



Supporting Information

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Gold nanoparticles and gold^{III} complexes as general and selective hydrosilylation catalysts**

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Experimental Section

General considerations

Except where noted, all manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen by use of standard Schlenk methods. Solvents were carefully degassed before use. colloidal Au,^[1] (tht)AuCl,^[2] (PPh₃)AuCl,^[3] and (Schiff base)Au^{III},^[4] complexes homogeneous and heterogenized were prepared employing reported methods. ¹H-NMR, ¹³C-NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers. Chemical shifts being referred to tetramethylsilane (internal standard). GC-MS were obtained with a Hewlett-Packard 5890 Series II. HPLC analysis were taken in an Agilent 1200 equipped with a chiralcel OD column. The inorganic support for anchoring was purely siliceous MCM-41.^[5]

Preparation of Au/CeO₂ catalyst.

Synthesis of nanoparticulated ceria.

A colloidal dispersion of CeO₂ nanoparticles was prepared by thermolysis of an acidified Ce(NO₃)₄ solution followed by re-dispersion. The dispersion was purified and concentrated using an ultra-filtration cell equipped with a 3KD membrane. The purification was monitored by the residual acidity of the dispersion, determined by an acid titration of the supernatant after ultra-centrifugation at 50000 rpm for 6h. The resulting cerium oxide has, owing to the small size of the nanoparticles, a very high surface area (180 m²·g⁻¹).

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Formation of Au/CeO₂

Au was deposited on the nanoparticulated cerium oxide by the following procedure: A solution of H₂AuCl₄·3H₂O (200mg) made in 40 mL of deionised water was brought to pH 10 by addition of a solution of NaOH 0.2M. Once the pH value was stable the solution was added to a slurry containing of colloidal CeO₂ (2.01 g) in H₂O (50 ml). After adjusting the pH of the slurry at a value of 10 by addition of a solution of NaOH 0.2M, the slurry was left under vigorous stirring for 18 hrs at room temperature. The Au/CeO₂ solid was then filtrated and exhaustively washed with distilled water until no traces of chlorides were detected by the AgNO₃ test. This is an important treatment since traces of Cl⁻ remain strongly bonded to Au⁺¹ and are highly detrimental for the overall activity. The catalyst was dried during 16 hours at vacuum. The total Au content of the final catalyst was 2.4% as determined by chemical analysis.

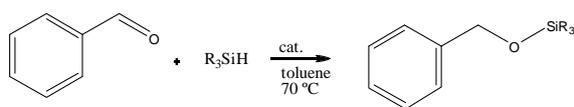
Recycling of heterogenized catalysts

The evolution of the reaction of hydrosilylated product was monitored by gas-chromatography. At the end of the hydrosilylation process, the mixture of reaction was filtered; the residue of zeolite-containing catalyst washed to completely remove the remains of products and/or reactants and used again.

Taking this into account, it is mandatory to find out if some gold has passed into the solution. To do this, we have investigated the residual activity of the supernatant solution after separation of the catalyst. The potential leaching was studied as follows: the organic phase of a first run was separated from the solid (Au-supported). New reagents were added to the clear filtrate, and the composition of the reaction mixture was determined by GC. This homogeneous reaction mixture was treated as a standard catalytic experiment (70 °C, 24 h). After 24 h, the composition was determined and no reaction was observed, which excludes the presence of active species in solution. Leaching of the gold complex can also be discarded because the amount of Au in the solid before (0.27 0.02 mmol/g) and after (0.25, 0.02 mmol/g) the consecutive catalytic reactions was mainly unchanged.

When the reaction mixture was filtered through a micropore filter, no residual Au was detected from the filtrate by ICP analysis (< 1 ppm) implying that leaching of Au from the support is negligible.

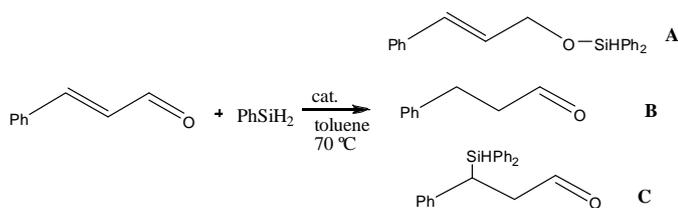
Table S1. Gold-catalyzed hydrosilylation of benzaldehyde with R_3SiH .^[1]



Cat.	Ph_2SiH_2	$PhMe_2SiH$	Et_3SiH
$KAuCl_4$	100	100	60
Au/CeO_2 ^[2]	100	100	100 (8h)
$1,2Au^{III}$	100	40	10
$(tht)AuCl$	100	30	5
$3Au^I$	15	<5	0
Au^0	100	80	30

^[1]The reactions were carried out with benzaldehyde (1 mmol), silane (2 mmol), and the gold catalyst (5 %) in toluene (1 ml) at 70 °C for 2 h while under a nitrogen atmosphere. Yields quoted with respect to aldehyde consumed based on GC-MS. Selectivity > 98 %. ^[2] Recycled 4 run.

Table S2. Gold-catalyzed hydrosilylation of cinnamaldehyde with Ph₂SiH₂.^[1]



Cat.	t(h)	Conv. (%)	S _A	S _B
(tht)AuCl	1	100	95	5
KAuCl ₄	1	100	98	2
1,2Au ^{III}	1	100	97	3
1,2Au ^{III} -(MCM-41)	1	100	98 ^[2]	2
Au/CeO ₂	1	100	95 ^[3]	5
Au ⁰	1	100	95	5

^[1]The reactions were carried out with cinnamaldehyde/silane ratio (1 mmol)/(2 mmol), and the gold catalyst (5 %) in toluene (1 ml) at 70 °C under a nitrogen atmosphere. Yields quoted with respect to aldehyde consumed based on GC-MS. Selectivity analyzed for ¹H NMR ^[2] Recycled 3 run. ^[3] Recycled 4 run.

Table S3a. Gold-catalyzed hydrosilylation with Ph₂SiH₂.^[1] Yields %

Cat.				
(tbt)AuCl	100	100	100	100
(PPh ₃)AuCl	5	0	<5	<5
KAuCl ₄	100	100	100	100
1,2Au ^{III}	100	100	100	100
1,2Au ^{III} -(MCM-41) ^[2]	100	100	100	100
Au/CeO ₂ ^[2]	100	100	100	100
Au ⁰	0	0	100	100
Au/TiO ₂	0	-	80 (110 C)	50 (110 C)

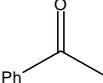
^[1]The reactions were carried out with alkenes (3 mmol)/silane (1 mmol) or carbonyl compound (1 mmol)/silane (2 mmol), and the gold catalyst (5-10 %) in toluene (1 ml) at 70 °C under a nitrogen atmosphere. Yields quoted with respect to substrate or silane consumed based on GC-MS. Selectivity > 98 %. ^[2] Recycled 4 run.

Table S3b. Gold-catalyzed hydrosilylation with Ph_2SiH_2 .^[1] Yields %

Cat.	$\text{Ph}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$	$\text{Ph}-\text{C}(\text{Ph})=\text{N}-\text{CH}_2-\text{CH}_2-\text{H}$	heptanal	1-octene
Au/CeO₂	100 (trans, traces cis)	20 (50) ^[2]	90	70
1Au^{III}	100(40 trans, 60 cis)	<10 (25) ^[2]	65	45
1Au^{III}-(MCM-41)	100 (trans, traces cis)	15 (30) ^[2]	95	80

^[1]The reactions were carried out with alkene, alkyne or imine (3 mmol)/silane (1 mmol) or carbonyl compound (1 mmol)/silane (2 mmol), and the gold catalyst (5%) in toluene (1 ml) at 70 °C under a nitrogen atmosphere. Yields quoted with respect to substrate or silane consumed based on GC-MS. ^[2]In parenthesis yield with 10% of gold catalyst, T = 90 °C.

Table S4. Heterogenized Gold-catalyzed hydrosilylation of α -methylstyrene and acetophenone with Ph_2SiH_2 .^[1]

Catalyst				
	Conv.(%) ^[2]	ee(%) ^[3]	Conv.(%) ^[2]	ee(%) ^[3]
1Au^{III}	100	15	100	12
1Au^{III}-(MCM-41) (1 run)	100	12	100	8
1Au^{III}-(MCM-41) (4 run)	100	15	100	10
2Au^{III}	100	25	100	25
2Au^{III}-(MCM-41) (1 run)	100	15	100	15
2Au^{III}-(MCM-41) (4 run)	100	13	100	13
Au/CeO₂ (1 run)	100	-	100	-
Au/CeO₂ (4 run)	100	-	100	-

^[1]The reactions were carried out with alkene (3 mmol)/silane (1 mmol) and the gold catalyst (5%) in toluene (1 ml) at 70 °C under a nitrogen atmosphere. ^[2]Yields quoted with respect to substrate or silane consumed based on GC-MS. Selectivity > 98 %. ^[3] Determined by HPLC (chiralcel OD column).

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