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Simple and efficient: Gold nanoparticles from triphenylphosphane gold(I) carboxylates without addition of any further stabilizing and reducing agent

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ABSTRACT

An innovative and straightforward methodology for the generation of gold nanoparticles (= NP) from $[(Ph_3P)\text{-}AuO_2CCH_2(OCH_2CH_2)_2OCH_3]$ without addition of any further stabilizing and reducing reagents is reported; particles of size 3–6 nm (average diameter 4 nm) with narrow size distribution are obtained.

Transition metal nanoparticles (= NP) are of high interest in many applications [1], due to their unique optical [2,3], electrical [4], magnetical [5], and catalytical [6] properties depending on the size, shape, and size distribution [7]. In particular, group-11 metal NP allow the design of new generations of nanodevices and smart materials [8–10]. Nanostructured metal colloids can be obtained by top-down or bottom-up methodologies [11–13]. The latter method includes mainly electrochemical [14] and photochemical [7,15] pathways. The most common and efficient synthesis strategy in this field is the chemical reduction of metal ions to zerovalent metal NP in aqueous [16,17] or organic solvents [18]. As stabilizing components mostly ethylene glycols [19,20] and polymers/co-polymers [21] or dendrimers [22] with donating functionalities including N, P, S, and O donor atoms are used.

We here discuss a novel methodology to form gold NP with size diameter of 3–6 (+/-1) nm using $[(Ph_3P)AuO_2CCH_2(OCH_2CH_2)_2OCH_3]$ (**3**) [23] as starting material. The formation of the NP was carried out by thermolysis at relative low temperature, whereas no further stabilizing and even reducing agent was necessary.

Molecule **3** is accessible by the reaction of $[(Ph_3P)AuCl]$ (**1**) with the silver carboxylate $[AgO_2CCH_2(OCH_2CH_2)_2OCH_3]$ [24] (**2**) in toluene at ambient temperature (Scheme 1). Compound **3** was characterized by elemental analysis, IR and NMR spectroscopy and mass-spectrometry [23]. Complex **3** crystallized in the triclinic space group $P\bar{1}$. The P1—Au1—O1 unit is almost linear (177.5°), the Au—P, Au—O as well as the C—C and C—O distances of the 2-[2-(2-methoxyethoxy)ethoxy]acetato ligand do not show any distinctive features (Fig. 1) [25].

The thermal decomposition of **3** was studied by thermogravimetric and differential scanning calorimetric experiments to obtain first information of the decomposition behavior of **3** (Fig. 2). Decomposition of **3** is observed at 232 °C, the overall mass diminution with 68.8% corresponds to the formation of elemental gold ($\Delta m/m_0 = 69.0\%$, theoretical). The melting point of **3** was determined by DSC experiments (133 °C). The decomposition of **3** shows an overlay of various exothermic and endothermic processes (Fig. 2). From TG–MS coupling experiments the formation of CO_2, PPh_3 and ethylene glycol fragments were observed which indicated the cleavage of the Au—O bond. Most probably, the *in-situ* formed organic and inorganic species are responsible for the narrow size distribution of the Au NP. Obviously, the thermal induced decomposition of **3** follows a similar mechanism as found for akin silver species [26].

Based on these studies we choose mesitylene as organic solvent for the thermal decomposition of **3** to generate Au NP, due to its high boiling point and *non*-coordinating behavior. In a typical experiment a 6.3×10^{-3} mol/l mesitylene solution containing **3** was heated to reflux for 10 min. The color of the solution turned from colorless to intensive purple which indicates the formation of gold NP. The UV-vis spectrum shows a plasmon band at 523 nm (Fig. 3). This result evinces that metal-organic **3** decomposes in solution at much lower temperature as found in the solid state (vide supra). TEM analyses gave an average size diameter of 4.0 (+/-1) nm with a sharp size distribution (Fig. 4). In addition, we carried out further thermolysis experiments at lower temperatures. At 138 °C (*para*-xylene) the reaction time increased to 1 h and at 111 °C (toluene) to 24 h, which shows that NP generation decelerates with decreasing reaction temperature. The received NP size

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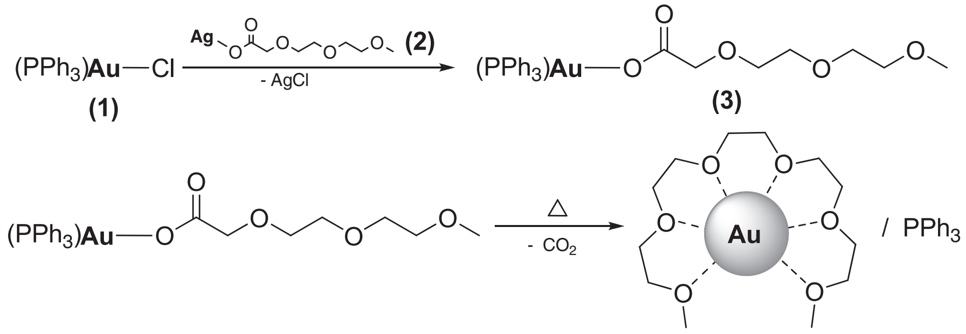

Scheme 1. Synthesis of **3** and thermal induced generation of Au-NP; schematic view of stabilized Au-NP by the *in-situ* generated organic/inorganic matrix.

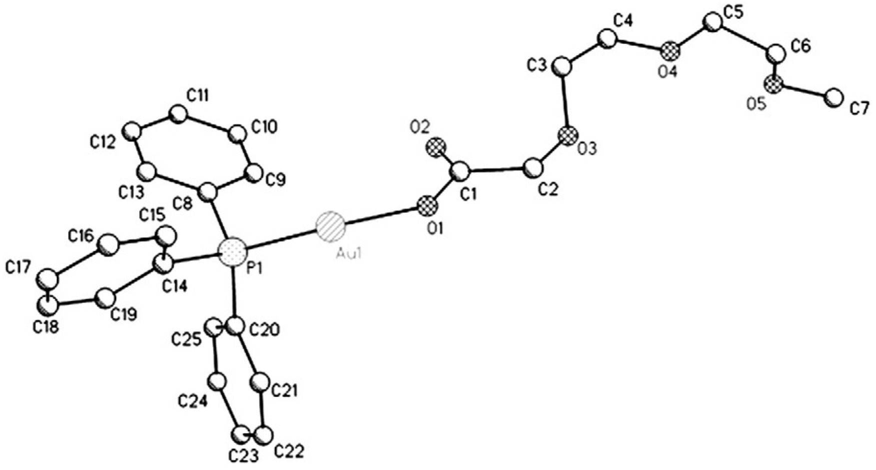

Fig. 1. ORTEP diagram (50% probability level) of the molecular structure of **3** with the atom-numbering scheme. All hydrogen and disordered atoms are omitted for clarity. Bond distances (Å) and angles (°): Au1—P1 2.214(3), Au1—O1 2.079(7), C1—O1 1.307(13), C1—O2 1.210(14); P1—Au1—O1 177.5(3), O1—C1—O2 125.3(11), C1—O1—Au1 113.3(7).

diameters are with 3.9 (+/-1) and 4.0 (+/-1) nm similar to the results obtained at 168 °C. The formation of gold NP at lower temperatures (benzene, 80 °C) could not be observed, which indicates that for NP formation from **3** a certain temperature is required. The thus formed NP are stable about several weeks in solution. The removal of the solvent gives a deep purple viscous residue which is able to re-disperse.

The NP size and size distribution are obviously not influenced by the reaction temperature but probably by the glycol chain and its decomposition products. Changing the concentration from $7.8 \cdot 10^{-4}$ mol/l (3.8 (+/-0.6) nm) to $1.6 \cdot 10^{-2}$ mol/l (4.4 (+/-0.5) nm) shows a slightly enlargement of the average NP size.

Transmission electron microscopy (TEM) data show that homogeneous, conformal NP were formed (Fig. 4).

Most likely after thermal induced decarboxylation of **3** the thus formed organic species recombine to form the ethylene glycols which acts as stabilizing component for the *in-situ* formed gold colloids. The formation of ethylene glycol derivatives could be determined by ^1H NMR studies, where it was found that during decomposition the *in-situ* generated Au NP are stabilized by ethylene glycol fragments as well as *non*-decomposed $[(Ph_3P)AuO_2CCH_2(OCH_2CH_2)_2OCH_3]$ as evidenced by a deep field shift of the signals of the ethylene glycol

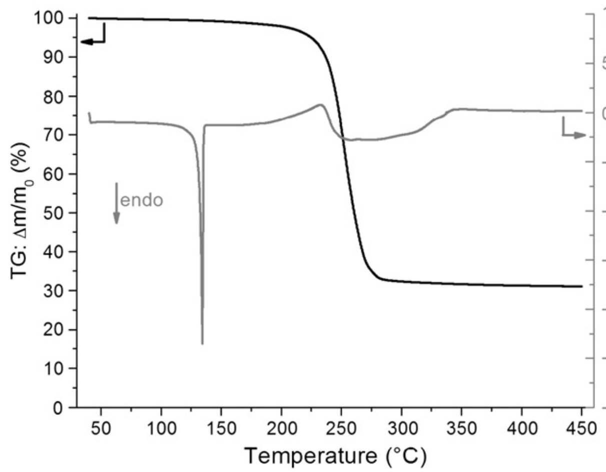

Fig. 2. TG (black) and DSC (gray) traces for the thermal heating of **3** in argon (flow rate 40 ml·min^{-1}, heating rate 5 K·min^{-1}).

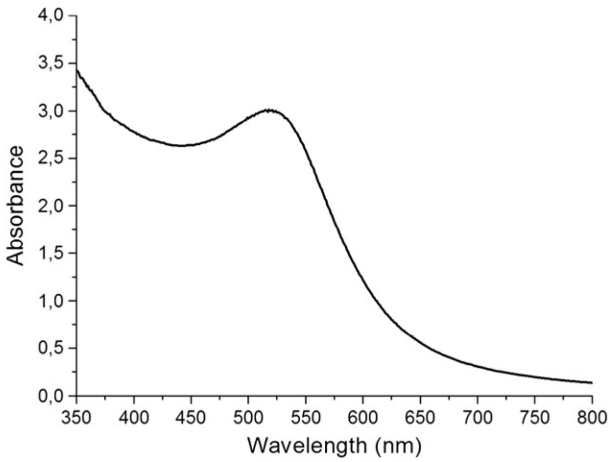

Fig. 3. UV–vis spectra of Au NP obtained by thermolysis of **3** (c = 6.3×10^{-3} mol/l) in mesitylene.

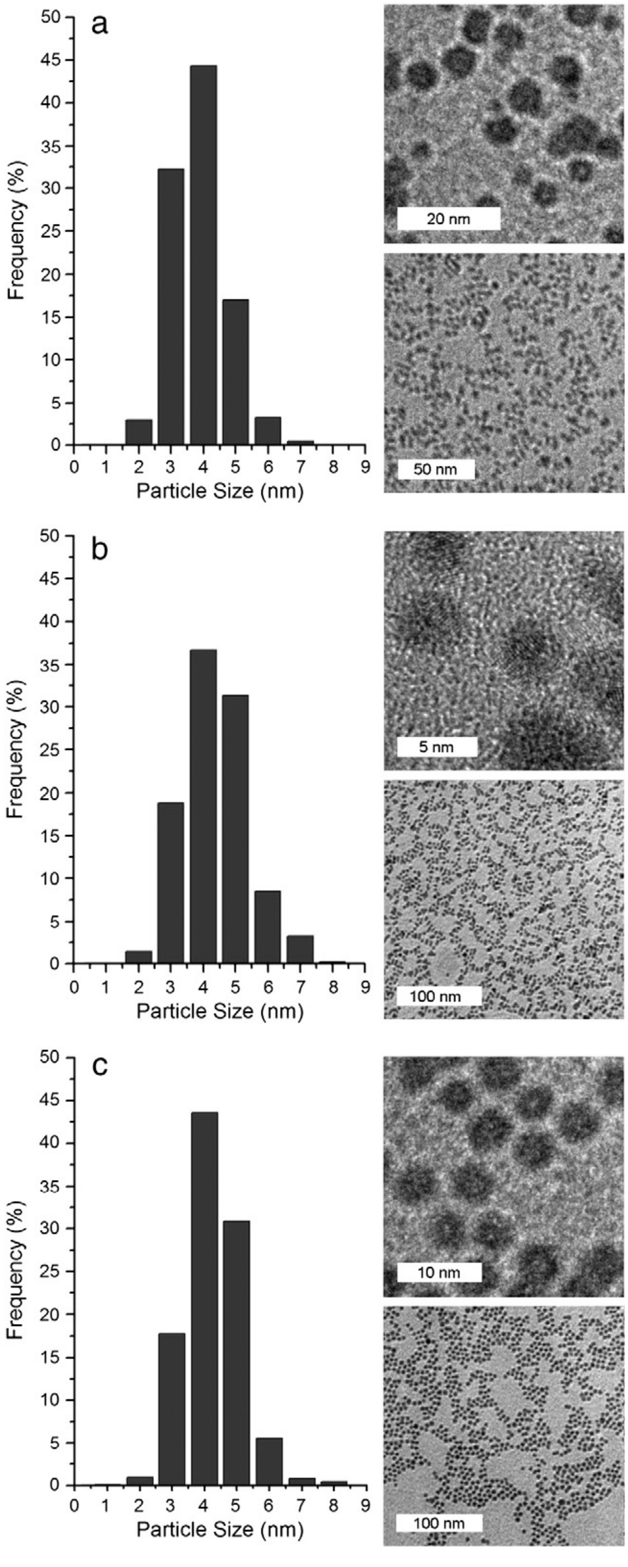

Fig. 4. TEM images and size distribution of Au NP derived from **3** generated in boiling mesitylene (3.9 (+/-1) nm) (a), *para*-xylene (4.0 (+/-1) nm) (b), and toluene (4.0 (+/-1) nm) (c).

fragments. From ^{1}H NMR and ^{31}P NMR studies we conclude that the stabilizing matrix of the Au NP consists of ethylene glycol fragments and PPh_3. In contrast to common bottom-up synthesis procedures, neither the addition of a stabilizing (*e. g.* polymers, co-polymers or dendrimers) nor a reducing reagent is necessary [27,28], which qualifies **3** as an efficient and simple precursor for the generation of metal NP.

We have developed a straightforward and efficient way to generate gold nanoparticles by thermolysis of a phosphane gold ethylene glycol carboxylate in organic solvents (toluene, *para*-xylene and mesitylene) at low temperatures. The advantage of this preparation methodology is that no reducing and stabilizing agents have to be added. The generated NP are of narrow size distribution and are stabilized by a small organic/inorganic matrix.

Actually, we are using the methodology described above for the formation and stabilization of various metal and metal oxide NP from further transition metal and main-group element carboxylates.

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Appendix A. Supplementary material

CCDC-793568 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[23] Synthesis of $[(Ph_3P)AuO_2CCH_2(OCH_2CH_2)_2OCH_3]$ (**3**). Triphenylphosphine gold(I) chloride (**1**) (0.32 g, 0.64 mmol) dissolved in toluene (10 mL) was treated with silver(I)-2-[2-(2-methoxyethoxy)-ethoxy]acetate (**2**). The slurry was stirred for 12 hrs at 25 °C in the absence of light, followed by a filtration through a pad of Celite. Afterwards, the remaining solid was washed twice with toluene (15 mL). Evaporation of all volatiles from the eluate in oil-pump vacuum gave colorless **3** (0.38 g, 94%). Mp 133 °C. Elemental analysis: Calcd. for $C_{25}H_{28}AuO_5P$ (636.43) C, 47.18%, H, 4.43%, Found: C, 47.38%, H, 4.52%. ^{1}H NMR ($CDCl_3$) 3.36 (s, 3H), 3.54 (m, 2H), 3.65 (m, 2H), 3.70 (m, 2H), 3.78 (m, 2H), 4.17 (s, 2H), 7.42–7.54 (m, 15H). ^{13}C NMR ($CDCl_3$) 58.94, 70.31, 70.40, 70.65, 71.30, 71.88, 128.45 (d, $^1J_{CP} = 64.5$ Hz), 129.1 (d, $J_{CP} = 11.9$ Hz), 131.90 (d, $^4J_{CP} = 2.3$ Hz), 134.1 (d, $J_{CP} = 13.6$ Hz). IR: $\upsilon CO = 1599$ (m), $\upsilon_{PC} = 1434$ (m), $\upsilon_{COC} = 1119$ (m).
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[25] Crystal data for $[(Ph_3P)AuO_2CCH_2(OCH_2CH_2)_2OCH_3]$ (**3**): $C_{25}H_{28}AuO_5P$, $M = 636.41$ g ·mol^{-1}, crystal dimensions $0.10 \times 0.05 \times 0.01$ mm, $T = 100$ K, triclinic, $P\bar{1}$, $a = 9.7833(8)$, $b = 10.3950(10)$, $c = 12.4782(9)$ Å, $\alpha = 81.125(7)$, $\beta = 74.972(7)$, $\gamma = 78.687(7)$ °, $V = 1194.60(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.769$ g cm^{-3}, $\mu = 12.484$ mm^{-1}, θ range = 4.36–62.00 °, reflections collected: 6954, independent: 3703 ($R_{int} = 0.0568$), $R_1 = 0.0621$, $wR_2 = 0.1647$ [$I > 2\sigma(I)$].
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