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$[Au_5Mes_5]$: Improved gram-scale synthesis and its use as a convenient precursor for halide-free supported gold nanoparticles

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A simple one-step and gram-scale synthesis of $[Au_5Mes_5]$ from $AuCl_3$ was developed, and this molecular precursor was used to generate Au nanoparticles on SiO_2 and Al_2O_3. While $[Au_5Mes_5]$ does not react with surface silanols and is only physisorbed, its incipient wetness impregnation followed by H_2 treatment leads to a narrow size distribution of 1.4 nm Au nanoparticles. In contrast, $[Au_5Mes_5]$ reacts with partially dehydroxylated Al_2O_3 to directly yield 1 nm Au nanoparticles along with adsorbed species. A subsequent treatment under hydrogen leads to a narrow size distribution of smaller 0.8 nm Au particles.

Introduction

Metallic gold has long been thought to be a chemically inert material. It was not until the pioneering work of Haruta showing that supported Au nanoparticles display high activity for low temperature CO oxidation that the field of heterogeneous gold catalysis began.[1] Since then, nanoparticulate Au has been demonstrated to be catalytically active in a wide range of reactions, from hydrogenation to water splitting.[1-4] Two factors dominate the performance of Au nanoparticles in these reactions: the nature of the supporting material and the size of the nanoparticles.[5, 6]

Most synthetic routes to gold nanoparticles are based on aqueous procedures using gold chloride precursors, allowing deposition of Au nanoparticles on a wide range of supports. Particles are typically formed by deposition-precipitation on supports such as Al_2O_3 and Fe_2O_3,[7, 8] or by photo-deposition on supports such as TiO_2.[9] However, these methods give a wide distribution of particle sizes, are typically limited to the 2-5 nm particle size range, and commonly result in contamination of the surface with halide impurities.[9-11] These halogen impurities have been found to be detrimental to the catalytic activity.[12]

In order to overcome these limitations, use of organometallic, halide-free, Au precursors have been proposed for nanoparticle deposition. These precursors offer the potential for smaller nanoparticles under relatively mild conditions through the treatment under H_2, He, or O_2.[13-16] For instance, Gates et al. have developed and characterized the grafting of $[AuMe_2(acac)]$ with a range of surfaces from MgO to Al_2O_3, and achieved a range of particle sizes, from 1-2 nm Au nanoparticles to Au_6 clusters in the case of MgO.[14, 15, 17] Similarly, 2 nm Au particles on Al_2O_3 and 6 nm particles on SiO_2 have been deposited using vapor deposition of $[AuMe_2(acac)]$ (Me = CH_3, acac = acetylacetonate).[18] Our group has demonstrated that the controlled grafting of $Au[N(SiMe_3)_2]$ onto partially dehydroxylated silica can result in the formation of a narrow particle size distribution of 2 nm Au on silica.[16] However, this approach is limited by the low yield and small scale synthesis of $Au[N(SiMe_3)_2]$; such precursors lead to the passivation of the surface with $SiMe_3$ groups since this precursor releases $HN(SiMe_3)_2$ upon grafting. While this can lead to improved catalyst performance in the previously studied reactions, it also changes the properties of the support,[19] which may not be desirable in all cases.

We reasoned that $[Au_5Mes_5]$ could constitute a valuable gold precursor to form halide-free gold nanoparticles on various supports. The work of Floriani on mesityl derivatives of the Group 11 metals has demonstrated a simple synthesis of $[Au_5Mes_5]$ (Mes ≡ 2,4,6-$Me_3C_6H_2$) by salt metathesis of [AuCl(CO)] with a mesityl Grignard reagent.[20] However, [AuCl(CO)] is light and temperature sensitive, and its synthesis requires the use of CO gas. Here, we present a one-step scalable synthetic route of $[Au^I_5Mes_5]$ from $Au^{III}Cl_3$ and demonstrate its use for the simple synthesis of pristine small Au nanoparticles on both SiO_2 and Al_2O_3 supports.

Experimental

General Procedures

All experiments were carried out under an inert atmosphere of argon using standard schlenk or high vacuum (10^{-5} mbar) techniques. Tetrahydrofuran (THF) was distilled from purple Na/benzophenone ketyl under Ar and stored over activated molecular sieves, toluene was dried by passage through two columns of activated alumina and degassed by three freeze-pump thaw cycles prior to use. H_2 was purified over R3-11 BASF catalyst/MS 4 Å prior to use. All glassware used was dried at 120 °C overnight. MesMgBr (Mes = 2,4,6-trimethylphenyl) was synthesized following literature procedures.[21]

Silica (Aerosil Evonik, 200 $m^2.g^{-1}$) was compacted with distilled water, and then dried for 72 h at 120 ^oC. After calcination at 500 °C under air for 4 h, silica was treated under high vacuum at 500 °C for 4 h and then at 700 °C (5 $^oC/min$) for 12 h (SiO_{2-700}). To form SiO_{2-500}, compacted silica was calcined at 500 °C under air for 4 h, and treated under vacuum (10^{-5} mbar) at 500 °C for 12 h.

Alumina (Alu-C, Evonik, 200 m^2g^{-1}) was compacted with distilled water, dried, calcined under air flow at 500 ^oC (1.5 $^oC/min$) for 14 h in a flow reactor and treated under high vacuum at 500 ^oC for 12 h, yielding Al_2O_{3-500}. Treatment of Al_2O_{3-500} under high vacuum for 12 h at 700 ^oC (5 $^oC/min$) yielded Al_2O_{3-700}. All synthesized samples were stored under inert atmosphere at -40 ^oC.

Synthesis of [Au_5Mes_5]

A solution of MesMgBr (10.6 mL, 1.24 M, 14.4 mmol, 2 equiv.) in THF was added dropwise to an orange suspension of $AuCl_3$ (2.18 g, 7.2 mmol, 1 equiv.) in cold THF (150 mL, -80 ^oC), resulting in a clear yellow solution. After 3h stirring at -80 °C, 10 equiv. of dioxane (12.3 mL, 144 mmol) were added to the reaction mixture, and the solution was allowed to warm to room temperature over 30 min. An off-white precipitate gradually formed. The resulting suspension was filtered on Celite®. The clear yellow filtrate was evaporated to dryness at room temperature under high vacuum for 1.5 h, affording a green/black solid. Addition of 150 mL of toluene led to the formation of a reddish suspension, which was filtered over Celite®. The yellow filtrate was concentrated by ~60% and cooled to -40 ^oC overnight To afford yellow crystals of [Au_5Mes_5] (1.25 g, 3.8 mmol, 55%), collected in three crops. ^1H NMR (300MHz, C_6D_6): δ (ppm) 6.62 (m, 2 H, C_6H_2), δ 2.89 (s, 6 H, *o*-Me), δ 1.87 (s, 2 H, *p*-Me); ^{13}C NMR (300MHz, C_6D_6): δ (ppm) 21.0, δ 28.2, δ 126.4, δ 135.1, δ 141.5, δ 155.9 (Fig. S.1). Elemental analysis shows 33.61 % C and 3.46 % H, compared to the calculated 34.19 % C and 3.50 % H.

Formation of Au-SiO_2

SiO_{2-700} (480 mg, 0.26 mmol –OH/g SiO_{2-700})[22] was impregnated with a solution of [Au_5Mes_5] (11.5 mg, 0.037 mmol Au) in toluene (5 mL) at room temperature. The suspension was stirred for 15 min and the solvent was evaporated *in vacuo* (10^{-2} mBar). After 2h drying under high vacuum (10^{-5} mBar) a yellow solid was isolated. The physisorbed [Au_5Mes_5] was then decomposed under flowing H_2 (60 ml/min for 12 h at 300 ^oC, 0.5 ^{o}/min) to afford a red powder (Au-SiO_2).

Formation of Au-Al_2O_{3-500}

A solution of [Au_5Mes_5] (45 mg, 0.14 mmol Au, 1.25 Au : -OH) in toluene (4.5 mL) was added to Al_2O_{3-500} (200 mg, 0.56 mmol –OH/g Al_2O_{3-500})[22] at room temperature. After 4 h stirring at room temperature, the color of the solid changed from white to reddish brown. The supernatant was removed via filtration, and the solid was washed with toluene (3 x 10 mL) leaving a colorless filtrate after the last washing. Volatiles were evacuated *in vacuo* (10^{-2} mBar), and the solid were further dried 3 h under high vacuum (10^{-5} mBar) to afford Au-Al_2O_{3-500}.

Formation of Au-$Al_2O_{3-500-H2}$

Au-Al_2O_{3-500} can be treated under flowing H_2 (60 ml/min H_2 for 12 h at 300 ^oC, 0.5 ^{o}/min ramp) to afford a reddish powder (Au-$Al_2O_{3-500-H2}$).

Formation of Au-Al_2O_{3-700}

A solution of [Au_5Mes_5] (38 mg, 0.12 mmol Au, 1.25 Au : -OH) in toluene (4.5 mL) was added to Al_2O_{3-700} (220 mg, 0.43 mmol –OH/g Al_2O_{3-700})[22] at room temperature. After 4 h stirring at room temperature, the color of the solid changed from white to reddish brown. The supernatant was removed via filtration, and the solid was washed with toluene (3 x 10 mL), leaving a colorless filtrate after the last washing. Volatiles were evacuated *in vacuo* (10^{-2} mBar) and the solid were further dried 3 h under high vacuum (10^{-5} mBar) to afford Au-Al_2O_{3-700}.

In situ monitoring of the grafting of [Au_5Mes_5] on Al_2O_{3-500}

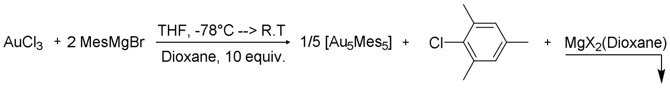
A solution of [Au_5Mes_5] (4.3 mg, 13.6 μmol Au, 1.25 Au : -OH) in C_6D_6 (1.0 mL) was added to Al_2O_{3-500} (25.5 mg, 0.56 mmol –OH/g Al_2O_{3-500})[22] at room temperature. After 5 h at room temperature with no stirring, the color of the solid changed from white to reddish brown. Quantitative ^1H NMR revealed the release of 0.13 μmol mesitylene with the consumption of 0.76 μmol Au (0.15 μmol [Au_5Mes_5]).

Characterization

TEM images were collected with a Philips CM12 transmission electron microscope. Samples were exposed to air for only a short time (<10 min) prior to insertion into the microscope. Particle size distributions were obtained by measuring the particles from 20-30 TEM images. Tests for chlorine content in [Au_5Mes_5] were negative and are detailed in the ESI. IR measurements were performed using a Bruker Alpha-T FTIR spectrometer inside an Ar filled glovebox. Samples were pressed into self-supporting disks using a manual press. [Au_5Mes_5] was diluted in KBr prior to pressing. Elemental analyses were performed by the Mikroanalytisches Labor Pascher; Remagen, Germany. GC measurements were performed with a GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. NMR spectroscopy was conducted using a 250 MHz Bruker AVANCE spectrometer.

Results and discussion

[Au_5Mes_5] was prepared in one step by addition of two equivalents of MesMgBr to a solution of $AuCl_3$ in THF in good yields (55%). A purification by recrystallization from toluene afforded pure [Au_5Mes_5]. This simple procedure was successfully scaled up from a 100 mg to a 1 g scale with similar yields. This synthesis represent a convenient alternative to the previously described synthesis from [AuCl(CO)].[20] Monitoring the reaction by GC and NMR indicates the release of one equivalent of chloromesitylene per Au center, consistent with the formation of a transient [$AuMes_2Cl$] species, which probably undergoes a reductive elimination to finally yield [Au_5Mes_5] (Scheme 1).



Scheme 1. Reaction of $AuCl_3$ with 2 equiv. MesMgBr to afford [Au_5Mes_5] via reductive elimination.

This simple synthetic route can likely be applied to obtain a wide range of Au organometallics from the appropriate Grignard reagents.

We then used [Au_5Mes_5] as a molecular precursor suited to the synthesis of supported Au nanoparticles by investigating two prototypical supports, SiO_2 and Al_2O_3.

Contacting SiO_{2-700} with a solution of [Au_5Mes_5] did not result in any reaction with the surface silanols, according to ^1H NMR indicating no formation of mesitylene and IR spectroscopy showing no consumption of silanols. Similar findings were obtained with SiO_{2-500}, which contains a higher density of silanols.[22] However, [Au_5Mes_5] can be deposited on SiO_{2-700} by incipient wetness impregnation (IWI). IR analysis of AuMes-SiO_{2-700} confirms the absence of reaction of the surface silanol groups (3747 cm^{-1}) after the IWI step (Fig. 1). The appearance of bands at ca. 2900 cm^{-1} identical to those of molecular [Au_5Mes_5] indicates that [Au_5Mes_5] is only physisorbed on SiO_{2-700} (Fig. S.2). In addition, the appearance of a broad band at ca. 3600 cm^{-1} is consistent with the interaction (no bond cleavage or formation) of [Au_5Mes_5] with surface silanols.[23]

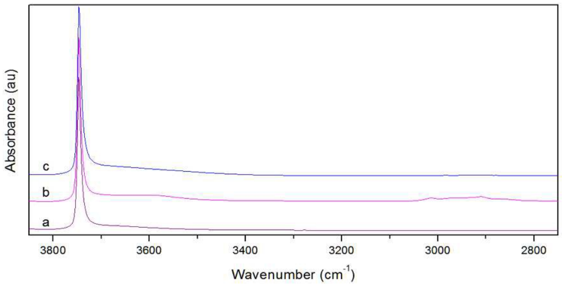


Figure 1. IR spectra of a) SiO_{2-700} , b) [Au_5Mes_5]@SiO_{2-700}, c) Au-SiO_2

A subsequent treatment under H_2 at 300 °C affords a reddish solid with 1.2 wt% Au, for which 1.4 ± 0.09 nm (st. dev. = 0.6 nm) Au nanoparticles are observed via TEM (Fig. 2). Such particles correspond to 60 atom Au-clusters.[24] Elemental analysis of the sample reveals only trace carbon remaining on the surface after this step and no signal intensity in the C-H region of IR (Fig. 1).

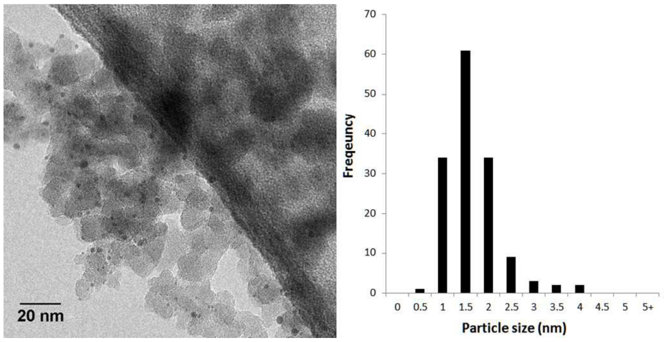


Figure 2. Representative TEM image of 1.2 wt% Au-SiO_2 (left) and particle size distribution with frequency representing the number of particles measured for each size bin (right)

The 1.4 nm Au particles formed on SiO_{2-700} are in the low range of alternative synthetic methods in the literature, but with the added benefit of a simple, halide free synthesis procedure. [12, 16, 18, 25-27]

Contrary to what is observed with SiO_{2-700}, upon contacting Al_2O_{3-500} (2 OH/nm^2)[22] with a [Au_5Mes_5] solution at room temperature, the color of the support changes from white to reddish brown, and analysis by TEM indicates formation of nanoparticles with an average size of 1.3 ± 0.2 nm (st. dev. = 1.2 nm) (Fig. 3). NMR characterization of the solution after the reaction and washing step shows the amount of [Au_5Mes_5] remaining in solution decreases to 0.025 mmol (for 200mg Al_2O_{3-500}), corresponding to approximately 1.5 wt% Au being deposited on the surface, in approximate agreement with the 2.0 wt% determined from elemental analysis (EA). EA also shows that a significant amount of carbon (2.1 wt%, 17 C/Au) remains on the surface of Al_2O_3. Since the C/Au in [Au_5Mes_5] is 9, the higher observed C/Au ratio is probably due to toluene/mesitylene which remains adsorbed after the grafting step by Al_2O_3.

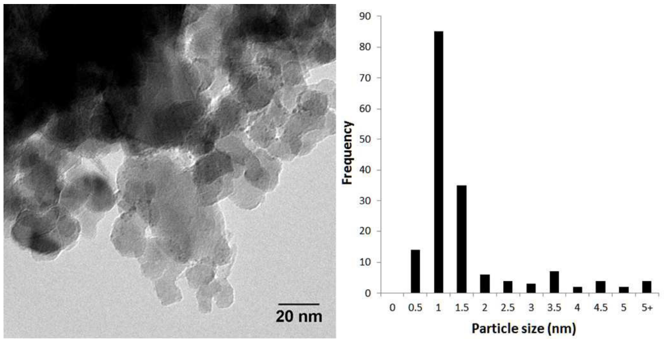


Figure 3. Representative TEM of 2.0 wt% Au-Al_2O_{3-500} (left) and particle size distribution with frequency representing the number of particles measured for each size bin (right)

Furthermore, monitoring the grafting of [Au_5Mes_5] on Al_2O_{3-500} by ^1H NMR shows the concomitant formation of mesitylene (0.13 μmol) and consumption of [Au_5Mes_5] (0.15 μmol), consistent with a surface reaction involving a protonolysis step. Comparison of the IR spectra of the pristine $Al_2O_{3\text{-}500}$ and Au-$Al_2O_{3\text{-}500}$ indicates that the –OH groups of $Al_2O_{3\text{-}500}$ at ca. 3700 cm^{-1} are partially consumed and that C-H stretches at ca. 2900 cm^{-1} appeared after reaction with [Au_5Mes_5] (Fig. 4).

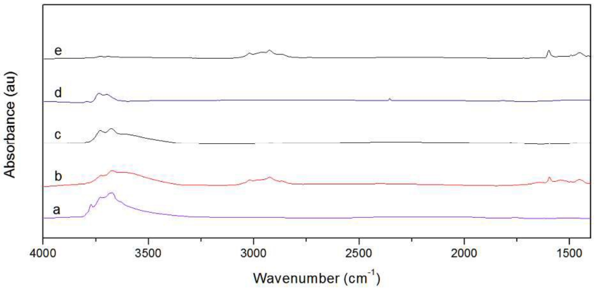


Figure 4. IR spectra of a) $Al_2O_{3\text{-}500}$, b) Au-$Al_2O_{3\text{-}500}$, c) Au-$Al_2O_{3\text{-}500\text{-}H2}$, d) $Al_2O_{3\text{-}700}$, e) Au-$Al_2O_{3\text{-}700}$,

From analyzing the –OH stretching region (ca. 3700 cm^{-1}, see Fig. S.2) we can conclude that grafting primarily occurs via a reaction with the most reactive HO-μ_1-Al_{VI} groups.[28] In the C-H region of the IR the main peak at 2906 cm^{-1} is shifted to 2927 cm^{-1} when [Au_5Mes_5] reacts with $Al_2O_{3\text{-}500}$, otherwise the spectra remains similar to that of molecular [Au_5Mes_5] (Fig. S.2). The observed remaining organic mesityl groups are either bound to metallic Au nanoparticles or associated with adsorbed Au clusters similar to [Au_5Mes_5].

In a manner analogous to the synthesis of Au-SiO_2, we treated of Au-$Al_2O_{3\text{-}500}$ under H_2. The disappearance of C-H stretches at ca. 2900 cm^{-1} of the IR (Fig. 1), and trace amounts of C determined by elemental analysis indicate the removal of most organic groups. Additionally, this treatment further disperses the Au particles, with their average size decreasing to 0.8 ± 0.04 nm, (st. dev. = 0.3 nm) corresponding to 15 atoms of Au per cluster (Fig. 5).[24]

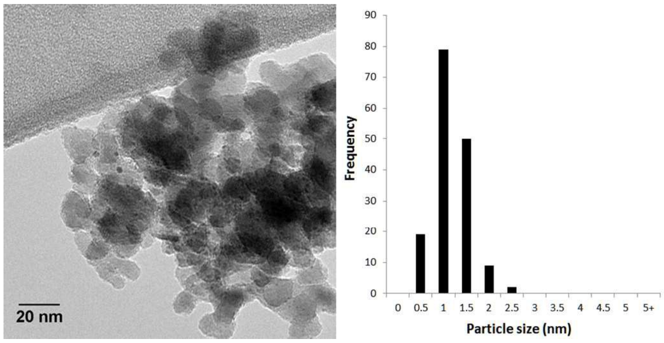


Figure 5. Representative TEM image of TEM image of 2.0 wt% Au-$Al_2O_{3\text{-}500\text{-}H2}$ (left) and particle size distribution with frequency representing the number of particles measured for each size bin (right)

In order to control the weight loading of Au on the surface, we sought to graft the precursor on more dehydroxylated alumina, which presents a lower density of –OH groups. For this purpose we grafted [Au_5Mes_5] onto $Al_2O_{3\text{-}700}$ (0.6 OH/nm^2).[22] NMR characterization of the solution after the reaction and washing step shows 0.020 mmol [Au_5Mes_5] remaining in solution (for 220 mg $Al_2O_{3\text{-}700}$), corresponding to approximately 1.9 wt% Au deposited on the surface. EA shows that 1.5 wt% Au is deposited, with similar IR spectra and amounts of carbon remaining as in Au-$Al_2O_{3\text{-}500}$ (Fig. 4, S.2). TEM indicates deposition of Au nanoparticles with an average size of 0.9 ± 0.06 nm (st. dev. = 0.4 nm) (Fig. 6).

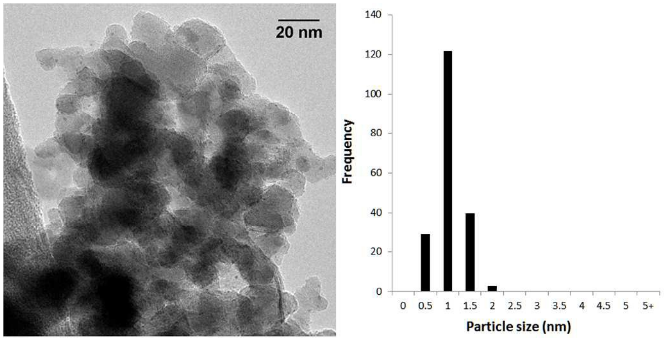


Figure 6. Representative TEM image of 1.5 wt% Au-$Al_2O_{3\text{-}700}$ (left) and particle size distribution with frequency representing the number of particles measured for each size bin (right)

While particle size slightly decreases, using a more dehydroxylated alumina containing a lower density of surface hydroxyl groups allows the control/decrease of Au loading. This simple halide-free synthesis allows for the formation of 1.2 and 1.0 nm Au nanoparticles onto Al_2O_3, which to the best of our knowledge correspond to the smallest sizes reported in literature.[8, 14, 18, 29]

Comparing formation of Au nanoparticles on SiO_2 and Al_2O_3 highlights the profound effect of surface reactivity on nanoparticle formation. The more inert dehydroxylated silica surface (isolated OH groups) does not react with [Au_5Mes_5], while alumina, which is always covered by hydroxyls related to chemisorbed water,[30] reacts readily, forming nanoparticles at room temperature. This data suggested that the particle formation process takes place via hydrolysis of [Au_5Mes_5], generating MesH and unstable Au_xO_y, which dismutate to yield Au clusters.[31]

Conclusions

We have developed a gram-scale synthetic route to [Au_5Mes_5] based on readily available and stable gold(III) precursors, and demonstrated the versatility of this precursor for the simple, scalable and halide free synthesis of Au nanoparticles on SiO_2 and Al_2O_3.

Depending on the nature of the supports nanoparticles can be obtained either directly upon grafting or necessitate a two-step procedure consisting in incipient wetness impregnation followed by a treatment under H_2 flow. While [Au_5Mes_5] only physisorbed on silica, it reacts with alumina, probably via chemisorbed water, to yield Au nanoparticles. Further treatment with H_2 for both silica and alumina leads to the removal of most organic ligands and the formation of small (1.4 nm, 60 atom clusters) to very small (0.8 nm, 15 atom clusters) Au nanoparticle on silica and alumina, respectively. This robust and simple synthetic method is readily applicable to a broad range of supports, easing the synthesis of supported small Au nanoparticles. We are currently exploring this avenue and the reactivity of these supported small clusters in catalytic processes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: ^1H and ^{13}C NMR of [Au_5Mes_5] in C_6D_6, full IR spectra of [Au_5Mes_5] and IR spectra comparing [Au_5Mes_5], [Au_5Mes_5]@SiO_2, Au-$Al_2O_{3\text{-}500}$ and Au-$Al_2O_{3\text{-}700}$ focused on the C-H region. See DOI: 10.1039/b000000x/

1. M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet and B. Delmon, *J. Catal.*, 1993, **144**, 175-192.
2. A. Corma and H. Garcia, *Chem. Soc. Rev.*, 2008, **37**, 2096-2126.
3. M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffin and C. J. Kiely, *Nature*, 2005, **437**, 1132-1135.
4. C. Gomes Silva, R. Juárez, T. Marino, R. Molinari and H. García, *J. Am. Chem. Soc.*, 2011, **133**, 595-602.
5. S. H. Overbury, V. Schwartz, D. R. Mullins, W. Yan and S. Dai, *J. Catal.*, 2006, **241**, 56-65.
6. M. Comotti, W.-C. Li, B. Spliethoff and F. Schüth, *J. Am. Chem. Soc.*, 2005, **128**, 917-924.
7. E. D. Park and J. S. Lee, *J. Catal.*, 1999, **186**, 1-11.
8. A. Wolf and F. Schüth, *Appl. Catal., A*, 2002, **226**, 1-13.
9. G. R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, *Catal. Lett.*, 1997, **44**, 83-87.
10. V. Aguilar-Guerrero and B. Gates, *Catal. Lett.*, 2009, **130**, 108-120.
11. S. Ivanova, V. Pitchon and C. Petit, *J. Mol. Catal. A: Chem.*, 2006, **256**, 278-283.
12. G. M. Veith, A. R. Lupini, S. Rashkeev, S. J. Pennycook, D. R. Mullins, V. Schwartz, C. A. Bridges and N. J. Dudney, *J. Catal.*, 2009, **262**, 92-101.
13. J. Guzman and B. C. Gates, *J. Phys. Chem. B*, 2002, **106**, 7659-7665.
14. J. Guzman and B. C. Gates, *Langmuir*, 2003, **19**, 3897-3903.
15. J. Guzman, S. Kuba, J. Fierro-Gonzalez and B. Gates, *Catal. Lett.*, 2004, **95**, 77-86.
16. D. Gajan, K. Guillois, P. Delichère, J.-M. Basset, J.-P. Candy, V. Caps, C. Coperet, A. Lesage and L. Emsley, *J. Am. Chem. Soc.*, 2009, **131**, 14667-14669.
17. J. Guzman and B. C. Gates, *Nano Lett.*, 2001, **1**, 689-692.
18. M. Okumura, S. Tsubota and M. Haruta, *J. Mol. Catal. A: Chem.*, 2003, **199**, 73-84.
19. F. Héroguel, G. Siddiqi, M. D. Detwiler, D. Y. Zemlyanov, O. V. Safonova and C. Copéret, *J. Catal.*, 2015, **321**, 81-89.
20. E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1989, **8**, 1067-1079.
21. I. Mutule and E. Suna, *Tetrahedron*, 2005, **61**, 11168-11176.
22. F. Rascon, R. Wischert and C. Coperet, *Chem. Sci.*, 2011, **2**, 1449-1456.
23. B. Rhers, A. Salameh, A. Baudouin, E. A. Quadrelli, M. Taoufik, C. Copéret, F. Lefebvre, J.-M. Basset, X. Solans-Monfort, O. Eisenstein, W. W. Lukens, L. P. H. Lopez, A. Sinha and R. R. Schrock, *Organometallics*, 2006, **25**, 3554-3557.
24. A. Jentys, *Phys. Chem. Chem. Phys.*, 1999, **1**, 4059-4063.
25. M. Turner, V. B. Golovko, O. P. H. Vaughan, P. Abdulkin, A. Berenguer-Murcia, M. S. Tikhov, B. F. G. Johnson and R. M. Lambert, *Nature*, 2008, **454**, 981-983.
26. R. Zanella, A. Sandoval, P. Santiago, V. A. Basiuk and J. M. Saniger, *J. Phys. Chem. B*, 2006, **110**, 8559-8565.
27. S. D. Lin, M. Bollinger and M. A. Vannice, *Catal. Lett.*, 1993, **17**, 245-262.
28. M. Digne, P. Sautet, P. Raybaud, P. Euzen and H. Toulhoat, *J. Catal.*, 2004, **226**, 54-68.
29. C. K. Costello, J. Guzman, J. H. Yang, Y. M. Wang, M. C. Kung, B. C. Gates and H. H. Kung, *J. Phys. Chem. B*, 2004, **108**, 12529-12536.
30. R. Wischert, P. Laurent, C. Copéret, F. Delbecq and P. Sautet, *J. Am. Chem. Soc.*, 2012, **134**, 14430-14449.
31. H. Tsai, E. Hu, K. Perng, M. Chen, J.-C. Wu and Y.-S. Chang, *Surf. Sci.*, 2003, **537**, L447-L450.

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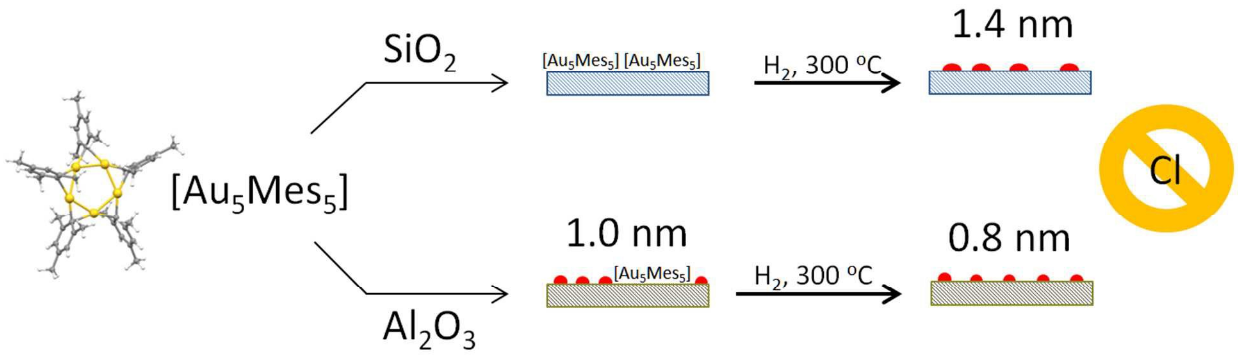

A novel, simplified synthesis of $[Au_5Mes_5]$ and its use for deposition of halide free Au nanoparticles on SiO_2 and Al_2O_3