array. The central Au(I) in an inversion center is coordinated by two chlorine atoms and another two cationic phosphine-ligated Au(I)-complex moieties in perpendicular direction. The bond angles of Au(1)–Au(2)–Au(1a) of 180° and P(1)–Au(1)–Cl(1) of 176° are observed. The Au–Au distance is 3.08 Å which is in the range of Au–Au metal bonding [22]. The selected bond distances and bond angles for compound **1A**–**1C** and **2A**–**4A** are given in Table 1.

Actually **1C** was not the direct aggregation of $[L–Au–Cl]^+$ cation with $AuCl_4^-$ anion in **1B**, but the aggregation of $[L–Au–Cl]^+$ cation with $AuCl_2^-$, the later was derived from the reduction of $AuCl_4^-$ anion by acetone solvent. The presence of $AuCl_2^-$ could be confirmed by the concomitant formation of **1B′** and **1C′** analogs as the minor products during the crystal generation of **1B** and **1C** (Fig. 1). As shown in Scheme 2, the trinuclear Au(I)-complex of **1C** is the exact adduct of **1B** with **1B′**. And the self-aggregation of **1B′** leads to the formation of **1C′** (Scheme 2).

The driving force for the aggregation of mononuclear Au(I)-complexes into multiple-nuclear ones has been usually ascribed to the strong aurophilic Au(I)–Au(I) bonding (d^{10}–d^{10}) interaction in the literature [4]. However, the absence of such aggregation of **1A**, **1B**, **2A**, **3A**, or **4A** themselves implied that the additional

Table 1
The selected bond distances (Å) and bond angles (°) for the ionic Au-complexes.

Au-complex	Bond distances (Å)			Bond angles (°)		Shortest distance between the ion-pair (Å)
	Au1–P1	Au1–Cl1	Au1–Au2	P1–Au1–Cl1	Au1–Au2–Au1a	
1A	2.2213(14)	2.2784(15)	–	176.74(6)	–	Au1···O3 3.4427(70)
1B	2.2214(14)	2.2720(15)	–	175.01(6)	–	Au1···Cl3 5.3514(22) Au1···Au2 7.1304(3)
1C	2.2199(13)	2.2816(14)	3.0831(2)	176.14(5)	180.000(5)	Au2···Cl3 7.3889(28)
2A	2.2209(7)	2.2838(7)	–	175.98(3)	–	Au1···F3 3.7012(41)
3A	2.2261(11)	2.2819(12)	–	175.26(4)	–	Au1···F5 4.9436(75)
4A	2.2268(9)	2.2761(10)	–	177.99(4)		Au1···O1 6.7506(33)
1B′	2.2218(15)	2.2826(17)	–	175.16(6)	–	Au1···Cl3 3.5449(20) Au1···Au2 3.2545(3)
1C′	2.2244(11)	2.2940(11)	3.0069(2)	172.22(4)	180.0	Au1···Cl3 4.7494(14)
$Au^{I}(PPh_3)Cl$ [21]	2.235(3)	2.279(3)	–	179.68(8)	–	–

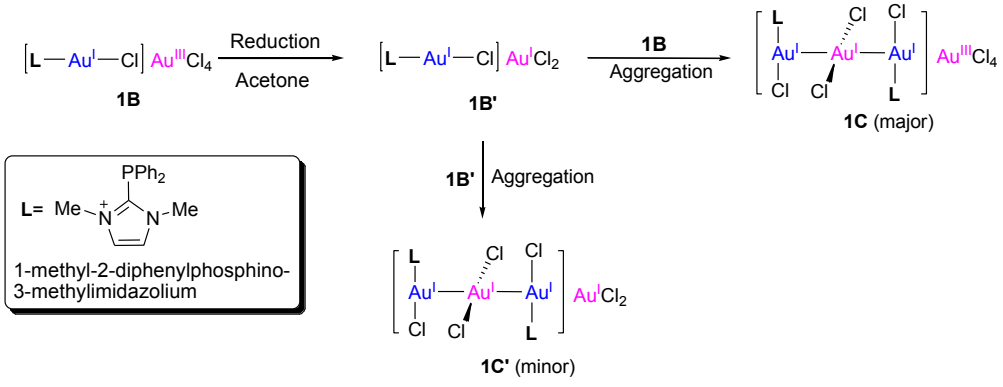
electrostatic interaction and steric preference are also crucial factors for the aggregation of the mononuclear Au(I)-complexes. As for **1A**–**4A**, the aggregation of $[L–Au–Cl]^+$ cation itself is not favored due to the repulsive electrostatic force; As for **1B**, the steric hindrance of the square-planar $AuCl_4^-$ anion with $[L–Au–Cl]^+$ cation also inhibits their aggregation. Only the aggregation between $[L–Au–Cl]^+$ cation and $AuCl_2^-$ anion (derived from reduction of $AuCl_4^-$ anion in **1B**) can lead to the formation of **1C**, due to the aurophilic Au(I)–Au(I) interaction, the electrostatic attraction, and the steric preference.

The comparative Au–P distances (2.221–2.227 Å) in the ionic Au(I)-complexes of **1A**–**1C**, **2A**–**4A**, **1B′** and **1C′** than that of $Au^{I}(PPh_3)Cl$ (2.235 Å, Table 1) indicate that the Au–P interactions in these ionic Au(I)-complexes are not weakened because of the electron-deficient nature of the phosphine-FILs of **1**–**4**. In comparison to PPh_3 as an electron-rich σ-donor, **1**–**4** in which the P(III) atoms are vicinal to the positive charge imidazoliums can mimic the behaviors of the electron-deficient ligands of phosphites, exhibiting the electron-withdrawing effect as a result of both σ-donation and π-back bonding. Resultantly, the linkages of Au–P in **1A**–**1C**, **2A**–**4A**, **1B′** and **1C′** got strengthened due to the additional π-back bonding interaction. In addition, the phosphine-FILs of **1**–**4** with the electron-deficient nature are more robust against oxidative degradation due to the delocalization of the lone-pair electrons in the P atom to the adjacent positive imidazolium ring, resulting in insensitivity to moisture and oxygen under ambient conditions. Hence, the corresponding ionic complexes of **1A**–**1C**, **2A**–**4A**, **1B′** and **1C′** ligated by **1**–**4** are also featured with moisture- and oxygen-insensitivity.

On the other hand, it is found that, as for **1A**, **1B**, **2A**, and **1B′** with the same Au(I)-complex cation, their ion-pair distances are dramatically influenced by the counteranions (Table 1). The ion-pair distance in **1B** (the shortest distance, Au1···Cl3 5.35 Å) is much longer than those in **1A** (the shortest distance, Au1···O3 3.44 Å), **2A** (the shortest distance, Au1···F3, 3.70 Å), and **1B′** (the shortest distance of Au1···Cl3, 3.54 Å). However, when the counteranion of $Au^{III}Cl_4^-$ in **1B** is replaced by $Au^{I}Cl_2^-$, the ion-pair relationship as shown in **1B′** becomes much closer (**1B**, Au1···Au2, 7.13 Å; **1B′**, Au1···Au2 3.25 Å). Reasonably, the closer ion-pair distance in **1B′** gives rise to Au(I)–Au(I) aurophilic interaction for the aggregation to the trinuclear Au(I)-complexes of **1C** and **1C′**. The similar phenomenon is observed in the cases of **1C** vs **1C′** (**1C**, Au1···Au3, 8.88 Å; **1C′**, Au1···Au3 6.38 Å). And the bulky steric hindrance of the cation impels the counteranion far away such as in the cases of **2A** vs **3A** and **1A** vs **4A**. It is supposed that not only the weak crystal packing force, but also the strong chemical interactions such as electrostatic force, aurophilic interaction, and hydrogen bonding may affect the ion-pair distance dramatically.

Catalytic performance of the ionic Au(I)-complexes for hydration of phenylacetylene

For the hydration of alkynes catalyzed by Au(I)-complexes, the involvement of the proton acid as co-catalyst has been found effective to promote the reactions [23]. Hence the inorganic acid of H_2SO_4 was used herein in considerations of the ionic compatibility with the ionic Au-complexes and the good solubility in H_2O. The insensitivity to moisture and oxygen of the ionic Au-complexes of **1A**–**1C** and **2A**–**4A** is the basic criteria for the precatalysts used in hydration of alkynes. In our experiments, the hydration of phenylacetylene was selected as a model reaction. The reaction conditions were optimized over **1A** firstly (Table 2).



Scheme 2. The proposed pathway for the formation of **1C**.

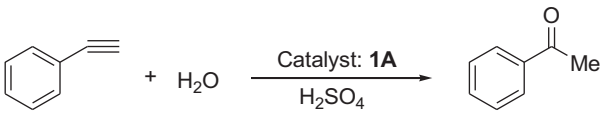
Since phenylacetylene and **1A** were insoluble in water, the co-solvent of MeOH was added to admit the accessibility of the substrates to the catalytic site. MeOH was also believed to promote hydration of alkynes through the formation of diacetal intermediate since the attack of MeOH to metalated-alkyne intermediate was faster in comparison to H_2O [9a,14]. Undoubtedly, neither **1A** nor H_2SO_4 alone was active under the applied conditions (entries 1 and 2). The involvement of H_2SO_4 as the additive was significantly important to spur the activity of **1A** (entries 3 vs 1 and 2). The indispensable role of H_2SO_4 to spur the activity of the Au(I)-catalysts was believed to cooperatively cleave the Au–Cl bond for the generation of the unsaturated $[R_3P–Au]^+$ species to accommodate phenylacetylene for transmetalation and inhibit the deactivation of the Au-catalyst [23]. The increased concentration of H_2SO_4 couldn't improve the yield of acetophenone further (entries 3 vs 4), while the prolonged reaction time from 2 h to 5 h increased the yield from 58% to 79% (entry 5). Unexceptionally, the hydration of phenylacetylene proceeded selectively according to Markovnikov's rule to afford acetophenone with 100% selectivity.

Under the selected reaction conditions (0.5 mmol H_2SO_4, 2 h, and 75 °C), the catalytic performance of **1A**–**3C** and **2A**–**4A** for hydration of phenylacetylene was investigated at the same benchmark (Table 3).

As for **1A**, **1B**, and **2A** with the same phosphino-imidazolium cations, it was found that the counteranion effect played significantly important role in tailoring the catalytic performance (Table 1). The obtained yields of acetophenone over **1A**, **1B**, and **2A** followed the order of PF_6^- > OTf^- > $AuCl_4^-$. **1B** with $AuCl_4^-$ counteranion exhibited the lowest activity with acetophenone yield of 47% (entry 2), which suggested that $AuCl_4^-$ as a gold(III)-center unit exhibit no additional contribution to the activation of phenylacetylene. Comparatively, the presence of counteranion OTf^- with the amphilicity in **1A** could accelerate the reaction rate to some extent (entry 1); whereas the presence of counteranion PF_6^- with absolute hydrophobicity in **2A** dramatically spurred the activity of the corresponding cation $[\mathbf{L}–Au^I–Cl]^+$, giving the yield of acetophenone up to 86% (entry 3). As for PF_6^-, OTf^-, and $AuCl_4^-$, the hydrophobicity is in the ranking of PF_6^- (hydrophobicity) > OTf^- (amphilicity) > $AuCl_4^-$ (hydrophilicity), which is in the same order for the observed activity of **2A** > **1A** > **1B**. Based on these results, it is supposed that the counteranions with hydrophobicity might act as the shields to besiege the hydrophobic $[\mathbf{L}–Au^I–Cl]^+$ cation through the hydrophobic pushing-force, and then protect $[\mathbf{L}–Au^I–Cl]^+$ cation (as the catalytic site) from deactivation before the coordination of the nucleophilic alkyne to $[\mathbf{L}–Au^I–Cl]^+$ for transmetallation [14]. Consequently, **2A** with the most hydrophobic PF_6^- counteranion exhibited the best activity towards hydration of phenylacetylene. Reasonably, the close ion-pair relationship of **2A** could further consolidate such shielding effect to expel water molecules out of the surroundings of $[\mathbf{L}–Au^I–Cl]^+$.

In comparison to **2A**, the increased bulky hindrance in the peripheral position of the imidazolium ring in **3A** and **4A**, led to the decreased reaction rate. Especially over **4A** with bulky benzimidazolium-substituted phosphine, the yield of acetophenone dropped to 34% (entry 5). The trinuclear Au(I)-complex of **1C** exhibited much better activity, in comparison to **1B** with the same $AuCl_4^-$ counteranion, giving 81% yield of acetophenone (entry 6). **1C** as a trinuclear Au(I)-complex was featured with the inherent catalytic nature, but not the simple adduct of two **1B**. Since when the concentration of **1C** was decreased to half (0.5 mol%), the much higher yield of acetophenone was obtained with **1C** than that with **1B** (entries 7 vs 2: yield 64% vs 47%).

Table 2
Hydration of phenylacetylene catalyzed by **1A** in conjunction of H_2SO_4[a]



Entry	Catalyst	H_2SO_4 (mmol)	Time (h)	Conv. (%)[b]	Sel. to acetophenone (%)[b]
1	–	0.5	2	0	–
2	**1A**	–	2	0	–
3	**1A**	0.5	2	56	100
4	**1A**	1.0	2	58	100
5	**1A**	1.0	5	79	100

[a] **1A** 1 mol%, phenylacetylene 1 mmol, solvent 5 mL [H_2SO_4 aqueous solution (1.0 mol/L) 0.5 mL, H_2O 1 mL, MeOH 3.5 mL], temperature 75 °C.
[b] GC analysis.

Table 3
Different Au(I,III)-complexes as the homogeneous precatalysts for hydration of phenylacetylene in conjunction of H_2SO_4.[a]

Entry	Cat	Conv. (%)[c]	Sel. to acetophenone (%)[c]
1	**1A**	56	100
2	**1B**	47	100
3	**2A**	86	100
4	**3A**	71	100
5	**4A**	34	100
6	**1C**	81	100
7[b]	**1C**	64	100

[a] Au-complex 1 mol% (0.01 mmol), phenylacetylene 1 mmol, solvent 5 mL [H_2SO_4 aqueous solution (1.0 mol/L) 0.5 mL, H_2O 1 mL, MeOH 3.5 mL], temperature 75 °C.
[b] **1C** 0.5 mol% (0.005 mmol).
[c] GC analysis.

Conclusions

A series of ionic Au(I)-complexes ligated by the phosphine-FILs were obtained and prove to be composed of the Au(I)-complex cation and the different counteranion of OTf^-, $AuCl_4^-$, or PF_6^- by the single crystal X-ray diffraction analysis. The Au(I)-centered vectors in **1A**, **1B**, **1B′**, **2A**, **3A**, and **4A** all possess the slightly twisted linear geometry in which the Au-center is coordinated by one chlorine atom and one imidazolium-based phosphine. The aggregation of **1B** with **1B′** leads to the formation of the trinuclear Au(I)-complexe of **1C**, in which the trimetalic-Au nucleus is arrayed in an ideal linear pattern. 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 the moderate to high yields of acetophenone. The catalytic performance of these ionic Au(I)-complexes can be affected by several factors including the counteranion effect, the steric hindrance of the involved phosphine, and the inherent nature of the Au-nucleus. **2A** possessing the hydrophobic anion of PF_6^- exhibited the best activity towards the activation of phenylacetylene, probably due to the protection of $[\mathbf{L}–Au^I–Cl]^+$ catalytic site by the peripheral hydrophobic PF_6^- through the hydrophobic pushing-force against the attack of water molecules. **1C** exhibited better activity due to the inherent catalytic nature of the trimetalic-Au nucleus, but not the result of the simple adduct of **1B**.

Experimental section

Reagents and analysis

The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. And Alfa Aesar China, and used as

received. ^{1}H NMR spectra and ^{31}P NMR spectra (with 75% H_3PO_4 sealed in a capillary tube as internal standard) were recorded on a Bruker Avance 500 spectrometer at 298 K. Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a RTx-Wax capillary column (30 m × 0.25 mm × 0.25 μm). GC–mass spectrometry (GC–MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector.

Synthesis

*1-Methyl-2-diphenylphosphino-3-methylimidazolium triflate (**1**)*

Under N_2 atmosphere, to a solution of 1-methylimidazole (2.055 g, 25 mmol) in 80 mL dry THF cooled to −78 °C, *n*-BuLi (1.6 M, in hexane, 16 mL, 25 mmol) was added dropwise. Chlorodiphenylphosphine (5.73 g, 25 mmol) was added dropwise after the mixture stirred for 1 h. The suspension stirred for another 1 h and then warmed to room temperature slowly, the mixture stirred continuously for another 2 h. After quenching excess *n*-BuLi with a small amount of deionized water, THF was removed on a rotary evaporator to obtain yellow mixture, which was dissolved in 5 mL diethyl ether. The obtained ether solution was repeatedly washed with deionized water, and then purified through silica gel column chromatography with eluent of petroleum ether/ethyl acetate (PE:EA = 1:3) to afford 1-methyl-2-diphenylphosphinoimidazole as the white solids (5.3 g, yield 80 wt%). Then the obtained solids (1.5 g, 5.7 mmol) dissolved in 35 mL dry CH_2Cl_2 were cooled down under N_2 atmosphere to −78 °C, which was treated with methyl triflate (1.0 g, 6.3 mmol). The reaction mixture was stirred vigorously at −78 °C for 1 h and then warmed up to ambient. After removed the solvent under vacuum, the obtained residue was recrystallized from $CH_3COOCH_2CH_3/Et_2O$ to yield **1** as the white solids (2.2 g, yield 90 wt%). ^{1}H NMR (*δ*, ppm, chloroform-*d*): 7.81 (s, 2H, NC*H*C*H*N), 7.52–7.50 (m, 6H, P*Ph*$_2$), 7.36–7.33(m, 4H, P*Ph*$_2$), 3.70 (s, 6H, 2NC*H*$_3$), ^{31}P NMR (*δ*, ppm, chloroform-*d*): −25.59 (s, *P*Ph$_2$).

*1-Methyl-2-diphenylphosphino-3-methylimidazolium hexafluorophosphate (**2**)*

Under N_2 atmosphere, iodomethane (3.9 g, 27.5 mmol) was added dropwise to a solution of 1-methylimidazole (2.1 g, 25 mmol) in 20 mL dry THF, there were a large amount of white solid precipitated after the mixture stirred in 30 °C oil bath for 2 h. After removal of the solvent under vacuum, the obtained residue dissolved in 20 mL deionized water with ammonium hexafluorophosphate (6.1 g, 37.5 mmol) added. 1-Methyl-3-methylimidazolium hexafluorophosphate was obtained after 2 h with the mixture was extracted with dichloromethane (6 mL × 3) and then stripped of dichloromethane under vacuum. The phosphine-FIL of 1-methyl-2-diphenylphosphino-3-methylimidazolium trifluoromethanesulfonate (**2**) was prepared according to the published methods [18] with some modifications. ^{1}H NMR (*δ*, ppm, chloroform-*d*): 7.59 (s, 2H, NC*H*C*H*N), 7.50–7.48 (m, 6H, P*Ph*$_2$), 7.36–7.32(m, 4H, P*Ph*$_2$), 3.64 (s, 6H, 2NC*H*$_3$), ^{31}P NMR (*δ*, ppm, chloroform-*d*): −25.50 (s, *P*Ph$_2$), −144.23 (sept, *P*F_6^-).

*1-Butyl-2-diphenylphosphino-3-methylimidazolium hexafluorophosphate (**3**)*

The phosphine-FIL of 1-butyl-2-diphenylphosphino-3-methylimidazolium hexafluorophosphate (**3**) was prepared according to the published methods [18].

*1-Butyl-2-diphenylphosphino-3-methylbenzo[d]imidazolium triflate (**4**)*

Under N_2 atmosphere, to a solution of 1-butyl-benzimidazole (8.6 g, 49.4 mmol) in 50 mL dry THF cooled to −78 °C was added *n*-BuLi (1.6 M in hexane, 37.0 mL, 59.3 mmol) dropwise. After stirring the mixture for 1 h, chlorodiphenylphosphine (13.0 g, 59.3 mmol) was added dropwise subsequently. The resultant mixture was stirred for another 1 h at −78 °C and then warmed up to ambient. After quenching excess *n*-BuLi with deionized water, the solvent of oily mixture was removed in vacuo. The obtained residue was purified by silica gel column chromatography with eluent of PE:EA = 8:1 to give 1-butyl-2-(diphenylphosphino)-benzimidazole as the white solids (10.27 g, yield 58 wt%). ^{1}H NMR (*δ*, ppm, acetone-d_6): 7.62 (d, 1H, *J* = 8 Hz, H$_{Ar}$), 7.59–7.53 (m, 5H, H$_{Ar}$), 7.39–7.36 (m, 6H, H$_{Ar}$), 7.27–7.18(m, 2H, H$_{Ar}$), 4.45–4.41 (t, 2H, *J* = 7.5 Hz, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.66–1.60 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.28–1.23 (m, 2H CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.81–0.78 (t, 3H, *J* = 7.5 Hz, CH$_2$CH$_2$CH$_2$C*H*$_3$).

Under N_2 atmosphere, to a solution of 1-butyl-2-(diphenylphosphino)-benzimidazole (1.29 g, 3.6 mmol) in dry CH_2Cl_2 (40 mL) cooled to −78 °C was added methyl triflate (0.62 g, 3.8 mmol). The solution was stirred with the reaction temperature increasing from −78 °C to ambient, and then stirred continuously at room temperature for another 2 h. After removal of the solvent under vacuum, the residue was washed with diethyl ether (10 mL × 3) to afford the white powder as the product of **2** (1.84 g, yield 98 wt%). ^{1}H NMR (*δ*, ppm, acetone-d_6): 8.17–8.14(m, 1H, H$_{Ar}$), 8.07–8.05 (m, 1H, H$_{Ar}$), 7.82–7.77 (m, 2H, H$_{Ar}$), 7.71–7.58 (m, 10H, H$_{Ar}$), 4.81–4.76 (t, 2H, *J* = 8 Hz, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.94 (s, 3H, NC*H*$_3$), 1.69–1.62 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.30–1.28 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.81–0.77 (t, 3H, *J* = 7.5 Hz, CH$_2$CH$_2$CH$_2$C*H*$_3$) ppm. ^{31}P NMR (*δ*, ppm, acetone-d_6): −20.4 (s, *P*Ph$_2$).

*(1-Methyl-2-diphenylphosphino-3-methylimidazolium)-chlorogold(I) triflate (**1A**)*

[Au^I(tht)Cl] was prepared according to the published methods [24]. 1-Methyl-2-diphenylphosphino-3-methylimidazolium triflate (430.4 mg, 1 mmol) was slowly added to a stirring solution of [Au^I(tht)Cl] (320.6 mg 1 mmol) in 10 mL of distilled dichloromethane, which was stirred at room temperature for adding 15 min. The solution was still colorless and then concentrated to 1 mL and 10 mL ether was added resulting in white precipitate. The solid was then filtrated, washed with ether (5 mL × 3), and dried under vacuum. Yield: 656.1 mg (98 wt%). The crystals of **1A** suitable for the single crystal X-ray diffraction analysis were obtained by recrystalization from an acetone-dichloromethane solution layered with *n*-hexane. ^{1}H NMR (*δ*, ppm, chloroform-*d*): 8.01–7.96 (4H, m, P*Ph*$_2$), 7.77–7.70(8H, m, P*Ph*$_2$, NC*H*C*H*N), 3.59 (6H, s, 2NC*H*$_3$). ^{31}P NMR (*δ*, ppm, chloroform-*d*): 20.32 (s, *P*Ph$_2$). CHN-elemental analysis found for **1A** (%): C 32.64, H 2.71, N 3.96 (Calcd., C 32.62, H 2.74, N 4.23).

*(1-Methyl-2-diphenylphosphino-3-methylimidazolium)-chlorogold(I) tetrachloroaurate (**1B**)*

1B was prepared by ion exchange for **1A** (132.6 mg 0.2 mmol) with chloroauric acid (82.4 mg 0.2 mmol) in 10 mL of dry dichloromethane. The obtained salmon pink solution after being concentrated to 1 mL was treated with 10 mL diethyl to precipitate the yellow solids. The yellow solids were collected with yield of 93 wt% (158.6 mg), after washing with diethyl ether (5 mL × 3) and drying under vacuum. The single crystals of **1B** suitable for the single crystal X-ray diffraction analysis were obtained from an acetonitrile-dichloromethane solution layered with dry diethyl ether. ^{1}H NMR (*δ*, ppm, methylene chloride-d_2): 7.97–7.92 (4H, m, P*Ph*$_2$), 7.84–7.83 (2H, m, P*Ph*$_2$), 7.78–7.75 (4H, m, P*Ph*$_2$), 7.65 (2H, s, NC*H*C*H*N), 3.61 (6H, s, 2NC*H*$_3$), ^{31}P NMR (*δ*, ppm, methylene chloride-d_2): 21.49 (s, *P*Ph$_2$). CHN-elemental analysis found for **1B** (%): C 23.93, H 2.08, N 3.05 (Calcd., C 23.95, H 2.13, N 3.29).

*[Au^{I}(**L**)Cl–AuCl$_2$–Au(L)Cl]AuCl$_4$ (**L** = 1-methyl-2-diphenylphosphino-3-methylimidazolium, **1C**)*

The yellow and clear solution of **1B** (103.5 mg, 0.12 mmol) in 4 mL of acetone was stirred vigorously for 72 h at room temperature and then concentrated to 1 mL. After addition of 15 mL dry diethyl ether to the concentrated solution, the orange solids were precipitated and then collected after washing with *n*-hexane and dryness in vacuo, with the yield of 78 wt% (76.8 mg). The crystals of **1C** were obtained by recrystallization from acetone-hexane. ^{1}H NMR (δ, ppm, acetonitrile-d_3): 7.87–7.81 (6H, m, P*Ph*$_2$), 7.74–7.70 (4H, m, P*Ph*$_2$), 7.60 (2H, s, NC*HCH*N), 3.51 (6H, s, 2NC*H*$_3$); ^{31}P NMR (δ, ppm, acetonitrile-d_3): 20.49 (s, *P*Ph$_2$). CHN-elemental analysis found for **1C** (%): C 24.26, H 2.08, N 2.96 (Calcd., C 24.99, H 2.22, N 3.43).

*(1-Methyl-2-diphenylphosphino-3-methylimidazolium)-chlorogold(I) hexafluorophosphate (**2A**)*

To a solution of [Au^{I}(tht)Cl] (320.6 mg, 1 mmol) in 10 mL dry dichloromethane was added slowly the phosphine-FIL of **2** (426.4 mg, 1 mmol). The obtained mixture was stirred vigorously at room temperature for another 15 min to afford the colorless solution, which was concentrated under vacuum to 1 mL. Then 10 mL diethyl ether was added into the above concentrated solution to precipitate the white solids, which was collected after washing with diethyl ether (5 mL × 3) and dryness under vacuum to give **2A** with the yield of 95 wt% (625.3 mg). The crystals of **2A** suitable for the single crystal X-ray diffraction analysis were obtained by recrystalization from an acetone-dichloromethane solution layered with *n*-hexane. ^{1}H NMR (δ, ppm, chloroform-*d*): 8.01–7.96 (4H, m, P*Ph*$_2$), 7.77–7.70 (8H, m, P*Ph*$_2$, NC*HCH*N), 3.59 (6H, s, 2NC*H*$_3$). ^{31}P NMR (δ, ppm, chloroform-*d*): 20.32 (s, *P*Ph$_2$), −143.52 (sept, *P*F$_6^-$). CHN-elemental analysis found for **2A** (%): C 30.90, H 2.74, N 3.89 (Calcd., C 31.00, H 2.75, N 4.25).

*(1-Methyl-2-diphenylphosphino-3-butylimidazolium)-chlorogold(I) hexafluorophosphate (**3A**)*

To a solution of [Au^{I}(tht)Cl] (320.6 mg, 1 mmol) in 10 mL dry dichloromethane was added slowly the phosphine-FIL of **3** (468.4 mg, 1 mmol). The obtained mixture was stirred vigorously at room temperature for another 15 min to afford the colorless solution, which was concentrated under vacuum to 1 mL. Then 10 mL diethyl ether was added into the above concentrated solution to precipitate the white solids, which was collected after washing with diethyl ether (5 mL × 3) and dryness under vacuum to give **3A** with the yield of 93 wt% (651.8 mg). The crystals of **3A** suitable for the single crystal X-ray diffraction analysis were obtained by recrystalization from an acetone solution layered with *n*-hexane. ^{1}H NMR (δ, ppm, acetonitrile-d_3): 7.89–7.84 (6H, m, P*Ph*$_2$), 7.76–7.73 (4H, m, P*Ph*$_2$), 7.74 (1H, s, NCHC*H*N), 7.64 (1H, s, NC*H*CHN), 4.06–4.03 (2H, t, J = 8.0 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$), 3.42 (3H, s, NC*H*$_3$), 1.71–1.65 (2H, m, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.15–1.10 (2H, m, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.84–0.81 (3H, t, J = 7.4 Hz, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{31}P NMR (δ, ppm, acetonitrile-d_3): 20.00 (s, *P*Ph$_2$), −143.11 (sept, *P*F$_6^-$). CHN-elemental analysis found for **3A** (%): C 34.35, H 3.39, N 3.69 (Calcd., C 34.28, H 3.45, N 4.00).

*(1-Butyl-2-diphenylphosphino-3-methylbenzoimidazolium)-chlorogold(I) triflate (**4A**)*

To a solution of [Au^{I}(tht)Cl] (320.6 mg, 1 mmol) in 10 mL dry dichloromethane was added slowly the phosphine-FIL of **4** (522.5 mg, 1 mmol). The obtained mixture was stirred vigorously at room temperature for another 15 min to afford the colorless solution, which was concentrated under vacuum to 1 mL. Then 10 mL diethyl ether was added into the above concentrated solution to precipitate the white solids, which was collected after

Table 4
Crystal data and structure refinement for **1A**, **1B**, **1C**, **2A**, **3A**, **4A**, **1B′**, and **1C′**.

	1A	**1B**·CH$_3$CN	**1C**	**2A**	**3A**	**4A**	**1B′**·0.5CH$_3$Cl	**1C′**
Empirical formula	[C$_{17}$H$_{18}$Au$_1$Cl$_1$N$_2$P$_1$][C$_1$F$_3$O$_3$S$_1$]	[C$_{17}$H$_{18}$Au$_1$Cl$_1$N$_2$P$_1$][Au$_1$Cl$_4$]·(C$_2$H$_3$N$_1$)	[C$_{34}$H$_{36}$Au$_3$Cl$_4$N$_4$P$_2$][Au$_1$Cl$_4$]	[C$_{17}$H$_{18}$Au$_1$Cl$_1$N$_2$P$_1$][F$_6$P$_1$]	[C$_{20}$H$_{24}$Au$_1$Cl$_1$N$_2$P$_1$][F$_6$P$_1$]	[C$_{24}$H$_{26}$Au$_1$Cl$_1$N$_2$P$_1$][C$_1$F$_3$O$_3$S$_1$]	[C$_{17}$H$_{18}$Au$_1$Cl$_1$N$_2$P$_1$][Au$_1$Cl$_2$]·0.5(C$_1$H$_3$Cl$_1$)	[C$_{34}$H$_{36}$Au$_3$Cl$_4$N$_4$P$_2$][Au$_1$Cl$_2$]
Formula weight	662.79	890.54	1634.08	658.69	700.77	754.94	806.85	1563.18
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P-1	P2(1)/n	P2(1)/n	P-1	P-1	P2(1)/n	P2(1)/c
a (Å)	13.1955(7)	7.6902(2)	9.8860(4)	13.0608(5)	9.6409(2)	9.5376(3)	11.0380(4)	15.9095(7)
b (Å)	11.1755(6)	8.7947(2)	16.5441(6)	11.1338(4)	10.2757(2)	11.0636(4)	17.8015(7)	12.8943(6)
c (Å)	15.5179(8)	19.9277(6)	13.9541(5)	15.1950(5)	13.6711(3)	13.8655(5)	11.5603(4)	9.9998(5)
α (°)	90	85.3500(10)	90	90	72.6770(10)	75.1930(10)	90	90
β (°)	105.346(2)	89.6860(10)	92.8200(10)	103.3270(10)	69.8350(10)	77.8470(10)	96.2530(10)	90.1720(10)
γ (°)	90	77.7360(10)	90	90	85.0800(10)	86.6220(10)	90	90
V (Å^3)	2206.8(2)	1312.58(6)	2279.50(15)	2150.10(13)	1213.46(4)	1382.78(8)	2258.00(14)	2051.37(17)
Z	4	2	2	4	2	2	4	2
d_{calc} (g cm^{-3})	1.995	2.253	2.381	2.035	1.918	1.813	2.369	2.531
μ (Mo-Kα) (mm^{-1})	7.002	11.746	13.401	7.172	6.361	5.600	13.469	14.759
T (K)	296(2)	296(2)	173(2)	296(2)	173(2)	296(2)	296(2)	296(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Total reflections	25,013	15,250	26,119	24,293	14,118	16,137	25,641	23,318
Unique reflections (R_{int})	3865 (0.0228)	4574 (0.0330)	4013 (0.0401)	3775 (0.0243)	4231 (0.0210)	4848 (0.0197)	3935 (0.0409)	3596 (0.0357)
R_1 [$I > 2\sigma(I)$]	0.0309	0.0303	0.0242	0.0170	0.0250	0.0223	0.0284	0.0202
wR_2 (all data)	0.0816	0.0826	0.0570	0.0426	0.0709	0.0612	0.0770	0.0475
F(000)	1272	822	1500	1256	676	736	1478	1432
Goodness-of-fit on F^2	1.052	1.065	1.071	1.065	1.060	1.098	1.072	1.021

washing with diethyl ether (5 mL × 3) and dryness under vacuum to give **4A** with the yield of 86 wt% (649.3 mg). The crystals of **4A** suitable for the single crystal X-ray diffraction analysis were obtained by recrystalization from a saturated methanol solution. ^{1}H NMR (δ, ppm, chloroform-*d*): 8.27–8.25 (4H, d, J = 8 Hz, benzimidazole), 7.80–7.76 (10H, m, PPh_2), 3.76–3.71 (5H, m, NCH_3, NCH_2), 1.68 (2H, br, NCH$_2$CH_2), 1.28–1.25 (5H, m, CH_2CH_3). ^{31}P NMR (δ, ppm, acetone-d_6): 93.13 (s, *P*Ph$_2$). CHN-elemental analysis found for **4A** (%): C 39.73, H 3.44, N 3.39 (Calcd., C 39.77, H 3.47, N 3.71).

General procedures for the hydration of phenylacetylene catalyzed by the ionic Au(I) complexes

In a typical procedure, phenylacetylene (1 mmol), H_2SO_4 aqueous solution (0.5 mL, 1.0 mol/L), MeOH (3.5 mL), the isolated crystalline Au-complex precatalyst (0.01 mmol), and the distilled water (1 mL) were added sequentially to a safe glass pressure reactor. The mixture was heated in oil bath at 75 °C for 2 h. Upon completion, the reaction mixture was cooled to room temperature and then filtered. The combined filtrate after washing the residue with MeOH (2 mL × 3) was analyzed by GC to determine the yield of the product (1-dodecane as the internal standard). The structures of obtained products were further confirmed by GC–Mass.

X-ray crystallography

Intensity data were collected at 298 K on a Bruker SMARTAPEX II diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data reduction included absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by fullmatrix least-squares using SHELXS-97 (Sheldrick, 1990), with all non-hydrogen atoms refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically. The crystal data and refinement details are given in Table 4.

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Appendix A. Supplementary material

CCDC 961119, 961120, 961121, 961122, 961123, 961124, 961125, and 961126 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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