

SUPPORTING INFORMATION

Formation and stability of 3–5 atom gold clusters from gold complexes during the catalytic reaction: Dependence on ligands and counteranions.

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General information.....Page S2

Reaction procedure and compound characterization.....Page S3

Figures S1–S3.....Page S4

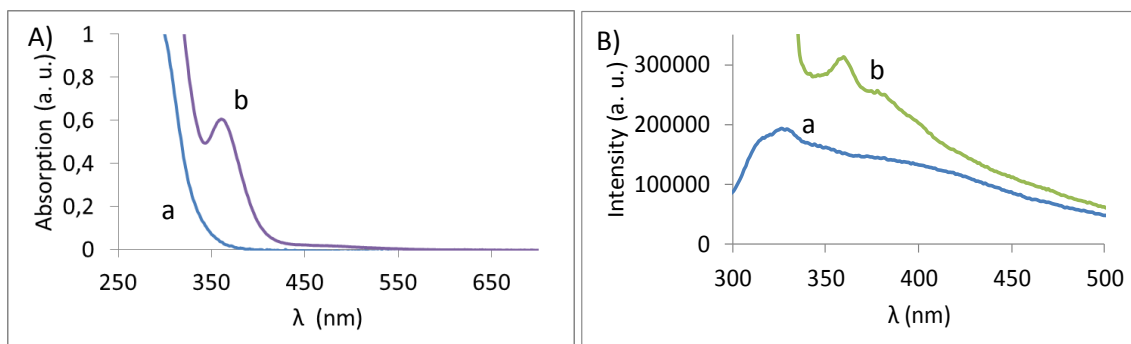
General information.

Reagents and solvents were obtained from commercial sources and were used without further purification otherwise indicated. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. Dodecane was used as an external standard. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. ^1H , ^{13}C , DEPT, ^{19}F and ^{31}P NMR measurements were recorded in a 300 MHz instrument using CD_3CN or CDCl_3 as solvents, containing TMS as an internal standard. Absorption spectra were recorded on a Cary 300 UV-Vis spectrophotometer (UV0811M209, Varian). Fluorescence spectra were obtained with a LP S-220B (Photon Technology International) equipped with 75 W Xe lamp. The photophysical measurements were performed under air at room temperature in a quartz cell of 1.0 cm optical path length.

Reaction procedure.

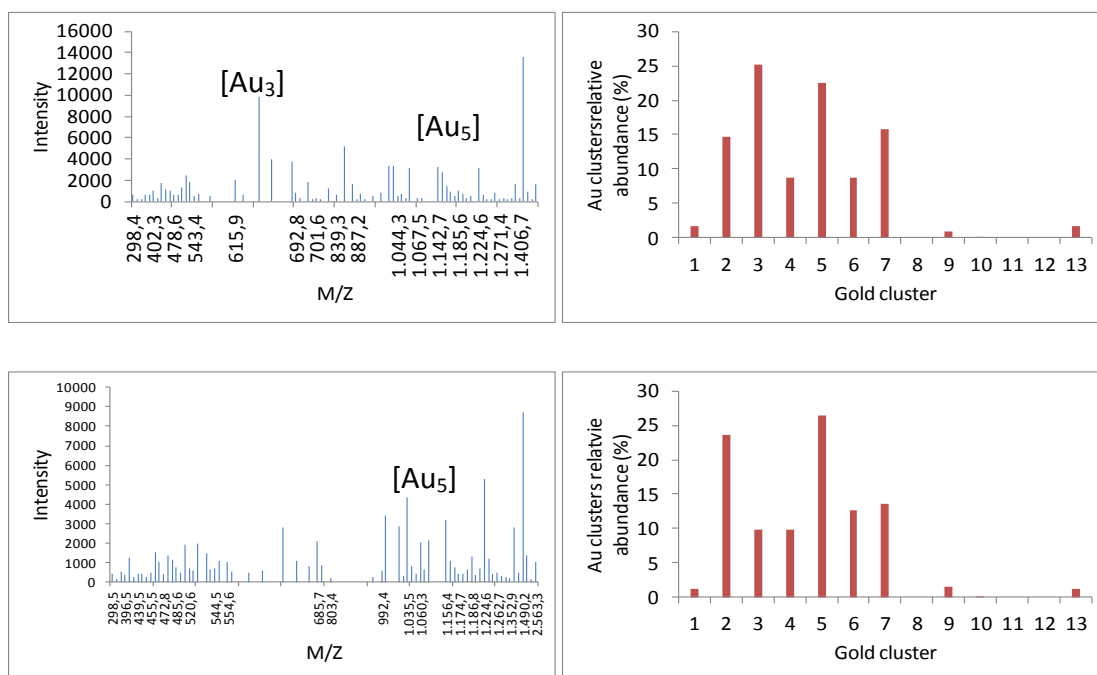
General procedure for the one-pot acylation-hydration reaction. The gold catalyst, heptanoyl chloride (1 mmol) and the propargylic alcohol (10 mmol) were placed in a 2 ml vial equipped with a magnetic stir bar. For small amounts of gold, the calculated amount of a dilution of an initial solution of AuCl (5 mg) in propargylic alcohol or acetonitrile (5 ml) was used. The same applies to gold complexes and additives. The vial was sealed and the resulting mixture was stirred for 0.5 h at room temperature. Then, water (1 mmol) was added and the resulting mixture was stirred at room temperature, and aliquots of 25 μ l were periodically taken, diluted in *n*-hexane, and analyzed by GC in order to follow the reaction, using dodecane as an external standard. Product **3** was characterized by GC-MS and ^1H , ^{13}C NMR and DEPT spectroscopy. GC-MS (*m/z*, relative intensity): 215 (M^+H , 1), 171 (17), 130, (1), 113 (100), 85 (29), 57 (9), 43 (23). ^1H NMR (CDCl_3 , 300 MHz): 2.26 (dd, $J=9.6, 9.6$ Hz, 2H), 2.04 (s, 3H), 1.61-1.51 (mult, 2H), 1.39 (s, 6H), 1.24 (mult, 6H), 0.84-0.80 (mult, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): 206.7 (C), 173.0 (C), 83.3 (C), 34.2 (CH_2), 31.2 (CH_2), 28.6 (CH_2), 24.6 (CH_2), 23.4 (2 CH_3), 23.2 (CH_3), 22.3 (CH_2), 13.8 (CH_3).

Fig. S1. A) UV–vis measurements for AuPPh₃Cl **4** before (a) and after (b) the addition of HCl. B) Fluorescence measurements of the quantum gold clusters formed from AuPPh₃Cl **4** irradiated at 290 nm (a) and 356 nm (b), corresponding with clusters between 3–5 gold atoms. C) Representative Matrix–Assisted Laser Desorption/Ionization Time–Of–Flight (MALDI–TOF) measurements of the gold clusters generated from AuCl.



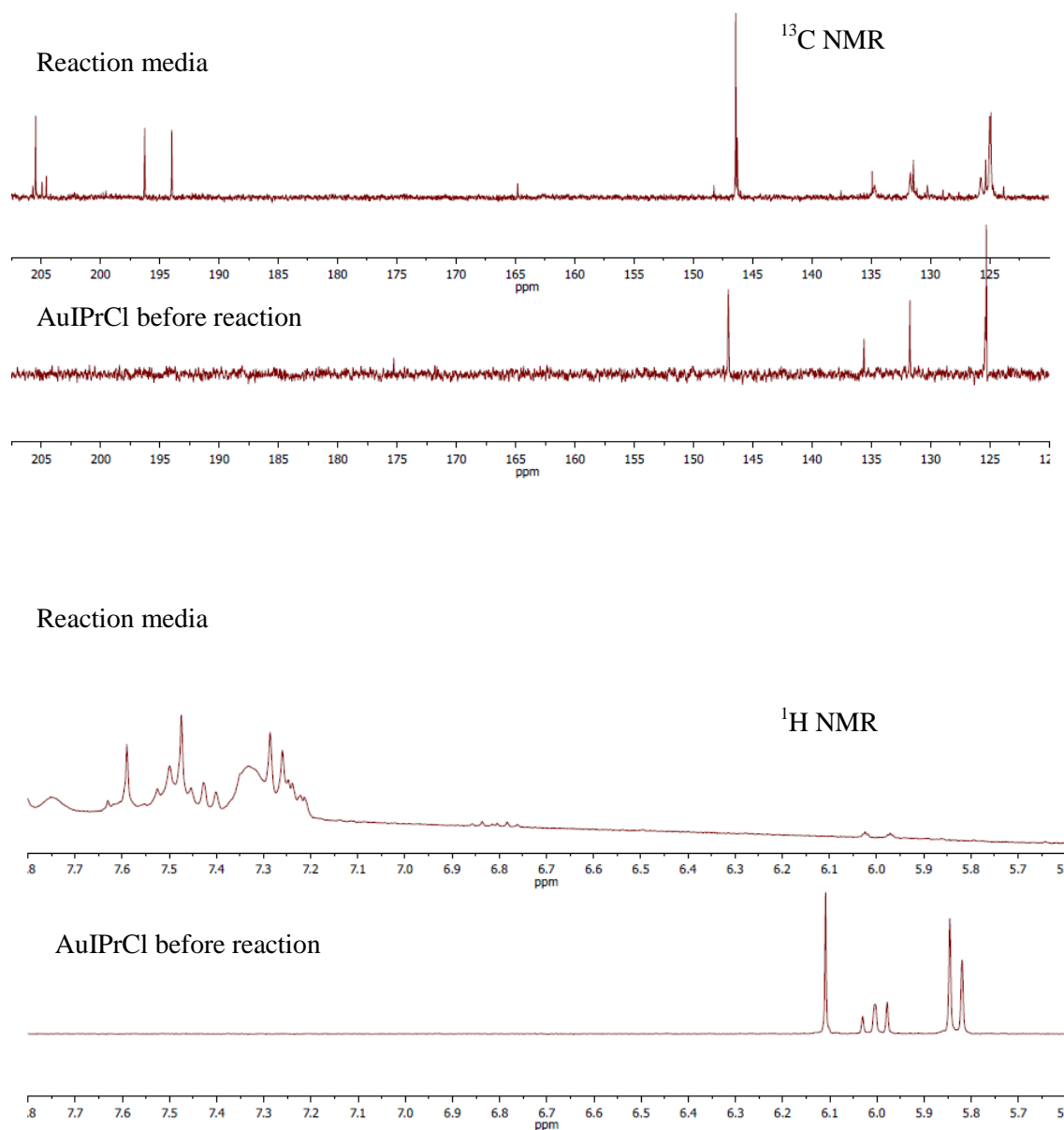
The results show that complex **4** decomposes immediately to gold clusters of 3-5 atoms after HCl addition.

C)



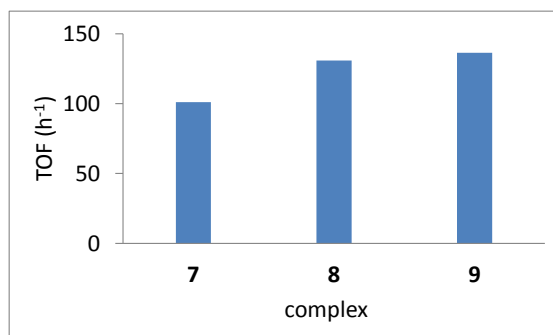
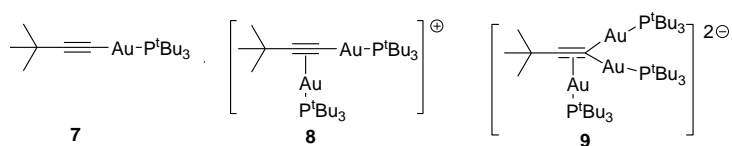
The MALDI-TOF results confirm the size of 3-5 atoms for the gold clusters after HCl addition.

Figure S2. ^1H (bottom) and ^{13}C NMR (top) spectra for the gold carbene complex AuIPrCl **5** fresh and during the hydration reaction.



The evolution of complex **5** was monitored by ^1H , ^{13}C and ^{19}F Nuclear Magnetic Resonance (NMR) spectroscopy and the disappearance of the original carbene signals together with the appearance of new downfield signals was observed in ^1H NMR. The peaks in ^{13}C NMR do not disappear completely but new peaks are also observed.

Figure S3. Initial rates *per gold atom* for the gold cluster-catalyzed one-pot acylation-hydration of propargyl alcohol **1** with complexes **7–9**.



The catalytic activity of three gold phosphine complexes having different number of gold atoms was tested in the reaction and the initial catalytic activity *per gold atom* increases as the number of gold atoms in the complex does.