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Amphiphilic Zwitterionic phosphine based Au(I)-complex as efficient and recyclable catalyst for hydration of alkynes free of additional additives



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Xia Chen^a, Xu Ye^a, Wen-Yu Liang^a, Qing Zhou^a, Giang Vo-Thanh^b, Ye Liu^{a,*}

^a Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, PR China

^b UMR 8182, Bat. 420, Université Paris-Sud 11, Orsay Cedex, France

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ABSTRACT

The unique amphiphilic Zwitterionic P,O-hybrid ligand (L1) containing phosphino-fragment and $-SO_3^-$ group was synthesized and firstly applied in Au-catalyzed hydration of alkynes. Without the aid of any auxiliary additive such as acid or silver salt, L1-based Au-catalyst exhibited excellent activity towards hydration of alkynes to yield ketones with 100% selectivity according to Markovnikov's rule. On the other hand, L1-based Au-catalyst could be recycled for 4 runs in room temperature ionic liquid of [Bmim]PF₆ without obvious activity loss, and also exhibited wide generality to the hydration of different alkynes.

1. Introduction

The hydration of terminal alkynes which is the nucleophilic addition of water to alkynes following Markovnikov's rule to generate the ketones represents an environmentally benign route to form carbonyl compounds because of water as reagent [1,2]. Acid-catalyzed hydration of electron rich alkynes such as alkynyl ethers and alkynyl thioethers has been well known to carry out satisfactorily [3-6]. However, the hydration of simple alkynes is quite sluggish and need toxic mercury(II) salts as co-catalysts along with the strong acids to improve the reaction rate [1,2,7-11]. More recent attentions have been focused on Au-catalyzed hydration of simple alkynes, due to the unique alkynophilicity of Au-complex catalyst with π -acidity [2,12,13] and the environmentally begin consciousness by replacing the uses of highly toxic mercury(II) salts [14-17]. Typically, an Au(I)-complex with the linear configuration is diagonally coordinated by one phosphine or carbene (L) and one halide ($X^- = Cl^-$ or Br^-) in the form of L-Au⁺-X⁻. In order to cleave Au(I)-X⁻ bond to expose Au⁺-center to activate the alkynes, the silver salts and/or strong acids have to be added additionally [17–19], which greatly sacrificed the merits of this green hydration. Hence, many efforts have been made to develop the Au(I)-catalysts which are coordinated by the weak anionic ligands such as $\rm NTf_2^-, \, OTf^-, \, TFA^-$ in place of X⁻ to eliminate the use of auxiliary additives such as silver salts and/or strong Bronsted acids [20-26]. For example, Corma [20] reported several (R_3P)Au^INTf₂ complexes (R_3P = SPhos, PPh₃, P^tBu₃) as the active catalysts for the hydration of a wide range of alkynes to the corresponding ketones. Gatto [21] developed a series of carbene-ligated

Au(I)-complexes [(NHC)Au⁺X, $X = BArF^{-}$ (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), BF4⁻, SbF6⁻, OTf⁻, NTf2⁻, ClO4⁻, OTs⁻, TFA⁻] for the efficient hydration free of silver salts and acids. However, in the preparation of such kinds of Au(I)-complex catalysts, the silver salts or strong Bronsted acids were still required without exception [20-22]. Encouragingly, Xu [26] made an advance to develop a unique acid- and silver-free catalytic system of (CyNC)Au^ICl/KB $(C_6F_5)_4$ for hydration. And Schmidbaur [27] discovered that carboxylate- and sulfonate-related Au(I)-complexes enabled the efficient hydration with the presence of Lewis acidic BF3·Et2O completely without the track of any silver salt. But to the best of our knowledge, a complete silver- and (Lewis/Bronsted) acid-free Au(I)-catalyzed hydration under mild conditions is still lacking in the literature. On the other hand, due to the strict requirements to the Au(I)-catalysts in terms of hydrophilicity as well good stability, the recycling uses of the corresponding Au(I)-catalysts has been rarely reported. The homogenous acid- and silver-free (NHC)AuOTf catalyst reported by Belanzoni [21] was the only example so far that was recyclable under the solvent-free condition. And Carriedo [28] and Li [29] respectively reported the porous organic polymer-supported NHC-Au heterogeneous catalysts.

It was believed that the uses of the poorly coordinated counter anions instead of X^- can render the corresponding Au(I)-complexes more activity towards hydration free of additives, due to the facilely exposed Au⁺-center to activate alkynes for the subsequent addition of H₂O molecules. In addition, Au⁺-center has to be coordinated by a proper ligand like phosphine or carbene in order to prevent Au-catalyst against deactivation. So we are inspired to develop a hybrid P,O-ligand

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

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^{*} Corresponding author.

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containing one hard (O-) donor and one soft (P-) donor with flexible ligations to Au^+ -center, in which the O-donor with weak coordinating ability can reversibly release during the catalytic cycle providing the unsaturation site at the metal center as widely reported before [27,30–35].

In this paper, we succeeded in developing an amphiphilic Zwitterionic P,O-hybrid ligand (L1) containing phosphino-fragment and $-SO_3^-$ group. Without the addition of any auxiliary additive such as acid or silver salt, L1-based Au-catalyst exhibited excellent activity towards hydration of alkynes to yield ketones. In addition, as an ionic phosphine, L1 based Au-catalyst in combination of the room temperature ionic liquid (RTIL) as the reaction medium could be easily recovered and recycled for 5 runs. This method has been accepted as an efficient alternative to immobilize the transition metal catalysts for recovery and recycling in green chemistry [36–40].

2. Experimental

2.1. Reagents and analysis

The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and Alfa Aesar China, which were used as received. The solvents were distilled and dried before use. The ¹H and ³¹P NMR spectra (85% H₃PO₄ sealed in a capillary tube as an internal standard) were recorded on a Bruker ARX 500 spectrometer at ambient temperature. Gas chromatography (GC) was performed on a SHIMAwith a DM-Wax DZU-2014 equipped capillary column $(30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ \mum})$. GC-mass spectrometry (GC-MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. The amount of Au and P in the sample was quantified by using an inductively coupled plasma optical emission spectrometer (ICP-OES) on an Optima 8300 instrument (the detection limit of $0.1 \,\mu g/g$).

2.2. Synthesis

2.2.1. Synthesis of L1 ligand

In N₂ atmosphere, the solution of Xantphos (1.73 g, 3.0 mmol) in 40 mL of dry toluene (refluxed with sodium and distilled freshly before use) was treated with 1,3-propanesultone (0.40 g, 3.3 mmol). The obtained mixture solution was stirred vigorously for 12 h at 70 °C. Then the white precipitates were formed gradually. The precipitates were collected after filtration and then washed with diethyl ether to give a white solid as the product of L1 (1.89 g, yield 90%). ¹H NMR (δ , 500 MHz, CD₂Cl₂): 7.93 (d, *J* = 7.5 Hz, 1H), 7.73-7.67 (m, 6H), 7.57-7.52 (m, 5H), 7.36-7.33 (m, 2H), 7.30-7.23 (m, 5H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.91(t, *J* = 7.5 Hz, 4H), 6.77 (br, s, 1H), 6.63-6.60 (m, 1H), 4.03-3.97 (m, 2H), 2.52-2.50 (m, 2H), 2.17-2.15 (m, 2H), 1.75 (s, 6H). ³¹P NMR (δ , 500 MHz, CD₂Cl₂): 26.38, -21.21. FT-IR (ν , KBr pellet, cm⁻¹): 3060 (w), 2977 (w), 1436 (s), 1402 (vs), 1225 (vs), 1124 (s), 1111 (s), 1039 (s), 696 (m). CHN-elemental analysis found for L1 (C₄₂H₃₈O₄P₂S₁, %): C 72.12, H 2.59 (Calcd., C 71.99, H 5.47).

2.2.2. Synthesis of L2 ligand

In N₂ atmosphere, the solution of Xantphos (1.74 g, 3.0 mmol) in 100 mL dry diethyl ether was treated with MeOTf (methyl trifluoromethanesulphonate, 0.54 g, 3.3 mmol). The obtained mixture solution was stirred vigorously for 3 h at -50 °C. Then the white precipitates were formed gradually. The precipitates were collected after filtration to give a white solid as the product of **L2** (2.0 g, yield 90%). ¹H NMR (δ , 500 MHz, CDCl₃): 7.92 (d, J = 8.0 Hz, 1H), 7.70-7.68 (m, 2H), 7.60–7.58 (m, 8H), 7.50 (d, J = 9.5 Hz, 1H), 7.34–7.25 (m, 7H), 7.07 (t, J = 8.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 4H), 6.77–6.72 (m, 1H), 6.60–6.58 (m, 1H), 2.89 (d, J = 14.0 Hz, 3H), 1.75 (s, 6H). ³¹P NMR (δ , 500 MHz, CDCl₃): 22.22, -21.02. CHN-elemental analysis found for **L2**

(C₄₀H₃₅O₁P₂, %): C 81.12, H 6.13 (Calcd., C 80.93, H 5.94).

2.2.3. Synthesis of L3 ligand

L3 were prepared according to the literature methods [41].

2.2.4. Synthesis of Au-L1 complex

In N₂ atmosphere, **L1** (0.35 g, 0.5 mmol) dissolved in dry dichloromethane (20 mL) was added to a solution of AuCl(THT) (0.18 g, 0.55 mmol) in dry dichloromethane (3 mL). The mixture was stirred vigorously at room temperature for 4 h. Then diethyl ether was added to the mixture solution to precipitate the white solids, which were collected after washing by diethyl ether, and then dried under vacuum as the product of **Au-L1** (0.41 g, yield 90%). ¹H NMR (δ , 500 MHz, CD₂Cl₂): 7.93 (d, J = 7.5 Hz, 1H), 7.73–7.67 (m, 6H), 7.57–7.52 (m, 5H), 7.36–7.33 (m, 2H), 7.30–7.23 (m, 5H), 7.09 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 7.5 Hz, 4H), 6.77 (br, s, 1H), 6.63–6.60 (m, 1H), 4.03–3.97 (m, 2H), 2.52–2.50 (m, 2H), 2.17–2.15 (m, 2H), 1.75 (s, 6H). ³¹P NMR (δ , 500 MHz, CDCl₃): 28.35, 23.51. FT-IR (ν , KBr pellet, cm⁻¹): 3070 (w), 2975 (w), 1436 (s), 1402 (s), 1216 (vs), 1109 (s), 1099 (s), 1039 (s), 694 (m). CHN-elemental analysis found for **Au-L1** (C₄₂H₃₈Au₁Cl₁O₄P₂S₁, %): C 54.18, H 4.22 (Calcd., C 54.06, H 4.10).

2.3. X-ray crystallography

Intensity data were collected at 296(2) K for Au-L1 on a Bruker SMARTAPEX II diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Data reduction included absorption corrections by the multi-scan method (Table 1). The structures were solved by direct methods and refined by full matrix 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.

2.4. General procedures for hydration of alkyne

In a typical experiment, phenylacetylene (1 mmol, or the other alkyne), 3 mL MeOH, deionized water (1 mL), AuCl(THT) (0.005 mmol) and L1 (0.025 mmol) (or the other ligand) were sequentially added in a safe glass pressure reactor. The obtained mixture was heated in oil bath at 120 °C for 3 h. Upon completion, the reaction mixture was cooled to room temperature. The solution was analyzed by GC to determine the conversions (*n*-dodecane as internal standard) and the selectivities

Table 1

The crystal data and structure refinement for Au-L1.

	Au-L1
Empirical formula	$\mathrm{C}_{42}\mathrm{H}_{38}\mathrm{Au}_{1}\mathrm{Cl}_{1}\mathrm{O}_{4}\mathrm{P}_{2}\mathrm{S}_{1}$
Formula weight	933.14
Crystal system	Monoclinic
Space group	P2(1)/n
a (Å)	14.2090(6)
b (Å)	16.7516(7)
c (Å)	22.8631(9)
α (°)	90
β (°)	101.6170(10)
λ (°)	90
V (Å ³)	5330.5(4)
Ζ	4
$d_{\rm calc} ({\rm gcm^{-3}})$	1.163
μ (Mo-K α) (mm ⁻¹)	2.939
<i>T</i> (K)	296(2)
λ	0.71073
Total reflections	61129
Unique reflections (R _{int})	0.0440
$R_1 [I > 2\sigma(I)]$	0.0262
wR_2 (all data)	0.0672
F(000)	1856
Goodness-of-fit on F^2	1.070

Table 2

Au-catalyzed hydration of phenylacetylene under different conditions^a.



Entry	Catalyst precursor	Ligand	Additive	P/Au ^b	Temp. (°C)	Conv. (%) ^c	Sel. (%) ^d	TON
1	AuCl(THT)	L1	-	1/1	100	29	100	58
2	AuCl(THT)	L1	-	3/1	100	60	100	120
3	AuCl(THT)	L1	-	5/1	100	75	100	150
4	AuCl(THT)	L1	-	6/1	100	48	100	96
5	AuCl(THT)	L1	-	5/1	120	97	100	194
6	AuCl(THT)	L1	-	5/1	80	30	100	60
7 ^e	AuCl(THT)	L1	-	5/1	80	95	100	190
8	AuCl(THT)	L1	AgOTf	5/1	120	< 5	-	-
9	AuCl(THT)	L1	AgOTf	5/1	80	21	100	42
10 ^e	AuCl(THT)	L1	AgOTf	5/1	80	23	100	46
11	Au-L1	-	-	1/1	100	30	100	60
12	AuCl(THT)	Xantphos	-	5/1	120	-	-	-
13	AuCl(THT)	L2	-	5/1	120	28	100	56
14	AuCl(THT)	L3	-	5/1	120	-	-	-
15	AuCl(THT)	L2	n-C ₈ H ₁₇ SO ₃ Na	5/1	120	35	100	70
16 ^f	AuCl(THT)	L1	-	5/1	120	50	100	100

^a AuCl(THT) 0.005 mmol (0.5 mol%), phenylacetylene 1 mmol, H₂O 1 mL, AgOTf (if required) 0.005 mmol, MeOH 3 mL, time 3 h.

^b P/Au representing the molar ratio of phosphino-fragment to Au.

^c Determined by GC with *n*-dodecane as internal standard.

^d Determined by GC with normalization method which was calibrated by the commercial sample of acetophenone.

^e 24 h.

f TBAF 0.025 mmol.



Scheme 1. The structures of Au(I)-complexes ligated by Xantphos and L1.

(normalization method), and the products were further identified by GC–MS spectrometry.

2.5. Protocols for the catalyst recycling experiments in $[Bmim]PF_6$

In the course of the recycling experiments, the room temperature IL of $[Bmim]PF_6$ was selected the co-solvent besides of MeOH. In the first run (with the fresh catalyst), $[Bmim]PF_6$ (3 mL) was mixed with MeOH (3 mL), deionized water (1 mL), phenylacetylene (1 mmol), AuCl(THT)



Fig. 1. The single crystal structure of Au-L1 (H-atoms and the solvent molecules were omitted for clarity). Selected bond distances (Å) and bond angles (°): Au-L1, Au1-P1 2.2343(8); Au1-Cl1 2.2855(9); P1-Au1-Cl1 174.61(3).

(0.005 mmol), and L1 (0.025 mmol) sequentially to form a homogenous reaction solution. Upon completion at the appointed conditions, the reaction solution was treated with diethyl ether ($3 \text{ mL} \times 3$) to completely extract the reactants and products out of the IL phase. The combined organic phase was analyzed by GC and ICP-OES analyses. The lower phase containing [Bmim]PF₆, MeOH and water was directly used without further treatment for the next run. Due to the partial loss of MeOH and water into the organic phase during the extraction, in the 3rd and 5th runs, 1 mL of MeOH and 0.5 mL of the deionized water were added additionally.



Scheme 2. The proposed catalytic mechanism over Au-L1 for hydration of phenylacetylene.

Table 3 The recycling uses of L1-based Au-catalyst for hydration of phenylacetylene.

Run	Ligand	RTIL	Conv. (%) ^b	Sel. (%) ^b	TON ^c	Accumulative TON
1 ^a	L1	[Bmim]PF ₆	99	100	198	940
2	-	-	94	100	184	
3 ^d	-	-	96	100	192	
4	-	-	96	100	192	
5 ^d	-	-	87	100	174	

^a AuCl(THT) 0.005 mmol, P/Au = 5/1 (molar ratio), phenylacetylene 1 mmol, H₂O 1 mL, MeOH 3 mL, [Bmim]PF₆ 3 mL, time 3 h, temperature 120 °C.

^b Determined by GC with *n*-dodecane as internal standard.

^c TON, turn over mumber in 3 h in each run.

 $^{\rm d}$ 1 mL MeOH and 0.5 mL deionized water were added additionally.

3. Results and discussion

The catalytic performance of L1-based Au-catalyst was investigated free of any auxiliary additives with hydration of phenylacetylene as a model reaction (Table 2). Since phenylacetylene and Au-L1 were highly polar and insoluble in water, the solvent of MeOH was added to admit the accessibility of the substrates to the catalytic site. In addition, MeOH with more nucleophilicity was believed to be able to promote hydration of alkynes due to its faster attack to the metalated-alkyne intermediate than that of H₂O [20]. Obviously the molar ratio of P/Au dramatically influenced the reaction rate. The best molar ratio of 5 gave 75% yield of acetophenone selectively according to Markovnikov's rule at 100 °C in 3 h (Entry 3). The increased temperature up to 120 °C resulted in the highest yield of 97% of acetophenone (TON = 194) (Entry 5) while at 80 °C only 30% yield was obtained (Entry 6). However, the prolonged reaction to 24 h at 80 °C also gave 95% yield of the product (Entry 7). Unexpectantly, the addition of AgOTf badly deteriorated the activity of the catalyst alone with the serious precipitation of Au-nanoparticles, implying the rapid deactivation of the Au-catalyst (Entries 8-10). It was found that the as-synthesized Au-L1 exhibited the same activity as the one in situ formed by mixing AuCl(THT)

Та	ы	e	4

Hydration of the different terminal alkynes catalyzed by L1-AuCl(THT) system^a.

Entry	Alkyne	Product of ketone	Conv. (%) ^b	Sel. (%) ^b
1	H ₂ N	H ₂ N	99	100
2	YO M	40 ⁱ	99	100
3			99	100
4		ČY.	99	100
5	Ŭ.		99	100
6			99	100
7	ci Ci		99	100
8	NC		0	-
9			99	100
10		ч С	74	100

 a AuCl(THT) 0.005 mmol, L1 0.025 (P/Au = 5/1 molar ratio), alkyne 1 mmol, H_2O 1 mL, MeOH 3 mL, time 3 h, temperature 120 °C.

^b Determined by GC and GC-MS.

[tetrahydrothiophene-gold(I) chloride] and L1 at molar ratio of 1/1 (Entries 11 *vs* 1). In contrast, the uses of analogues of L1 such as Xantphos, L2, and L3 in place of L1 all corresponded to the poor yields of acetophenone (Entries 12–15). Especially over the diphosphines of Xantphos and L3, no reaction occurred under the applied conditions (Entries 12 and 14). The physical mixture of L2 and *n*-C₈H₁₇SO₃Na also led to the uncompetitive result in comparison to L1 (Entries 15 *vs* 5), which implied the intramolecular concerted effect of phosphino-fragment and $-SO_3^-$ in L1 on the catalytic performance of Au-complex.

As for the diphosphines of Xantphos, it had been verified that the Au (I)-center of the corresponding complexes as shown in Scheme 1 was either chelated by two phosphino-fragments[Au-Xantphos-a: P1-Au1-P2, 116.73(3)°] [42] or coordinated by one-phosphino-fragment along with the developed Au(I)-Au(I) aurophilic interaction [Au-Xantphos-b: Au–Au bond, 2.9947(4) Å] [43]. In this way, the fused ring-configurations rendered Au-Xantphos-a or Au-Xantphos-b the good stability. Hence the dissociation of Cl⁻ to release the Au(I)-center to activate alkyne substrate was quite difficult without the aid of the auxiliary scavenger (H^+ or Ag^+) over the diphosphines such as Xantphos and L3, leading to the poor activities towards hydration of phenylacetylene as observed in Table 2 (Entries 12 and 14). Comparatively, L1 was a typical mono-phosphine tailed with SO_3^- group. The complexation of L1 and AuCl(THT) led to the formation of a complex of Au-L1. Au-L1 is a Zwitterionic mononuclear Au(I)-complex containing a linearly coordinated Au(I)-center (Fig. 1).

As for **Au-L1** complex, the strong electron-withdrawing effect coming from the positive-charged phosphonium might be an inherent driving force to rupture Au^+ - Cl^- bond. Then the active P- Au^+ species could be formed without the requirement of the addition of auxiliary acids or silver salts. This conjecture was tentatively supported by the following fact. When the equal equivalent F⁻ (coming from TBAF) was added into the reaction system to quench the Lewis acidity of phosphonium site due to its strong fluorophilicity [44,45], the activity of L1based Au-catalyst deteriorated obviously along with only 50% conversion of phenylacetylene (Table 2, Entry 16 *vs* 5). In the catalytic cycle, the active P-Au⁺ species was protected timely by available SO_3^- group again against deactivation (Scheme 2). On the other hand, the hydrophilic nature of SO_3^- group rendered H₂O molecule better accessibility to the Au-catalytic sites, which was believed to be another merit of L1 to promote the reaction rate.

In addition, as an ionic phosphine, L1-based Au-catalyst could be used with the room temperature ionic liquid (RTIL) solvent to fulfill the recovery and recycling of transition metal catalysts. The recycling uses of L1-based AuCl(THT) system in [Bmim]PF₆ (1-butyl-3-methylimidazolium hexaflurophosphate) were investigated in Table 3. It was found that, in the first 4 runs, L1-AuCl(THT) system could be successfully recycled corresponding to 94-96% conversion of phenylacetylene and 100% selectivity to acetophenone. In the 5th run, the conversion of phenylacetylene dropped obviously due to the deactivation of the Aucatalyst as well its loss in the upper organic phase. In the 5th run, the precipitation of Au-blacks was observed obviously. In addition, the ICP-OES analysis demonstrated that the leaching of Au (coming from AuCl (THT) precursor) and P (coming from L1 and [Bmim]PF₆) in the combined organic phase was 0.16% and 6.6%, indicating the loss of L1based Au-catalyst and the co-solvent of [Bmim]PF₆ during the extraction for the catalyst separation and recovery. Upon the recycling uses for 5 runs, the accumulative TON reached 940 for L1-based Au-catalyst.

The generality of L1-AuCl(THT) catalytic system for hydration of different alkynes was summarized in Table 4. It was found that all the phenylacetylene derivatives, except of 4-ethynylbenzonitrile, were converted to the corresponding ketones with the excellent yields (95–99%) without discrimination on the steric and electronic effects of the *para*-positioned substituents (Entries 1–7). As for *para*-ethy-nylbenzonitrile, the presence of cyano group in excess as a kind of strong σ -donors dramatically competed with L1 to coordinate to Aucenter, leading to the completely inhibited activitation of alkynyl group and then the stopped hydration (Entry8). As for linear aliphatic alkynes such as 1-hexyne and 1-octyne, the corresponding hexan-2-one and octan-2-one were obtained respectively with the yield of 99% (Entry 9) and 74% (Entry 10). The increased carbon-chain obviously decelerated the reaction rate.

4. Conclusion

fragment and $-SO_3^-$ group was synthesized and found efficient to promote Au-catalyzed hydration of alkynes without the addition of any auxiliary additives for the first time. In the developed L1-based AuCl (THT) catalytic system, the active P-Au⁺ species could be protected timely by available SO_3^- group again against deactivation (Scheme 2). On the other hand, the amphiphilic nature of L1 rendered both H₂O molecules and alkynes better accessibility to P-Au⁺ catalytic sites, which also gave rise to the reaction rate. As an ionic ligand, L1-based Au-catalyst not only could be recycled in RTIL medium of [Bmim]PF₆, but also exhibited wide generality to the hydration of different terminal alkynes including aryl ones and linear aliphatic ones.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.01.035.

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