

Small Gold Clusters Formed in Solution Give Reaction Turnover Numbers of 10^7 at Room Temperature

Judit Oliver-Meseguer, Jose R. Cabrero-Antonino, Irene Domínguez,
Antonio Leyva-Pérez,[†] Avelino Corma[†]*

Instituto de Tecnología Química. Universidad Politécnica de Valencia–Consejo
Superior de Investigaciones Científicas. Avda. de los Naranjos s/n, 46022
Valencia, Spain.

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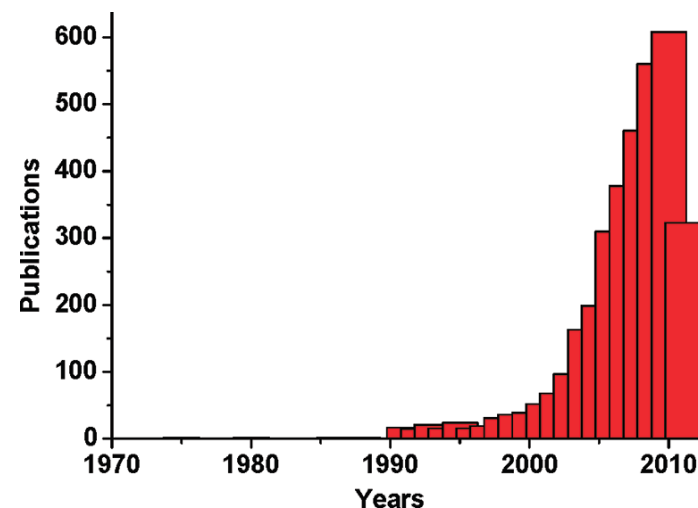
Sub-Nanosized Gold Catalysts

By

A. Stephen K. Hasmi

❖ Gold was long considered to be “**catalytically dead**”, but since 1985, triggered by observations of Haruta and Hutchings, heterogeneous gold catalysis has become a **highly active field**.

1. Vapor Phase Hydrochlorination of Acetylene: Correlation of Catalytic Activity of Supported Metal Chloride Catalysts. *Journal of Catalysis* 96, 292-295 (1985) by G. J. HUTCHINGS.
2. Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature far Below 0°C. *Chemistry Letters*, 2, 405 (1987) by M. Haruta.



❖ Innovative results from homogeneous gold catalysis have also triggered considerable research interest in this area.

❖ Crucial factors in these cases are Turnover number (TON) and Turnover frequency (TOF).

❖ Turnover number (abbreviated *TON*) is the number of moles of substrate that a mole of catalyst can convert before becoming inactivated.

❖ In the case of a catalyst loading of 5 mol%, a yield of 100% corresponds to a TON of 20 — a number that is ridiculously low in the eyes of any industrial chemist.

❖ An ideal catalyst would have an infinite turnover number in this sense, because it wouldn't ever be consumed, but in actual practice one often sees turnover numbers which go from 100 upto 40 million for Catalase.

❖ The term turnover frequency (abbreviated *TOF*) is used to refer to the turnover per unit time, as in enzymology. For most relevant industrial applications, the turnover frequency is in the range of 10^{-2} - 10^2 s^{-1} (enzymes 10^3 - 10^7 s^{-1}).

History of increasing TON: Efficient Gold Catalysis

❖ Teles *et al.* have explored the homogeneous gold(I)-catalyzed addition of alcohols to alkynes on a multi kilogram scale and achieved an impressive **TON of 100,000 and a TOF of 5400 hour⁻¹**.

J. H. Teles et al., Angew. Chem. Int. Ed. 37, 1415 (1998).

❖ Through the use of CO and acid as promoters and cocatalysts in this homogeneous catalysis, Mizushima *et al.* subsequently almost tripled this **TOF to 15,600 hour⁻¹**.

E. Mizushima et al., Angew. Chem. Int. Ed. 41, 4563 (2002).

❖ For heterogeneous gold-catalyzed oxidation of glucose by oxygen, Comotti *et al.* achieved an even higher **TOF of 50,120 hour⁻¹**.

M. Comotti et al., Angew. Chem. Int. Ed. 43, 5812 (2004).

❖ Marion *et al.* recently reported a homogeneous and highly efficient hydration of alkynes, reaching a **TON of 84,000 and a TOF of 4667 hour⁻¹** with some substrates.

N. Marion et al., J. Am. Chem. Soc. 131, 448 (2009).

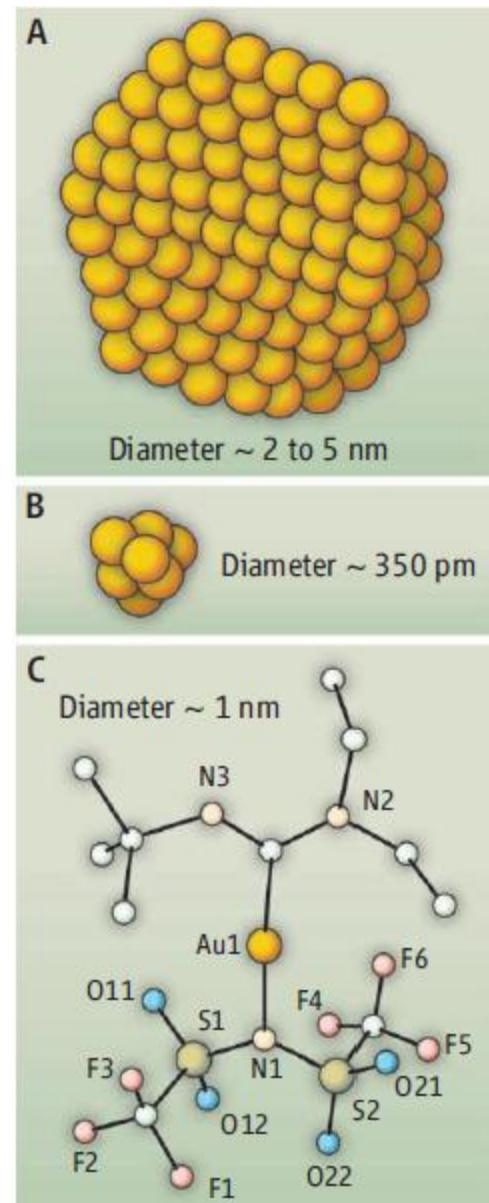
Examples of highly efficient heterogeneous gold catalysts also stem from the field of alcohol addition to alkynes; last year Bouhrara *et al.* reported a **TON of 800,000 and a TOF of 294,000 hour⁻¹**. These water or alcohol additions to alkynes seem to be by far the most efficient gold-catalyzed reactions.

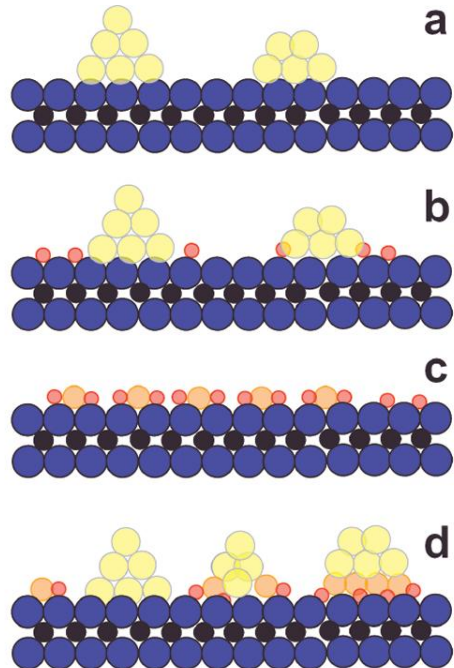
M. Bouhrara *et al.*, *Dalton Trans.* 40, 2995 (2011).

Oliver-Meseguer *et al.* have now achieved remarkable values of **TON (10,000,000) and TOF (100,000 hour⁻¹)** for the ester-assisted hydration of alkynes.

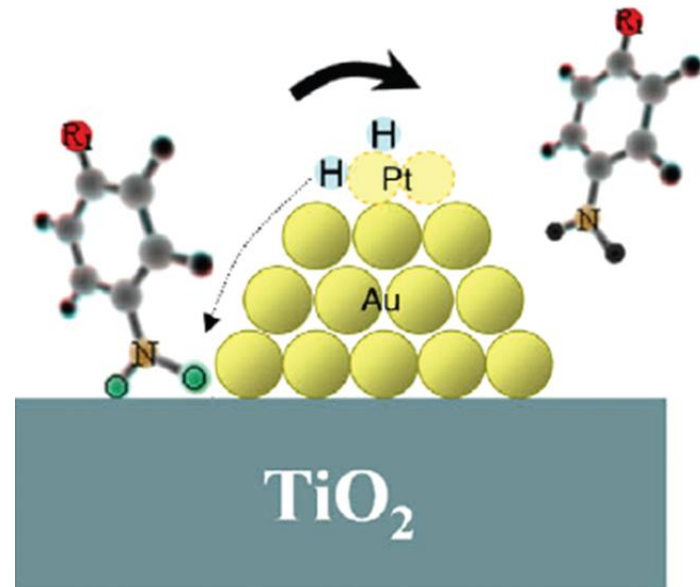
J. Oliver-Meseguer *et al.*, *Science* 338, 1452 (2012).

Gold catalysis. Oliver-Meseguer et al.'s sub-nanosized gold clusters (B) show catalytic activities that are much higher than those obtained with small gold nanoparticles (A) and mononuclear homogeneous gold catalysts (C).



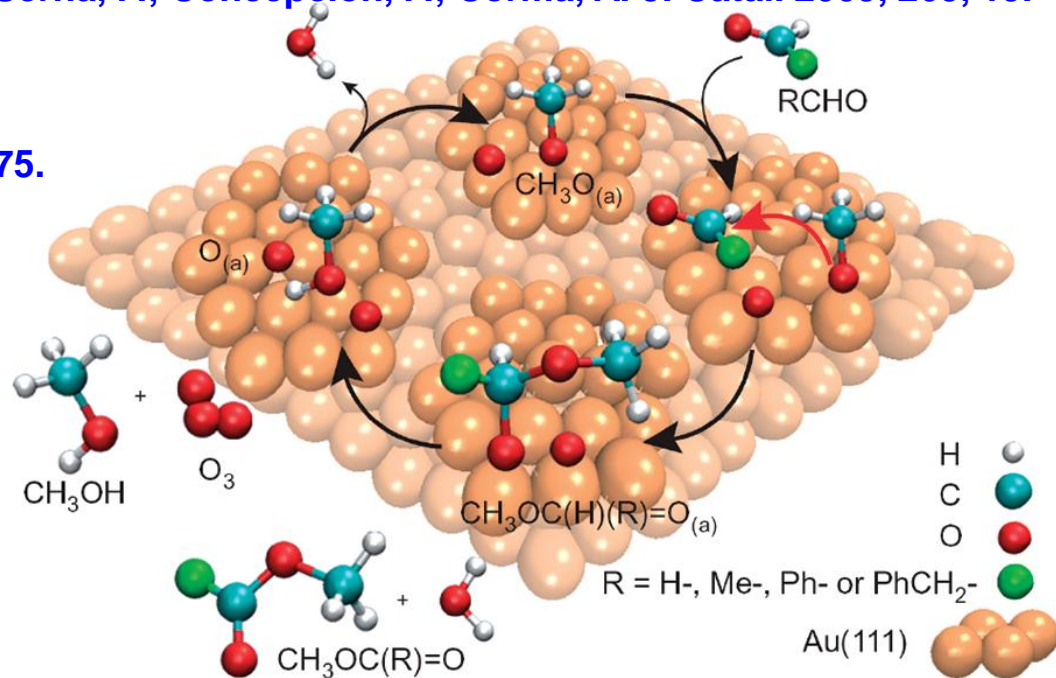
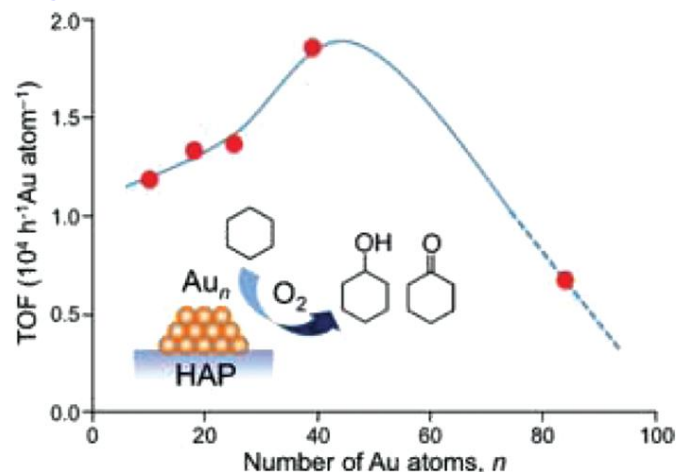


Y. Zhang, X. Cui, F. Shi,
Y. Deng, Chem. Rev.
112, 2467 (2012).



Serna, P.; Concepcion, P.; Corma, A. J. Catal. 2009, 265, 19.

Zhang, X.; Shi, H.; Xu, B.-Q. J. Catal. 2011, 279, 75.



Liu, Y.; Tsunoyama, H.; Akita, T.; Xie, S.; Tsukuda,
T. ACS Catal. 2011, 1, 2.

Xu, B.; Liu, X.; Haubrich, J.; Friend, C. M. Nat.
Chem. 2011, 2, 61.

❖ Gold salts and complexes have catalytic activity in solution, particularly for unsaturated C-C bonds; new routes for organic synthesis have taken advantage of this activity. In particular, readily available Au(I) and Au(III) chloride salts or complexes have **been** used as Lewis catalysts for many of these homogeneous reactions.

❖ However, their ubiquity has puzzled chemists because these catalysts perform similarly irrespective of the gold oxidation state. Some authors have speculated that Au(III) is reduced to Au(I) under reaction conditions and that the latter is the true catalyst; others have attributed this similar catalytic performance to the disproportionation of Au(I) to Au(III) and Au(0).

In this paper,

They have shown that different Au(I) and Au(III) salts or gold complexes form 3 to 10 atom gold clusters in solution at room temperature and can act as extremely active catalysts, with turnover number (TON) values up to $\sim 10^7$ and turnover frequency (TOF) values up to $\sim 10^5 \text{ hour}^{-1}$. They present results for two types of representative Au-catalyzed reactions in solution: **the ester-assisted intermolecular hydration of alkynes and **the bromination of arenes**. Efficient formation of these very small gold clusters in diluted suspensions achieved a catalytic activity nearly five orders of magnitude higher than those previously reported.**

Results and Discussion

Hypothesis:

When catalytic species form during a reaction, a reaction-induction period can generally be observed, provided that the rate of formation of the catalyst is slower than the rate of the reaction.

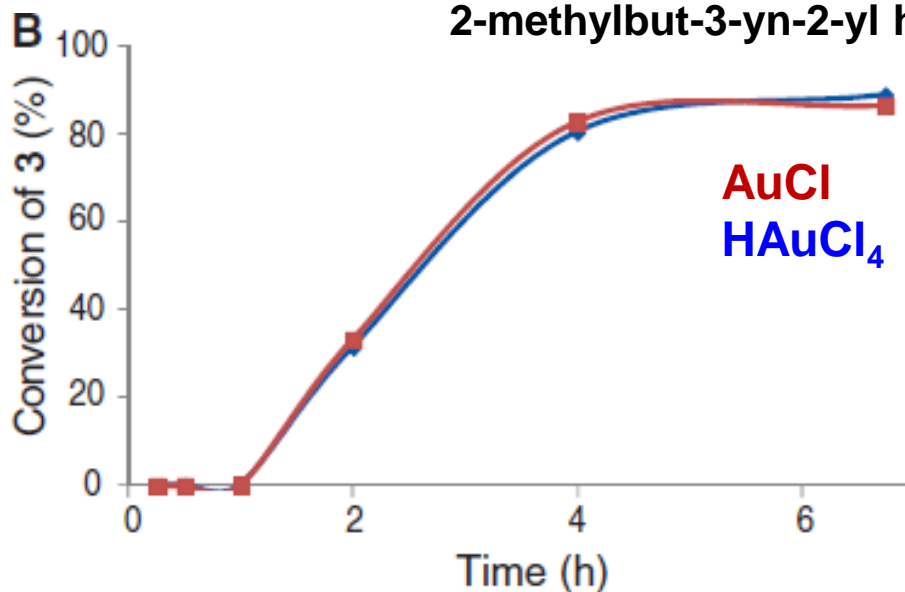
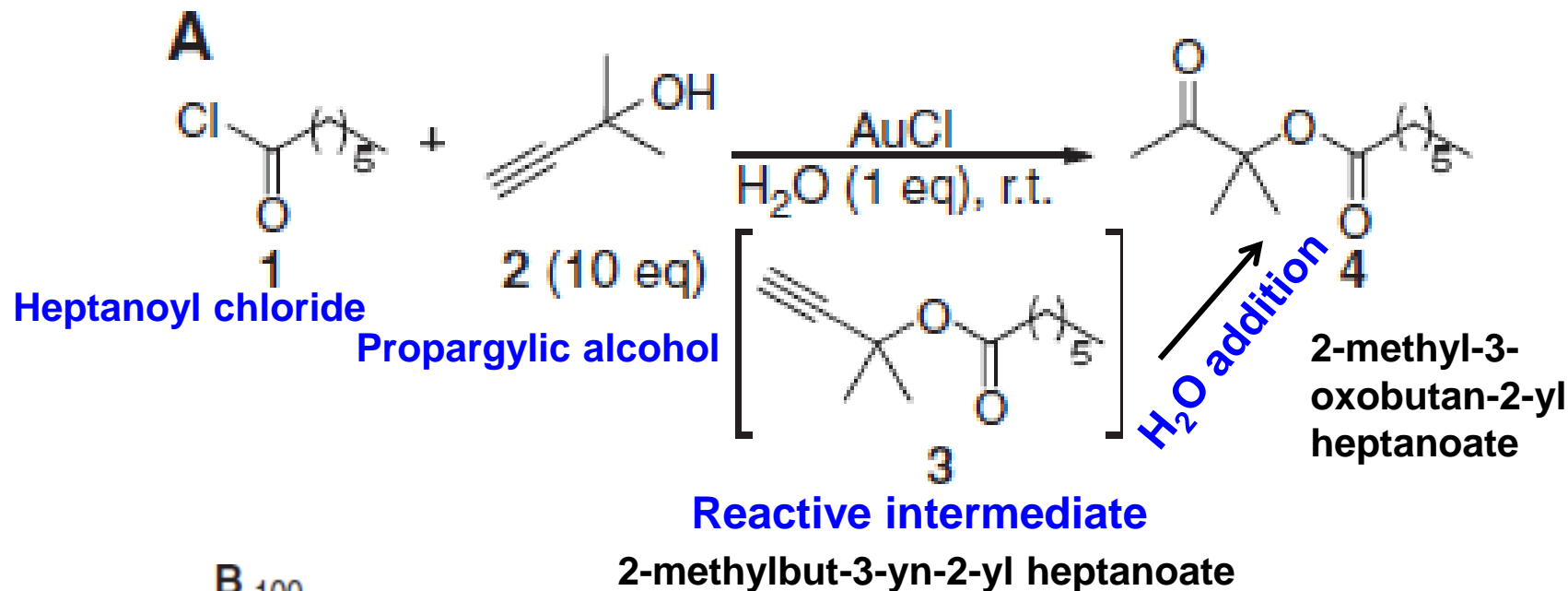
Induction period in chemical kinetics is defined by an initial slow stage of a chemical reaction, after the induction period, the reaction accelerates.

For Au catalyzed reactions no induction period is observed and can be explained assuming active species forms very quickly and cannot be detectable.

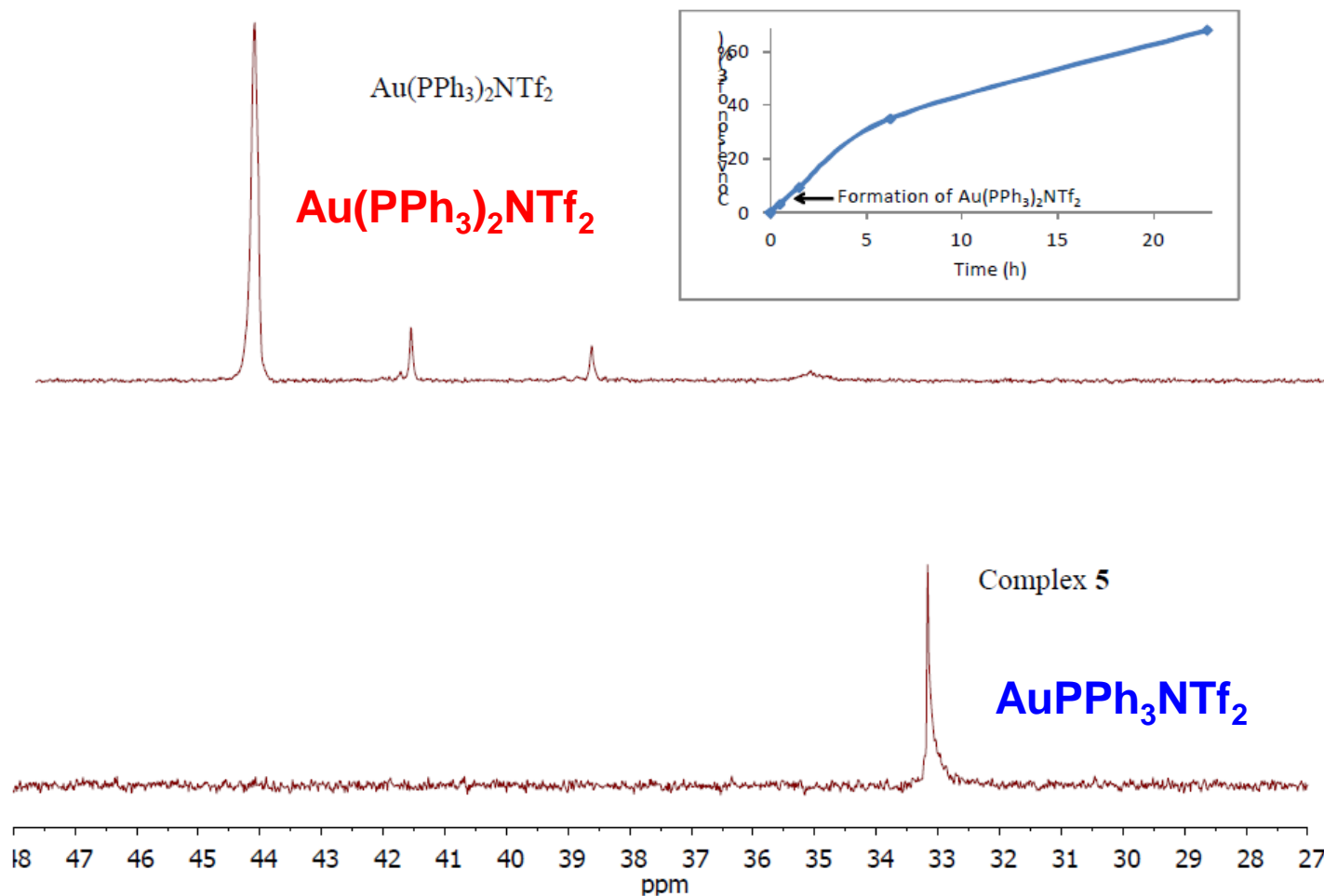
The hypothesis was cross checked using AuCl and HAuCl_4 as gold source at 100 ppm concentration showing same kind of kinetic profile indicating active gold species must have formed before the catalysis starts and is same regardless the nature of gold source.

$\text{Au}(\text{OH})_3$ of 100 ppm was also used and showed same behavior, so the induction period is not due to autocatalytic or exothermic process.

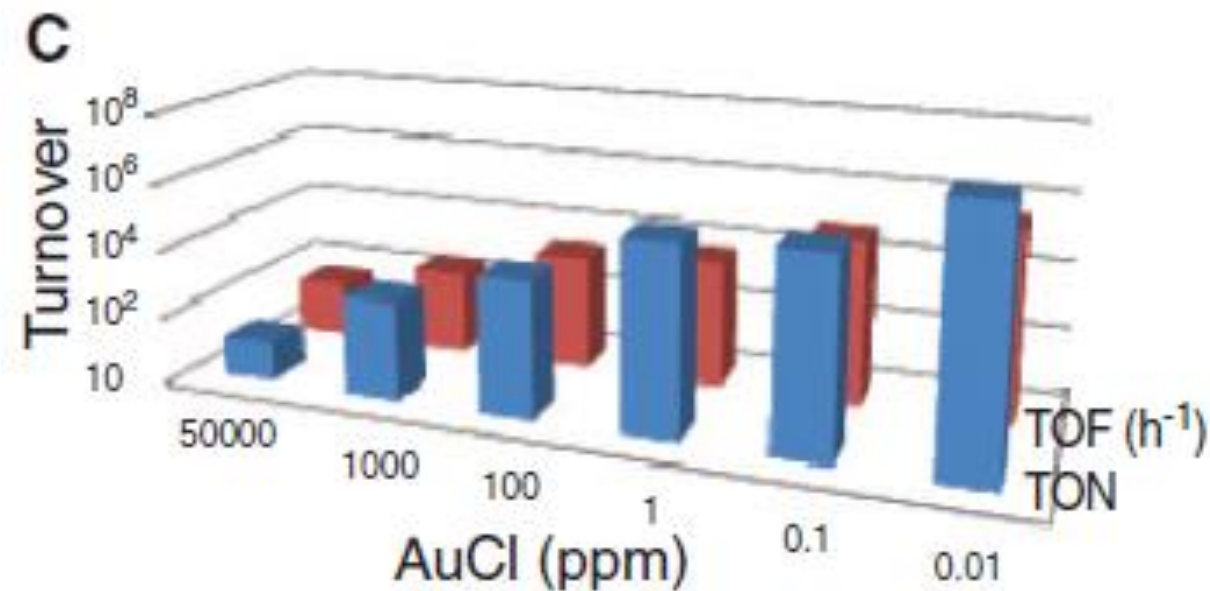
Ester-assisted intermolecular hydration of alkynes



Catalytic activity does not change with different oxidation state of Au

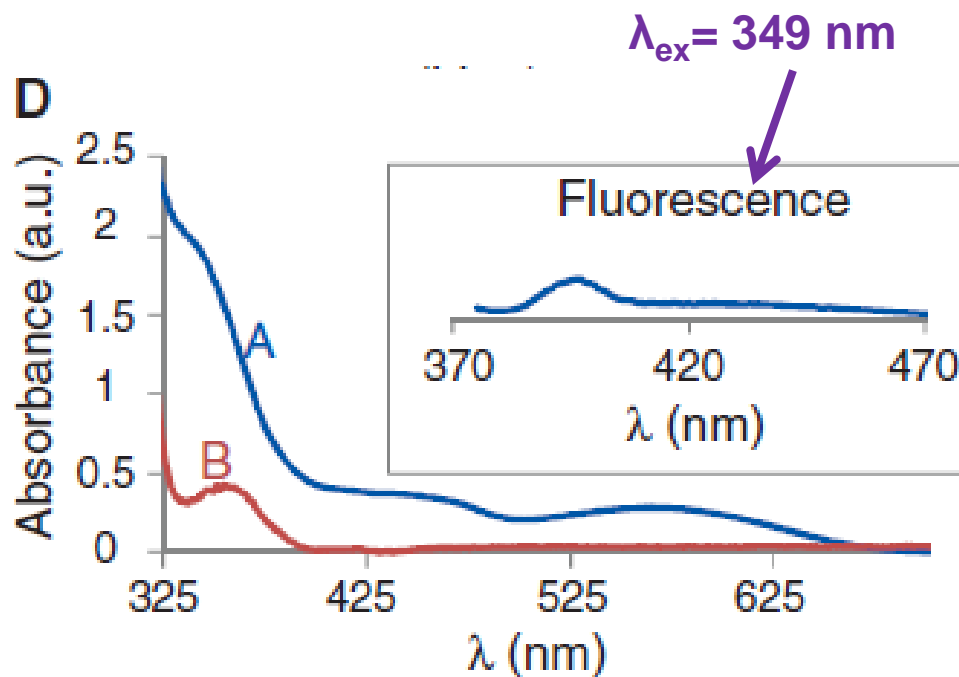


^{31}P -NMR spectra for complex *before* (bottom) and *after the addition of the reactants* (up). The inset shows the evolution of the reaction.

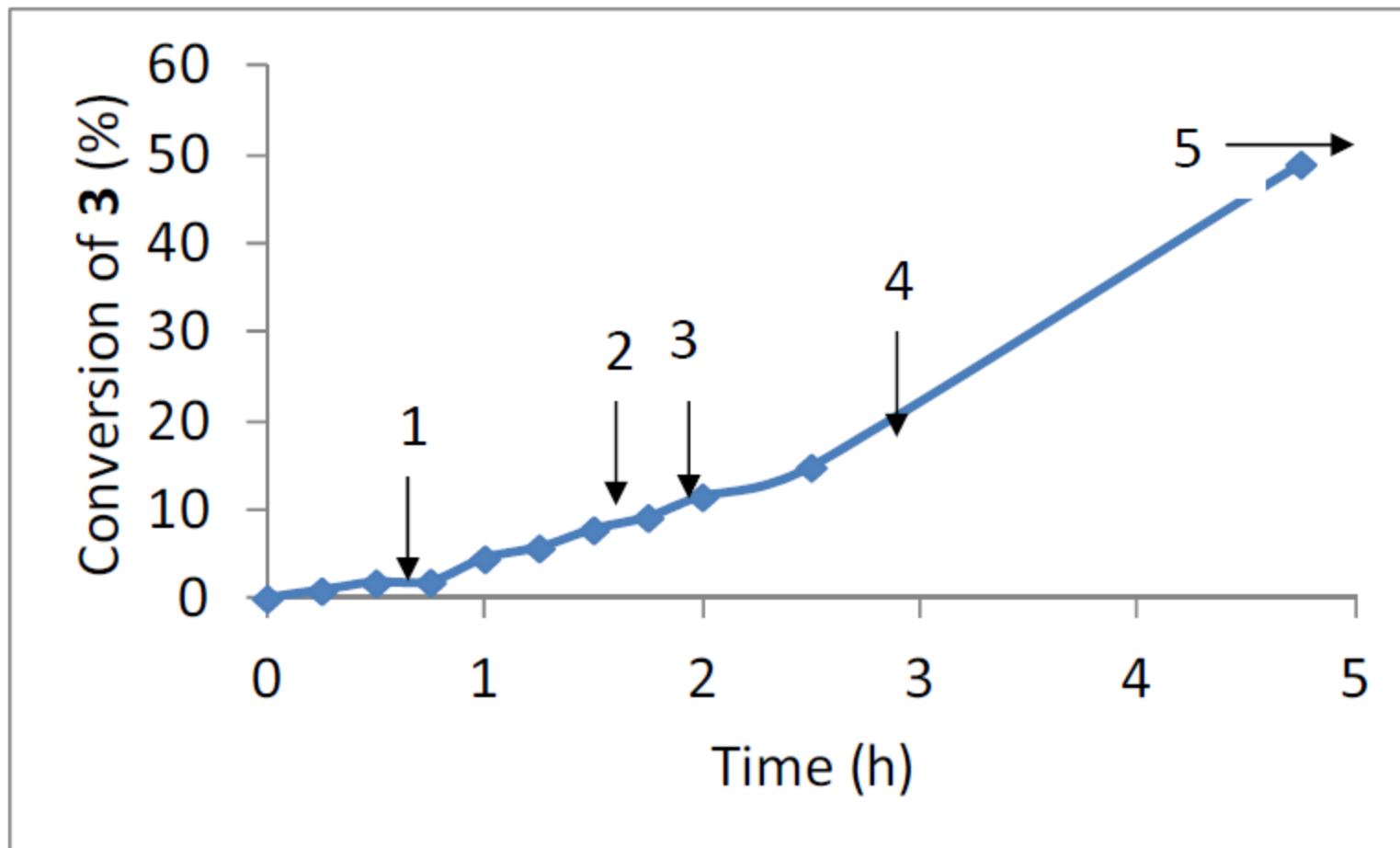


In all the cases yield is over 90%. Only for 0.01 ppm yield 50%.

Absorption measurements for the hydration of the reactive intermediate containing the Au active species along induction time A) and the reaction proceeds B) with the corresponding fluorescence.

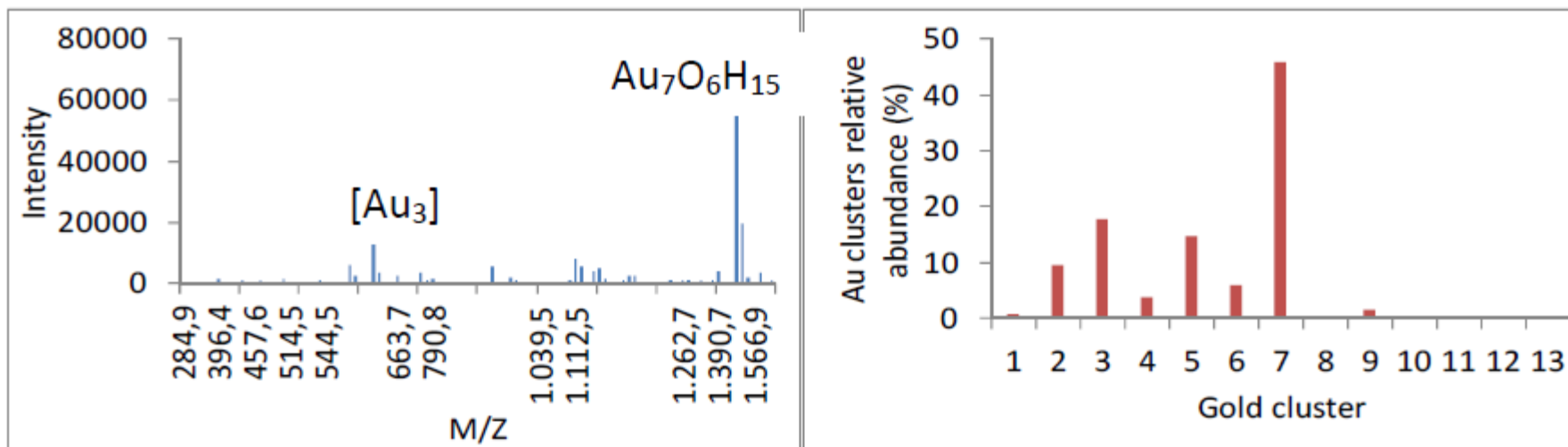


Kinetic curve for reaction progression

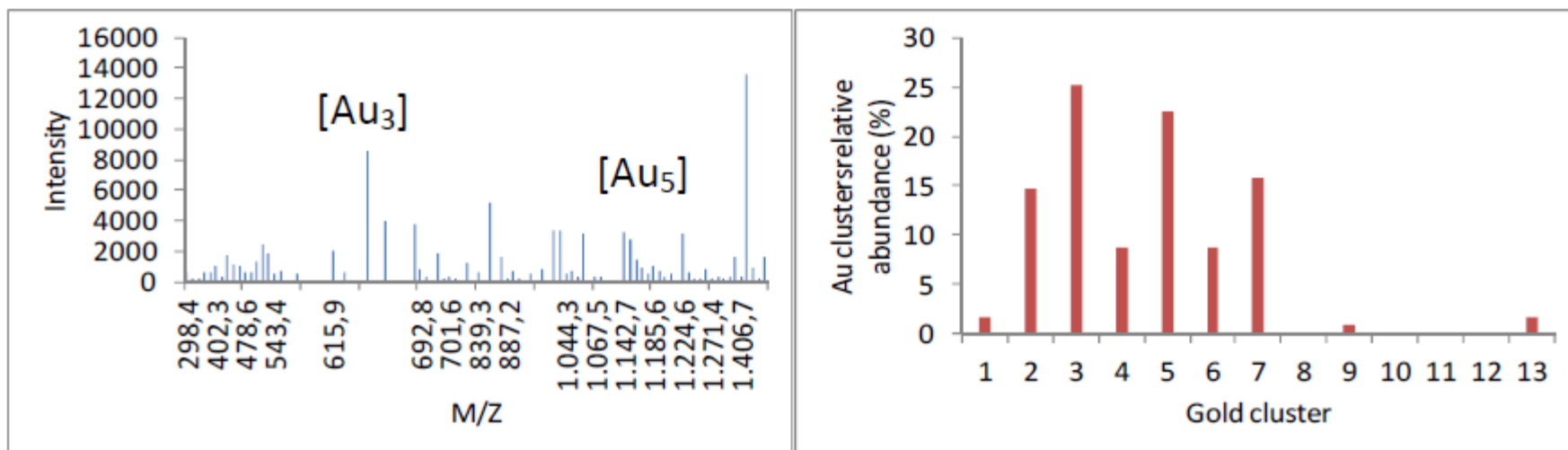


At different time reaction mixture was analyzed by MALDI-TOF and UV-Vis spectroscopy

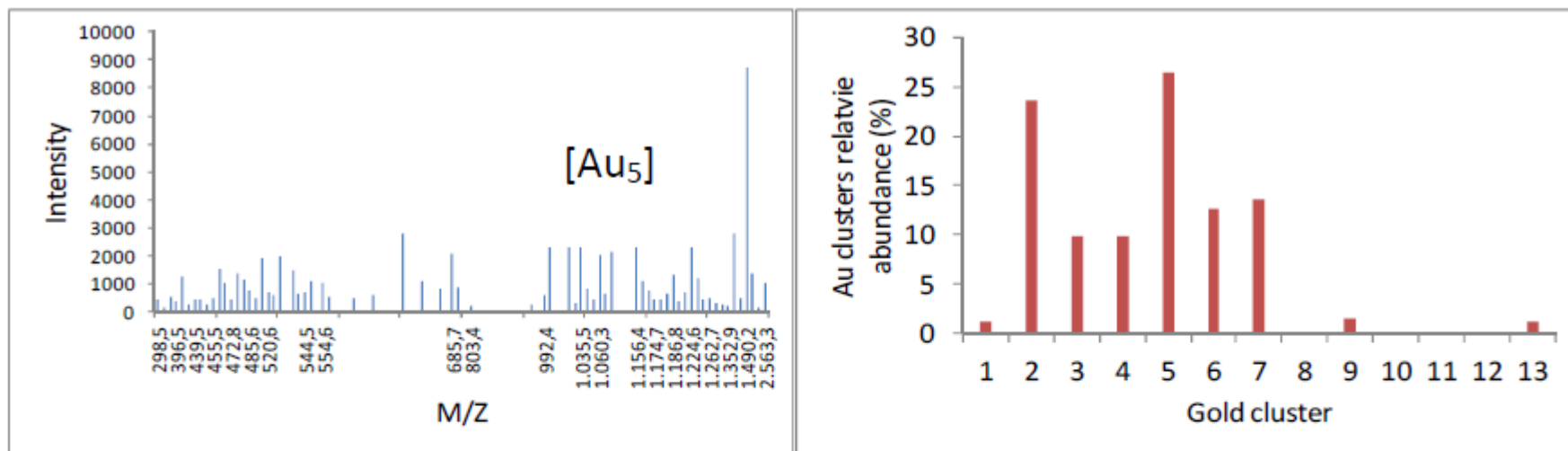
Aliquot 1



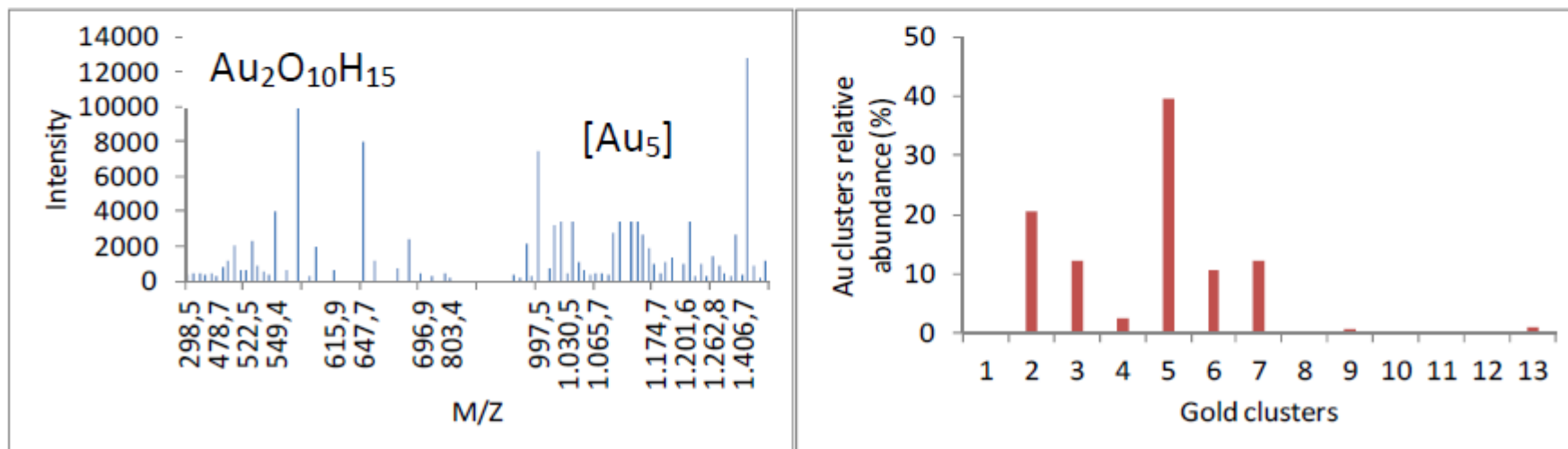
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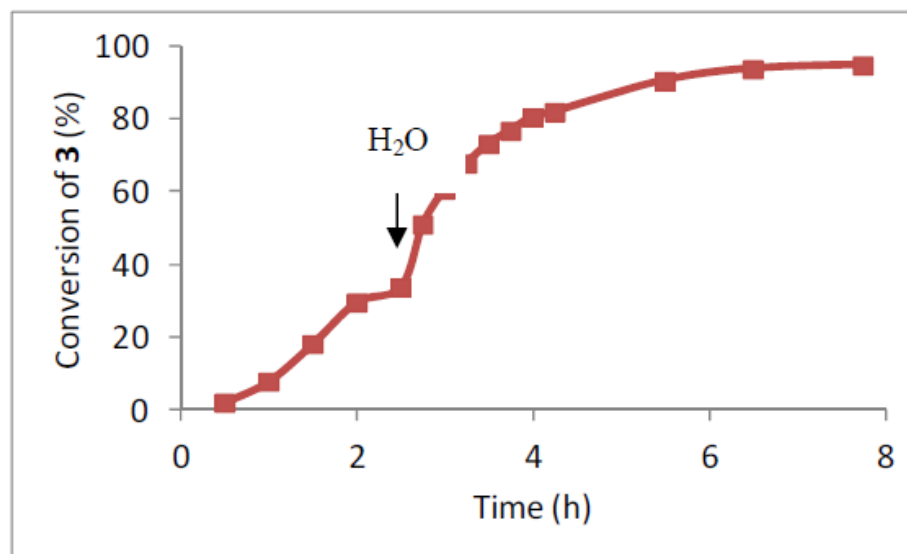
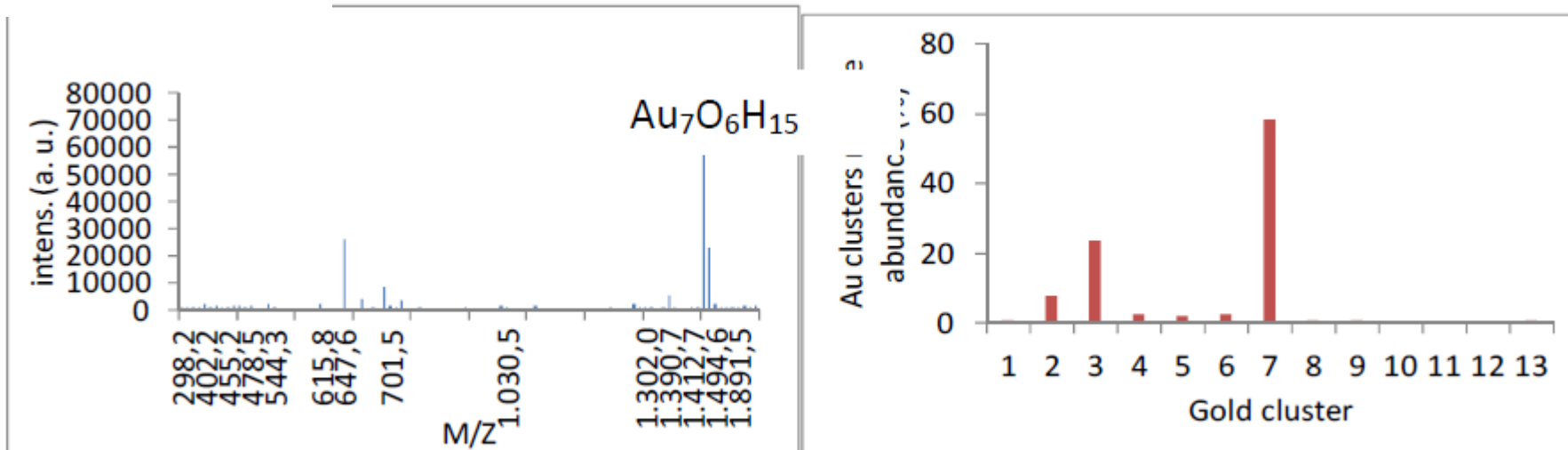
Aliquot 3



Aliquot 4



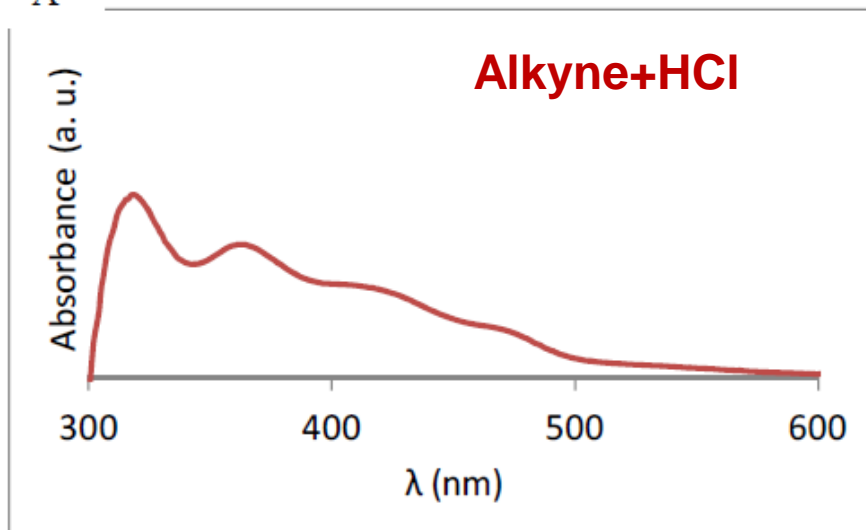
Aliquot 5



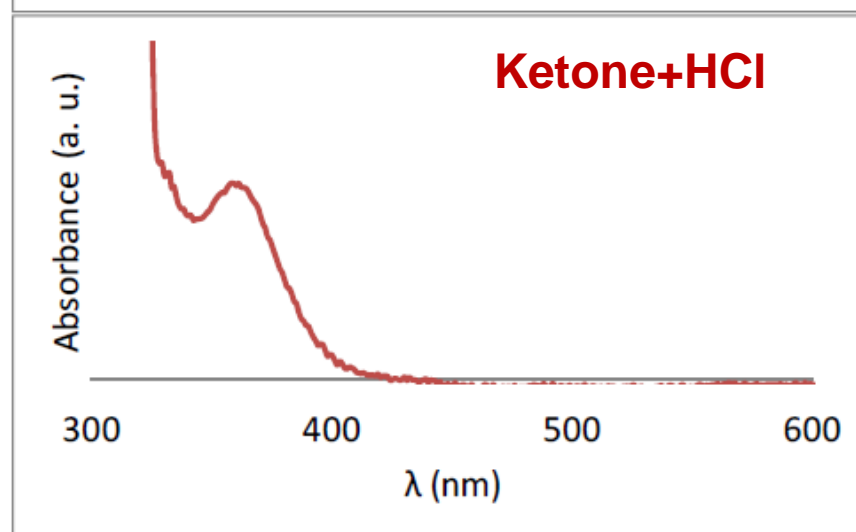
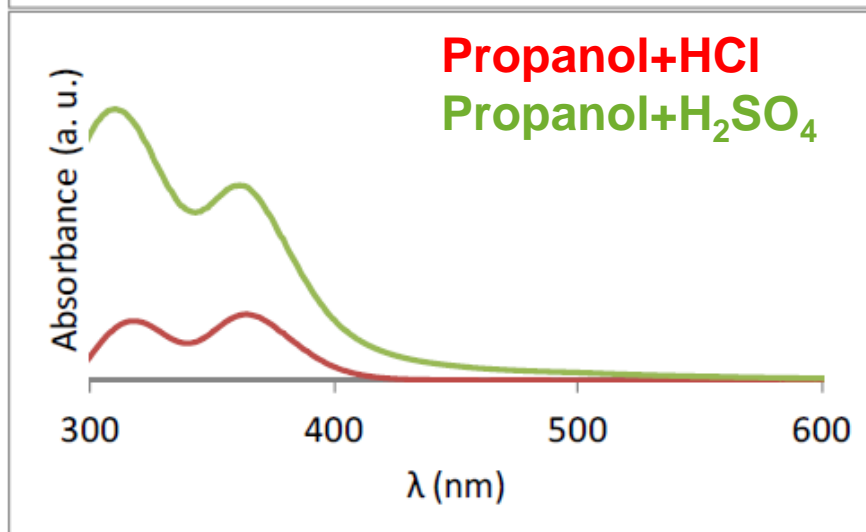
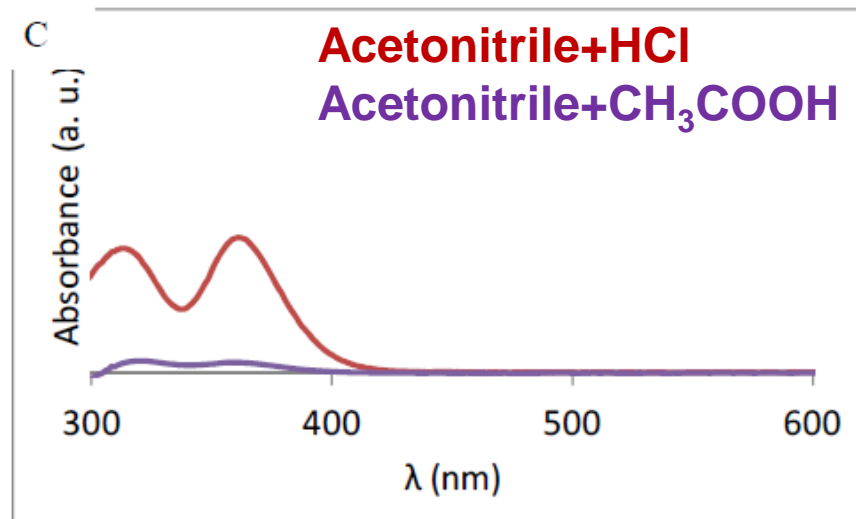
Water is not needed for the formation of gold clusters but alkyne is needed for the same.

Role of HCl

A

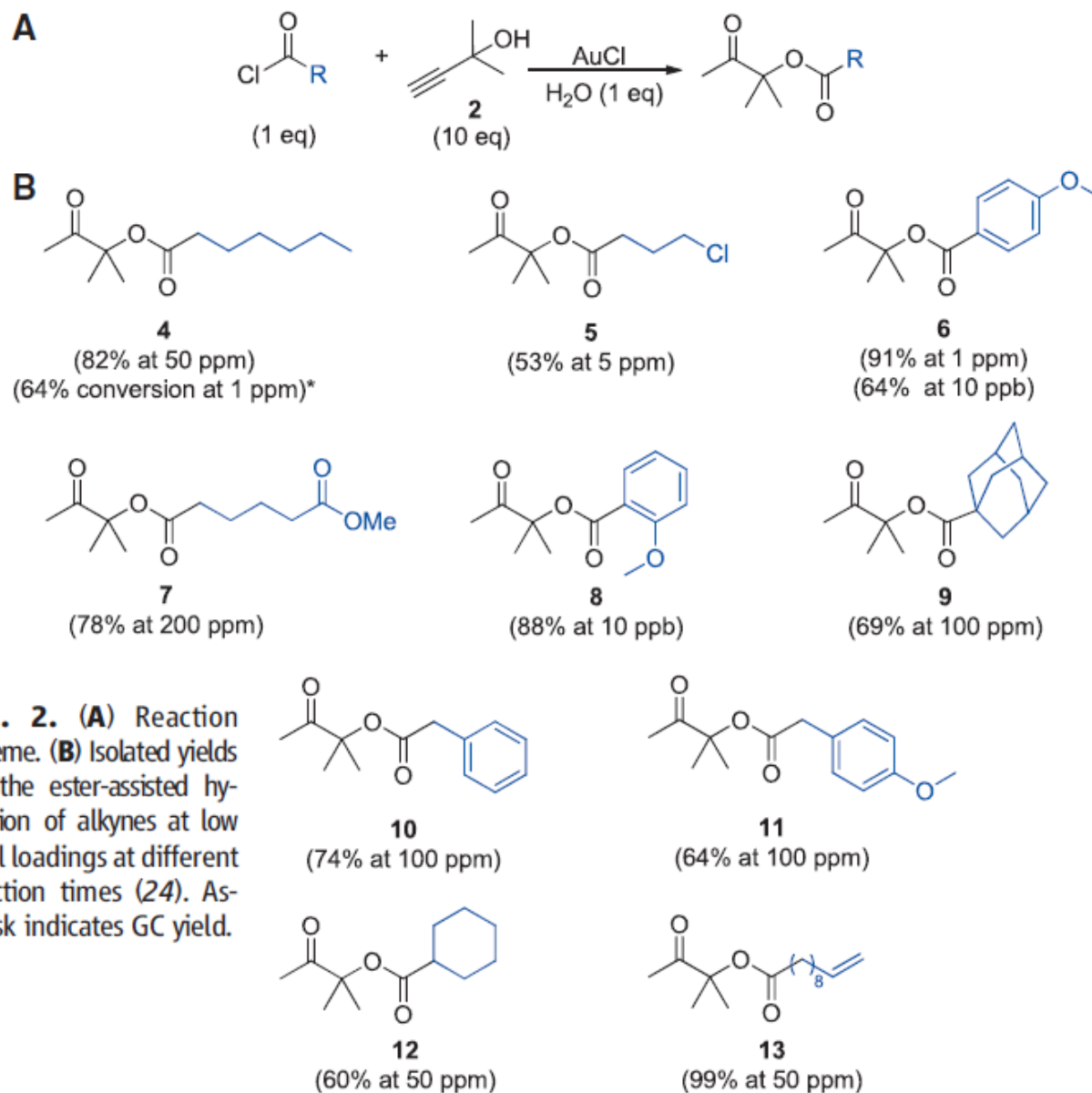


C



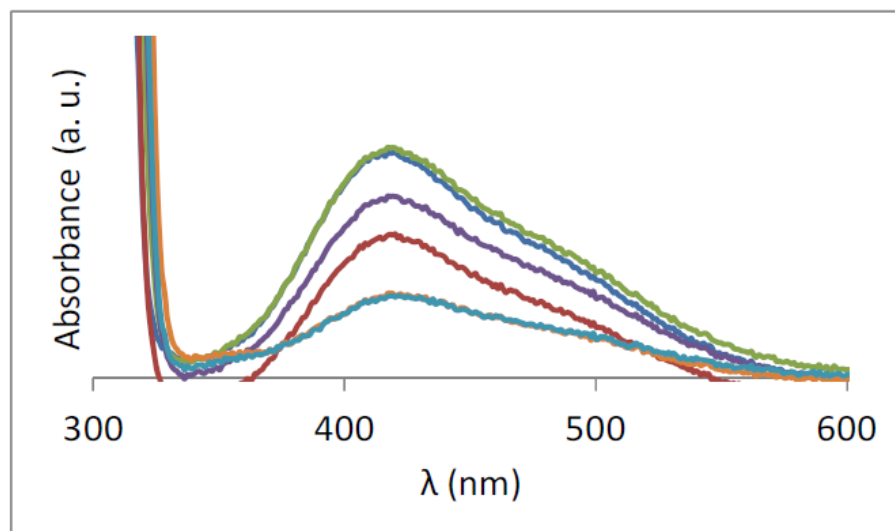
Reaction proceeds with HBr also but not with alkyl ammonium or sodium chloride salt. Low pH is the key for active catalyst formation.

Efficient catalyst for other ketones also

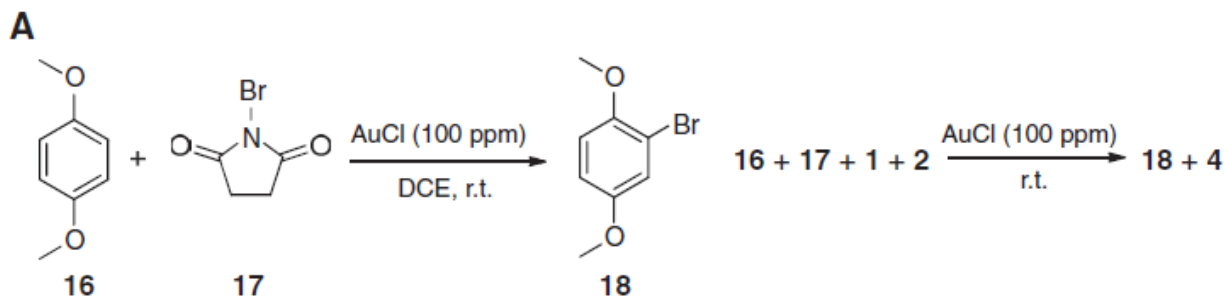


These results indicate that very small Au clusters of 3 to 5 atoms were formed from different Au sources at room temperature in acidified propargyl alcohol, and that these clusters could catalyze the ester-assisted intermolecular hydration of alkynes with catalytic efficiencies up to five orders of magnitude greater than those previously reported.

To determine whether small gold clusters, rather than cationic gold, were the active species for other homogeneous reactions, they tested the AuCl_3 catalyzed bromination of arenes. The results show that when using AuCl at ppm concentrations under the reported reaction conditions—namely, dichloroethane (DCE) as a solvent at room temperature—a catalytic efficiency similar to that with AuCl_3 after an induction period was observed, and UV-vis measurements indicate that small clusters of 7 to 9 atoms were responsible for the catalysis. Thus, it seems that different-sized clusters catalyze the two homogeneous reactions studied here.



Bromination of arene



Bromination Hydration

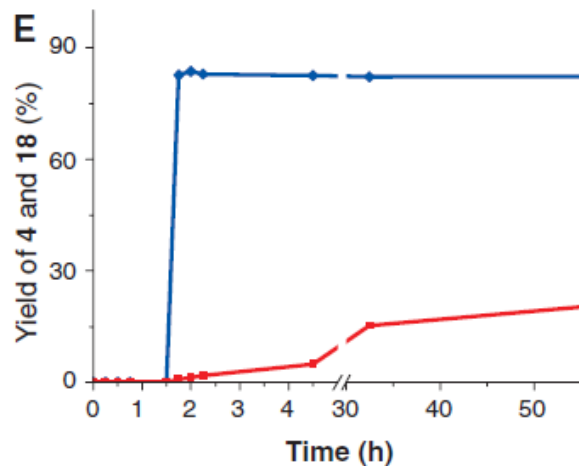
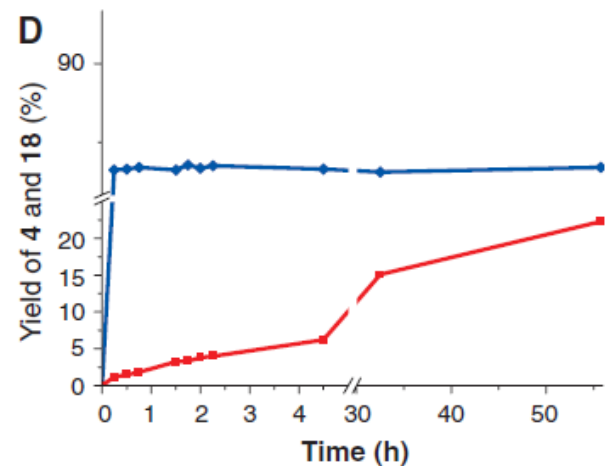
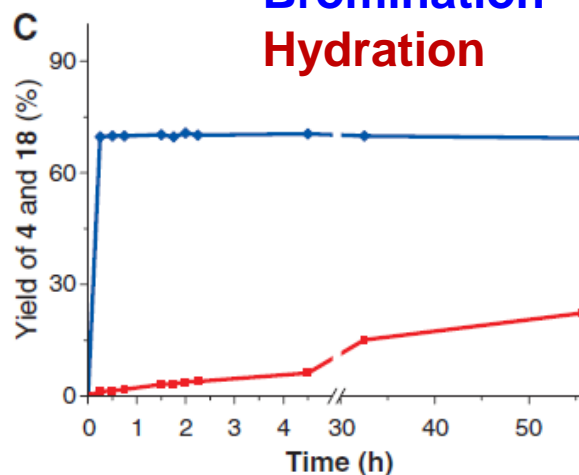
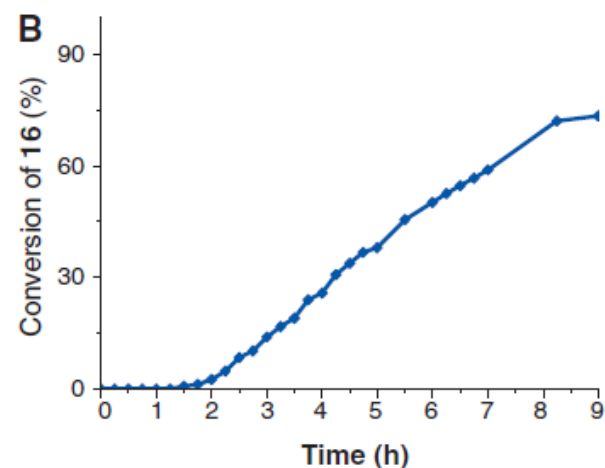


Fig. 3. (A) Studied reaction schemes. (B to E) Plot-time conversion for the bromination of arene 16 (B) and for the same reaction in the presence of the reactants for the ester-assisted hydration of alkyne under the following reaction conditions (bromination, diamonds; hydration, squares): (C) All the reactants are added from the beginning. (D) The reactants 2, 16, and 17 are added from the beginning; at 1.5 hours of reaction time, 1 and 1 equivalent of water are added to start the hydration reaction. (E) The reactants 1, 2, and water are added from the beginning; at 1.5 hours of reaction time, 16 and 17 are added.

Bromination of arene

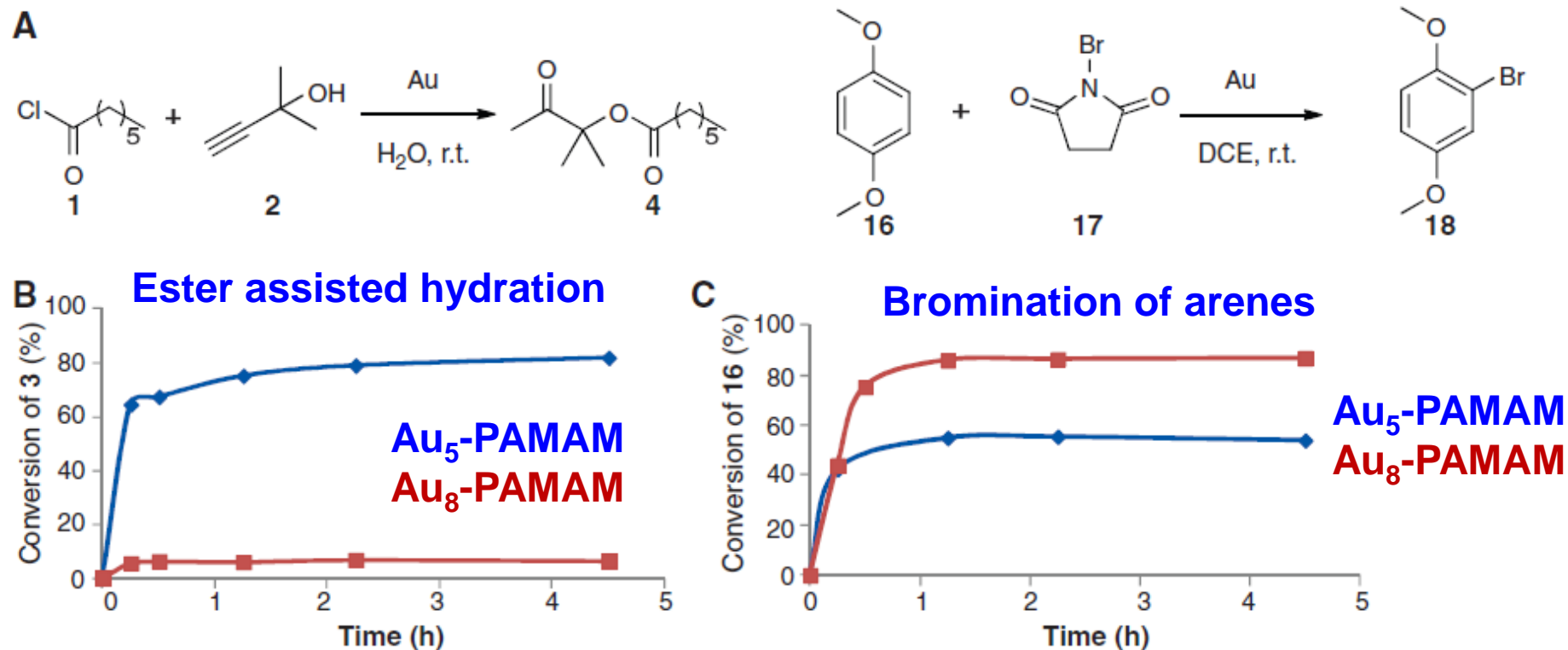


Fig. 4. (A) Studied reaction schemes. (B and C) Plot-time conversion for the ester assisted hydration (B) and for the bromination of p-dimethoxybenzene (C) with $\text{Au}_5\text{-PAMAM}$ (diamonds) and $\text{Au}_8\text{-PAMAM}$ (squares).

Summary

- ❖ Regardless of the gold salt [AuCl , AuCl_3 , $\text{Au}(\text{OH})_3$] or gold complex (AuPPh_3Cl , $\text{AuPPh}_3\text{NTf}_2$) used, rapid decomposition during the reaction to give gold clusters preferentially formed by 5 to 13 atoms was observed. These clusters formed new Au_3 - Au_5 clusters.
- ❖ Only when a critical concentration of the last clusters formed did the ester-assisted hydration of alkynes occur. However, when Au_3 - Au_5 clusters were added at time zero, the ester-assisted hydration of alkynes immediately started with no induction period. With a second reaction (i.e., bromination of *p*-dimethoxybenzene), no induction period was observed with gold salts in acidified propargyl alcohol, indicating that the larger Au_5 - Au_9 clusters initially formed are active for this reaction.
- ❖ The bromination of *p*-dimethoxybenzene readily stopped when the Au_5 - Au_9 clusters were transformed into Au_3 - Au_5 clusters. When both reactions were performed simultaneously, the bromination of *p*-dimethoxybenzene readily started, but no hydration reaction was observed. After ~2 hours, the bromination reaction stopped and the hydration rapidly proceeded, which reflected the transformation to a different type of clusters in solution.
- ❖ An independent synthesis of the different clusters and their use as catalysts confirmed the nature of the catalytic species. These results may lead to more efficient Au catalytic systems and to a greater understanding of the chemistry of subnanosized particles in general.

THIS WEEK IN Science

Gold Cluster Catalysis

A variety of gold salts and complexes have been used to catalyze different organic reactions. Often, the catalytic rates for these reactions are similar. Oliver-Meseguer et al. (p. 1452; see the [Perspective by Hashmi](#)) observed an induction period for the onset of catalysis of organic reactions, such as the ester-assisted hydration of alkynes, for different gold salts and complexes. Mass spectrometry and absorption spectroscopy revealed that small gold clusters (three to ten atoms) formed during these induction periods and are likely to represent the active catalysts. The catalytic reaction rates could be extremely high—up to 10^5 turnovers of the catalyst per hour.

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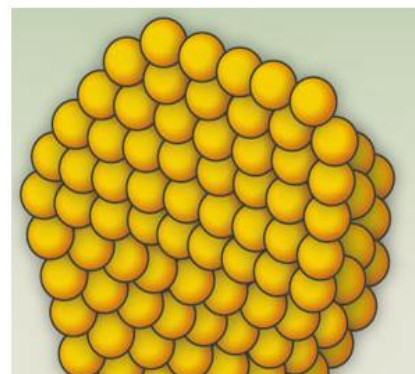
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Pico-gold clusters break catalysis record

14 December 2012

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Chemists in Spain have shown that small clusters of gold atoms are excellent inorganic catalysts with record-breaking efficiency. The clusters, which have been used in the hydration of alkynes, exhibit catalytic turnover frequencies of up to 100,000 per hour at room temperature.

Interest in gold as a catalyst began 25 years ago when chemists realized that nano-sized gold particles could catalyse the oxidation of carbon monoxide better than anything previously known. Since then, gold has been found to catalyse a host of other important reactions, such as the formation of azo compounds, which are used as leather and textile dyes, or intermediates for the production of polyurethane.

Future aspects:

- ✓ Efficient enzyme like catalysis is possible with small clusters if right system is chosen.
- ✓ Real time monitoring of the intermediates is possible. It will be better if we do solution phase study like ESI MS.
- ✓ There are several clusters available which can be used as catalyst for several reactions.

Thank You