

Gold Nanoparticles and Gold(III) Complexes as General and Selective Hydrosilylation Catalysts**

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Gold salts and soluble complexes have provided access to reactions that could not be reached before with more traditional catalysts.^[1] Moreover, when Au is prepared in the form of nanoparticles, it becomes an active and selective catalyst for reactions such as CO oxidation,^[2] chemoselective reduction of substituted nitroaromatics by H₂,^[3] selective oxidation of alcohols,^[4] and some C–C bond-forming reactions.^[5] Together with solids, the use of Au complexes in homogeneous catalysis has undergone a renaissance and numerous publications have recently emphasized the beneficial role of Au.^[6–10] A broad range of transformations catalyzed by inorganic Au^{III} salts have also been reported; examples include hydroamination^[11] and functionalization of aromatic C–H bonds.^[12] Most often, AuX₃ (X = Cl, Br) salts are used directly and only a limited number of examples are known of well-defined organogold(III) complexes acting as catalysts.^[6b,13] Recently, we have shown that Au^{III} phenolic Schiff base complexes catalyze the homocoupling of aryl boronic acids but are unable to catalyze the Suzuki cross-coupling.^[14] However, Au^I, which has the same d¹⁰ electronic configuration as Pd⁰, is an active catalyst for performing Suzuki couplings and the copper-free Sonogashira cross-coupling.^[15] We have also reported that stable unsymmetrical N-heterocyclic carbene (NHC) Au^I complexes (soluble and heterogenized) are effective catalysts for the Suzuki cross-coupling and enantioselective hydrogenations.^[16]

Hydrosilylation reactions are a very important route to silicon polymers.^[17] In general, organosilicon compounds have found industrial applications as photoresistors, semiconductors, adhesives, binders, and for preparative organic synthesis. Hydrosilylation catalysts normally involve Pt, Pd, Ir, Ru, Rh, Co, and Ni complexes,^[18] while gold was believed not to be

active for hydrosilylation until Hosomi and co-workers^[10] showed the possibility to hydrosilylate aldehydes with [(PPh₃)AuCl]. Unfortunately, low conversions are observed with this and similar catalysts as a result of precipitation of inactive metallic gold, unless a large excess (20 mol %) of tributylphosphine is added.^[19–20]

To date, hydrosilylation with gold has been restricted to aldehydes and alkynes,^[21] but the process is still far from ideal as it is hampered by the use of phosphine derivatives and owing to the lack of results for the hydrosilylation of olefins and imines. It is therefore of interest to synthesize new phosphine-free homogeneous gold catalysts and, even better, to design recyclable solid gold catalysts for hydrosilylation of a variety of groups.

Herein we show that nanoparticles of gold, on carriers which are able to stabilize cationic forms of gold, can be a general recyclable catalyst for the hydrosilylation of a large variety of functionalities (aldehydes, ketones, olefins, imines, and alkynes). To discuss the nature of the active gold species on solid catalysts, Au^I and Au^{III} phosphine-free complexes both homogeneous and heterogenized on MCM-41^[22] (Figure 1) have been prepared and tested. We show that solid gold catalysts are not only active catalysts for a large variety of hydrosilylation reactions but are also chemoselective for the hydrosilylation of aldehydes in the presence of olefins.

Recently, we demonstrated that nanoparticles of CeO₂ can stabilize cationic forms of gold (Au^I and Au^{III}).^[23] If this is so, a solid catalyst formed by gold on nanoparticulated CeO₂ could act as a catalyst for hydrosilylation reactions. Indeed, results show that Au/CeO₂ with an average gold particle size of 4 nm is active and selective for the hydrosilylation of olefins, aldehydes, ketones, alkynes, and imines (Table S3a and S3b in the Supporting Information). The catalyst can be filtered and recycled at least four times without loss of activity or selectivity.

Three gold species, that is, Au^I, Au^{III}, and Au⁰ were identified by different spectroscopic techniques on the Au/CeO₂ catalyst used in this work, with relative abundances of Au⁰ > Au^{III} > Au^I.^[23] To find which, among those species, are the active sites for hydrosilylation, we tested a series of Au^I [(PPh₃)AuCl], [(carbene)AuCl] (**3Au**), and [(tbt)AuCl]; tbt = tetrahydrothiophene) and Au^{III} complexes (**1,2Au^{III}**) and salts (KAuCl₄), as well as colloidal Au⁰ with a mean diameter of 5 nm, which is very similar to that observed for gold nanoparticles supported on the nanocrystalline ceria.

When [(PPh₃)AuCl] is used as catalyst, it shows no activity toward the hydrosilylation of either carbonyl or olefinic compounds as a result of the formation of inactive gold metallic particles that agglomerate. However, when the Schiff

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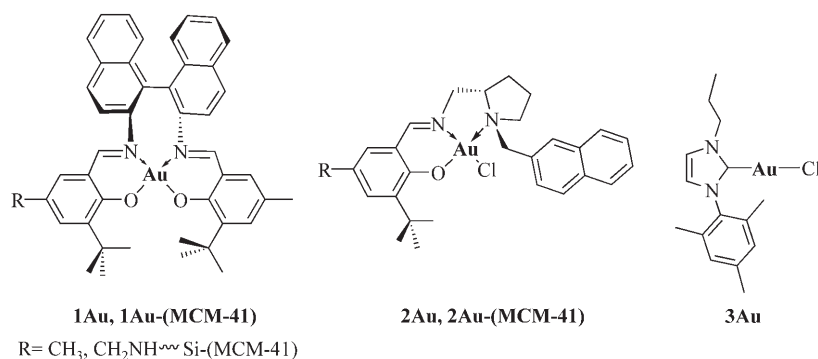


Figure 1. Gold compounds studied as hydrosilylation catalysts.

base Au^{III} complexes were used, they showed very high activities and selectivities for the hydrosilylation of the different compounds. Good results were also obtained with Au^{III} in the form of KAuCl₄. However, the salt decomposes with time and the gold is reduced to metallic gold thereby losing most of its activity. Au^I, on the other hand, is generally less active than Au^{III} (Table 1; see also Tables S1–S3 in the Supporting Information). Finally, colloidal gold is only active

Table 1: Gold-catalyzed hydrosilylation of styrene with R₃SiH.^[a]

Catalyst	Ph ₂ SiH ₂	PhMe ₂ SiH	Et ₃ SiH
KAuCl ₄	100 (2 h)	80 (8 h)	20 (8 h)
Au/CeO ₂ ^[b]	100 (2 h)	100 (8 h)	100 (8 h)
1Au^{III}	100 (2 h)	50 (8 h)	30 (8 h)
[(tht)AuCl]	100 (15 h)	47	traces
[(PPh ₃)AuCl]	5 (15 h)	traces	0
3Au^I	50 (15 h)	20	2–5
Au ⁰	0 (24 h)	0	0

[a] The reactions were carried out with styrene (3 mmol), silane (1 mmol), and gold catalyst (10 mol %). Yields are quoted with respect to the amount of silane consumed based on GC-MS. Selectivity > 98 %.

[b] Recycled: fourth run.

for the hydrosilylation of carbonyl compounds. From the above results, we could conclude that Au^I and, specially, Au^{III} species are both active for the hydrosilylation of carbonyl compounds and olefins, while nanoparticles of metallic gold (colloidal Au) are only active for the hydrosilylation of carbonyls. If we extrapolate these results to those obtained with Au/CeO₂, it could be concluded that the presence of stabilized Au^{III} on that catalyst should be responsible for hydrosilylation of olefins and carbonyl groups, while nanoparticles of Au⁰, probably through unsaturated atoms at corners and axis of the crystallites, are only active for carbonyls compounds. Note that Au/CeO₂ as well as the homogeneous catalysts studied here are chemoselective for the hydrosilylation of the carbonyl group (Table S2 in the Supporting Information). Moreover, when the Schiff base Au^{III} complexes, **1,2Au^{III}**, are grafted on a mesoporous MCM-41 support, they are active and chemoselective, and can be recycled without any decrease in activity.

To discuss the relative catalytic activity of the different gold species for olefin hydrosilylation, we treated styrene with a series of alkyl and aryl silanes, which follow the order of activation, Ph₂SiH₂ > PhMe₂SiH > Et₃SiH. Results from Table 1 indicate that Au^{III} is more active than Au^I as the former gives higher conversion with the less activated silanes. Interestingly, Au/CeO₂ is the most active catalyst, affording 100 % conversion in all cases. In the case of the hydrosilylation of benzaldehyde (Table S1 in the Supporting Information), again Au^{III} is the most active, followed by Au⁰ and Au^I. When Au/CeO₂ was used as catalyst, the reaction was complete

even in the presence of an aliphatic silane such as Et₃SiH.

The generality of gold for hydrosilylation was demonstrated by reacting various substrates such as phenyl acetylene, *anti-N*-benzyl(1-phenylethylidene)imine, heptanal, and 1-octene. Phenyl acetylene was chosen as model compound for the hydrosilylation reaction of terminal acetylenes. As shown in Table S3b in the Supporting Information, Au/CeO₂ is highly selective and only produces the *trans* isomer. When soluble **1Au^{III}** was used as catalyst, a considerable loss of selectivity was detected and the yield of the *cis* isomer increased up to 60 % of the product mixture. The supported catalyst **1Au^{III}**-MCM-41 gives only the *trans* isomer. Hydrosilylation of an imine (*anti-N*-benzyl(1-phenylethylidene)imine) was also carried out with diphenylsilane in the presence of a Schiff base Au^{III} complex or Au/CeO₂ (Table S3b in the Supporting Information), and a moderate yield of the corresponding silylated product was obtained. The reaction with a linear aldehyde (heptanal) or alkene (1-octene) leads to the corresponding silyl derivative in good yields, with Au/CeO₂ again being the most active. The hydrosilylation of cinnamaldehyde (Table S2 in the Supporting Information), which contains a conjugated double bond, at the carbonyl group affords the 1,2-addition product with high chemoselectivity (> 95 %).

To study the asymmetric catalytic activity of the homogeneous and heterogenized chiral **1,2Au^{III}** complexes, we investigated the hydrosilylation of α -methylstyrene and acetophenone (Table S4 in the Supporting Information). The oxidation of diphenyl(1-phenylethyl)silane with H₂O₂ or the hydrolysis of diphenyl(1-phenylethoxy)silane gave 1-phenylethanol with an enantiomeric excess of less than 25 %. The results indicate further possibilities of gold catalysts, and work on the design of new ligands is currently in progress.

In conclusion, we have found that gold supported on CeO₂ and well-defined phosphine-free organogold(III) complexes can selectively catalyze the hydrosilylation of aldehydes, ketones, olefins, imines, and alkynes. Au/CeO₂ is able to efficiently catalyze those reactions owing to the presence of stabilized Au^{III} on the surface. This catalyst can be recycled without loss of activity, and it is regio- and chemoselective. Schiff base Au^{III} complexes can catalyze the hydrosilylation of carbonyls and olefins without the need to introduce any phosphine groups to avoid formation of metallic gold, as was required with previously reported homogeneous catalysts.

Heterogenized Au^{III} complexes also can be recycled by simple filtration without any loss of activity or metal leaching.

Experimental Section

Experimental procedures: 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. In See Supporting Information for experimental details with respect to catalyst preparation and reaction procedures.

General protocol for hydrosilylation experiments. The protocol used for hydrosilylation reactions employing 5–10 mol % catalyst loading in toluene is provided as a representative procedure. A solution or suspension of the catalyst (5–10 mol %) in dry toluene (2 mL) in a 5-mL Schlenk flask was allowed to equilibrate for 5 min with stirring, at which point, styrene (343 μ L, 3 mmol), α -methylstyrene (390 μ L, 3 mmol), acetophenone (114 μ L, 1 mmol), benzaldehyde (101 μ L, 1 mmol), or cinnamaldehyde (126 μ L, 1 mmol) was added. The resultant mixture was stirred for an additional 5–10 min, after which time H₂SiPh₂, HSiMePh₂, or HSiEt₃ (1 mmol for styrenes or 2 mmol for benzaldehyde, acetophenone, and cinnamaldehyde) was added. The reaction mixture was stirred at 70°C for 1–15 h, and the reaction course was monitored by GC-MS analysis. The mixture was filtered through a short column (celite), from which a clear, colorless solution was eluted. Products of each reaction were identified by the use of GC-MS^[24] or ¹H NMR spectroscopy.

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