



Enhancement of gold catalytic activity and stability by immobilization on the surface of graphene



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ABSTRACT

The catalytic performance of gold complexes is evaluated at the molecular level and when supported onto reduced graphene oxide (rGO). Gold complexes of general formula [(NHC)AuX] catalyse the synthesis of indoles via intramolecular hydroamination reaction of alkynes. The catalytic properties of the molecular gold complexes are highly improved when supported onto graphene. Faster reaction rates and higher catalyst stability are observed for the immobilized gold complexes. The use of graphene as support of molecular complexes has a positive benefit in the catalytic gold properties in terms of activity and stability.

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1. Introduction

The use of gold as catalyst has acquired a great impact over the last years [1–3]. Although initially considered as an inert noble metal, gold has proved his potential application in catalysis [4]. The gold catalytic activity is very high in the form of solid catalysts [5–7], nanoparticles [8–11], clusters [12], or molecular complexes [13–19]. Despite the advances of gold in homogeneous catalysis, one of the main drawbacks that still need to be tackled is stability. In particular, stability of gold complexes towards decomposition under common catalytic conditions. Stability issues of gold complexes should address to a rational design of more active and robust catalysts that inhibit regular decomposition pathways [20–23]. At the molecular level, decomposition of gold complexes comes from the nature and number of intermediates involved in a catalytic cycle and its inherent facile reduction to form inactive gold metallic mirrors. In order to improve catalytic efficiency and activity it is important to develop systems in which deactivation or reduction pathways are minimised or avoided. An alternative to circumvent this problem consists of the immobilization of organometallic complexes onto solid surfaces capable of enhancing their stability [24–28]. Immobilization of molecular complexes combines the advantages of homogeneous and heterogeneous catalysis of selectivity and robustness [29–32]. Catalytic applications of well-defined molecular complexes onto supports are

widened as they can be recovered and reused for several catalytic cycles. In addition, separation of the solid catalyst from reaction products is crucial for many applications. The use of solid supports for immobilization of molecular complexes allows the controlled incorporation of catalytic active sites. Structural characterization of the active sites facilitates the understanding of structure-reactivity relationships that govern the catalytic performance and stability.

In this work, we aim to study different factors that may play a role over the control of stability of gold complexes during catalytic reactions. In this context, we have developed a methodology that allows the immobilization of well-defined gold complexes onto the surface of graphene. The structure of the hybrid material is composed of a regular distribution of active sites completely characterized. Here, we show that the rationale ligand design and immobilization of organometallic complexes on the surface of graphene enhance the gold catalytic properties.

2. Results and discussion

The gold/graphene hybrid materials were prepared using a general procedure previously described in our laboratory that allows the controlled introduction of molecular complexes onto the surface of graphene [33]. The method consists in the direct immobilization of gold complexes onto the surface of reduced graphene oxide (rGO) by π -stacking interactions [34–36]. These types of interactions are important in the case of polyaromatic hydrocarbons (PAHs) including graphene and related materials [37]. We

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have used a pyrene tag for the preparation of two imidazolium salts that serve as NHC ligand precursors and allow the direct immobilization of the organometallic gold complexes onto the surface of graphene (Scheme 1). The imidazolium salts **1** and **2** containing the pyrene tag were prepared in good yields by alkylation of methyl (or mesityl) imidazole with 1-bromomethylpyrene. Deprotonation of the imidazolium salts using a transmetalation procedure or an external base in the presence of AuCl(SMe₂) allows the formation of the well-defined organometallic gold complexes **3** and **4**. The gold complexes were fully characterized by NMR spectroscopy, ESI-MS spectrometry and elemental analysis. The ESI-MS analysis requires the addition of an external sodium or potassium salt to detect the molecular peak. For instance, in the case of complex **3**, the base peak corresponds to an adduct with potassium at 567.03 *m/z*. The mass/charge relation and the isotopic pattern confirm the molecular composition. Single crystal X-ray diffraction completes the characterization of **3** and **4** (Figs. 1 and 2). The Au-C_{carbene} distance is 1.974(4) Å for **3** and 2.000(3) Å for **4** and both lie in the expected range for gold NHC complexes. The packing diagram of complex **3** shows an intermolecular π -stacking interaction between the pyrene groups (Fig. 1). The interplanar distance is 3.5 Å, indicating an interaction between the polyaromatic groups. The same situation is observed in the case of the gold complex **4**. The packing diagram shows a π -stacking interaction between the pyrene groups with an interplanar distance of 3.6 Å (Fig. 2). We have previously observed the formation of π - π interactions in palladium [33] and ruthenium [38] NHC complexes functionalized with pyrene tags. The formation of these π - π interactions gives an indication of the tendency of the pyrene tag to interact with PAHs such as graphene.

Gold complexes **3** and **4** are immobilized on rGO at room temperature using ultrasounds (US). The exact amount of gold complex anchored on the surface of graphene was analysed by ICP-MS. The results accounted for a 3.9 wt% of complex **3** in the hybrid material **5** and 0.9 wt% of complex **4** in the hybrid material **6**. The hybrid materials were characterized by UV/Vis, FTIR and HRTEM. Analysis by X-ray photoelectron spectroscopy (XPS) provides evidence of the structure of the molecular complexes on the surface of graphene. Fig. 3 shows a comparative XPS analysis of the molecular complex **4** and the hybrid material **6**. Complex **4** shows three characteristic peaks corresponding to the core-levels of N1s, Au4f and Br3d. These peaks are also observed in the XPS of the hybrid material **6** at the same binding energy. XPS analysis confirms the presence of the molecular complex **4** on the surface of the reduced graphene oxide and that the structure of complex **4** is maintained after immobilization.

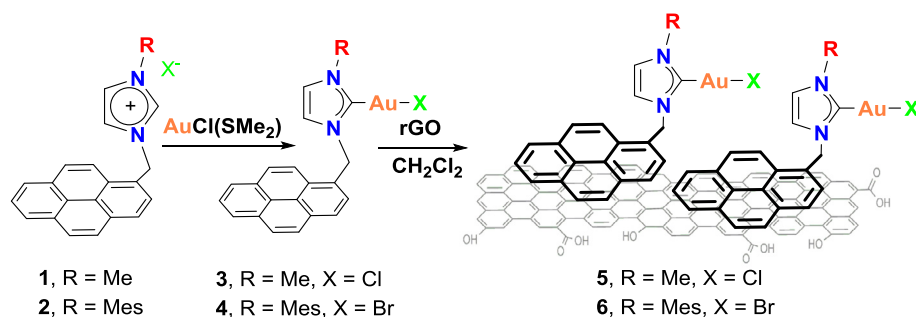
2.1. Catalytic properties

We tested the catalytic properties of the molecular gold complexes and the hybrid materials using the intramolecular

hydroamination of alkynes as model reaction [39–42]. The catalytic formation of indole derivatives is an elegant approach for the synthesis of sophisticated organic molecules. The reaction mechanism is well established and requires the addition of AgBF₄ to activate the gold precatalyst. The gold catalysts (**3–6**) are active in the cyclisation reactions (Table 1) at low temperatures. Initial control experiments show that Au is required in the reaction to proceed, AgBF₄ or rGO material is not active. (Data not shown Table 1, see SI for details). Results show that the catalytic performance of **3–6** is particularly different. For instance, the performance of catalyst **3** is very low, and only 20% yield is obtained after 6 h reaction (Entry 1). However, under the same reaction conditions, **4** and **5** afforded 91% and 82% yield respectively (Entries 3 and 8). We observed that the overall turnover was even better in the case of catalyst **6**, which afforded quantitative yields in 1.5 h with a catalyst loading of 0.08 mol% (Entry 9). These results are remarkably considering that standard conditions on gold-catalysed intramolecular hydroamination of alkynes require catalyst loadings in the range of 1–2 mol% [43–46]. The reaction affords quantitative yields when using acetonitrile or toluene as solvents, but only 15% yield is obtained when using thf (Entry 6). We have not observed differences on mass balances in the presence of the support when monitoring the reactions by gas chromatography. This result suggests that the π -stacking interactions of substrates with the support are weak and therefore they are not adsorbed. The use of catalyst **6** allows the reduction in reaction time to minutes at a low catalyst loading of 0.56 mol% (Entry 10). These results show that better outcomes are obtained when using catalyst **6** in toluene at low temperature.

A hot filtration experiment was carried out to establish the heterogeneous nature of catalyst **6** during the intramolecular hydroamination. We performed the experiment under the reaction conditions described in entry 9 (Table 1), but after 45 min. (GC yield 53%), the catalytic hybrid material **6** was separated from the solution by cannula-filtration at the working temperature (50 °C). The filtrate was stirred under the same conditions for 5 h at 50 °C. After this time, GC analysis reveals that there is no more indole formation. This result suggests that there are not catalytic active species in solution. On the other hand, the isolated catalyst **6** was treated with toluene and substrate. After 2 h reaction, we observed the formation of indole in 97% yield. The results suggest the heterogeneous nature of catalyst **6**. The hot filtration experiment confirmed the absence of leached species in solution due to desorption from the graphene surface.

The catalytic performance evaluation of **3–6** was compared by monitoring the cyclisation reaction during time (Fig. 4). The catalytic rate of the molecular gold complexes **3** and **4** is remarkably different (Fig. 4a). Under the same reaction conditions and catalyst loading, complex **3** affords only 20% yield but complex **4** affords 100% yield. As observed in the monitoring of the reaction, catalyst **3** is completely deactivated after 300 min. The results show that



Scheme 1. Synthesis of gold complexes and hybrid materials.

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