Sulphonated NHC-gold(I) complexes in aqueous catalysis. An experimental and DFT computational analysis

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ABSTRACT

A series of sulphonated NHC gold(I) complexes, with different steric bulk around the metal center, [1,3-bis(2,6-diisopropyl-4-sodiumsulfonatephenyl)imidazol-2-ylidene] gold(I) chloro (**C1**), [1-(2,6-diisopropylphenyl)-3-(3-sodiumsulfonatopropyl)imidazol-2-ylidene] gold(I) chloro (**C2**), [1-mesityl-3-(3-sodiumsulfonatopropyl)imidazol-2-ylidene] gold(I) chloro (**C3**), [1-methyl-3-(3-sodiumsulfonatopropyl)imidazol-2-ylidene] gold(I) chloro (**C4**) and [(3-sulfonatopropyl)imidazol-2-ylidene gold(I) chloro] (**C5**), have been studied in the hydration of phenylacetylene in aqueous media, resulting to be active and even recycled.

All reactions were performed in water and water:methanol. Notably, except **C1**, there was no reaction with any of other complexes (**C2**-**C5**) in water. In contrast to these results, all the reactions carried out in water:methanol were positive. In order to explain the experimental results, we decided to study the reactivity of these complexes applying Density Functional Theories (DFT) methods. For this purpose, we considered complexes **C1** and **C5** as representative compounds taking into account that their structure and reactivity are completely different. Thus, **C1** has two bulky substituents (*2,6-diisopropyl-4-sodiumsulfonatephenyl*) attached to the nitrogen atoms, while **C5** has a less bulky moiety as an alkyl chain (*sulfonatopropyl*). The 100% conversion of phenylacetylene to acetophenone was obtained after drastically different induction periods: 30 min for **C1** and 100 h for **C5**. The DFT computational studies support the experimental results showing that the alkyl chain folds generate a strong steric hindrance around the metal center causing a decrease of the catalytic effect.

Keywords: Water-soluble Au(I), N-heterocyclic carbene, DFT methods

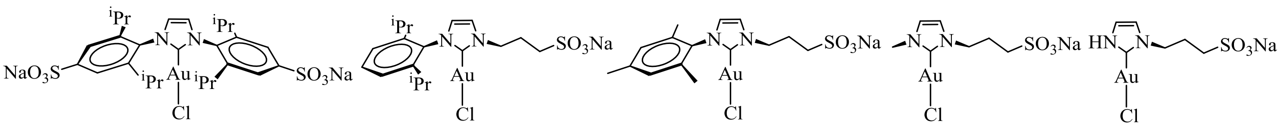
INTRODUCTION

Although the water is considered as a natural enemy of the organometallic compounds, in recent decades the field of organic chemistry in aqueous media has been increasing. 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.

Since the first discovery of N-heterocyclic carbenes (NHCs) by Arduengo in 1991, work on the synthesis of NHC-metal organometallic 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]. Even though most of the transition metals is coordinated with NHC ligands and the majority of the resulting complex was used in organometallic catalysis [2], only a few of them, predominantly Ru and Pd and in a few examples with Ag, Cu, Rh, Pt and Ir have been investigated in aqueous phase [3]. Is worth noting that, although the chemistry of water soluble NHC-gold(I) complexes is still a relatively young field, has given successful results in various application areas such as catalysis, medicine and luminescence [4].

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.

In our group, complexes NHC-gold(I) were synthesized (Figure 1) from the corresponding imidazolium salts. The complexes have been studied in the oxidation of terminal alkynes in aqueous media, resulting to be active and even recycled [4b]. In this communication, in order to explain the experimental results, a computational analysis of **C1** and **C5** complexes was performed applying DFT methods.

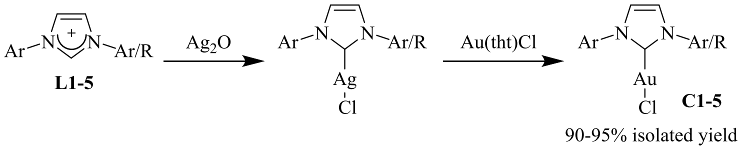


C1 **C2** **C3** **C4** **C5**

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

RESULTS AND DISCUSSION

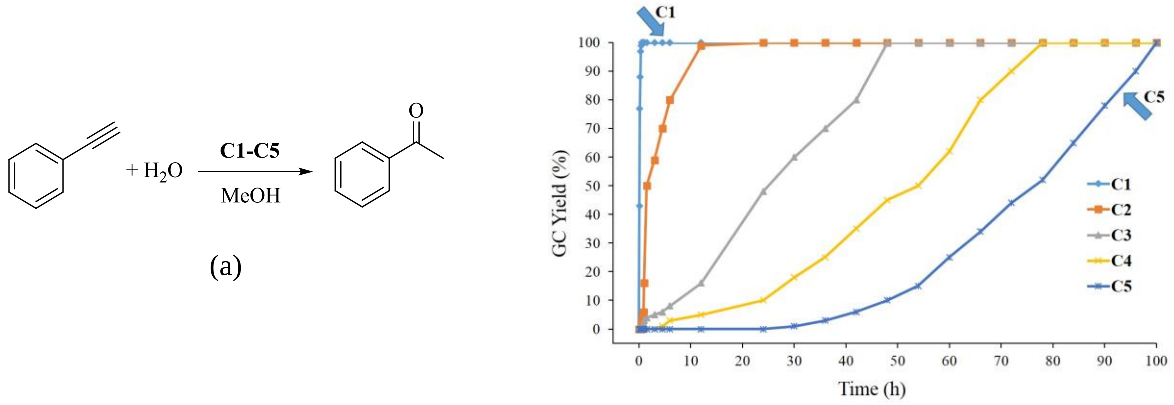
All complexes (**C1-C5**) were synthesized from AuCl(tht) and the corresponding imidazolium salt (**L1-L5**) through the silver oxide route, based on Ag-NHC-Cl complexes as NHC transfer agents [5] (Scheme 1). In previous work, we have determined that this synthetic route turned out to be the most effective (90 to 95% of isolated complex), avoiding the formation of the respective bis-carbene complexes $[Au(I)\text{-}(NHC)_2]^+$ [4a].



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

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 our complexes (**C1-C5**). All reactions were performed in water and water:methanol. Notably, except for **C1**, there was no reaction in water with any of other complexes (**C2-C5**). In contrast to the results obtained in pure water, all the reactions carried out in water:methanol (100° C) were positive.

Kinetic information about the influence of the steric bulk around the metal center was obtained by monitoring the reaction (GC) over time. As can be seen in Figure 2, the 100% conversion of phenylacetylene to acetophenone was obtained after drastically different induction periods: 30 min for **C1** and 100 h for **C5**. The induction is less favored with the incorporation of alkyl chains as substituents on the N atoms.



(a)

(b)

Figure 2. (a) Hydration of phenylacetylene; (b) Comparison of reaction progress: **C1** (0.5 h); **C2** (13 h); **C3** (48 h); **C4** (72 h) and **C5** (100 h)

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 (**C1**) 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 [6]. However, the introduction of less bulky structural moiety such as *sulfonatopropyl* (**C5**) caused long reaction times.

These experimental observations prompted us to study, through computational calculations, **C1** and **C5** complexes, considering that they are structurally very different. At first, we modeled the neutral complexes corresponding to **C1** and **C5** derivatives, applying the density functional theory (DFT) [7] with the B3LYP [8] functional, the LANL2DZ [9] pseudopotencial for the Au atom and 6-31G* basis set for the other atoms, which is known to be an appropriate methodology for the theoretical study of these reactive systems [10].

For the neutral **C1** complex we find a Au-C bond length of 1.99 Å and a Au-Cl distance of 2.37 Å, whereas, no structural peculiarities are observed. This means that the *2,6-diisopropyl-4-sodiumsulfonatephenyl* groups are located symmetrically at both sides of the ligand as can be seen in Figure 3.

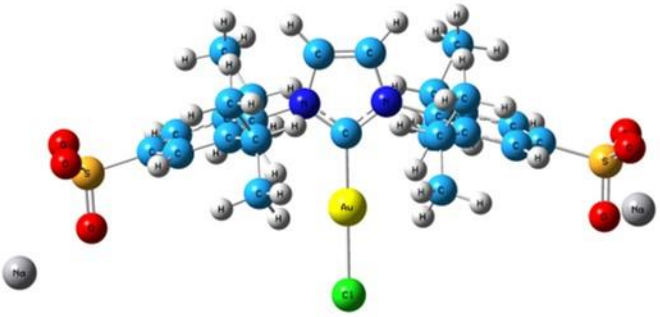


Figure 3. Calculated geometry of neutral **C1** complex

Then, we modeled the neutral **C5** complex, which has a *sulfonatopropyl* moiety attached to the N atom. For this complex, the Au-C bond length is the same that for **C1**, 1.99 Å, but the Au-Cl distance is shorter than **C1**, 2.28 Å, and surprisingly, the alkyl chain is folded up around the metal center as shown in Figure 4.

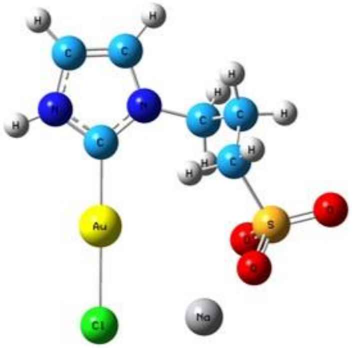
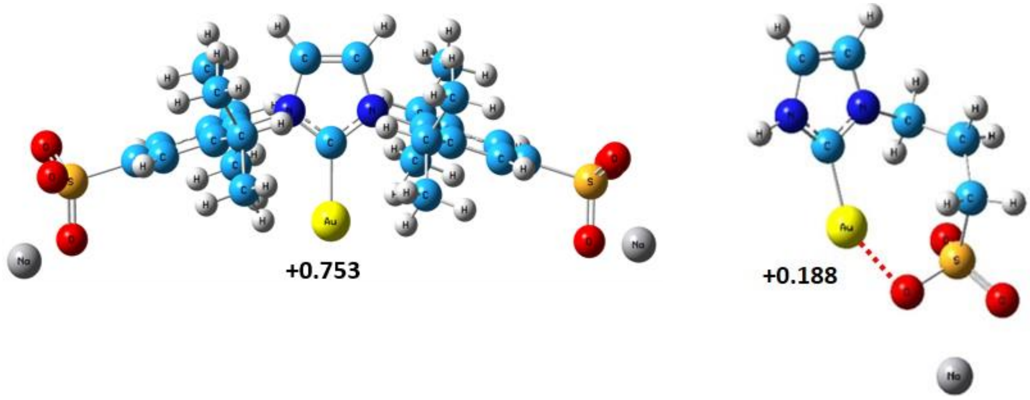


Figure 4. Calculated geometry of neutral **C5** complex

Considering that the metal should be Au(+1) in the complex, in order to the hydration of alkynes take place, we modeled the charged of **C1** and **C5** complexes, that is, without the Cl atom attached to the metal. As result, we showed the geometries corresponding to **C1** and **C5** complexes in Figure 5, and besides, we computed the atomic charges by fitting the electrostatic potential (ESP charges). The DFT calculations showed significant differences between the complexes. In **C1**, the geometric parameters between the neutral and charged species remain without changes, but the **C5** shows a strong interaction between the metal and the oxygen atom of sulfonate group (shown with a red dashed line in Figure 5b). The distance Au-O in the neutral **C5** is 3.52 Å, and it is shortened to 2.17 Å in the charged complex, giving evidence of the strong interaction aforementioned.



(a) (b)

Figure 5. Calculated geometry and ESP charges of the Au(+1): (a) **C1**; (b) **C5**

Based on the results of computational calculations, we could assume that the lack of reactivity of **C5** compared with **C1** would be related to steric factors, that is, the alkyl chain is folded up over the metal center, generating a significant steric hindrance. In addition to electronic factors, also related to this folding, that produce a strong interaction between the metal and the oxygen atom of sulfonate group, directly affecting the distribution of positive charge on this center, being lower in the **C5** (+0.188) that in the **C1** (+0.753).

CONCLUSIONS

In summary, we have shown that the bulkiness of the ligands influences in the stability and the catalytic properties of the complexes; thus, higher yields in shortest times are obtained with bulkier NHC ligands but without steric hindrance around the metal center. Besides, through DFT calculations, we were able to explain the lack of reactivity of **C5** in term of steric arrangements of the *sulfonatopropyl* chain, showing to be a successful computational approach for studying these complexes.

EXPERIMENTAL SECTION

All operations were performed under a nitrogen atmosphere by using Schlenk techniques. Organic solvents were dried and distilled under nitrogen and degassed prior to use. Unless otherwise stated, reagents were obtained from commercial sources and used as received. [AuCl(tht)] was prepared according to reported procedures [11]. ^{1}H and ^{13}C spectra were recorded with a Bruker 300 spectrometer.

General procedure for preparation of sulphonated NHC-gold(I) complexes

All complexes (**C1-C5**) were prepared according to reported procedures [4b]. In a 25 mL Schlenk tube was prepared a solution of [Ag(I)-NHC-Cl], from the imidazolium salt (0.60 mmol), silver oxide (0.083 g, 0.36 mmol) and sodium chloride (0.035 g, 0.60 mmol) in 3 mL of MeOH or DMSO. The mixture was stirred over night at room temperature. AuCl(tht) (0.192 g, 0.60 mmol) and NaCl (0.035 g, 0.60 mmol) were added and the mixture was stirred for 4 hours. The final solution was filtered through a plug of celite. The gold complex was precipitated with 10 mL of dry acetone, separated by filtration and dried under vacuum.

[1,3-bis(2,6-diisopropyl-4-sodiumsulfonatephenyl)imidazol-2-ylidene] gold(I) chloro (**C1**). White solid (95%). ^{1}H-NMR (300 MHz, DMSO-d$_6$): δ 8.00 (s, 2H, Imz), 7.58 (s, 4H, Ar), 2.17 (h, $^{3}J_{H-H}$ = 6.0 Hz, 4H, C*H*Me$_2$), 1.22 (t, $^{3}J_{H-H}$ = 6.5 Hz, 24H, CH*Me*$_2$); ^{13}C-NMR (75 MHz, DMSO-*d*$_6$): δ 173.0 (s, Imz C^2), 149.8 (s, Ar C^4), 144.8 (s, Ar C^2) 134.0 (s, Ar C^1), 124.6 (s, Ar C^3), 121.1 (s, Imz C^{4,5}), 28.4 (s, *C*HMe$_2$), 23.9 (s, CH*Me*$_2$), 23.5 (s, CH*Me*$_2$).

(3-sulfonatopropyl)imidazol-2-ylidene gold(I) chloro (**C5**). White solid (90%). ^{1}H-NMR (300 MHz, DMSO-d$_6$): δ 7.82 (s, 1H, NH), 7.25 (d, $^{3}J_{H-H}$ = 1.4, 1H, Imz), 6.99 (d, $^{3}J_{H-H}$ = 1.4, 1H, Imz), 4.10 (t, $^{3}J_{H-H}$ = 7.0, 2H, NCH$_2$), 2.36 (t, $^{3}J_{H-H}$ = 7.5, 2H, CH$_2$S), 1.99 (q, 2H, CH$_2$C*H*$_2$CH$_2$); ^{13}C-NMR (75 MHz, DMSO-d$_6$): δ 164.2(s, Imz C^2), 123.0 (s, Imz C^5), 121.7 (s, Imz C^4), 48.4 (s, NCH$_2$), 45.9 (s, SCH$_2$), 27.6 (s, CH$_2$*C*H$_2$CH$_2$).

General method for the alkyne hydration reactions in water or water:methanol. 0.005 mmol of catalyst were added to a solution of phenylacetylene (0.5 mmol, 56 μL) in water:methanol (1.5:1.5 mL). The mixture was vigorously stirred at 100 °C (oil bath) in an ampoule tube equipped with a PTFE valve. Reaction time was monitored by GC by taking samples at different times.

Computational Procedure

The calculations were performed with Gaussian09 [12]. The initial conformational analysis of selected compounds was performed with the semiempirical PM3 method. The geometry of the most stable conformers thus obtained was used as starting point for the B3LYP studies of the corresponding complexes with the LANL2DZ pseudopotential for heavier elements (Au) and the 6-31+G* (C, H, O, S). The characterization of all stationary points (minimum) was done by Hessian matrix calculations of geometries obtained with full optimization. The energies in solution were obtained with full geometry optimization within the Tomasi's polarized continuum model (PCM) [13] as implemented in Gaussian09. Figures were built with the GaussView program.

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