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Aurophilic complexes as gold atom sources in organic media†

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The decomposition, either thermal or under H_2, of $[O(Au^IPR_3)_3](CF_3SO_3)$ (R = Ph 1, R = Me 2) in organic solvents has been studied by $^{31}P\{^1H\}$ NMR, UV–vis spectroscopy and TEM; during the reaction, the phosphine acts as an efficient oxygen trap and gold nanoparticles are produced which may be stabilized by PVP in acetonitrile (mean diameter 4.5 nm) or oleylamine in toluene (mean diameter 9 nm).

In recent years intensive work has been focused on the synthesis and properties of nanoparticles. These properties were shown to differ from those of the corresponding bulk materials and to be highly dependent on the surface state.[1] Many applications are expected in catalysis,[2] gas sensors technology,[3,4] high density recording media[5] and microelectronics,[3] *etc*., which require well characterized nanoparticles assemblies, with narrow size distributions and well controlled surface states. Furthermore, the properties of these objects may be modulated through the formation of bimetallic species.[6] In this respect, nanoparticles including gold atoms could be of particular interest for their optical and catalytic properties.[7] This requires the use of a gold precursor, which would decompose in conditions close to those of the other metals in the absence of contaminants such as water. Besides, strongly coordinating ligands such as thiols should be avoided since they alter the surface of the particles which is thus distorted[8] or passivated, with modified magnetic properties.[9] Halide ions also form strong bonds with gold or silver surfaces. For instance, chloride ions are used to anchor nanoparticles on gold surfaces[10] and their presence is essential for the stabilisation of gold–phosphine clusters[11] such as $[Au_{39}(PPh_3)_{14}Cl_6]Cl_2$[12] and $[Au_{55}(PPh_3)_{12}Cl_6]$[13] or even of nanoparticles.[14] There is therefore a need for alternatives to gold chloro derivatives as nanoparticle precursors[15,16] and for conditions allowing the use of labile and non-contaminating ligands.

We report here our investigations on the gold(I) complexes $[O(Au^IPR_3)_3](CF_3SO_3)$ (R = Ph **1**, R = Me **2**)[17] as potential gold atom precursors in organic media. These complexes are easily prepared, they display short gold–gold distances and are available with two phosphines of different electronic and steric properties. These complexes have been widely used to carry out auronation reactions and as alternative precursors for the synthesis of small gold clusters (4–8 gold atoms).[18] In the context of this work, the phosphine would act both as a reducing agent and as an oxygen trap. The counter-anion is non-coordinating and should not alter the surface properties of the nanoparticles.

Thermal decompositions of these salts were carried out in refluxing acetonitrile. Typically, 5 mg of the oxonium salt were dissolved in 20 mL degassed acetonitrile and the solution was refluxed under argon for 2 h. At this temperature phosphine or phosphine oxide ligands alone were not able to stabilize gold nanoparticles, and a brown powder was formed, thought to contain finely divided gold metal. Most of this powder sticks to the walls of the reactor and could not be isolated for further characterisation. Hence, to better characterise the system, the reaction was reproduced in the presence of 100 mg of poly(*N*-vinylpyrrolidone) (PVP, 40 000 g mol^{-1}). The reaction was monitored by UV–vis spectroscopy. Once the reflux started, a brown colloidal solution formed, probably containing small clusters, which rapidly transformed into a typical ruby-coloured colloidal solution: λ = 525 nm for colloid 1 (obtained from complex **1**) and 515 nm for colloid 2 (obtained from complex **2**). The observation of the typical plasmon band implies the presence of gold nanoparticles with sizes in the range 4–30 nm.[19] The nanoparticles could be stored for a long time by evaporating to dryness the solution to give a red/violet residue, which could then be redissolved in chlorinated solvents or acetonitrile. Transmission electron microscopy (TEM) images of colloid 1 display nanoparticles of 4.5 ± 0.5 nm mean diameter and narrow size distribution. In the case of colloid 2, nanoparticles of similar size (4.3 ± 0.5 nm mean diameter) and also narrow size distribution are observed (Fig. 1). As PVP is not a stabiliser of choice for gold,[20] these results suggest that the phosphine contributes to the stabilisation of the nanoparticles. However, since a powder is obtained in the absence of polymer, the interactions between the phosphine ligand and the gold surface is probably weak.

Since our precursors contain phosphines, ^{31}P NMR can be used to follow the decomposition reaction. The $^{31}P\{^1H\}$ NMR

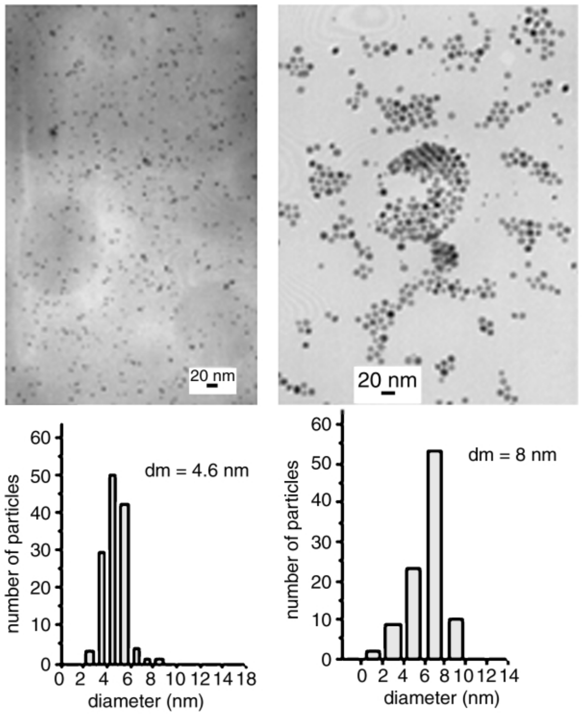

Fig. 1 TEM images and size histograms of colloids 2 (a) and 5 (b).

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† Electronic supplementary information (ESI) available: UV–vis spectra, TEM images and size histograms of colloids 1, 3 and 4. See http://www.rsc.org/suppdata/cc/b1/b111679g/

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spectrum of colloid 1 showed both the presence of free phosphine oxide and a broad resonance at 41.2 ppm. When running the experiment at −55 °C, this broad peak splits into a sharp signal assigned to $[Au(PPh_3)_2]^+$ and several small signals assigned tentatively to phosphino-clusters present in the solution. It is well-known that the presence of a small amount of extra phosphine can induce fast exchanges in phosphino–gold derivatives.[21] As determined through integration of the NMR signals, one third of the initial phosphine was transformed into phosphine oxide. $[Au(PPh_3)_2](CF_3SO_3)$ has been heated for more than 9 h in refluxing acetonitrile without any change in its NMR spectrum. In the case of colloid 2 the corresponding $[Au(PMe_3)_2](CF_3SO_3)$ complex and phosphine oxide were the only products observed. Therefore the ^{31}P NMR experiments demonstrate that the thermal decomposition of the oxonium salts is an intramolecular redox process which produces gold(0), and $[Au(PR_3)_2](CF_3SO_3)$. Furthermore, these experiments show that the phosphines effectively behave as oxygen traps. This contrasts with the observation that these oxonium salts give three phosphino–gold(I) units in auronation reactions.

We have carried out experiments under a reducing atmosphere of H_2, in order to lower the decomposition temperature and to get cleaner reactions. The decomposition occurred at 40 °C under 3 bar H_2 and even at room temperature under 5 bar H_2. $^{31}P\{^1H\}$ NMR spectra of the colloidal solution formed at room temperature from complex **1**, denoted colloid 3, show only phosphine oxide and a broad signal at 34 ppm. No traces of $[Au(PPh_3)_2](CF_3SO_3)$ were present even at −55 °C. Therefore, we assume that the full reduction of the oxonium complex affords free phosphine oxide and gold nanoparticles. Removal of phosphine oxide was attempted by washing with diethyl ether, however traces of the phophine oxide remained trapped within the polymer framework. In the case of complex **2**, traces of $[Au(PMe_3)_2](CF_3SO_3)$ were observed on the $^{31}P\{^1H\}$ NMR spectra of the corresponding colloidal solution, *i.e.* colloid 4. This can be related to the fact that the thermal decomposition of complex **2** is easier and thus this path could not be totally suppressed, even under 5 bar of dihydrogen. Surprisingly, though the decomposition under dihydrogen is easier, the growth of the gold nanoparticles is less controlled. TEM images of colloids 3 and 4, evidence bimodal size distributions which correspond to particles of 2.8 and 6.6 nm mean diameter for colloid 3, and 3 and 6.2 nm for colloid 4. The nanoparticles are however stable in solution.

We have further investigated this route in a non-polar organic medium. As PVP is not readily soluble in such media, we turned to amine ligands as stabilizing agents. These ligands have been recently used by our group to stabilise ruthenium[22] or nickel nanoparticles.[23] They have been shown to be fluxional[22] and to induce the formation of rod-shape nanoparticles.[23] Hence, the decomposition of complex **1** (3 mg) has been studied in toluene (3 mL), in the presence of oleylamine (100 μL). Full decomposition of the gold precursor was achieved after refluxing the solution for 20 mn: UV–vis spectra are consistent with the formation of gold nanoparticles, λ_{max} = 528 nm (colloid 5). TEM images display spherical gold nanoparticles of narrow size distribution centered around 9 ±0.5 nm. Interestingly, these nanoparticles tend to self-assemble on the microscope grid as can be observed in Fig. 1; additionally, the colloidal solution remained unchanged for several days. This is different from previous observations for THF solutions of gold nanoparticles stabilised by primary alkyl amines such as RNH_2, R = C_8H_{17}, $C_{12}H_{25}$ or $C_{16}H_{33}$.[16] Most probably, the bending of the oleyl chain insures better protection against coalescence.

In conclusion, we have shown that phosphino–gold oxonium salts can act as gold atom sources in organic media under mild conditions. In acetonitrile, in the presence of poly(*N*-vinylpyrrolidone), UV–vis spectroscopy and TEM measurements evidence the formation of gold nanoparticles of 4.5 nm diameter and narrow size distribution. In toluene, the use of a weaker stabiliser, oleylamine, also leads to gold nanoparticles of narrow size distribution centered around 9 nm. We now intend to develop these precursors with the aim of synthesizing bimetallic Au/M nanoparticles and study their physical properties.

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