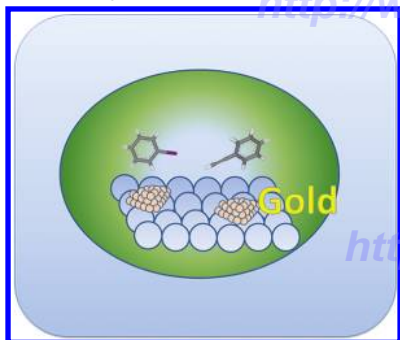


Catalysis by Supported Gold Nanoparticles: Beyond Aerobic Oxidative Processes

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1. INTRODUCTION

Bulk gold, being the most stable among all metals, was for many years considered as an inert catalyst. However, gold particles with size on the scale of nanometers (gold nanoparticles, Au NPs) have been recognized as surprisingly active and extraordinary effective green catalysts, generating a highly popular research topic in the frontier between homogeneous and heterogeneous catalysis.^{1,2} The first major discovery in the field of catalysis by Au NPs was their high

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potency to oxidize CO into CO₂ by atmospheric air.⁵ This oxidation has a huge environmental and commercial potential due to the feasibility to achieve the selective oxidation of CO without oxidizing the valuable H₂ in the presence of a large hydrogen concentration for the use of the treated gas in fuel cells. The reaction is now optimized to operate at ambient conditions,^{4–16} and even at –80 °C,¹⁷ allowing the development of several other practical applications, such as the use of supported gold nanoparticles as additives in gas masks or as sensors in analytical instruments. Following this early discovery, several valuable Au NP-catalyzed industrial processes toward a sustainable chemistry^{18,19} were also developed, such as the aerobic oxidation of methanol to the important chemical methyl formate,²⁰ or the bulk production of vinyl acetate and vinyl chloride, basic raw chemicals for the synthesis of polymers.²¹ Au NPs supported on metal oxide surfaces²² (Au/M_xO_y, e.g., Au/TiO₂ or CeO₂ or Fe₃O₄ or MgO, etc.) with controllable shape²³ can be prepared by the adsorption or deposition-precipitation methods,^{24,25} and by other means.²⁶ They can be easily handled, are fairly air-stable,²⁷ and in case of deactivation can be redispersed and reactivated upon treatment with CH₃I.²⁸ In addition, gold nanoparticles supported on carbonaceous materials (e.g., carbon nanotubes),^{29–32} on polymers or biopolymers,³³ and in the form of ultrathin films³⁴ have received considerable attention. Catalysis by bimetallic or trimetallic gold-bearing nanoalloys is also a rapidly expanding field.³⁵ The structure and surface chemistry of such materials has been recently reviewed,³⁶ while several synthetic applications are presented within the sections of this article.

Following the mild aerobic CO oxidation methodology, Au nanoparticles have been applied as powerful catalysts for various other oxidative transformations such as the oxidation of alcohols, aldehydes, amines, hydrocarbons, and in the epoxidation of alkenes utilizing oxygen or air as oxidant. Such processes have been thoroughly reviewed over the past few years.^{37–41} Additionally, the reaction between hydrogen and oxygen for the direct production of the industrially valuable hydrogen peroxide has been extensively studied,⁴² having recently achieved significant progress.⁴³ The mechanism of the Au NP-catalyzed processes, especially the aerobic ones, is questionable and under continuous debate. The main issue deals with whether small metallic clusters of Au⁰, partly oxidized gold particles (Au^{δ+}), partly reduced gold particles by interacting with electron-rich metal defects on the support (Au^{δ-}), undercoordinated gold atoms, or cationic Au^I and/or Au^{III} species are the actual catalytic sites.^{44–50} The mechanistic complexity is apparent, as, for example, catalytic sites bearing Au species of different gold oxidation states within the same Au NP-supported catalyst may be responsible for the catalysis of dissecting pathways.^{51–53} Apart from the questionable oxidation level(s) of the reactive species, the size, shape, and location of nanoparticles on the support is also crucial.^{54–59} It has been shown that the catalytic sites on the material's surface are located at dual perimeter positions at the interface between Au NP and the support.^{60,61}

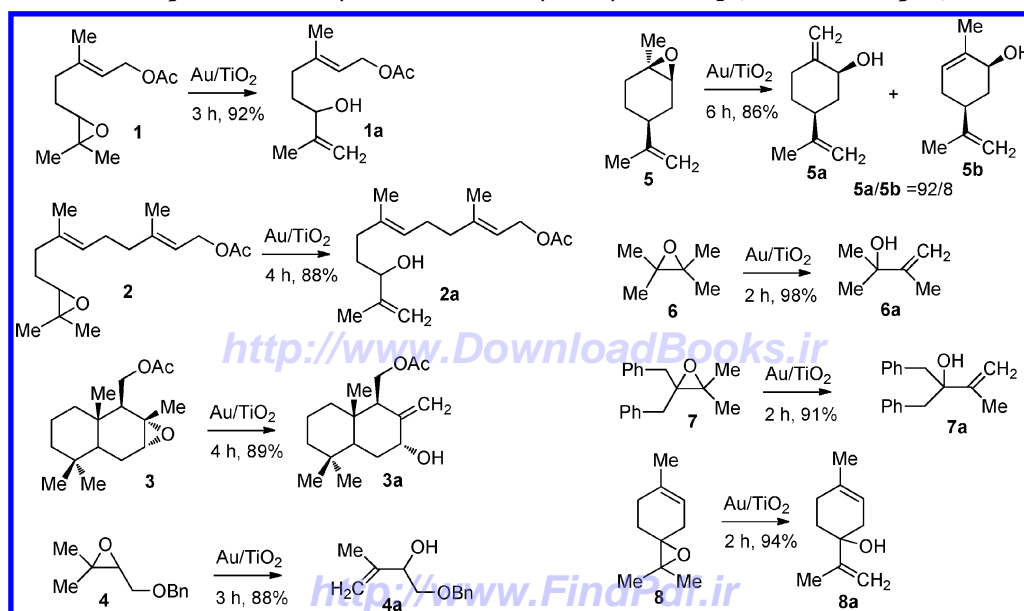
Gold nanoparticles supported on metal oxide surfaces are typically prepared upon reduction of Au(III) substances such as HAuCl₄ or NaAuCl₄. Although it is expected that cationic gold will certainly be completely reduced to metallic gold clusters, recent experiments have shown that Au NPs/M_xO_y may also contain cationic gold species in either the oxidation state of +1 or +3.^{62–64} Such species have been titrated^{65–70} and can be quantified with X-ray photoelectron spectroscopy (XPS) by

deconvolution of the characteristic Au 4f_{7/2} peak.⁷¹ Oxidized gold particles may also be formed by the interaction of small metallic gold clusters with a specific type of hydroxyl groups on the metal oxide surface.⁷² Norskov and co-workers⁷³ proposed low-coordinated Au atoms on the corners and edges of supported Au NPs as active sites. On the other hand, for Au/CeO₂ an interplay was suggested⁷⁴ between reversible Ce⁴⁺/Ce³⁺ and Au³⁺/Au⁺ reductions, which underpins the high catalytic activity of the dispersed Au atoms. In the case of Au/TiO₂, it was postulated⁷⁵ that TiO₂(110) surface contains positively charged Au ions that catalyze CO activation. In general, the synergism between gold nanoparticles and the support seems to be an essential factor in Au NP catalysis, and besides stabilization of particle size and agglomeration minimization, one of the main reasons for this synergism is the generation of positive Au ions on the surface of nanoparticles.

Although metallic Au(111) surface^{76–79} and even bulk gold^{80–82} have been shown to be catalytically active, especially in aerobic oxidative processes, we emphasize that Au NPs supported on metal oxide surfaces contain a part of small metallic gold clusters,^{83,84} oxidized gold particles bearing either Au^{δ+}, or even Au(I) and Au(III) species. These support-stabilized cationic species⁴⁵ may act as soft Lewis acids or participate in reactions involving gold redox catalysis and have been proposed on many occasions to be responsible for the catalytic activity of Au NPs (several examples will be presented throughout this review article). In other words, supported Au NPs might be considered to a certain extent to be counterparts of homogeneous ionic gold catalysts. Comparison of the catalytic activity of supported Au NPs with that of gold(I) or gold(III) complexes has been used as an experimental methodology to clarify/suggest the nature of the active sites of supported Au NPs. Because it seems, based on the proposals, that ionic and nonionic gold species present on supported Au NPs are involved in catalytic processes, metaphorically they could be considered as “Swiss army knife” multipurpose heterogeneous catalysts.⁸⁵

Heterogenized ionic gold catalysts, which are prepared by covalent binding of their ligands into solid supports (typically resins) or porous materials, is also a class of catalysts that could be applied in heterogenized gold-catalyzed reactions, but they have attracted limited attention so far.^{86–92} Probably the main reason for this paucity of reports describing heterogenization of homogeneous gold complexes on insoluble large-area solids is the lack of stability, as these complexes generally tend to decompose during the course of the reaction. It would be of interest to assess stability of gold complexes, because this would be a prerequisite for their covalent anchoring in solids and their use as heterogeneous catalysts, an area that remains rather unexplored and should probably undergo a future development similarly to the work that has been performed for other transition metals, and to develop recoverable and reusable heterogeneous catalysts from successful homogeneous catalysts.^{93–95} In this area of heterogenization of homogeneous complexes, micro/mesoporous solids are among the preferred supports due to the large surface of these materials, but attention has to be paid to the possibility of diffusion limitation of substrates and reagents to the catalytic sites. To facilitate diffusion, solids with larger pore size in the mesoporous range can be preferred.

However, apart from being excellent catalysts in aerobic oxidative processes, supported Au NPs have also found in

Scheme 1. Isomerization of Epoxides into Allylic Alcohols Catalyzed by Au/TiO₂ (Selected Examples)

recent years numerous applications as unique catalysts in novel and unprecedented reactions. This review focuses on the recent achievements in the activation of dihydrogen, epoxides, alcohols, carbonyl compounds, alkynes, hydrosilanes, or boron hydrides, as well as on CO₂ fixation, C–C cross-coupling reactions, hydrogen transfer catalysis, etc. As a general comment, it appears that the reactivity of supported Au NPs in the current presented examples is controlled by a variety of different oxidation states of Au with the same catalyst, which makes gold nanoparticles a polyfunctional catalyst. Hopefully, further research in the near future will shed light on the obscure nature of reactive species on the increasing number of Au NP-catalyzed reactions.

2. OXOPHILIC ACTIVATION OF EPOXIDES, CARBONYL COMPOUNDS, AND ALCOHOLS

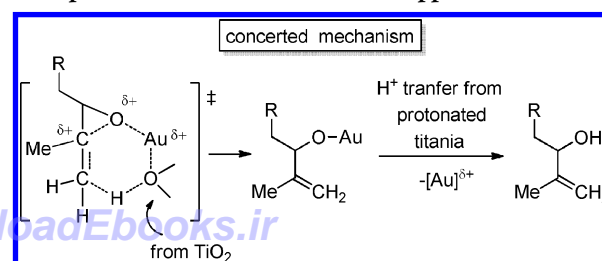
2.1. Isomerization of Epoxides into Allylic Alcohols

An unexpected catalytic property of Au/TiO₂ was uncovered in the clean and highly regioselective isomerization of tri- and tetrasubstituted epoxides into allylic alcohols (Scheme 1).⁹⁶ The Au/TiO₂-catalyzed (~1% mol) reaction proceeds in a slurry of refluxing 1,2-dichloroethane. Under acid catalysis, epoxides are known to undergo isomerization into carbonyl compounds through the Meinwald rearrangement. On the other hand, the isomerization of an epoxide into an allylic alcohol requires the synergism of a bifunctional acid/base catalyst, such as amphoteric aluminum alkoxides or amides.⁹⁷ For the Au/TiO₂-catalyzed isomerization, it was suggested that the soft Lewis acidic sites are provided by ionic gold species on the surface of the catalyst, whereas the basic sites could possibly be the oxygen atoms of the support. Titania, being an amphoteric oxide, also promotes the epoxide to an allyl alcohol isomerization, however, at least 2–3 orders of magnitude more slowly and unselectively. The reaction was found to be highly selective in cases where more than one regioisomer could formally have been formed (e.g., epoxides **3**, **5**, **7**, and **8**; Scheme 1), and that was rationalized in terms of a kinetic formation of the new double bond through abstraction of a hydrogen atom from the least hindered allylic position with

respect to the epoxide functionality. The catalytic efficiency is very high; as in the case of tetramethylethylene oxide (**6**), the turnover number (TON) was measured to be close to 10³.

On the basis of stereoisotopic studies and intermolecular kinetic isotope effects, a six-membered ring concerted transition state was proposed, as shown in Scheme 2. Isomerization of the

Scheme 2. Mechanistic Proposal for the Au/TiO₂-Catalyzed Isomerization of Epoxides through a Synergism of Ionic Gold Species and Basic Sites on the Support



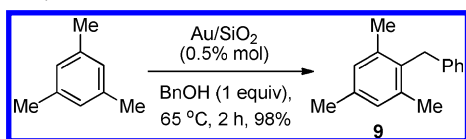
epoxide through the intermediate formation of an open carbocation was clearly ruled out. The concerted mechanism nicely rationalizes the observed regioselectivity. For example, the epoxide **5** (1R,4S-limonene oxide) yields mainly one regioisomer (**5a**) due to an inappropriate conformational orientation of intraring C–H bonds, whereas its 1S,4S-epimer forms a mixture of regioisomers. Cationic gold has been shown under homogeneous conditions to be not only π -carbophilic but also oxophilic^{98–100} It is possible that ionic gold species on TiO₂ (designated as Au^{δ+} in Scheme 2) are responsible for the activation of the epoxide, acting as a Lewis acid.

2.2. Benzylation of Aromatics

The alkylation of aromatics by alcohols is a typical Friedel–Crafts-type reaction catalyzed by Lewis or Brønsted acids, as well as by Au(III),¹⁰¹ under homogeneous conditions. Hardacre and co-workers¹⁰² used heterogenized Au nanoparticles supported on silica (0.5–1.5% mol) to achieve good to excellent selectivity in the benzylation of substituted benzenes with benzyl alcohol. As expected, the more electron-rich

aromatic compounds underwent the more facile alkylation, as shown for the case of mesitylene in Scheme 3 that provides

Scheme 3. Benzylation of Mesitylene by Benzyl Alcohol Catalyzed by Au/SiO₂

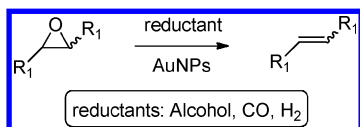


benzylmesitylene (**9**) in almost quantitative yield. The recyclable catalyst was prepared by an ionic liquid-mediated deposition procedure. This example clearly indicates the oxophilic nature of Au NPs. However, their catalytic efficiency is still below that of conventional Lewis acids.

2.3. Deoxygenation of Epoxides

Traditionally, the stereospecific deoxygenation of epoxides into the corresponding alkenes takes place using stoichiometric amounts of reagents¹⁰³ (e.g., reaction with Ph₂PLi followed by addition of MeI, with low-valent Ti, and many others) or under catalytic protocols with poor efficiency. Recently, novel and highly efficient methodologies for the deoxygenation of epoxides catalyzed by gold nanoparticles have been reported,^{104–109} which exceed by far the effectiveness (TON and turnover frequency (TOF)) of all previously developed homogeneous catalytic versions. A common logic behind these processes is the use of an inexpensive stoichiometric reductant that is oxidized through a gold-mediated indirect oxygen atom transfer from the reacting epoxide (Scheme 4). In situ-formed

Scheme 4. Deoxygenation of Epoxides into Alkenes in the Presence of a Reducing Agent Catalyzed by Au NPs



gold hydride species with an often unspecified oxidation state of gold were proposed in all protocols as the active epoxide reducing agents. Reductions of other functional groups involving transient gold hydrides generated by the interaction of alcohols, CO/H₂O, formates, or dihydrogen with supported Au NPs will be also presented in sections 6 and 7.

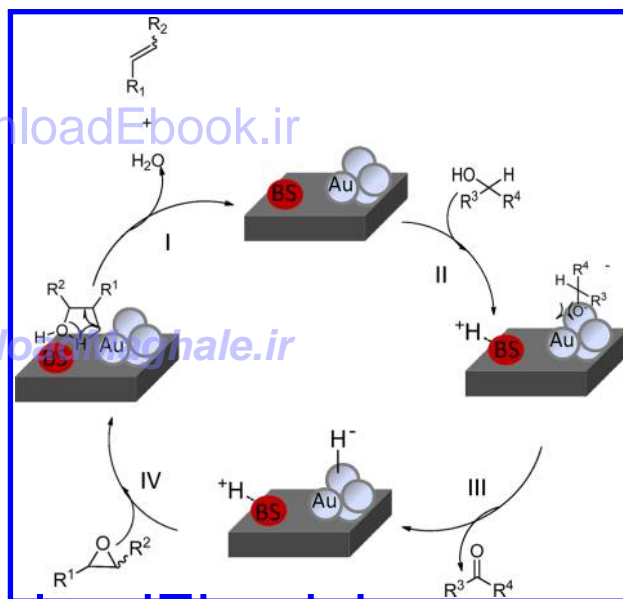
The first example of this deoxygenation concept was reported by Kaneda and co-workers,^{104–106} who showed that Au NPs supported on hydrotalcite, Au/HT [HT, hydrotalcite, Mg₆Al₂(OH)₁₆CO₃·*n*H₂O], catalyze the deoxygenation of a series of epoxides in high selectivity (>99%) and yield (up to 99%), using alcohols as reducing agents. Isopropanol was proven as the most practical and suitable (Table 1). The optimum reaction conditions require a 10 molar excess of 2-propanol (that is eventually oxidized into acetone), refluxing toluene as solvent, 0.45% mol of catalyst, and inert atmosphere (Ar). Under those conditions, remarkable catalytic efficiency was observed with TOF and TON being up to 270 h^{−1} and 2 × 10⁴, respectively, regarding the deoxygenation of *trans*-stilbene oxide at 150 °C. The monosubstituted epoxides are more reactive and provide higher deoxygenation yields relative to di- or trisubstituted ones. Furthermore, the reaction is heterogeneous in nature, as in the supernatant solution the gold content measured by inductively coupled plasma (ICP) analysis was

Table 1. Selected Examples in the Deoxygenation of Epoxides Catalyzed by Au/HT, Using 2-Propanol As Reductant

Substrate	Product(s)	Conversion/Time (h)
10	10a	99%/4
11	11a (Z/E=3/2)	99%/4
12	12a	94%/6
13	13a	93%/6
14	14a (Z/E=3/2)	81%/12
15	15a	88%/24

below the detection limit (0.1 ppm). A synergism between Au NP and the basic sites of HT was invoked in the proposed catalytic cycle of deoxygenation. First, oxidation of the alcohol occurs through proton abstraction by the basic support, followed by β -hydride transfer (intermediate B, Scheme 5) to the Au NPs, thus forming [Au–H][−] species (intermediate C).

Scheme 5. Proposed Mechanism for the Au/HT-Catalyzed Deoxygenation of Epoxides in the Presence of an Alcohol (BS, Basic Site; HT, Hydrotalcite)^a

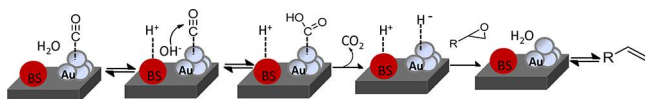


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Subsequently, protonation of the epoxide by the conjugate acid of hydrotalcite (HT-H^+) and attack by the $[\text{Au-H}]^-$ species (cyclic transition state D) provides the product (alkene) and a molecule of H_2O . Because HTs are layered materials constituted by positively charge sheets of a few atoms thickness having anions in the interlamellar space, one key issue that has been not sufficiently addressed is the possibility to make available the intergallery space of these materials. Typically this space is not accessible to reagents due to the strong Coulombic interactions, the short distance between the layers, and the lack of porosity. It would be of interest if the surface area of HT could be much larger by making available the internal surface that normally is not accessible to the reagents due to the lack of diffusion.

The same group¹⁰⁷ provided immediately after a new method for the Au/HT-catalyzed (0.9% mol) deoxygenation of epoxides using CO (1 atm) as reductant and water as solvent. This methodology is much milder as it can be performed at room temperature. Yields up to 99% were reported, while the product selectivity was always >99%. Other metal nanoparticles supported on HT (e.g., Ag, Pt, Rh, Ru, and Pd) are completely inefficient, thus highlighting the uniqueness of Au NPs in such a process. Again $[\text{Au-H}]^-$ species were suggested as the active reducing agents. The authors postulated coordination of CO on the Au NPs, HT-assisted basic hydrolysis of the catalyst-bound carbon monoxide to form $[\text{Au}]$ -carboxylates that eliminate CO_2 , thus forming gold hydride species (Scheme 6). The cooperation between the basic sites of hydrotalcite and Au NPs was emphasized.

Scheme 6. Proposed Mechanism for the Au/HT-Catalyzed Deoxygenation of Epoxides in the Presence of CO (BS, Basic Site; HT, Hydrotalcite)^a



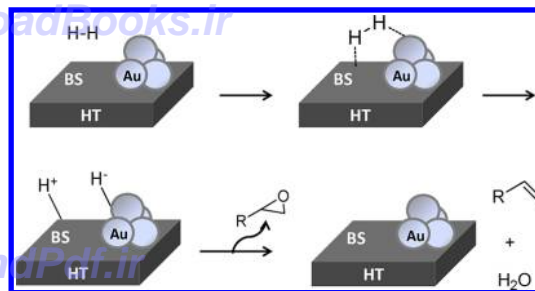
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Almost simultaneously, Cao and co-workers¹⁰⁸ reported a similar mild (room-temperature) CO-mediated deoxygenation, catalyzed by very small Au NPs supported on titania (Au/TiO_2 -VS). Typical commercially available Au/TiO_2 catalyst (AUROLite) is less efficient. The authors proposed the intermediacy of highly reactive transient $\text{Au}^0\text{-H}$ species, generated by a similar mechanism as proposed by Kaneda and co-workers.¹⁰⁷ The participation of H_2 as the reducing agent was ruled out. Hydrogen gas could formally have been generated from an ambient temperature water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) within the reaction mixture, yet it was found that the deoxygenation of an epoxide in the presence of H_2 (2 atm) under Au/TiO_2 -VS catalysis conditions proceeds sluggishly.

Following the alcohol and CO-mediated methodologies, a simple procedure for the deoxygenation of epoxides was reported by the group of Kaneda,¹⁰⁹ using hydrogen gas as reductant and Au/HT (0.9% mol) as catalyst (1 atm H_2 , 60 °C, 8–24 h, toluene). Among several gold-based catalytic systems tested, Au/HT was highly product selective in favor of alkene formation. Au/TiO_2 is also highly selective; however, the reaction proceeds slowly. $\text{Au/Al}_2\text{O}_3$ provides mainly over-reduction of the initially formed alkene to the corresponding

alkane, whereas Pd or Pt/HT catalyze the reductive opening of the epoxides into terminal alcohols, without any formation of alkenes. The size of Au NPs is essential for the observed product selectivity, as Au NPs <3 nm provide 97% selectivity in favor of the alkenes, whereas nanoparticles with size ~20 nm lead primarily to over-reduction, forming alkanes. A concerted effect among Au NPs and the basic sites of the support was invoked to rationalize the mechanism (Scheme 7). Thus, most

Scheme 7. Proposed Mechanism for the Au/HT-Catalyzed Deoxygenation of Epoxides through Heterolytic Dissociation of H_2 (BS, Basic Site; HT, Hydrotalcite)^a

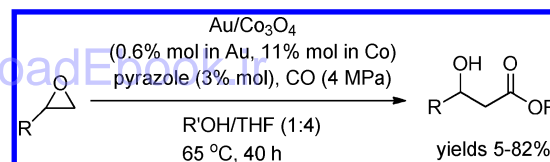


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likely, heterolytic dissociation of H_2 at the interface between the basic sites of HT and Au NPs generates HT-H^+ and Au-H^- species, with the latter being responsible for the deoxygenation reaction. Bands assigned to such species (1748 cm^{-1} for Au-H^- and 3200 cm^{-1} for HT-H^+) were recorded by Fourier transform infrared (FTIR) spectroscopy.

Alkoxycarbonylation of epoxides by CO in the presence of an alcohol to form β -hydroxy esters is a well-known transformation,^{110,111} catalyzed by $\text{Co}(\text{CO})_8$. A major problem in this process is the instability of $\text{Co}(\text{CO})_8$, which has to be freshly prepared and sublimed prior to use. Tokunaga and co-workers¹¹² reported that Au nanoparticles supported on Co_3O_4 provide in situ $\text{Co}(\text{CO})_8$ species under a 4 MPa CO atmosphere (Scheme 8). Yields up to 82% were obtained for

Scheme 8. Au/ Co_3O_4 -Catalyzed Alkoxycarbonylation of Epoxides by CO in the Presence of Alcohols



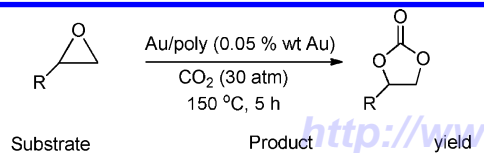
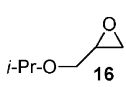
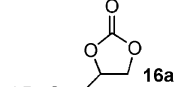
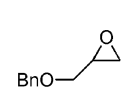
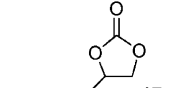
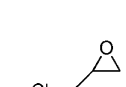
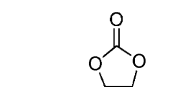
the reaction of a series of epoxides in the presence of methanol or ethanol as cosolvents to tetrahydrofuran (THF). It was proposed that the active cobalt catalytic species are formed by reduction of the support metal (cobalt) and subsequent binding to CO.

2.5. Formation of Cyclic Carbonates via Insertion (Fixation) of CO_2 on Terminal Epoxides

The transformation of the global carbon-based fuels combustion product, CO_2 , into useful chemicals is an urgent priority of modern green chemistry.¹¹³ The CO_2 -epoxide fixation to form cyclic carbonates is a well-studied reaction toward that direction and is typically catalyzed by bifunctional acid–base cata-

lysts.^{114–117} Deng and co-workers reported an amazing catalytic efficiency of polymer-supported gold nanoparticles (Au/poly, 0.05% wt in Au) in the CO₂-epoxide fixation reaction, limited yet to terminal monosubstituted epoxides (Table 2).¹¹⁸

Table 2. Insertion of CO₂ on Epoxides to Form Cyclic Carbonates Catalyzed by Au NPs Supported on a Cationic Polymer

Substrate	Product	yield
		
		90%
		93%
		94%

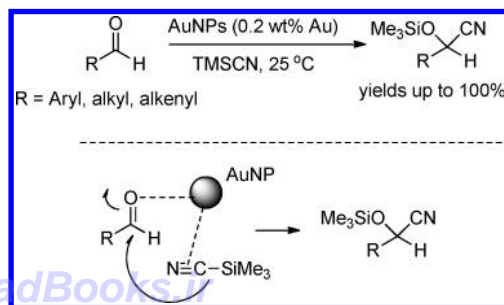
Unprecedented high turn over frequencies (TOFs) of >50 000 mol/mol/h were achieved. The functional group of the polymer was cationic quaternary ammonium, which probably stabilizes the Au nanoparticles against deactivation. Additionally, the authors reported in the same manuscript that in the presence of amines (cyclohexyl amine and benzyl amine), CO₂ is smoothly transformed into disubstituted ureas (carbamates). The yields are excellent, and the process is highly efficient, as a turnover frequency for product (TOFP) \approx 3000 mol/mol/h was measured. The mechanism of CO₂ fixation on epoxide is unclear in the sense of whether the carbonyl functionality of CO₂ or the epoxide is activated, or even both, and is more likely attributed to a synergism between nanogold species and the peculiar cationic microenvironment of the indispensable polymer surface.

Following this report, Sun and co-workers reported¹¹⁹ a convenient route for the direct synthesis of styrene carbonate from styrene and CO₂ over a nanogold catalyst supported on R201 resin (a quaternary cationic ammonium polymer). Anhydrous *tert*-butyl hydroperoxide (TBHP) was used in situ as oxidant to epoxidize styrene into styrene oxide, which then couples in one pot with carbon dioxide to form the cyclic carbonate. It was proposed that not only Au NPs play a vital role on both reactions (epoxidation and CO₂ fixation), but the quaternary ammonium functionalities of polymer as well. In this process, CO₂ was used as a reagent and solvent as well.

2.6. Cyanosilylation of Aldehydes

Choi and co-workers¹²⁰ reported that a variety of aldehydes (aromatic, unsaturated, saturated) can be smoothly cyanosilylated by trimethylsilyl cyanide under 1-octanethiol-passivated Au NPs (0.2 wt %) catalysis conditions in a variety of solvents (Scheme 9). The reaction is also feasible in the presence of a thin gold film. Detailed experiments indicated that the reaction proceeds via combined pathways of heterogeneous and homogeneous catalysis. The homogeneous pathway is due to leaching of gold into the solution. A rough estimation of the

Scheme 9. Cyanosilylation of Aldehydes by TMSCN Catalyzed by 1-Octanethiol-Passivated Au NPs and a Proposed Mechanism

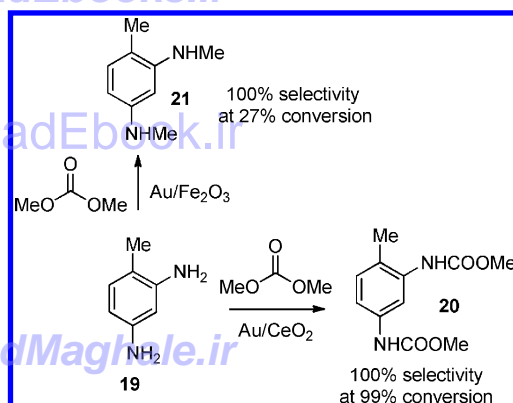


two pathways showed that the ratio of homogeneous and heterogeneous catalysis is \sim 4/1. The competing homogeneous path was independently shown by the same group in the AuCl₃-catalyzed cyanosilylation of carbonyl compounds.¹²¹ It was proposed that the driving force of the reaction is the simultaneous coordination of aldehyde (via the carbonyl group) and trimethylsilyl cyanide (TMSCN) (via the cyanide group) onto the oxophilic gold nanoparticles. Although the authors suggested catalysis by Au(0) in the case of Au NPs, the fact that Au(III) is also active implies that possibly oxidized Au particles might be the active heterogeneous catalytic sites.

2.7. N-Carbamoylation of Anilines with Dimethyl Carbonate

A heterogeneous gold-catalyzed phosgene-free synthesis of polyurethane precursors was recently presented, which mechanistically involves activation of the carbonyl group of dimethyl carbonate over gold nanoparticles.¹²² Thus, Au NPs supported on nanoparticulated CeO₂ are highly efficient catalysts for the selective *N*-carbamoylation of aromatic amines, while emphasis was given to dicarbamoylation of 2,4-diaminotoluene (**19**, Scheme 10) with dimethyl carbonate

Scheme 10. Divergent Activity (*N*-Methylation or *N*-Carbamoylation) for the Reaction of 2,4-Diaminotoluene (19**) with Dimethyl Carbonate Catalyzed by Supported Au NPs**



(DMC), which is an important aromatic amine for the production of polyurethane. The current industrial route for manufacturing polyurethanes is based on the use of the highly toxic phosgene (COCl₂), which reacts with amines forming isocyanates, the immediate polyurethane precursors. Several supported metal nanoparticles (Au, Pt, and Pd) were also tested as catalysts and Au/CeO₂ (0.44% mol) provides the desired

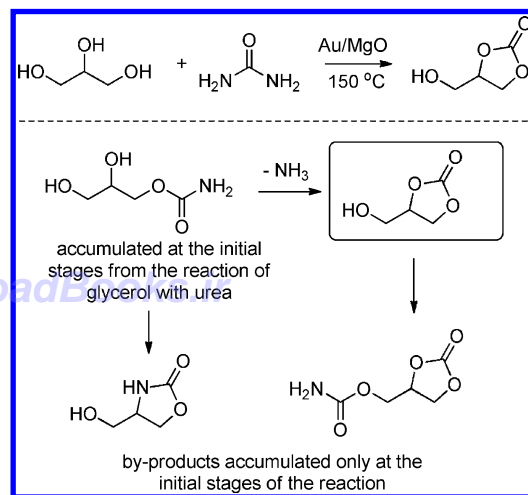
N,N-dicarbamylation of 2,4-diaminotoluene in up to 100% yield (product **20**). Surprisingly, the same reaction catalyzed by Au/TiO₂ or Au/Fe₂O₃ proceeds slowly and leads mainly to the corresponding dimethylated diaminotoluene (**21**) without any dicarbamylation seen. On the other hand, Lewis acids provide mixtures of carbamylation and dimethylation pathways. Although it was shown that nanocrystalline CeO₂ catalyzes by itself the carbamylation, yet unselectively, the presence of supported gold strongly boosts activity to the desired dicarbamylation product. Given that Au/CeO₂ also catalyzes the reduction of –NO₂ to –NH₂ functionality in the presence of hydrogen (see also section 5.3), the one-pot reduction/carbamylation of 2,4-dinitrotoluene in the presence of H₂ (5 bar) and DMC (150 °C, 12 h) was achieved in high yield. Through in situ FTIR spectroscopy studies, it was found that DMC adsorbs dissociatively on the surface of CeO₂, giving methoxy and carbonate species. When aniline is introduced into the reaction mixture, the carbonate species slowly start to disappear, whereas the methoxy groups have only partially disappeared. On the contrary, for Au/TiO₂, DMC also adsorbs dissociatively but the methoxy groups are much easily desorbed than in Au/CeO₂; therefore, undesired *N*-methylated amines are primarily formed. Further studies¹²³ revealed that the low-energy {111} facets of ceria show high activity and selectivity toward the desired carbamylation. In addition, a continuous-flow methodology for the carbamylation of aniline with dimethyl carbonate was developed,¹²⁴ using a microreactor coated with a thin film of Au/CeO₂.

2.8. Synthesis of Carbonates from Diols and Their Transalkylation

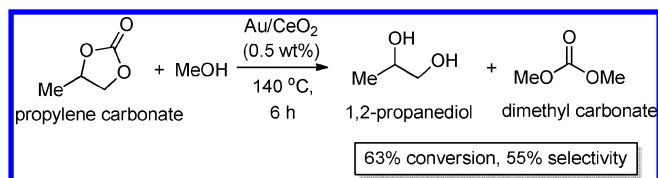
The reaction of glycerol with urea to form glycerol carbonate, an important raw chemical, is mostly reported in the patent literature. This process utilizes two inexpensive and readily available compounds and additionally provides a route to upgrade the excedent production of glycerol formed in large quantities as byproduct during the production of biodiesel. Previous reports are largely based on the use of high concentrations of metal sulfates or oxides as catalysts, which suffer from low intrinsic activity and selectivity. The group of Hutchings presented¹²⁵ an efficient methodology using supported Au NPs as catalysts. By following an extensive screening, it was found that MgO was the support of choice (Scheme 11). Au/MgO (2.5 wt % in Au) was calcined to 400 °C and reused 10 times without activity loss. The molar ratio of glycerol to urea was 1/1.5, and the reactions were carried out at 150 °C. The yields of glycerol carbonate obtained are superior to those under homogeneous conditions using conventional Lewis acids, such as ZnSO₄. This beneficial effect might occur by promoting the intramolecular cyclization of the initially generated intermediate carbamate to form glycerol carbonate (see proposed mechanism in Scheme 11 as concluded on the basis of intermediate products characterization by FTIR spectroscopy and GC-MS analysis). The mechanistic study suggested that the main effect of the catalyst is the promotion of the intramolecular reaction for the formation of glycerol carbonate from the intermediate 2,3-dihydroxypropyl carbamate, via gold coordination to the carbonyl group, which facilitates nucleophilic attack by the secondary hydroxyl group.

The Au NP-catalyzed methanolysis of propylene carbonate into propanediol and dimethyl carbonate was also reported (Scheme 12) and proceeds in moderate yields and selectivity.¹²⁶ Ceria nanocrystals, by themselves, are poor

Scheme 11. Synthesis of Glycerol Carbonate from Glycerol and Urea Catalyzed by Au/MgO and the Proposed Reaction Mechanism



Scheme 12. Methanolysis of Propylene Carbonate into Propanediol and Dimethyl Carbonate Catalyzed by Au/CeO₂



active catalysts regarding this transalkylation. However, the presence of gold nanoparticles on ceria at appropriate loading significantly increases the activity and selectivity, probably via carbonyl group coordination. The alcoholysis by ethanol and higher homologues proceeds in lower yield, apparently due to steric reasons.

3. ALKYNE ACTIVATION

The proposal that ionic gold species are present on the surface of supported gold nanoparticles on metal oxides^{62–70,127} implies that Au NPs could possibly catalyze alkyne activation, as alkynes are highly σ -acidic against Au(I) and Au(III) salts or complexes. Alkyne σ -acidicity has resulted to an explosive growth of homogeneous ionic gold catalysis during the past decade,^{128–143} and this topic has become an essential branch of modern synthetic organic chemistry. Yet, despite the remarkable development of π -acid catalysis by Au(I or III) under homogeneous conditions, the use of Au NPs in alkyne activation under heterogeneous conditions still remains rather underdeveloped,^{144,145} mostly due to the failure of many of the conventional metal oxide-supported Au catalysts to behave similarly to Au(I) complexes in homogeneous phase. A search for heterogeneous versions of Au-catalyzed reaction is extremely important because these processes are generally cleaner, safer, and environmentally friendly and allow for the recycling of the catalysts. In this section we will cover the recent achievements in alkyne activation by Au NPs, with the topic of hydrochlorination of alkynes excluded, as it already has been extensively reviewed.^{41,42} We briefly highlight in this reaction a recent mechanistic study¹⁴⁶ in which through deuterium labeling experiments it was concluded that the major product

is formed by *anti*-addition of HCl to the triple bond (catalyst, Au/C) in accordance to homogeneous Au-catalysis proposed mechanisms.

3.1. Cyclization of Aryl Propargyl Ethers

Following the unprecedented epoxide activation by Au/TiO₂,⁹⁶ where ionic gold species were suggested as the active catalytic sites, Stratakis and co-workers¹⁴⁷ presented an example of alkyne activation by the same catalyst in the heterogeneous cyclization of aryl propargyl ethers (Table 3). Such trans-

Table 3. Selected Examples from the Cyclization/Oxidative Dimerization of Aryl Propargyl Ethers Catalyzed by Au/TiO₂

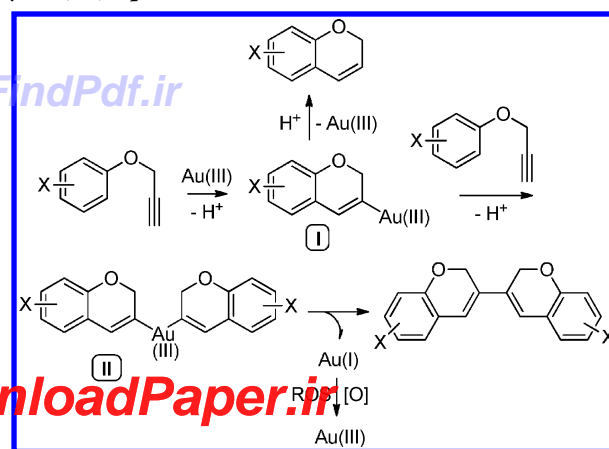
Substrate	Products	Yield/Time (h)
	 	83%/17
	 	74%/3
	 	88%/23
		~2% of dimer 94%/1
		no dimer 96%/2
	 	94%/26
	 	92%/25

formation catalyzed by Au(I) is well-known under homogeneous conditions.^{148–150} Interestingly, Au NPs supported on CeO₂ have been reported to be inactive against [1,6]-enyne cyclization,¹⁵¹ substrates with similar structural features to aryl propargyl ethers. It was found that a variety of functionalized aryl propargyl ethers undergo, in the presence of Au/TiO₂ (1.2% mol) and in refluxing dichloroethane (DCE), selective cyclization into 2H-chromenes. Surprisingly, for the majority of the reacting substrates, dimeric 2H,2'H-3,3'-bichromenes are formed as byproduct in relative yields up to 20%. Blank experiments revealed that the bichromenes are formed not

from an oxidative dimerization of monomeric 2H-chromenes but directly from the starting material. Also, ICP analysis revealed that the gold content in the supernatant solution is extremely low (~0.4 ppb); thus, the cyclization is heterogeneous in nature. The efficiency of the method allowed the synthesis of the naturally occurring pyranocoumarins seselin (28a) and xanthyletin (28b) from the simple aryl propargyl ether precursor 28.

Although monomeric 2H-chromenes could possibly be formed either through Au(I)- or Au(III)-catalysis on the surface of the catalyst, dimeric bichromenes require Au(III) species through a cycle that involves Au(I)–Au(III) redox catalysis.^{152,153} It was postulated that the initially formed auric-monocyclic I (Scheme 13) acts as an electrophilic center to

Scheme 13. Proposed Mechanism for the Cyclization/Oxidative Dimerization of Aryl Propargyl Ethers Catalyzed by Au(III) Species

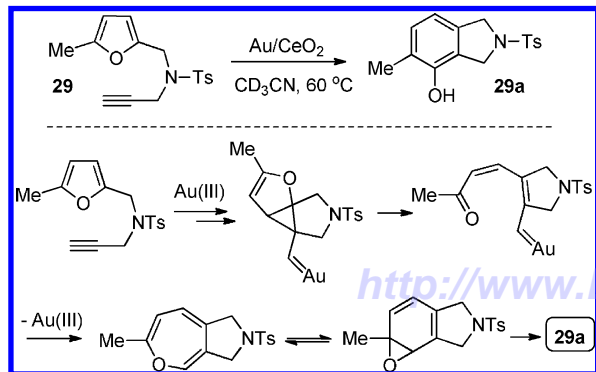


cyclize, attached on it, a second molecule of propargyl ether, thus forming the diorganogold II. Intermediate II undergoes intermolecular C–C coupling to form the dimeric products with elimination of Au(I)-species. The required oxidant to regenerate Au(III) from Au(I) after dimeric C–C bond formation is apparently atmospheric air, as under an inert atmosphere dimers are formed in <3% relative yield, whereas by occasionally blowing air into the reaction mixture, the relative amount of dimer 22b (for the case of substrate 22) may reach 25% relative yield. It was postulated that the required reoxidants are reactive oxygen species (ROS),^{154–157} the proposed transient oxidizing species in the aerobic oxidation of alcohols to carbonyl compounds by gold nanoparticles on various supports. More recently, Wong and co-workers¹⁵⁸ reported the homogeneous Au(III)-catalyzed synthesis of amides by coupling of aldehydes and amines via a Au(I/III) redox cycle promoted by molecular oxygen.

3.2. Cyclization of ω -Alkynylfurans

In 2006 the collaborating groups of Corma and Hashmi reported¹⁵⁹ that Au NPs supported on nanocrystalline ceria (Au/CeO₂) catalyze the cyclization of the ω -alkynylfuran 29 to the substituted phenol 29a (Scheme 14), a well-established transformation under homogeneous conditions in the presence of Au(III),¹⁶⁰ which proceeds through a mechanism involving detectable and interconverting via an electrocyclic reaction oxepines and benzene oxides as intermediates.¹⁶¹ Although this example was the first time that a heterogeneous gold catalyst showed activity in the Au-catalyzed phenol synthesis, and in

Scheme 14. Phenol Synthesis from the Cyclization of *o*-Alkynylfuran 29, Catalyzed by Au/CeO₂, and the Proposed Mechanism

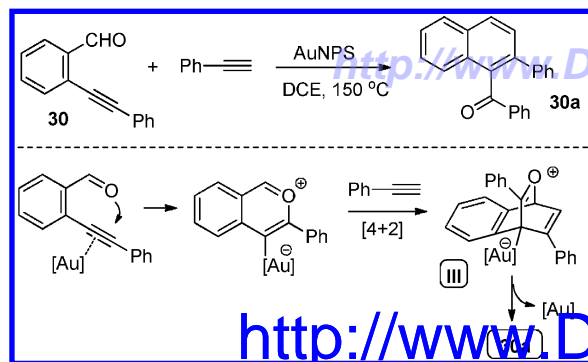


general in C–C bond-forming reaction arising from alkyne activation, the pure heterogeneous nature of the reaction was not obvious due to the significant leaching of gold into the supernatant solution, as verified by analysis through atomic absorption spectroscopy (AAS). The leaching of gold into solution can be minimized by calcination of the catalyst, and surprisingly it was found that leaching strongly decreases after its second reuse and practically disappears after the third run, accompanied by reduced activity, however. By carefully monitoring the catalytic efficiency of Au(III) under homogeneous and heterogeneous conditions, it was concluded that the TON obtained on the basis of cationic gold present on the surface of the heterogeneous catalyst is superior to the one obtained from homogeneous gold(III) catalysts. This can be explained on the basis of a surface concentration effect.

3.3. Benzannulation between *o*-Ethynyl Benzaldehydes and Alkynes

Following the lead of homogeneous gold catalysis,¹⁶² it has been found that Au NPs deposited on various supports (Fe₂O₃, CeO₂, TiO₂, and C) are able to catalyze the benzannulation reaction between *ortho*-(phenylethynyl) benzaldehyde (30) and phenylacetylene yielding 1-benzoyl-2-phenylnaphthalene (30a) with high selectivity and yields (Scheme 15).¹⁶³ Surprisingly, there is no significant influence of the support on the catalyst's efficiency, with all tested supported catalysts working equally well at ~3–4 wt % of Au. Under the typical reaction conditions, 1 equiv of *o*-alkynyl benzaldehyde 30, 3 equiv of phenylacetylene, and 5% mol of the catalyst were heated at 150 °C

Scheme 15. Benzannulation between *o*-(Phenylethynyl) Benzaldehyde (30) and Phenylacetylene Catalyzed by Supported Au NPs and the Proposed Mechanism



(DCE as solvent in a sealed tube) under an inert atmosphere. Such benzannulation reactions have been earlier reported¹⁶² to proceed under homogeneous Au(III) catalysis, via a [4 + 2]-cycloaddition of alkynes to an ate complex generated by intramolecular nucleophilic attack of the aldehyde functionality to the Au(III)-coordinated triple bond of *ortho*-(ethynyl-substituted) benzaldehydes. The TON measured for the heterogeneous reaction was 4–7 times higher as compared to the homogeneous AuCl₃-catalyzed version. Asao and co-workers¹⁶⁴ used a recoverable and reusable nanoporous gold material (20% mol) as a heterogeneous catalyst for such benzannulation reactions (150 °C, *o*-C₆H₄Cl₂) in good to moderate yields. Substituted naphthalenes were also formed as byproduct via hydrative capture of intermediate III (Scheme 15), followed by carboxylic acid elimination (benzoic acid for the paradigm shown in Scheme 15). The Au material possessing pores around 25 nm provided the optimum results, whereas increasing the size of pores to 100 nm caused the catalyst to become inactive. Furthermore, a gold film-catalyzed benzannulation in a flow reactor, under microwave irradiation, was shown by Organ and co-workers.¹⁶⁵

A mechanistically analogous version of the above benzannulation reaction was presented¹⁶⁶ in the intermolecular [3 + 2]-dipolar cycloaddition of the 1,6-allenyl benzaldehyde 31 (Scheme 16), extending previous homogeneous Au(III)

Scheme 16. Intermolecular [3 + 2]-Cycloaddition of 1,6-Allenyl Benzaldehyde 31, Catalyzed by In Situ-Generated Au NPs

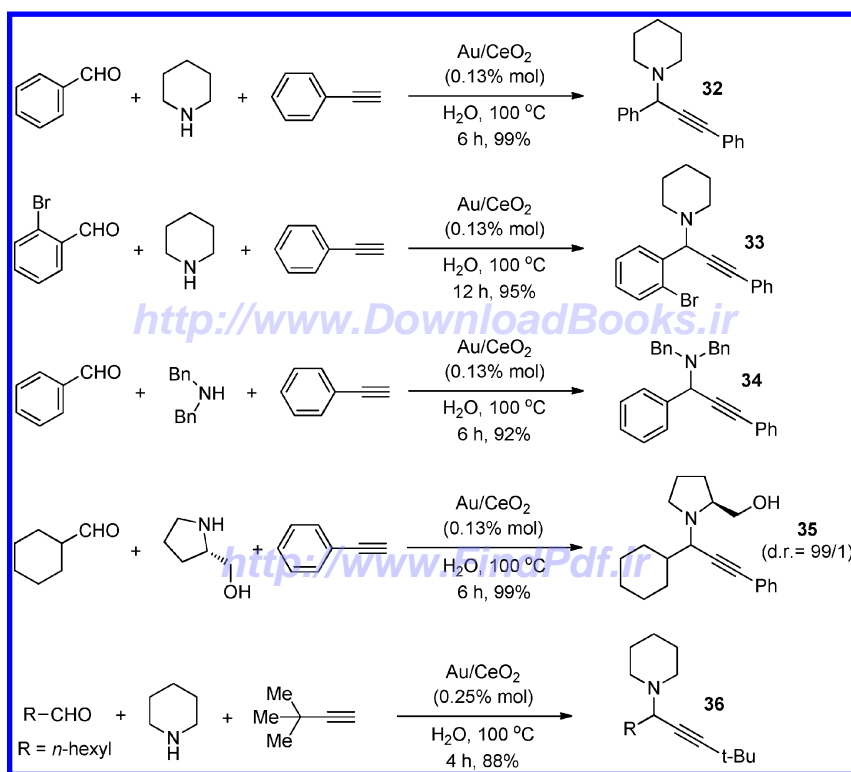


studies.¹⁶⁷ The active catalytic species proved to be spherical-shaped monodispersed 12–14 nm range Au NPs. Mechanistically, a cationic pyrylium intermediate, as shown in Scheme 15, most likely undergoes an intermolecular [3 + 2]-cycloaddition with the pentand double bond of the allene. The carbonyl group is introduced by a dehydrogenative water molecule capture in the intermediate [3 + 2]-cycloadduct. This polycyclization may have a potent synthetic value, as motif 31a appears on the core skeleton of several guaiane-type sesquiterpenes.

3.4. Synthesis of Propargylamines via Three-Component Coupling Reactions

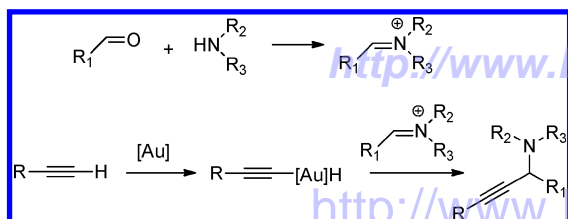
The Au(I)- or Au(III)-catalyzed synthesis of propargylamines under homogeneous conditions by a three-component coupling between an aldehyde, an amine, and an alkyne in water as solvent was documented in 2003.¹⁶⁸ Attempting to bridge the gap between homogeneous and heterogeneous gold catalysis, Zhang and Corma reported¹⁶⁹ that Au NPs supported on ceria or zirconia are excellent catalysts for such three-component coupling reactions, applicable to a variety of functionalized substrates (Scheme 17). Upon screening several supported gold catalysts, Au/CeO₂ (~0.1–0.25% mol) was the most efficient, providing excellent yields and high TONs. Au/ZrO₂ works equally well but requires higher catalyst loadings. Under the optimized reaction conditions, 1 equiv of aldehyde, 1.2 equiv of amine, and 1.2 equiv of the alkyne were mixed with water (1 mL of H₂O per 1 mmol of aldehyde), and the system was

Scheme 17. Synthesis of Propargylamines via a Three-Component Coupling Reaction Catalyzed by Au/CeO₂ (Selected Examples)



heated to 100 °C. Excellent conversion yields up to 99% were seen. Gold thin films are also perfect catalysts in this three-component coupling reaction by using a microwave-assisted continuous-flow apparatus.¹⁷⁰ It was postulated that Au(III) species (designated as [Au] in Scheme 18) stabilized by the

Scheme 18. Postulated Mechanism for the Au/CeO₂-Catalyzed Three-Component Coupling Reaction to Yield Substituted Propargylamines



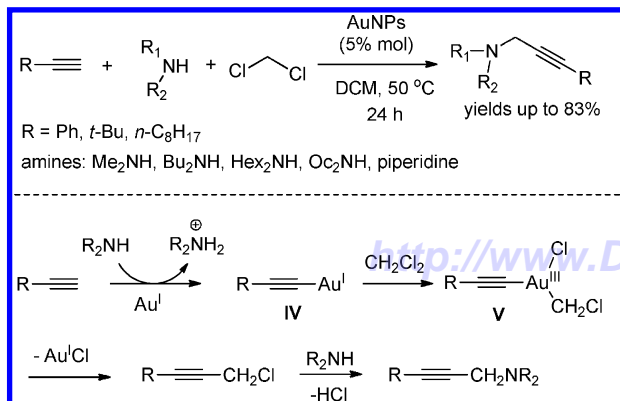
support are the active catalytic sites. However, Au(I) sites might also be active, and their participation cannot be excluded. Thus, according to the mechanistic proposal, an oxidative insertion of the C_{sp}-H bond of alkyne to Au(I) takes place that generates gold acetylide hydrides, in which gold is in the stable oxidation state of Au(III). Following the C-H activation, the gold acetylides attack nucleophilically the iminium ion (formed by the condensation of the aldehyde and the amine), to form substituted propargylamines.

Prior to the development of the highly efficient Au/CeO₂-catalyzed three-component coupling reaction by Corma's group, Kidwai and co-workers¹⁷¹ have used recyclable Au NPs (10% mol) for the high-yield synthesis of substituted propargylamines. The high loading of catalyst is a drawback of this process. The gold NPs had rather large shape ranging from 15 to 70 nm and were prepared in an aqueous solution of reverse

micellar droplets. Later on, Ying and co-workers¹⁷² used successfully a heterogeneous air- and water-stable reusable PbS-supported gold catalyst for the above-mentioned three-component coupling reaction. Au/CdS or Au/CdSe were less efficient. Vinu and co-workers¹⁷³ succeeded the encapsulation of ultrasmall Au nanoparticles over highly-ordered mesoporous carbon nitride, thus avoiding particle agglomeration, and applied this catalyst to the three-component coupling reaction with good selectivity. More recently, the same group¹⁷⁴ presented the synthesis of gold nanoparticles on nanocrystalline magnesium oxide (0.24% mol), which exhibits excellent catalytic activity (TON up to 400) without requiring an inert atmosphere.

A novel Au-catalyzed three-component coupling methodology for the synthesis of propargylamines was recently presented.¹⁷⁵ The three components are an amine, a terminal acetylene, and surprisingly dichloromethane (the reaction solvent), which provides the -CH₂- unit in condensation product structures (Scheme 19). The reaction is catalyzed either by Au(III)-complexes under homogeneous conditions or by in situ-generated Au NPs from the reduction of KAuCl₄ with the amine. The XPS deconvolution spectra of Au NPs revealed their preferential appearance in the oxidation state of +1. In a typical experiment under heterogeneous conditions, 1 equiv of alkyne and 1 equiv of amine and the gold catalyst (5% mol) were mixed in CH₂Cl₂ (solvent), and the slurry was heated to 50 °C for 24 h. The isolated yields of the products were from moderate to good. Evidence for the participation of a solvent molecule was confirmed by using CD₂Cl₂ as solvent, which resulted in the incorporation of the -CD₂- unit into the products. The authors proposed Au(I) as the active catalytic species of the process. Thus, the terminal alkyne is generated in the presence of the amine alkynylgold(I) species and

Scheme 19. Synthesis of Propargylamines via a Three-Component (Alkyne, Amine, and Dichloromethane) Coupling Reaction Catalyzed by Au NPs and a Possible Mechanism

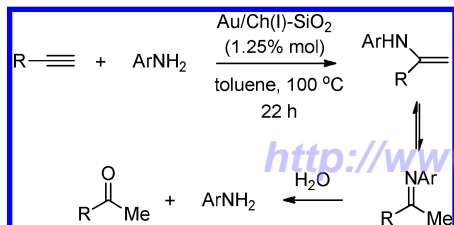


protonated amine (see proposed mechanism in Scheme 19). The intermediate IV undergoes oxidative addition on the carbon–chlorine bond of CH_2Cl_2 , forming Au(III) species (V). Reductive elimination of AuCl is expected to provide the corresponding propargyl chloride that readily alkylates the amine to form the final coupling product. The possibility that propargyl chloride undergoes oxidative addition by AuCl, followed by replacement of chloride by the amine, and a final reductive elimination to form the propargylamine, was not excluded.

3.5. Hydroamination of Alkynes

Hydroamination of alkynes is a useful transformation leading to enamines in equilibrium to their isomeric imines, which readily form ketones upon hydrolysis. This reaction is catalyzed by a variety of metals (e.g., Ag^+ , Cu^{2+} , and Zn^{2+}) as well as by Au(I)^{176–178} under homogeneous conditions. Searching for a heterogeneous version, Corma and co-workers performed an extensive screening among several Au NP-supported catalysts (Au/TiO_2 , SiO_2 , Fe_2O_3 , or CeO_2) and found all of them to be active.¹⁷⁹ However, Au NPs supported on a biopolymer (chitosan)–silica composite hybrid $[\text{Au}/\text{Ch}(\text{I})-\text{SiO}_2]$ exhibited the highest activity regarding the hydroamination of 1-octyne and phenylacetylene with substituted anilines (Scheme 20). The role of chitosan is to interact with the

Scheme 20. Hydroamination of Terminal Alkynes with Substituted Anilines Catalyzed by Au NPs Supported on Chitosan– SiO_2 Hybrid $[\text{Au}/\text{Ch}(\text{I})-\text{SiO}_2]$



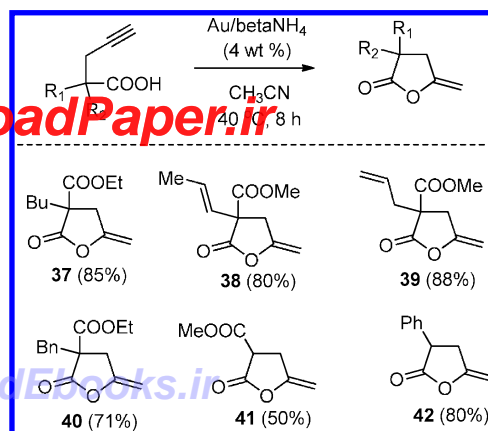
surface of silica, stabilizing nanoparticles of small size and providing a material with a large surface area. Internal alkynes are unreactive, whereas aliphatic amines, being stronger bases, are also unreactive, possibly due to their tendency to form stable complexes with the Au NPs. The reactions were carried out using 1 equiv of alkyne and amine, 1.25% molar loading of

catalyst, and toluene as solvent. The yields were moderate to excellent, and the isolated products are mixtures of imines (not enamines), and inevitably their hydrolysis products (ketones). The ratio of imine/ketone depends on the water content within the reaction mixture. The reason for the enhanced efficiency of $[\text{Au}/\text{Ch}(\text{I})-\text{SiO}_2]$ might be that the chitosan– SiO_2 hybrid protects the Au nanoparticles against agglomeration or leaching. The extra stability as demonstrated by spectroscopic techniques (Raman, IR, UV, and NMR) was attributed to the interactions of Au NPs with the oxygen and nitrogen functionalities of biopolymer.

3.6. Cycloisomerization of γ -Acetylenic Carboxylic Acids

The intramolecular nucleophilic attack of a carboxyl functionality to an activated triple bond in γ -acetylenic carboxylic acids is a versatile methodology for the synthesis of functionalized lactones. The catalytic activation of the alkyne has been achieved under homogeneous conditions by Ru, Rh, Pd, Ag, or Hg and more recently also by Au(I or III).^{180,181} Additionally, Au_2O_3 was found to be a superior catalyst, providing selectively cyclization toward γ -alkylidene γ -butyrolactones (5-*exo* mode) and $\text{TON} \approx 1000$.¹⁸² An effective Au-catalyzed heterogeneous version was immediately thereafter presented,¹⁸³ by using recyclable supported Au NPs (Scheme 21). Au/zeolite β - NH_4^+

Scheme 21. Cyclization of γ -Acetylenic Carboxylic Acid into γ -Alkylidene γ -Butyrolactones Catalyzed by Au/Zelite β - NH_4^+



afforded the best results after a screening among several other supported gold catalysts. The catalyst was prepared by the deposition-precipitation method, and in situ XPS studies suggested the presence of cationic gold (possibly Au^{III}) as the most reasonable active catalytic sites. In a typical cyclization reaction, the γ -acetylenic carboxylic acid is dissolved in CH_3CN and 4 wt % of catalyst is added. After 8 h at 25–40 °C, generally quantitative reactions are seen while isolated yields of up to 88% were reported.

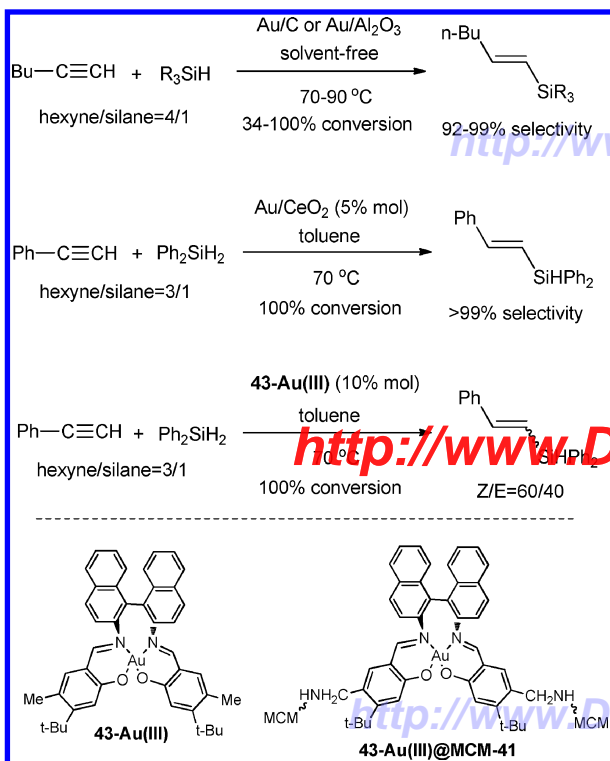
4. HYDROSILANE ACTIVATION

It is likely that hydrosilanes undergo in the presence of Au NPs oxidative metal insertion on the Si–H bond, similar to what occurs with other transition or noble metals. As a consequence, hydrosilanes add to alkynes or carbonyl compounds and readily undergo hydrolysis or alcoholysis with hydrogen gas elimination.

4.1. Hydrosilylation of Alkynes

The hydrosilylation of alkynes yields alkenyl silanes, valuable building blocks in organic synthesis.¹⁸⁴ A variety of metals are well-known to catalyze this addition reaction, including Pt, Ru, Rh, and organolanthanide complexes.^{185–188} Recently, gold has been shown to be also an active catalyst; however, few reports appear in the literature and deal mostly with heterogeneous conditions. Surprisingly, no effective homogeneous Au(I)-catalyzed hydrosilylation protocol of alkynes is known. The group of Caporusso¹⁸⁹ reported in 2005 the solvent-free hydrosilylation of 1-hexyne using several hydrosilanes, acetone-solvated Au NPs supported on carbon and γ -alumina as catalysts at 70 °C (Scheme 22). Moderate to excellent yields

Scheme 22. Hydrosilylation of Alkynes Catalyzed by Gold Nanoparticles and Homogeneous Au(III) Complexes



were found, while the selectivity was close to 100% in favor of β -isomer formation. A drawback of this process is the poor atom economy, as a 4/1 ratio of alkyne/silane was used in all experiments. The catalytic behavior of the gold-based systems is comparable to analogous supported Pt catalysts. The same group¹⁹⁰ extended their studies, focusing again on the hydrosilylation of 1-hexyne (molar ratio alkyne/silane = 4/1). A screening of the size of Au NPs obtained from gold vapor and acetone via the metal vapor synthesis (MVS) technique, and deposited on a variety of different supports (C, Al_2O_3 , Fe_3O_4 , CeO_2 , TiO_2 , and ZrO_2), was performed. The best results were obtained in the presence of Au/ γ - Al_2O_3 (0.05% mol). ZrO_2 - and TiO_2 -supported Au atoms are less efficient, as according to their proposal, the strong interfacial contact between gold and metal oxide reduces the number of active sites on the catalyst's surface.

In the mean time, Corma's group reported¹⁹¹ that Au NPs supported on CeO_2 (5% mol) catalyze the hydrosilylation of phenylacetylene in high yield and β -E selectivity (toluene, 70

°C). The molar ratio of phenylacetylene to the hydrosilane was 3/1. This selectivity is in contrast to the homogeneous hydrosilylation reaction catalyzed by catalyst **43-Au(III)** (R = Me, Scheme 22), which provides a ratio of β -E/ β -Z = 2/3. On the other hand, the heterogenized **43-Au(III)** covalently bound through the R groups to the mesoporous MCM-41 (**43-Au(III)@MCM-41**, Scheme 22) provided identical selectivity to Au/ CeO_2 . Unfortunately, these alkyne hydrosilylation studies were limited to a single substrate (phenylacetylene), and it would be of interest to determine the scope and limitations of the process. The advantage of MCM-41 with respect to other solids is the large surface area and pore dimensions in the range of 3 nm or larger that facilitate reagent and product diffusion to the complex.

Shore and Organ¹⁹² showed that gold oxide thin films on the surface of glass (borosilicate) capillaries are highly active catalysts for the rapid hydrosilylation of alkynes in a continuous-flow reactor heated by microwave irradiation (Table 4). The films are reusable with no detectable loss of

Table 4. Typical Examples in the Hydrosilylation of Terminal Alkynes Catalyzed by Thin Gold Films Coated on Glass Capillary under Microwave Irradiation

$\beta\text{-E}$ $\beta\text{-Z}$ α -

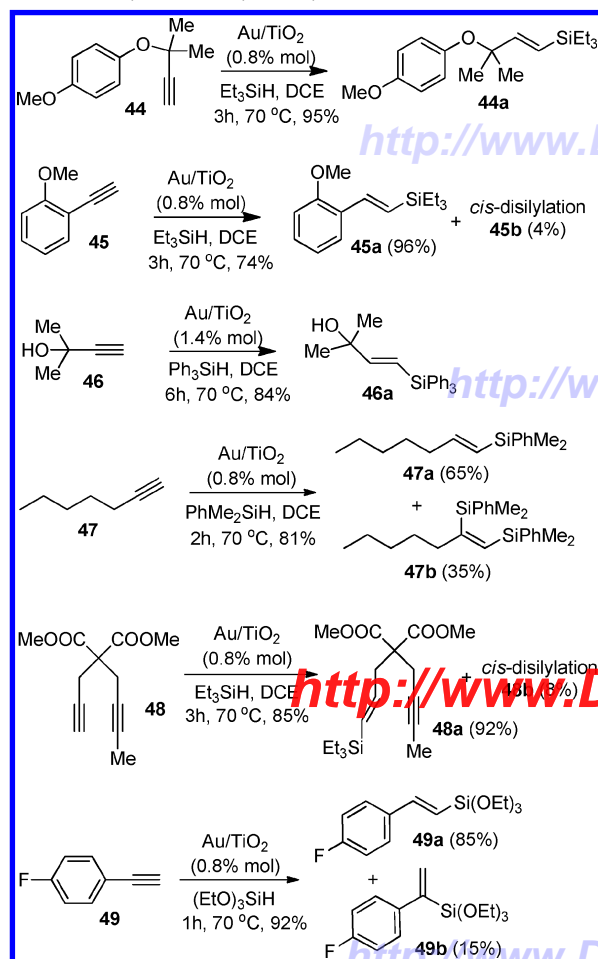
R—C≡C—	silane	$\beta\text{-E}$	$\beta\text{-Z}$	α -	isolated yield
		(relative yield)			
n-Bu—C≡C—	Et ₃ SiH	82%	9%	9%	70%
HO—C≡C—	Ph ₃ SiH	85%	4%	11%	74%
Cl—C≡C—	Et ₃ SiH	75%	4%	21%	68%
Ph—C≡C—	Ph ₃ SiH	90%	2%	8%	80%
NC—C≡C—	Ph ₃ SiH	97%	1%	2%	78%
BnO—C≡C—	Et ₃ SiH	97%	1%	2%	80%
S—C≡C—	Ph ₂ SiClH	74%	0%	26%	62%
Me ₃ Si—C≡C—	Ph ₂ SiClH	76%	0%	24%	50%

activity. The heterogeneous catalyst was prepared by treatment of the borosilicate capillaries with AuCl_3 followed by reduction with trisodium citrate and finally calcination. In all experiments, the molar ratio of alkyne to silane was 2/1, and the reactants were dissolved in toluene. The hydrosilylation studies were limited to terminal alkynes, and the yields were good in general. Regarding product selectivity, the β -E products were always the major, the β -Z adducts were formed in up to 9% relative yield, while in certain cases α -isomers were seen in up to 26% relative yield. The temperature reached on the gold film inside the microwave apparatus during the continuous-flow experiments was 185–195 °C.

Au/ TiO_2 (0.8–1.4% mol) was also tested as a hydrosilylation catalyst in α -chloroacetone (70 °C).¹⁹³ Terminal alkynes

form regioselectively and in very good yields β -E addition products. β -Z isomers were not detected, whereas depending on the nature of silane (specifically for triethoxysilane), α -regioisomers can be formed in up to 15% relative yield (Scheme 23). Surprisingly, for the less-hindered triethyl- and

Scheme 23. Typical Examples in the Hydrosilylation of Terminal Alkynes Catalyzed by Au/TiO₂



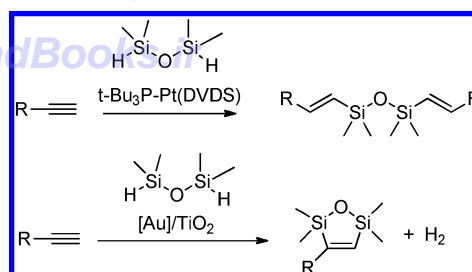
dimethylphenylsilane, minor products from an oxidative *cis*-disilylation pathway were detected in up to 35% relative yield (e.g., diaddition product **47b**). The experiments were carried out by using 1 equiv of alkyne and 1.5–2 equiv of hydrosilane to compensate its partial oxidative hydrolysis by the moisture present in the solvent. Internal alkynes are less reactive or even completely unreactive. This was clearly shown in the exclusive regioselective hydrosilylation of the terminal triple bond of diyne **48**. Kinetic experiments are in agreement with a mechanism that involves silyl carbometalation of the triple bond in the rate-determining step of the reaction. The formation of the oxidative disilylation byproduct might involve gold–disilyl species $R_3Si-Au(III)-SiR_3$ most likely generated by the dehydrogenative direct coupling of two hydrosilane molecules with Au(I) species on the surface of Au/TiO₂.

4.2. Oxidative Cycloaddition of Tetramethyldisiloxane to Alkynes

Although monohydrosilanes primarily add regioselectively to terminal alkynes under Au/TiO₂ catalysis conditions,¹⁹³ 1,1,3,3-tetramethyldisiloxane (TMDS), dihydrodisilane, undergoes a

fast cycloaddition with a variety of functionalized alkynes, forming substituted 2,5-dihydro-1,2,5-oxadisiloles with evolution of hydrogen gas.¹⁹⁴ This chemoselectivity is in sharp contrast with that obtained in the presence of *t*-Bu₃P-modified Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane, Pt(DVDS),¹⁹⁵ which provides the typical dihydrosilylation products that are exclusively formed (Scheme 24). The process catalyzed by Au/

Scheme 24. Divergent Pathways in the Reaction of Tetramethyldisiloxane with Terminal Alkynes Catalyzed by Pt(0) and Au/TiO₂

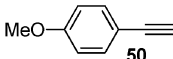
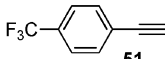
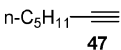
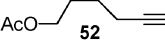

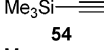
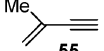
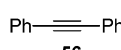
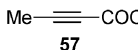


TiO₂ resembles, however, the dehydrogenative cycloaddition of 1,2-bis(dimethylsilyl)benzene to alkynes, alkenes, and dienes, in the presence of Pt(CH₂=CH₂)(PPh₃)₂,¹⁹⁶ and the Pd(PPh₃)₄-catalyzed double silylation of bis-(dichlorosilyl)methanes with acetylenes.¹⁹⁷

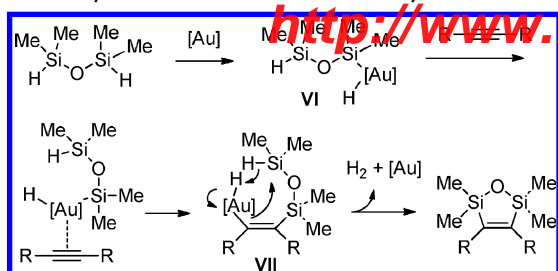
The Au/TiO₂-catalyzed TMDS cycloaddition takes place at room temperature in many solvents and tolerates a variety of functional groups, while in certain cases, as low as 0.1% mol of catalyst loading is enough to drive the reaction to completion. Increasing the amount of catalyst at >1% mol results in an instantaneous reaction with violent evolution of H₂. Terminal alkynes react faster as compared to internal alkynes, providing yields up to 99% (Table 5). Under dry conditions, typically a 1/1 molar ratio of alkyne versus TMDS is employed, yet upon using nondried solvents, a 20–30% molar excess of TMDS is necessary to compensate its hydrolytic oxidation from the moisture present in the solvent. The products arising from the hydrolysis of tetramethyldisiloxane are highly nonpolar compounds and can be easily removed by column chromatography. From the mechanistic point of view, a modified Crabtree–Ojima mechanism was postulated, as shown in Scheme 25. Thus, silylmatalation (intermediate **VII**) in the insertion of the gold hydride intermediate **VI** to the alkyne, followed by an intramolecular elimination of H₂ and [Au], leads to the cycloadducts.

The gold-catalyzed oxidative cycloaddition of TMDS to alkynes represents an indirect example of double silyl addition to a triple bond, a long-known reaction by insertion of Pd to 1,2-disilanes.^{198,199} The isolobal analogy among Au(I/III) and Pd(0/II) complexes is currently stimulating the search for “gold versions” of the rich palladium- and other late transition metal- or Hg-catalyzed transformations,²⁰⁰ especially in Si–Si bond-insertion reactions. Yet no gold-catalyzed methodology appears for these processes so far. In a promising observation, Bourissou and co-workers²⁰¹ described that a σ -Si–Si bond undergoes under homogeneous conditions a rapid oxidative intramolecular addition to a Au(I) complex (generated by the reaction of ligand **58** with AuCl), forming the Au(III) bis-silyl complex **59** (Scheme 26). This example might be a milestone toward such an expansion of Au catalysis. We will comment later on further similarities and dissimilarities between Au(I/

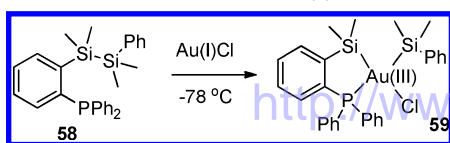
Table 5. Typical Examples in the Oxidative Cycloaddition of Tetramethyldisiloxane to Alkynes Catalyzed by Au/TiO₂

$\text{R}-\text{C}\equiv\text{C}-\text{R}' \xrightarrow[\text{DCM, 25 } ^\circ\text{C}]{\text{TMDS (1 equiv) [Au]/TiO}_2 \text{ (0.3\%)}} \text{Me}_2\text{Si}(\text{O}-\text{Si}(\text{Me})_2)_2\text{C}(\text{R})=\text{C}(\text{R}') + \text{H}_2$			Yield/Time
	50a		96%/40 min
	51a		91%/20 min
	47c		97%/30 min
	52a		98%/30 min
	53a		92%/30 min
	54a		87%/1 h
	55a		78%/40 min
	56a		88%/24 h
	57a		64%/45 min

Scheme 25. Postulated Mechanism for the Gold-Catalyzed Oxidative Cycloaddition of TMDS to Alkynes



Scheme 26. Oxidative Insertion of Au(I) into a σ -Si-Si Bond



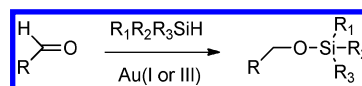
III) and Pd(0/II) pairs when reviewing the C-C coupling reactions in section 7. In contrast to Cu and Pt, Au nanoparticles do not catalyze the double boronation of alkynes by bis(pinacolato)diboron.²⁰² Yet alkenes can be diborated in the presence of binap-stabilized gold(0) nanoparticles²⁰³ in very good yields. The postulated mechanism for this process does not require oxidative insertion of gold into the diborate but rather requires a heterolytic B-B bond cleavage promoted by Au(0).

4.3. Hydrosilylation of Carbonyl Compounds

In 2000, Hosomi and co-workers²⁰⁴ reported the first example of the homogeneous gold-catalyzed (3% mol of Ph₃PAuCl, 20% Bu₃P, 2 equiv of hydrosilane, dimethylformamide, 70 °C) hydrosilylation of aldehydes and silyl-protected alcohols

(Scheme 27). Ketones were shown to be unreactive, while an example of aldimine hydrosilylation was also presented. Later

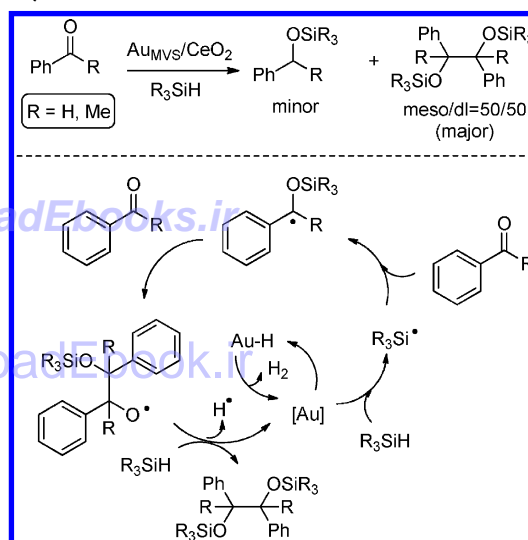
Scheme 27. Gold-Catalyzed Hydrosilylation of Aldehydes



on, these studies were expanded to other Au(I)- and Au(III)-based homogeneous catalysts.^{92,205–207}

Regarding gold-based heterogeneous approaches, Corma and co-workers have shown¹⁹¹ that Au NPs supported on CeO₂ (5% mol) catalyze the hydrosilylation of benzaldehyde, cinnamaldehyde, and heptanal in high yields (toluene, 70 °C) using a variety of hydrosilanes. Even acetophenone was highly reactive, in contrast to the homogeneous methodology (Ph₃PAuCl/Bu₃P).²⁰⁴ A molar ratio of carbonyl compound/silane = 1/2 was used. As in the case of alkyne hydrosilylation, Au(III) was shown to be a more active catalyst, compared to Au(I). Afterward, Raffa and co-workers²⁰⁸ studied the hydrosilylation of benzaldehyde and acetophenone catalyzed by Au/CeO₂ (0.1–0.15% mol, 100 °C, 18–24 h). Au NPs were prepared either by the metal vapor synthesis (Au_{MVS}) or by the deposition-precipitation method (Au_{DP}). Under those conditions, the authors reported, in addition to the typical silylated alcohols, the unexpected formation of disilylated pinacol products in 40–80% relative ratio, with a *meso*/DL ratio \approx 50:50 (Scheme 28). It was proposed that Au(I) species catalyze

Scheme 28. Hydrosilylation of Carbonyl Compounds Catalyzed by Au_{MVS} or Au_{DP}/CeO₂ and the Proposed Catalytic Cycle Regarding the Pinacol-Type Coupling Pathway

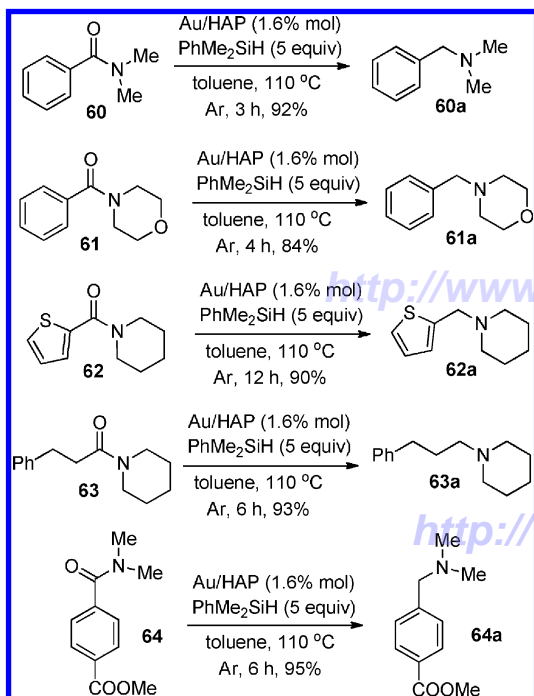


the hydrosilylation pathway, whereas Au(0) can act as a radical initiator forming R₃Si· radicals, which undergo addition to the carbonyl followed by pinacol-type dimerization (see the catalytic cycle in Scheme 28).

4.4. Deoxygenation of Amides, Sulfoxides, and Pyridine N-Oxides

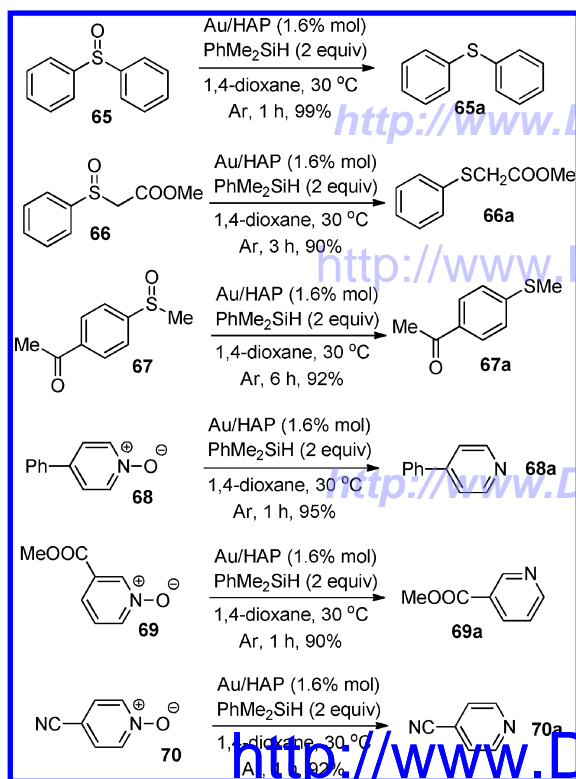
Kaneda and co-workers²⁰⁹ reported that hydroxyapatite-supported Au NPs (Au/HAP) catalyze in excellent yields the reduction of amides into amines (Scheme 29), sulfoxides into

Scheme 29. Deoxygenation of Amides into Amines by Dimethylphenylsilane Catalyzed by Au/HAP (Selected Examples)



sulfides, and pyridine *N*-oxides into pyridines (Scheme 30), using 1.6% mol of catalyst in all cases and dimethylphenylsilane as the reducing agent. Au/HAP was prepared by mixing

Scheme 30. Deoxygenation of Sulfoxides and Pyridine *N*-Oxides by Phenyldimethylsilane Catalyzed by Au/HAP (Selected Examples)



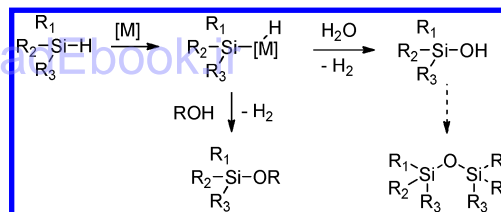
hydroxyapatite [HAP, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$] with HAuCl_4 in aqueous ammonia, followed by reduction with KBH_4 . Concerning the amide-to-amine reduction, the reaction was carried out in the presence of 5 equiv of silane in refluxing toluene under an inert atmosphere (3–24 h). The reported conversion yields range from 80 to 99%, while the reaction tolerates several functional groups. Other supported Au NPs, such as Au/TiO_2 and $\text{Au}/\text{Al}_2\text{O}_3$, also gave good yields; however, Au/HAP was superior. The TON for the deoxygenation reaction with Au/HAP was close to 10 000, which is 2 orders of magnitude higher as compared to known catalytic systems. The proposed mechanism is similar to known Lewis acid-catalyzed analogous reductions by silanes,²¹⁰ and it is likely to involve oxidative insertion of the Si–H bond on gold. This was supported by FTIR spectroscopy, as a significant shift of the Si–H stretching vibration to lower frequencies was observed upon treatment of dimethylphenylsilane with Au/HAP , whereas no change in the C=O stretching frequency of the reacting amide was seen.

The scope of deoxygenation ability of Au/HAP /hydrosilane system was extended by the same group.²⁰⁹ Thus, a variety of sulfoxides and pyridine *N*-oxides are almost quantitatively reduced to the corresponding sulfides upon treatment with 2 equiv of dimethylphenylsilane under mild conditions (30 °C) in 1,4-dioxane as solvent (Scheme 30). It is notable that the deoxygenation reactions were carried out in substrates bearing formally reducible functional groups that remained intact. The TONs for the deoxygenation of sulfoxides are up to 10 000 (at 130 °C), which is 3 orders of magnitude greater than previously reported catalytic systems. Although these deoxygenations can be of wide applicability in organic synthesis, it would be of interest to have a more affordable hydrosilane than dimethylphenylsilane by other more affordable hydrogen sources, in a similar manner to the systematic work that has been carried out for the deoxygenation of epoxides into alkenes.

4.5. Silane Hydrolysis/Alcoholysis

Hydrolytic oxidation of silanes to form silanols and/or disiloxanes with H_2 elimination is catalyzed by a variety of metals, including In, Cu, Re, Ir, Pd, and Ru. Analogous is the process of alcoholysis of hydrosilanes (Scheme 31) forming

Scheme 31. Metal-Catalyzed Oxidation of Silanes to Silanols/Disiloxanes in the Presence of H_2O or Alcohols



silyl alkoxides, an alternative to the classical methodology for the protection of alcohols with chloro trialkylsilanes under basic conditions. Following the first report²¹¹ on the homogeneous $\text{AuCl}(\text{xantphos})$ [xantphos , 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene] catalyzed dehydrogenative silylation of alcohols, a reaction that proceeds via the intermediacy of gold hydrides,²¹² Raffa and co-workers showed that, in addition to the hydrosilylation of carbonyl compounds, Au/CeO_2 also catalyzes silane alcoholysis under heterogeneous conditions.²⁰⁸ The experiments were focused on primary alcohols and carried out under solvent-free conditions at 100 °C (3–16 h). The

conversion yields range from moderate to excellent. It is notable that as low as 0.05% mol of catalyst loading was used.

Kaneda and co-workers²¹³ reported that Au/HAP can act as a highly efficient and reusable catalyst for the oxidation of diverse silanes into silanols in water as solvent and under open air conditions (Table 6). For 1 mmol of silane, 3 mL of water

Table 6. Selected Examples in the Au/HAP-Catalyzed Hydrolysis of Silanes into Silanols

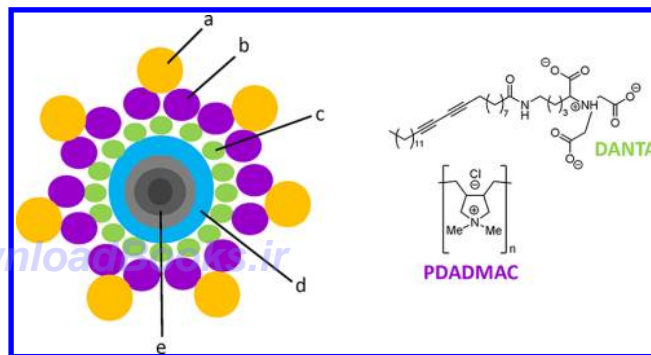
$\begin{matrix} R_1 \\ R_2-Si-H \\ R_3 \end{matrix}$	$\xrightarrow[\text{H}_2\text{O (3 mL/mmol of silane)}]{\text{Au/HAP (0.8\% mol)}} \xrightarrow{80\text{ }^\circ\text{C}}$	$\begin{matrix} R_1 \\ R_2-Si-OH \\ R_3 \end{matrix}$	
Reactant	Product	Time (h)/yield (%)	
$\begin{matrix} Et \\ Et-Si-H \\ Et \end{matrix}$	$\begin{matrix} Et \\ Et-Si-OH \\ Et \end{matrix}$	2/99	
$\begin{matrix} i-Pr \\ i-Pr-Si-H \\ i-Pr \end{matrix}$	$\begin{matrix} i-Pr \\ i-Pr-Si-OH \\ i-Pr \end{matrix}$	24/96	
$\begin{matrix} Ph \\ Ph-Si-H \\ Me \end{matrix}$	$\begin{matrix} Ph \\ Ph-Si-OH \\ Me \end{matrix}$	10/97	
$\begin{matrix} Ph & H \\ & \\ Si-H \\ & \\ Ph \end{matrix}$	$\begin{matrix} Ph & OH \\ & \\ Si-OH \\ & \\ Ph \end{matrix}$	8/92	
$\begin{matrix} H & Me \\ & \\ Si \\ & \\ \text{C}_6\text{H}_4 \\ & \\ Si \\ & \\ Me \end{matrix}$	$\begin{matrix} OH & Me \\ & \\ Si \\ & \\ \text{C}_6\text{H}_4 \\ & \\ Si \\ & \\ Me \end{matrix}$	8/98	

were used, the catalyst load was close to 1% mol, and the conversions were almost quantitative (80 °C, 2–24 h reaction time, depending on the bulkiness of the silane). The reaction is highly selective in favor of silanols, relative to their intramolecular dehydration products, disiloxanes, which are formed in <1% relative yield. This catalytic methodology is a benign procedure for the environmentally friendly oxidation of silanes and has several advantages such as (i) there is no requirement for organic solvents; (ii) water is used as a clean oxidant; (iii) the catalyst is reusable; and (iv) it is applicable to a variety of silanes, including aliphatic.

Later on, Asao and co-workers²¹⁴ presented a novel and milder methodology for the gold-catalyzed (1–3% mol) oxidative hydrolysis of silanes into silanols using a nanoporous material prepared by selective leaching of silver from an alloy consisting of Au₃₀Ag₇₀ upon treatment with 70% w/w HNO₃. The size of nanopores in the resulting gold-based catalyst were ~30 nm, and therefore, no diffusion limitations are expected even for large reagents. The catalyst is easily recoverable and was reused 5 times in the row without losing catalytic activity, while the reaction conditions are very mild. The hydrolyses were run at ambient temperature in acetone as solvent, water was in 5–6 times molar excess, and the reported isolated yields range from 80 to 98%. Additionally, the calculated TON was very high, in the range of 10 000.

More recently, Doris and co-workers²¹⁵ showed that a carbon nanotube–gold nanohybrid (AuCNTs, Scheme 32) has superior activity in the oxidative hydrolysis of silanes into silanols. The reaction is highly selective in favor of silanols

Scheme 32. Schematic Representation of the Au/Carbon Nanotube (CNT) Nanohybrid: (a) Au NP; (b) PDADMAC Layer; (c) DANTA Nanorings; (d) Polymerized Region (Green); and (e) Multiwalled CNT



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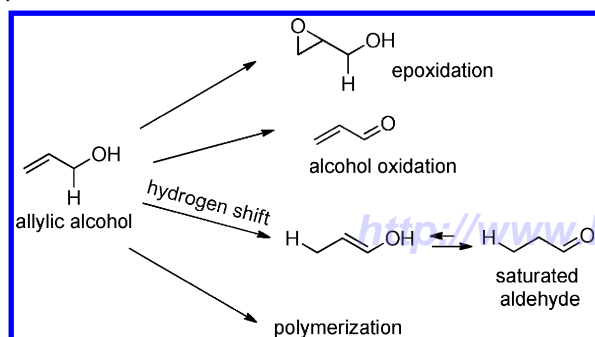
relative to disiloxanes and can be performed at room temperature; the catalyst load is only 0.1% mol, the reaction times varies between 1 and 4 h, and the yields of isolated products are in the range of 93–99%. Additionally, the catalyst can be easily recovered and reused without significant loss of catalytic activity even after 5 consecutive runs. In the hydrative oxidation of dimethylphenylsilane catalyzed by AuCNTs, striking and unprecedented TON and TOF (72 000 and 12 000 h^{−1}, respectively) were measured. It was proposed that the high catalytic efficiency of AuCNTs might be related to the stabilization of transient higher oxidation states of gold by the electronically “active” nanotubes. However, some experimental problems related to the use of CNTs as supports can arise, particularly the difficulty of catalyst recovery and its dispersion in the liquid phase. In addition, the present AuCNT catalyst has additional limitations derived from the availability of the two polyelectrolytes needed to coat CNT acting as interphase with Au NPs.

5. DIHYDROGEN ACTIVATION

One of the major differences between gold and other noble metals is the stability of the corresponding metal hydrides.^{216,217} Although platinum and palladium hydrides are easy to be formed and are relatively stable, gold hydride is considerably more unstable and difficult to be formed,²¹⁸ although there are recent reports concerning the spectroscopic characterization of these long elusive species.^{219–222} This relative stability has consequences in catalytic activity and product selectivity. Thus, one of the steps in alcohol oxidation is hydride transfer and the formation of a metal hydride from the metal alcoholate.^{223–226} In the case of palladium, the higher concentration of Pd–H is responsible for the notorious lack of selectivity of Pd catalysts for the oxidation of allylic alcohols that gives a complex product distribution including the saturated carbonyl compounds and alcohols.^{227,228} In contrast, supported Au catalysts are remarkably selective for the oxidation of allylic alcohols, and the obtained evidence indicates that the main reason is the low concentration of Au–H due to its instability. Scheme 33 summarizes the different catalytic behavior for Pd and Au catalysts in alcohol oxidation that reflects the relative stability of the two metal hydrides.

As we have commented earlier in section 2.3 when discussing the mechanism of the decygenation of epoxides using hydrogen as reagent, spectroscopic evidence including inelastic

Scheme 33. Possible Products Arising from the Oxidation of Allylic Alcohols; Au/CeO₂ Is Selective for Alcohol Oxidation, Whereas Pd Catalysts Promote Also Other Processes, Reflecting the Relative Stability of Au and Pd Hydrides



neutron scattering indicates that on the surface of Au NPs supported on metal oxides hydrogen can undergo a heterolytic and heterotopic dissociation, giving rise to H⁺ protonating the metal oxide support and H⁻ bonded to Au, as illustrated in Scheme 7.^{229,230} Experimental and theoretical calculations have shown that the slow step for most hydrogenations catalyzed on supported gold catalysts is hydrogen dissociation, and this process can be significantly accelerated by adding a small loading of platinum into the system.²³¹

5.1. Hydrogenation of Unsaturated C–C Bonds

Historically, the first known catalytic property of gold is its involvement in the hydrogenation of π -systems (alkenes, dienes, alkynes, and aromatics). This topic was reviewed by Hashmi and Hutchings in 2006.²³² In contrast to the widely used Pd catalysts that operate typically at ambient conditions, gold-catalyzed hydrogenations require higher temperatures (100–250 °C), thus making this catalytic property of low synthetic importance. Perhaps in the most efficient example from the past studies, Au/SiO₂ (0.01 wt %), and less efficiently Au/Al₂O₃ or Au/boehmite, catalyze the hydrogenation of pentene, 1,3-butadiene, and 2-butyne at 100 °C.²³³ In the case of 1,3-butadiene, no diastereoselection (*cis*- versus *trans*-2-butene formation) was observed, whereas for 2-butyne, 80% selectivity in favor of *cis*-2-butene was found. Okumura and co-workers²³⁴ studied the same hydrogenation reaction and achieved the best results using Au/Al₂O₃ prepared by deposition-precipitation with quantitative conversion and ~60% selectivity in favor of 2-butyne. Surprisingly, they found that the catalytic activity of their supported Au catalysts is almost structure-insensitive in terms of the size effect of Au particles, contrary to other reports.²³⁵ A significant improvement in the efficiency of 1,3-butadiene hydrogenation was reported by the group of Xu,²³⁶ who used gold nanoparticles supported on ZrO₂ (<0.1% Au) as catalyst and proposed that isolated Au(III) ions on the support are the active catalytic sites. It is likely that the mechanisms for dihydrogen activation by isolated Au(III) ions and metallic Au(0) atoms are different.²³⁷ The same group exemplified the vital role of surface hydroxyl groups in zirconia in the catalytic efficiency of Au/ZrO₂ for 1,3-butadiene hydrogenation.²³⁸ Density functional theory (DFT) calculations were performed by Liu and co-workers²³⁹ to uncover the active species in the Au/ZrO₂-catalyzed hydrogenation. The suggested ionic Au(I) as the heterogeneous catalytic sites are possibly produced from the reduction of Au(III) under the reaction conditions. Farvolden

and co-workers²⁴⁰ uncovered the beneficial role of gold present in Pd colloids embedded on SiO₂ during the hydrogenation of π systems (3-hexyn-1-ol, cinnamaldehyde, and styrene). It was shown that alloying Pd with Au (~1 wt % each component) in the bimetallic colloids leads to enhanced activity and most importantly to improved selectivity. Also, the combination of the two metals resulted in novel catalysts that were very stable against poisoning, as was evidenced during the hydrogenation of styrene contaminated with thiophene.

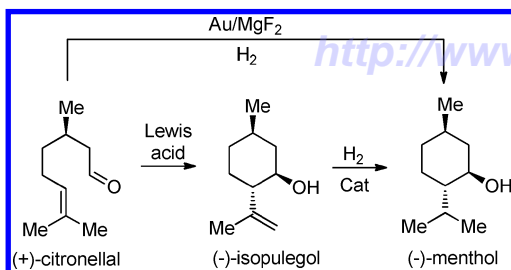
In the presence of Au NPs supported on metal oxides, alkynes are selectively hydrogenated over alkenes.^{241,242} The origins of this chemoselectivity were uncovered experimentally and on the basis of DFT calculations.²⁴³ Although based on thermodynamics the activation energy for the hydrogenation of a triple bond is comparable to that of a double bond, the chemoselectivity was rationalized in terms of the binding energy of the reactants on the catalyst (gold), which is significantly higher for alkynes. By contrast, palladium catalysts are unselective, because both double and triple C–C bonds are more or less equally adsorbed on Pd surface. On several occasions, a beneficial synergism between Au and other metal nanoparticles was noticed in π -system hydrogenation. Thus, in the hydrogenation of acetylene and phenylacetylene catalyzed by Au–Ni/Al₂O₃,²⁴⁴ the conversions of alkynes over the Au–Ni catalysts was higher than the sum of conversions on Au- and Ni-supported catalysts (independently studied), by an order of magnitude. This effect was rationalized in terms of formation of new catalytic sites with improved adsorption and catalytic properties due to an electron transfer from gold to oxidized Ni. In addition, a synergism between Au and Pt nanoparticles^{245,246} improves significantly the activity of conjugated π -systems (e.g., cinnamaldehyde), providing mainly reduction of the double bond relative to the carbonyl functionality, in contrast to the general trend for the hydrogenation of conjugated carbonyls under Au NP catalysis conditions (section 5.2). Finally, hydrogenation of aromatics is difficult to be achieved, and a few examples appear in the literature. Thus, the hydrogenation of biphenyl into bicyclohexyl (a classical model study) was recently reported by the group of Fierro²⁴⁷ under forcing conditions (5 MPa, 488 K) using Au nanoparticles supported on Fe-, Ce-, and Ti-modified mesoporous silica (HMS). Also, a gold-promoted Pd catalyst supported on mesoporous hollow silica spheres (PdAu/MHSS)²⁴⁸ exhibits significant enhancement of activity in the hydrogenation of several phenols forming cyclohexanones, relative to monometallic supported Pd catalysts. HMSs can be prepared having a large variety of transition metals in the framework. These transition metals can cooperate with Au NPs or introduce sites of different activity for tandem reactions. The mesoporosity of the material minimizes diffusion limitations generally encountered in liquid-phase reactions with zeolites and other microporous solids.

Generally, there is no unified mechanistic picture of the Au NP-catalyzed hydrogenation processes,²⁴⁹ and the question for the nature of oxidation state(s) of gold nanoparticles is complicated by the fact that additionally ionic gold salts and complexes are active hydrogenation catalysts under homogeneous conditions. For example, Guzman and Gates²⁵⁰ provided evidence for Au(III) as the active species forming alkylgold (from alkenes and H₂) as reactive intermediates, whereas the generality of Au(III) complexes as active hydrogenation catalysts was exemplified by Corni and co-workers,²⁵¹ who

commented on the similarity among complexes of Pd(II), which have the same d^8 electronic structure as Au(III).

A practical application was presented by Negoi and co-workers,²⁵² who described the synthesis of a bifunctional ionic gold/magnesium fluoride catalyst (Au/MgF₂, 4 wt % in Au) that effectively catalyzes the one-pot synthesis of menthol (diastereomeric ratio (dr) = 92.5%) from citronellal in the presence of 15 atm H₂, at 80 °C (Scheme 34). Although metal

Scheme 34. One-Pot Synthesis of (–)-Menthol from (+)-Citronellal Catalyzed by Au/MgF₂ in the Presence of H₂



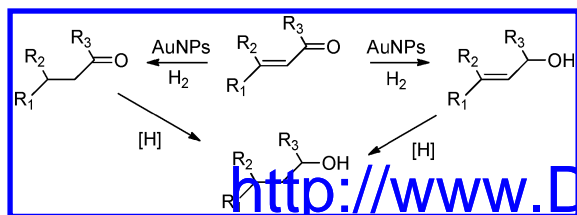
oxides together with active carbon are the most widely employed supports for metal NPs, the use of metal fluorides remains almost unexplored in spite of their interesting properties derived from their acid/base character. Menthol, an important fine chemical, is typically obtained in two steps²⁵³ using a Lewis acid-promoted diastereoselective cyclization of citronellal to isopulegol, and then separately isopulegol undergoes hydrogenation. MgF₂, being a Lewis acidic solid, catalyzes the intramolecular carbonyl–ene reaction of citronellal to form isopulegol, while Au nanoparticles catalyze the hydrogenation into menthol. It was proposed that Au(III) ionic species are the active catalytic sites, which through heterolytic activation of H₂ facilitated by the support form Au(III)–H species that add to the double bond of isopulegol to form auric intermediates. Upon protonation, these intermediates yield menthol, with Au(I) elimination. It was postulated that the reoxidation of Au(I) to Au(III) can occur either through the generation of H⁺ in the media or possibly more effectively by air.

5.2. Hydrogenation of Carbonyl Compounds and CO₂

Although saturated carbonyl compounds are rather unreactive under typical hydrogenation conditions (to form alcohols), in the presence of supported gold catalysts, α,β -unsaturated carbonyl compounds are surprisingly reactive and undergo preferential reduction on the carbonyl group relative to the C=C double bond under relatively mild conditions (Scheme 35), yet more slowly compared to supported Pd, Pt, or Ru catalysts.²⁵⁴

The group of Hutchings was the first to demonstrate such chemoselectivity in the gas-phase hydrogenation of but-2-enal

Scheme 35. Possible Products from the Hydrogenation of α,β -Unsaturated Carbonyl Compounds

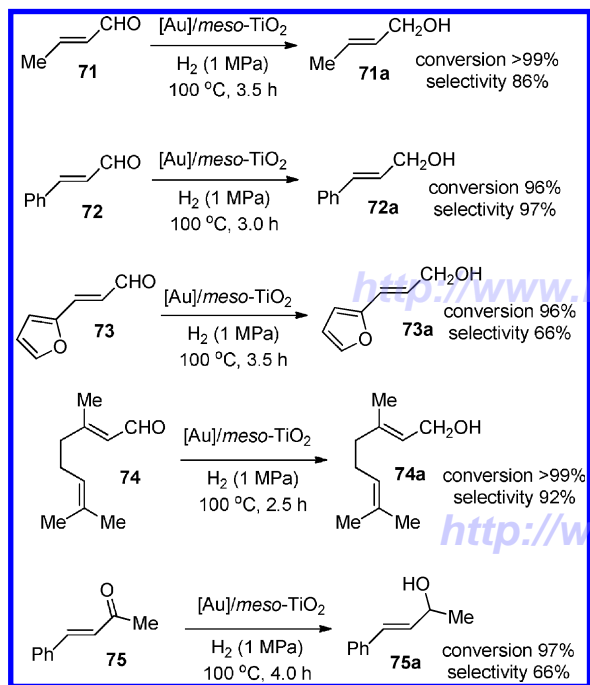


using Au/ZnO and Au/ZrO₂ as catalysts.^{255,256} These catalysts were found to be selective for the formation of the unsaturated alcohol (but-2-en-1-ol) rather than the corresponding saturated aldehyde. Addition of thiophene enhances the relative yield of the unsaturated alcohol. The thiophene-promoted beneficial enhancement is associated only with smaller Au nanoparticles. Au/ZnO is more efficient compared to Au/ZrO₂. The highest but-2-en-1-ol selectivities (81%) were observed by using 5 wt % Au/ZnO reduced at 400 °C prior to use, yet the conversions of ~5–10% were too low.

Following these early steps in chemoselective gold-catalyzed hydrogenation, several improved approaches using Au/SiO₂, Au/TiO₂, Au/CeO₂, Au/ZnO, Au/Fe₂O₃, Au/ZrO₂, and Au–In/ZnO as catalysts were presented in the literature,^{257–270} applied to a variety of α,β -unsaturated carbonyl compounds, such as acrolein, citral, benzalacetone, and pent-3-en-2-one. More recently, the hydrogenation of α,β -unsaturated aldehydes was studied using Au/ α -Fe₂O₃ (isopropanol, 100 °C, 1.0 MPa H₂),²⁷¹ Au/Fe(OH)₃ (isopropanol, 65–100 °C, 1.0 MPa H₂),²⁷² Au/Fe₃O₄ (hexane, 120 °C, 2.0 MPa H₂),²⁷³ Au/Mg₂AlO (ethanol, 120 °C, 0.9 MPa H₂),²⁷⁴ and Au–In/APTMS-SBA-15 (APTMS, γ -aminopropyltrimethoxysilane; SBA-15, a mesoporous siliceous material; reaction conditions: hexane, 120 °C, 2.0 MPa H₂).²⁷⁵ The highest yield and selectivity regarding the hydrogenation of crotyl aldehyde in favor of crotyl alcohol were found with Au–In/APTMS-SBA-15, while it is notable that Au NPs on flowerlike magnetite (Au/Fe₃O₄)²⁷³ significantly improve the kinetics of the reduction. Mesoporous SBA-15 as host of Au NPs can provide certain stabilization against particle growth but avoids diffusion limitation of small reagents inside the pores. Additionally, a support chemoselectivity up to 100% for carbonyl reduction was shown by Jin and co-workers²⁷⁶ regarding the hydrogenation of α,β -unsaturated ketones and aldehydes catalyzed by atomically precise Au₂₅(SR)₁₈ nanoparticles, whereas the hydrogenation of cinnamaldehyde over Au/TiO₂ in ethanol as solvent may directly provide cinnamyl ethyl ether, yet in low yield.²⁷⁷ The mechanism of carbonyl hydrogenation is unclear and may depend on the size/type of nanoparticles and the support as well as the reaction conditions. Notably, different oxidation states of gold (Au⁰, Au^I, and Au^{III}) have been invoked as possible active catalytic sites. For example, theoretical calculations by Liu and co-workers²⁷⁸ provided evidence that minor Au(I)-cationic species on Au/ZrO₂ rationalize the obtained catalytic selectivity in the hydrogenation of acrolein. On the other hand, Au(0) nanocolloids^{279,280} selectively reduce α,β -unsaturated aldehydes to allylic alcohols, whereas with increasing the Au(III)/Au(0) ratio on Au/Mg₂AlO,²⁸¹ both reactivity and selectivity were increased.

A practical green methodology was reported by Cao's group in 2011,²⁸² by using Au NPs supported on meso-structured ceria (Au/meso-CeO₂) in neat water (Table 7). The optimum reaction conditions require 1% mol of catalyst and 1 MPa pressure of H₂ (100 °C). For the cases of highly lipophilic substrates, a 4/1 volume ratio of H₂O/EtOH was used. Generally the reductions go to completion within 2–6 h, and the reported selectivities for carbonyl relative to C=C double-bond reduction are the highest reported so far, reaching 97% in certain cases. The beneficial role of water as a solvent was not rationalized in terms of higher H₂ availability under steady-state conditions, as the solubility of hydrogen in isopropanol (3.9 mmol/L) and other organic solvents is considerably higher

Table 7. Chemoselective Hydrogenation of α,β -Unsaturated Carbonyl Compounds in Water Catalyzed by 1% mol Au/*meso*-CeO₂ (Selected Examples)



compared to water (0.8 $\mu\text{mol/mL}$). Instead, it was proposed that, within the water environment, the hydrophilic C=O moiety is preferentially oriented to the active sites on catalyst surface. This assumption is supported by the fact that on competing hydrogenation among benzaldehyde and styrene in water, benzaldehyde is reduced ~ 100 times faster, whereas upon employing nonpolar cyclohexane as solvent, a remarkable reverse chemoselectivity was observed, with styrene reacting ~ 10 times faster. Prior to this report, Au/CeO₂ has been used as catalyst for the hydrogenation of crotonaldehyde in isopropanol (80 $^\circ\text{C}$, 1.0 MPa H₂), with lower conversions and selectivity under comparable reaction times.²⁸³

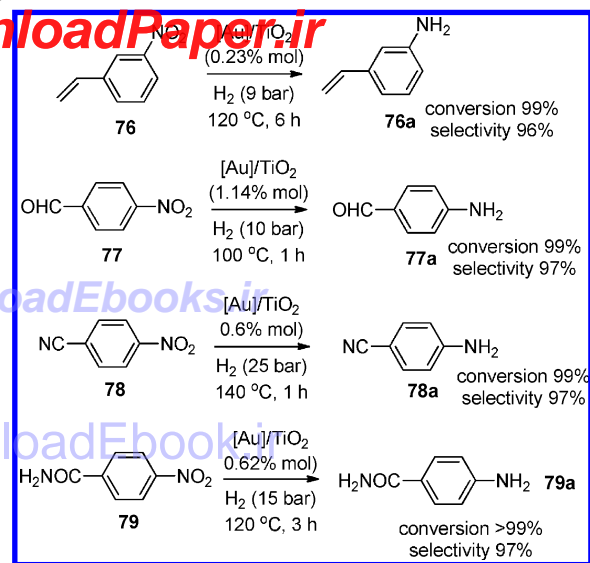
Although the literature regarding the Au NPs-catalyzed chemoselective hydrogenation of α,β -unsaturated carbonyl compounds is very rich, a few reports are known concerning the hydrogenation of simple carbonyls. Budroni and Corma²⁸⁴ found that Au/TiO₂ is a highly active and selective catalyst for the hydrogenation of succinic anhydride into γ -butyrolactone, an important fine chemical (97% selectivity and conversion). Additionally, it is possible to use the same catalytic system for the one-pot conversion of succinic anhydride into pyrrolidones if an amine is present. The reaction is facilitated by the presence of molecular sieves to capture the produced H₂O. The catalytic activity can be further improved without loss of selectivity, by adding a very small amount of Pt (100 ppm) to increase the rate of hydrogen dissociation. This hydrogenation concept was further extended to the synthesis of phthalide from phthalic aldehyde.^{285,286} Gold/platinum bimetallic core/shell nanoparticles stabilized by Frechet-type dendrimer catalyze the hydrogenation of 3-phenoxybenzaldehyde.²⁸⁷ Additionally, Keane and co-workers²⁸⁸ found recently that benzaldehyde can be hydrogenated under continuous gas-phase conditions into benzyl alcohol over Au/Al₂O₃. Other nanometal-supported catalysts led to over-reduction, yielding to benzyl

hydrogenation of the abundant combustion waste carbon dioxide for the production of formic acid (HCOOH) would complete the long-desired chemical loop for indirect hydrogen storage using CO₂. Such a concept has not received thus far significant attention. Formic acid is known to provide directly H₂ or hydride species in the presence of metals (see also section 6.1) and is a highly promising chemical for hydrogen storage. The group of Fachinetti extended previous efforts in this concept using a Ru(II) catalyst²⁸⁹ under homogeneous conditions, into heterogeneous, using Au/TiO₂ as catalyst.²⁹⁰ This commercially available catalyst (known also as AUROLite) promotes efficiently the CO₂ hydrogenation in the presence of neat Et₃N to form HCOOH/NEt₃ adducts.

5.3. Hydrogenation of Nitro Compounds and Subsequent Transformation of Amines

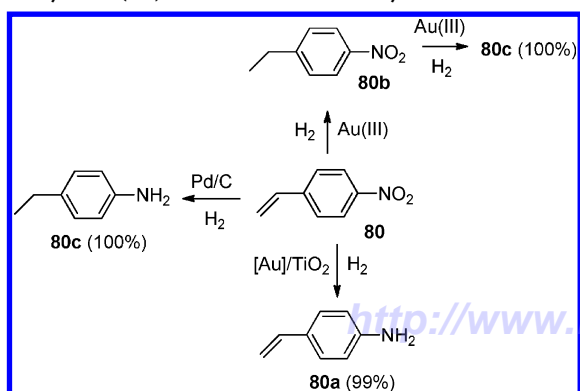
The reduction of nitro compounds into amines is an important process for the chemical industry. It is generally achieved by hydrogenation over supported Pt and Pd catalysts, or more traditionally by Fe or Sn/HCl. These procedures have several drawbacks such as the requirement of stoichiometric reagents, whereas for the case of metal-catalyzed catalytic protocols, the selectivity is low if other reducible functionalities are present (e.g., halides, C=C, and C=O double bonds). In 2006, Corma and Serna reported^{291,292} that supported Au catalysts (Au/TiO₂ or Fe₂O₃) promote the reduction of functionalized nitro arenes into anilines in yields close to 100% (Table 8). The significant

Table 8. Chemoselective Hydrogenation of Nitro Arenes in the Presence of Other Reducible Functionalities Catalyzed by Au/TiO₂



observation was that the nitro functionality is selectively reduced in the presence of other reducible functionalities (C=C double bond, carbonyl, nitrile, or amide), in sharp contrast to supported Pd and Pt catalysts or homogeneous Au(I or III) and Pd(II), complexes which provide either unselective reduction or different chemoselectivities (see, for example, the comparable results in Scheme 36).²⁹³ This highly efficient hydrogenation was used as a key step for the synthesis of aromatic azo-compounds,²⁹⁴ via the reduction of nitro aromatics followed by an oxidative coupling of the produced anilines under aerobic conditions. Almost simultaneously to Corma's pioneering work on the Au/TiO₂-catalyzed selective

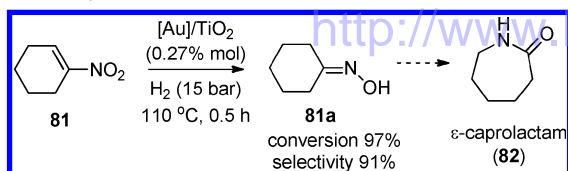
Scheme 36. Selectivity in the Hydrogenation of 4-Nitrostyrene (80) under Various Catalytic Conditions



nitro group hydrogenation, Qiu²⁹⁵ and co-workers had prepared and applied highly dispersed gold nanoparticles supported on silica for the chemoselective hydrogenation of aromatic nitro compounds. Later, Keane and co-workers studied in detail the influence of support and particle size on activity and selectivity regarding the hydrogenation of *m*-dinitrobenzene^{296–298} and chloronitrobenzene.^{299–301} Over Au NPs supported on TiO₂ or Fe₂O₃, mainly *m*-nitroaniline is formed. The over-reduction product (*m*-phenylenediamine) was exclusively produced over Au/CeO₂, whereas the hydrogenation over Au/Al₂O₃ is unselective. Hammett kinetics regarding the Au/TiO₂-catalyzed hydrogenation of a series of *p*-substituted nitrobenzenes³⁰² provided $\rho = +0.93$, consistent with a typical hydride nucleophilic reaction mechanism. The analogous Ag/TiO₂-catalyzed reduction provided a lower ρ value of +0.22, indicative of a more early transition state in the latter case. Very recently, Kaneda's group reported that the core-shell nanocomposite of AgNPs@CeO₂ is an excellent and highly selective catalyst for the hydrogenation of nitroaromatics,³⁰³ in contrast to typical AgNPs/CeO₂. It would be interesting to apply this reverse micelle technique for the synthesis of analogous Au NPs with higher durability in reductive processes.

The Au-catalyzed hydrogenation of 1-nitro-1-cyclohexene (81) renders cyclohexanone oxime, 81a (Scheme 37),²⁹¹ that

Scheme 37. Simple Route Towards ϵ -Caprolactam (81) from 1-Nitro-1-cyclohexene



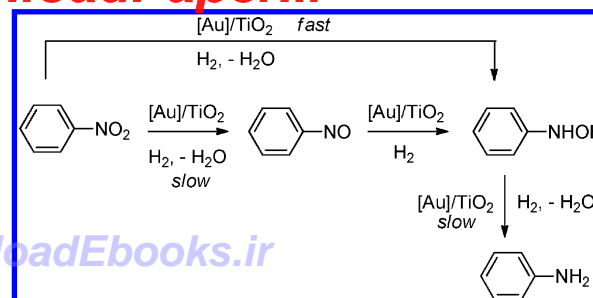
can be transformed into ϵ -caprolactam (82). ϵ -Caprolactam is a valuable chemical whose polymerization forms nylon-6. The conventional synthesis of cyclohexanone oxime proceeds through the condensation of hydroxylamine (toxic and unstable compound) with cyclohexanone. A current challenge might be a practical methodology for the synthesis of 1-nitro-1-cyclohexene from either benzene or nitrobenzene, which are readily available raw chemicals. More recently, the formation of cyclohexanone oxime (up to 83% selectivity) from the Au/Al₂O₃-catalyzed hydrogenation of 1-nitro-1-cyclohexene was re-

ported.³⁰⁴ The size of gold particles on this specific catalyst was ~2.5 nm.

By designing a bimetallic gold-platinum catalyst supported on titania (1.5% mol Au@Pt/TiO₂), a more effective hydrogenation catalyst for nitro arenes was uncovered.³⁰⁵ As commented at the introduction of this section, platinum nanoparticles are more efficient in enhancing the rate of H₂ dissociation (essentially the rate-limiting step of the overall hydrogenation process), thus increasing significantly the rate of the reduction by ~1 order of magnitude as compared to Au/TiO₂. Furthermore, the chemoselectivity observed in cases where other reducible functionalities are present was maintained. An analogous beneficial effect of Pt on Au was reported in the chemoselective hydrogenation of the nitro group in chloronitrobenzene by a Au-Pt/TiO₂ catalyst.³⁰⁶ Deng and co-workers²⁷² compared the hydrogenation of aromatic nitro compounds (100 °C, 1 MPa, H₂) over gold nanoparticles supported on ferric hydroxide and ferric oxide and found that the TOF values over Au/Fe(OH)_x were 2–6-fold higher than that of the corresponding ferric oxide-supported catalyst. In addition, it was reported that deactivation of the catalytic hydrogenation process over Au NPs may occur in the presence of CO₂.³⁰⁷

A mechanistic study of the hydrogenation of nitrobenzene into aniline was undertaken by Corma and co-workers.³⁰⁸ It was concluded that the main pathway involves formation of an intermediate phenylhydroxylamine (fast step) directly from nitrobenzene. Subsequently, the hydroxylamine is reduced in a slower step to aniline (Scheme 38). The possible pathway for

Scheme 38. Proposed Mechanism for the Au/TiO₂-Catalyzed Hydrogenation of Nitrobenzene into Aniline



the formation of phenylhydroxylamine involving the intermediacy of nitrosobenzene was established to be a minor one, as the amounts of hydroxylamine formed when nitrosobenzene was subjected to the reaction conditions were much lower, compared to the conditions where nitrobenzene was used. The fact that generally very low amounts of azoxybenzene are formed strongly suggests that the steady-state concentration of nitrosobenzene is always low. Otherwise, the percentage of azoxybenzene detected should be much larger, because this specific compound results from the condensation among phenylhydroxylamine and nitrosobenzene.

The activation of dihydrogen by dissociation on Au nanoparticles of different shape, supported on stoichiometric and reduced TiO₂ surfaces, was investigated by means of periodic DFT calculations.^{309,310} Gold nanoparticles become positively charged when supported on TiO₂ and negatively charged when adsorbed on the reduced surface, although this finding does not appear to be relevant for H₂ dissociation activity. It was uncovered that Au atoms active for H₂

dissociation must be either neutral or with a net charge close to zero. Also, they must be located at corner or edge low-coordinated positions and not directly bound to the support. Shimizu and co-workers³¹¹ examined the hydrogenation of some substituted nitroaromatics in the presence of Au/Al₂O₃ (size of nanoparticles 2.5 nm) and found higher intrinsic activity than with Au/TiO₂. On the basis of FTIR studies, they proposed a cooperation of the acid–base pair site on alumina and the coordinatively unsaturated Au atoms on the Au NPs that is responsible for the dissociation of H₂, to yield a H⁺/H[−] pair at the metal/support interface. Bokhoven and co-workers³¹² studied the Au/CeO₂-catalyzed hydrogenation of nitrobenzene at high pressure, monitored simultaneously by means of online attenuated total reflectance–Fourier transform infrared spectroscopy. They found no evidence that cationic gold particles contributed to the catalytic activity. The reasons for the superior Au/TiO₂-catalyzed chemoselectivity in the hydrogenation of nitroaromatics if other reducible functionalities are present were also rationalized.²³¹ Thus, by combining kinetics, quantum mechanical calculations, and in situ IR spectroscopy, it was found that this selectivity derives from the preferential adsorption of the reactant on the catalyst surface through the nitro group. Thus, nitro or olefinic groups are weakly and unselectively adsorbed on Au(111) or Au(001) surfaces. In contrast, an energetically favored adsorption occurs on the titania support, and more specifically in the interface between Au NPs and TiO₂, with the nitro group oriented perpendicular to the surface. Such preferential and oriented adsorption was not predicted or observed with silica for the case of Au/SiO₂. On the basis of these observations, it was concluded that the high chemoselectivity upon using Au/TiO₂ might be attributed to a synergism between Au NPs and the support that preferentially activates the nitro group. This support-driven reaction facilitation was corroborated by the fact that other supports (e.g., SiO₂ and C) provide a non-chemoselective hydrogenation of 3-nitrostyrene. In contrast, other metal nanoparticles (e.g., Pt)³¹³ strongly interact with any type of functional groups, with it being hard to control the selectivity of the hydrogenation process when several simultaneous or sequential reduction pathways are possible.

Following the reports in the chemoselective hydrogenation of nitro aromatics, a unique methodology for the transformation of α,β -unsaturated nitro compounds into oximes was presented (Table 9).³¹⁴ In a continuation of the studies regarding the Au/TiO₂-catalyzed hydrogenation of 1-nitro-1-cyclohexene²⁹¹ into cyclohexanone oxime (Scheme 37), it was found that a series of substituted *trans*- β -nitrostyrenes hydrogenate into the corresponding oximes in excellent yields and selectivities up to 97% by using Au/TiO₂ (0.6–0.9% mol) as catalyst. For comparison, although Pt or Pd/C under approximately identical reaction conditions reacts much faster, it provides lower selectivity. A striking example is the case of β ,2-dinitrostyrene (**86**), which affords in the presence of Pt or Pd/C primarily 1H-indole (**86b**) via an over-reduction/cleavage sequence, in contrast to Au/TiO₂, which catalyzes the exclusive formation of the corresponding oxime **86a**.

The utility of the Au/TiO₂-catalyzed hydrogenation of nitro compounds was extended to the synthesis of substituted imines, secondary amines, and β -amino carbonyl compounds through cascade reactions, if a carbonyl compound (saturated or unsaturated) is present along with a nitro compound.³¹⁵ Typical examples of such transformations are presented in Table 10. For instance, by mixing nitrobenzene and an aromatic

Table 9. Chemoselective Hydrogenation of α,β -Unsaturated Nitro Compounds into Oximes Catalyzed by Au/TiO₂

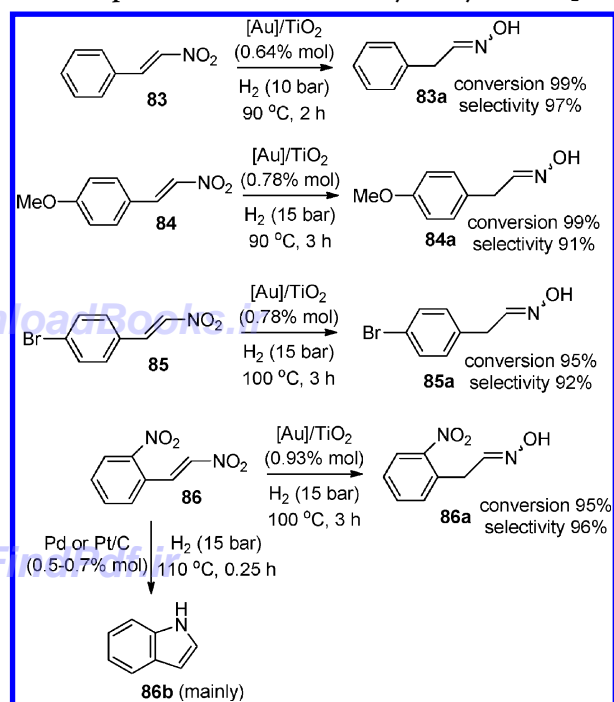
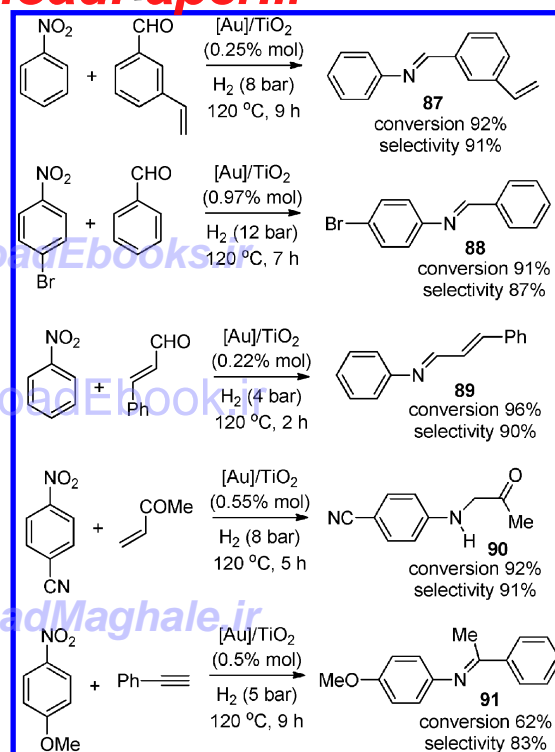


Table 10. Chemoselective Synthesis of Substituted Imines and β -Amino Carbonyls via Condensation of Nitro Aromatics with Carbonyl Compounds, α,β -Enones, and Acetylenes in the Presence of H₂ Catalyzed by Au/TiO₂

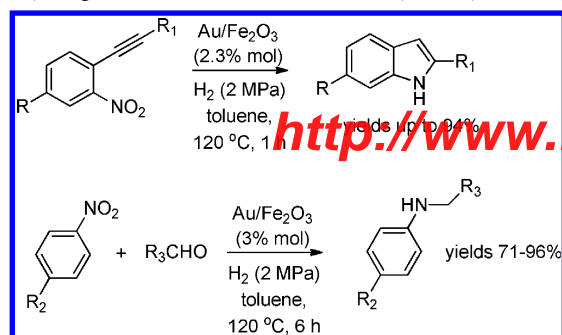


aldehyde under a certain pressure of H₂ in the presence of Au/TiO₂ (0.25–1% mol) and heating to ~120 °C, the nitro compound is reduced selectively, and the resulting aniline form an imine by coupling to the aldehyde. The reported

product selectivity was high (~90%). This approach is complementary to the Au/TiO₂-catalyzed methodology for the synthesis of imines, which uses amines and alcohols under aerobic conditions.³¹⁶ Under further forcing hydrogenation conditions, the imine C=N double bond can be reduced, leading thus to the one-pot synthesis of secondary amines. The imine reduction of the second step occurs selectively over any existing C=C double bond within the molecule. By replacing the aromatic aldehyde with an α,β -unsaturated carbonyl compound (e.g., methyl vinyl ketone), the initially formed aniline undergoes a Michael addition to the enone, forming substituted β -amino carbonyl compounds in high yields and selectivity. An alternative indirect approach for the synthesis of imines involves the hydrogenation of a nitroarene in the presence of an aryl acetylene. The acetylene undergoes nucleophilic attack by the aniline¹⁷⁹ (from the hydrogenation of a nitroarene), yielding a trisubstituted imine. The yield and selectivity for imine formation through this procedure is moderate, as the trisubstituted imines are very prone to hydrolyze into anilines and acetophenones from the water (byproduct of the nitroarene oxidation step) present in the reaction mixture.

An example of potent synthetic utility for the one-pot synthesis of indoles and substituted anilines (Scheme 39) via a

Scheme 39. One-Pot Synthesis of Indoles and Anilines from the Hydrogenation of Nitroarenes Catalyzed by Au/Fe₂O₃



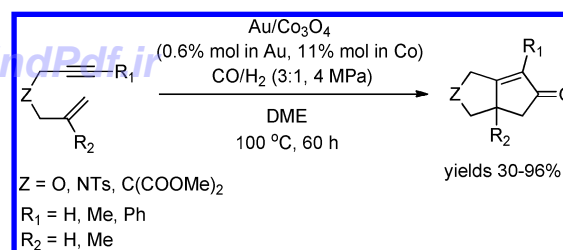
Au/Fe₂O₃-catalyzed hydrogenation of suitably functionalized nitroarenes was presented by Tokunaga and co-workers.³¹⁷ Thus, a series of (2-nitroaryl)alkynes lead to indoles in up to 94% yield through a preceding –NO₂ to –NH₂ reduction, followed by intramolecular hydroamination of the alkyne functionality (see also section 3.5). It was shown that the nitro functionality is more quickly reduced to an amine compared to the C–C triple bond, thus allowing selectively the intramolecular hydroamination taking place prior to alkyne reduction. Additionally, in the presence of aldehydes, nitroarenes initially yield anilines that condensate with the aldehydes forming imines. Finally imines are hydrogenated to amines within an one-pot operation. An intramolecular version of the latter procedure was also shown in the case of 2-(2-nitrophenyl)acetaldehyde, which afforded parent indole in 71% yield. Analogous synthetically valuable cascade-type examples involving reduction of nitroarenes by other means, and in situ coupling of the produced amines with carbonyls, are presented in the accompanying section 6.

5.4. Hydroformylation of Alkenes

Tokunaga and co-workers³¹⁸ showed that gold nanoparticles deposited on Co₃O₄ exhibit good activity in the heterogeneous hydroformylation of olefins by CO/H₂ mixture under relatively

mild conditions (100–140 °C, pressure 3–5 MPa). The selectivity was >85% in favor of the desired aldehydes. It was proposed that gold nanoparticles provide spillover H atoms from transient Au–H that reduce in situ Co₃O₄ into small Co nanoparticles. Mechanistically, the alkene undergoes one-electron reduction by Au–H on the surface of Co nanoparticles, accompanied by CO insertion. Finally, a second reduction, probably by Au–H species, generates an aldehyde (hydroformylation product). The catalyst can be easily recycled by simple decantation and reused, thus providing advantage over existing homogeneous catalysts. A synthetically useful extension of this observation was presented by the same group,¹¹² employing Au/Co₃O₄ as catalyst and a mixture of H₂/CO (3/1) in intra- and intermolecular versions of the Pauson–Khand reaction, a formal [2 + 2 + 1]-cyclization among an alkene, an alkyne, and CO (Scheme 40). The

Scheme 40. Au/Co₃O₄-Catalyzed Intramolecular Pauson–Khand Reaction



reported isolated yields range from moderate to excellent. There is no clear picture regarding the nature of the active CO species based on IR studies. Thus, an absorption at 1965 cm^{–1} indicates the presence of CO-bound species; however, it was not ascribed to Co₂(CO)₈, HCo(CO)₄, or Co₄(CO)₁₂.

5.5. Au Nanoparticle-Catalyzed Fischer–Tropsch Reaction

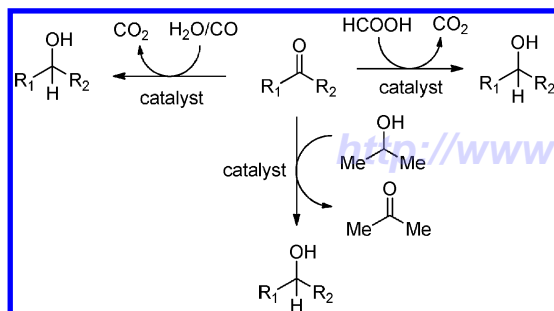
The Fischer–Tropsch reaction is a known methodology since the 1920s for the synthesis of hydrocarbons and other aliphatic compounds by activation of mixtures of H₂ and CO, if reacted in the presence of an iron or cobalt catalyst at elevated temperatures. A typical catalyst for this process is cobalt nanoparticles supported on titania. Hutchings and co-workers³¹⁹ examined the effect of Au doping on 10% Co/TiO₂, by varying the amount of Au (0.2–5 wt %). It was concluded that the addition of Au improves Co dispersion on the catalyst's surface and shifts the reduction temperature for the cobalt oxides in interaction with the support to lower temperatures. The catalyst activity for the Fischer–Tropsch reaction increases with an increase in Au loading and passes through a maximum in activity at ~1 wt % Au. Additionally, the methane and light-product selectivity monotonically increase with Au loading. The same group³²⁰ studied later on the effect of Au addition on the structure of Co/Al₂O₃ and Co/SiO₂ systems and their performance in the Fischer–Tropsch reaction. An improvement in Co reduction was observed by adding Au to the supported Co catalysts. For both catalysts the activity increased significantly after the addition of gold up to 1.5 wt %. The Au also improved the catalyst's reducibility and activity. The most significant effect was found for 5% Au on 10% Co/Al₂O₃, where the maximum conversion was 6 times higher compared to the uncatalyzed reaction.

6. REDUCTION VIA TRANSFER HYDROGENATION

6.1. Reduction of Carbonyl Compounds

Metal-catalyzed transfer hydrogenation (Scheme 41) employing hydrogen donors such as sacrificial alcohols, HCOOH, or

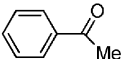
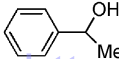
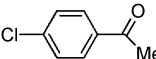
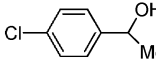
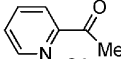
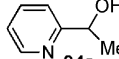


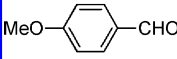
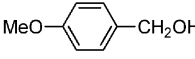
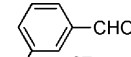
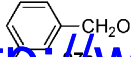
Scheme 41. Reduction of Carbonyl Compounds via Transfer Hydrogenation from Isopropanol, HCOOH, or CO/H₂O



CO/H₂O for the reduction of carbonyl compounds is a well-established methodology, especially for asymmetric synthesis purposes.^{321,322} In the transfer hydrogenation concept, sacrificial alcohols are oxidized into carbonyl compounds while “borrowing hydrogens” to a certain substrate that is finally reduced. Also, formic acid, as well as the mixture CO/H₂O, eliminates CO₂ after reducing a substrate (formally borrowing to it two hydrogen atoms).

In 2008, Cao and co-workers³²³ reported that Au NPs catalyze the transfer hydrogenation of aromatic ketones using isopropanol as the hydrogen donor (Table 11). The reduction was carried out under an inert atmosphere in the presence of Au/TiO₂ (0.8% mol) as catalyst at 80 °C and 0.3 equiv of KOH. Through catalyst screening it was proven that Au/TiO₂

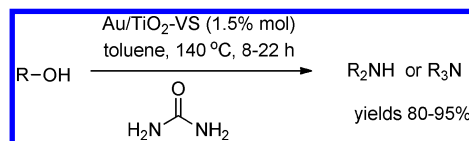
Table 11. Selected Examples for the Au/TiO₂-Catalyzed Reduction of Aromatic Carbonyl Compounds through Transfer Hydrogenation from Isopropanol

$\text{R}_1-\text{C}(=\text{O})-\text{R}_2 \xrightarrow[\text{[Au]/TiO}_2 \text{ (0.8\% mol)}]{\text{2-propanol (solvent)}} \text{R}_1-\text{CH}(\text{OH})-\text{R}_2$		Yield/Time (h)
82-120 °C		
		99%/4
92	92a	
		92%/3.5
93	93a	
		93%/8
94	94a	
		44%/9
95	95a	
		98%/9
96	96a	
		99%/2.5
97	97a	

was superior, and after five consecutive runs no changes in either activity or selectivity were seen. Additionally, the product selectivity was excellent, and the conversion yields were from moderate (in the case of hindered aromatic or aliphatic ketones) to excellent (for methyl aryl ketones). Aromatic aldehydes require more harsh conditions to be reduced (120 °C). For such reductions, K₂CO₃ was added to avoid undesirable Cannizzaro-type reactions promoted by the more basic KOH. It was proposed that the reaction proceeds through the formation of [Au]–H complexes, as hydride donors.

A highly efficient gold-catalyzed (Au/TiO₂–VS) heterogeneous method for the direct synthesis of tertiary or secondary amines upon coupling alcohols and urea was very recently presented.³²⁴ The process requires a 6-fold excess of the alcohol and mechanistically involves the reduction of urea through “borrowing hydrogen activation” by the alcohol. The reduction of urea yields ammonia that couples with the aldehyde (formed by the indirect alcohol oxidation), thus forming an imine. Reiteration of the reductive steps by the sacrificial alcohol finally yields tertiary or secondary amines depending on the substrate and reaction conditions (Scheme 42).

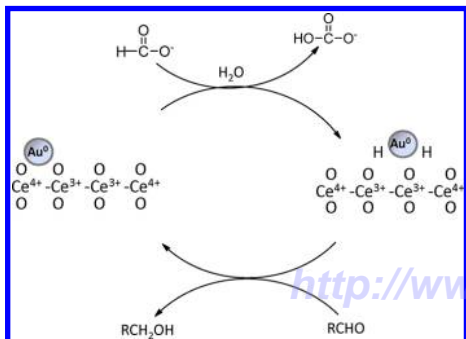
Scheme 42. Direct Amination of Alcohols with Urea Catalyzed by Au/TiO₂–VS



The same group³²⁵ made use of HCOOK (5 equiv) in H₂O as a mild hydrogen donor for the reduction of a variety of carbonyl compounds, catalyzed by Au NPs (3% mol). The utility of formic acid or formates as hydrogen donors in gold catalysis is well-documented.^{326,327} Among several catalysts, Au/meso-CeO₂ (meso = mesoporous) was proven as the most efficient, probably due to the combination of large surface area and still favorable diffusion. The reactions were run at 80 °C, and the reductions go to completion within 4–21 h, depending on the substrate (isolated yields range from 80 to 99%). A series of α,β -unsaturated aldehydes were reduced to allylic alcohols without significantly affecting the entity of C=C double bonds. That was exemplified in the competing reduction of benzaldehyde and styrene, where the aldehyde was quantitatively reduced, whereas ethylbenzene (hydrogenation product of styrene) was formed in merely 7% yield. It was postulated that ceria sites (Ce³⁺ and Ce⁴⁺) facilitated by H₂O catalyze the dehydrogenation of formate to bicarbonate species (rate-limiting step). The hydrogen species transfer to vicinal Au⁰ clusters, thus forming Au⁰–H species, which rapidly reduce the carbonyl compounds through hydride transfer (Scheme 43).

The generation of H₂ from mixtures of CO + H₂O, through the so-called “water gas shift reaction”, is a key step in fuel processing.³²⁸ This process has been shown to be efficiently catalyzed by supported Au nanoparticles at low temperatures.^{329–338} It was revealed that the dominant active catalytic sites are corner atoms with fewer than seven neighboring gold atoms supported on rutile TiO₂.³³⁹ The water gas shift reaction was successfully utilized³⁴⁰ for the chemoselective reduction of α,β -unsaturated aldehydes, through the postulated intermediacy of transient Au⁰–H species. Au/CeO₂ (2.8% mol) was the most efficient catalyst with Au/TiO₂ being equally product-selective

Scheme 43. Tentative Mechanism for the Au/*meso*-CeO₂-Catalyzed Reduction of Carbonyl Compounds through Transfer Hydrogenation from Formate^a

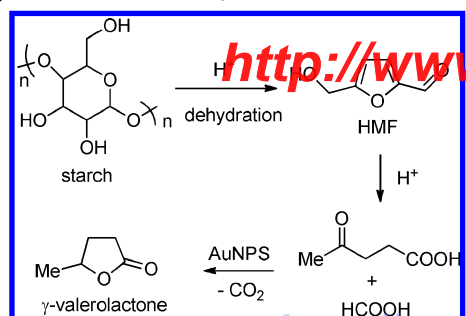


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but less reactive. The reactions were carried out at 96 °C, the conversions were always >94%, and the product selectivity in favor of aldehyde reduction was between 85 and 95%, relative to the competing reduction of the C–C double bond or over-reduction (double bond + aldehyde).

A practical Au NP-catalyzed transfer hydrogenation from in situ-generated HCOOH was reported in the transformation of 5-hydroxymethylfurfural (HMF) to γ -valerolactone (GVL),³⁴¹ an important industrial chemical (Scheme 44). The acid-

Scheme 44. Process for the Catalytic Conversion of Carbohydrate Biomass into γ -Valerolactone



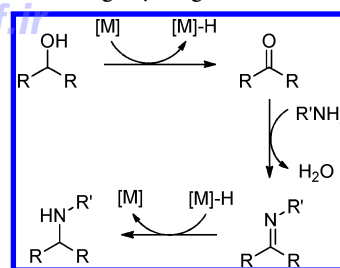
catalyzed decomposition of HMF yields levulinic acid and HCOOH, with the latter being the hydrogen donor under gold-catalysis conditions that intramolecularly reduces/cyclizes levulinic acid into GVL, without requiring external hydrogen gas addition. HMF is well-known to derive from the acid-catalyzed decomposition/dehydration of carbohydrate biomass (e.g., starch),³⁴² whereas Au NPs (Au/Al₂O₃)³⁴³ or MOF-immobilized Au–Pd nanoparticles³⁴⁴ catalyze the dehydrogenation of formic acid under near ambient conditions to form H₂ + CO₂. These observations are of high importance, because HCOOH might be a convenient hydrogen carrier in fuel cells designed for portable use. The optimum conditions to convert levulinic acid + HCOOH into GVL (~95% yield) were achieved in the presence of 0.1% mol Au/ZrO₂–VS (VS, very small; reaction conditions: 150 °C, 8 h). ZrO₂ is the most suitable support for Au NPs in this process because of its excellent acid-tolerance under the harsh conditions required in the previous steps. Other supports such as Al₂O₃, Fe₂O₃, ZnO, or CeO₂ undergo leaching or even dissolution under the acidic required for the production of levulinic acid from HMF. The Au/ZrO₂ catalyst was also used for the direct one-pot synthesis

of highly valuable pyrrolidone derivatives if a primary amine is present in the reaction mixture, under milder conditions compared to those applied in GVL synthesis.

6.2. N-Alkylation of Amines by Alcohols via Borrowing Hydrogen Activation

The one-pot selective N-alkylation of amines by alcohols via the so-called “borrowing hydrogen activation” of alcohols^{345–347} is catalyzed by a variety of metals. This reaction has profound implications to transfer hydrogenation reactions. For instance, the activation of alcohols (dehydrogenation) by Au NPs is well-known.³⁴⁸ Tentatively this one-pot stepwise procedure could be simplified as follows: (a) oxidation of the alcohol to a carbonyl compound catalyzed by a metal through the formation of metal hydride species; (b) reaction of the carbonyl compound with the amine to form an imine; and finally (c) reduction of the imine by the hydride species produced during the alcohol oxidation step (Scheme 45). Au/TiO₂–VS was reported as a

Scheme 45. Metal-Catalyzed N-Alkylation of Amines by Alcohols via Borrowing Hydrogen Activation of Alcohols



metal catalyst for the N-alkylation of amines by alcohols (Table 12).³⁴⁹ The reactions were performed at 120 °C under inert conditions, 0.5% mol of catalyst loading, equimolar amounts of amine and alcohol, and toluene as solvent. The main reaction byproduct (<8% relative yield) was the corresponding imine. Notably, this transformation can be applied for large-scale experiments (0.1 mol of aniline with 0.1

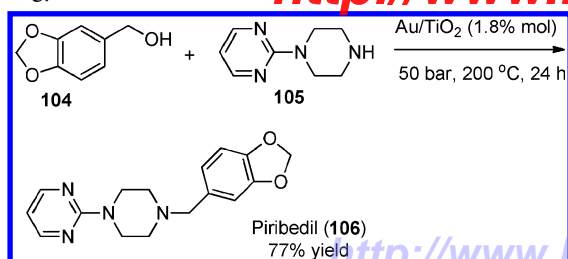
Table 12. N-Alkylation of Amines with Alcohols Catalyzed by Au/TiO₂–VS (Selected Examples)

R–NH ₂ + R'–OH		[Au]/TiO ₂ –VS (0.5% mol)	Yield/Time (h)
		toluene, 120 °C	
PhNH ₂	BnOH	PhNHBn 98	90%/14
PhNH ₂	Me Ph–CH–OH	Me Ph–CH–NHPh 99	90%/36
PhNH ₂	Ph–CH ₂ –OH	Ph–CH ₂ –NHPh 100	96%/19
Cl–C ₆ H ₄ –NH ₂	BnOH	Cl–C ₆ H ₄ –NHBn 101	87%/20
Cyclohexyl–NH ₂	Ph–CH ₂ –OH	Cyclohexyl–NH–CH ₂ –Ph 102	51%/49
PhNH ₂	BnOH	PhNH–CH ₂ –Ph 103	97%/50

mol of benzyl alcohol) under solvent-free conditions. Thus, by heating at 180 °C for 96 h under a N₂ atmosphere, and in the presence of merely 0.008% mol of catalyst, benzylphenylamine was isolated in 96% yield. The mechanism is unclear, although some clues were provided by Hammett kinetics. Thus, a value of $\rho = -1.32$ in the reaction of *p*-substituted benzyl alcohols with aniline indicates the development of a positive charge on the benzylic position, most likely due to a β -hydride transfer in the transition state of the rate-limiting step of the reaction. Alkylation of amines by alcohols was also shown by Ishida and co-workers³⁵⁰ using gold clusters deposited on Al-MIL35 (a metal organic framework). The same group studied the support effects in the Au-catalyzed *N*-alkylation of amines by alcohols and found that ZrO₂ exhibited the best selectivity.³⁵¹ The importance of surface hydroxyls on zirconia was highlighted. An analogous transformation (reaction between an amine and an alcohol) catalyzed by Au NPs immobilized on polystyrene-based polymers (Au/PICB), yet under aerobic conditions, leads to amides instead.³⁵² Under these oxidative conditions, the intermediate addition product of the amine to the aldehyde is oxidized to the amide prior to its dehydration to form an imine.

Hii and co-workers³⁵³ developed a flow reactor for the highly selective direct alkylation of amines by alcohols using Au/TiO₂ (0.9–1.8% mol) as catalyst, without the requirement for an inert atmosphere or base. The high yielding coupling is applicable to aromatic, aliphatic, and chiral amines by primary and secondary alcohols and was utilized for the straightforward single-operation synthesis of Piribedil (**106**, Scheme 46), a

Scheme 46. Single-Operation Synthesis of Piribedil (106**) through a Au/TiO₂-Catalyzed Amine–Alcohol Coupling Strategy in a Flow Reactor**



common drug for the treatment of Parkinson's disease, by the reaction among piperonyl alcohol (**104**) and 2-(1-piperazinyl)pyrimidine (**105**). Through kinetics and measurement of thermodynamic parameters, it was concluded that the origin of selectivity is due to the accessibility of a high temperature (>150 °C), while water was found to be essential for the activity of the catalyst.

6.3. Reduction of Nitro Compounds and Subsequent Transformation of Amines

In addition to catalytic hydrogenation, several Au NP-catalyzed transfer hydrogenation methodologies for the nitro to amine transformation were recently presented. A simple room-temperature catalytic methodology (Table 13) was developed by Cao and co-workers,³⁵⁴ using a mixture of CO and H₂O (syngas) as a hydrogen source and very small Au NPs supported on titania (Au/TiO₂-VS) as catalyst. At 1% mol catalyst loading, 5 atm CO, in EtOH/H₂O (2:1) solvent system, quantitative conversions of nitro compounds to amines were found within 0.5–4 h, depending on the substrate. The advantages of this method were exemplified in a large-scale

Table 13. Reduction of Nitro Compounds to Amines Using CO/H₂O As Hydrogen Donor, Catalyzed by Au/TiO₂-VS (Selected Examples)

$\text{R-NO}_2 \xrightarrow[\text{EtOH/H}_2\text{O, 25 } ^\circ\text{C}]{\text{[Au]/TiO}_2\text{-VS (1\% mol), CO (5 atm)}} \text{R-NH}_2$		Yield/Time (h)
 107	 107a	99%/3.5
 108	 108a	99%/1
 78	 78a	99%/2.5
 109	 109a	98%/4
 110	 110a	99%/1.2
 111	 111a	99%/4
<hr/> <div style="display: flex; align-items: center; justify-content: center;"> <div style="margin: 0 10px;"> $\xrightarrow[\text{100 } ^\circ\text{C, CO (15 atm), 2.5 h}]{\text{[Au]/TiO}_2\text{-VS (0.01\% mol)}}$ </div> </div> <div style="display: flex; justify-content: space-between; width: 100%;"> 0.25 mol scale 2.5 h 97% isolated yield </div>		

experiment, where nitrobenzene (0.25 mol scale) was reduced within 2.5 h to aniline in 97% isolated yield, using 0.01% mol Au/TiO₂-VS, under a 15 atm pressure of CO at 100 °C. The reduction was performed to a variety of ring-substituted nitrobenzenes, as well as to aliphatic substrates, always with excellent selectivity and yields. Several potentially reducible functionalities coexisting with the nitro group remain intact. The mechanism is unclear, and it is likely to involve gold hydride species as the reducing agent. An intermolecular kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 1.54$ was observed upon switching the solvent from H₂O to D₂O; however, this observation does not necessarily provide solid evidence regarding the rate-determining step of the reduction. Prior to this publication, Deng and co-workers³⁵⁵ presented a highly chemoselective hydrogenation of aromatic nitro compounds in the presence of CO and H₂O over Au/Fe(OH)₃, yet elevated temperatures are required (100–120 °C, 1.5–6 h depending on the substrate). Because H₂ was not detected during the course of the reaction, the authors suggested the formation of gold hydride species generated from a typical water gas shift reaction.

Ammonium formate (HCOONH₄) could be also used³⁵⁶ as an alternative reagent to effect the hydrogenation of a variety of nitro arenes. The significant improvement in this reduction process is that HCOONH₄ is a readily available and cheap chemical, easy to handle compared to toxic CO, while the reactions are commonly carried out at ambient temperature. Typically the reactions were performed under an inert atmosphere (N₂) employing 1% mol Au/TiO₂, 5 equiv of HCOONH₄, and ethanol as solvent. The reaction time varies from 0.25 to 8 h depending on the electronic nature of the substituents on the nitrobenzene, and the reported isolated yields are

good to excellent. By studying the reactivity of all possible intermediate reduction products from nitrobenzene (nitrosobenzene, azobenzene, hydrazobenzene, and phenyl hydroxylamine) under the reaction conditions, it was concluded that Au–H species, initially formed from HCOONH_4 , reduce PhNO_2 through a pathway forming directly phenyl hydroxylamine (PhNHOH), which in turn is the precursor of the final product (aniline). An analogous conclusion had been drawn³⁰⁸ regarding the Au-catalyzed hydrogenation of nitro aromatics (Scheme 38). By switching the solvent from ethanol to refluxing CH_3CN , it is possible to transform a variety of functionalized nitro aromatics into *N*-aryl formamides instead of anilines, also making use of the CO_2 byproduct (Table 14).³⁵⁶ The conversion yields are excellent and the reaction

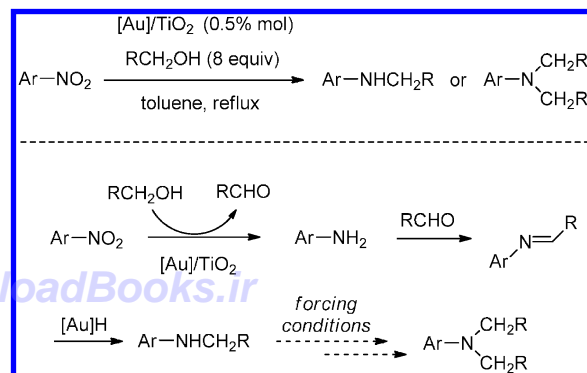
Table 14. Direct Synthesis of *N*-Formyl Anilines from Nitroarenes by HCOONH_4 in CH_3CN Catalyzed by Au/ TiO_2 (Selected Examples)

$\text{Ar}-\text{NO}_2 \xrightarrow[\text{CH}_3\text{CN, reflux}]{[\text{Au}]/\text{TiO}_2 (1\% \text{ mol}), \text{HCOONH}_4 (7 \text{ equiv})} \text{Ar}-\text{NHCHO}$		Yield/Time (h)
		88%/3
		93%/2.5
		90%/7
		71%/9
		66%/8

time is relatively short, making this approach superior to the known HCOONH_4 –Pd/C protocol.³⁵⁷ A complementary Au/ NiO -catalyzed process for the *N*-formylation of amines is known, employing the aerobic oxidation of methanol in the presence of an amine.³⁵⁸ The Au NP-catalyzed transfer hydrogenation by formate was successfully applied in the selective reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid into the 4,4'-diamino substance,³⁵⁹ which is an important intermediate for the production of dyes and mothproofing agents.

By following the one-pot selective *N*-alkylation of amines with alcohols catalyzed by Au/ TiO_2 –VS,³⁴⁹ it was found that nitro compounds can replace amines and lead to the high-yield formation of di- or trialkylated amines without any external hydrogen source, under ligand- and base-free conditions (Scheme 47).³⁶⁰ This unique methodology was proposed to proceed through an initial reduction of the nitro compound to the amine through transfer hydrogenation from the alcohol (forming an aldehyde), formation of an intermediate imine by coupling of aldehyde and the newly formed amine, and finally reduction of the imine by Au–H species formed during the oxidation of the alcohol, which is in excess. By forcing the reaction conditions through increasing the temperature from 120 to 150 °C, further alkylation of the primarily formed

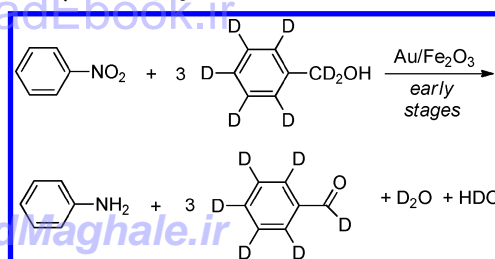
Scheme 47. General Methodology for the Coupling of Nitroarenes with Alcohols to Form Substituted Amines Catalyzed by Au/ TiO_2 –VS and a Possible Reaction Pathway



dialkylated amines may occur, thus leading to the formation of trialkylated amines.

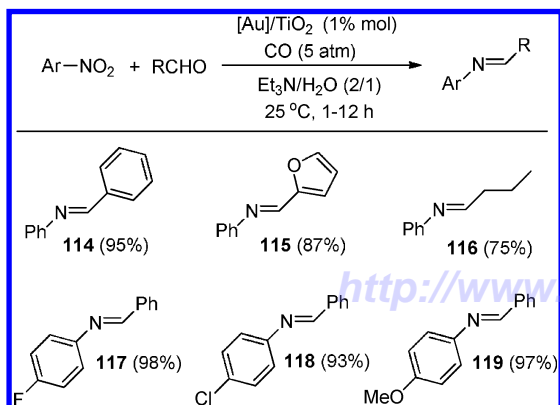
Almost simultaneously, the same concept (synthesis of *N*-mono- or *N,N'*-dialkylated amines from nitroarenes and alcohols) was reported³⁶¹ employing Au/ Fe_2O_3 as catalyst, through a fine-tuning of the reaction conditions to achieve mono- or dialkylation. The authors used more or less similar reaction conditions and stoichiometries to the Au/ TiO_2 –VS-catalyzed³⁶⁰ condensation. Excellent yields, especially for the synthesis of trisubstituted amines, were reported. Additionally, *N,N*-disubstituted amines may be formed from the alkylation of *N*-substituted amines. For instance, the reaction of *N*-benzylaniline (2 mmol) with *p*-methoxybenzyl alcohol (10 mmol) in the presence of Au/ Fe_2O_3 afforded after 30 h at 170 °C *N,N*-(benzyl-*p*-methoxybenzyl)aniline in 97% yield. By monitoring the reaction between nitrobenzene and benzyl alcohol- d_7 at the initial stages through GC-MS, <5% of deuterium incorporation was found on aniline (the intermediate product of the process). Also, only benzaldehyde- d_6 could be detected (no D scrambling on the aldehyde), which suggests that the one proton on the nitrogen of aniline derives from the proton of the hydroxyl group of benzyl alcohol, while one benzylic C–H proton is transferred into water (see stoichiometry at the early stages of the reaction in Scheme 48).

Scheme 48. Isotopic Studies in the Alkylation of Aniline with Benzyl Alcohol- d_7 at the Early Stages of the Reaction, Catalyzed by Au/ Fe_2O_3



Finally, the one-pot controlled reductive imination of nitroarenes with aldehydes by $\text{CO}/\text{H}_2\text{O}$ catalyzed by Au/ TiO_2 –VS (1% mol) can be achieved in good to excellent yields (Scheme 49).³⁶² Stoichiometric amounts of nitro arenes and aldehydes were used and the solvent of choice was triethylamine, while the reaction conditions are very mild (25 °C). From the mechanistic point of view, the nitro compounds are reduced to the corresponding amines, which directly couple

Scheme 49. Direct Synthesis of Imines from Nitroarenes and Aldehydes in the Presence of CO/H₂O Catalyzed by Au/TiO₂–VS (Selected Examples)



with the aldehydes, forming the imines. Apparently, the nitro functionality is selectively reduced over the coexisting aldehydes. It was also demonstrated in a single example that the in situ-formed imine (from nitrobenzene and benzaldehyde) can react with Danishefky's diene to form the corresponding aza-Diels–Alder product. Desilylation provided a dihydropyridone, a useful scaffold of biologically active compounds, in 85% overall yield. Prior to this report, Li and co-workers³⁶³ had developed the one-pot synthesis of imines from nitroarenes and carbonyl compounds using bimetallic Au–Pd/Al₂O₃ as catalyst and employing methanol as reductant. This procedure requires rather harsh conditions in terms of temperature (130 °C) or pressure as well as prolonged reaction times. It is not clear whether the reduction takes place via the aqueous-phase reformation of methanol or through hydrogen transfer from the methanol. It should be pointed out that Au or Pd particles were supported on Al₂O₃, without the modification of each other.

6.4. Photochemical Reduction of Nitro Arenes under Transfer Hydrogenation Conditions

The Au NPs-catalyzed photochemical reduction of nitroaromatic compounds in the presence of isopropanol and visible or ultraviolet light was reported by Zhu and co-workers.³⁶⁴ This unique methodology leads to the formation of aromatic azo compounds, instead of hydroxylamines or anilines, in a single step (Table 15). It has been known that supported Au NPs strongly absorb both visible light and ultraviolet light,³⁶⁵ and surprisingly they can also sensitize the formation of singlet molecular oxygen (¹O₂).³⁶⁶ Thus, by irradiating (400 nm) a slurry containing a nitroarene, Au/ZrO₂ in isopropanol, the corresponding aromatic azo compounds were formed in moderate to excellent yields. The process is facilitated by catalytic amounts of KOH. From the mechanistic point of view, based on the kinetics of reactant consumption, as well as intermediate and product formation, it was proposed that the reaction involves two processes. In the first process corresponding to the early stages of the reaction, isopropyl alcohol is oxidized. In the second process (later stages of reaction), the aromatic azo compounds are produced, with the intervention of species formed in the first process. The second process does not rely on the oxidation of isopropyl alcohol. Thus, in the first process azoxyarenes and Au–H species are primarily formed. The gold hydride species form in the presence of N–O bonds (from azoxyarenes, Au–H species

Table 15. Synthesis of Aromatic Azo Compounds from Nitroarenes in the Presence of Isopropanol under UV/Vis Irradiation Catalyzed by Au/ZrO₂

reactant	product	conversion (%) /selectivity (%) /time (h)
		100/99/5
		100/95/3
		100/56/6
		58/99/3
		100/82/3

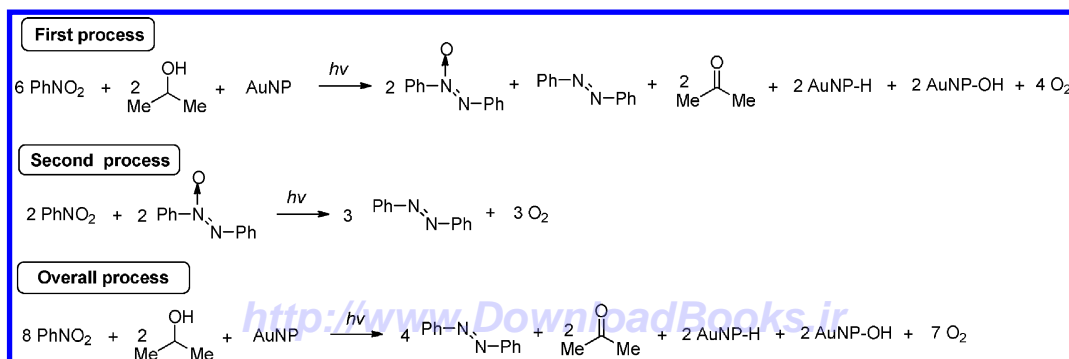
via a photocatalytic process. Finally, the Au–OH release O₂ and transform into Au–H that are recycled in the subsequent reaction process. In the second process, the oxidation of isopropanol is negligible and the large amount of azoxybenzene formed in the first process is reduced into azobenzene, releasing O₂. The proposed stoichiometry of the two processes and the overall sum are shown in Scheme 50.

The irradiation of nitroarenes in ethanol under Au/ZrO₂ catalysis conditions provides an unusual direct route to the synthesis of quinaldines in 19–91% yield (Scheme 51).³⁶⁷ The construction of the quinaldine bicycle requires the participation of 2 molecules of ethanol (the reaction solvent). The condensation mechanism is not completely understood, and according to the most likely proposed pathway, it proceeds by initial transfer hydrogenation from ethanol to the nitroarene that generates acetaldehyde and a substituted aniline, which couple to form an imine. Then vinylogous aldol-like homodimerization of the imine, followed by aniline elimination and dehydrogenative aromatization, leads to quinaldines. This mechanistic rationale is supported by the fact that some of the postulated intermediates were detected by GC–MS during the course of the reaction.

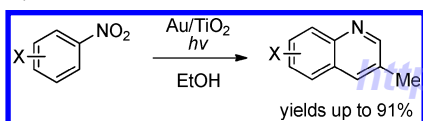
6.5. Reductions via Activation of Boron–Hydride Bonds

The activation of NaBH₄ by gold nanoparticles toward the reduction of nitroarenes in the corresponding anilines has been shown by several groups (Scheme 52). NaBH₄ by itself is essentially inefficient regarding the –NO₂ to –NH₂ reduction in the absence of the catalyst. The studies were mainly focused on the reduction of *p*-nitrophenol to *p*-aminophenol as a model transformation and include dendrimer (PAPAM or PPI) Au nanocomposites;^{368,369} polymer-stabilized gold nanocolloids;³⁷⁰ resin-bound Au NPs;³⁷¹ polystyrene sulfonate-stabilized Au NPs;³⁷² Au–Ag alloy nanoprisms;³⁷³ Au@SiO₂ yolk/shell particles;³⁷⁴ Au NPs stabilized by collagen³⁷⁵ or poly(*N*-isopropylacrylamide)-*co*-poly(4-vinylpyridine);³⁷⁶ Au NPs@membranes;³⁷⁷ polyvinylpyrrolidone-supported Au NPs;³⁷⁸ Au poly(methyl methacrylate);³⁷⁹ resorcinarene-functionalized Au NPs;³⁸⁰ Au@Ag core-shell nanoparticles stabilized on a

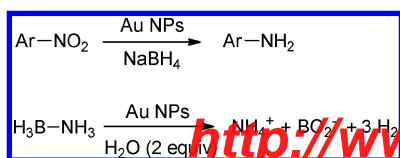
Scheme 50. Proposed Mechanism for the Au/ZrO₂-Catalyzed Photochemical Synthesis of Azobenzene from Nitrobenzene in Isopropanol



Scheme 51. Synthesis of Quinaldines from the Photochemical Coupling of Nitroarenes with Ethanol Catalyzed by Au/ZrO₂



Scheme 52. Reduction of Nitroarenes by NaBH₄ and the Hydrolysis of Ammonia Borane Complex Catalyzed by Au NPs



MOF (metal organic framework)³⁸¹ and, more recently, by Au-PNIPA yolk/shell particles;³⁸² Au NPs grown in situ within a lysozyme protein crystal;³⁸³ Au/AgInS₂;³⁸⁴ and polypyrrole nanotube-supported Au NPs.³⁸⁵ Surprisingly, the Au nanoparticle-catalyzed activation of NaBH₄ has not found any attention so far in other reductive processes.

Relevant to the activation of B-H bond of NaBH₄ by Au NPs is the hydrolysis of ammonia borane (BH₃-NH₃) Lewis acid-base complex for the production of hydrogen gas (Scheme 52), thus making this compound a promising chemical tool for fuel cell applications/hydrogen storage in the future.³⁸⁶ This reaction is known to take place primarily in the presence of non-noble metals as catalysts, whereas among noble metals Pt and Rh exhibit high efficiency.³⁸⁷ Au/γ-Al₂O₃ is a rather poor catalyst;³⁸⁸ however, bimetallic nanoparticles such as Au-Ni supported on SiO₂,³⁸⁹ Au@Co core-shell nanoparticles,³⁹⁰ and trimetallic Au/Co/Fe triple-layered core-shell nanoparticles³⁹¹ show promising activity. It is expected that Au-catalyzed reductive transformations by BH₃-NH₃ may find novel applications in organic synthesis.

7. C-C COUPLING REACTIONS

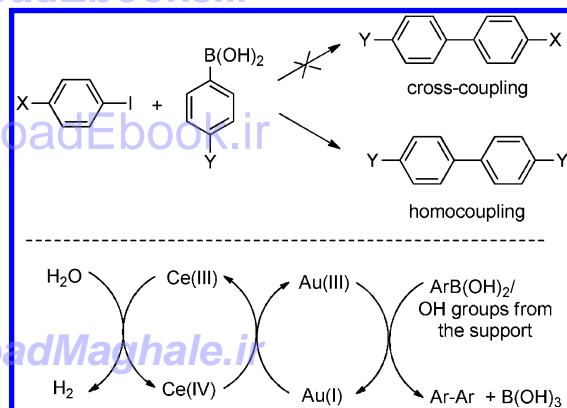
One key point in gold catalysis is to delineate the specific activity of gold compared to other noble metals, and palladium in particular. As we have already commented in section 4.2, a line of research in gold catalysis has been aimed at establishing gold versions of palladium catalysis. In this context, even though Au⁺ and Au³⁺ are isoelectronic with Pd⁰ and Pd²⁺, it is clear that the different redox behavior between the two Au

Au³⁺ and Pd⁰/Pd²⁺ redox pairs derived from the easier reoxidation of Pd⁰ to Pd²⁺ can make a difference from a mechanistic point of view with respect to Au catalysis in which reoxidation of low to higher oxidation states is less favorable. Therefore, Pd salts, complexes, and nanoparticles are able to catalyze an array of C-C coupling reactions that have gained relevance as a powerful toolbar in organic synthesis because of their general applicability, mild conditions, and compatibility of the C-C bond formation with the presence of a wide array of functional groups.^{385–389} It is of large interest to check the activity of supported gold catalysts for this type of reactions. The outcome of the available experimental data points to a remarkably low catalytic activity of Au compared to Pd and the importance of having the catalyst sites that can be ascribed either to Au⁺ or Au³⁺ ions.

7.1 Homocoupling of Arylboronic Acids—Suzuki Cross-Coupling

It has been reported that gold supported on nanoparticulate ceria does not catalyze the Suzuki–Miyaura cross-coupling between phenylboronic acid and iodobenzene (Scheme 53).³⁹⁷

Scheme 53. Catalytic Activity of Au/CeO₂ for the Homocoupling of Phenylboronic Acid versus Its Cross-Coupling with Aryl Iodides and a Mechanistic Rationalization Involving Au(III) Species



In contrast, under the typical reaction conditions for cross-coupling, Au/CeO₂ promotes the quantitative homocoupling of arylboronic acids to the corresponding symmetric biphenyls (5% mol Au/CeO₂, 55 °C, 15 h, toluene). Intriguingly, the reaction requires oxygen and water to occur. Homocoupling also has been promoted by small Au(0) clusters stabilized on biopolymers such as poly(1-vinyl-2-pyrrolidone) under aerobic

conditions,^{398,399} or chitosan,⁴⁰⁰ by other metal oxide-supported Au NPs,⁴⁰¹ upon using homogeneous or heterogenized Au(III) Schiff base complexes,^{402–405} ferrocenyl-stabilized Au NPs,⁴⁰⁶ or even in the presence of simple Au(III) salts.⁴⁰⁷

Among these studies, it is not clear what is the catalytically active oxidation state of gold, as the proposals diverge. Sakurai's colloidal gold nanocatalyst (Au/poly(*N*-vinyl-2-pyrrolidone)) is formally Au⁰; however, it possesses Lewis acidic character,⁴⁰⁸ as revealed by its ability to promote intramolecular heterocyclization of γ -hydroxyalkenes and γ -aminoalkenes under aerobic conditions,^{409,410} typical reactions also catalyzed by homogeneous Au(I) catalysts. A reasonable redox mechanism involving Au(III) catalysis was provided by Corma and co-workers³⁹⁷ as shown in Scheme 53, in which cerium also participates, while the OH groups on the surface of the support interact with boronic acid to form boric acid. The characterization of the Au sites responsible for the catalytic activity in Au/CeO₂ by means of IR spectroscopy using CO as probe shows the presence of a band at 2148 cm⁻¹ that is specific of Au³⁺ sites. This assumption also agrees with the Au(4f_{7/2}) peak in XPS spectrum (86.2 eV) attributable to Au³⁺. Apparently one of the roles of ceria as support is to stabilize the presence of this type of site. Concerning the nature of the active sites and the experimental information, it should be commented that theoretical models consider that charges in Au clusters should be largely delocalized with the charge density distributed throughout the atoms. In this regard, no real atoms with +III or +I oxidation states should be expected. However, depending on the location of the gold atoms in the cluster and, particularly, its coordination number and coordination sphere, it is expected that the density of positive charge varies.

Although trinuclear homogeneous Au(I) complexes⁴¹¹ catalyze, in addition to homocoupling of arylboronic acids, competitively the classical Suzuki–Miyaura cross-coupling in the presence of aryl iodides, Guo and co-workers⁴¹² reported an unexpected and clean Suzuki cross-coupling between aryl halides and aryl boronic acids (Table 16) in the presence of reusable polymer (PATP)-stabilized Au NPs (0.05% mol). The reactions were run in water at 80 °C with the aid of 4 equiv of KOH and proceed in high yield. Notably, aryl chlorides are almost as reactive as the corresponding bromides and iodides. More recently, Stevens and co-workers⁴¹³ showed that biodeposited Pd/Au bimetallic nanoparticles (2 wt % Au) catalyze efficiently the Suzuki coupling between aryl iodides and a series of aryl boronic acids.

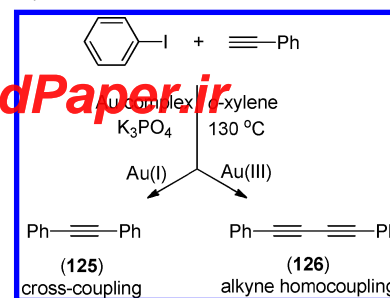
7.2. Sonogashira Cross-Coupling

Au/CeO₂ is also able to promote the Sonogashira cross-coupling between iodobenzene and phenylacetylene in moderate yields. The corresponding product 1,2-diphenylacetylene (**125**) is accompanied by biphenyl and 1,4-diphenyl-1,3-butadiyne (**126**) arising from iodobenzene or phenylacetylene homocoupling reactions, respectively (Scheme 54).⁴¹⁴ Although DMF and polar solvents are more suited in homogeneous phase to promote the Sonogashira reaction, by using this solvent at 150 °C in the presence of Au/CeO₂ as catalyst complete conversion of iodobenzene after 24 h was seen, yet leaching of gold from the solid to the solution was noticed. The occurrence of leaching is always detrimental for the long-term stability of the solid gold catalyst. To avoid leaching, the preferred experimental conditions made use of *o*-xylene as solvent with 5% mol Au and 1:1 molar ratio of

Table 16. Suzuki–Miyaura Cross-Coupling Catalyzed by Polymer-Stabilized Au NPs in H₂O (Selected Examples)

$\text{Ar-X} + \text{Ar'-B(OH)}_2 \xrightarrow[\text{H}_2\text{O, 4 h}]{\text{Au/PATP (0.05\% mol), KOH (8 equiv)}}$		yield (%)
Aryl halide	Arylboronic acid	
		95
		91
		82
		90
		56

Scheme 54. Product Distribution Observed for the Reaction of Iodobenzene and Phenylacetylene Promoted by Au(I) or Au(III) Catalysts



iodobenzene with respect to phenylacetylene. Comparison of the results for the Sonogashira coupling using Au/CeO₂ as catalyst with the catalytic behavior of metallic complexes of Au⁺ with Ph₃P and imine ligands, as well as Au³⁺ with Schiff bases, has allowed concluding the specificity of the Au sites promoting either the Sonogashira cross-coupling (as Au⁺) or phenylacetylene homocoupling (as Au³⁺). The reactions can be carried out in xylene at 130 °C using K₃PO₄ as base. It is notable that homogeneous Au(I) Sonogashira coupling is well-known,⁴¹⁵ whereas organogold complexes smoothly couple with alkynes, yet in the presence of Pd(II).⁴¹⁶ A recent study⁴¹⁷ sheds light on the puzzling question of the Au-catalyzed Sonogashira coupling under homogeneous conditions. The active catalytic species as proven by experiments and theory are trinuclear cationic gold clusters [Au₃L⁶⁺]⁺, where L is a biphosphine ligand.

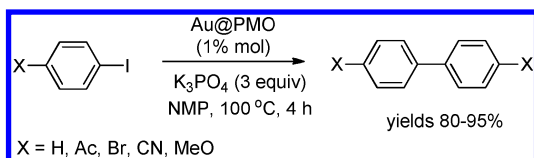
Following Corma's work, it was reported that Au/SiO₂ (3% mol) provide efficiently the Sonogashira coupling to a series terminal alkynes and aryl iodides in DMF under microwave irradiation.⁴¹⁸ Apart from ionic gold, Lambert and co-workers⁴¹⁹ found that Sonogashira coupling between phenylacetylene and iodobenzene takes place on an extended Au(111) surface under vacuum. The same group^{420,421} reported

immediately after that several supported Au NPs are selective in the above-mentioned Sonogashira coupling reaction. Au/La₂O₃ exhibited the best catalytic properties compared to other Au NPs on various supports (e.g., γ -alumina and BaO). On the basis of XPS and TEM analysis, it was proposed that the active catalytic species is Au(0) and not ionic gold. The strong promoting effect of lanthanum oxide on Sonogashira selectivity was tentatively ascribed to hydrogen spillover from the metal to the support. Although certainly the above results indicate that supported Au catalysts have some activity for C–C coupling reactions, it is clear that, from the practical point of view, additional catalysts still need to be developed and that at the present Pd is by far the metal of choice for these transformations.

7.3. Ullmann Coupling of Aryl Iodides

An unexpected catalytic activity of gold nanoparticles supported on a bifunctional periodic mesoporous organosilica (Au@PMO) was recently described in the Ullmann-type coupling of aryl iodides (Scheme 55).⁴²² This observation arose in an

Scheme 55. Ullmann Coupling of Aryl Iodides Catalyzed by Au@PMO



attempted etherification reaction among iodobenzene and phenol, which produced biphenyl instead. PMO is similar in structure to periodic mesoporous MCM-41 aluminosilicate, but they contain organosilanes as building units. The reaction is applicable to aryl iodides, while the corresponding bromides are highly unreactive. By using 1% mol of catalyst and 3 equiv of K₃PO₄, a series of aryl iodides afford, upon heating for 16 h at 100 °C (NMP as solvent) under air, the symmetrical biaryls in 80–95% yield.

7.4. Role of Palladium in C–C Bond-Formation Reactions Promoted by Supported Gold Catalysts

The accepted mechanism for many Pd-catalyzed C–C coupling reactions involves the oxidative addition of Pd⁰ atoms or complexes to C–X bonds. Data using organometallic Au complexes indicate that Au⁺ species are reluctant to undergo oxidative additions. On the basis of these data from homogeneous catalysis, the fact that supported gold catalysts can promote C–C couplings and, in particular, the Sonogashira coupling mentioned previously in section 7.2 has also been recently questioned.^{423,424} It has been proposed that, for this reaction, gold is not the real active metal promoting the C–C Sonogashira coupling⁴²⁵ but rather the palladium impurities that unavoidably are present accompanying gold in ppb levels. High-purity HAuCl₄ can contain Pd in concentrations about 3 $\mu\text{g} \times \text{g}^{-1}$, and lower qualities of HAuCl₄ can contain comparatively much higher concentrations above 1000 $\mu\text{g} \times \text{g}^{-1}$ of Pd and other metals. In fact, Cu is among the most abundant impurities present in HAuCl₄ samples. This proposal of Pd impurities as being responsible for the attributed catalytic activity of Au follows the finding that some of the reports describing Fe³⁺ as active to promote C–C coupling reactions were in reality due to the presence of Cu impurities in the Fe salts used, as revealed by the lower catalytic activity observed

when high-purity Fe salts were used as precursors.^{426,427} In this controversy, it is pertinent to remind that, because of their chemical inertness, Au can be obtained in higher purity than other transition metals and the concentration of impurities can be comparatively low.

To address this important issue of the role of Pd impurities on the catalytic activity, several Au/CeO₂ samples with known percentages of Pd in the ppb range were prepared and the initial reaction rate for the Sonogashira coupling of PhI and PhC \equiv CH in DMF was plotted against Pd concentration present in the Au/CeO₂ catalysts (Figure 1).⁴²⁸ It was

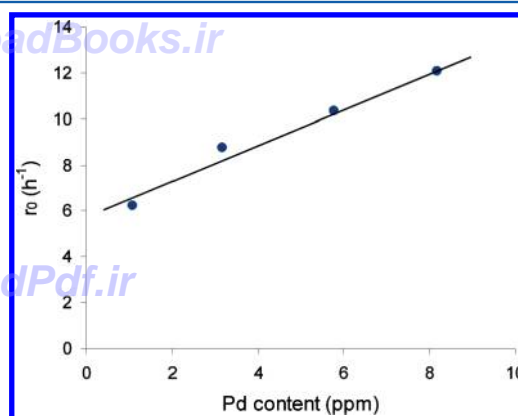


Figure 1. Plot of the initial reaction rate (r_0) for diphenylacetylene formation from Sonogashira coupling, as a function of Pd impurities in the presence of Au/CeO₂. Reprinted with permission from ref 428. Copyright 2011 Royal Society of Chemistry.

determined that extrapolation to a zero Pd concentration of the best linear fit of the experimental data indicates that above 80% of the catalytic activity for the Sonogashira coupling of the Au/CeO₂ starting with the highest HAuCl₄ purity should be attributed to Au.

7.5. Catalysis of Au NPs versus Au Complexes for C–C Couplings

One interesting point to be commented is the difference in the catalytic activity between Au complexes characteristic of homogeneous catalysis and Au nanoparticles. In the latter case, the presence of a surface of Au atoms that can cooperate and contribute to the overall mechanism by adsorbing simultaneously more than one substrate and reagent molecule in close vicinity can open new reaction pathways that are not available for monometallic Au complexes in which most of the coordination positions around the Au atoms are already compromised by the complex ligand. For this reason, the catalytic activity of nanoparticles arises from the low coordination of surface gold atoms compared to the gold atoms in the interior of the particle.

Another aspect to be considered when comparing the catalytic activity of Au complexes and supported Au nanoparticles is the possibility that the complexes act as precursors of colloidal Au NPs that will develop during the initial stages of the reaction. In fact, stability of gold complexes under the reaction conditions has frequently not been checked and the observation of induction periods in some C–C coupling reactions can be explained as the time required for development of some Au nanoparticles that can be the real catalysts.

7.6. Theoretical Calculations of C–C Coupling-Reaction Mechanism

Compared to the vast number of reports providing experimental data about the catalytic activity of supported Au NPs, the list of theoretical studies aimed at providing a deeper and detailed understanding on the reaction mechanism is considerably much limited. Considering the current stage of development in heterogeneous gold catalysis and the fact that there are several controversial issues regarding the role of the support, the optimal number of gold atoms in the NP, the appropriate range of particle size and particle morphology, the state of charge density of the active sites, and so on, there is an urgent need for gaining insights from computational chemistry. Theoretical calculations and modeling are powerful tools that should be applied systematically to shed light into the reaction mechanisms and to clarify the obscure points remaining in gold catalysis. We have already commented on some relevant calculations about dihydrogen activation in section 5.

One example of the type of information that can be obtained from quantum chemistry that is relevant for the present section is the study of the homocoupling of phenylboronic acid on naked or partially oxidized Au₃₈ NP.⁴²⁹ The aim of this study was to determine the role of cationic gold species and adsorbed oxygen on the homocoupling. As commented earlier in section 7.1, one of the intriguing facts of this C–C bond-forming reaction is the need of oxygen, since the yield in its absence is considerably reduced and the process becomes quasi-stoichiometric from the point of view of gold. Calculation of the adsorption energy of phenylboronate indicates that this anion should be preferentially adsorbed on neutral gold atoms rather than in positive Au^{δ+} sites. After adsorption on gold, dissociation of the C–B bond with a low activation energy (estimated as 6.5 kcal × mol^{−1}) leads to boric acid and a phenyl group strongly bonded to low-coordinated gold atom. Figure 2 shows the geometries and energy profile of the various states considered for this reaction. Two possibilities with similar high activation energy were considered for the transition state leading to biphenyl, i.e., coupling of two phenyl groups located either on the same gold atom at a corner of the Au₃₈ cluster or located on two neighbor gold atoms. The fact that the energy of these two transition states is high (>30 kcal × mol^{−1}) was taken as an indication that positively charged gold atoms should intervene at this stage, lowering this barrier. Thus, calculations based on the partially oxidized Au₃₈ NP give 6.5 kcal × mol^{−1} as the activation energy, making the coupling feasible.

According to this view, the role of oxygen is the generation of partially oxidized (positive) gold clusters. Previous calculations have indicated that molecular oxygen adsorption on gold clusters or the interaction of gold with the surface oxygens of TiO₂ generates a positive charge density on the gold cluster due to inductive and polarization effects.⁴³⁰ It must be stressed that the cationic gold species existing in the models are not Au³⁺ ions but rather Au^{δ+}. These positive clusters are generated by removing electrons from the whole clusters and the positive charge distributes throughout all Au atoms in various charge densities depending on the coordination of the gold atom. As has been indicated, one characteristic of Au NPs with respect to molecular Au complexes is delocalization of the electron vacancy in the cluster.

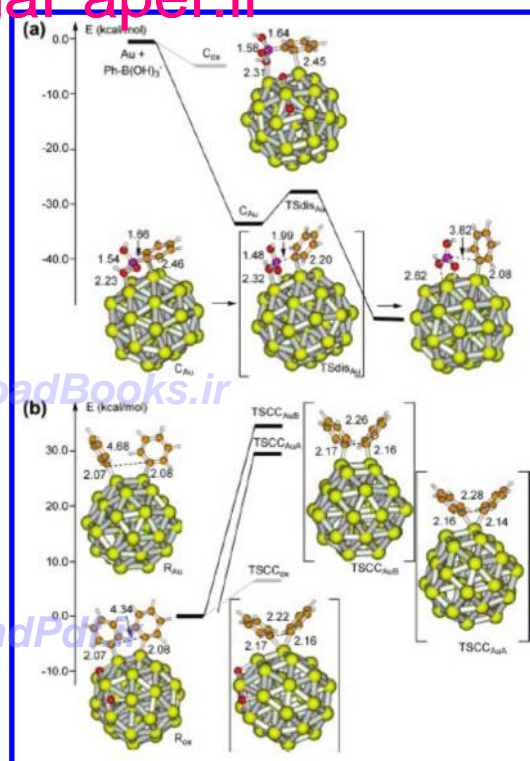


Figure 2. Calculated energy profiles for (a) dissociation of PhB(OH)₃ anion and (b) coupling of two phenyl fragments yielding biphenyl on a naked Au₃₈ nanoparticle (black line) and on a partially oxidized Au₃₈ nanoparticle (gray line). The optimized distances are given in Å. Reprinted with permission from ref 429. Copyright 2011 Elsevier.

8. CONCLUDING REMARKS AND FUTURE PROSPECTS

It is widely accepted that supported Au NPs are among the most active and general catalysts for the aerobic oxidations of alcohols. The purpose of the present review has been to summarize the reports describing the catalytic activity of supported Au NPs for other organic reactions beyond oxidations. Data have been presented showing that, following the lead of homogeneous Au catalysts, supported Au NPs can also be extremely active and selective in promoting some complex organic transformations, paradigmatic examples being the rearrangement of *ω*-alkynylfurans to phenols and the benzannulation of *o*-ethynyl benzaldehydes, two nonintuitive processes that can hardly have been included in retrosynthetic analyses. Considering that Au NP catalysts can be manipulated at the open air, under ambient conditions, and that they are not sensitive to moisture and can be prepared reproducibly, it can be easily anticipated that their use in organic synthesis will experience a rapid growth as they are becoming commercially available. As the application of gold catalysis in organic synthesis is still in its infancy, it can easily be foreseen that supported Au NPs can promote more rearrangements, C–X couplings, and cycloadditions that those that have been currently uncovered, and further work is expected in this area.

In this context, one surprisingly underdeveloped field is the heterogeneization of successful gold complexes by covalent anchoring of suitable derivatized ligands on insoluble solids. This strategy will allow the recovery and reuse of these complexes generally containing expensive ligands and the possibility to use them under continuous-flow operation. These types of heterogeneous Au catalysts would widen the scope of Au catalysis in organic synthesis to any reaction promoted by

soluble Au complexes. The key issue for the anchoring of an Au complex on a support should be the stability of the complex under operation under the reaction conditions.

Theoretical calculations and modeling are urgently needed in the field of heterogeneous Au catalysis to shed light on various aspects including the structure of the active sites and the influence of partial charge on Au NPs, the role of the nature of the supports, the different catalytic activity depending on the crystallographic phases, and the most likely reaction mechanism. There is no doubt that the development of Au catalysis in organic synthesis will be a large benefit by complementing the experimental work with computational calculations.

From the point of view of catalyst preparation, there is a need for innovative preparation procedures aimed at reducing the Au particle size to the point of defined, uniform clusters and also to prepare samples with the optimal NP morphology. Control at the atom-by-atom level of the size and morphology of the clusters will represent a real breakthrough in the area of catalyst preparation and would allow becoming closer to experimental work and theory.

The role of impurities in transition metal catalysis and Au NP in particular should be addressed to firmly determine the intrinsic activity of Au NPs. Perhaps in this point the most important developments will be the preparation of nanoalloys and structured core-shell bimetallic catalysts in which the activity found for Au is boosted and fine-tuned by the presence of some other metal in the appropriate percentage and in the most adequate spatial configuration. The very limited examples already reported for alcohol oxidation have clearly shown the enormous potential of this field. In view of the above comments, there is no doubt that the importance of supported gold nanoparticles as heterogeneous catalysts for organic transformations will undergo a burst in the near future, and it will continue to be an active research front in chemistry.

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Notes

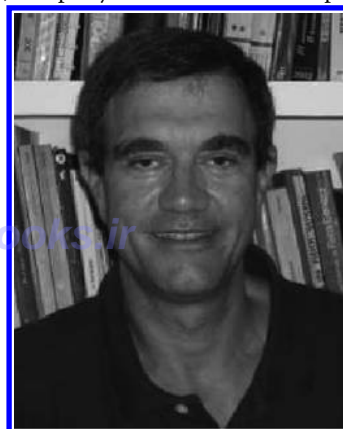
The authors declare no competing financial interest.

Biographies



Manolis Stratakis studied chemistry at the Aristotle University of Thessaloniki, Greece. After obtaining a Ph.D. from the University of Crete (Greece) in 1991 and performing postdoctoral studies at the University of California at Berkeley and UCLA, he joined the faculty at

the Department of Chemistry, University of Cyprus. In 1999 he moved to the Department of Chemistry, University of Crete, where he is currently a full professor. His recent research interests focus on novel catalytic applications of supported gold nanoparticles in organic transformations, and partly in biomimetic natural product synthesis.



Hermenegildo García is full Professor at the Technical University of Valencia in 1996 and staff member of the Instituto de Tecnología Química, a joint center of the Technical University of Valencia and the Spanish National Research Council. He made postdoctoral stays at the University of Reading with Professor Andrew Gilbert and several sabbatical leaves in the group of Professor J. C. Scaiano at the University of Ottawa. Prof. Garcia has been active in the field of heterogeneous catalysis working with porous catalysts and nanoparticles, has published over 450 papers, and has filed over 25 patents, two of them in industrial exploitation. Prof. Garcia is Doctor Honoris Causa from the University of Bucharest and the recipient of the 2011 Jussieu Prize awarded by the French Royal Society of Chemistry and the 2008 Alpha Gold of the Spanish Society of Glass and Ceramics.

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