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# **ARTICLE TYPE**

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## **Covalently anchored homogeneous gold complex on carbon nanotubes:** a reusable catalyst

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The gold complex [Tf<sub>2</sub>NAuPPh<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>] was synthesized and covalently anchored on modified carbon nanotubes in order to obtain a supported gold homogeneous catalyst. Simple 1,6 enynes were chosen as benchmark substrates to assess its <sup>10</sup> behaviour in cyclization catalysis as well as study its recycling.

Homogeneous catalysts display often high activities and selectivities towards the targeted product but suffer from various drawbacks: they are often expensive and most of the time single 15 use meaning that a potential recycling of these catalysts is of paramount importance. The concept of supported homogeneous catalysis combining advantages of both homogeneous and heterogeneous catalysis opens promising perspectives. A highly active catalyst coupled with ease of separation from products 20 allows reusability. Many strategies have been carried out for the

- <sup>20</sup> anows reusability. Many strategies have been carried out for the covalent and non-covalent immobilization of various metal complexes on different materials. Amorphous and ordered silica, clays and highly cross-linked polymers are the standard supports to create a heterogeneous catalyst from a homogeneous one <sup>1</sup>.
- <sup>25</sup> Carbon nanotubes as supports for the immobilization of homogeneous catalysts are surprisingly not developed in relation with the rich chemistry dealing with the functionalization of these tubes <sup>2</sup>. Among the different possible functionalization strategies, the most common is the covalent one <sup>3</sup> and to our knowledge only
- <sup>30</sup> a few papers deal with the covalent anchoring of homogeneous catalysts on carbon nanotubes <sup>4</sup>. In addition, gold complexes have been increasingly used in homogeneous catalysis in the past decade thanks to their ability to promote a myriad of chemicals transformations with impressive turnover numbers, particularly
- <sup>35</sup> C-H activation followed by C-C bond formation <sup>5</sup>. This communication aims at reporting a simple methodology to transform a homogeneous gold catalyst into a heterogeneous one using modified Multi-Walled Carbon Nanotubes (MWNTs) as support and at showing the potential of this supported
- 40 homogeneous catalyst in terms of recyclability using enynes as benchmark substrates.

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45 +32 10-472810; E-mail: <u>sophie.hermans@uclouvain.be</u>; <u>olivier.riant@uclouvain.be</u> †Electronic Supplementary Information (ESI) available: [synthesis of gold complex, XPS analysis, NMR of cyclized products and recycling]. See DOI: 10.1039/b000000x/

The present strategy was based on the use of the bifunctional 50 ligand 1 (Scheme 1) able to interact both with a gold complex thanks to the phosphine group and with modified MWNTs using the amine group to obtain a homogeneous gold complex supported onto MWNTs. The bifunctional ligand 1 can be <sup>55</sup> obtained on a multi-gram scale <sup>6</sup>. A ligand exchange between the gold complex ClAuSMe<sub>2</sub> 2 and bifunctional ligand 1 provided the modified gold complex  $3^{7}$ . The chlorine atom was then replaced by the bis(trifluoromethanesulfonyl) imidate moiety (NTf<sub>2</sub>) by adding 1 equivalent of AgNTf<sub>2</sub> leading to the gold complex 4 60 (Scheme 1). This gold complex tailored for immobilization was obtained in 80% yield starting from 1 and was extensively characterized by TGA, HR-MS, <sup>1</sup>H NMR, <sup>31</sup>P NMR, <sup>19</sup>F NMR and <sup>13</sup>C NMR (see ESI for experimental section and characterizations). This synthesis affords a stable and non-65 hygroscopic gold (I) complex which is isolable and easy to handle, thanks to the NTf<sub>2</sub> moiety. When other counter-anions are used (TfO', SbF<sub>6</sub>', BF<sub>4</sub>'), silver salts are added to a solution containing the gold pre-catalyst to form the catalytic species in situ<sup>4</sup>. In those cases, the active complex is not isolated and 70 residual Ag might also play an active role in catalysis. In addition, complex 4 is able to interact in one single step with modified MWNTs to cause its covalent anchoring.

Pristine MWNTs (Thin MWNTs, 95+ % C purity, Nanocyl S.A.) were firstly modified by the most common method to <sup>75</sup> generate carboxylic acids at the surface of carbon nanotubes, i.e. refluxing in concentrated HNO<sub>3</sub> according to a general procedure aiming at oxidizing these nanotubes without degrading them<sup>8</sup>. The oxidized MWNTs were submitted to chlorination using SOCl<sub>2</sub> in toluene under reflux to obtain acyl chloride functions at the surface of the tubes (see ESI)<sup>9</sup>. These modified MWNTs (*m*-MWNTs) were dispersed in dichloromethane under ultrasound before addition of the gold complex **4** (Scheme 1). The reaction that should occur would lead to an amide bond between the ligand and surface acyl chlorides. Various periods of time were stested (from 2h to 24h). The resulting functionalized MWNTs (*f*-MWNTs) were filtrated in order to separate them from the

MWNTs) were filtrated in order to separate them from the solution containing the unreacted gold complex **4**. The solids were analysed by X-ray photoelectron spectroscopy (XPS) to check if incorporation indeed occurred at the surface of the tubes.

<sup>90</sup> These XPS results (see ESI, *Table S1*) show that a non-negligible amount of gold was present on the support after reaction and that the ratios between the different elements (N, P, S, F, Au) were in agreement with the theoretical numbers. The incorporation duration was not found to be a decisive factor. The incorporated gold amount was nearly the same irrespective of the time. A similar observation can be made concerning the atomic ratios between N, P, S, F and Au. A duration of 7h was selected and <sup>5</sup> reproducibility assays produced similar results (see ESI, Table S1). Furthermore, the oxidation state of gold was analysed by XPS and remained Au<sup>I</sup> after incorporation (see ESI). These results prove that catalyst **5** was covalently anchored and remained unaffected by this anchoring process. ICP analyses <sup>10</sup> were realized to determine the bulk Au amount on MWNTs: the numbers found (between 3.5 and 4.1 weight %) fall within the range of covalently supported homogeneous catalysts on carbon nanotubes<sup>10</sup>.



Scheme 1. Synthesis and covalent grafting of the gold catalyst.

The homogeneous gold catalyst **4** and its supported counterpart <sup>30</sup> **5** were both tested in the cyclization of the model substrate enyne **6** (scheme 2). The gold complex **4** was catalytically effective and gave complete conversion of **6** using 2 mol% of gold catalyst in dichloromethane at room temperature in 28h. The cyclization reaction afforded predominantly the 5-exo-dig product **7** and a <sup>35</sup> minor amount of 6-endo-dig product **8** in a ratio 88/12 as outcome of the reaction. Compared to the structurally close gold catalyst Tf<sub>2</sub>NAuPPh<sub>3</sub>, the catalytic activity of **4** is much lower (*i.e.* 28 hours instead of 10 min for complete conversion) (see

- ESI). This drop in catalytic activity can only be explained by the <sup>40</sup> presence of the dangling amine group. An inhibition of the cyclization reaction could have been explained if the amine group played an active role in the enyne cyclization mechanism but this possibility can be ruled out. One postulated hypothesis consists in a head-to-toe complex dimerization meaning that the amine group
- <sup>45</sup> could act as ligand taking up the position of NTf<sub>2</sub> as ligand and leading to a loss of the complex activity.

Cyclization of enyne **6** was next performed similarly using the supported homogeneous catalyst **5** (Scheme 2). This supported homogeneous catalyst (2 mol % based on ICP results) was first

- <sup>50</sup> dispersed under ultrasound in distilled dichloromethane before addition of enyne 6. A complete conversion was obtained after 6 hours giving cyclized products. Compared to its homogeneous counterpart, a decrease in the reaction time was observed here. Indeed, due to the formation of an amide group for incorporation
- <sup>55</sup> onto MWNTs, the above-mentioned effect about the deleterious role of the dangling amine group does not take place in this case. Based on these results, enynes 9 and 12 were tested with the supported homogeneous catalyst 5 in order to verify if the

heterogenized catalyst is active in other cyclization reactions 60 (Scheme 2). Similar results were obtained considering the quantitative conversion of 9 into 10 and 11 (ratio 55/45) and of 12 into 13. Nevertheless, longer time and higher catalytic loadings were required (*i.e.* 18 h hours and 5 mol%, Scheme 2) than with enyne 6.

The covalently anchored gold catalyst **5** was finally tested in terms of recyclability in the cyclization of enyne **6**. After 6 hours, the solvent was removed in order to separate the filtrate containing the cyclized products from **5**. These *f*-MWNTs were vacuum dried before being used in a new catalytic run and the <sup>70</sup> collected solutions were analysed by <sup>1</sup>H NMR. The covalently anchored gold catalyst was found to be reusable according to the results shown in Scheme 2. Indeed, a quantitative conversion of enyne **6** into the cyclized products **7** and **8** in a constant ratio 88/12 was found for the first four catalytic runs before a slight <sup>75</sup> decrease appeared during the last three runs. Conversions of 94 %, 81% and finally 43% were observed respectively for runs 5 to 7. When quantitative conversion occurred, an isolated yield of 85 % was obtained (see ESI).



100 Scheme 2. Cyclization of enynes 6, 9, 12 with 5 (top). Recycling of catalyst 5 (2 mol%) in the cyclization of enyne 6 (bottom).

XPS was performed after run 3 and run 7 to check the gold oxidation state and the obtained results were in agreement with a <sup>105</sup> gold(I) oxidation state proving that it remained unchanged during the recycling tests. Although the XPS atomic percents of gold(I) decreased after each run, the ratios between the constitutive elements of the catalysts (F,N,P,S,Au) remained globally constant (see ESI, Table S3). Furthermore, solutions were analysed by ICP <sup>110</sup> after each run in order to quantify the gold leaching. These results are given in Table 1 and show that gold losses along the runs were quite constant and really weak. These results prove the strength of the covalent bond between the gold complex and the carbon support. Leaching explains more than half of the activity <sup>115</sup> loss observed after the sixth run. The rest must be due to Au

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complex degradation/rearrangment.

Table 1. Solutions analyzed by ICP after each catalytic run.

Run	Au leaching (ppm) <sup>[a]</sup>	Gold lost (%) [b]
1	0.95	1.1
2	0.85	1.0
3	3.3	4.0
4	1.35	2.8
5	0.95	1.6
6	0.62	1.1
7	1.56	0.7
Total 1-7	9.58	12.3

Gold loaded in *f*-MWNTs **5** before catalysis: 82.4 ppm. [a] Leaching of gold in ppm 5 run by run. [b] Percentage of gold lost run by run (Au leaching (ppm) divided by the initial quantity: 82.4 ppm)

Heterogenization of Gold (I) complexes is rare irrespective of the support: it is still at an early stage. MCM-41, polystyrene, P-10 functionalized coordination polymers and delaminated zeolite were selected so far as supports to covalently heterogenize and recycle gold(I) catalysts 11. These supported homogeneous catalysts were typically recycled four or five times and accompanied by a slight decrease of the catalytic activity 15 throughout the catalytic cycles, which falls in the range of the supported gold catalyst 5 anchored onto MWNTs. Compared to the only other supported gold catalyst onto MWNTs immobilized by a non-covalent strategy <sup>12</sup>, the required time to reach a complete conversion of enyne 6 is longer using the same 20 conditions (i.e. 2 mol% gold catalyst, dichloromethane), most probably due to the reaction occurring at the solid/liquid interface. In the non-covalent case, a boomerang effect was unravelled which allows the gold complex to act as soluble species. Nevertheless, the covalent anchoring realized in the 25 present work enabled to obtain significant advantages. Considering the same envne 6 cyclization reaction, an increase in the number of runs realized before deactivation as well as a

- higher conversion along the runs were obtained. The gold leaching along the runs was much lower and reached barely 11% <sup>30</sup> after 5 consecutive runs, which is lower than the gold boomerang
- catalyst (29% after 5 runs) and undoubtedly due to the covalent linkage between catalyst **4** and *m*-MWNTs.

### Conclusions

- A gold complex with a pendant amine group was designed for <sup>35</sup> its covalent anchoring onto modified MWNTs in order to give a supported homogeneous catalyst. Compared to its homogeneous counterpart, the selectivity to the cyclized products was unchanged but the activity was considerably improved. Recycling is conceivable and is combined with a fairly low gold leaching.
- <sup>40</sup> To the best of our knowledge, this is only the second case of reported supported gold homogeneous catalyst onto carbon nanotubes and the first example of supported homogeneous gold catalyst onto carbon nanotubes via covalent anchoring.

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