Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Structure/Catalytic Activity Study of Gold(I)-NHC Complexes, Recyclable and Reusable, in the Hydration of Alkynes in Aqueous Medium

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ABSTRACT

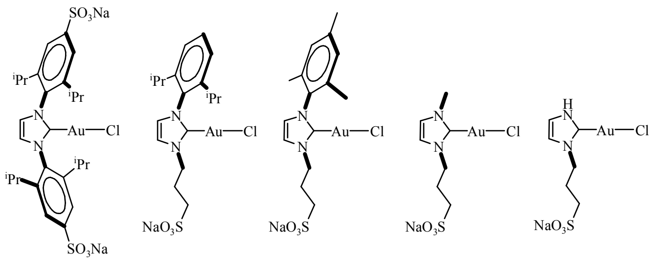
We conducted a structure/catalytic activity study of water-soluble gold(I) complexes -supporting sulfonated NHC ligands- in the hydration of alkynes in pure water or water:methanol (1:1), as well as their recyclability. Comparative studies were carried out with the addition of different silver salts. Our results indicate that the bulkier complex is the most effective and that the addition of methanol as co-solvent not only shortens reaction times but also stabilizes the less bulky complexes.

KEYWORDS: water-soluble N-heterocyclic Carbene; NHC-Gold(I); recyclability

INTRODUCTION

Since the first discovery of N-heterocyclic carbenes (NHCs) by Arduengo, work on the synthesis of metal-NHC compounds has revolutionized the field of catalysis, gradually displacing the typical phosphine and amine-type ligands in view of their higher stability and reactivity [1]. Besides, aqueous catalysis has become an important topic in Green Chemistry due to the positive implications of the use of water as a reaction medium. Also, it is important to mention that water insolubility of many organic products facilitates separation process and, in the case of water-soluble catalysts, opens the way for their recycling and reuse. Although most of the transition metals has been coordinated with NHC ligands and most of the resulting complexes has been used in organometallic catalysis [2], only a few of them, predominantly with Ru [3] and Pd [4] and, in a few examples with Ag [5], Cu [6], Rh [7], Pt [5, 8] and Ir [9] have been investigated in aqueous phase catalysis [10]. It is noteworthy that, although the chemistry of water-soluble NHC-gold(I) complexes is still a relatively young field, it has yielded successful results in various areas of application such as medicine, luminescence and catalysis [11, 12].

It is known that hydration of alkynes is an appropriate reaction for the synthesis of aldehydes and ketones. In order to replace the initial Hg-catalysts, efficient methodologies using catalysts containing Rh [13], Pd(II) [14], Ru(III) [15], Cu(II) [16], or Pt [5] have been reported. Since 1991, when Fukuda and Utimoto reported the hydration of alkynes catalyzed by Na[AuCl$_4$] [17], a development of research on the use of gold catalysts has been initiated [11]. The synthesis of new water soluble NHC-gold complexes, the study of their physicochemical properties as well as their application to various chemical transformations -including their potential recovery- is a very significant contribution to organometallic catalysis and to sustainable organic chemistry in general. Continuing with our research on water-soluble NHC-gold(I) complexes [11c], herein we report the structure/catalytic activity study of five complexes (**C1**-**C5**, Figure 1) in the hydration of alkynes in aqueous medium, as well as their recyclability.

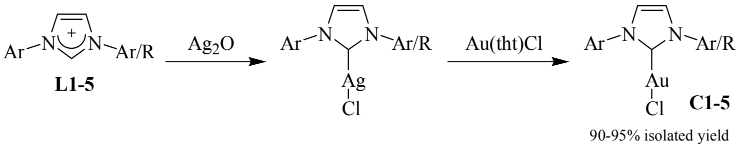


C1(w) 111 g/L **C2** (w) 80 g/L **C3** (w) 180 g/L **C4** (w) 645 g/L **C5**

Figure 1. Structure and water solubility of sulphonated NHC-gold(I) complexes.

RESULTS AND DISCUSSION

1. Synthesis of Gold(I) Complexes. Complexes **C1-C5** were synthesized from [AuCl(tht)] (tht = tetrahydrothiophene) [18] and the corresponding imidazolium compounds **L1-L5** through the silver oxide route developed by Lin and co-workers [19], based on [Ag-NHC-Cl] complexes as NHC transfer agents [20] (Scheme 1). Previously, we have determined that this synthetic route turned out to be the most effective (90 to 95% of isolated complex), avoiding the formation of the respective bis-carbene complexes $[Au(I)\text{-}(NHC)_2]^+$ [11c].

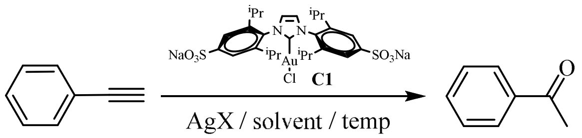


Scheme 1. General procedure for the synthesis of NHC-gold(I) complexes.

As far as we now, [(3-sulfonatepropyl)imidazol-2-ylidene] gold(I) chloride (**C5**) has not been previously reported. Once the complex is isolated as a solid by removal of the solvent (methanol) under vacuum it should be stored under a moisture-free atmosphere. Otherwise, the immediate appearance of the characteristic violet coloration, indicating the presence of Au nanoparticles in the medium, is detected. The complex is stable in a methanol solution.

2. Catalytic Experiments. Our initial exploration started with the hydration of phenylacetylene, using **C1** as catalyst, as a model system. The reactions were carried out in pure water. The results obtained are summarized in Table 1.

Table 1. Hydration of phenylacetylene catalyzed by complex **C1**. [a]

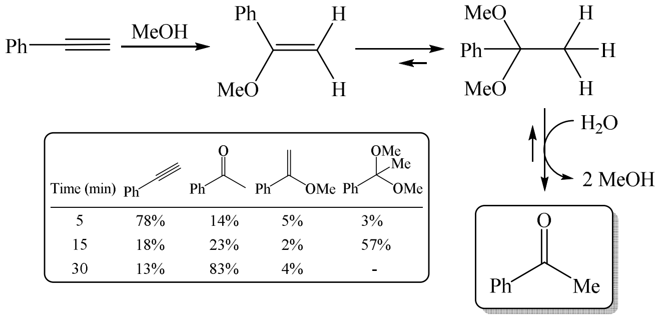


Entry	**C1** (mol%)	AgX salt (mol%)	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	1	-	H_2O	80	5	100
2	1	SCN (1)	H_2O	80	5	100
3	1	SCN (2)	H_2O	80	4	100
4	2	SCN (1)	H_2O	80	3	98
5	2	-	H_2O	80	3	70
6	1	-	H_2O	90	3	100
7	1	-	H_2O	100	1.17	100
8	1	SCN (1)	H_2O	100	0.5	55
9	1	SbF_6 (1)	H_2O	100	0.5	68
10	2	-	H_2O	100	0.5	100
11	1	-	H_2O:MeOH	100	0.5	100
12	1	-	H_2O:MeOH	80	0.75	100
13	2	-	H_2O:MeOH	100	0.25	100
14	1	SCN (1)	H_2O:MeOH	100	0.66	100
15	1	OTs (1)	H_2O:MeOH	100	0.33	100
16	1	SbF_6 (1)	H_2O:MeOH	100	0.13	100
17[c]	1	-	MeOH[d]	100	0.5	83[e]

[a]Experiments were carried out with 0.5 mmol of phenylacetylene, in 3.0 mL water or 1.5 mL:1.5 mL water:methanol. [b]Isolated yield. [c]Quantitative yield was obtained after 40 min. [d]Stoichiometric amount of pure water. [e]Together with 4% of (1-methoxyvinyl)benzene.

We decided to initiate the study working at 80°C with addition of 1 mol % of **C1**. Under these reaction conditions, acetophenone was obtained in a quantitative yield after 5 h (entry 1). Next, with the main goal of reducing reaction time, we studied the effect of different parameters such as the addition of a silver salt [21] and the increment of either the catalyst loading or the temperature. Results resumed in Table 1 show that, although the addition of 1 mol% of AgSCN was ineffective, it was possible to reduce reaction time to 4 h by doubling the load of salt (entries 2 and 3); on the other hand, reaction time was further reduced by an increment of catalyst loading (2 mol%), with the addition of 1 mol% of AgSCN, (entry 4) as well as by an increment of the bath temperature (90 ºC, 3 h; 100 °C, 70 min) (entries 6 and 7). Meanwhile the addition of 1 mol% of either AgSCN or $AgSbF_6$ caused no benefits to the reaction carried out at 100ºC, showing a decline in the catalytic activity giving 55% and 68% yield respectively (compare entry 7 with entries 8 and 9), the use of 2 mol% of catalyst reduced the reaction time to 30 min (entry 10).

Although these reactions -carried out in pure water- gave excellent results we considered interesting to study the effect of methanol as co-solvent, specially taking into account the results reported by Laguna [22]. So, we performed a series of reactions in a water:methanol (1:1) mixture where we analyzed the effect of temperature as well as the catalyst loading and the addition of different silver salts. As expected, a decrease of the temperature from 100 ºC to 80 °C increased the reaction time from 30 to 45 min (Table 1, entries 11 and 12); on the other hand, an increase in the load of the catalyst (2 mol%) reduced the reaction time to 15 minutes (entry 13). A comparative analysis on the addition of different silver salts (1 mol%) shows that $AgSbF_6$ was the most effective: the desired product was obtained in 100% yield in only 8 minutes in the presence of 1 mol% of **C1**! (entries 14-16). Taking into account that the reactions in pure water are slower than in a water:methanol mixture, we carried out a reaction in methanol adding a stoichiometric amount of pure water. This reaction was slower than in water:methanol, giving 83% of ketone after 30 min. (compare entries 11 and 17) together with a small amount of (1-methoxyvinyl)benzene (4%). The results obtained in two experiments carried out at shortest reaction times (5 to 15 min) enable us to propose the generation of the ketone through the hydrolysis of a ketal intermediate (Scheme 2). Similar results have been reported by other authors. [21, 23]



Time (min)				
5	78%	14%	5%	3%
15	18%	23%	2%	57%
30	13%	83%	4%	-

Scheme 2. Reaction carried out in methanol.

In order to obtain some kinetic information about co-solvent effect we monitored the conversion of phenylacetylene over time. The kinetic plot, Figure 2, shows a rapid activation in the reactions carried out in water:methanol.

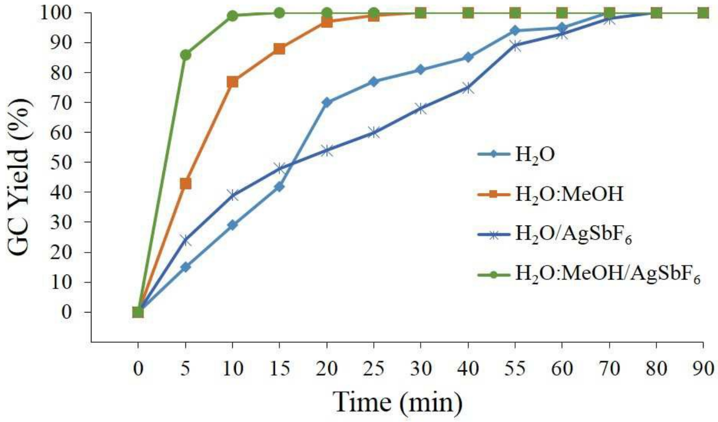
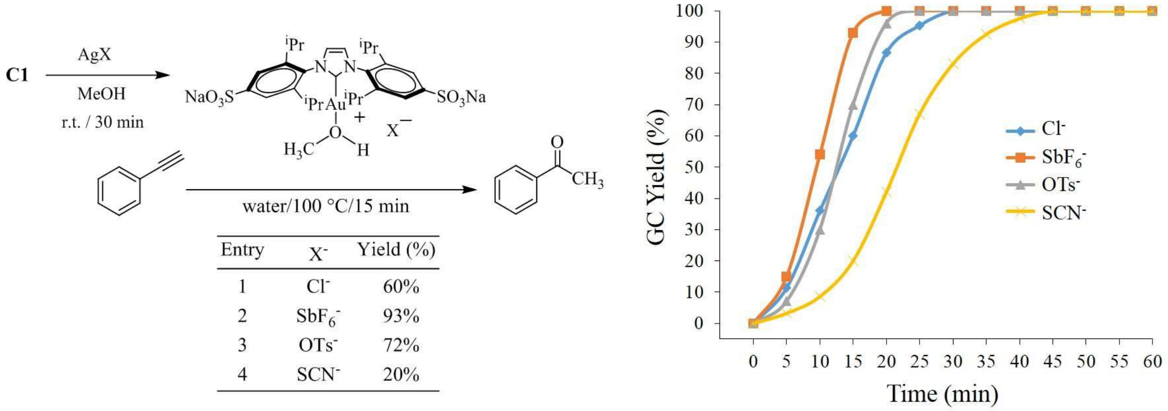


Figure 2. Hydration of phenylacetylene with **C1** (1 mol%). Reactions were run at 100 °C.

Taking into account that the effect of weakly coordinating anions, introduced as silver salts additives, is an issue of growing concern in gold catalysis [23, 24], we considered interesting to obtain a kinetic plot in order to compare experiments 11 and 14-16 (Table 1). For this purpose, the active specie, prepared in methanol from **C1** and the corresponding silver salt (see Supporting Information), was added to a solution of phenylacetylene in water. Scheme 3 shows that, under this condition, the lower activity shown by **C1**/SCN^- is due to a longer induction period.

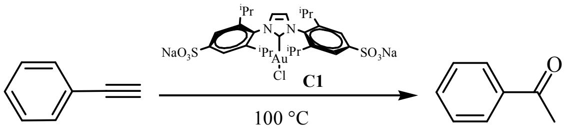


Entry	X$^-$	Yield (%)
1	Cl$^-$	60%
2	SbF$_6^-$	93%
3	OTs$^-$	72%
4	SCN$^-$	20%

Scheme 3. Anion effect with catalyst **C1**. Reactions were run in water:methanol at 100 °C.

2.2. Catalyst loading. A series of experiments was performed in water as well as in water:methanol, at 100 °C, gradually reducing catalyst loading from 1 to 0.05 mol%. The results are summarized in Table 2. It is important to mention that complex activation was performed working at 100 ° C and not by the addition of silver salts. As can be seen, the catalyst turned out to be active in all cases. The drawback was that halving the catalyst loading leads to a doubling of the reaction time to obtain similar results. In all cases the reactions carried out in water were slower (from 1.17 h to 13 h) (entries 1-5) than in water:methanol (from 30 min to 7 h) (entries 6-10). Furthermore, it is noteworthy that the catalyst besides being active at 0.05 mol% was recycled and reused five times without losing catalytic activity.

Table 2. Effectiveness of **C1**. Catalyst loading.[a]

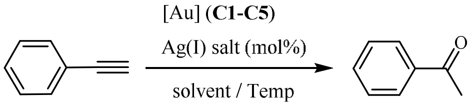


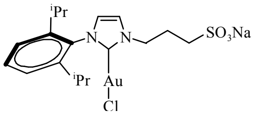
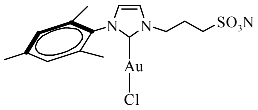
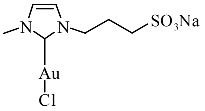
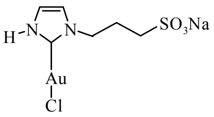
Entry	**C1** (mol%)	Solvent	Time (h)	Yield (%)[b]
1	1.0	H_2O	1.17	100
2	0.5	H_2O	2	100
3	0.25	H_2O	4	100
4	0.10	H_2O	8	100
5	0.05	H_2O	13	100
6	1.0	H_2O:MeOH	0.5	100
7	0.5	H_2O:MeOH	1	100
8	0.25	H_2O:MeOH	2	100
9	0.10	H_2O:MeOH	4	100
10	0.05	H_2O:MeOH	7	100

[a]Conditions for a typical experiment: 0.5 mmol of phenylacetylene; water (3 mL); water:methanol (1.5 mL:1.5 mL); heating (oil bath). [b]Isolated yield.

2.3. Steric Hindrance Effect. Next, in order to evaluate the steric hindrance effect over the catalytic activity, caused by the substituents attached to the nitrogen atoms, we studied the hydration of phenylacetylene in the presence of 1 mol% of NHC-gold(I) less bulky complexes (**C2**-**C5**). All reactions were performed in water and water:methanol, with and without the addition of a silver salt, at the appropriate temperature considering the thermal stability of the complexes. Table 3 summarizes the principal results obtained.

Table 3. Hydration of phenylacetylene catalyzed by complexes **C2-C5**.[a]



Entry	NHC-Au	[Au] mol%	AgX salt (mol%)	Solvent	Temp (°C)	Time (h)	Yield[b]
1	 **C2**	1	-	H_2O	100	24	0
2		1	SCN (1)	H_2O	100	24	0
3		1	SbF_6 (1)	H_2O	100	24	0
4		5	-	H_2O	100	24	0
5		5	SbF_6 (10)	H_2O	30	24	0
6		1	-	H_2O:MeOH	100	13	100
7		1	OTs (1)	H_2O:MeOH	100	6	100
8		1	SbF_6 (1)	H_2O:MeOH	100	7.5	100
9		1	-	TMS	80	24	0
10	 **C3**	1	SbF_6 (1)	H_2O	80	3	0
11		5	SbF_6 (10)	H_2O	30	3	0
12		1	-	H_2O:MeOH	80	48	95
13		1	SCN (1)	H_2O:MeOH	80	48	35
14		1	OTS (1)	H_2O:MeOH	80	48	80
15		1	SbF_6(1)	H_2O:MeOH	80	48	56
16		1	-	H_2O:MeOH	100	24	44
17		1	-	TMS	80	48	0
18	 **C4**	1	-	H_2O	80	24	0
19		1	SCN (1)	H_2O	80	24	0
20		1	SbF_6 (1)	H_2O	80	24	0
21		5	-	H_2O	80	24	0
22		5	SbF_6 (10)	H_2O	30	24	0
23		1	-	H_2O:MeOH	80	60	62
24		1	OTs (1)	H_2O:MeOH	80	60	52
25		1	SbF_6 (1)	H_2O:MeOH	80	60	48
26		1	-	H_2O:MeOH	100	24	14
27		1	-	TMS	80	24	0
28	 **C5**	5	SbF_6 (10)	H_2O	30	0.5	0
29		1	-	H_2O:MeOH	80	60	20
30		1	SbF_6 (1)	H_2O:MeOH	80	60	35
31		1	-	H_2O:MeOH	100	24	19

[a] Experiments were carried out with 0.5 mmol of phenylacetylene, in 3.0 mL water or 1.5 mL:1.5 mL water:methanol. [b] Isolated yield.

Notably, there was no reaction in water with any of these complexes. First, the reactions carried out with **C2** were negative although reaction times were extended to 24 h, even using either Au loadings of 5 mol% or adding different silver salts (entries 1-4). Similar results were obtained with **C4** (entries 18–21). It should be mentioned that the substrate was completely recovered and the generation of Au nanoparticles (violet coloration of the solution) was not detected. We supposed that these unexpected results could be due to a probable thermally sensitive intermediate, so, we carried out two reactions at 30 ºC. In order to activate these reactions we used loadings of 5 mol% and 10 mol% of catalyst and $AgSbF_6$, respectively. Once more, the reactions were negative (entries 5 and 22). Up to now we cannot explain these results.

On the other hand, taking into account that **C3** and **C5** are unstable in water, we carried out an experiment with **C3** adding the complex over a mixture of the silver salt (1 mol%) and the substrate in water, considering that the active species could be generated prior to the decomposition of the complex. Gradually, the solution turned to violet and, after 3 h, the complex was totally decomposed. Similar results were obtained at 30 ºC with loadings of 5 mol% and 10 mol% of catalyst and $AgSbF_6$, respectively (entries 10 and 11). Experiment 28 shows that, under similar conditions, **C5** was completely decomposed in just 30 min. It is noteworthy that these reactions were negative, indicating that gold nanoparticles did not act as catalyst.

In contrast to the results obtained in pure water, all the reactions carried out in water:methanol were positive. The results obtained showed that a decrease of steric hindrance caused a decrease of catalytic effect. For example, using 1 mol% of **C2** a quantitative yield was obtained, although after a prolonged reaction time (13 h) (entry 6). As shown in experiments 7 and 8, the addition of 1 mol% of AgOTs and $AgSbF_6$ reduced the reaction time to 6 h and 7.5 h, respectively. At this point is appropriate to cite that similar conclusions about counterion effects has been previously reported about gold(I) catalysts [25].

The reactions catalyzed with **C3** gave an excellent yield but after 48 h (entry 12). In this case the addition of different silver salts [AgSCN, AgOTs and $AgSbF_6$] caused no beneficial effects, providing conversions of 35%, 80% and 56% respectively, in a similar reaction time (entries 13-15). On the other hand, complex **C4** gave moderate conversions even after 60 h [26] showing that, once more, the addition of silver salts negatively affects the reaction (entries 23 to 25). Finally, complex **C5** showed lower activity giving 20% yield after 60 h; in this case the addition of $AgSbF_6$ produced a positive effect (35%, 60 h) (entries 29 and 30). In order to determine whether the unexpected negative effect produced by the addition of salts is due to different induction periods or, the catalytic rate is really different and anion-dependant, we considered interesting to obtain a kinetic plot in order to compare experiments 12-15 (Table 3). Figure 3 shows that the reaction rates are anion-dependent.

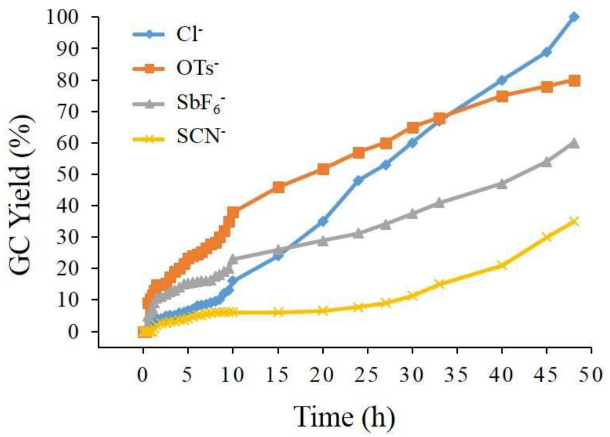
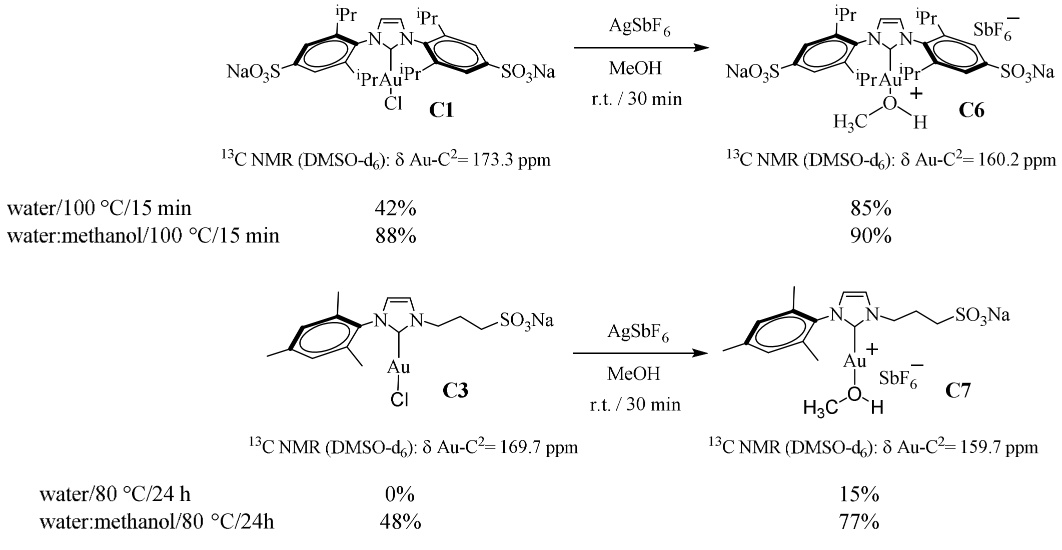


Figure 3. Anion effect with complex **C3**. Reactions were run in water:methanol.

Experiments 16, 26 and 31, carried out at 100 °C, show that an increase in temperature caused no significant benefits in reducing reaction times or increasing the yields. It is worth mentioning that, in none of the experiments carried out with complexes **C3** and **C5** the characteristic violet coloration was observed.

It is tempting to speculate that the positive influence of the addition of methanol as co-solvent may be due to the generation of a more effective precatalyst. Two methanol coordinated cationic complexes, **C6** and **C7**, were prepared from **C1** and **C3** respectively, according to reported procedures [27]. Next, we carried out a series of reactions in order to compare the catalytic activity of **C1** and **C6** as well as of **C3** and **C7**, either in water or in water:methanol. The results obtained, sketched in Scheme 4, support our hypothesis. Thus, **C6** was found to be more active than **C1** working in water (85% *vs*. 42% yield) while their catalytic activity were similar in water:methanol (90% *vs.* 88% yield). On the other hand, **C7** was more active than **C3** under both conditions. Even more, the reaction carried out in water was positive, yielding 15% of the desired product after 24 h. It should be mentioned that no violet coloration was detected working with **C7** in water.

The ^{13}C-NMR spectra confirm the presence of a more acidic gold center; thus, a slight upfield shift of the signal of carbenic carbons was observed: 173.3 ppm (**C1**) *vs* 160.2 ppm (**C6**); 169.7 ppm (**C3**) *vs* 159.7 ppm (**C7**). Stability and catalytic activity of different precatalysts in water are currently being examined in our laboratory. The results will be published in due course.



Scheme 4. A comparison of the catalytic activity of **C1** and **C3** with the corresponding methanol coordinated cationic complexes **C6** and **C7**.

2.4. Kinetic Information. Thereafter, in order to obtain some kinetic information about the influence of the steric bulk around the metal center we monitored the reaction over time, in the absence of silver salts at 100 °C. As seen in Figure 4, the 100% conversion was reached after a given period. The kinetic plot shows that all gold complexes reveal similar active catalyst systems after drastically different induction periods. Thus, the induction is less favored with decreasing size of the N-substituents.

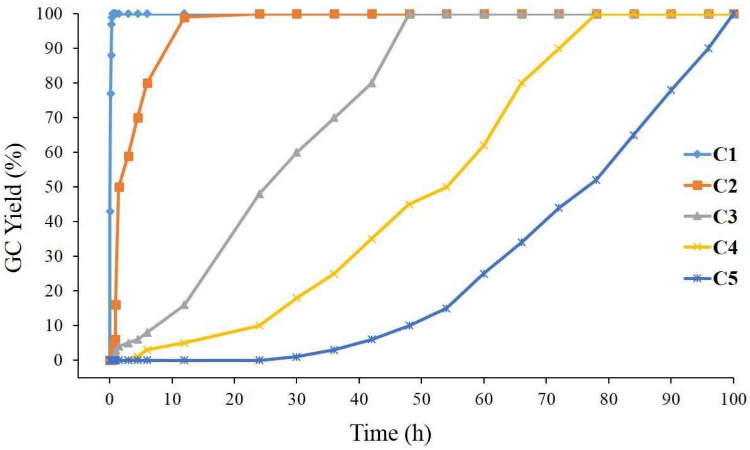


Figure 4. Comparison of reaction progress: (•) **C1** (0.5 h); (♦) **C2** (13 h); (■) **C3** (48 h); (▲) **C4** (72 h) and (-) **C5** (100 h). Reactions were run in water:methanol at 100 °C.

Our results confirm that the steric bulk is an important factor in both the stability and the catalytic activity of gold(I) complexes in aqueous medium, being the bulkier NHC complex the most effective catalyst in the studied reaction. These results are consistent with those reported by other authors on different reactions carried out in conventional organic solvents [28].

Probably, the lower activity exhibited by complexes **C2** to **C5** (pH between 6.4 and 7.2) could be due to the sulfonated moiety which is flexible enough to coordinate the metal or to interfere with the reaction center. Such coordination could be eliminated working at an acidic pH. The graph presented in Figure 5 shows that the induction time is drastically reduced in the reaction carried out with the less active catalyst (**C5**) at pH = 2, improving the catalytic effect. This result supports the existence of coordination between the metal and the sulfonate group.

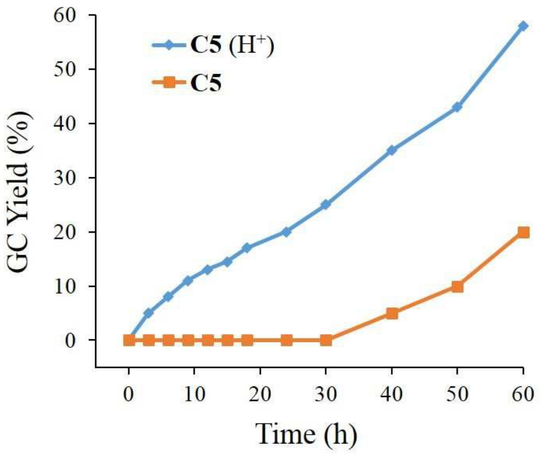
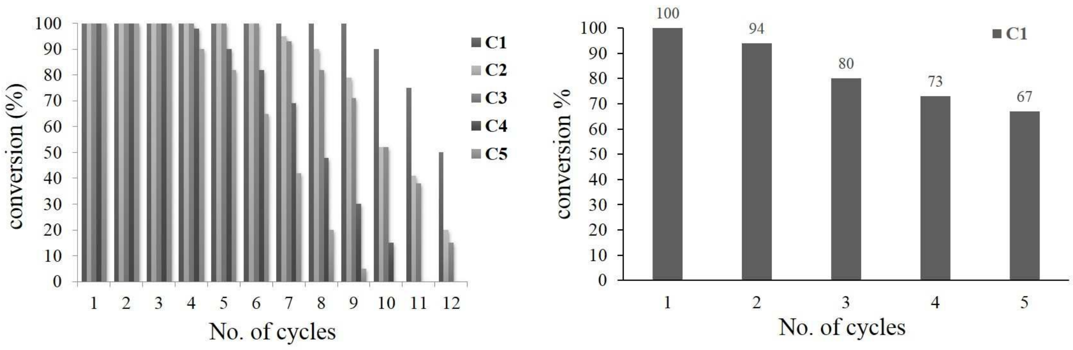


Figure 5. Comparison of reaction progress: (■) **C5**; (♦) **C5** in acid medium. Reactions were run in water:methanol at 80 ºC.

A preliminary Density Functional Theory (DFT) computational study supports the experimental results showing that the alkyl chain folds generate a strong steric hindrance around the metal center. In addition, the strong interaction between metal and oxygen atom of sulfonate affected the positive charge distribution on the metal center. We continue working on the topic and the results will be published in due course.

2.5. Catalyst Recycling. This study was carried out in water:methanol taking into account that all the catalysts were stable in this medium. Each recycling experiment was repeated until the catalyst was almost inactive. The number of cycles that attained this conversion can be found in Figure 6a. Recovery experiments showed that the smaller gold(I)-NHC complexes (**C4** and **C5**) suffered from significant activity losses after the initial cycles (4 and 3 cycles, respectively) whereas the bulky complexes (**C1-C3**) have attained high levels of recyclability (9, 6 and 6 cycles, respectively) [29]. The decline in catalytic activity could be due either to degradation or losing of the catalyst in each process of extraction and reloading of reagent [11b], which would be noted when the remaining amount of catalyst is not sufficient to reach the 100% conversion. For example, a recycling experiment using 0.5 mol% of **C1**, showed a loss of catalytic activity in the first recycling loop (Figure 6b).



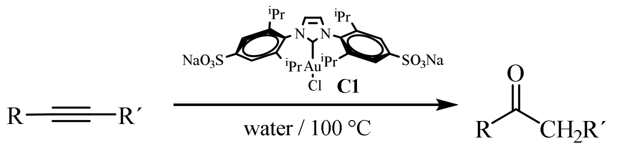
(a) (b)

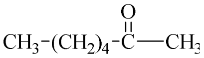
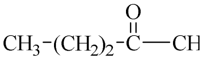
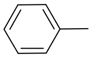
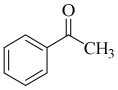
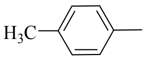
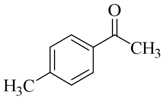
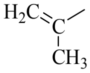
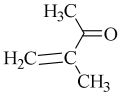
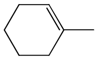
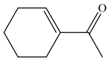
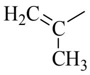
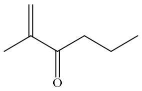
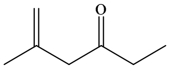
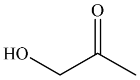
Figure 6. (a) Recycling experiment: cycle numbers *vs* percentage conversion of (a) different [Au] complexes (1 mol%); (b) **C1** (0.5 mol%).

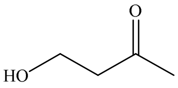
Thermomorphic multicomponent solvent (TMS) systems, which consist of a mixture of three solvents of high, intermediate and low polarity, forms two phases at low temperature but becomes homogeneous at high temperature [30]. The catalytic reaction is then run homogeneously at high temperature and phase separation is performed at low temperature. Considering our experience in the use of TMS systems as an alternative of catalyst recycling [8], experiments in water:toluene:DMF (TMS system at 80 °C) were performed with complexes **C2-C4**. Unfortunately, in all cases, the desired product was not obtained even heating for 24 h, recovering the starting material (Table 3, entries 9, 16 and 25).

2.6. Scope and Limitation. Next, taking into account the higher catalytic activity shown by **C1**, we studied the reactivity of selected terminal alkynes catalyzed by **C1** in water at 100 °C in absence of silver salts. Table 4 shows that these terminal alkynes were oxidized to the corresponding ketone [31] in quantitative yields, according to Markovnikov's rule, in acceptable reaction times (entries 1-6). Moreover, entries 5 and 6 show that the catalytic system can be extended to enines yielding the corresponding α,β-unsaturated ketone. As expected, the reaction carried out with an internal enyne was not regioselective and a mixture of ketones was obtained (entry 7).

Table 4. Hydration reaction of terminal and internal alkynes catalyzed by **C1** in water.[a]



Entry	R	R’	Time (h)	Product	Yield (%)[b,c]
1	$-C_5H_{11}$	H	1.17	 $CH_3-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-CH_3$ **1**	100 (96)
2	$-C_3H_7$	H	1.17	 $CH_3-(CH_2)_2-\overset{O}{\overset{\Vert}{C}}-CH$ **2**	100 (97)
3		H	1.17	 **3**	100 (99)
4		H	2	 **4**	100 (96)
5		H	2	 **5**	100 (98)
6		H	2	 **6**	100 (97)
7		C_2H_5	6	 **7**  **8**	23 40
8[d]	$HO-CH_2-$	H	2	 **9**	100 (99)

9[d]	$\mathrm{HO}{-}(\mathrm{CH_2})_2{-}$	H	2	 10	100 (99)

[a]Conditions for a typical experiment: 0.5 mmol of alkyne; 1 mol% of **C1**; water (3.0 mL); heating (oil bath). [b]Quantified by GC, using the external standard method. [c]Isolated yields between brackets. [d]Heating at 60 ºC with the addition of $AgSbF_6$ (1 mol%).

It is important to notice that although **C1** is highly soluble in water, some of alkynes tested in Table 4, do not. If surface effects are really important, higher alkyne amounts per volume of water could lead to different results. So, we carried out a series of reactions with the double and triple amount of phenylacetylene, *p*-methylphenyl acetylene and 1-ethynylcyclohex-1-ene, in the same volume of water. In all cases, the increase in the concentration led to similar results as those resumed in Table 4.

It should be mentioned that the reactions carried out with prop-2-yn-1-ol and but-3-yn-1-ol under the general conditions (100 ºC) gave a mixture of products in which none of the expected ketones were detected. In order to obtain the corresponding hydroxy ketones, the reactions must be carried out at 60 ºC, activating the catalyst by the addition of $AgSbF_6$ (entries 8 and 9).

CONCLUSIONS

In summary, we have shown that water-soluble Au(I) complexes, supporting sulfonated NHC ligands, are active and recyclable catalysts in the alkyne hydration in water:methanol (1:1), even in the absence of silver salts. Moreover, the bulkiness of the ligands influences the catalytic properties; thus, higher yields, in shortest times, are obtained with bulkier NHC ligands. In addition, we have shown that the bulkier catalyst **C1** is highly effective in water. Thus, the hydration reaction carried out with different alkynes gave a quantitative yield of ketone in acceptable reaction times (1.17 to 2 h). The use of pure water as reaction medium facilitates the catalyst recycling. Further work, in progress in our laboratory, is aimed to assess the influence of different co-solvents in both the stability and the effectiveness of the catalysts.

Finally, it should be mentioned that the effect of the less effective catalyst **C5** could be improved working at acidic pH. A preliminary DFT study shows that the sulfonated chain generates a strong steric hindrance around the metal center. A complete DFT study is in progress in our laboratory.

Supporting Information. Experimental results and ^{1}H and ^{13}C NMR spectra for compounds **C5-C7**.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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Acknowledgments

This work was partially supported by CONICET, CIC, ANPCYT (PICT 2012-1449), and the Universidad Nacional del Sur, Bahía Blanca, Argentina. CONICET is thanked for a research fellowship to G.A.F.. We thank the Empresa Neuquina de Servicios de Ingeniería S.E., Argentine, for the provision of D_2O.

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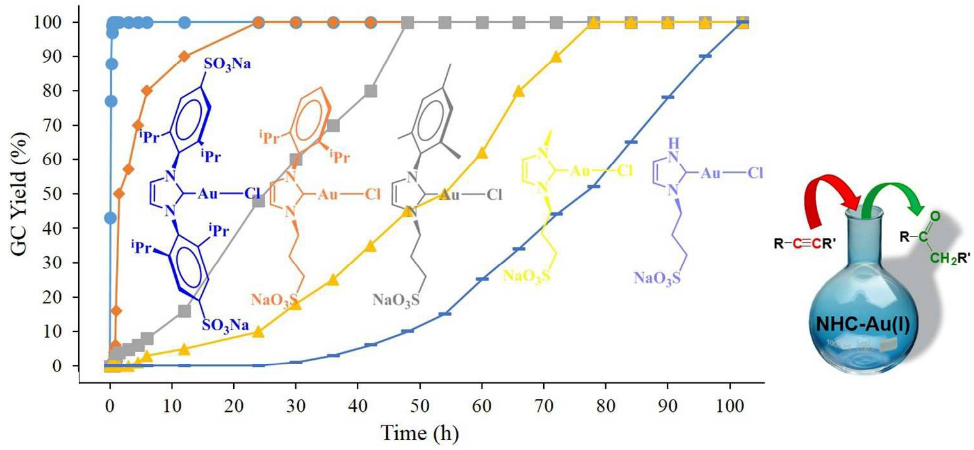

Graphical Abstract
249x124mm (150 x 150 DPI)