CHEMICAL REVIEWS

REVIEW

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Gold-Catalyzed Carbon−Heteroatom Bond-Forming Reactions

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CONTENTS

1. INTRODUCTION

After the long-held assumption of the unreactivity of gold, numerous reactions catalyzed by this noble metal have been increasingly emerging in the literature over the past 2 decades.[1−3]

The majority of these reactions are based on the propensity of gold to act as a soft and carbophilic Lewis acid in the activation of carbon−carbon π-bonds,[4] thus allowing the formation of C−C, C−O, C−N, and C−S bonds by nucleophilic attack on these activated multiple bonds. Computed enthalpies of formation (as well as selected structural parameters of optimized structures) of complexes formed between an alkyne and different electrophiles (Brønsted acids, iodine, iodonium compounds, gold and silver complexes) confirm that the binding energies of complexes formed with gold catalysts are the strongest one, so that gold can be considered as one of the most powerful activators of a carbon−carbon triple bond. In this respect, gold has revealed

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itself as alkynophilic, but not as oxophilic as most Lewis acids, and this brings a true advantage to the chemists in the sense that oxygen, water, and alcohols are often well-tolerated in sharp contrast to most air- and moisture-sensitive Lewis acids or transition-metal transformations.[5]

However, this superiority of gold to induce the π-activation is not the only factor responsible for its activity and effectiveness, but also the good functional group compatibility that has been shown in a number of important reactions, such as methatesis, cycloisomerization reactions of enynes and related substrates, and hydrofunctionalization of alkenes, alkynes, allenes with carbon−heteroatom nucleophiles. Moreover, besides activation of C−C multiple bonds, other functional groups, such as carbonyls, imines, are also activated through coordination with gold, providing an useful and important method for facilitating many different organic transformations with high atom efficiency. In accordance with these premises, gold catalysis has been used as the key step in the synthesis of natural products and as a powerful tool for cascade or domino reaction processes.[6]

Besides this, it is important to remark that the intermediates involved in gold-catalyzed transformations have a nonclassical carbocation or carbenoid feature (they are not classical carbocations), and this point often leads to well-controlled product selectivity.[5] An additional characteristic is that carbon−gold bonds are labile toward protodeauration but not susceptible to β-hydride eliminations, which is something that frequently occurs in other transition-metal-catalyzed reactions (vs with palladium), and this also contributes to increase the product selectivity for certain reactions.

Furthermore, Au-catalyzed reactions can often occur efficiently using gold with oxidation state +1 and +3.[7a] In many transformations, gold catalysts do not need any other ligand to exert their catalytic activity, being active in extremely small amounts.

Besides all the above-mentioned possibilities, gold can also accomplish nucleophilic substitutions, so that it can activate, for instance, a propargyl alcohol through coordination.[7b] This reaction proceeds under very mild conditions (dichloromethane, room temperature) with a commercially available gold catalyst, giving water as the only byproduct. In general, these types of nucleophilic substitutions have been traditionally carried out using the Nicholas reaction, which presents some limitations, since cobalt protects the triple bond, it involves several steps, and requires stoichiometric amounts of the metal complex $[Co_2(CO)_8]$.[7c−e] In this case, gold catalyzes the propargylic substitution with various C-, O-, and S-nucleophiles and simultaneously acts as a Lewis acid and as a transition metal, so that no other metal complex is needed to catalyze the reaction.

With respect to redox reactions, it is important to notice that despite both gold oxidation states, i.e. Au(I) and Au(III), being stable, there are few examples where Au(I) participates in a redox-based processes involving both oxidation states. In fact, the high oxidation potential of Au(I) to Au(III) allows most Au(I)-catalyzed reactions to proceed in the presence of air, this being an important issue for chemical applications. Anyway, it has been reported that gold can substitute for palladium in reactions where redox catalytic cycles are involved, such as C−C coupling reactions, even supported on solids.

With respect to heterogeneous catalysts based on gold nanoparticles, they are very active and selective for a broad range of redox reactions.[8a] Although primarily known as active and selective for oxidation reactions,[8b−d] gold nanoparticles are also highly efficient for selective hydrogenation.[8e−i] Moreover, the tendency of gold(I) and gold(III) species in many homogeneous systems is to precipitate with time, in particular gold(III), which suggests that supported gold nanoparticles are more stable catalytic systems.

Beyond all these chemical benefits, gold is more abundant than platinum, palladium, rhodium, and other metals that are largely used as catalysts, and their stoichiometric technical applications, in addition to the production in mines every year, is an incentive to use gold instead of Pt or Rh, provided that the adequated gold-based catalyst can be prepared.[9]

The rapid development of gold catalysis in the past decade has not been widely extended to enantioselective catalysis, and few examples of enantioselective gold catalysis have been reported.[10] One reason for this relies on the trend of gold(I) to form linear two-coordinate complexes, in which the reacting substrate is positioned far from the potential source of chirality. This problem associated with substrate−ligand proximity gets worse if one takes into account the outer-sphere nature of the π-activation in some cases, which bypasses nucleophilic interaction prior to C−X formation. The preferred linear coordination mode of gold(I) also precludes approaches based on bidentate coordination of chiral bis(phosphines) and related ligands that have become the cornerstones of enantioselective catalysis employing four-, five-, and six-coordinate transition-metal complexes.

This challenge has been approached by looking for new strategies from the point of view of ligand construction (identification of enantiomerically pure bis(gold)−phosphine complexes of the form $[(AuX)_2(P-P)]$ as well as the recognition of the pronounced effect of the counterion on the efficiency and selectivity of these transformations).[10f−i] In accordance with this, since 2005, the number of examples of enantioselective gold(I)-catalyzed transformations has increased markedly.[10]

In the future, the pursuit of an organic ligand able to tune the acidity and/or redox features of the coordinated metal atom will be the key to design a highly selective gold metal based complex. The punctual hardness at the gold atom will depend on the hardness−softness of the ligand considered as a base. The harder the ligand, the harder the gold atom in the complex will be, and a rational design of the catalyst for specific reactions could, in principle, be achieved.

2. AIMS AND SCOPE OF THE REVIEW

Given the tremendous impact of gold catalysis in the past decade, many reviews have appeared in the last years, covering different aspects. Nowadays, one or two publications *per day* on gold-catalyzed processes appear in the literature. This fast development of gold catalysis hampers efforts to summarize every new single transformation in one report. The last comprehensive reviews on gold catalysis cover until 2007[1−3] and, despite their interest, the ability of gold to catalyze the formation of carbon−heteroatom bonds[10e] has not been specifically covered nor related with the behavior of other metal catalysts. Therefore, we will review here and will put in perspective gold-catalyzed transformations involving any carbon−heteroatom bond formation with special emphasis on those that have been reported since the end of 2007 up to now.[10j]

The review has been primarily organized from the point of view of the formation of different carbon−heteroatom (oxygen, nitrogen, sulfur, silicon, etc.) bonds, no matter the type of gold

catalyst that is involved in the reaction. In fact, the reader will find that different gold complexes with different oxidation states of gold have been used to catalyze the same reaction. Further subdivision has been focused on the type of functional group or final substrate class formed by the gold catalysis activation. We hope this review will be useful to readers interested in reactions involving C−heteroatom formation and lead to (1) an understanding of the ability of gold to produce known and new compounds, (2) a comparison of the new gold-catalyzed procedures with those well-known and others possible, and (3) application of the gold-catalyzed process for obtaining target products of interest. In this respect, we also include the last applications of gold catalysis in the synthesis of natural products, since we think that gold catalysis will become a regular tool in organic synthesis in the next years.

The reactions compiled in this revision include oxidations, isomerizations, additions, substitutions, cyclizations and, in general, any gold-catalyzed reaction that generates a new carbon−heteroatom bond, regardless of the procedure. The oxidation of amines to give imines as well as C−O forming reactions (derived from oxidation of alcohols) has been included, while carbon monoxide oxidation and hydrogenations have not been specifically considered.

When possible, intra- and intermolecular processes have been conveniently separated and both homogeneous and heterogeneous catalysts are discussed. Since modern catalysis needs to be embedded into sustainability criteria, those processes where the catalyst can be recovered and recycled have been highlighted.

3. FORMATION OF CARBON−HALOGEN BONDS

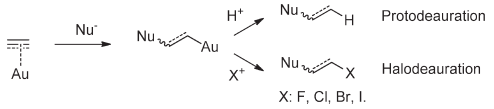
The formation of new carbon−halogen bonds via electrophilic addition to unsaturated carbon−carbon bonds is a classical process in organic synthesis, since the direct radical substitution of alkanes is difficult to control.[11] For instance, the obtention of haloalkanes from alkenes and HX or X_2 are well-known processes.[12] They follow Markovnikov's rule, and polyhalogenation is obtained in the case of alkynes. As it was early shown, gold catalysis is a powerful tool for controlling the chlorination of alkynes to obtain vinyl chlorides.[13] During the period covered by this review, this process has been improved. Furthermore, it has been reported that the formation of the four different C−X bonds (X = F, Cl, Br, I) from unsaturated C−C bonds can be made by using a final halodeauration (instead of a protodeauration) step at the end of the catalytic cycle, for a given gold-catalyzed reaction. In other words, releasing the gold atom bonded to a carbon bond with a source of cationic halogens instead of protons allows easy carbon−halogen bond formation (Scheme 1). These two strategies constitute the basis of the reactions shown below.[14,15]

3.1. Formation of Carbon−Fluoride

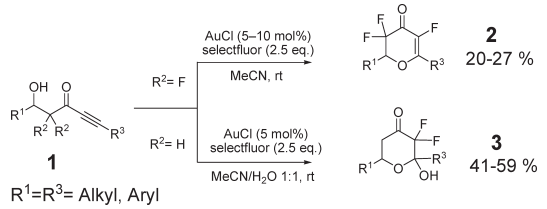
The first gold(I)-catalyzed hydrofluorination of alkynes was reported in 2007.[16] The addition of fluoride resulted in trans-hydrofluorination products. Since then, other gold-catalyzed C−F bond formations have been reported. Gouverneur and co-workers[17] have reported the gold(I)-catalyzed alkoxyhalogenation, including fluorination, of hydroxydifluoroynones **1** (Scheme 2). Trifluoro- and difluorooxocarbocycles **2** and **3** were obtained in low to moderate yields together with other byproduct.

Miller and co-workers[18] reported later the direct Au-catalyzed hydrofluorination of a range of functionalized alkynes having a carbonyl functionality as directing group. The presence of these groups allows achieving a good conversion and regioselectivity to the *Z*-vinyl fluoride.

Scheme 1



Scheme 2



3.2. Formation of Carbon−Chloride

The first gold-catalyzed hydrochlorination of alkynes was reported in 1976.[19] However, the seminal work by Hutchings,[13] namely a gold-supported catalyst for the hydrochlorination of acetylene with HCl to produce vinyl chloride monomer (VCM), is probably the most important finding in this area and is still being revisited.[20] For instance, gold-based bimetallic catalysts have been described,[21] showing that undoped Au seems to be the catalyst of choice. Thus, Wang and co-workers[22] have studied the kinetics of acetylene hydrochlorination over bimetallic Au−Cu/C catalysts, by both theoretical and experimental methods. Conversions and selectivities >99 % were reported. In addition, studies on the reactivation of a carbon-supported gold catalyst have been reported.[23] Deactivation is considered to be due to reduction of active Au^{3+} species to Au^0, which is reoxidized by treatment with aqua regia.

One of the most important reactions in gold-catalyzed chemistry is the cycloisomerization of substituted unsaturated bonds, in particular alkynes and allenes. In this sense, Gevorgyan and co-workers[24] have reported several metal-catalyzed 1,2-shifts of diverse migrating groups in allenyl systems, including the gold(III)-catalyzed 1,2-halogen migration/cycloisomerization of allenyl derivatives **4** to form halofurans **5** (Scheme 3). However, only one example of chloride derivative was given, in moderate yield.

Remarkably, Wang and co-workers[25] have reported a general Au-catalyzed halogenation of aromatics by *N*-halosuccinimides, including *N*-chlorosuccinimide, and the procedure will be discussed in detail in the next section. In another work, Barluenga and co-workers[26] have reported that gold or platinum can catalyze a tandem process from alkynol derivatives, where the final intermediate can be trapped with CH_2Cl_2, leading to chloro-substituted, oxygen-containing [3.3.1]bicyclic compounds. Gold(III) halides, particularly chloride and bromide have been successfully used in substoichiometric amounts for the head-to-head dimerization of difluoropropargyl amides.[27] The gold salt acts as both catalyst and halogenating agent. Finally, Hashmi and co-workers[28] have performed the direct halogenation of styryl-gold intermediates with NCS to obtain *E*-chlorostyrene in

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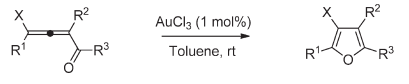
Scheme 3



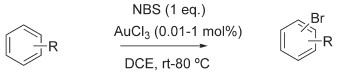
4

a) X= Cl; R^1= $(CH_2)_2OTBS$, R^2=R^3= Ph
b) X= Br, I; R^1= H, Alkyl, R^2=R^3= H, Alkyl, Ph

5

a) 48 %
b) 61-97 %

Scheme 4



6

R= Me, OMe, CO_2Me, Cl, F, $-OCH_2O-$

7

80-99 %

excellent yield. The gold compound is used in this case in stoichiometric amounts.

3.3. Formation of Carbon−Bromide and Carbon−Iodide

No gold-catalyzed hydrobrominations or hydroiodinations have been reported yet. However, other gold-catalyzed methods allow the formation of C−Br and C−I bonds. As above-commented, Wang and co-workers[25] have reported a general Au-catalyzed halogenation of aromatics by *N*-halosuccinimides. The work mainly uses *N*-bromosuccinimide as halogen source (Scheme 4).

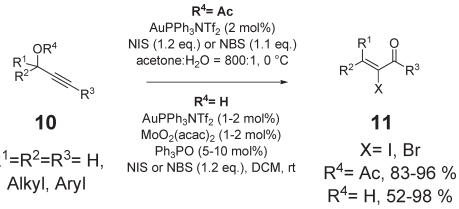
Yields were excellent and good regioselectivies were found in many examples. Moreover, the process is suitable to engage palladium-catalyzed reactions. Thus, sequential transformations were carried out after the halogenations of the aromatics, including the Suzuki−Miyaura cross-coupling, the Miyaura borylation, or the Sonogashira coupling. The succinimide fragment can also be incorporated using Cu(0) as catalyst under microwave conditions at high temperature.

The above-commented method by Barluenga and co-workers[26] provided one example of formation of bromo-derivative oxygen-containing bicycles. It is a common formation of new C−Br and C−I bonds by the same gold-catalyzed method. For instance, the gold(I)-catalyzed fluorohalogenation of hydroxydifluoroynones **1** (see Scheme 2 above), reported by Gouverneur and co-workers,[17] was also used for the obtention in good yields of vinyl iodides and bromides **9** (as **2**, but Br or I atoms instead of F atom on the alkene).

As has been seen above, it was possible to obtain iodo- and bromofurans **5** in good yields from allenyl derivatives **4** by a gold(III)-catalyzed 1,2-halogen migration/cycloisomerization (see Scheme 3),[24] while *E*-iodo- and bromostyrene were obtained in excellent yields from stoichiometric amounts of styrylgold intermediates with NIS or NBS.[28]

Zhang and co-workers[29,30] have designed a gold(I)-catalyzed preparation of linear α-iodo and bromo enones **11** from propargylic compounds **10** (Scheme 5), and the previous methodology[29] involving 1,3-migration of the propargyl acetate and later hydrolysis to obtain the α-haloenone was improved[30] by using a combination of two catalyst, the same gold(I) complex and

Scheme 5



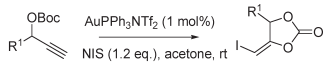
10

R^1=R^2=R^3= H, Alkyl, Aryl

11

X= I, Br
R^4= Ac, 83-96 %
R^4= H, 52-98 %

Scheme 6



12

R^1= Alkyl

13

35-76 %

a molybdenum compound, which allows directly reacting the propargyl alcohol and avoiding the need for preparing the ester.

Concerning the obtention of new C−I bonds exclusively, Gagosz and co-workers[31] have reported the synthesis of *Z*-iodomethylenedioxolanones **13** in moderate yields (Scheme 6) during their work on gold(I)-catalyzed rearrangement of propargylic *tert*-butyl carbonates (see Scheme 87, carbonate formation).

Later, Krause and Gockel[32] also reported a similar procedure for the cyclization of β-hydroxyallenes, in the presence of NIS, but using AuCl or $Ph_3PAuCl/AgBF_4$ as catalysts. The reaction is extremely fast (less than 1 min reaction time), working at room temperature. Unfortunately, yields are still moderate (<70%). The so-obtained iododihydropyranes can subsequently react in a Pd-catalyzed coupling and in an Au-catalyzed cyclization to give access to furopyrans. In a related way, a recent patent claims the direct iodination of nonactivated aromatic and heteroaromatic compounds with I_2, catalyzed by gold(III)−pyridine complexes in the presence of base.[33]

4. FORMATION OF CARBON−OXYGEN BONDS

The carbon−oxygen bond is, after C−H and C−C bonds, the most widespread type of bond in nature. Gold catalysis is playing an important role in the development of new methodologies to form C−O bonds in more convenient ways. Cationic gold is a soft Lewis acid in the third row of the periodic table that, furthermore, experiences relevant relativistic effects over its 6s valence electron. This makes gold a high π-acid with a low oxyphilicity,[34,35] and consequently, cationic gold can activate unsaturated C−C bonds in the presence of H_2O, alcohols, or any other oxygen-containing functionality. Once the carbocationic species is generated, the nucleophilic oxygen couples to form the new C−O bond.

4.1. Formation of Alcohols

Activation of C−H bonds to form C−OH bonds is of paramount importance in organic chemistry and the direct formation of alcohols from alkanes is performed in industry. For instance, cyclohexanol is produced by the oxidation of cyclohexane in air, typically using cobalt catalysts. However, significant amounts of ketone are coproduced. This can be avoided in particular cases such as, for instance, the selective oxidation of alkanes to tertiary

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alcohols with ozone over silica gel at −78 °C.[36] Unfortunately, the low temperature of the reaction and the high amounts of silica needed make this reaction difficult to scale-up. Different catalysts have been described for this free-radical hydroxylation, including an Fe(III)−phorphirin that allows moderate levels of enantioselectivity by using iodosylbenzene as oxidant of secondary carbons.[37] Nevertheless, the search for selective alkane hydroxylation methods is still a matter of interest. It will be shown that gold-supported nanoparticles have provided interesting results in the last years. In another way, the formation of alcohols from alkenes and H_2O is a process that requires highly acidic conditions (e.g., H_2SO_4 or strongly acid zeolites[38a]), and for preparative laboratory uses, indirect methods such as a hydroboration−oxidation route are frequently preferred. Alternatively, hydration of alkenes under mild conditions[38b] has been achieved by using the so-called oxymercuration process (addition of mercury and oxygen in Markornikov's fashion followed by in situ reduction with $NaBH_4$). However, this process does not follow the environmental standards currently required for organic transformations. In this sense, gold catalysis has provided new environmentally benign synthetic methodologies for the obtention of alcohols from alkynes and allenes by simple addition of H_2O, by intramolecular oxygen rearrangements, and by combination of both (H_2O as external oxygen source and later rearrangement of the C−O bond thus formed). In many cases, unprecedented transformations have been found, leading to new synthetic methods. The "phenol synthesis" reported in 2000 by Hashmi and co-workers[39] is a clear example. The last advances on this reaction since 2008, together with other methods appeared during the same period based on the transformations commented above, are shown in this section.

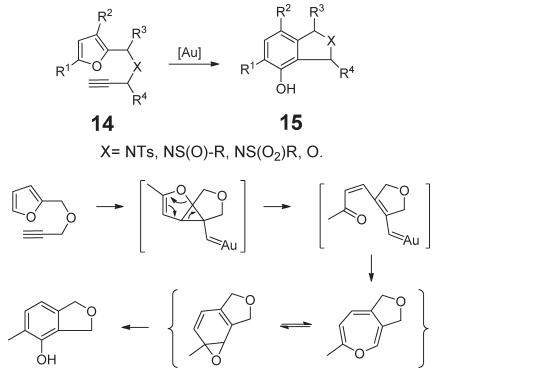
4.1.1. Heterogeneous Catalysis for C−OH Formation: Direct Hydroxylation of Alkanes. The first studies on the direct oxidation of cyclohexane to cyclohexanone and cyclohexanol were reported in 2004.[40,41] Recently, cyclohexane has also been oxidized to cyclohexanol and cyclohexanone using Au NPs (size 3−8 nm) uniformly located on the walls of SBA-15.[42] In contrast, some authors have got evidence that the oxidation of cyclohexane over different Au-supported catalysts is not a heterogeneous catalytic process but proceeds through metal dissolved or even by a radical-chain mechanism, well-known from autoxidation.[43] Thus, gold may not act as catalyst for producing cyclohexanol and cyclohexanone. In fact, important amounts of different acids are apparently formed.

In another approach, a mesoporous silica containing well-dispersed gold nanoparticles on the walls acts as a reusable catalyst for the oxidation of *n*-hexadecane to a regioisomeric mixture of alcohols.[44] Furthermore, the oxidation of methane to methanol has been achieved by using a gold-supported catalyst[45] and electrochemically.[46]

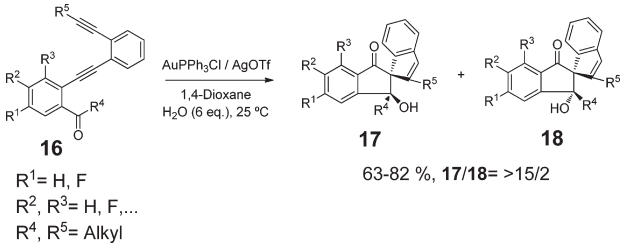
4.1.2. Intramolecular C−OH Formation. The formation of phenol **15** from furan **14** using gold catalysts (phenol synthesis, Scheme 7), originally reported by Hashmi and co-workers,[39] is already considered a "classical" reaction that can be carried out with both homogeneous[39a] and with solid gold catalysts.[39b]

The same authors have widened their studies, achieving success for propargyl-*N*-tosyl derivatives (X = NTs),[47−49] propargyl chiral sulfoxides [X = NS(O)R or NS(O_2)R],[50] and propargyl ethers (X = O).[48,51] Mechanistic studies based on deuterium isotopes have been also carried out.[52] Recently, Shi and co-workers[53] have applied the "triazole strategy" to the

Scheme 7



Scheme 8



Hashmi phenol synthesis, in such a way that a triazole molecule coordinates the active cationic gold center so that when the catalyst is not acting over the substrates, it relies on a more stable form than the "naked cation", avoiding decomposition to gold(0) and prolonging the catalyst life.

A particularly interesting case corresponding to substrates **14** is when the molecule contains two diastereotopic alkynyl groups. In this case, regio- and stereoselective ring-closure reactions are theoretically possible, leading to stereochemically enriched phenol derivatives. Hashmi and co-workers[54] have studied both possibilities and while highly diastereoselective ring-closure reactions with $AuCl_3$ as catalyst were achieved,[54] only moderate enantioselectivities could be obtained after exploring different chiral auxiliars.[55]

In another type of reaction, Liu and co-workers[56] have reported the formation of tricyclic spiro ketones **17**/**18** with PPh_3AuOTf as catalyst (Scheme 8). A possible mechanism involves the hydration of the triple bonds, followed by Conia-ene and aldol condensation. The gold species gives different regioselectivity for the hydration of **16** than $PtCl_2$.

Vinyl alcohols can be achieved by an intramolecular reaction between α,β-epoxy ketones and alkynes cocatalyzed by $AuPMe_3Cl$ and $Yb(OTf)_3$.[57] This new catalytic system gives novel indene derivatives in moderate to good yields under mild conditions. As will be shown (see furan formation), one of the most successful Au-catalyzed intramolecular reactions is the synthesis of furan derivatives from hydroxyl-containing alkynes, allenes, and alkenes. Recently, Krause and co-workers[58] have reported the inverse process: a regioselective ring-opening allylation of 2,5-dihydrofurans in the 2-position to get 2,6-dien-1-ols. The process needs the presence of catalytic amounts of $HAuCl_4 \cdot 3H_2O$.

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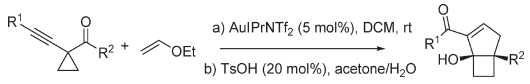
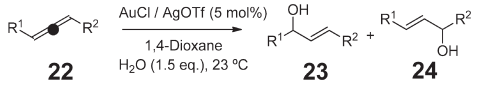
Scheme 9



19 **20** **21**

R^1= Alkyl, Aryl; R^2= H, Alkyl, Aryl — 48-98 %

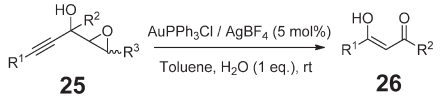
Scheme 10



22 **23** **24**

R^1, R^2= H, Alkyl, Aryl. — 25-72 % (**23**+**24**)

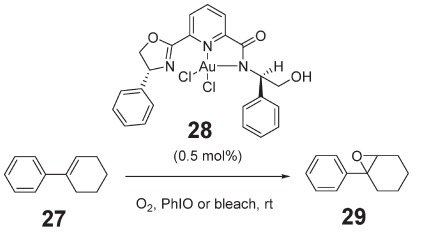
Scheme 11



25 **26**

R^1, R^2, R^3= Alkyl, Aryl. — 76-91 %

Scheme 12



28

27 **29**

53-66 %, ee 10-32 %

Scheme 13

R^1= H, R^2= H	**30**	R^1= H, R^2= H	**31**
R^1= Me, R^2= H	**32**	R^1= Me, R^2= H	**33**
R^1= Ethyl, R^2= H	**34**	R^1= Ethyl, R^2= H	**35**
R^1= Hexyl, R^2= H	**36**	R^1= Hexyl, R^2= H	**37**
R^1= R^2= -$(CH_2)_3$-	**38**	R^1= R^2= -$(CH_2)_3$-	**39**
R^1= R^2= -$(CH_2)_2$-CH=$)_2$	**40**	R^1= R^2= -$(CH_2)_2$-CH=$)_2$	**41**
R^1= Ph, R^2= H	**42**	R^1= Ph, R^2= H	**43**
R^1= Ph, R^2= Ph	**44**	R^1= Ph, R^2= Ph	**45**

4.1.3. Intermolecular C−OH Formation. Zhang and co-workers[59] have reported the Au(I)-catalyzed synthesis of bicyclo-[3.2.0]heptanes **21** in good yields from the starting materials **19** and **20** (Scheme 9).

The proposed mechanism theoretically involves up to 10 different steps, including a 1,3-dipolar cycloaddition with the ethyl vinyl ether **20** and a final acid-generated carbocation that is trapped by water, generating the final alcohol **21**. This carbocation can be trapped by others nucleophiles, including methanol, to form the corresponding methyl ether.[59]

The hydration of allenes **22** to form allylic alcohols **23**/**24** has been reported by Widenhoefer and co-workers,[60] although in moderate yields and regioselectivities (Scheme 10).

Shi and Dai[61] reported a gold-catalyzed isomerization of 1-alkynyl-2,3-epoxy alcohols **25** to the enolic form of 1,3-diketones **26** in good yields (Scheme 11).

One example can be found reporting the oxidation of allyl alcohol with molecular oxygen in distilled water in the presence of Au/C or Au/TiO_2 to form 3-hydroxypropionic acid.[62]

4.2. Formation of Ethers

Ethers can mainly be produced by environmentally convenient methods in two ways: (1) addition of alcohols to unsaturated C−C bonds[63] and (2) dehydration of alcohols.[64] For the first approach, Lewis acid catalysis is usually required, mercury cationic salts [e.g., $Hg(OCOCF_3)_2$] being the catalysts of choice. For the second approach, liquid and solid Brønsted acid catalysts can perform the reaction. Gold catalysis has been successfully applied through the two approaches described above. Within the first route, it is noteworthy to highlight the seminal work by Haruta and co-workers[65] in which propylene is oxidized to propylene oxide by using Au/TiO_2 as catalyst. Further advances of this method since 2008 will be shown in this section. The direct addition of alcohols to form allyl and propargyl ethers will be also shown. Furthermore, intramolecular additions of alcohols to alkenes, alkynes, or allenes are nicely performed with gold cationic species, competing with well-established methods such those using palladium catalysts.[66] This allows one to obtain oxygen-containing heterocycles such as furans, pyranes, and bigger *O*-heterocycles, including the different hydro-derivatives. In the second approach, simple gold salts are able to catalyze the chemoselective dehydration of alcohols to form unsymmetric ethers in water.[67]

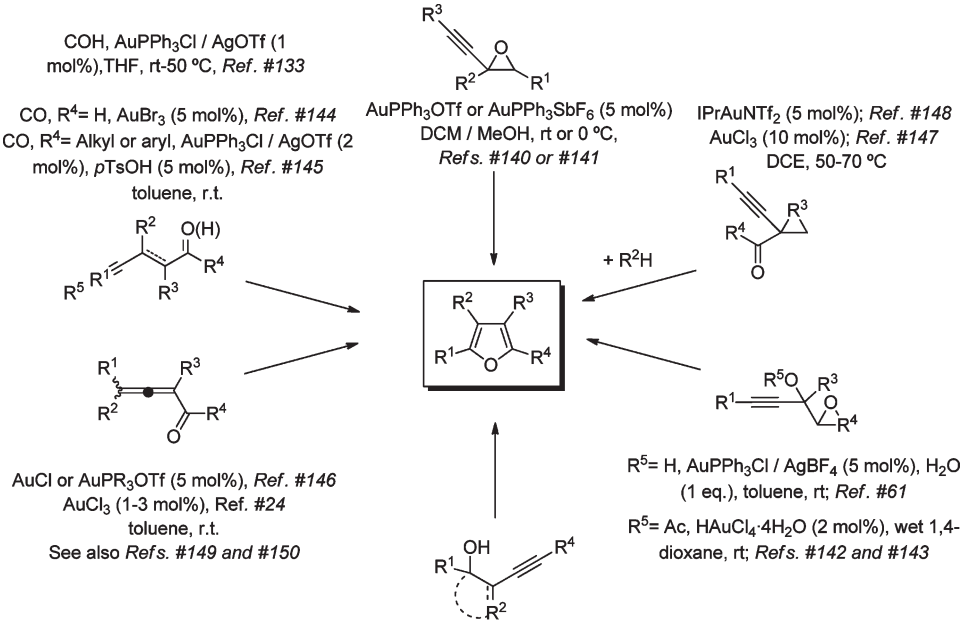
4.2.1. Cyclic Ethers. *4.2.1.1. Three-Membered Rings (Oxiranes).* The gold-catalyzed synthesis of epoxides from alkenes is usually performed on heterogeneous catalysts; however, one example on homogeneous catalysts was recently found.[68] In this work, 1-phenylcyclohexene **27** and other alkenes were transformed to the corresponding epoxide **29** in the liquid phase by using the chiral gold(III) complex **28** as catalyst, although with moderate yields and enantioselectivities (Scheme 12).

4.2.1.1.1. Heterogeneous Catalysis. As was commented before, gold-supported catalysts are commonly used to obtain epoxides from alkenes. Propene, styrene, and stilbene are mainly used; however, the epoxidation of other alkenes can also be performed (Scheme 13). Many patents for Au-catalyzed propylene epoxidation,[69−80] propylene oxide from propane,[81] styrene epoxidation,[82] and general alkene epoxidation[83−85] can be found.

The synthesis of ethylene epoxide **31** from ethene **30** with dioxygen is a commercial process with high selectivity using a supported Ag catalyst.[86] However, the use of different Au-containing solids as catalysts has also been addressed in patents. Au nanoparticles as catalysts for this reaction have been compared with the Au(111) surface by means of density functional theory.[87] Quantum mechanical computer simulations have also been performed.[88]

The synthesis of propylene epoxide **33** from propene **32** is much more complicated that the epoxidation of ethene, since the presence of allylic hydrogens hampers selectivity. The seminal work from Haruta and co-workers[65] in which propylene oxide

Scheme 14



33 was obtained from **32** by using Au/TiO_2 as catalyst is still being revisited by other authors. Haruta's group was the first to introduce H_2 as sacrifitial reductant, allowing the activation of O_2 under milder conditions.[89] The morphology of the support has been recently varied, including titania,[90−93] Ti-SBA-15,[90,94] Ti-containing hexagonal mesoporous silicas (Ti-HMS) with wormhole structure,[95] titanosilicalite (TS),[96−99] and TiO_2-SiO_2.[100] Al_2O_3 films have also been used as support.[101] A combination of H_2/O_2 is the oxidant system, although H_2O can replace hydrogen in particular cases.[91,101,102] The use of this O_2/H_2O oxidizing system is still an unresolved problem that would, if successful, greatly improve the present industrial process. In one of the recently reported works, Haruta and co-workers[102] remarkably showed the better performance of gold clusters of <2 nm compared to silver- and copper-based catalytic systems by using O_2/H_2O as oxidant of propylene. Although the yield is still very low, the selectivity was >50%. N_2O[93] or air[100] have also been used as oxidants. The role of the gold nanoparticles during the epoxidation has been studied. Spectroscopic evidence for the adsorption of propene on gold nanoparticles during hydroepoxidation has been observed,[103] and an experimental and theoretical study of the catalytic activity of soft-landed subnanometer gold clusters (Au_6-Au_{10}) has been performed,[101] as well as model calculations on the oxidation over Au(111) surfaces.[104] The role of the support on the epoxidation has also been studied. For instance, in situ Ti K-edge X-ray absorption near-edge structure (XANES) spectroscopy has allowed detecting hydroperoxide species on an Au−titanosilicate catalyst and estimating the net epoxidation rate.[105] Moreover, steady-state isotopic transient kinetic experiments, using oxygen-18, provided information on the types and quantities of species present on Ti-SBA-15 during the reaction.[90] It has been found that a postsynthesis ammonium treatment induces a substantial increase in the catalytic activity of Au/Ti-SBA-15 for the direct vapor-phase epoxidation of propylene using hydrogen and oxygen.[94]

A combination of two catalysts, Au/TiO_2 and TS-1, were used to catalyze the epoxidation of 1-butene **34** to butylene oxide **35** in aqueous solution using molecular oxygen under very mild reaction conditions.[106] Carbon monoxide was needed as a sacrificial reductant. The one-pot epoxidation of 1-octene **36** with O_2 has been performed using nanoparticulated Au/CeO_2 and Ti-MCM-41 silylated materials as catalytic system in the presence of a hydrocarbon and azobisisobutyronitrile (AIBN) as a promoter, in reasonable yields and high selectivities.[107] Other alkenes were also oxidized with high selectivities.

A solvent-free selective epoxidation of cyclooctene **38** to form **39** using supported gold catalysts has been described.[108] Thus, air and *tert*-butyl hydroperoxide (TBHP) as a peroxide initiator were the oxidizing system, and the order of activity for the different supports for gold was graphite > SiO_2 > TiO_2. For the preparation of the solids, the use of a sol-immobilization method significantly enhanced catalyst activity with retention of selectivity. Au-modified Si nanowires (SiNWs) have been described as a superior catalyst for the selective oxidation of *cis*-dicyclooctene **40** to epoxycyclooctane **41** with high selectivity (90%) and high efficiency (38%) using air as oxidant.[109]

In contrast to the uniqueness of TiO_2 as support for gold nanoparticles in the epoxidation of **32**, a wide number of different solids can act as supports for the epoxidation of styrene **42** to styrene oxide **43**. Among them, different alkaline earth oxides;[110,111] IIIa group metal oxides, transition metal oxides, or rare earth metal oxides;[111] boron nitride, silicon dioxide, or carbon;[112] carbon nanotubes;[113] SBA-12;[114] SBA-15;[115] organic−inorganic hybrid mesoporous silicas;[116] Au(111) surfaces;[117]

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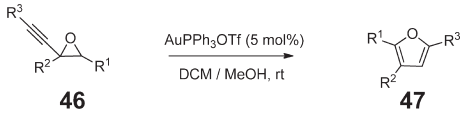
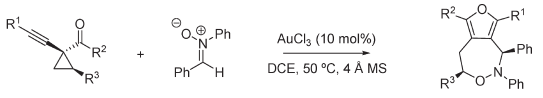
Scheme 15



46 **47**

R^1= H, Alkyl; R^2= Alkyl; R^3= H, Alkyl, Ph 70-93 %

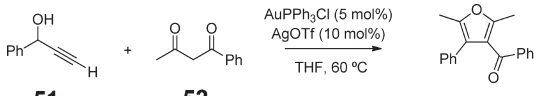
Scheme 16



48 **49** **50**

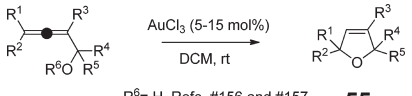
R^1= Ph, *n*Bu; R^2= Me, *n*Pr, Ph; R^3= H, Ph 54-84 %

Scheme 17



51 **52** **53** (80 %)

Scheme 18



54 R^6= H, Refs. #156 and #157; R^6= MOM, Ref. #158 **55**

manganese−porphyrin;[118] and ionic liquids can be found.[119] Remarkably, Turner and co-workers[112] have showed that 55-atom gold clusters of ~1.4 nm, supported on inert materials, are efficient and robust catalysts for the selective oxidation of styrene by dioxygen, while particles with diameters of 2 nm and above are completely inactive. Interestingly, Jiang and co-workers[120] studied later the styrene epoxidation on these 55-atom clusters compared to 38-atom clusters by density functional theory, claiming that the latter should be the size threshold for the epoxidation catalysis.

Caps, Copéret, and co-workers[121] have prepared 1.8 nm gold nanoparticles on passivated silica via controlled functionalization of the silica surface with a Au(I) complex followed by mild reduction under H_2. This OH-free material was used as a highly efficient catalyst for the aerobic epoxidation of *trans*-stilbene **44** to stilbene oxide **45** in methylcyclohexane, using *tert*-butyl hydroperoxide as initiator. The use of peroxides in catalytic amounts to initiate the oxidation of alkenes with O_2 was first reported in 2005.[122] Nearly full conversion and 80% epoxide selectivity were achieved, these being the best catalytic performances observed to date for a liquid-phase epoxidation of *trans*-stilbene under aerobic conditions. As for propene **32**, the aerobic epoxidation of stilbene **44** to form **45** has been also accomplished with Au/TiO_2 by Caps and co-workers[123,124] and an hybrid titania nanocrystallite as support for the Au species has also been used.[125]

4.2.1.2. Five-Membered Rings. 4.2.1.2.1. Furans. Palladium is arguably the most used metal to catalyze the synthesis of oxygen-containing heterocycles, including medium- and large-size rings, from C−C unsaturated bonds, particularly alkynes.[66] On the other hand, gold-catalyzed syntheses of furan derivatives were reported by different groups in the past decade,[126−131] including a recyclable catalytic system in ionic liquids.[132] In general, the furan core is constructed by intramolecular addition of alcohol to unsaturated C−C catalyzed by gold salts and complexes, and the recent examples are summarized in Scheme 14.

The alcohol can already be present in the precursor[133−139] or be formed in situ from epoxides,[61,140−143] carbonyls,[24,144−149] or acetates.[150] The addition of carbonyls to gold-activated alkynes has been studied by computational methods.[151,152] The unsaturated C−C bond is usually a triple bond or an allene. In general, regioselectivities and yields are good. As a typical example, Pale and co-workers[141] have transformed alkynyloxiranes **46** to trisubstituted furans **47** by using Au or Ag catalysts (Scheme 15). The reaction is run at room temperature with high yields. Mechanistic studies showed that a cascade pathway rather than a direct intramolecular nucleophilic addition of the oxirane oxygen atom to the intermediate acetylene−metal π-complex occurs.

In some cases, the formation of the furan ring can be coupled with a second reaction in a one-pot tandem process. For instance, Wang and co-workers[147] have reported a highly diastereoselective $AuCl_3$-catalyzed cycloaddition of 1-(1-alkynyl)cyclopropyl ketones **48** and nitrones **49** to obtain bicyclic 5/7 furanyl oxazepines **50** in good yields (Scheme 16). A one-pot reaction using **48**, an aldehyde, and a hydroxylamine derivative as nitrone surrogate also leads to **50**.

The same author has reported a similar procedure where the new fused oxazepine is a six-membered ring (see Scheme 33).[153] In another example of tandem process, the furan ring is formed after a first in situ reaction. Thus, Arcadi and co-workers[154] achieved furan **53** in good yield by the coupling of propargyl alcohol **51** with the 1,3-dicarbonyl compound **52** following cyclization (Scheme 17).

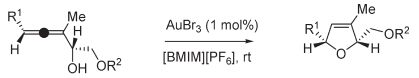
4.2.1.2.2. Dihydrofurans. Dihydrofuran derivatives were synthesized early on from alkynes by palladium-catalyzed intramolecular hydroalkoxylation reactions.[155] The more common way to achieve dihydrofurans through gold catalysis is the cyclization of vinyl allenols. For instance, $AuCl_3$ catalyzes the cyclization of vinyl allenols **54** to form 2,3-dihydrofurans **55** (Scheme 18).[156−160]

The same transformation was achieved by Krause and Winter[161] in a more environmentally friendly way, by using water as solvent, $HAuCl_4$ (5 mol %) as catalyst, and LiCl (1 equiv) as additive. Krause and Aksin[162] have also achieved this cyclization in ionic liquids, using $AuBr_3$ instead of $AuCl_3$ (Scheme 19). Yields of 2,3-dihydrofurans **57** were good, and remarkably, the solution containing the catalyst could be reused up to five times. In a related reaction, Krause and Poonoth achieved bis(2,5-dihydrofuran) derivatives by combining $AgNO_3$ and $AuBr_3$ catalysis.[163]

Z-5-Ylidene-2,5-dihydrofurans **59** were obtained in a regioselective manner and with good yields from substituted *Z*-enynols **58** (Scheme 20).[133] If heating, the furan ring is obtained (see Scheme 14).

In a similar approach, Akai and co-workers[164] prepared substituted 3(2*H*)-furanones by intramolecular cyclization of γ-hydroxyalkynones under mild conditions in good yields. The method is also applicable to the preparation of 2,3-dihydro-4*H*-pyran-4-ones. Tandem reactions that direct to the formation of

Scheme 19

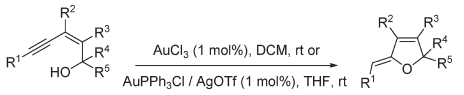


56 57

R^1= Alkyl, Aryl; R^2= TBS, Bn

45-89 %

Scheme 20

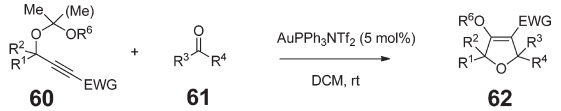


58 59

R^1=R^2=R^5= Alkyl, Aryl
R^3=R^4= H, Alkyl, Aryl

83-97 %

Scheme 21

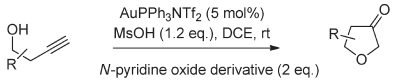


60 61 62

55-84 %

EWG= CO_2R, Mes, Cl_2PhSO
R^1=R^2=R^3=R^4=R^5= Alkyl, Aryl, H
R^6= Me, Et

Scheme 22

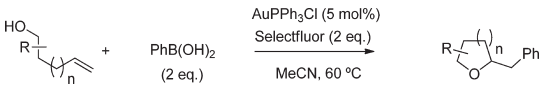


63 64

R= Cyclic alkyl, Aryl, $-(CH_2)_n$-X (X= H, OBn, Br, N_3, OMOM, NHBoc, Ph; n=1-4)

55-88 %

Scheme 23

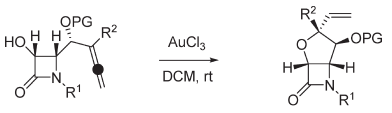


65 66

R= Alkyl, Benzyl

35-71 %

Scheme 24



67 68

R^1= benzyl, allyl
R^2= Me, Ph
PG= TBS, COPMP

50-58 %

polysubstituted 2,5-dihydrofurans have also been designed. Thus, Zhang and Zhang[165] have reported an unprecedented gold(I)-catalyzed migration/fragmentation of acetals to form an all-carbon 1,3-dipole, which undergoes in situ [3 + 2] cycloaddition with various enones/enals to form the highly substituted dihydrofuran core **62** (Scheme 21). A similar strategy was employed by the same authors in the synthesis of furans (see Scheme 14).[148]

Kirsch and co-workers,[166] during their studies on the preparation of cyclopentane rings by combining gold catalysis with amino catalysis, have reported an example of preparation of a 2,3-dihydrofuran derivative, while Hasmi and co-workers[51] have obtained 2,5-dihydrobenzofurans by the gold-catalyzed phenol synthesis.

Another remarkable example of intramolecular construction of the dihydrofuran ring was later reported by Zhang and co-workers (Scheme 22).[167]

The strategy is based on a gold-catalyzed intermolecular oxidation of terminal alkyne **63** with *N*-pyridine oxides derivatives under mild reaction conditions, followed by in situ cyclization of the α-oxo gold carbene formed. The method provides good yields and presents a good functional group tolerancy.

4.2.1.2.3. Tetrahydrofurans. In 2006, Widenhoefer and co-workers[168] reported the Au-catalyzed synthesis of tetrahydrofurans via intramolecular hydroalkoxylation of allenes. One year later, the same group developed the enantioselective version.[169] In the same year, Toste and co-workers[170] designed a very smart strategy to induce chirality in the final tetrahydrofuran ring. To do that they used a chiral counteranion in the silver salt, so the removal of the chloride anions of the gold complex by precipitation rendered a chiral gold catalyst. The procedure allowed high enantioselectivities for the intramolecular hydroalkoxylation of γ-hydroxyallenes. Concerning alkenes, the first example of intramolecular hydroalkoxylation was reported by He and Yang in 2005.[171]

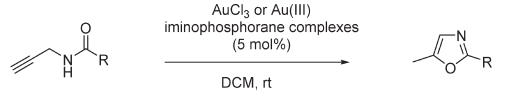
With these precedents in hand, other approaches have been envisaged during this period. For instance, Zhang and co-workers[172] have developed a carboalkoxylation procedure for terminal alkenes via oxidative gold catalysis, which provides access to various substituted *O*-heterocycles, including tetrahydrofurans (Scheme 23).

This reaction constitutes a clear example of redox Au(I)/Au(III) cross-coupling catalysis. Alcaide, Almendrós, and co-workers[158,173] have reported the $AuCl_3$-catalyzed regioselective formation of tetrahydrofurans **68** from γ-allenols **67** (Scheme 24). The formation of tetra- or dihydrofurans depends on the protecting group (PG) of the molecule: if PG = TBS, the tetrahydrofuran **68** is formed, but if PG = MOM, the dihydrofuran **55** (see Scheme 18) is obtained instead. Remarkably, only gold as catalyst is able to form hydrofurans, while other metals such as La or Pd lead to six- or seven-membered rings. These findings were also corroborated by theoretical studies.[173]

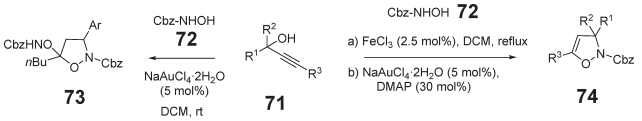
Helmchen and co-workers[174] have presented a full account on a gold(I)-catalyzed cycloaddition of carbonyl compounds to enynes, yielding 2-oxabicyclo[3.1.0]hexanes with four stereogenic centers and high diastereoselectivity. As that of Alcaide, Almendrós, and co-workers,[158,173] this is a rather complete study that includes the scope of the reaction, mechanistical experiments, and DFT calculations. Hashmi and co-workers[51] have

dx.doi.org/10.1021/cr100414u |*Chem. Rev.* 2011, 111, 1657–1712

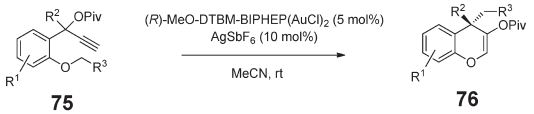
Scheme 25



Scheme 26



Scheme 27



also reported an example of cyclization of γ-allenols by using gold(I)−triflimide complexes of H-KitPhos and *o*-MeO-KitPhos as catalysts, while one example of a gold-catalyzed formation of tetrahydrofuran has been reported during studies directed to the formation of tetrahydropyranes (see Scheme 31).[175] Similarly, the gold(I)-catalyzed cascade cyclization of allenyl epoxides **87** (see Scheme 32) produced tetrahydrofurans and tetrahydropyrans concominantly.[176]

4.2.1.2.4. Oxazoles and Dihydrooxazoles. When nitrogen and oxygen functionalities that could act as nucleophiles are present in the reaction medium, a competition between them for the gold-activated carbon electrophile could be expected, though one of them usually prevails. In 2004, Hashmi and co-workers[177] published a report on the $AuCl_3$-catalyzed synthesis of oxazoles from the *O*-cycloisomerization of *N*-propargylcarboxamide, and recently, this work has been expanded. For instance, oxazoles **70** have been obtained in good yields via cycloisomerization of *N*-propargylcarboxamides **69** catalyzed by gold(III) salts or iminophosphorane gold complexes (Scheme 25), where a new C−O is formed.[178] A similar $AuCl_3$-catalyzed reaction has been reported by Padwa and Verniest.[179]

Hashmi and co-workers further developed their precedented work[180] and reported that oxazoles **70** were indeed obtained when using Au(III) ($AuCl_3$) as catalyst, since the intermediate methylendihydrooxazole was isomerized in situ at room temperature. In other words, the whole process was an *O*-cycloisomerization. However, when using Au(I) ($AuPPh_3NTf_2$) as catalyst instead, the product obtained from the corresponding propargylic amide is the intermediate methylendihydrooxazole, since only cyclization occurs.

Perhaps a more illustrative example is the one-pot synthesis of isoxazoles **73** and 2,3-dihydroisoxazoles **74** from propargylic alcohols **71** and *N*-protected hydroxylamine **72**, reported by Campagne and co-workers (Scheme 26).[181]

If the reaction was catalyzed by gold(III), the reaction pathway involved a nucleophilic substitution on the propargylic carbon of **71** by the hydroxylamine **72**, cyclization to form the new cyclic C−O bond, and a second addition of **72**, in this case through the hydroxyl group, to form eventually the 5*O*-substituted isoxazole **73**. In contrast, with iron(III) as catalyst for the nucleophilic substitution and DMAP as additive for the gold(III)-catalyzed cyclization, the later *O*-intermolecular addition was suppressed, and now the 2,3-dihydroisoxazoles **74** were the main product of the reaction. Hashmi and co-workers have performed the same transformation with the gold(I)−triflimide catalysts mentioned above.[51]

4.2.1.3. Six-Membered Rings. Pyrane derivatives can be prepared by catalyzed reactions with different metals and, as occurs with furan derivatives, palladium seems to be the most studied catalyst.[66] Nevertheless, the catalytic behavior of gold is remarkable for these transformations.

4.2.1.3.1. Pyranes and Hydropyranes. Krause and Belting[145] have obtained 4*H*-pyrans from alkynones by using a combination of $AuPPh_3OTf$ (generated in situ from $AuPPh_3Cl$ and AgOTf) and *p*-TsOH as catalysts, in a way analogous to their procedure to obtain furans (see Scheme 14). In the same way, Arcadi and co-workers[154] (see Scheme 17) also obtained 4*H*-pyrans by conveniently combining the propargylic alcohol **51** with other 1,3-dicarbonyl compounds **52** during the Au(I)-catalyzed formation of furans.

Cascade-type procedures have led to the obtention of hydropyranes, and for instance, the formation of complex 2*H*-pyran compounds from nonaromatic epoxides, catalyzed by $AuPPh_3Cl$/$AgSbF_6$ (5 mol %), has been reported by Liu and co-workers.[182] In that transformation, a 6-exo-dig attack of the epoxide at the Au(I) activated alkyne occurs, which triggers a Nazarov-type cyclization to give the cyclized products. In another relevant example, Toste and co-workers[183] have described a gold(I)-catalyzed enantioselective synthesis of benzopyrans **76** via rearrangement of allylic oxonium intermediates (Scheme 27).

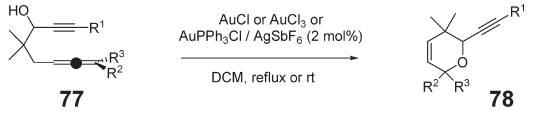
A chiral biarylphosphinegold(I) complex is able to provide benzopyrans containing quaternary stereocenters in moderate to good yields and with excellent enantioselectivities. The carboalkoxylation of the propargyl esters proceeds through the reaction of a carbocation with a chiral allylgold(I) intermediate.

4.2.1.3.2. Dihydropyranes and Dioxanes. The Au-catalyzed synthesis of dihydropyranes was early reported by the Krause's group.[184,185] In general, dihydropyranes can usually be made by the same methods reported to prepare dihydrofurans. For instance, 2*H*-2,3-dihydropyranes have been obtained in water, working in the same $HAuCl_4$-catalyzed conditions as the synthesis of 2,5-dihydrofurans **55** (see Scheme 18).[161] Similarly, substituted 2,3-dihydro-4*H*-pyran-4-ones can be prepared by the same method to cyclize γ-hydroxyalkynones.[164] Gold(I) is able to catalyze the alkoxyhalogenation of hydroxydifluoroynones **1** to produce ketodihydropyranes **2** and **9** (see Scheme 2).[17] The cycloisomerization of hydroxylated 1,5-allenynes to 2*H*-2,3-dihydropyranes **77** occurs with gold salts and complexes (Scheme 28),[186] while $PtCl_2$ gave C−C rather than C−O coupling.

Liu and co-workers[187] have observed a high stereoselectivity for the $AuCl_3$-catalyzed hydrative cyclization of 1-epoxy-1-alkynylcyclopropanes to form (5*H*)2,3-dihydropyranes, which allows engaging the corresponding in situ formed 1-oxyallyl cations to dienes and enones, to provide finally (5*H*)2,3-dihydropyrane derivatives with excellent diastereoselectivity. Regarding benzopyranes, Hashmi and co-workers[51] have reported one example of preparation of

dx.doi.org/10.1021/cr100414u |*Chem. Rev.* 2011, 111, 1657–1712

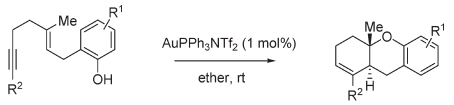
Scheme 28



R^1= $SiMe_3$, CH_2iPr, CH_2OMe;
R^2= Alkyl; R^3= H, Alkyl

41-96 %

Scheme 29



R^1= H, Halogen, Me, OAlkyl;
R^2= H, Me, Ph

76-96 %

3,4-benzopyrane using the phenol synthesis strategy, with gold(I)−triflimide catalysts. More elaborated benzopyranes have been obtained by other cascade-type procedures, and for instance, the intramolecular phenoxycyclization reaction of 1,5-enynes **79** has been reported with $AuPPh_3NTf_2$ as catalyst (Scheme 29).[188]

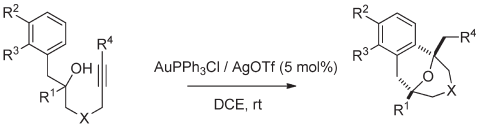
Tricyclic 2,3-benzopyranes **80** were obtained by a 6-endo cyclization process in good yields. In another relevant work, Barluenga and co-workers[189] performed a tandem intramolecular hydroalkoxylation−hydroarylation to obtain the enantiopure benzofused cyclic ethers **82** in good yields (Scheme 30). Moreover, an enantioselective version of this reaction was also developed in the same work.[189]

An efficient and highly selective approach for the synthesis of functionalized 4*H*-chromenes via a gold(III)-catalyzed condensation/annulation tandem reaction of ketones with phenols has been recently reported.[190] The gold catalyst ($AuCl_3$ + 3AgOTf) provided the products in good yields and selectivities. Another example of formation of a 1,4-dioxane ring by using gold catalysis has been reported by Cheng and co-workers.[191] They obtained complex vinyl alcohols by a copper- and palladium-catalyzed three-component coupling of benzynes, allylic epoxides, and terminal alkynes. The so-formed suitable precursors were employed as substrates for an intermolecular cascade reaction catalyzed by $AuPPh_3Cl/AgSbF_6$ to yield an elaborated 1,4-dioxane compound. In a last example, a tandem 3,3-rearrangement/transannular [4 + 3] cycloaddition reaction of macrocyclic propargyl acetates containing a furan ring has been performed.[192] A gold(III) complex was the catalyst of choice to obtain the bicyclic ethers. In contrast, when gold(I) complexes in combination with $AgSbF_6$ were used as catalysts, the corresponding ketones were obtained instead. 1,2-Acetoxy or 1,2-alkyl migration can occur, and the core structure of the natural product cortistatin A may be prepared.

4.2.1.3.3. Tetrahydropyranes. Aponick and co-workers[175,193] have reported the synthesis of tetrahydropyrans **85** by an Au-catalyzed cyclization of monoallylic diols **83**, in good yields and diastereoselectivities, under very mild conditions (Scheme 31).

The reaction can be easily scaled up.[193] A similar strategy can be used starting with 2-alkynyl-1,5-diols as substrates.[194] In that case, a ketal intermediate further reacts to the corresponding

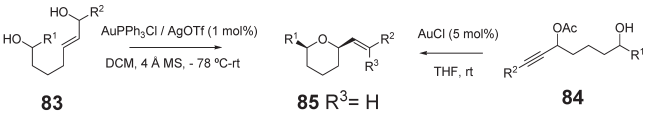
Scheme 30



X= O, CH_2, NTs;
R^1= H, Alkyl; R^2= H, Alkyl, OMe;
R^3= H, Alkyl; R^4= H, Ph

70-96 %

Scheme 31



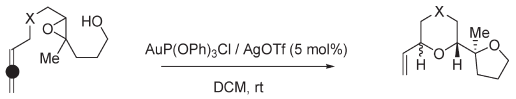
83 R^1=R^2= H, Alkyl, Aryl

85 R^3= H
76-99 % dr >4:1

86 R^3= OAc
81-99 %

84 R^1= H, Alkyl;
R^2= Alkyl, Aryl

Scheme 32



X= O-, $(PhO_2S)_2C$-, $(MeO_2C)_2C$-

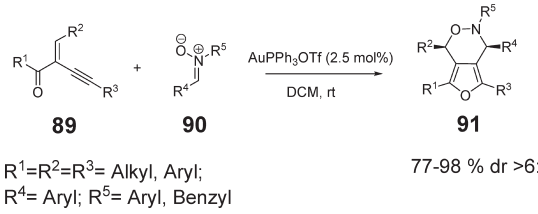
60-65 %

tetrahydropyrane under the action of AuCl as catalyst, and tetrahydropyranyl-β-substituted ketones are obtained in good yields under mild conditions. Bisubstituted tetrahydropyrans **86** were also obtained in good yields from ω-hydroxy propargylic esters **84** by a cycloisomerization reaction (Scheme 31).[195] Alternatively, the gold(I)-catalyzed cascade cyclization of allenyl epoxides **87** led to the bisubstituted tetrahydropyrans **88** in moderate yields (Scheme 32).[176]

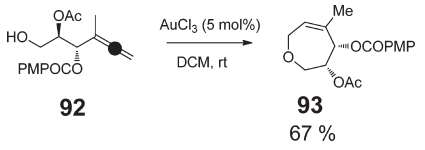
Fürstner and Morency,[196] during their studies on the gold-catalyzed cycloisomerization of enynyl esters **201** to δ-lactones **202** (see Scheme 77), were able to reproduce the same reaction for enynyl alcohols, obtaining the corresponding cyclic fused tetrahydropyranes. A particular case of this approach corresponds to the Au/Ag-catalyzed intramolecular ring-opening of vinylidenecyclopropane, later reported by Shi, Li, and co-workers.[197] In this work, vinylidenecyclopropanes tethered with hydroxyl groups undergo intramolecular cyclization catalyzed by a mixture of $[(Ph_3PAu)_3O]BF_4$ and AgOTf (4 mol % each) to afford allene-functionalized tetrahydropyrans, although in moderate yields. Barluenga and co-workers[26] have reported a gold- or platinum-catalyzed tandem process that involves an intramolecular hydroalkoxylation of a triple bond followed by a Prins-type cyclization. This strategy constitutes an efficient method for the synthesis of oxygen-containing [3.3.1]bicyclic compounds. Finally, Zhang and co-workers[172] provided an example of tetrahydropyrane formation during their studies on carboalkoxylation of alkenes (see Scheme 23).

dx.doi.org/10.1021/cr100414u |*Chem. Rev.* 2011, 111, 1657–1712

Scheme 33



Scheme 34



4.2.1.3.4. Oxazepines. Gold catalysis has been successfully used not only to form oxygen-containing six-membered cyclic ethers but also to prepare fused oxazepines **91** (Scheme 33).[153] The reaction involves a diastereoselective 1,3-dipolar cycloaddition, and a new C−O bond from the N−O of the nitrone **90** is formed, in good yields and diastereoselectivities.

4.2.1.4. Seven-Membered Rings. 4.2.1.4.1. Seven-Membered Cyclic Ethers. As previously mentioned, Alcaide, Almendrós, and co-workers[158,173] (see Scheme 24) have reported the $AuCl_3$-catalyzed regioselective formation of tetrahydrofurans **68** from γ-allenols **67**. By protecting the γ-OH in **67** as a MOM group, the regioselectivity changes dramatically in such a way that bicyclic β-lactames/tetrahydrooxepines are then formed as major product. The enantiopure tetrahydrooxepine **93** can also be formed from the γ-allenol **92** derived from D-glyceraldehyde (Scheme 34).[198]

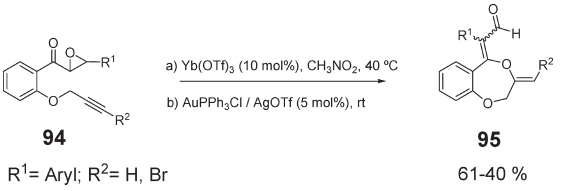
The gold(I)-catalyzed cascade cyclization of allenyl epoxides **87** (see Scheme 32) can lead to fused 7−6 bicyclic ethers by appropriately choosing the substitution pattern.[176] The seven-membered dioxanes **95** can be formed by combining ytterbium and gold catalysis (Scheme 35).[199]

Pericàs and co-workers[200] have developed an iron-catalyzed cyclization/rearrangement of benzyl glycidyl ethers **96** to tetrahydrobenzo[*c*]oxepin-4-ols **97** that can be performed using $AuCl_3$/3AgOTf as catalytic system (Scheme 36).

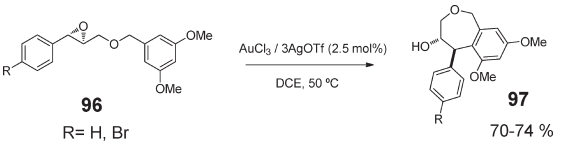
The synthesis of seven-membered ether rings by means of a stereoselective gold-catalyzed [2 + 2 + 2] cycloaddition of ketoenynes substituted at the propargylic position has been reported.[201] The catalyst of choice is the carbene−gold(I) complex **264**, and this methodology was applied to the synthesis of the natural product (+)-orientalol F (**266**) (see Scheme 96). It has been seen above (see Scheme 16) that N−O bonds can be incorporated in medium-size rings by forming a new C−O bond via gold catalysis. Thus, bicyclic 5/7 furanyl oxazepines **50** have been prepared in a tandem reaction from ketones **48** and nitrones **49** in good yields.[147] Czekelius and co-workers[202] have recently described a gold-catalyzed cyclization of 1,4-diynols to dihydrodioxepines by employing typically $Au(PCy)_3Cl$/$AgBF_4$ as catalyst in toluene. The cyclization occurs exclusively in an endo-fashion, although yields are only moderate.

4.2.2. Acyclic Ethers. *4.2.2.1. Vinylic Ethers.* In a seminal contribution on gold-catalyzed processes, Teles and co-workers[203] described the addition of alcohols to alkynes, achieving the corresponding vinyl ethers when using unsymmetrical and terminal alkynes, while acetals were formed with internal symmetrical alkynes. Rhee and co-workers[204] have reported the only recent example of an intramolecular formation of acyclic ethers, particularly vinyl methyl ethers (Scheme 37). In this work, the gold(I)-catalyzed cycloisomerization of 3-methoxy-1,6-enynes **98** led to the formation of **99** in excellent yields after cyclization and later [3,3] sigmatropic rearrangement. Additionally, in situ hydrolysis of the vinyl ether allowed obtaining the corresponding ketones in good yields.

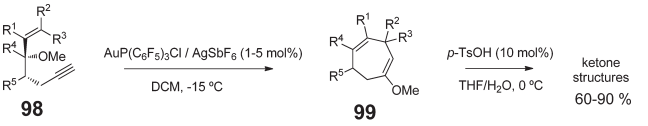
Scheme 35



Scheme 36



Scheme 37



Vinyl transfer reactions between vinyl ethyl ether and alkyl and benzyl alcohols have been performed using in situ generated $AuPPh_3OAc$ as catalyst to obtain the corresponding new vinyl ethers in good yields.[205]

4.2.2.2. Allylic Ethers. Allylic ethers can be obtained with gold catalysis in several ways.[206] The common procedure to obtain allylic ethers using gold catalysis is the direct nucleophilic addition of alcohols to allenes (Scheme 38),[207−211] and DFT calculations have been performed for Au(I)−carbene complexes as catalysts.[212]

Another route is the addition of the alcohol to an allyl is *O*-nucleophuge activated by a gold catalyst in a $S_{N'}$ reaction (Scheme 39).[213] A different silyloxy group and different reactions conditions did not change the result.[214]

When the allyl *O*-nucleophuge is acetate, the reaction proceeds worse, and only allyl alcohol reacts to form the corresponding diallyl ether.[215] A third possible electrophilic carbon to add the alcohol is cyclopropene **105** (Scheme 40).[216] Two possible gold(I) catalytic systems are active, $AuPPh_3NTf_2$ being superior. This method allows the synthesis of the quaternary allylic alcohols **106** in good yields. Moreover, this unexpected regioselectivity inspired the authors to test allenes as substrates, observing that,

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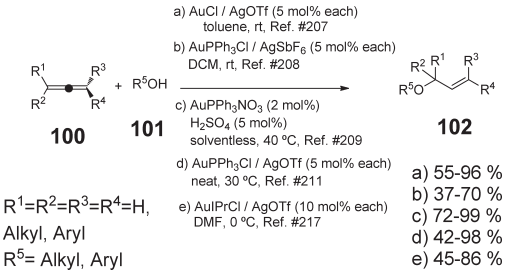
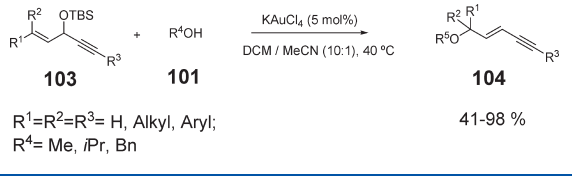
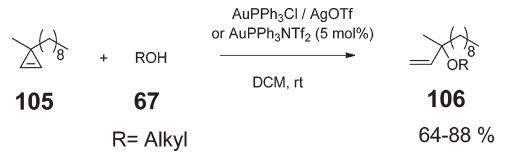
Scheme 38



Scheme 39



Scheme 40



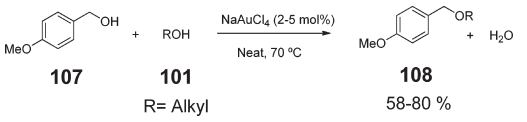
indeed, *tert*-allylic ethers were regioselectivelly obtained (see Scheme 38, condition e).[217]

An unexpected allylic alcohol product was reported by Arcadi and co-workers[154] during their studies on gold-catalyzed formation of furans (see Scheme 17). The direct formation of allylic ethers by addition of allylic alcohols to alkenes under gold-catalyzed conditions has been reported by Michelet and co-workers.[218] In this work, it is noteworthy that the gold-catalyzed formation of ethers was coupled with another typical gold-catalyzed process, namely, the cycloisomerization of enynes. Finally, a gold(I)-catalyzed cascade reaction of propargyl propiolates **162** (see Scheme 65) has been reported and allows formation of allylic ethers **165**.[219]

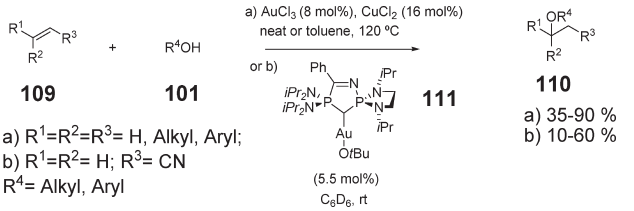
4.2.2.3. Propargylic Ethers. As mentioned above, $NaAuCl_4 \cdot 2H_2O$ activates propargylic alcohols **71** toward the nucleophilic substitution of the hydroxyl group by amines (see Scheme 26). In a similar reaction, different nucleophiles including alkyl alcohols could be introduced, leading to new propargylic ethers.[214] The methoxycyclization of 1,6-enynes leads also to propargylic ethers. One example of this transformation is found in the work recently reported by Espinet, Echavarren, and co-workers[220] using gold(I) carbene as catalysts.

4.2.2.4. General Synthesis of Ethers. The direct hydroalkoxylation of alkenes with alcohols to form dialkyl ethers is a challenging reaction. A particular case has successfully been addressed by Tokunaga and co-workers,[221] by coupling unactivated olefins with alcohol substrates bearing coordination functionalities such as halogen or alkoxy groups, using a combination of gold(I) and electron-deficient phosphine ligands as the catalytic system. Although yields were generally moderate, this constitutes a relevant step toward the direct hydroalkoxylation of alkenes. In a more general method, as occurred for propargylic alcohols, $NaAuCl_4$ is also able to activate benzylic alcohols toward a possible nucleophilic substitution with other alcohols. Thus, Asensio and co-workers[67] have designed a very simple method to obtain ethers from alcohols using $NaAuCl_4$ as catalyst (Scheme 41). Several combination of alcohols can be used in addition to those shown in Scheme 41, leading to unsymmetrical ethers in good yields.

Scheme 41



Scheme 42



Corma and Zhang[222] have reported the addition of alcohols, including phenols, to alkenes, mediated by a combination of Au(III)−Cu(II) as catalyst (Scheme 42, condition a). Gold catalysts alone are otherwise rapidly reduced.

Other Au(III) salts are also active as cocatalysts, and Markovnikov addition occurs. However, regarding this, a different regioselectivity can be found in the literature (Scheme 42, condition b)[223] when using the gold(I) carbodiphosphorane complex **111** as catalyst and acrylonitrile as alkene. In this case, the anti-Markovnikov addition of the alcohol was observed.

Asao and co-workers[224] have employed a smart strategy to transform alcohols to ethers. They found that alkyl esters **112** containing an *o*-alkynylbenzoic acid as substituent, behave as alkylating agents in the presence of gold species (Scheme 43). Thus, asymmetric ethers were formed by using in situ formed $AuPPh_3OTf$ as catalyst.

It has been already mentioned that the formation of allylic ethers by addition of an allylic alcohol to an alkene can be coupled with the gold-catalyzed cycloisomerization of enynes.[218] In fact, the *O*-addition triggers this cascade reaction. This tandem reaction can be applied to other nucleophiles, including different alcohols (Scheme 44).[225]

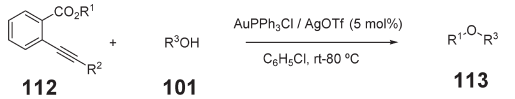
The catalyst is an isolable, highly acidic $AuPR_3NTf_2$ complex, and the bicycle **115** was obtained in moderate to good yields.

4.3. Formation of Acetals

Acetals, particularly cyclic acetals, are important functionalities in organic synthesis since they appear in many natural products and, moreover, they are extremely useful as protecting groups.[226−228] They are traditionally obtained from the addition of an alcohol to the corresponding aldehyde or ketone under Brønsted acid conditions, making necessary the removal of the water generated in the medium to shift the equilibrium toward

dx.doi.org/10.1021/cr100414u |*Chem. Rev.* 2011, 111, 1657–1712

Scheme 43

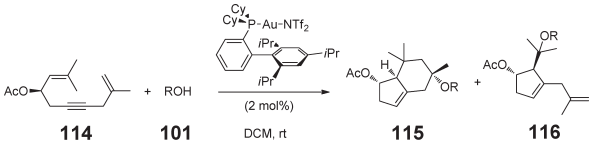


112 **101** **113**

50-90 %

R^1=R^3= Alkyl; R^2= Alkyl, Aryl

Scheme 44

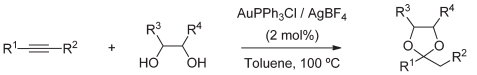


114 **101** **115** **116**

R= H, Alkyl, Aryl

40-82 % (**115**:**116** > 3:1)

Scheme 45



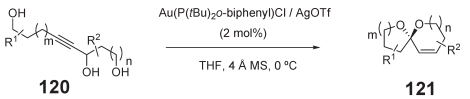
117 **118** **119**

35-87 %

R^1= Alkyl, Aryl; R^2= H, Alkyl

R^3=R^4= H, Me, Et

Scheme 46

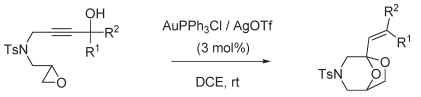


120 **121**

R^1= H, Cyclohexyl, Ph; R^2= H, Me; m=n= 0,1

75-99 %

Scheme 47



122 **123**

R^1= H, Alkyl; R^2= Alkyl, Aryl

12-56 %

the acetal. The addition of diols to unsaturated C−C bonds bypasses this problem, leading to a 100% atom-economical process. Gold catalysis has turned out to be an excellent tool for this second approach. In fact, intra- or interaddition of alcohols to alkynes has provided access to spyroketals, different monocyclic ketals, and even acyclic ketals under mild conditions.

4.3.1. Cyclic Acetals. In 2005, Michelet, Genêt, and co-workers[229] showed a gold-catalyzed double intramolecular hydroxylation of alkynes to give bicyclic acetals in high yields. The catalyst could be AuCl or $AuCl_3$. More recently, Pericàs and co-workers[200] obtained dioxolanes during their studies on the cyclization/rearrangement of benzyl glycidyl ethers (see Scheme 36), using $AuCl_3$/3AgOTf as catalytic system. The method reported by Helmchen and co-workers,[174] describing the gold(I)-catalyzed cycloaddition of carbonyl compounds to enynes to yield 2-oxabicyclo[3.1.0]-hexanes, is also applicable to obtain hexahydrocyclopenta[*d*][1,3]-dioxins, by simply varying the substitution pattern of the alkene moiety of the enyne. Corma and co-workers[230] have obtained dioxolanes **119** by direct addition of 1,2-diols **118** to alkynes **117** (Scheme 45). The addition could be expanded to 1,3- and 1,5-diols, obtaining larger dioxolane cycles in good yields.

However, bicyclics and even tricyclis acetals are more commonly obtained by using gold-catalyzed processes through cascade reactions. For instance, the Au-catalyzed cyclization of monopropargylic triols **120** to spiroacetals **121** has been described in excellent yields (Scheme 46), as well as the enantiomeric version.[231]

In a similar approach, 2-alkynyl-1,5-diols have been used as substrates to obtain dioxabicyclo[4.2.1] ketals by using AuCl as catalyst, in good yields under mild conditions.[194] This ketal can react further to the corresponding tetrahydropyrane. Shi and Dai[232] have developed the gold(I)-catalyzed intramolecular reaction of propargylic and homopropargylic alcohols with oxiranes. Starting from **122**, the bicyclic acetals **123** are obtained in low to moderate yields (Scheme 47).

The obtention of bicyclic acetals in good yields has been reported,[233] and remarkably, the authors have expanded the $AuCl_3$-catalyzed transformation to obtain tricyclic acetals **125** in moderate yields and good selectivities (Scheme 48).

An example of hemiaminal formation has recently been reported.[234] The procedure consists in a gold(I)-catalyzed tandem coupling/cyclization of alkynes and *o*-aminobenzyl alcohols leading to the corresponding tricyclics compounds in one-pot.

4.3.2. Acyclic Acetals. Acyclic acetals can also be obtained by gold catalysis.[235] In fact, the first observed products in gold-catalyzed reactions involving oxygen-containing nucleophiles were acyclic acetals, as shown by Utimoto[236] and Teles.[203] These acetals come from the bis-addition of the corresponding alcohol to alkynes, since stopping the reaction in the intermediate vinyl ether is difficult. Furthermore, these acetals are also unstable under the acidic conditions provided by the gold catalyst and undergo hydrolysis to give the ketone. However, acyclic acetals are more stable when one of the oxygen is embedded into a cycle. Thus, in an early report, gold(I) catalysis allowed obtaining 2-*O*-substituted tetrahydrofurans.[237] More recently,[17] the gold(I)-catalyzed alkoxyhalogenation of hydroxynones **1** in MeCN/H_2O to form acetals **3** (see Scheme 2) has been reported. In an analogous way, the same authors have obtained tetrahydrofuranyl ethers from alkynones and alcohols by using in situ generated $AuPPh_3OTf$ as catalyst (see Scheme 14).[145,238]

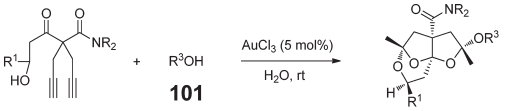
Enantiomerically pure (2*H*)3,4-polysubstituted dihydrofuranyl ethers were obtained in a smart protocol developed by Krause, Alexakis, and co-workers (Scheme 49).[239]

The strategy consists in taking advantage of the high enantioselective induction generally provided by organocatalysts, which is difficult to obtain with chiral gold complexes. Thus, the organocatalytic reaction between **126** and **127** was successfully engaged to the gold(I)-catalyzed cyclization of the so-obtained adduct, leading to the corresponding nitro-substituted tetrahydrofuranyl ethers **128** in good yields and excellent diastero- and enantioselectivities.

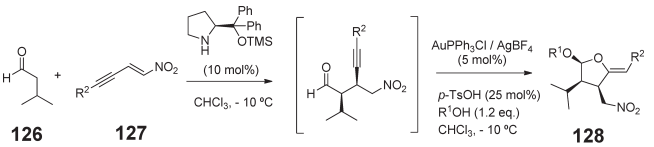
The $AuCl_3$-catalyzed hydroalkoxylation of conjugated alkynoates **129** to obtain acetals **130** in good yields has also been described (Scheme 50),[240] and the tetrahydrofuranyl derivatives could also be obtained.

dx.doi.org/10.1021/cr100414u |*Chem. Rev.* 2011, 111, 1657–1712

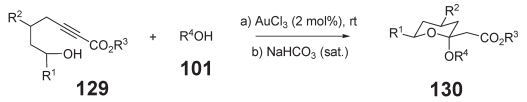
Scheme 48



Scheme 49



Scheme 50

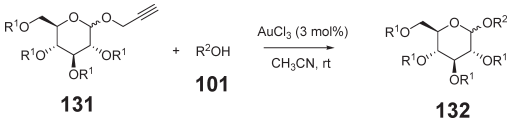


The glycosylation of sugars has also been accomplished, and Hotha and Sureshkumar[241,242] have reported a seminal contribution in this area using the propargyl moiety as a leaving group under gold-catalyzed conditions (Scheme 51).

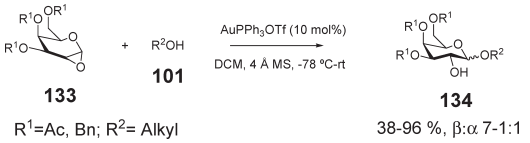
For instance, propargyl ethers, as $AuBr_3$-activated leaving group, have been used to give access to disaccharides by addition of glucosides in fair yields at room temperature.[242] Moreover, propargyl 1,2-orthoesters can also be selectively activated with $AuBr_3$ at room temperature in the presence of *n*-pentenyl glycosides.[243] In contrast, orthoester formation with alcohols was accomplished by using $AuPPh_3OTf$ as catalyst in the presence of 2,6-di-*tert*-butylpyridine as an additive.[244] Curiously, if a combination of $BF_3 \cdot Et_2O$ and DBU was used instead, a gold(I)-catalyzed glycosylation of carboxylic acids with glycosyl *o*-hexynylbenzoates occurred chemoselectively.[244] This line of work has been followed by other authors, who have used terminal propargyl glycosides of glucose, galactose, and mannose for the synthesis of saccharides using $AuCl_3$ as catalyst under heating conditions.[245] Balamurugan and Koppolu[246] attempted to engage this glycosylation of propargyl ether derivatives with a previous Ferrier reaction of the acetyl-substituted glucal, galactal, and rhammal. This Ferrier reaction also proceeds under $AuCl_3$-catalyzed conditions.[246] AuCl-catalyzed glycosidations have been performed over trichloroacetamide-substituted substrates.[247]

In other approaches, Yu and co-workers[248] have found that $AuPPh_3OTf$ is a superior catalyst for the gluco- and galactopyranose derivatives (Scheme 52). The galactopyranose derivative **133** was glycosidated with diverse alkyl alcohols **101** to form **134** in good yields.

Scheme 51



Scheme 52



The same authors employed a similar strategy to that described for the formation of ethers[224] (see Scheme 43) by using an *o*-alkynylbenzoic acid as leaving group in the presence of $AuPPh_3OTf$.[249] Thus, several alkyl and phenolic alcohols could be incorporated into glycosyl *o*-hexynylbenzoates. *o*-Alkynylbenzoates were also employed[250] to perform $AuPPh_3X$ (X = OTF or NTf_2) catalyzed glycosylations. This strategy was used to construct the cyclic triterpene saponin (see Scheme 98).

4.4. Formation of Aldehydes

Aldehydes are produced industrially in millions of tons each year, since they are important precursors for manufacturing plasticizers and detergents, among others. Moreover, they are the base of many fragances. The dominant process to manufacture aldehydes is the hydroformylation reaction.[251] Other large-scale preparations involve the oxidation of alkenes (Wacker process) and the oxidation of alcohols. The latter, for instace, is the method of choice for the obtention of formaldehyde from methanol and oxygen, and the reactions of methanol over gold-supported catalysts have been recently studied.[252]

Gold nanoparticles supported on CeO_2 early showed their ability to catalyze the oxidation of alcohols to aldehydes under oxygen.[253] Other systems such as polymer-incarcerated Au nanoparticles also showed a remarkable activity.[254] The mechanism of oxidation over these gold-based catalysts have been studied,[253,255,256] suggesting Au−H intermediates. In fact, the formation of the carbocation of benzylic alcohol under gold-catalyzed oxidation conditions has also been reported.[257] This methodology has been expanded in the last years by using air, instead of oxygen, as oxidant. Tsukuda and co-workers[258,259] prepared Au clusters of size as small as <1.5 nm on poly(*N*-vinyl-2-pyrrolidone) (PVP) to catalyze the aerobic oxidation of *p*-hydroxybenzyl alcohol **135** (Scheme 53).

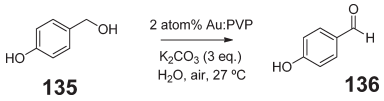
Mullins and Gong[260] have studied the oxidative conversion of ethanol into acetaldehyde on Au(111) by employing in situ techniques such as temperature-programmed desorption and molecular beam reactive scattering. Acetaldehyde can aso be formed from ethanol by using gold-supported nanoparticles in the presence of oxygen.[261]

The oxidation of benzyl alcohol **137** to benzaldehyde **138** is a benchmark reaction and has been widely reported during this period (Scheme 54).

For this reaction, bimetallic nanoparticulated systems enhance the activity of the catalyst compared to gold nanoparticles alone. For instance, Au−Pd supported on polyaniline was a better

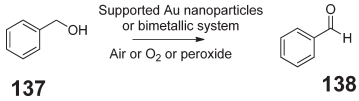
dx.doi.org/10.1021/cr100414u |*Chem. Rev.* 2011, 111, 1657–1712

Scheme 53



135 136

Scheme 54



137 138

catalyst for the aerobic oxidation of **137** than the corresponding Au- or Pd-supported system.[262] The same effect was observed when using Au−Pd confined in mesoporous silica SBA-15[263] or PVP.[264] This effect is attributed to the size decrease of the gold nanoparticles in the presence of the palladium nanoparticles. The bimetallic system is also active if supported on PVP,[265,266] β-MnO_2 nanorods,[267] or carbon,[268,269] in this case using O_2 as oxidant. The system could be used five times without depletion of the activity or selectivity.[265] Bimetallic gold−copper[270] or gold−platinum[271,272] catalysts have also been employed for the aerobic oxidation of **137** in good yields. Monometallic gold-supported systems also catalyze the oxidation of **137** to **138**.[273−282] Different oxidants can be employed, including peroxides,[111,283] and either batch or continuous reactors have been successfully used for this type of reaction.[284]

The general aerobic oxidation of alcohols to aldehydes and ketones has been reported for different gold-supported systems, including Au-supported on CeO_2,[256] Cs_2CO_3,[274] aluminum oxyhydroxide,[285] hydrotalcite,[275] bimetallic Au−Pt nanoparticles immobilized on spherical polyelectrolyte brushes[271] or cross-linked polystyrene derivative,[272] Au−Pd nanoparticles on PVP,[266] and colloidal gold nanoparticles,[286] most of the catalysts being recoverable and recyclable. An example is that using mesostructured Ga−Al mixed-oxide as support, which presents unique dehydrogenation properties.[281]

A final procedure to obtain aldehydes catalyzed by gold is depicted in cycloisomerization reactions, oxidative or not, that ultimately lead to highly substituted aldehydes.[3]

4.5. Formation of Ketones

As was mentioned before for alcohols, ketones can be manufactured industrially by aerobic oxidation of alkanes under harsh conditions, cyclohexanone being a typical example. The synthesis of ketones by oxidation of secondary alcohols is also common. Air and oxygen are the common oxidants either in industrial plants or at laboratory scale. In some cases, strong oxidants such as permanganate or cromate are used instead. A third important way corresponds to the hydration of alkynes. This method involves the direct addition of H_2O to the corresponding alkyne to form the ketone in a 100% atom-economical method.[287a] Unfortunately, the catalyst of choice for this transformation is a salt of mercury, and the Minamata Bay's disaster showed the high toxicity of mercury (notice that the mercury residues that poured into the bay came from the hydration reaction of ethylene to form acetaldehyde). The oxidation of alcohol is the method more commonly employed on a laboratory scale.

Gold catalysis has been successfully reported for both the oxidation of alcohols, usually by gold nanoparticles in heterogeneous phase,[253] and for hydration of alkynes, usually by gold salts in homogeneous phase.[203,236,287b] For the latter, gold exceeds the activity of any other metal catalyst (except banned mercury). Moreover, H_2O can be replaced for any other oxygen-containing functionality as nucleophile, so the new ketone is formed after rearrangement of the intermediate. All these methods have been improved during the period covered by this review.

4.5.1. Intramolecular Formation of Ketones.

The formation of ketones by using gold catalysis can be accomplished intramolecularly from six different functional groups: alcohols (Meyer−Schuster rearrangement),[288] cyclic ethers (epoxides and furans), silyloxy groups, pre-existing ketones, esters (Rautenstrauch rearrangement), and amine oxides. In all these cases the oxygen atom attacks a gold-activated alkyne to form the final ketone after suitable rearrangements of the molecule.

4.5.1.1. Ketones from Alcohols. In 2005, Toste and co-workers[289] reported the ring expansion of strained alkynyl cyclocarbinols to cyclic ketones. In this period, the Meyer−Schuster rearrangement[288] of propargyl alcohols **139** under gold-catalyzed conditions to achieve α,β-unsaturated ketones **140** has been studied (Scheme 55).[290−293]

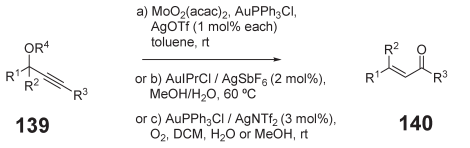
Akai and co-workers[290] used a combination of Mo and Au as catalysts to obtain the α,β-unsaturated ketones **140** in good yields (Scheme 55, condition a). In a similar reaction and using also a similar combination of catalysts, Zhang and co-workers[30] have prepared the linear α-iodo and bromo enones **11** from propargylic alcohols **10** (see Scheme 5, C−halogen formation). Nolan and co-workers[291] obtained similar results using carbene gold complexes at higher temperatures with external water assistance (Scheme 55, condition b). A last unusual strategy to achieve a couple of these ketones in good yields involved the gold-catalyzed oxidative cleavage of aryl-substituted alkynyl ethers by using molecular oxygen (Scheme 55, condition c).[292]

After these works, Toste and Kleinbeck[294] expanded their original work[289] and reported a gold(I)-catalyzed enantioselective ring expansion of allenylcyclopropanols **141** to form cyclobutanones **143** with a vinyl-substituted quaternary stereogenic center (Scheme 56).

A chiral phosphine−gold(I) complex **142** was used as catalyst, and the yields and enantiomeric excesses were excellent. Moreover, this method constituted the first report of an enantioselective gold-catalyzed 1,2-alkyl migration. In another work, Yeh and co-workers[295] reported the intramolecular attack of the hydroxyl group onto a gold-activated alkyne belonging to cyclic 8-aryl-2,7-enyn-1-ols, which allows an in situ [3,3] sigmatropic rearrangement of the structure to generate a spirocyclic ketone. This gold(I)-catalyzed Claisen-type rearrangement proceeds via cationic allylic vinyl ether gold intermediates. Liang and co-workers[296] have reported a gold-catalyzed rearrangement of α-hydroxy epoxides to afford unsymmetrical 1,5 or 1,6-diketones and monoketones, depending on the substituents and ring strain in the substrates. The catalyst of choice is $NaAuCl_4 \cdot 2H_2O$ and the yields were good to moderate.

4.5.1.2. Ketones from Oxiranes and Furans. A second way to obtain ketones intramolecularly under gold-catalyzed conditions is by means of epoxides. The method of Liang and co-workers[296] from α-hydroxy epoxides (see previous section) has already been mentioned, while Liu and co-workers[182] and Hashmi and co-workers[51,297] employed substrates **144** as precursors of 3-1*H*-indenyl ketones **145** after cycloisomerization under gold-catalyzed conditions (Scheme 57).

Scheme 55

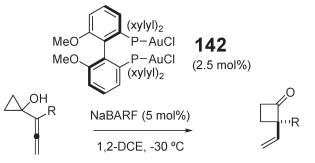


139 **140**

R^1=R^2= H, Alkyl, Aryl
R^3= H, Alkyl, Aryl, OAlkyl
a,b) R^4= H; c) R^4= H, Me

a) 61-97 %
b) 58-96 %
c) 72-83 %

Scheme 56



141 **143**

R= Alkyl, Aryl

61-99 %
e.e. 84-94 %

Thus, Liu employed in situ generated $AuPPh_3SbF_6$ as catalyst[182] to obtain ketones **145** in fair yields (condition a), and similar yields were obtained by Hashmi, but using isolable $AuP(Ad)_2$-(*n*Bu)NTf_2[297] (condition b) or AuKitPhosNTf_2[51] complexes as catalysts. The same author found a ketone as product during his studies on the gold-catalyzed phenol synthesis.[47]

Pale and co-workers[298] have reported a second type of alkynyloxiranes that undergo the gold(I)-catalyzed rearrangement (Scheme 58).

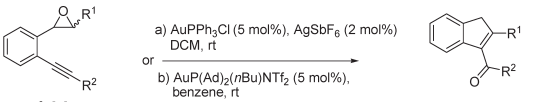
Divinyl ketones **147** were obtained in moderate to good yields by using in situ generated $AuPPh_3SbF_6$ as catalyst. The mechanism of this transformation could involve the anchimeric assistance of the ester group, although the actual mechanism seems to be more complicated, as it has been presented by computational studies.[299]

Regarding furans as source of ketones, Hashmi and co-workers[300,301] have obtained different α-aryl-substituted methyl ketones from furanyne derivatives by using phosphane−gold(I) complexes as catalysts. DFT calculations support the different pathways suggested for the reactions. Liu and co-workers[302] went a step forward in the gold(I)-catalyzed Friedel−Crafts reaction of a furan derivative with the corresponding propargyl alcohol. $AuPPh_3NTf_2$ was the catalyst of choice, and different *Z*-enones and *Z*-enals were obtained in good yields under mild conditions.

4.5.1.3. Ketones from Silyloxanes. Kirsch and co-workers[303] have expanded their seminal work on the cycloisomerization of 3-silyloxy-1,5-enynes.[304] In that case, the trialkylsilyloxy group was bound to a secondary carbon, leading to aldehydes after the pinacol rearrangement. If using a tertiary silyloxy-substituted carbon instead, a ketone is formed. Thus, silyloxyenynes **148** in the presence of $AuP(C_6F_5)_3Cl$ and $AgSbF_6$ gave fused 5/7 membered-ring ketones **149** in good yields (Scheme 59).[303]

The mechanism involves a carbocyclization followed by a pinacol-type rearrangement. Curiously, a change in the electronic properties of the gold-bound phosphane ligand leads to a completely different reaction pathway and, consequently, to other products.

Scheme 57



144 **145**

a) R^1= Me, Bn, *n*Pr; R^2= Alkyl, Aryl, NMeTs
b) R^1= Alkyl; R^2= Alkyl, Aryl

a) 46-81 %
b) 56-80 %

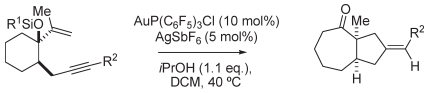
Scheme 58

146 **147**

R^1=R^2= H, Alkyl;
R^3=R^4= H, Alkyl, Aryl;
R^5= Me. *t*Bu. Bn

32-85 %

Scheme 59



148 **149**

R^1= Me, Et; R^2= Me, Aryl

62-96 %

The [4 + 3] cycloaddition of 5-silyloxydioxins to cyclopentadiene or furan with $AuCl_3/AgSbF_6$ to form cyclic (cyclohexane or tetrahydropyrane) α-hydroxy ketones has been published.[305] Finally, a gold(I)-catalyzed synthesis of highly substituted 2-cyclopentenones from 5-siloxypent-3-en-1-ynes has been published.[306] The catalyst of choice was a combination $AuCl[P(C_6F_5)_3]$/$AgSbF_6$ and the reaction proceeds at room temperature in good yields.

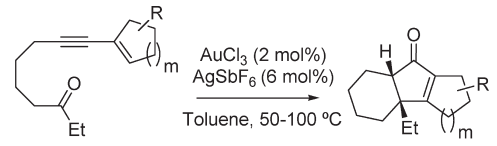
4.5.1.4. Ketones from Pre-Existing Ketones. Alkynylcarbonyl compounds suffer unexpected cycloisomerizations in the presence of gold catalysts, which can leave the newly formed ketone group far away from the original position in the molecule. For instance, Yamamoto and Jin[307] have reported Au(III)-catalyzed synthesis of polycyclic enones **151** from enynyl carbonyls **150** via tandem heteroenyne metathesis and Nazarov reaction (Scheme 60).

Zhang and co-workers[308] have prepared indolizinones **153** from β-lactames **152** through an intriguing mechanism involving gold-mediated 5-exo-dig cyclization of the β-lactam nitrogen to the C−C triple bond followed by heterolytic fragmentation of the amide and cyclization (Scheme 61).

Nakamura and co-workers[309] have prepared naphthylmethyl ketones from alkynyltetralones in good yields by using in situ prepared $AuPPh_3OTf$ as catalyst, in THF at 50 °C. However, a different way to obtain ketones has been described by Organ and co-workers.[310] In their methodology, the benzaldehydes **154** are flowed through glass capillaries laying down a thin gold-on-silver film on the inner surface, which acts as catalyst for the benzannulation reaction under microwave irradiation (Scheme 62).

dx.doi.org/10.1021/cr100414u |*Chem. Rev.* 2011, 111, 1657–1712

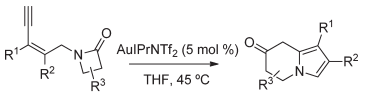
Scheme 60



150 **151**

R= H, Alkyl; m= 1-4 60-85 %

Scheme 61



152 **153**

R^1=R^2= H, Alkyl, Ph; R^3= H, Alkyl 66-90 %

4.5.1.5. Ketones from Esters. Rautenstrauch[311] reported in 1984 the synthesis of 2-cyclopentenones from 1-ethynyl-2-propenyl acetates using $PdCl_2(MeCN)_2$ as catalyst. The first gold(I)-catalyzed version was reported by Toste and co-workers in 2005,[312] the work being further expanded by others. Rautenstrauch's rearrangement under gold-catalyzed conditions allowed the formation of ketones **159** from propargyl esters **158** (Scheme 63).[29,313−317]

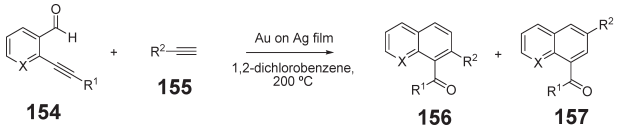
When an allylic alkene is present in **158**, the Rautenstrauch rearrangement occurs under gold-catalyzed conditions (Scheme 63, condition a, 1,2-shift of the pivaloate followed by Nazarov-type carbocyclization) to produce **159** in fair yields.[313] If a halogen is used as trapping agent instead (Scheme 63, condition b), α-haloenones are obtained in good yields (see Scheme 5).[29] The use of cyclopropyl alkynyl acetates **160** is particularly interesting (Scheme 63, condition c), since five-, six-, and seven-membered carbocycles **161** can be obtained (Scheme 64).[314]

A particular case of this approach is the oxidative dimerization of the propargyl acetate, reported by Zhang and co-workers.[318] In this case, oxidation of Au(I) to Au(III) by Selectfluor allows the catalytic cycle to occur, completed by the transmetalation and the reductive elimination steps. This mechanism leads to enone dimers bounded by a new C−C bond. Schreiber and Luo[219] have reported a gold(I)-catalyzed cascade reaction of propargyl propiolates **162** (Scheme 65).

The intermediate **163** can be opened up in two ways, leading to the ketone **164** or the ether **165**, depending on the gold(I) catalysts and conditions used. Remarkably, this reaction can be coupled with other processes such as the ruthenium-catalyzed ring-closing metathesis to achieve longer cascade reactions. Zhang and Cao[319] have reported the formation of 2-acylcyclohexenones with an electron-rich arene ring fused at the 4,5-positions from propargylic carboxylates through two sequential transformations in a one-pot process: a gold(III)-catalyzed rearrangement and a $Sc(OTf)_3$-catalyzed cyclization.

4.5.1.6. Ketones from Amine Oxides. Zhang and co-workers[320] have reported an interesting one-pot conversion of butynyl anilines **166** to tetrahydrobenzazepinones **167** (Scheme 66),

Scheme 62

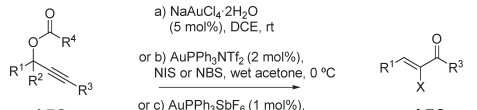


154 **155** **156** **157**

R^1= Aryl; R^2= Alkyl, Aryl, Silyl ; X= CH, N

40-78 % (sum of products) **156:157** 100:0 to 58:42

Scheme 63

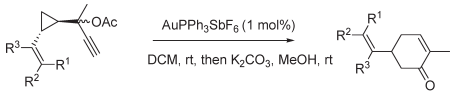


158 **159**

R^1=R^2=R^3= H, Alkyl, Aryl
a) R^4= *t*Bu; b) and c) R^4= Me

a) X= carbon, 60-75 %
b) X= iodo or bromo, 75-97 %
c) X= carbon, 56-96 %

Scheme 64



160 **161**

R^1=R^2=R^3= H, Alkyl, Aryl 56-96 %

in addition to the intermolecular reaction reported by the same group.[167]

The amine oxide was generated in situ and then the gold catalyst allowed the transfer of the oxygen to the alkyne moiety to generate **167** after cycloisomerization. Curiously, the reaction proceeds without gold catalyst if the alkyne has a EWG as terminal substituent instead of H. The reaction was expanded by the same group to butynyl alkyl amines.[321] The corresponding piperidones were recovered in good yields and diastereoselectivities and allowed the diastereoselective synthesis of racemic cermizine C. Anyway, the nitrone can already be present in the substrate. Finally, Shin and co-workers[322] have reported geometry-dependent divergence in the gold-catalyzed cyclization of *o*-alkynylaryl ketoximes and nitrones, leading to 2-acyl-substituted isoindoles.

4.5.2. Intermolecular Formation of Ketones. The hydration of alkynes is the method of choice to form ketones in an environmentally friendly, 100% atom-economical way. The seminal work by Utimoto,[236] Tanaka[287b] and Teles[203] on the gold-catalyzed hydration of alkynes have been revisited by different authors. Nolan and co-workers[323] reported that gold(I)−carbene catalysts are able to catalyze the hydration of alkynes at loadings <10 ppm under acid-free conditions. In a similar approach, Corma and Leyva[324] have used gold(I)−phosphine complexes as catalysts at room temperature and without acidic cocatalysts (Scheme 67). Ketones **169**, including those containing acid-labile functionalities such as propargyl alcohols or silyloxy-protecting groups, were obtained in good yields.

The hydration of alkynes has also been reported to proceed smoothly in aqueous media by using water-soluble phosphine−Au(I)

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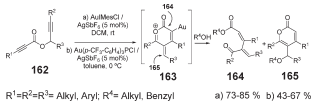
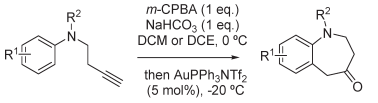
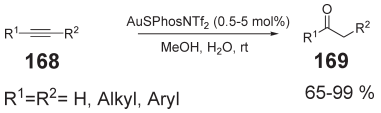
Scheme 65



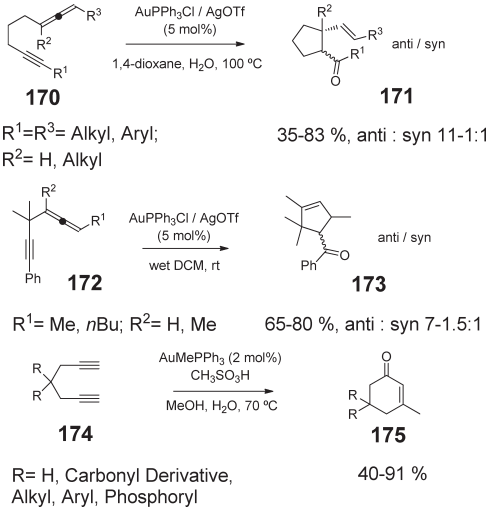
Scheme 66



Scheme 67



Scheme 68



dendrimers as catalysts.[325] Remarkably, the nano-order size of the dendritic catalyst Au(I) allowed recycling by membrane separation without deactivation of the catalyst. In a related patent, allylamine polymer-supported phosphine ligands were used and recycled for the gold(I)-catalyzed hydration of alkynes.[326] A gold(III)-catalyzed hydration of homopropargyl alcohols has also been reported.[327] The corresponding γ-hydroxy ketones were directly reduced by Ph_3SiH in the presence of a Lewis acid to achieve 2,5-disubstituted tetrahydrofurans.

The gold-catalyzed hydration of the alkynes can also be accompanied by cycloisomerization processes (Scheme 68).

First, Liu, Liao and co-workers[328] have reported the gold(I)-catalyzed hydrative carbocyclization of 1,5- and 1,7-allenynes **170** and **172** to form the α-cyclopentyl ketones **171** and **173** in good yields and selectivities. Second, Zhang, Hayashi and co-workers[329] have reported the same process but for 1,6-diynes **174**, obtaining cyclohexenones **175** in good yields, with a sulfonic acid as both co-catalyst and promoter of the gold(I) catalyst. The same reaction has been performed recently in ionic liquids by Cui and co-workers,[330] using $[bmim]BF_4$ as ionic liquid, MeOH as cosolvent, $AuPPh_3NO_3$ as catalyst, $MeSO_3H$ as substoichiometric catalyst, and water as reagent. The system was recycled up to six times without loss of activity. Finally, Cossy, Meyer, and Couty[331] have reported the AuCl-catalyzed cycloisomerizations of enynamides to cyclobutanones in moderate yields at room temperature, including a diastereoselective version.

Not only water and/or alcohol can be the external oxygen source in ketone formation from alkynes. Indeed, Ujaque, Asensio, and co-workers[332] have reported a gold(I)-catalyzed oxyarylation between terminal acetylenes **176** and sulfoxides **177** (Scheme 69). The product **178** arises from the electrophilic aromatic alkylation at the position adjacent to the sulfur atom concominantly with the hydration in the other position of the alkyne, which leads to a new β-arylated ketone. DFT calculations suggest a concerted mechanism for the reaction.

It can be seen that the use of an external source of oxygen to hydrate alkynes is a common way to obtain ketones under gold-catalyzed conditions. However, both intra- and intermolecular oxygen addition are sometimes involved (Scheme 70).

Typically, alkynyl esters **179** can undergo the anchimeric assistance of the carbonyl group under gold-catalyzed conditions to form an intermediate which is opened back up by one water molecule, leading finally to carbonyl compounds **180**. This mechanism has already been commented on during the synthesis of α,α′-acyloxiranyl alkynes **146** (see Scheme 58).[298,299] As H_2O is used now as an additional oxygen source, the epoxide functionality is not necessary. For instance, Hammond and co-workers[333] have reported the $NaAuCl_4$-catalyzed synthesis of β- and γ-keto esters from 2- or 3-alkynoates, respectively, in good yields, through this neighboring ester-assisted mechanism. The same anchimeric assistance is proposed to occur in the Au(I)-catalyzed hydrative rearrangement of 1,1-diethynylcarbinol acetates, reported by Oh and Karmakar.[334] The use of in situ formed $AuPPh_3SbF_6$ as catalyst and external water allows producing cyclopentenones or allenones in good yields, depending on the reaction conditions. This oxo-assisted, gold-catalyzed hydration of alkynes is not exclusive of alkynyl esters; for instance, another ketone present in the molecule can act as preactivator of the alkyne, as found by Liu and co-workers.[56,335] Curiously, the regioselectivity of the oxo-assistance on the alkyne can vary depending on the catalyst (in situ generated $AuPPh_3OTf$ or $PtCl_2$) and the gold(I) catalyst leads to spiroketones in good yields and selectivities.[56] The same catalyst allows one to obtain diyn-3-ones in fair yields.[335]

The neighboring ester-assisted mechanism shown in Scheme 70 can be tuned, as has been shown (Scheme 71).[336] 1-Benzoxyvinyl ketones **186** were obtained in good yields by oxidizing Au(I) to Au(III) with Selectfluor in the catalytic cycle, whereby a final reductive elimination of the Au(III) allows the coupling of the esters and the regeneration of the catalyst.

A third way to obtain ketones by gold-catalyzed processes is the oxidation of secondary alcohols. 1-Phenylethanol **187** has been commonly used as benchmark substrate for this reaction (Scheme 72, equation A).

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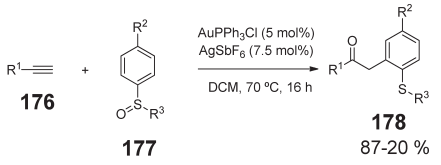
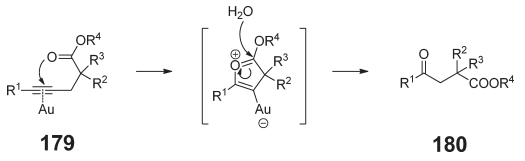
Scheme 69



Scheme 70



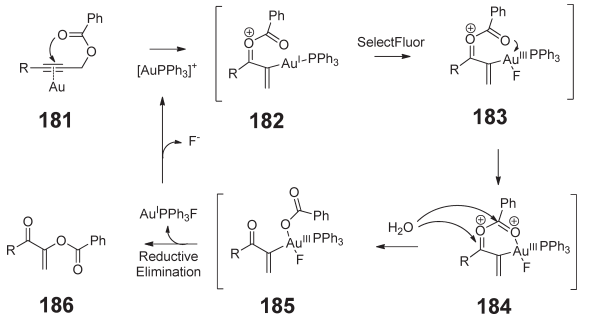
Acetophenone **188** has been obtained by oxidation using different gold-supported nanoparticles as catalysts under air or O_2. Among the supports used during this period in the aerobic oxidation of **187** we found Mg, Al, and Cu mixed oxides;[337] basic metal carbonates;[338] aluminum oxyhydroxide;[285] poly(*o*-phenylenediamine) hollow microspheres;[339] and hydrotalcites.[275] For oxidations under O_2 we found microchannel flow reactors,[284] polymer-incarcerated, carbon-stabilized gold nanoclusters,[340] porous coordination polymers,[341] and CeO_2.[342] The Au−Pd bimetallic system can also carry out the oxidation under O_2,[265] and H_2O_2 can also be used as oxidant.[343]

Not only **187** can be oxidized to the corresponding ketone. In fact, many of these gold-based catalysts as well as those reported for the oxidation of aldehydes have been used for the oxidation of alcohols under air[275,281,285,344b,c] or O_2.[265,266,284,340,344a,b] Cyclooctanone has been obtained by using colloidal gold nanoparticles as catalysts,[286] but supported nanoparticles work better when the proper support and reaction conditions are used. Thus, supercritical carbon dioxide has been used as solvent for the Au/TiO_2-catalyzed oxidation of alcohols to ketones and aldehydes with O_2.[277] Oximes can be used instead of alcohols as substrates to obtain ketones under O_2 using Au-supported CeO_2 as catalyst.[342]

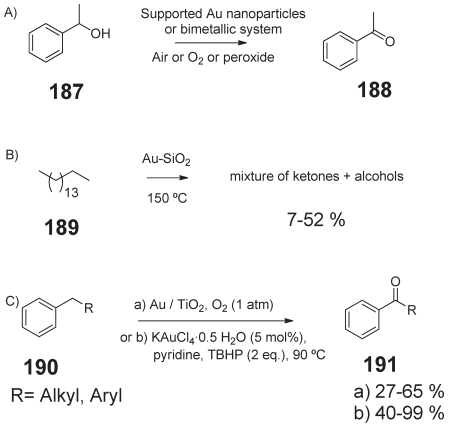
The mechanism of the gold-catalyzed oxidation of secondary alcohols to ketones has been studied during this period, analogously to that of aldehydes formation. Then, Mullins and coworkers[345] described the selective oxidation of 2-butanol on oxygen precovered Au(111) surface. Similar studies for 2-propanol oxidation were also performed.[346]

A last strategy to form ketones intermolecularly under gold-catalyzed conditions involves the direct oxidation of alkanes. As we mentioned before, the first studies on the direct oxidation of cyclohexane to cyclohexanone were reported in 2004,[40,41] using gold-supported zeolites, Au/ZSM-5, and gold-supported mesoporous materials, Au/MCM-4, as catalysts. More recently, different works confirm the important role that heterogeneous catalysts play in this regard (Scheme 72, equations B and C).[44,347,348] However, special care should be taken on product analysis to avoid misleading results. Well-dispersed gold nanoparticles into the walls

Scheme 71



Scheme 72



of mesoporous silica act as recyclable catalysts for the solvent-free aerobic oxidation of *n*-hexadecane **189** to a mixture of ketones and alcohols with poor regioselectivity,[44] while in another example, Au/TiO_2 catalyzes the solvent-free oxidation of benzylic compounds **190** to ketones **191** at 1 atm O_2 (Scheme 72, equation B).[347] The heterogeneous catalyst could be recycled. The yield of **191** could be improved with a homogeneous gold catalyst and TBHP as oxidant (Scheme 72, equation C).[348]

4.6. Formation of Carboxylic Acids

Formation of acids by Au-catalyzed reactions is less common. The work described usually involves the oxidation of aldehydes or alcohols to acids by molecular oxygen in the presence of gold nanoparticles on different supports,[349,350] as described for glycerol as starting alcohol in different patents.[351−354] Supported platinum and palladium nanoparticles are effective catalysts for the oxidation of polyols, for example, for the above-commented oxidation of glycerol to glyceric acid and for the oxidation of glucose to gluconic acid. However, these catalysts show poor selectivity with complex substrates. In this context, Prati and coworkers[355] have expanded their previous work[356] and have studied the role of different stabilizers, such as polyvinyl alcohol, tetrakishydroxypropylphosphonium chloride, and citrate, in the activity of the gold nanoparticles for the liquid-phase oxidation of glycerol. It was found that the phosphonium salt−Au nanoparticles catalytic system gave the best results. The same group studied and compared different Au catalysts and experimental conditions[357] and used a catalyst consisting of gold−palladium

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nanoparticles supported on activated carbon and studied different parameters for this reaction.[358] Hutchings and co-workers[359] obtained glycolate from glycerol by employing Au/C as catalyst and using hydrogen peroxide as oxidant and enhanced the reaction rate by using multiphase structured reactors.[360] Other groups have investigated different aspects of this reaction.[361]

Corma and co-workers[362] have reported the aerobic oxidation of 5-hydroxymethyl-2-furfural, a biomass-derived chemical, into 2,5-furandicarboxylic acid with gold nanoparticles supported on CeO_2 and TiO_2, the former being more active and selective. The reaction is performed in basic water at moderate temperatures. The same reaction was performed by Riisager and co-workers,[363] using gold nanoparticles on TiO_2 as catalyst at 30 °C.

The production of acetic acid from ethanol by liquid-phase oxidation with air and oxygen has been studied, using Au catalysts supported on various metal oxides.[364] ZnO and TiO_2 gave the best results, achieving yields and selectivities >99%. Silica can also be used as support.[365] With this catalyst, it was demonstrated that acetaldehyde is an intermediate in the formation of acetic acid from ethanol.[365] Acetic acid was found as one of the products during the oxidation of ethanol on gold (111) surfaces.[366]

A patent claiming that glucose can be oxidized to gluconic acid in the presence of a gold catalyst can be found during this period.[367] Haruta's group has deeply studied this gold-catalyzed oxidation, showing that glucose can be oxidized to sodium gluconate in basic conditions using gold nanoparticles directly deposited on ion-exchange resins.[368] Gluconate was also obtained by employing gold nanoparticles deposited on carbon supports.[369] The poisoning effect of different molecules on carbon-supported gold catalysts has also been studied.[370] Gold nanoparticles were also active for the same transformation when deposited on cellulose,[371] their catalytic activity being comparable to that of Au/C when the size of the Au particles is similar. Another method to obtain gluconic acid is starting from cellobiose.[372] The authors used carbon-nanotube-supported gold nanoparticles to catalyze the oxidation of cellobiose into gluconic acid with molecular oxygen in aqueous medium, achieving yields of 80%.

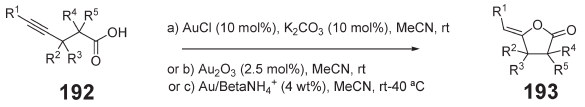
3-Hydroxypropionic acid can be directly obtained from allyl alcohol by employing Au/C or Au/TiO_2 as catalyst under O_2 atmosphere.[62] The direct oxidation of amino alcohols to amino acids have been accomplished by using Au supported on different metal oxides as catalyst, in basic conditions under O_2. TiO_2 was the most versatile support.[373] Different alcohols have been oxidized to acids by using gold-supported poly-(*o*-phenylenediamine) hollow microspheres as catalyst in basic aqueous conditions under air[339] or by using Au/TiO_2 as catalyst and H_2O_2 as oxidant in water.[343] Other supports did not work as well.

An exception to the use of alcohols or aldehydes as substrates corresponds to the direct oxidation of methane into formic acid using an O_2-H_2 mixture in a catalytic wall reactor functionalized with plasma-activated gold nanoparticle films.[374]

4.7. Formation of Esters

Oxidation of ethers to esters through C−H activation in the α position is less common that alkane oxidation to form alcohols and ketones. Nevertheless, some metal-catalyzed α-oxidation of ethers can be found and, as will be shown, gold is not an exception. Gold nanoparticles supported on inorganic supports are used as reusable heterogeneous catalysts for the oxidation of ethers to esters, using air as the oxidant. Moreover, the direct gold-catalyzed oxidation of alcohols to acids, (see formation of carboxylic acids) namely oxidative esterification, can give esters by in situ addition of the alcohol to the acid. However, the formation of esters at lower scale, including the laboratory, involves the addition of an alcohol to a preactivated acid derivative, such as the classical Fisher or Steglich esterifications. These transformations can be catalyzed by many Brønsted and Lewis acid, including gold. Once again, the intrinsic advantage of gold in this particular strategy relays on its capability of activating unsaturated C−C bonds toward oxygen-containing nucleophiles. In the simplest approach, the hydroxycarbonylation reaction between carboxylic acids and gold-activated C−C bond allows forming new ester groups. A third gold-catalyzed reaction pathway engages the two commented processes: a tandem hydroxylation−oxidation of the triple bond with an alcohol. A fourth approach, and probably the most intriguing, particularly for gold when forming new esters bonds, is the possibility of 1,2- and 1,3-intramolecular migrations of esters group. The latter is probably the most studied gold-catalyzed transformation in the period covered by this review.

Scheme 73



192 → 193

a) R^1= H, *n*Bu, Ph, Br; R^2=R^3= H, Me; R^4=R^5= H, NHFmoc
b) R^1= H, Alkyl, Aryl; R^2=R^3= H; R^4=R^5= H, Cl, Alkyl, Aryl, Ester
c) R^1=R^2=R^3= H; R^4=R^5= H, Alkyl, Aryl, Ester

a) 75-96 %
b) 54-99 %
c) 50-88 %

4.7.1. Cyclic Esters. *4.7.1.1. γ-Lactones.* The intramolecular addition of carboxylic acids to alkynes yields lactones. Palladium is the most acknowledged catalyst for this transformation.[66] In 2006, Genêt, Michelet, and co-workers[375] used AuCl as catalyst for this reaction, obtaining good yields. Toste and co-workers[170] also used the chiral counteranion strategy to obtain γ-lactones from allenyl-substituted acids under gold-catalyzed conditions (see Tetrahydrofurans). In this period, the Au-catalyzed cyclization of γ-acetylenic acids **192** to form γ-lactones **193** has been accomplished either with homogeneous[376,377] or heterogeneous catalysts[378] (Scheme 73).

The use of AuCl[376] (condition a) or Au_2O_3[377] (condition b) allowed obtaining the corresponding lactones **193** in good yields. However, Au-deposited onto β-zeolite (condition c) behave as an efficient and reusable catalyst.[378] Phosphaalkene−Au(I) complexes have also been used as catalysts for this reaction.[379]

The cyclization can also be done with γ-allenyl acids. For instance, $AuKitPhosNTf_2$ complexes have been employed as catalysts to afford the corresponding γ-lactones in good yields.[51] In a remarkable example, Blum and co-workers[380] employed a combination of $AuPPh_3Cl/AgOTf/Pd_2dba_3$ to form substituted butenolides **195** from allenoates **194** (Scheme 74).

The mechanism involves a first gold(I)-catalyzed cyclization step of the allenoate to form the gold(I)−substituted lactone adduct. This adduct can be detected by NMR and, in fact, these apparently unstable gold(I) complexes have been isolated as phosphine complexes (see compound **197**, Scheme 75). It is now when the palladium(II) activates the allyl moiety to couple with the sp^2-carbon of the lactone and release both the gold(I) and the Pd(0) complexes, for a new catalytic cycle. This mechanism has

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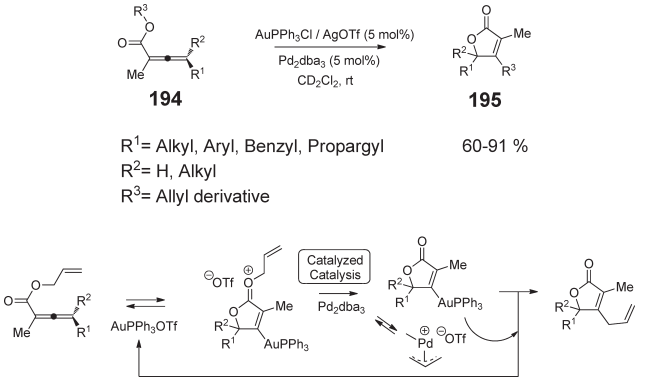
Scheme 74



been called "catalyzed catalysis". The unsaturated γ-lactones **195** were obtained in good yields. γ-Butyrenolactones have also been obtained by similar approaches.[381,382] Importantly, when gold(I) complexes are reacted as reagents with allenoates **196**, the corresponding gold(I)-substituted γ-butyrenolactones are isolated in good yields (Scheme 75, condition a).[381]

Compounds **197** constitute a proof of structure of intermediates in gold(I) catalysis. Indeed, **197** was converted into the corresponding butyrenolactone and iodobutyrenolactone by protodeaureation and iodization, respectively.[381] These compounds can also be synthesized in good yields from *Z*-enynols **198** (condition b), using in situ generated $AuPPh_3OTf$ as catalyst under a dioxygen atmosphere.[382] Examples of γ-lactones formed from γ-alkenyl acids have also been described by Fürstner and Morency[196] in the course of their studies on gold-catalyzed δ-lactones formation (see below).

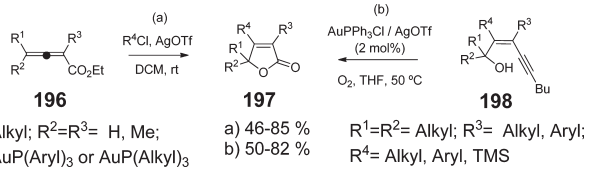
In a different synthetic approach, γ-butyrolactone **200** has been obtained from 1,4-butanediol **199** under heterogenously catalyzed conditions (Scheme 76).[383−385]

Au nanoparticles on iron oxides were used as catalyst, and a support crystal phase effect was observed on the oxidative dehydrogenation reaction.[383] Milder reaction conditions could be obtained by using O_2 over supported gold nanoparticles on hydrotalcite.[386] The catalyst can be recycled and reused without any loss of activity. A third example of oxidative cyclization of 1,4-butanediol has been reported using bimetallic Au−Pd polyvinylpyrrolidone-stabilized nanoparticles as catalysts in aqueous solution.[264]

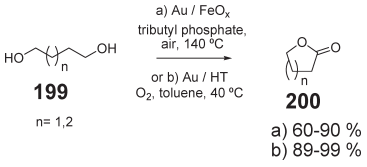
γ-Vinylbutyrolactones have been synthesized through a gold-catalyzed diastereoselective cyclization of the malonate-substituted allylic acetates by Chen and co-workers.[215] $AuPPh_3Cl/AgSbF_6$ or $AuBr_3$ were the catalysts of choice and they were employed depending on the nature of the substrate. This was, apparently, the first report of a gold-catalyzed intramolecular nucleophilic addition of esters onto allylic acetates. A possible gold-catalyzed intermolecular nucleophilic addition of alcohols onto allyl acetate was also attempted.[215] Unfortunately, only allyl alcohol worked well, providing the corresponding diallyl ether. Allyl tosyl amine did not work as nucleophile.

4.7.1.2. δ- and Seven-Membered Lactones. Lengthening the chain of the precursor by one atom allows the obtention of δ-lactones by some of the approaches reported for γ-lactones. For instance, δ-lactones are obtained in good yields from δ-acetylenic acids using AuCl as catalyst[376] (see Scheme 73, condition a) or from benzoate derivatives using the combination

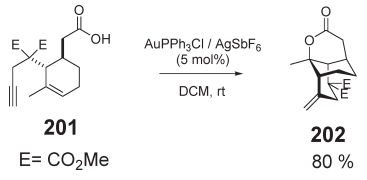
Scheme 75



Scheme 76



Scheme 77



$AuPPh_3Cl/AgOTf/Pd_2dba_3$ (catalyzed catalysis) as catalyst (see Scheme 74).[380] A gold-facilitated 6-exo-dig intramolecular cyclization of 2-[(2-nitrophenyl)ethynyl]phenylacetic acids has also been reported.[387] Dihydrocumarines have been synthetized from allyl aryl ethers by using $AuCl_3/3AgOTf$ as catalyst.[388] The control of the temperature allows one to get a [1,3] or a [3,3] sigmatropic rearrangement, thus affording different cyclic esters.

Similarly, δ-valerolactone can be obtained from 1,5-pentanediol using Au nanoparticles on iron oxides as heterogeneous catalyst,[383a] although in low yields (see Scheme 76), or by using O_2 over supported gold nanoparticles on hydrotalcite.[386] The gold support can also be titanium oxide.[61,389]

As was mentioned above, Fürstner and Morency[196] have performed the formation of δ-lactones **202** from enynyl esters **201** through gold-catalyzed cycloisomerization reactions (Scheme 77). Remarkably, small changes in the substitution pattern of the double bond dramatically changed the outcome of the gold-catalyzed reaction. Schreiber and Luo[219] have reported a gold(I)-catalyzed cascade reaction of propargyl propiolates **162** (see Scheme 65) to achieve δ-lactones **165**.

Concerning bigger lactones, one example of a seven-membered lactone has been reported,[376] although in very low yield and the product could not be isolated.

4.7.2. Acyclic Esters. *4.7.2.1. Intramolecular O-Migrations.* One of the most studied gold-catalyzed reaction is perhaps the intramolecular migration of acetoxy groups,[390] and this reaction is also the most studied during the period covered by this review. The mechanism typically involves the 1,2- or 1,3-migration of a propargyl ester (Scheme 78).[391] It is accepted that terminal or electronically demanding alkynes react via 1,2-migration,

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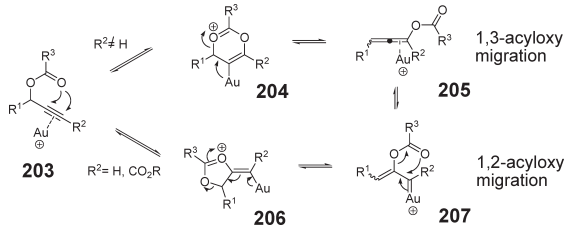
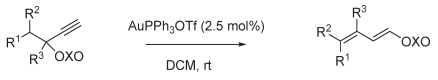
Scheme 78



Scheme 79



R^1= H, Me, CyHex, Ph; R^2= H, Me, CyHex;
R^3= H, CyHex; OXO= OAc, OPiv, OP(O)(OEt)$_2$

whereas internal alkynes prefer 1,3-migration.[391] These intermediates are evidenced by theoretical studies,[392] and relevant theoretical and experimental studies on **205**-type gold complexes have been performed.[393]

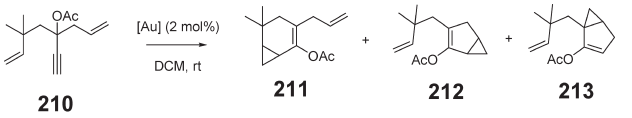
These mechanisms have already been seen in the neighbor-group-assisted intermolecular synthesis of ketones (see Schemes 58, 70, and 71). Consequently, some methods seen before for the synthesis of ketones have been used for the synthesis of esters. For instance, Nolan and co-workers[291] obtained esters by hydration of alkynyl ethers (see Scheme 55, condition b). In many cases the ester persists in the molecule and, obviously, no external source of oxygen is needed. Some examples have already been seen: starting from alkynyloxiranes **146**, divinyl keto esters **147** were obtained (see Scheme 58);[298,299] from alkynyl esters **181**, 1-benzoxyvinyl ketones **186** were obtained (see Scheme 71);[336] from benzylic esters **75**, vinyl esters **76** were obtained (see Scheme 27);[183] from cyclopropyl alkynyl acetates **160**, enol acetates were obtained (see Scheme 64);[314] from 1,1-diethynylcarbinol acetates, acetoxy cyclopentenones or allenones were obtained (see Scheme 71);[334] and from ω-hydroxy propargylic esters **84**, bisubstituted tetrahydropyrans **86** were obtained (see Scheme 31).[195]

However, exceptions to the mechanisms described in Scheme 78 can be found (see Schemes 79, 82, and 84). For instance, simple alkynyl esters lacking of any other functionality can form different esters under gold-catalyzed conditions through 1,3-acyloxy migration,[394,395] 1*E*,3*E*-dienes **209** being obtained in good yields from propargylic esters **208** (Scheme 79).

This 1,3-acyloxy migration often operates together with a gold-catalyzed cycloisomerization process. For instance, Nolan and co-workers[396] have performed an exhaustive study of the cycloisomerization of the enynyl ester **210**, including theoretical calculations and labeling experiments (Scheme 80).

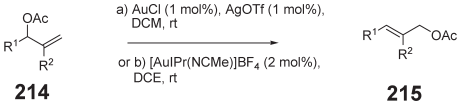
Different gold salts and complexes, including carbenes, gave the cycloisomerization reaction. Remarkably, compound **213** would come from a first 1,3-OAc shift/allene−ene cyclization followed by a second 1,2-OAc shift. In addition, the reactivity of related allenelyl acetates was examined and found to be different. The selectivity of the reaction can be improved using ionic liquids

Scheme 80



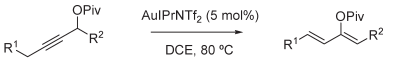
63-95 % (sum of products)

Scheme 81



a) R^1= Alkyl, Aryl; R^2= CO_2Me — a) 78-92 %
b) R^1= Heptyl; R^2= H — b) 73 %

Scheme 82



R^1= Alkyl, NPG; R^2= Alkyl — 36-85 %

as solvents.[397] Another example of 1,3-OAc migration was found during some studies on platinum-catalyzed reactions.[398]

The gold-catalyzed 1,3-acyloxy migration is not exclusive for propargyl esters, but allyl esters **214** can isomerize as well (Scheme 81).[399,400]

Xu and co-workers[399] showed that allyl acetates **215** are obtained in good yields and, importantly, with complete *E* selectivity (condition a). Nolan and co-workers[400] obtained a similar product (condition b) during their studies on cationic NHC−gold(I) complexes. Computational studies of the latter reaction were done.[401]

The second possible pathway of gold-catalyzed cycloisomerization is the 1,2-migration (see Scheme 78). Zhang and co-workers[402] have reported the 1,2-acyloxy migration in internal propargylic pivalates **216** (Scheme 82). The corresponding 1*Z*,3*E*-pivaloxydienes **217** are isolated in good yields.

This eliminative rearrangement can operate together with other processes, such as, for instance, the nucleophilic adition of the unsaturated imines **219**, reported by Toste and Shapiro[403] (Scheme 83, condition a). This reaction is a formal [4 + 3] cycloaddition catalyzed by the gold(III) complex PicAuCl$_2$ to form azepines **220** in good yields and diastereoselectivities.

In a related process, Davies and Albrecht[404] have reported the nucleophilic addition of sulfurs after a gold-catalyzed 1,2-rearrangement of **218**, which generated in situ sulfur ylides that led to **221** (b). A gold(I)-catalyzed 1,2-cycloisomerization of 1,7- and 1,8-enynes-3-propargyl esters has been reported by Hanna and co-workers,[405] leading to cyclopropyl vinyl ester derivatives containing seven- and eight-membered rings, respectively. This methodology was applied in the synthesis of a new allocolchicinoid, **279** (see Scheme 100).

Finally, Nevado and co-workers[391] have described the Au-catalyzed tandem 1,2-/1,2-bis (acetoxy) rearrangement of 1,4-bis(propargyl acetates) **222** to provide access to 2,3-bis-(acetoxy)-1,3-dienes in high yields (Scheme 84).

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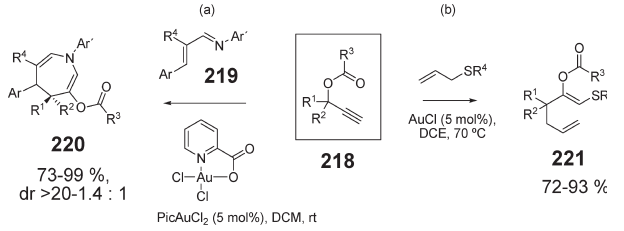
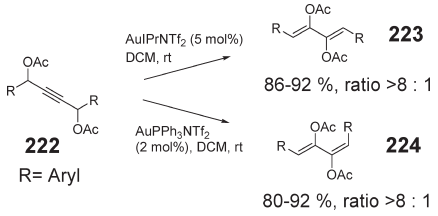
Scheme 83



a) R^1=R^2= H, Alkyl, Aryl;R^3= *t*Bu, Bn; R^4= Me, Br
b) R^1= Ph, *o*-BrC_6H_4; R^2= H; R^3= Me, *t*Bu, Ph; R^4= Aryl

Scheme 84



Remarkably, one or another stereoisomer **223** or **224** was obtained, depending on the gold(I) catalyst used. Nonsymmetrically substituted 1,4-bis(propargyl acetates) were also prepared.

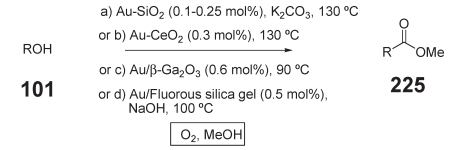
4.7.2.2. Intermolecular Ester Formation. As was mentioned for lactones, the intermolecular addition of acids to alkynes is the simpler way to obtain (vinyl) esters. Ruthenium is acknowledged as the most effective metal for this transformation.[66] A first example of gold-catalyzed intermolecular addition of acids to alkynes was reported in 2004 by Schmidbaur and co-workers,[406] using acetic acid and 3-hexyne under gold(I)-catalyzed conditions.

Other strategies to obtain acyclic esters under gold catalysis have been envisaged in this period. Some gold(I)-catalyzed transesterifications have been already commented. Schreiber and Luo[219] (see Scheme 65) have reported the gold(I)-catalyzed cascade reaction of propargyl propiolates **162** to achieve keto esters **164** in good yields after addition of the alcohol. Asao and co-workers[224] (see Scheme 43) have transformed alcohols to ethers by employing alkyl esters **112** as alkylating agents in the presence of gold species. If the reaction is run in the presence of EtOH for particular substrates, a simple transesterification process occurs.[407] A one-pot formation of ethyl acetate from ethanol has been reported by Friend and co-workers.[408] In this work, the formation of ethyl acetate over oxygen-covered Au(111) surfaces is followed in situ by GC−MS and vibrational (high resolution electron energy loss, HREEL) spectroscopy, the reaction occurring below room temperature. The work was further studied later.[366,409]

The most convenient method for the preparation of esters from alcohols under gold-catalyzed conditions is the oxidative esterification. Gold nanoparticles supported in different inorganic oxides are efficient and reusable catalysts for this reaction (Scheme 85).[410−412]

Rossi and co-workers[410] have reported the obtention of methyl esters **225** using Au/SiO_2 as catalyst under basic conditions. These basic conditions can be avoided by using Au/CeO_2 as catalyst.[411] Au/β-Ga_2O_3 can also act as catalyst under milder

Scheme 85



a) and c) R= Alkyl, Allyl, Benzyl
b) R= Methyl-2-furfural
d) R= cinnamyl

a) 20-100 %
b) >99 %
c) 80-99 %
d) 89 %

conditions.[412] These three solid catalysts can be reused without loss of activity. Finally, cinnamyl acid can also be obtained using as catalyst perfluoro-tagged gold nanoparticles immobilized on fluorous silica gel.[413] Hardacre and co-workers[414] have studied the carbonylation reaction of methanol to methyl acetate over heterogeneous gold-based catalysts and identified the active sites as dimers/trimers of gold with the iodide being critical for the activation of the catalyst and to maintain the catalyst in the active form. Other gold-based active systems for the oxidative esterification are gold nanoparticles supported on aluminum oxyhydroxide,[285] porous coordination polymers,[341] and potassium titanate nanowires.[415] In some cases one of the starting materials is the aldehyde, which is dissolved in the corresponding alcohol to obtain the ester by using gold nanoparticles as catalysts and air as oxidant.[416]

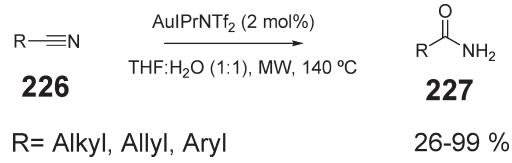
A last unusual strategy to get esters has already been commented on (see Scheme 55, condition c), where propargyl ethers **139** (not alkynyl ethers) undergo a gold-catalyzed oxidative cleavage by using molecular oxygen to achieve R^1COOR^4 as product in good yields.[292]

Tokunaga and Nakamura[205] have performed gold-catalyzed vinyl transfer reactions between vinyl acetate and alkyl, vinyl, benzyl, and aryl carboxylic acids to obtain the corresponding new vinyl esters in good yields, in a similar way as that to obtain vinyl ethers (see vinyl ethers formation). A special case of intermolecular synthesis of esters in which gold plays a specific role (dilution of Pd sites), but not as catalyst, is the vinylation of acetic acid with ethylene catalyzed by PdAu alloys.[85,417−436] This alloy has been revealed as a powerful catalyst toward the production of vinyl acetate monomer (VAM), of paramount importance in the manufacture of polymers. Worldwide VAM capacity is 5 million metric tonnes per year, 80% of which is produced via the ethene route.[437] Goodman and co-workers[438] reported that the high activity and selectivity of this catalyst for the coupling of acetic acid and ethylene comes from isolated Pd dimers on the Au surfaces, gold acting as a disperser and stabilizer of the Pd sites. These issues have been recently studied by computational methods,[439,440] and the deactivation of $PdAu/SiO_2$ has also been studied under industrial conditions.[441]

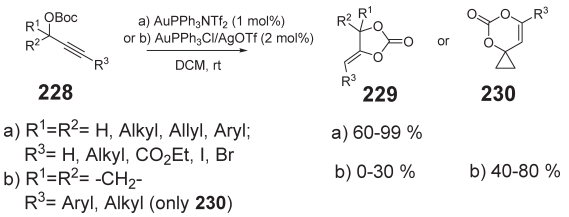
4.8. Formation of Amides

Amides are typically formed by addition of the *N*-nucleophile to an activated carboxylic group. However, the direct hydration of nitriles provides a suitable method to obtain amides through C−O formation. The hydrolysis of nitriles typically does not stop in the amide but goes further to the carboxylic acid.[442] Thus, chemoselective procedures for the synthesis of amides from nitriles are of interest. In this sense, Nolan and co-workers[443] have reported the gold(I)-catalyzed hydration of nitriles to amides (Scheme 86).

Scheme 86



Scheme 87



Many nitriles including aliphatics and (hetero)aromatics were hydrated by using a carbene gold(I) complex as catalyst under microwave heating. The same group reported later the intramolecular process, namely, the aldoximes rearrangement to amides.[444] The reaction proceeds via gold/silver cocatalysis under solvent and acid-free conditions.

4.9. Formation of Carbonates

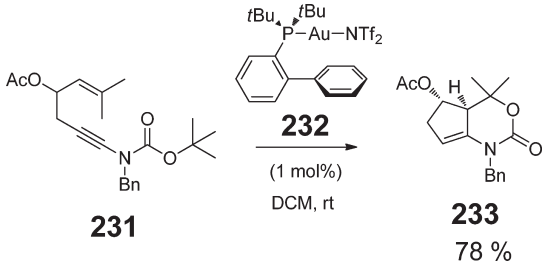
Carbonates have typically been formed from phosgene and alcohols. This method is currently being substituted by safer, environmentally better methods. These are based in the use of CO/O_2 or directly CO_2 as carbonate sources and R−X (X = nucleophuge) as alkyl parts. In this sense, gold can act as Lewis acid to activate alkyne groups toward CO_2 or ester addition, generating the new carbonate functionality in a convenient way.

4.9.1. Cyclic Carbonates. Gagosz and Buzas[445] reported in 2006 the gold(I)-catalyzed cyclization of propargyl *tert*-butyl carbonates to carbonates. The *tert*-butyl group is eliminated as isobutene and a proton.[446,447] Extending their work, Gagosz and co-workers[31] have obtained alkylidenyl dioxolanones **229** in good yields from propargylic *tert*-butyl carbonates **228** by this gold(I)-catalyzed rearrangement, using low amounts of catalyst (Scheme 87, condition a).

However, Chen and co-workers[448] reported later that six-membered rings **230** were preferentially formed for other substrates, through a 6-endo-dig addition, when using a gold(I) cationic complex (Scheme 87, condition b). The selectivity depends on stereoelectronic and steric effects, alkyl alkynes leading exclusively to the six-membered carbonates. Additionally, Rhee and co-workers[449] have reported a gold(I)-catalyzed tandem cyclization of 3-(*tert*-butoxycarbonyloxy)-1,6-enynes to form cyclic carbonates in good yields, using phosphine gold(I) complexes as catalysts.

4.9.2. Acyclic Carbonates. During this period, a three-component catalyst composed of $Au/Fe(OH)_3$, $ZnBr_2$, and Bu_4NBr was shown to be very efficient for the direct oxidative carboxylation of styrene to styrene carbonate.[450] In this reaction, CO_2 acts as both reagent and solvent. The same group[451] improved the method by using the strong basic resin R201, containing quaternary ammonium groups, to support the gold. TBHP was used as oxidant and the catalyst could be reused.

Scheme 88



4.10. Formation of Carbamates

The formation of carbamates is usually conducted via C−N formation, since *N*-containing compounds (typically amines) are better nucleophiles that the corresponding *O*-containing counterparts (typically alcohols). However, the addition of a certain nucleophile to activated carbon centers in gold catalysis is frequently not proportional to its nucleophilicity. In fact, it is well-known that alcohols and anilines add to alkynes better than alkyl amines do under standard gold-catalyzed conditions, which confirms this tendency. This particularity of gold catalysis allows designing the synthesis of carbamates based on *O*-addition rather than *N*-addition. For instance, in 2006, several authors[452,453] employed the same strategy that was used for the synthesis of carbonates to obtain cyclic carbamates from *N*-alkynyl *tert*-butyloxycarbamates. Boc-protected propargylamines were transformed to the corresponding 3-alkylidene-2-oxazolidinones in good yields using gold(I) catalysis. The work has been extended by Gagosz and co-workers,[454] who have used $AuPPh_3(NCMe)SbF_6$ as catalyst in low loadings for this transformation. Interestingly, this procedure could also be employed in the synthesis of the bicyclic carbamate **233** following a formal [4 + 2] cycloaddition process from the *N*-(hex-5-enynyl) *tert*-butyloxycarbamates **231** (Scheme 88).[455]

In this case, the biphenylphosphine-based gold(I) complex **232** was the catalyst of choice, and other substrates could be cyclized to the corresponding bicyclic carbamates in moderate yields and generally good diastereoselectivites.

4.11. Formation of Sulfonates

The first direct formation of sulfonates by addition of sulfonic acids to gold-activated alkynes has been accomplished in the last 2 years. Cui, Zhang, and co-workers[456,457] have reported the synthesis of vinyl tosylates or vinyl mesylates in good yields and regioselectivity from the corresponding alkynes and toluenesulfonic acid or methanesulfonic acid, in the presence of a catalytic amount of $AuPPh_3NO_3$ and phthalimide (Scheme 89).

The corresponding sulfonates **236** were formed in good yields and excellent regio- and stereoselectivity (regio- and stereoselectivity changes in single cases).[456]

4.12. Formation of Phosphonates

As has been seen before (see Scheme 79), the obtention of 1*E*,3*E*-dienephosphonates **209** has been reported in good yields from the gold(I)-catalyzed phosphatyloxy group migration in propargyl phosphonates **208**.[395]

4.13. Application of Gold Catalysts in Total Synthesis

The use of gold catalysis in total synthesis has increased in the last years, owing to the publication of an increasing number of gold-catalyzed reactions. The retrosynthetic strategy is based in carbon−oxygen disconnection, since gold-catalyzed C−O formation is the

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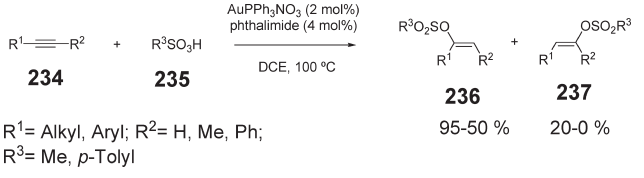
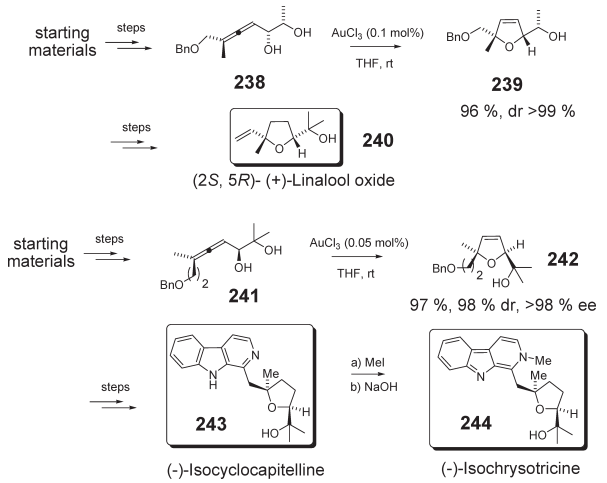
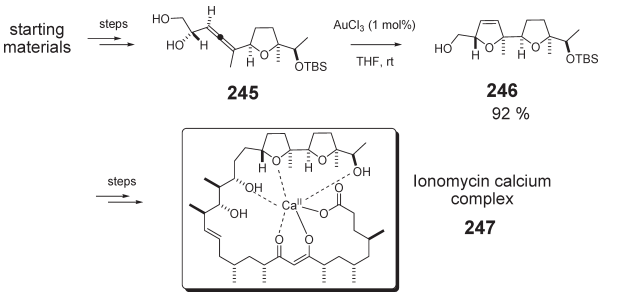
Scheme 89



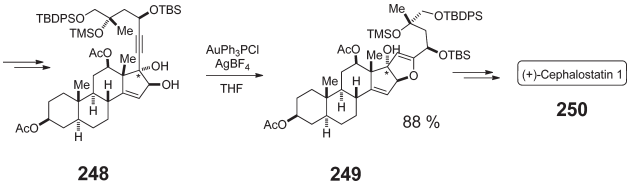
Scheme 90



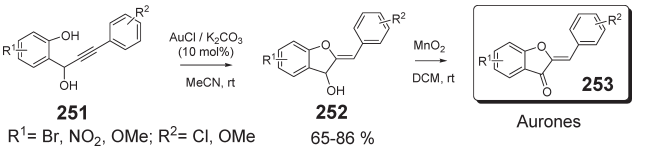
Scheme 91



Scheme 92



Scheme 93



most developed method. As we will see, retrosynthetic disconnections include formation of acetals, furans, pyranes, esters and ketones. A particular impressive example corresponds to the total synthesis of bryostatin 16 (**256**, see Scheme 94), reported by Trost and Dong,[458] where a new dihydropyrane functionality is formed by a gold(I)-catalyzed cycloisomerization of the corresponding alkyne, in a later step of the >40-step synthesis. Other interesting examples are also shown in this section. Previous works in total synthesis, where gold was employed at some stage as catalyst, can be found in a previous review by Hashmi and Rudolph.[6]

4.13.1. Dihydrofurans. The dihydrofuran core is ubiquitous in natural product structures. Gold catalysis is rapidly achieving a wide use to install this functionality in advanced steps of long syntheses. Over all, the same strategy is used: activation of an unsaturated C−C bond (allene or triple bond) by gold and then attack by the hydroxyl group.

The gold-catalyzed cycloisomerization of allyl allenes (see Scheme 18) to produce dihydrofurans has been employed in the total synthesis of diverse natural products. Krause and co-workers[459] have prepared stereoselectively three different tetrahydrofuran-containing natural products: (2*S*,5*R*)-(+)-linalool oxide **240**, (−)-isocyclocapitelline **243**, and (−)-isochrysotricine **244** (Scheme 90).

The corresponding dihydrofurans **239** and **242** were achieved by high-yielding, $AuCl_3$-mediated chirality transfer cycloisomerizations. Later reduction of the double bond gave the desired tetrahydrofurans. Kocienski and co-workers[460] used the same strategy in the synthesis of the ionomycin calcium complex **247**, which is a narrow-spectrum ionophore antibiotic (Scheme 91).

The bis(tetrahydrofuranyl) upper moiety of the molecule was achieved through a high-yielding $AuCl_3$-mediated cycloisomerization.

Regarding cyclizations of alkynols, Shair and co-workers[461] have recently reported a remarkable example during the enantioselective total synthesis of cephalostatin 1 (**250**), a potentially lethal synthetic with the *p16* tumor suppressor gene (Scheme 92).

Au(I)-catalyzed 5-endo-dig cyclization of the homopropargylic group in **248** afforded the dihydrofurane **249** in high yield. The advanced state of the synthesis is noteworthy at this point. Aurones **253** are flavonoids with a broad range of biological activities. Pale and co-workers[462] have designed a general synthesis for these compounds using a gold(I)-catalyzed cyclization of hydroxynyl phenols **251** (Scheme 93).

4.13.2. Dihydropyranes. Some of the gold-catalyzed strategies for the synthesis of dihydropyranes have been employed in total synthesis. Trost and Dong[458] have reported the total synthesis of bryostatin 16 (**256**), a macrolactone exhibing anticancer activity in vivo (Scheme 94). In the last steps of the synthesis, a gold(I)-catalyzed cycloisomerization of the alkyne **254** (see also Scheme 30) under basic conditions led to the dihydropyrane **255** in good yield. Apparently, a methoxy group is concominantly hydrolyzed.

Krause and co-workers[463] used the gold(I)-catalyzed cycloisomerization of the enantiomerically pure hydroxyallenes **257** and **258** (see Scheme 28) to the corresponding dihydropyrans **259** and **260** in order to obtain the sesquiterpenoids bejarols **261** and **262** in pure form (Scheme 95).

4.13.3. Seven-Membered Ether Rings. As was mentioned before, Echavarren and co-workers[201] have prepared the natural

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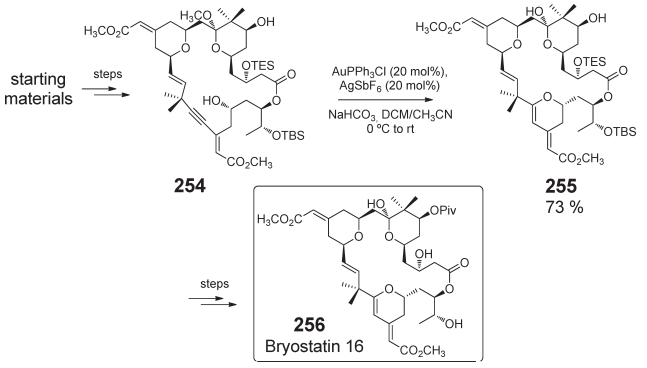
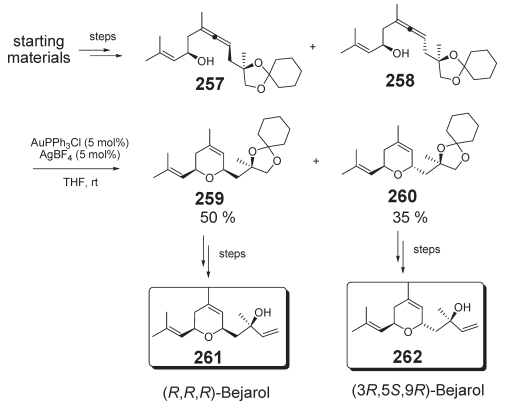
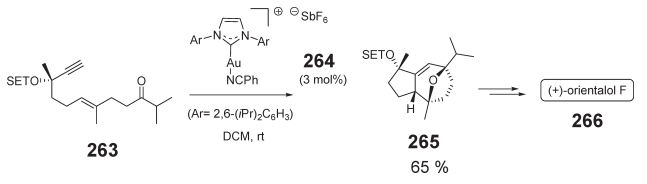
Scheme 94



Scheme 95



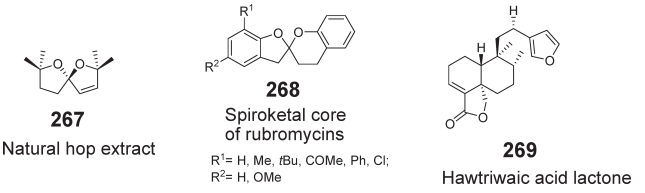
Scheme 96



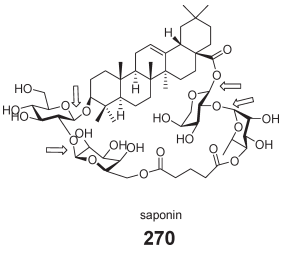
product (+)-orientalol F (**266**), using in one of the steps a stereoselective gold-catalyzed [2 + 2 + 2] cycloaddition of the ketoenyne **263** (see Scheme 96).

4.13.4. Acetals. Gold-catalyzed reactions for the synthesis of acetals have also been employed in natural product synthetic studies (Scheme 97). For instance, Aponick and co-workers[231] used the Au-catalyzed cyclization of monopropargylic triols **120** for preparing the natural hop oil extract **267** (see Scheme 46, spiroacetal **121**, $m = 1$, $n = 0$, 2,2,7,7-tetramethyl) in good yield. In addition, a gold-catalyzed double intramolecular alkyne hydroalkoxylation was performed in order to obtain the bisbenzannelated spiroacetal core of rubromycins **268**.[464] Finally, Miranda, Marrero, and co-workers[465] have reported the microwave-assisted Au(I)-catalyzed cleavage of the pyran ring of brevifloralactone to form an acetal which, after oxidation, gives access to the hawtriwaic acid (**269**) core.

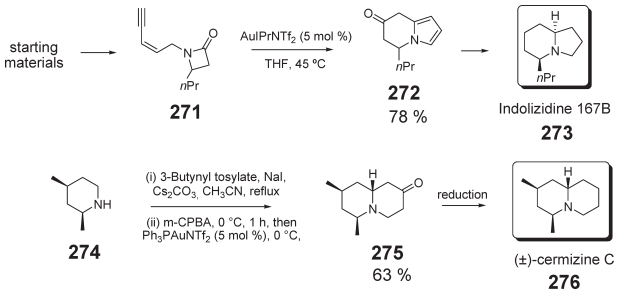
Scheme 97



Scheme 98



Scheme 99



A last impressive example of gold(I)-catalyzed glycosylations for natural product synthesis was shown by Yu and co-workers.[250] As was already commented, they employed glycosyl *o*-alkynylbenzoates as glycosylating agents. This allowed constructing the cyclic triterpene **270** (Scheme 98). The new C−O bonds (marked with arrows) were formed under $AuPPh_3OTf$ catalysis in good yields.

4.13.5. Ketones. Zhang and co-workers[308] have followed their gold-mediated 5-exo-dig cyclization of β-lactams (see Scheme 61) to prepare the intermediate **272** during the synthesis of the alkaloid indolizidine 167B (**273**) (Scheme 99). As has also been commented, the same group reported the diastereoselective synthesis of (±)-cermizine C (**276**) by the Au(I)-catalyzed synthesis of piperidone **275** from the amine **274** through the in situ generated *N*-oxide of the butynylalkyl amine intermediate (Scheme 99).[321]

4.13.6. Esters. As was mentioned before (see acyclic esters preparation, 1,2-acyloxy migrations), Hanna and co-workers[405] have prepared the new allocolchicinoid **279** by a gold(I)-catalyzed 1,2-cycloisomerization of the 1,7-enyne-3-propargyl ester **277** (Scheme 100). The intermediate vinyl ester (not shown) was hydrolyzed to afford the corresponding ketone **278** in good yield in two steps.

In another example of metal-catalyzed [1,2] acyl migrations, a gold(I) catalyst has been tested for the cycloisomerization

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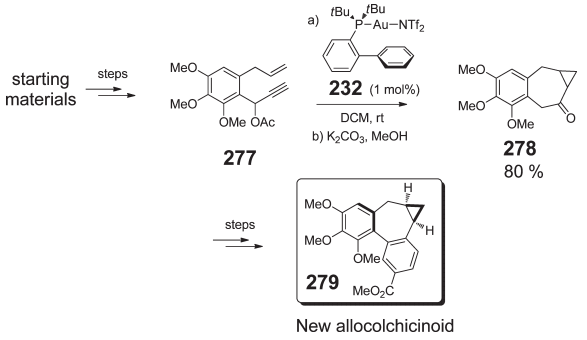
Scheme 100



reaction of enantioenriched propargyl pivalates toward the synthesis of the sesquiterpene (−)-cubebol.[466] However, $PtCl_2$ showed better catalytic activity.

5. FORMATION OF CARBON−NITROGEN BONDS

Many organic compounds of biological and pharmaceutical importance in human life contain nitrogen, and hydroamination, that is, the formal addition of a N−H bond across an unsaturated C−C bond, is a direct and efficient procedure for the synthesis of nitrogen containing compounds of industrial importance.[467]

Taking into account that the intermolecular hydroamination reaction is more difficult to achieve and far less developed than the intramolecular one (which is kinetically and thermodynamically favored), here it will shown that gold has surprisingly been applied to a wide number of examples of nitrogen-containing compound additions which proceed intermolecularly, either as the only reaction or prior to a subsequent gold-catalyzed evolution of the substrate. For example, it is very common to find gold-catalyzed processes in which an intermolecular addition of a nitrogen-containing compound to a multiple bond takes place prior to a cyclization reaction. Alternatively, other unsaturated functions may also be involved in different subsequent reactions instead of this ring closure, and accordingly, numerous examples involving ring expansions, cyclizations, cycloisomerizations, etc., which proceed through hydroamination of allenes, alkynes, etc., have been collected in different subsections throughout this section, hence evidencing the rich chemistry of gold. Other examples will show the opposite case, a reaction that takes place in which the heteroatom is introduced first and then a gold-catalyzed intramolecular cyclization occurs.[468]

Besides hydroaminations, several alkyl esters have also been shown to be efficient alkylating agents for forming C−N bonds, whereas examples on gold-catalyzed oxidations of amines, aldol condensations, allylic aminations, dihydroaminations, etc. will open up the way for benign routes to the synthesis of interesting nitrogen-containing compounds.

5.1. Intermolecular C−N Bond Formation

5.1.1. Formation of Amines. Acid- and metal-promoted hydroamination of alkenes is a general and atom-economical method for the synthesis of amines and derivatives.[469−472] This area of transition-metal-catalyzed hydroaminations has been usually dominated by catalysts based on early transition metals (groups 3−5, as well as lanthanide and actinides) or late transition metals (groups 8−10).[472] However, most of the reported catalytic systems for this reaction show a limited scope of substrates, modest selectivities, and sluggish rates for reactions involving unactivated substrates. Particularly, the hydroamination of unactivated alkenes remains limited.

Meanwhile ruthenium,[406] platinum,[473a,b] and palladium complexes[473c−e] have been shown to catalyze such reactions, but these processes are not efficient enough under mild conditions and, in the case of palladium, β-hydride elimination to afford unsaturated products is usually encountered as a side reaction. With respect to the group of organometallic rare earth metal compounds, they have shown a great capacity as catalysts for the hydroamination of alkenes even with nonactivated double bonds;[473f] however, they are air- and moisture-sensitive and require elaborate Schlenk and glovebox techniques to work with them. Furthermore, many functional groups are often not tolerated (e.g., alcohols, acids) or significantly reduce the catalytic performance (e.g., ethers) in a particular reaction.

Along with all these drawbacks associated with metals, it must be taken into account that the high ligating ability of amines often leads to nonproductive displacement of the unsaturated fragment (in preference to outer-sphere attack), and equally problematic is that the M−alkyl complexes formed by nucleophilic attack are often resistant toward protonolysis or are susceptible to β-hydride elimination.[474]

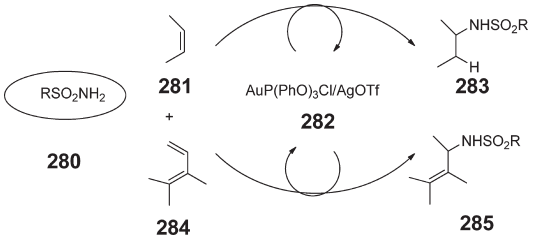
However, the ability of gold to catalyze this reaction in particular is superior in many aspects compared to other metals. In principle, gold complexes [particularly Au(I) complexes], usually catalyze the intra- and intermolecular hydroamination of unactivated olefins under relatively mild conditions.[10j] Even more, as they possess little oxophilic character, they tend to display good functional-group compatibility as well as low air and moisture sensitivity, being also stable with respect to β-hydride elimination. Nonetheless, as with other metals, the gold-catalyzed intramolecular hydroaminations are faster and more general than the intermolecular processes, while the regioselectivity of these bimolecular processes is more difficult to control, not only for alkenes but also for 1,3-dienes, which can afford either 1,2- or 1,4-addition products.[10j]

Another interesting feature of hydroaminations of alkenes catalyzed by gold is that gold salts are often used along with a silver salt (vs the catalytic system $AuPPh_3Cl/AgOTf$),[1,2,475] which is in most of the cases not a cocatalyst but works through counterion exchange to form the active gold catalyst. Nonetheless, despite the remarkable reactivity toward the electrophilic activation of carbon−carbon mutiple bonds, one challenge for this popular catalyst $PPh_3Au^+OTf^-$ is to overcome their poor stability at high temperature (leading to formation of gold mirror and gold nanoparticles).

In this respect, the work carried out by Nájera et al.[476] was focused on the identification of potential improvements in catalysts, especially with respect to activity. They envisaged that the use of stronger electron-withdrawing ligands would increase the interaction of the LAu^+ with the C−C double bond and consequently a greater catalytic activity could be achieved. Thus, they reported that the simple triphenylphosphitegold(I) chloride and silver triflate, as a catalytic mixture **282**, could be used as a very efficient and general catalyst for the intermolecular addition of sulfonamides **280** to alkenes **281** and conjugated dienes **284**, even at a low loading levels of catalysts **282** (Scheme 101).

The reaction could be performed under conventional thermal or microwave conditions, and even at room temperature in the case of dienes. On the other hand, terminal alkenes underwent regioselective hydroamination at the internal carbon atom and dienes at the less substituted double bond.

Scheme 101



Other similar catalytic systems that employ gold(I) salts in combination with $AgSbF_6$ were able to catalyze the Markovnikov intermolecular hydroamination of unactivated alkenes with cyclic ureas 1-methylimidazolidin-2-ones **286** with good yields and high regioselectivity below 100 °C (Scheme 102).[477a] This methodology was extended to the unprecedent enantioselective hydroamination of unactivated 1-alkenes. For example, the enantioselective version of this highly regioselective hydroamination can be carried out by gold(I)−phosphine complexes such as [(*S*)-**289**]−$(AuCl)_2$ [(*S*)-**289** = (*S*)-3,5-*t*-Bu-4-MeO-MeOBIPHEP] in combination with AgOTf, giving up to 78% ee (Scheme 102).

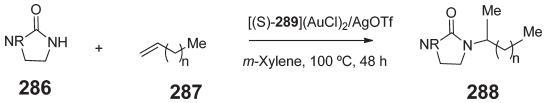
Another example within the field of asymmetric catalysis refers to a highly enantioselective tandem intermolecular hydroamination/transfer hydrogenation of alkynes using a protocol composed of gold(I) complex−chiral Brønsted acid. Here, a wide variety of aryl, alkenyl, and aliphatic alkynes as well as anilines with different electronic properties were tolerated. This approach combines the advantages of both gold(I) and organocatalysis, leading to an efficient synthesis of highly enantiomerically enriched chiral secondary amine compounds.[477b]

Another recent example of gold-catalyzed hydroamination reaction has to do with gold(I) catalysts of 1,2,4-triazole-based *N*-heterocyclic carbenes[478] and cyclic carbodiphosphoranes,[223] which have been recently reported for the hydroamination of terminal alkynes and the hydroamination of acrylonitrile, respectively.

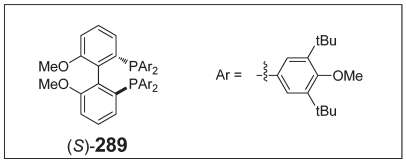
Other related cationic gold(I) and gold(III) complexes, either in the form of inorganic salts or as $Au(PPh_3)$ and Au(III) phorphyrin derivatives, have been used for the hydroamination of alkynes and alkenes; however, in most cases an acid has to be added to achieve conversion.[479] Here, the role of acid promoters is to contribute with a protonolysis reaction of the precatalyst $AuPPh_3CH_3$ to give $Au(PPh)_3^+$, which is the true active species involved in the mechanism.

Besides the hydroamination reaction, there is another way to obtain amines, which is based on the alkylation reaction of amines to get secondary amines. In particular, the synthesis of secondary amines has long been of interest because of their potential as robust pharmacophores and as useful synthetic intermediates. General synthetic methods for the preparation of dialkylamines have included direct *N*-alkylation,[480a] amide reduction,[480b] or the more popular reductive amination protocol.[480c−h] Although these methods are quite reliable, practical success is relatively limited, since concomitant overalkylations also occur. To avoid this problem, while still using traditional techniques, the amine has been occasionally introduced in large excess, so that further purification to remove the starting amine is necessary after completing the reaction. Besides this, *N*-protecting groups have been also typically used to overcome[480i] these shortcomings, although they add lengthy synthetic steps in the desired

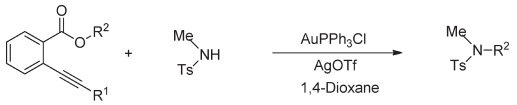
Scheme 102



nucleophile	alkene	yield (%)	ee (%)
R = Me	n = 5	86	76
R = Ph	n = 5	80	71
R = 4-C_6H_4F	n = 5	81	74
R = *t*-Bu	n = 5	89	78
R = CH_3	n = 7	83	73



Scheme 103



R^1= Ph, R^2= allyl, 98 %

R^1= Bu, R^2= allyl, 90 %

R^1= Ph, R^2= Ph—≡—, 87 %

transformations. Therefore, considerable interest exists in developing efficient protocols for the construction of carbon−nitrogen bonds through substitution reactions.

Lewis acids are frequently used as catalysts for these substitution reactions,[481] and gold has not been an exception. In fact, gold complexes that have recently emerged as soft and carbophilic Lewis acids have been reported to catalyze the alkylation reaction of amines and alcohols with *o*-alkynylbenzoic acid alkyl esters **290** as alkylating agents (Scheme 103).[224]

The reaction with alcohols occurs smoothly in the presence of catalytic amounts of $AuPPh_3Cl$ and AgOTf under mild conditions to produce the corresponding ether products in high yields (see Scheme 43). Similarly, *o*-alkynylbenzoic acid alkyl esters **290** have been also used as alkylating agents of sulfonamides **291** to give a series of monoalkylated products **292** with very high yields (Scheme 103).[224]

The reaction likely proceeds through the gold-induced in situ construction of leaving groups and subsequent nucleophilic attack of the nucleophile.

In another example, gold(III) catalyzes the 1,4-nucleophilic addition and subsequent regioselective oxidation of different substrates to prepare 2-amino-1,4-naphtalenedione and 6-amino-5,8-quinolinedione derivatives. Amines such as allyl and propargyl amines, which are well-tolerated under these conditions, gave moderate to good yields as well as different substituted primary, secondary, and aromatic amines.[482]

Finally, gold(III) can also catalyze the nucleophilic substitution of propargyl, benzylic, and allylic alcohols with various nucleophiles, among them various sulfonamides.[483a] Similarly,

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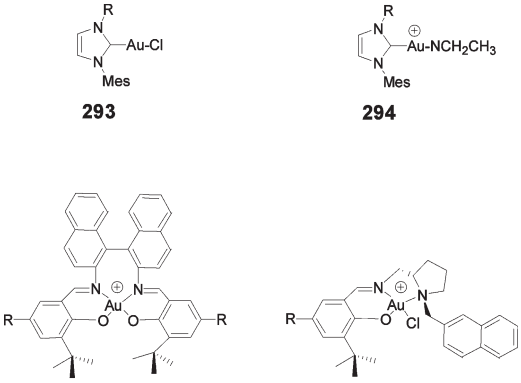
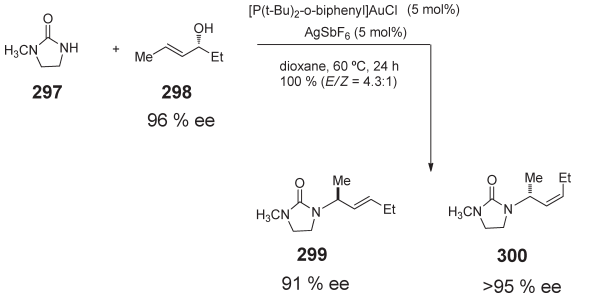
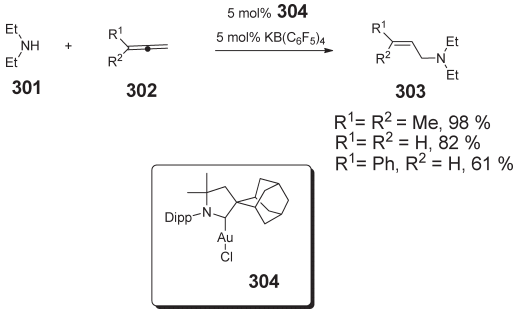
Scheme 104



Scheme 105



Scheme 106



Au(I) catalyzed the NH-triazole addition to alkynes with excellent yields and stereoselectivity (trans-addition) to give vinyl-substituted triazoles.[483b]

5.1.1.1. Heterogeneous Catalysis. The use of acid promoters in hydroamination reactions has not been common after the development of catalysts with poorly coordinating counterions. In these cases, the use of such promoters can be avoided when heterogenizing the gold complexes **293**−**296** on the surface of a Sn-containing MCM-41 (Scheme 104).[483c]

Indeed, this material itself behaves as an efficient recyclable catalysts for the hydroamination of alkenes and alkynes without requiring the incorporation of acids.

5.1.2. Formation of Allylic Amines. Allylic amines are versatile intermediates in synthesis, being important components of many naturally occurring and biologically active molecules and of products of industrial interest.[484,485]

This fact explains the ongoing interest in the direct catalytic amination of underivatized allylic alcohols as a route to allylic amines and related derivatives. Initial headway in this area was realized through the in situ activation of the hydroxyl functionality with Lewis acid cocatalysts.[486a−c] Later, Ozawa reported the amination of allylic alcohols with anilines catalyzed by a cationic Pd(II) π-allyl complex in the absence of a Lewis acidic cocatalyst.[486d] Since that time, a number of metals including Pd(0), Pt(II), Mo(VI), Bi(III), Au(I), and Au(III) have been shown to catalyze the intermolecular amination of underivatized allylic alcohols without assistance of a Lewis acidic cocatalyst.[486e−h,487] Although a number of these transformations display high regio- and/or stereoselectivity, the regiospecific amination of allylic alcohols remains problematic, presumably due to the intermediacy of π-allyl complexes or allylic carbocations.

Interestingly, a gold(I)-catalyzed protocol for the intermolecular amination of allylic alcohols with 1-methylimidazolidin-2-one **297** and related nucleophiles that, in γ-unsubstituted or γ-methyl-substituted allylic alcohols, occurs with high γ-regioselectivity and *syn*-stereoselectivity has been described (Scheme 105).[488]

The hydroamination reaction of allenes can also be a straightforward method to get allylic amines. In fact, depending on the regiochemistry, this reaction can lead to imines, enamines, or allylamines as main products. Recently, an intermolecular hydroamination of allenamides with arylamines has been achieved under mild Au(I) catalysis conditions, delivering allylamino *E*-enamides stereoselectively and in high yield.[489a] Similarly, it has been shown that cationic gold(I) complexes **304** promote the addition of all types of nontertiary amines to a variety of allenes, affording allylic amines **303** in good to excellent yields.[489b] Here, the amino fragment always adds to the less substituted terminus of the CCC skeleton (Scheme 106).

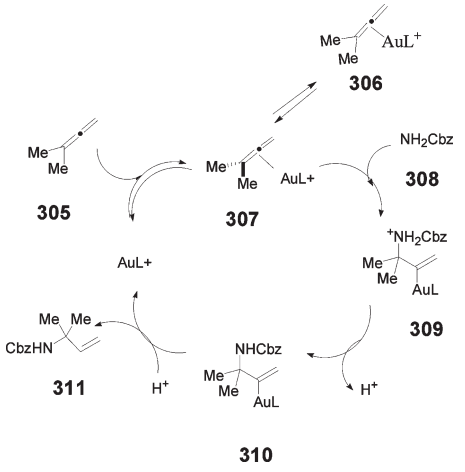
A closely related gold catalyst can be used with a wide diversity of nontertiary amines (included ammonia), as well as a variety of allenes.[490] Importantly, the regiochemistry observed with this gold catalyst (Markovnikov addition) is opposite or complementary to that obtained with early transition-metal catalysts (anti-Markovnikov).[489,491,492]

Interestingly, this regioselectivity was also different from that reported by Widenhoefer et al. in the hydroamination of allenes using carbamates in the presence of a cationic gold(I) complex.[493a] In this case, the protocol was effective for a number of *N*-unsubstituted carbamates and for monosubstituted, 1,1- and 1,3-disubstituted, trisubstituted, and tetrasubstituted allenes, and as previously pointed out, the Markovnikov adduct was formed but at the more substituted terminus of the allene (Scheme 107).

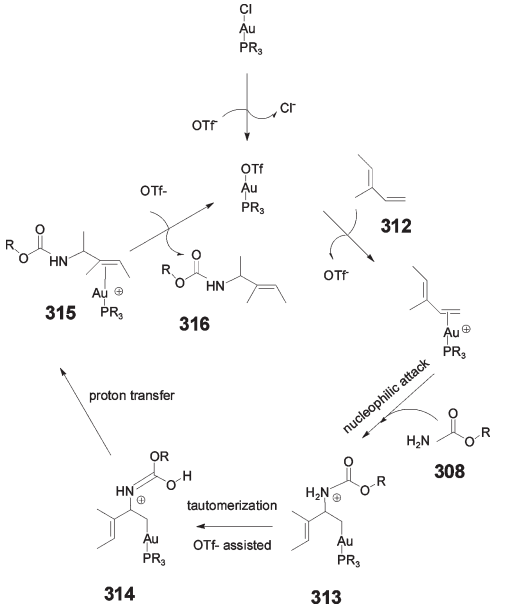
In this case, it appears likely that the intermolecular hydroamination of allenes occurs via outer-sphere attack of the carbamate on gold−π-allene complex **307** to initially form the cationic gold α-alkenyl complex **309** that loses a proton to form **310**. Protonolysis of the Au−C bond of **310** then releases the *N*-allylic carbamate with regeneration of the cationic Au(I) catalyst.[493a]

More recently, the intermolecular hydroamination of allenes has been reported to occur with hydrazide nucleophiles in the presence of $AuPPh_3NTf_2$. Mechanistic studies have established the resting state of the gold catalyst, the kinetic order of the reaction, the effect of ligand electronics on the overall rate, and the reversibility of the last steps in the catalytic cycle. The studies suggest that the rate-limiting transtition state for the reaction

Scheme 107



Scheme 108



does not involve the nucleophile and that the active catalyst is monomeric in gold(I). Computational studies support also an "outer-sphere" mechanism and predict that a two-step, no-intermediate mechanism may be operative. In accordance to this, the reaction can be accelerated with the use of more electron-deficient phosphine ligands on the gold(I) catalyst.[493b]

In close connection to this, the reaction mechanism of a gold(I)−phosphine catalyzed hydroamination of 1,3-dienes **312** to give allylic amines **316** has been analyzed by means of density functional methods combined with polarizable continuum models (Scheme 108).[494] Here the formation of the active species AuR_3POTf facilitates the subsequent coordination of the alkene.[494]

It was found that the most favorable series of reaction steps include (i) the ligand substitution reaction in the catalytically active $AuPh_3POTf$ species between the triflate OTf^- and the substrate **312**, (ii) subsequent nucleophile attack of the *N*-nucleophile (benzyl carbamate) **308** on the activated double bond to give **313**, (iii) $NH_2—C{=}O \leftrightarrow NH{=}C-OH$ tautomerization (triflate-assisted), (iv) proton transfer, and (v) replacement of the product by OTf^- regenerating the catalytic species, thereby closing the catalytic cycle.[494] Here, a novel pathway involving tautomerization of benzyl carbamate **313** to **314** assisted by triflate anion acting as a proton shuttle was characterized by the lowest barrier, which is consistent with experimental findings (Scheme 108).[494]

Turning to asymmetric gold-catalyzed reactions, it has been reported a method for the synthesis of enantiomerically enriched secondary amines with excellent ee values through the tandem intermolecular hydroamination/transfer hydrogenation of alkynes using a gold(I) complex−chiral Brønsted acid system. The catalyst works for a wide variety of aryl, alkenyl, and aliphatic alkynes as well as anilines with different electronic properties.[495a]

Finally, looking for greener and sustainable processes to get allylic amines, the gold(I)-catalyzed decarboxylative amination of allylic *N*-tosylcarbamates via base-induced aza-Claisen rearrangement has been described. In this case, a variety of tosyl allylic amines were obtained in good yields, excellent regioselectivity, and high to excellent stereoselectivity.[495b] This transformation could be performed either in water or one-pot directly from allylic alcohols and therefore represents an efficient and environmentally benign protocol for the synthesis of *N*-tosyl allylic amines.

5.1.3. Formation of Propargyl Amines. Propargylamines are versatile synthetic intermediates in organic synthesis and are also important structural elements in natural products and therapeutic drug molecules. These compounds have been traditionally synthetized by nucleophilic attack of lithium acetylides or Grignard reagents on imines or their derivatives.[496a,b] However, these reagents must be used in stoichiometric amounts, and they are highly moisture sensitive and require strictly controlled reaction conditions. An alternative atom economical approach to perform their synthesis is by means of a catalytic coupling of an alkyne, an aldehyde, and an amine (A^3 coupling) by C−H activation, giving water as the only theoretical byproduct. Recent progress in this area has been reported using homogeneous catalysts such as gold salts ($AuBr_3$ or AuCl), organic gold complexes, silver salts, copper salts, Hg_2Cl_2, and a Cu/Ru^{II} bimetallic system, among which the cationic gold species showed the highest catalytic activity.[496c−f] However, besides the potential limitations of homogeneous catalysis for achieving a sustainable catalytic process, the rapid reduction of cationic gold species into inactive metallic atoms is unavoidable when gold salts activate alkynes/alkene.[203,478,496g,h]

With gold(III) C−N complex, excellent diastereoselectivities (up to 99:1) were achieved when chiral prolinol derivatives were employed as the amine component of this A^3 coupling. Notably, the Au(C−N) complex could be repeatedly used for 10 reaction cycles, leading to an overall turnover number of 812.[497a]

Gold(I) compounds with phosphanes and gold(III) compounds with phosphinamide-based molecules have also shown to be very good catalysts for this multicomponent (A^3) coupling process,[497b,c] whereas $AuCl_3$ catalyzed a related coupling reaction between terminal alkynes, 1-(arylsulfonyl)cyclopropanol, and disubstituted amines to give 1-alkynyl cyclopropylamines with moderated yields in water.[498a] Similarly, propargylamines have been obtained from secondary amines and terminal alkynes in chlorinated solvents by a three- and two-component synthesis catalyzed by gold compounds and nanoparticles under mild conditions. The use of dichloromethane allows for the activation

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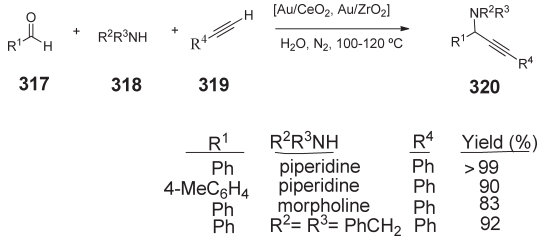
Scheme 109



R^1	R^2R^3NH	R^4	Yield (%)
Ph	piperidine	Ph	> 99
4-MeC_6H_4	piperidine	Ph	90
Ph	morpholine	Ph	83
Ph	R^2= R^3= $PhCH_2$	Ph	92

of two C−Cl bonds and a clean transfer of the methylene fragment to the final product.[498b]

5.1.3.1. Heterogeneous Catalysis. Heterogeneous catalysts are an attractive and sustainable solution to carry out any transformation in chemistry. Indeed, supported Au nanoparticles on nanocrystalline ZrO_2 and CeO_2 (Au−ZrO_2 and Au−CeO_2, respectively) have been successfully applied in many interesting transformations including this one under consideration.[499a] Effectively, these heterogeneous catalysts were highly active, selective, and recyclable catalysts for this A^3 coupling reaction in water as solvent. In this case, propargylamine derivatives **320** were synthetized via a gold supported-catalyzed three-multicomponent coupling reaction of different aldehydes **317**, amines **318**, and acetylenic derivatives **319** in water with very high yields (Scheme 109).[499a]

Gold nanoparticles, this time embedded in a mesoporous carbon nitride stabilizer, have been reported to efficiently catalyze this three-component coupling reaction.[499b] Interestingly, other heterogeneous catalysts that were highly active in this reaction were actually semiconductor gold nanocomposite catalysts. These materials, which were based on lead sulfide gold, were also successfully developed for the synthesis of propargylamines via a three-component coupling reaction of aldehyde, amine, and alkyne, in water as well.[499c]

5.1.4. Formation of Enamines and Enamides. With respect to the synthesis of enamines, a gold-catalyzed three-component tandem process for the synthesis of two new types of butenolides has been described. The protocol utilizes three commercially available starting materials such as glyoxylic acid **321**, alkynes **322**, and amines **323** to assemble highly functionalized butenolides **324**. Some examples obtained through this strategy are shown in the Scheme 110.[500a]

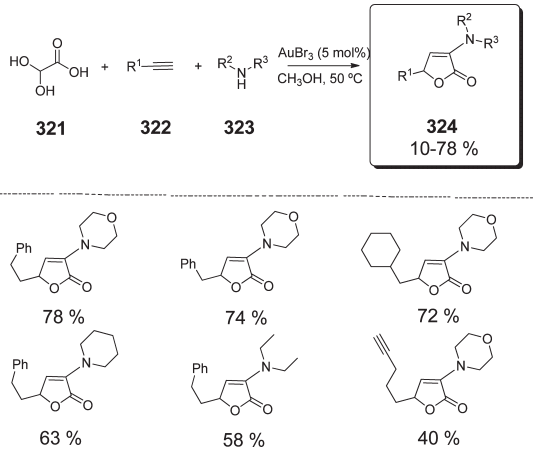
This tandem reaction consists of two catalytic processes in which more than four chemical bonds are formed. In this case, two sequential carbon−carbon bond-forming reactions are involved in the construction of the butenolide skeleton **324**, providing a useful synthetic method that expands the area of gold-catalyzed reactions.

Another mild and facile synthesis of enamides has been developed, this time on the basis of nucleophilic additions of electron-rich aromatic and heteroaromatics to an allenamide unit catalyzed by a gold(I) salt. Yields for the transformation were 29−98%.[500b]

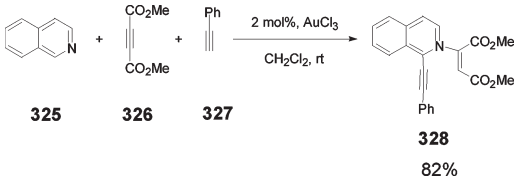
Another alternative to get enamines was based on a gold-catalyzed reaction of diazoalkanes with amines and O_2. Curiously, gold particles consisting of approximately 5−50 μm diameter, that is, the gold metal need not be nanosized, was enough to have high activity.[500c]

Gold(III) chloride has been found to be an effective catalyst for the addition of alkynes on activated quinoline/isoquinolines to produce a series of alkynyl-substituted 1,2-dihydroquinolines

Scheme 110



Scheme 111



and isoquinolines in a single-step operation. The easy availability of starting materials, convenient synthetic procedure, operational simplicity, and high regioselectivity make this strategy very useful for the preparation of enyne derivatives of aza-aromatic compounds **328** (Scheme 111).[501a]

Bertrand et al. reported that a gold(I) complex **333** allowed the addition of secondary dialkyl amines to internal alkynes, which is another process that has little precedent.[501b] In this case, a 95/5 mixture of *cis*- and *trans*-2,4-dimethyl-3-cyclohexenecarboxaldehyde (trivertal), a common fragrance and flavor material produced in bulk quantities, serves as the precursor for the synthesis of a stable spirocyclic alkylaminocarbene, in which the 2-methyl-substituted cyclohexyl group provides steric protection to an ensuing metal in the complex **333**. The efficiency of this carbene as ligand for transition-metal-based catalysts is illustrated by the gold(I)-catalyzed hydroamination of internal alkynes with secondary arylalkylamines to give 1,2-dihydroquinoline derivatives **332** (Scheme 112).[501b]

The feasibility of this reaction allowed for significantly enlarging the scope of the one-pot three-component synthesis of 1,2-dihydroquinoline derivatives **332** and related nitrogen-containing heterocycles from aryl amines and internal and terminal alkynes. Indeed, two different alkynes can be used, which includes an internal alkyne for the first step.[501b]

More recently, α,α′,*N*-triarylbisenamines have been efficiently formed and isolated for the first time. It is interesting to remark that in this case the synthesis is based on an unprecedent gold(I)-catalyzed double intermolecular hydroamination between *N*-arylamines and arylalkynes.[501c]

5.1.5. Formation of Azides. In the presence of catalytic amounts of $HAuCl_4 \cdot 3H_2O$, the nucleophilic attack of 2,5-dihydrofurans **334** by Me_3SiN_3 **335** is accomplished, leading to

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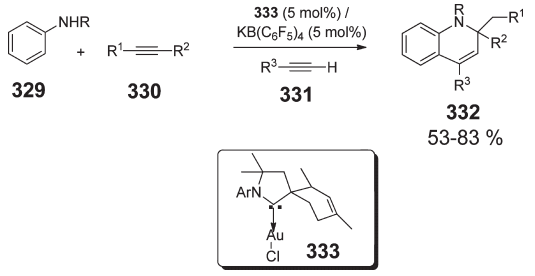
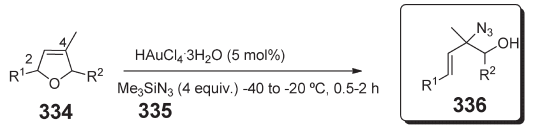
Scheme 112



Scheme 113



R^1= 4-$MeOC_6H_4$; R^2= CH_2OBn	(*dr*= 55:50)	70 %
R^1= 4-BrC_6H_4; R^2= CH_2OBn	(*dr*= 60:40)	85 %
R^1= 4-$MeO_2CC_6H_4$; R^2= CH_2OBn	(*dr*= 70:30)	12 %

ring-opening. The reaction is regioselective, since the azidation takes place in the 4-position exclusively (Scheme 113).[502a]

The reaction gave the azido alcohol **336**, resulting from exclusive attack of the nucleophile at C-4 with high yields at −40 to −20 °C, being the first example for a ring-opening reaction of an unsaturated cyclic ether with a nitrogen nucleophile. Curiously, the ring-opening allylation of 2,5-dihydrofurans has been accomplished with allyltrimethylsilane in the presence of the same catalyst, but in this case, the allylation proceeded regioselectively in the 2-position to afford 2,6-dien-1-ols.

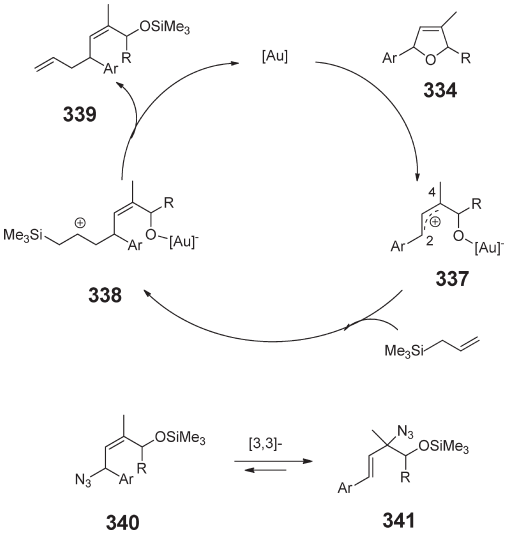
With respect to the mechanism, it is assumed that (in the case of allylation) the formation of the zwitterionic intermediate **337** from starting material **334** and the gold(III) catalyst (Scheme 114) is followed by a kinetically controlled attack of the allylsilane at C-2 of the benzyl cation moiety, affording β-silyl cation **338.** Cleavage of the carbon−silicon bond then leads to the ring-opening product **339** and regenerates the gold catalyst. However, the products of the gold-catalyzed allylation (and azidation) of dihydrofurans and pyrans can undergo [3,3] sigmatropic rearrangements.[502b,c]

Thus, there are two possible explanations for the formation of the allylazides, either the zwitterionic intermediate **337** is attacked by Me_3SiN_3 directly in the 4-position or the initially formed regioisomer (vs regioisomer **340**) rearranges rapidly to the (thermodynamically) more stable product **341** (Scheme 114).

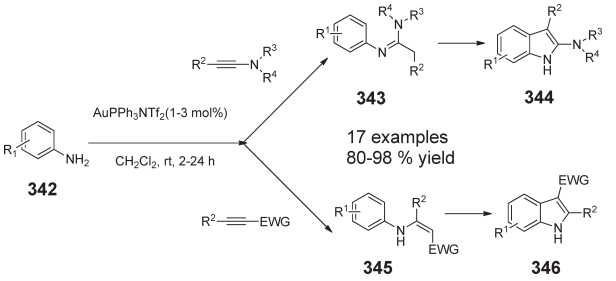
5.1.6. Formation of Imines. The standard protocol for the synthesis of imines involves condensation of an amine and a carbonyl compound (aldehyde or ketone). However, on occasion, owing to the unstable and reactive nature of the electrophilic carbonyl compound, it would be desirable to obtain imines by different pathways.

One approach to the obtention of imines was based on the application of gold(I)−phosphine complexes bearing a low coordinating bis(trifluoromethanesulfonyl) imidate counterion, namely $AuSPhosNTf_2$ and $AuPPh_3NTf_2$, for the regioselective intermolecular hydroamination of both internal and terminal

Scheme 114



Scheme 115



alkynes under mild reaction conditions.[503a] These gold(I) complexes operated under solvent-free conditions, without exclusion of air, and are quantitatively recovered and reused by a simple precipitation in hexane. The catalysts showed regioselectivity based on electronic rather than steric factors, which allowed the preferential synthesis of regioisomers opposite to those described previously.[503b−d]

It is necessary to indicate that the regioselectivity based on electronics rather than sterics using $AuPPh_3NTf_2$ was reported earlier and with complete regioselectivity by Skrydstrup et al.[503e] Here, a highly regioselective Au(I)-catalyzed hydroamination of unsymmetrical electron-poor and electron-rich alkynes (represented by ynamides and propiolates/propiolamides) with anilines catalyzed by Au(I) under mild conditions has been reported (Scheme 115).[503e] Because of its simplicity and mild reaction conditions and for the most cases short reaction times, this method has been applied to the one-pot synthesis of indoles starting from nonfunctionalized anilines (Scheme 115).

Despite the remarkable reactivity toward the electrophilic activation of carbon−carbon multiple bonds, one challenge of the popular catalyst $AuPPh_3OTf$ is to overcome its poor stability at high temperature (leading to formation of gold mirror and gold nanoparticles). Therefore, new Au(I) catalysts that may overcome the reactivity−stability dilemma are highly desirable and should open new temperature ranges for this rapidly growing

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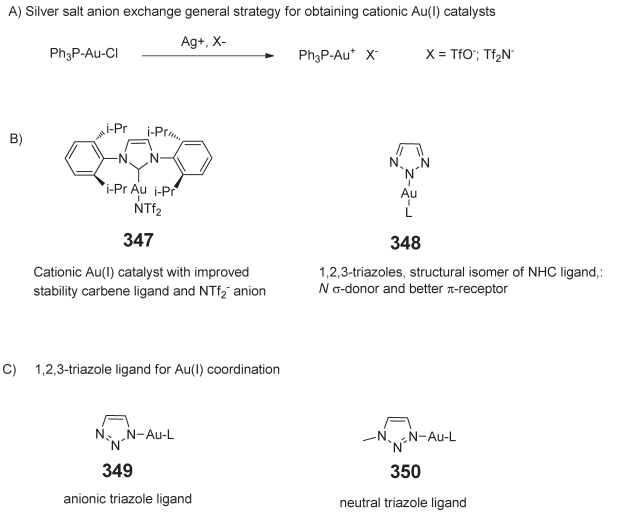
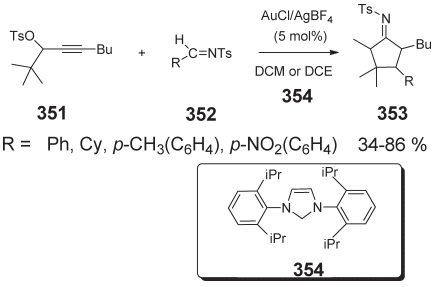
Scheme 116



Scheme 117



research field. Interestingly, investigation of diverse gold(I) complexes **347**−**350**, shown in Scheme 116, revealed a dynamic coordination between the triazole moiety and the Au(I) cation in triazole Au(I) complexes **348**−**350**, leading to the discovery of a new class of Au(I) catalyst with improved thermal stability (Scheme 116; see also comments on the phenol synthesis, Scheme 7).[503f]

The superior stability and reactivity of these catalysts was evidenced for achieving successful challenging transformations, such as the intermolecular internal alkyne hydroamination and reactions with unprotected aliphatic amines.[503f]

Another alternative to build related cyclopent-2-enimines has been reported recently.[504] Here, internal alkynes and imines such as propargyl tosylates **351** and *N*-tosylaldimines **352** respectively reacted to afford cyclopent-2-enimines **353** in a gold-catalyzed process that involves a deep reorganization of both substrates. The formal [4 + 1] cyclization is initiated by a 1,2-migration of the tosylate that eventually generates a substituted diene. Subsequent interaction with the imine launches a series of reaction steps prior to a Nazarov-like cyclization to yield the final product **353** (Scheme 117).[504a]

A cationic gold(I) complex has also been applied to the intermolecular hydroamination of internal alkynes with primary (and secondary) amines.[504b] More recently, a highly convenient regioselective intermolecular hydroamination of alkynes yielding ketimines has been reported to be catalyzed by gold(I) complexes of 1,2,4-triazole-based *N*-heterocyclic carbenes.[504c]

5.1.6.1. Heterogeneous Catalysis. Amines are stable and easily accessible compounds and would therefore be suitable precursors for imines by dehydrogenation or by other alternative oxidation procedures, such as aerobic amine oxidation.[505]

The importance of the aerobic amine oxidation is at least 2-fold: (1) the products of the reaction, that is, imines or nitriles, are valuable intermediates in organic synthesis, and (2) on the basis of catalytic amine oxidation, it is possible to develop kinetic resolution methods to access enantiomerically enriched secondary amines.

Although several oxidation procedures that use stoichiometric reagents for the synthesis of nitriles and imines from amines are known,[506−509] only a few catalytic procedures have been reported.[510−513]

In preliminary studies on this topic, a number of ruthenium and palladium complexes have been used for the oxidation of amines with dioxygen,[512,513] iodosylbenzene,[513] and persulfate ions[514a] as oxidants. However, these systems are not generally useful because of their low turnover numbers (TONs) and frequencies (TOFs), the formation of significant amounts of byproducts, severe deactivation of the catalysts, and narrow applicability to a limited number of amines.

Nonetheless, among the transition metals used in aerobic oxidations, Pd can be considered as the most attractive one, and there is one Pd-catalyzed aerobic oxidation reaction (i.e., the Wacker process) that is being applied in an industrial process.[514b−d] However, there still remain some important oxidative transformations for which it has been extremely difficult to find an effective Pd catalyst system. One example is the aerobic oxidation of amines to yield nitriles or imines.

Oxidation of amines with molecular oxygen using Au(0) supported on carbon, TiO_2, Al_2O_3, CeO_2, CeO_2/FeOx, etc. opened up benign routes to the synthesis of imines (among other interesting compounds), hence offering new opportunities for chemists.[515−521] Alternatively, the formation of amides could be accomplished through the amidocarbonylation of aldehydes using gold nanoparticles supported on Co_2O_3, although the main feature in this case is the use of CO/H_2 pressure or the acylation of amines mediated by oxygen atoms on metallic gold surfaces.[522a,b]

A closely related strategy to get imines was based on the preparation of gold clusters and nanoparticles deposited on three kinds of porous coordination polymers, MOFs, CPL-2, and Al-MIL53, by the solid grinding method. These metal-based materials catalyzed the one-pot synthesis of secondary amines from primary amines by sequential oxidation/hydrogenation.[522c]

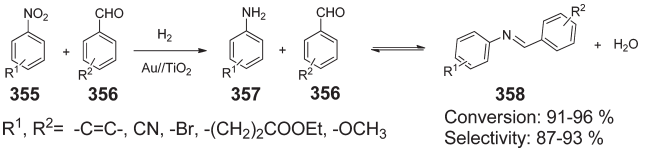
A quite different way to get imines has to do with the design of a cascade reaction. In this particular case, substituted imines could be prepared from nitroaromatic compounds **355** and aldehydes **356**, with results showing that the method is efficient even for synthesizing imines such as **358** (Scheme 118).[523]

In this paper, the unknown properties of gold to reduce selectively the nitro group in the presence of other sensitive functional groups such as double bonds was discovered, which opened up the possibility of easily preparing substituted secondary amines through a cascade reaction.

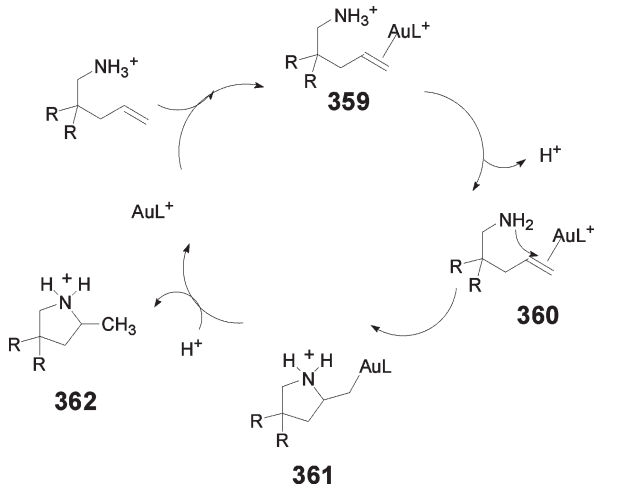
5.2. Intramolecular C−N Bond Formation

5.2.1. Five- and Six-Membered Rings. *5.2.1.1. Pyrrolidine.* The intramolecular hydroamination of unactivated double bonds with primary and secondary amines to afford pyrrolidines has been reported to be catalyzed by a mixture of (X)AuCl [X = $[PCy_2[2\text{-}(2,6\text{-}C_6H_3(OMe)_2)C_6H_4]$ and AgOTf.[524]

Scheme 118



Scheme 119



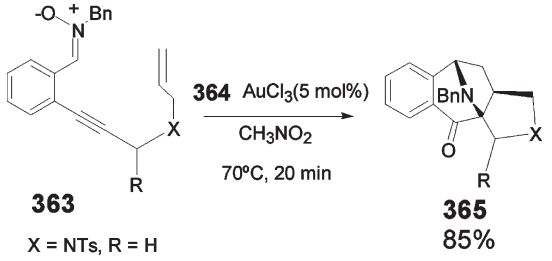
Stereochemical analysis of gold(I)-catalyzed hydrofunctionalization has consistently supported an outer-sphere mechanism for C−X bond formation. As such, the mechanism was envisaged as initiated by formation of a gold−π-alkene complex **359**. Then, deprotonation of the pendant ammonium salt, followed by outer-sphere attack of the free amine on the complexed alkene **360**, would form the cationic pyrrolidine complex **361**. Finally, protonolysis of the Au−C bond in the complex **361** with NHR_3 would release the protonated pyrrolidine **362** (Scheme 119).

Another efficient synthetic route to pyrrolidines that relies on the use of AuCl/AgOTf as catalyst has been reported to proceed through the tandem amination/ring expansion of substituted cyclopropyl methanols with sulfonamides.[525]

Interestingly, besides the classic intramolecular hydroamination reaction, the 1,3-dipolar addition offers a wide range of utility in the synthesis of five-membered heterocycles. In a classical 1,3-dipolar cycloaddition, one 1,3-dipole combines with a multiple bond system (the dipolarophile) in a cycloaddition to form an uncharged five-membered ring. Due to the concerted nature and the remarkably high degree of regioselectivity of this polar cycloaddition reaction, only a limited number of product isomers are formed, and attempts to control the selectivity with respect to the four possible stereoisomers formed by this reaction have attracted still more attention during the past decade.[526−528]

However, the fruitful development of this synthetic methodology relying on gold complexes is very recent. Indeed, the utility and attributes of gold as catalyst could be extended with the application of certain cationic gold(I) complexes to 1,3-dipolar additions, since these are examples of chemical transformations that are not based on typical π-bond activations.

Scheme 120



To this end, the development of a bisphosphinegold(I)-catalyzed enantioselective 1,3-dipolar cycloaddition reaction of mesoionic azomethine ylides (münchnones) with alkenes for the synthesis of complex *N*-heterocycles has been described.[529a]

Similarly, Shin et al. described a novel gold-catalyzed generation of an azomethine ylide, featuring an internal redox reaction between a tethered nitrone and an alkyne under electrophilic metal catalysis. The azomehine ylide that is formed underwent an efficient cycloaddition cascade in a highly diastereoselective manner. The benefit of atom economy (100%) as well as environmental safety is apparent from this approach (Scheme 120).[529b]

Recently, a gold-catalyzed aminoarylation reaction of alkenes and arylboronic acids has been reported. The reaction is proposed to proceed through a redox cycle involving the initial oxidation of gold(I) into gold(III) with Selectfluor.[529c]

Within the frame of asymmetric catalysis, the work of Mikami et al. has shown a relevant example on enantioselective intramolecular hydroamination of allenes, which proceeds with the intervention of biphep−gold complexes.[529d] Here, the axial chirality of these biphep−gold complexes can be imprinted by the use of phosphates (*S*)-**370** (as well as *N*-triflyl phosphoramides) as chiral anions and memorized at room temperature even after the dissociation of chiral anions. Scheme 121 represents the key strategy followed in this work.

The work has focused on the tropos (chirally flexible) bis(phosphanyl)biphenyl (biphep) ligand **366**. It is known that **366** can behave dynamically as chiral bidentate ligands for many metal complexes when the axial chirality is controlled by chiral diamines or diene ligands. But here, in gold−biphep complexes **367** and **369**, the axial chirality was controlled in a highly stereospecific manner by using the binaphtol-derived-phosphate anion (S)-**370**. In fact, high levels of enantioselectivity could be attained in chiral hydroaminations, since the resulting enantiopure complexes **368** efficiently catalyzed the intramolecular hydroamination as atropoisomeric asymmetric catalysts.

5.2.1.1.1. Heterogeneous Catalysis. In the heterogeneous phase, gold nanoclusters stabilized by the hydrophilic poly(*N*-vinyl-2-pyrrolidone) (Au-PVP) catalyzed the intramolecular addition of toluenesulfonamides to unactivated alkenes under mild, basic, and aerobic conditions. This reaction led to pyrrolidine derivatives in quantitative yields, albeit these results were strongly depending on the presence of oxygen and/or the size of Au−PVP catalysts.[530]

5.2.1.2. Piperidine. Highly substituted piperidines are found in numerous bioactive alkaloid natural products and pharmaceuticals.[531] Thus, considerable attention has been paid to the synthesis of this moiety, which includes the use of gold as catalyst.

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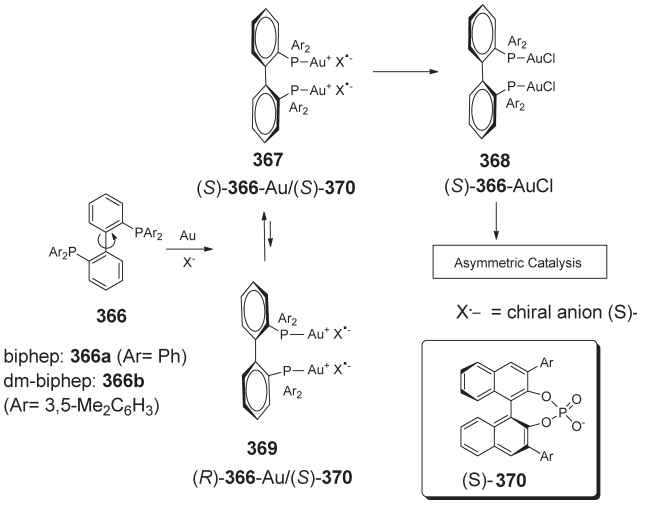
Scheme 121



In this respect, the cycloisomerization of functionalized allenes in water with chloroauric acid ($HAuCl_4$) induced the stereoselective cycloisomerization of various functionalized allenes to five- or six-membered oxygen or nitrogen-containing heterocycles.[161]

Besides this, a mild and efficient gold-catalyzed tandem cyclization to piperidinyl enol esters and piperidinyl ketones has been developed with readily available ε-*N*-Boc-protected propargylic esters. (Scheme 122).[532]

Compared to intermolecular catalyzed propargylic substitution and nucleophilic addition to propargyl carboxylates, this intramolecular piperidine cyclization methodology shows different reactivity and different substrate applicability.[533a,b]

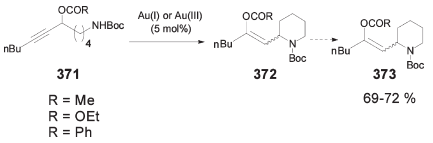
Recently, Bates et al. have reported a formal synthesis of swainsonine (a potent mannosidase inhibitor isolated from different fungus and plants), which has been prepared using a highly efficient and diastereoselective gold(III)-catalyzed allene cyclization (Scheme 123).[533c]

In this case, deprotection of the nitrogen of compound **375** by simple treatment with trifluoroacetic afforded piperidine derivative **376**. Then allyl carbamate (alloc) formation, followed by palladium(0)-catalyzed "alloc contraction", gave the diene **378** in 85% yield from the piperidine. The formal synthesis was completed by ring-closing methatesis using Grubbs second-generation catalyst in the presence of 1 equiv of *p*-toluenesulfonic acid, followed by workup (NaOH) to give the indozilidine **379** in good yields. The synthetic material was spectroscopically identical to the intermediate reported by Pyne (an intermediate precursor of the indolizine alkaloid swainsonine).

5.2.1.3. Pyrazolidine. A series of 1,2-diazacycles have been synthetized through gold-catalyzed hydroamination reactions. For example, a series of enantioselective gold(I) hydroamination of allenes with hydrazines has been recently developed. In particular, biarylphosphinegold(I) complexes **381** have been found to be suitable catalysts for the enantioselective addition of nitrogen nucleophiles to allenes, allowing rapid access to chiral vinyl-protected 1,2-diazacycles or pyrazolidines **382** (Scheme 124).[534a]

Besides this, a gold(III)-catalyzed synthesis of 1,2-diazabicycles from readily available materials has been devised through a formal cycloaddition between alkenyl metal carbenoids and 1,3-dipoles. In contrast to the previously reported cycloaddition, this

Scheme 122



reaction highlights the difference in the reactivity of alkenyl Fischer carbenes and the alkenyl Au−carbenoids generated from the rearrangement of propargyl esters.[534b]

5.2.1.4. Imidazolidine. Vicinal diamines are an important class of compounds as a result of their useful biological activities and their utility as chiral auxiliaries and ligands in asymmetric synthesis.[535]Among the methods usually employed to generate such scaffolds, the direct oxidative alkene diamination presents an attractive strategy, albeit until 2005 catalytic approaches for these reactions were unprecedented.[536−539] In fact, in contrast to the ubiquity of the corresponding dihydroxylation of alkenes, methods for the direct diamination of alkenes are rare. The main justification for this fact, as already pointed out, is the high reactivity of diamines in the presence of transition metals, which leads to metal coordination and, consequently, to catalyst deactivation.

Because of these reasons, current diamination methods generally suffer from limited substrate scope and/or protecting group versatility or are limited to the reactions of activated alkenes. Initially, the palladium(0)- and copper(I)-catalyzed diamination investigated by Shi and co-workers provided a completely new approach to diamination,[540−542] as they were the first group to devise catalytic and asymmetric diamination processes simultaneously. Notably, they discovered the possibility to address the regioselectivity of diene diamination by simply switching the catalytic system.

Recently, a complementary diamination of alkenes by using homogeneous gold catalysts has been described.[543] This reaction is one of very few examples of homogeneous gold oxidation catalysis and proceeds with high selectivity under mild conditions. In this work, the authors find strong evidence that a gold(I)/gold(III) cycle is responsible of performing this oxidation catalysis.[543] This diamination procedure [on the basis of gold(I)/gold(III) catalysis] is reminiscent of earlier findings with palladium catalysts.[544] Moreover, although the two protocols are very similar in nature, they are complementary in diastereoselectivity, due to the difference in stereochemistry for the initial step of aminometalation. In the second step, the gold(III) catalyst enables reductive elimination in a similar manner as does the postulated Pd(IV) intermediate. Besides this, the reaction proceeds with gold with high selectivity under mild conditions.

A gold(I)/silver(I) system has also been shown recently to catalyze the hydroamination of allenes as a redox-neutral and atom economic alternative to alkene diamination for the synthesis of vicinal dimines (Scheme 125).[545a]

In fact, reaction of *N*-δ-allenyl urea **383** with a catalytic 1:1 mixture of gold(I) heterocyclic carbene complex AuCl−**354** [**354** = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine] and $AgPF_6$ at room temperature led to isolation of bicyclic imidazolin-2-one derivatives **384** in 93−94% yield with >98% diastereomeric purity. In general, this gold-catalyzed dihydroamination was effective for a number of *N*-δ and *N*-γ-allenyl ureas to form the corresponding bicyclic imidazolidin-2-ones in good yield with high diastereoselectivity.

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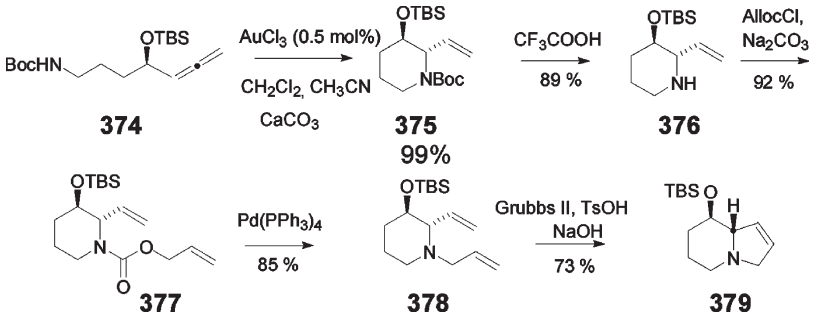
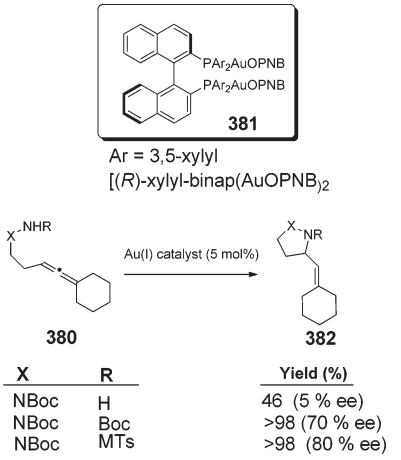
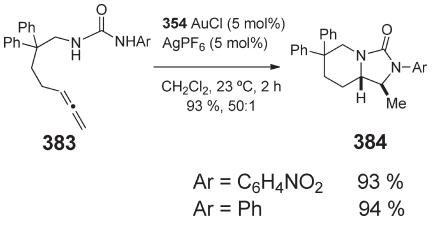
Scheme 123



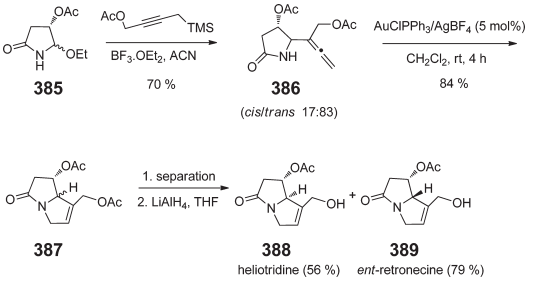
Scheme 124



Scheme 125



Scheme 126



Enantiopure vinylimidazolidinones could be also obtained through the classic intramolecular hydroamination of α-amino-allenamides.[545b]

Finally, substituted *N*-propargylamides also have proven to be valuable substrates for alkyne-activated cycloisomerization reactions. For example, *N*-tosyl-*N*-propargylurea underwent reaction with $AuCl_3$ to give the corresponding dihydroimidazolone, while *N*-propargyl-3-oxobutanamides and esters were used to construct fused pyrrolidinones and dihydrofuranones via Ag(I)-mediated alkyne activation.[179]

5.2.1.5. Pyrrolizidine. Pyrrolizidine is a heterocyclic organic compound that forms the central chemical structure of a variety of alkaloids known collectively as pyrrolizidine alkaloids. For this reason, pyrrolizidine-related structures are well-studied synthetic targets.[546]

Gold has not escaped attempts to obtain these interesting structures, through a sequence of propargylsilane addition to *N*-acyliminium ions followed by gold-catalyzed cyclization of the resulting allenyl lactams.[547] For substituted α-allenyl amide substrates, mild cationic cyclizations gave the expected products in good yields. However, when dealing with unsubstituted allenyl lactams and linear amides, elevated temperature $AuCl_3$ cyclization turned out to give the best yields. The sequence has shown to be useful for the short total synthesis of the alkaloids heliotridine **388** and *ent*-retronecine **389** from **385** (Scheme 126).[547]

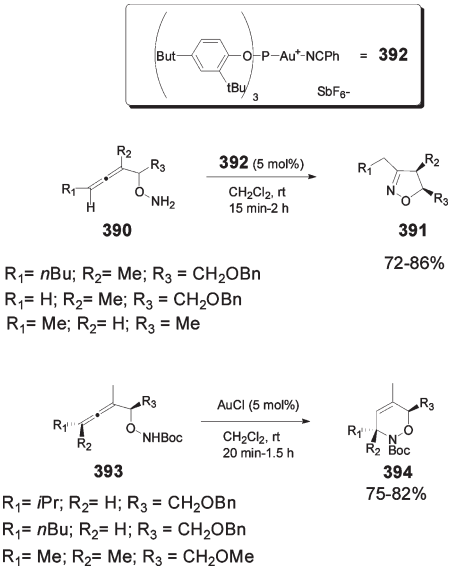
5.2.1.6. Isoxazole, Dihydroisoxazole, Oxazine, Oxazoline. Krause et al. reported a highly regio- and stereoselective route to different chiral heterocycles such as 4,5-dihydroisoxazole and 3,6-dihydro-1,2-oxazines. The reaction consisted of a gold-catalyzed cycloisomerization of allenic hydroxylamine derivatives. In all cases, the nitrogen atom acted as a nucleophile and attacked the allene in a 5- or 6-endo-cyclization. In the case of the allenic hydroxylamine ethers **390**, the regioselectivity could be shifted toward dihydrooxazoles **391** by employing a cationic Au catalyst **392** or in favor of dihydrooxazine **394** by using *N*-Boc-protected precursor **393** (Scheme 127).[548a]

Another alternative to get a closely related heterocycle came from a gold(I)-catalyzed 1,3-dipolar [3 + 3] cycloaddition of 2-(1-alkynyl)-2-alken-1-ones with nitrones. This reaction provided a practical, regiospecific, and diastereoselective access to highly substituted fused heterocyclic furo[3,4-*d*][1,2]oxazines under mild reaction conditions. In addition to this, when (*R*)-MeO-biphep was used as chiral ligand, the cycloadducts could be obtained with moderate ee values.[548b]

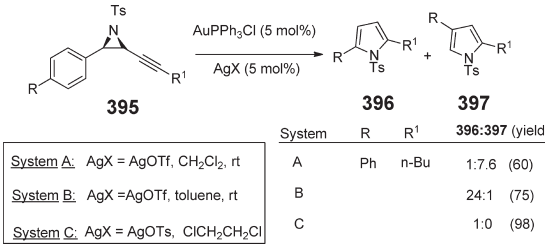
Another interesting approach for obtaining of 4-arylideneisoxazol-5(4*H*)-ones and 3,5-disubstituted isoxazoles with gold catalysts took place in both cases through the initial cyclization of oxime derivatives via C−N bond formation. In the case of

dx.doi.org/10.1021/cr100414u |*Chem. Rev.* 2011, 111, 1657–1712

Scheme 127



Scheme 128



4-arylideneisoxazol-5(4*H*)-ones, the reaction was followed by arylidene group transfer. In both cases, the reaction proceeded in good to excellent yields.[548c,d]

Curiously, formation of one oxazoline ring was observed as a dominant side reaction in the Overman rearrangement of δ-methoxy trichloroacetimidates with gold salts. In fact, the gold(I) and gold(III) salts AuCl and $AuCl_3$ afforded only moderated yields of the Overman rearranged product, whereas formation of trichloromethyloxazoline ring was observed as the dominant side reaction.[549]

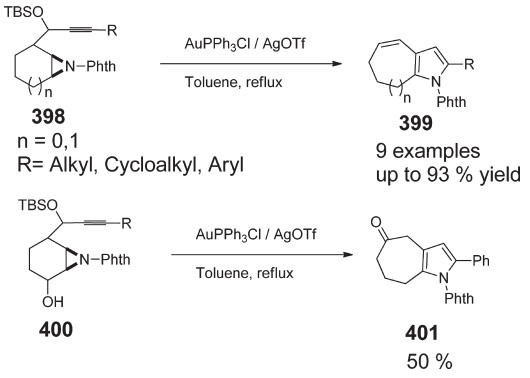
5.2.1.7. Pyrrole/Pyrroline. Aryl-substituted *N*-tosyl alkynyl aziridines **395** underwent a gold-catalyzed ring expansion to afford 2,5-substituted pyrrole products **396**. Under certain conditions, a ring expansion and rearrangement led to 2,4-substituted pyrroles **397**. The reaction pathway was determined by the counterion of the gold catalyst (Scheme 128).[550]

Similarly, $AuPPh_3Cl$/AgOTf catalyzed the rearrangement reaction of propargylic aziridines, leading to formation of trisubstituted and cycloalkene-fused pyrroles (Scheme 129).[551]

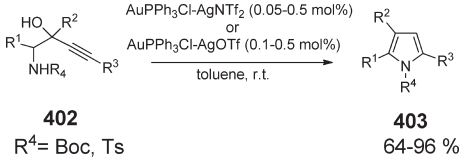
This reaction involves an unusual tandem cyclization−opening/Wagner−Meerweein process. The unique structures of the products demonstrate its potential application for synthesizing structurally diverse alkaloids.

Similarly, Au(I)/Ag(I)-catalyzed cycloisomerization reactions of acetylenylaziridines provided 2,5-disubstituted pyrroles in high yields. The presence of protic species accelerated the reaction rate and improved the yields of pyrrole products.[552a] In another example, functionalized pyrroles including pyrrole-2-carboxylates or 2-pyrrolyl ketones were easily constructed in good yields with a similar method from *N*-Phth-alkynylaziridines. The resulting pyrroles could be further converted to *N*-amino-pyrrole or 2-acylpyrroles, which are important synthetic intermediates for amplification of molecular complexity.[552b]

Scheme 129



Scheme 130



Another way to obtain pyrroles came from the intramolecular cyclization of amino-3-alkyn-2-ols with different Au(I)/Ag(I) catalytic systems, which proceeded at room temperature to provide a variety of furans and substituted pyrroles **403** in excellent yields (64−96%, Scheme 130).[139]

For example, in the presence of AuP(*t*-Bu)$_2$(*o*-biphenyl)]Cl/AgOTf, pyrrole derivatives were efficiently prepared by dehydrative cyclizations of readily available heteroatom-substituted propargylic alcohols. The reactions were rapid, high yielding, and procedurally simple, giving essentially pure aromatic heterocycles with catalyst loadings as low as 0.05 mol %.

A similar gold/silver catalytic system catalyzed an efficient one-pot synthesis of multisubstituted pyrroles **405** with high diversity and in a regioselective manner from suitably substituted (*Z*)-enynols **404** with amines or sulfonamides under mild reaction conditions. This synthesis was accomplished via a cascade process in the presence of the gold/silver catalytic system $(p\text{-}MeOC_6H_4)_3PAuCl/AgBF_4$ or the boron trifluoride·etherate/gold/silver system $BF_3\cdot Et_2O/(p\text{-}MeOC_6H_4)_3PAuCl/AgBF_4$, which could catalyze amination and cycloisomerization reactions in the same vessel (Scheme 131).[553]

Gold, albeit this time in the absence of any silver salt, catalyzed the synthesis of substituted pyrrolin-4-ones from amino acid derivatives under mild conditions. In fact, the gold-catalyzed cyclization of various α-amino ynone derivatives **406** gave the corresponding pyrrolin-4-ones **407** in high yields (Scheme 132).[554]

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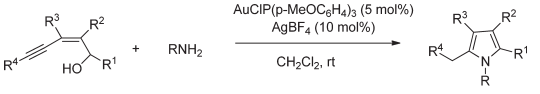
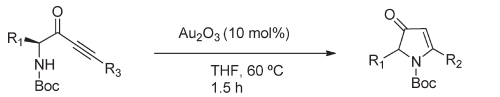
Scheme 131



Scheme 132



Here, the use of gold(III) oxide as catalyst allowed a moderate to total stereocontrol during the cyclization. Indeed, the use of a chiral pool of amino acids in this process led to pyrrolin-4-ones with moderate to excellent stereocontrol during the cyclization.

In the absence of any silver salt, other pyrrole derivatives were obtained through a gold(III)-catalyzed cyclization and dehydrofluorination of *gem*-difluorohomopropargylamines[555] or rhodium alkyne-catalyzed head-to-tail dimerization and subsequent gold-catalyzed cyclization.[556]

Similarly, a gold(III)-catalyzed tandem amination−intramolecular hydroamination reaction of 1-en-4-yn-3-ols with sulfonamides led to highly substituted pyrroles.[557]

Other efficient methodologies for the synthesis of regioisomeric 3-pyrrolines by reaction of electron-deficient imines and sulfur-containing allenyl derivatives are presented. Hence, lithiated thioallenes gave 2-aryl-3-phenylsulfonyl-3-pyrrolines, whereas allenyl sulfones furnished the isomeric 2-aryl-4-phenylsulfonyl-3-pyrrolines through migration of the sulfonyl group, which catalyzed the nucleophilic [3 + 2] cycloaddition.[558a]

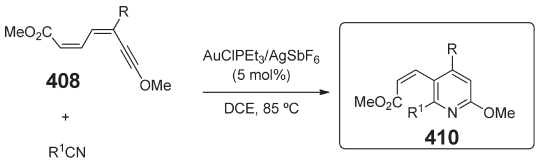
One cationic *N*-heterocycle carbene−gold(I) complex catalyzed the formation of tri- and tetrasubstituted pyrroles via the amino-Claisen rearrangement of *N*-propargyl β-enaminone derivatives and the cyclization of α-allenyl β-enaminone intermediates.[558a]

On the other hand, a general and efficient 1,2-migration/cycloisomerization methodology toward multisubstituted 3-thio-, seleno-, haloaryl- and alkylfurans and -pyrroles as well as fused heterocycles (valuable building blocks) for synthetic chemistry has been developed by Gevorgyan et al.,[24] whereas a short route to the synthesis of pyrrolocoumarin and pyrroloquinolone derivatives by Sonogashira cross-coupling has been reported through cross-coupling and gold-catalyzed cycloisomerization of acetylenic amines.[558b]

More recently, highly substituted furans and pyrroles have been efficiently formed by a new gold(I)-catalyzed tandem rearrangement−nucleophilic substitution of acetoxylated alkynyloxiranes and aziridines in the presence of various nucleophiles.[558c]

Finally, the gold(I)-catalyzed cycloisomerization of β-allenylhydrazones provides also an efficient access to multisubstituted *N*-aminopyrroles, which are obtained in good to excellent yields. This intramolecular cyclization method can be applied either to alkyl- or aryl-substituted allenes.[558d] In close connetion to this, the tandem hydroamination annulation reaction of 4-pentynenitriles in the presence of amine nucleophiles and a cooperative catalyst system [$AuPPh_3Cl$ and $Zn(ClO_4)_2$] provided an efficient route to 2-aminopyrroles.[558e]

Scheme 133



5.2.1.8. Pyridine. The Diels−Alder reaction provides a general and facile entry for the synthesis of six-membered cyclic structures. Consequently, it has been used extensively by organic chemists for the construction of complex compounds, especially those with pharmaceutical potential, so it is not surprising that gold had been explored as a catalyst for achieving such a transformation.

In this respect, Barluenga et al. have described the first example of a catalyzed intermolecular heterodehydro-Diels−Alder reaction that occurs between captodative 1,3-dien-5-ynes **408** and nonactivated nitriles **409**. The sequence was promoted by both gold(I) and gold(III) catalysts and led to the regioselective formation of tetrasubstituted pyridines **410** (Scheme133).[559a]

Gold(III) chloride catalyzed the synthesis of pyrrolopyridines, pyrrolocoumarins, and pyrroloquiniline derivatives in excellent yields without the use of bases, acids, *N*-protecting groups, and any silver salt.[559b]

5.2.1.9. Indole, Isoindole. Besides pyrrole, the indole skeleton occupies a privileged position in pharmaceuticals, material sciences, and natural products, being recently validated as a privileged structure, in particular as a scaffold capable of providing useful ligands for diverse receptors.[560] Consequently, methods to synthesize and functionalize these heterocycles are of utmost importance in organic chemistry,[561] and gold has not been passed over as a potential catalyst to achieve their preparation.

It was found that 3-substituted 1-(*o*-ethynylaryl)ureas selectively undergo 5-endo-dig cyclization through an intramolecular hydroamination to give indole derivatives. In general, ureas bearing an internal alkyne lead to the 5-endo-dig cyclization mode, regardless of the gold(I) complex employed.[562a]

Another interesting approach comes from the PPh_3Au^+OTf-catalyzed carboamination of alkynes for the synthesis of C-3-substituted indoles. The procedure utilizes easily accessible starting materials such as 2-alkynylanilines and alkynols. Here, a series of C3-functionalized indoles was accessible by using this one-pot strategy.[562b]

3-Sulfonylindoles were smoothly synthetized through gold-catalyzed reaction of *o*-alkynylsulfonanilides.[562c] The reaction proceeded through a formal addition of a nitrogen−sulfur bond to a triple bond, the so-called aminosulfonylation.

Similarly, gold(III) chloride catalyzed the synthesis of ring-fused isoindoles **412** starting from *N*-(*o*-alkynylphenyl)imines **411** through a tandem reaction and the synthesis of 3-substituted-1-cyanoisoindoles starting from ethynylbenzaldehyde.[563a,b] In the

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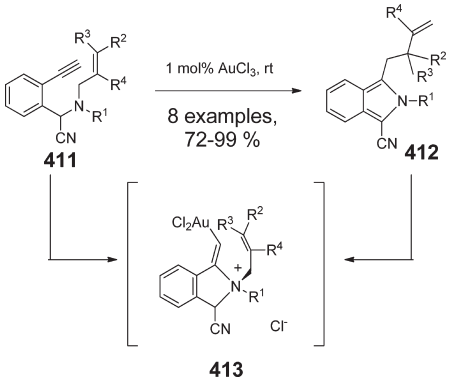
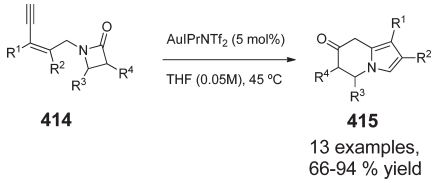
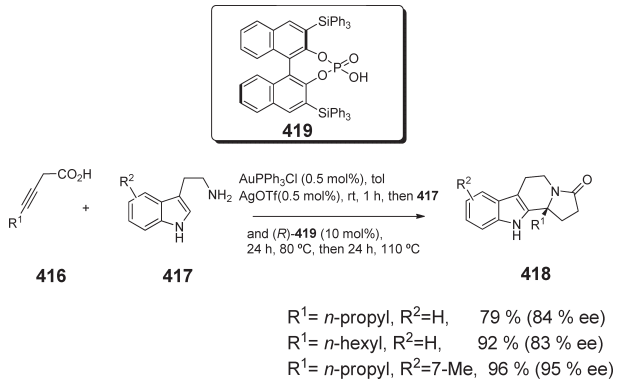
Scheme 134



Scheme 135



Scheme 136



case of 1-cyanoisoindole, the reaction underwent a rearrangement involving a 5-exo-dig cyclization followed by [1,3] alkyl shift and 1,5-prototropic aromatization. The key step was proposed to be a mild, high yielding, gold-catalyzed rearrangement of *N*-allylic aminonitrile (Scheme 134).[563b]

Indeed, there are clear indications that the gold catalyst induces a concerted mechanism rather than a stepwise one, as is the case upon microwave irradiation.[563c] In this case, the formation of **413** (Scheme 134) as a likely intermediate for the gold-catalyzed conversion of *N*-allylic aminonitriles has been proposed. The gold catalyst completes its coordination sphere by complexation with the alkene, and in this way it aligns the nucleophilic and electrophilic moieties for further conversion. This intermediate could not be trapped in the presence of nucleophiles (e.g., methanol), and no changes in the rate of both reactions or in the outcome were observed.

The gold-catalyzed intramolecular hydroamination of terminal alkynes in aqueous media has been reported for the synthesis of indole-1-carboxamides.[564] In this case, in the presence of $AuPPh_3Cl/Ag_2CO_3$ as catalyst, the 5-endo-dig-cyclization of *N*-substituted-*N*-(2-alkynylphenyl)ureas took place in water under microwave irradiation to afford indole-1-carboxamides. The method was tolerant to a variety of functional groups, including *N*-aryl, alkyl, heterocyclic, *N*-(substituted-2-ethynylphenyl), and *N*-(2-ethynylphenylpyridin-3-yl)ureas, affording moderate yields of the desired products.

Gold(I) catalyzed the intramolecular hydroamination of cyclo-1,3-dienes bearing an arylsulfonamide at the C-5 position in a 1,4-addition manner to afford hexahydroindole derivatives in a diastereoselective fashion and good yields.[565]

Zhang et al. have reported the synthesis of 5,6-dihydro-8*H*-indolizin-7-ones **415** from readily available *N*-(pent-2-en-4-ynyl)-β-lactams **414**. In this reaction a 5-exo-dig cyclization of the β-lactam nitrogen **414** to the Au-activated C−C triple bond was followed by heterolytic fragmentation of the amide bond, forming a highly nucleophilic acyl cation (Scheme 135).[566]

The method offered an expedient and novel approach to the synthesis of indolizidine alkaloids.

Perumal et al. reported the efficient synthesis of 3-substituted indoles through a domino gold(I)-catalyzed cycloisomerization/C_3 functionalization of 2-alkynyl aniline.[567a]The same authors described the synthesis of bis(indolyl)methanes and diindolylindolin-2-ones by a similar sequential approach involving gold(I)-catalyzed cycloisomerization/bis-addition of *o*-ethynylanilines with various aldehydes and isatins, respectively.[567b]

Dixon et al. have described an interesting example of C−N bond formation for the construction of nitrogen-containing ring systems.[568] In this case, different alkynoic acids **416** were treated with $Ph_3PAuCl/AgOTf$ (0.5 mol %) and then different tryptamines **417** in the presence of (*R*)-3,3′-bis(triphenylsilyl)BPA **419**. The multicatalyst cascade products were isolated in good yields with high ee's (Scheme 136).

The cascade sequence was a powerful strategy for the one-pot production of chiral polycyclic reaction products.[568]

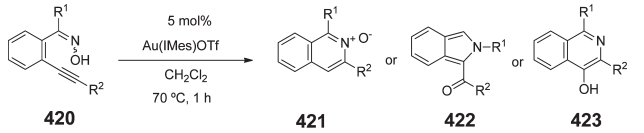
A last example for the synthesis of isoindoles (and/or isoquinolines) refers to an interesting geometry-dependent cyclization of *o*-alkylnylaryl ketoximes **420** and nitrones catalyzed by gold complexes. For example, (*E*)-ketoximes underwent *N*-nucleophilic attack, to give isoquinoline *N*-oxides **421**. In sharp contrast, (*Z*)-ketoximes underwent unprecedent *O*-nucleophilic attack, followed by a redox cascade, leading to a novel catalytic entry to isoindoles **422** of diverse scope (Scheme 137).[322]

The structure of the isoindole was unambiguously supported by X-ray crystallography. The generality of the isoindole synthesis was demonstrated, and a mechanistic model about this redox cascade was proposed on the basis of the reaction profiles of various substrates. The key mechanistic feature of this redox cyclization is that the mechanistic divergence into isoquinoline-*N*-oxides or isoquinoline is strictly dictated by the geometry of the starting ketoxime. In addition to the formation of isoindoles, the formation of 4-hydroxyisoquinoline derivatives **423** was also observed.

More recently, a synthetic route to indenyl-fused and 2,3-disubstituted indoles has been reported to occur in the presence of combined gold and silver catalyst system. In this case, a common vinyl gold species is generated in situ from accessible propargylic alcohol substrates under mild conditions.[569a]

Similarly, a novel gold-catalyzed intramolecular cascade cyclization for the synthesis of aryl- and heteroaryl-annulated[*a*]carbazoles

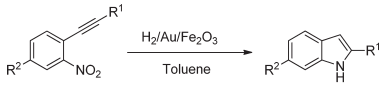
Scheme 137



420 **421** **422** **423**

oxime	R^1,R^2	**421**/**422**/**423** (yields, %)
(*E*)-**420a**	Me, Me	**421a**, 83
(*Z*)-**420a**	Me, Me	**422a**, 66
(*E*)-**420b**	Me, *n*-Bu	**421b**, 91
(*Z*)-**420b**	Me, *n*-Bu	**422b**, 42
(*Z*)-**420c**	Me, Ph	**421c**, 46
(*E*)-**420c**	Me, Ph	**422c**, 46/**423c**, 41

Scheme 138



424 **425**

R^1= Ph; R_2= H	87 %
R^1= 4-MeC_6H_4; R_2= H	87 %
R^1= 4-FC6H4; R_2= H	86 %

(compounds with a structure based on the indole structure) has been developed. The reaction was applicable to various aryl-annulated[*a*]carbazoles containing an alkyl or aryl substituent and provides a potent methodology for the fields of drug discovery and materials chemistry.[569b]

5.2.1.9.1. Heterogeneous Catalysis. Another one-pot sequence of hydrogenation/hydroamination to form indoles **425** from 2-nitroarylalkynes **424** was catalyzed by Au nanoparticles supported on Fe_2O_3. Here, the selective nitro group hydrogenation as successive reactions was efficiently catalyzed under the same reaction conditions (Scheme 138).[569c]

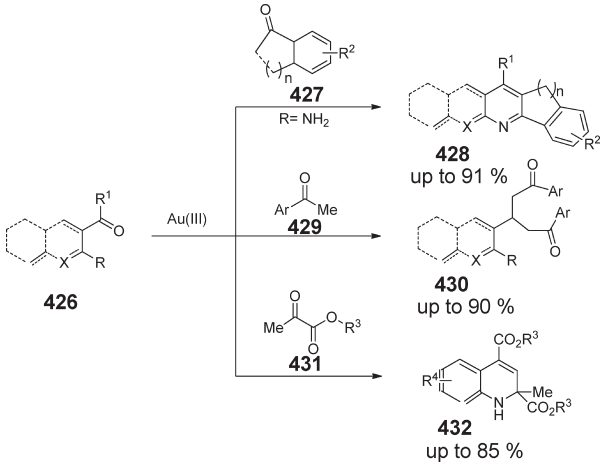
5.2.1.10. Quinoline, Isoquinoline. Quinolines, dihydroquinolines, and azaxanthones could be synthetized efficiently by means of a reaction sequence employing Au(III)-catalyzed aldol reactions as the key step under mild reaction conditions (Scheme 139).[570]

The aldol condensation is a powerful reaction to form carbon−carbon bonds in organic chemistry. This reaction is widely used in nature for the formation of carbon−carbon bonds in living systems (metabolism) and can be catalyzed by acids and bases. Many gold salts have moderate Lewis acidity, and researchers have made efforts to extend the applications of gold to catalyze the aldol reaction. Despite this, there are not many reports on this topic, so in principle, this reference can be considered as one of the few examples where gold compounds have been applied as catalyst in aldol transformations.[570] In this case, it is proposed that the formation of quinolines possibly begins with imine formation facilitated by the Lewis acidity of the gold catalyst, followed by enamine addition to a ketone. Water elimination eventually leads to quinoline formation.

Another interesting alternative to afford quinoline derivatives makes use of a bimetallic ruthenium/gold complex. This catalyst catalyzed the dimerization of 2-ethynylaniline, resulting in the formation of a quinoline derivative. The reaction proceeded in high yield, even in the absence of solvent.[571a]

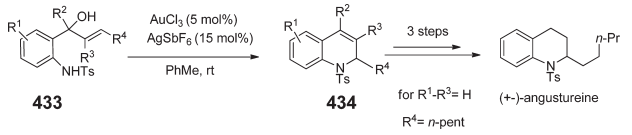
A facile assembly of fused isoquinolines by gold(I) has been recently described. The reaction makes use of two coupling

Scheme 139



426 **427** **428** **429** **430** **431** **432**

Scheme 140



433 **434**

partners, such as *o*-alkynylbenzaldehydes and aromatic amines, having tethered nucleophiles. The reaction is easy to perform, broad in scope, and allows the generation of a number of biologically important heterocyclic motifs from readily accessible starting materials.[571b]

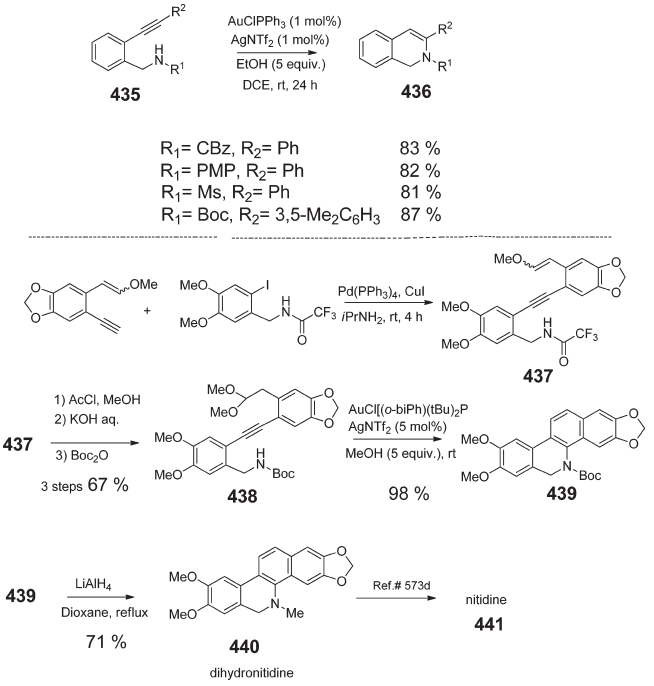
In the presence of $AuCl_3$, some alkynyl amides (and alkynyl ethers) provided access to tetrahydroquinolines (as well as dihydroindoles) very quickly and in good to excellent yields.[48]

An efficient synthetic route to 1,2-dihydroquinolines **434** that relies on $AuCl_3$/$AgSbF_5$-catalyzed intramolecular allylic amination of tosylaminophenylprop-1-en-3-ols **433** has been described. Uniquely, the reactions were found to only proceed rapidly at room temperature in the presence of the gold and silver catalyst combination and produce 1,2-dihydroquinolime products **434** in yields of 40−91% (Scheme 140).[572a] The method was shown to be applicable to a broad range of tosylaminophenylprop-1-en-3-ols containing electron-withdrawing, electron-donating, and sterically demanding substrate combinations. The mechanism is suggested to involve activation of the alcohol substrate by the $AuCl_3$/$AgSbF_6$ catalyst. This is followed by ionization of the starting material, which causes intramolecular nucleophilic addition of the sulfonamide unit to the allylic cation moiety and construction of the 1,2-dihydroquinoline. The utility of this *N*-heterocyclic ring forming strategy as a synthetic tool that makes use of alcohols as proelectrophiles was exemplified by its application to the synthesis of the bioactive tetrahydroquinoline alkaloid (±)-angustureine (Scheme 140).[572a]

Similarly, the intramolecular cyclization of (2-alkynyl)benzyl azides in the presence of AuCl and $AgSbF_6$ in THF under a pressured vial at 100 °C gave the corresponding isoquinolines in good yields.[572b]

In close connection to this, a sequential catalytic process has been developed based on gold-catalyzed nucleophilic addition of

Scheme 141



terminal alkynes to imines and gold-catalyzed intramolecular reaction of aromatic ring to alkynes. This one-pot reaction of aldehydes, amines, and alkynes gave quinoline derivatives in good yields.[573a]

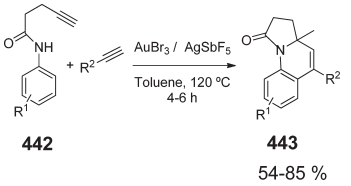
As a convenient and direct syntheses of tetrahydroquinazolones and 1,2-dihydroisoquinolines, the formal Markovnikov double hydroamination of alkynes[573b] and the gold(I)-catalyzed intramolecular hydroamination of (2-alkynyl)benzyl carbamates[573c] have been developed, respectively. In the case of dihydroisoquinolines, a convenient and direct synthesis of these compounds with a gold(I)-catalyzed intramolecular hydroamination of (2-alkynyl)benzyl carbamates **435** has been developed (Scheme 141).[573c]

The reaction with cationic gold(I) complex took place at room temperature, giving the desired 6-endo adducts. The addition of alcohol efficiently promoted the reaction, and the amount of the catalyst could be reduced to 1 mol %. However, the alkynes bearing either an electron-deficient aryl group or an alkyl group result in predominant production of 5-exo adducts. In such cases, use of a bulky gold catalyst, AuCl[*o*-biPh)(tBu)$_2$P]Cl/AgNTf$_2$, improved the regioselectivity, giving the 6-endo adducts in better yields. Furthermore, the hydroamination of alkynylcarbamates **438** bearing an acetal or enone was successfully applied to the concise synthesis of tetracyclic heterocycles such as nitidine via the single catalyst mediated tandem cyclization, which consisted of condensation or a Michael addition of the resulting enecarbamates (Scheme 141).[573c]

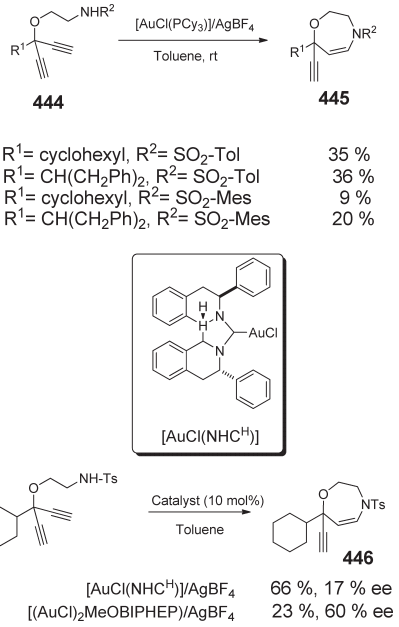
Other intramolecular amination of the chiral nonracemic allylic alcohol conjugated with a benzene ring afforded the tetrahydroisoquinoline containing a newly formed alkene in the presence of a catalytic amount of Lewis acid.[574]

The synthesis of fused heterocyclic multiring compounds pyrrolo[1,2-*a*]quinolin-1(2*H*)-ones via a AuBr$_3$/AgSbF$_6$-catalyzed cascade transformation is a straightforward approach to the construction of tricyclic lactam molecular architectures in

Scheme 142



Scheme 143



which two new C−C bonds and one new C−N bond are formed in a one-pot synthetic operation from simple starting materials. In this case, a broad spectrum of substrates can effectively participate in the process to produce the desired products in good yields and with excellent regio- and chemoselectivities (Scheme 142).[575]

5.2.1.11. Tricyclic Xanthines. A simple, convenient, and green synthetic approach to diverse fused tricyclic xanthines has been developed via gold(I)-complex-catalyzed intramolecular hydroamination of terminal alkynes under microwave irradiation in water.[576] This reaction is atom-economical and has high functional group tolerance.

5.2.2. Seven-Membered Ring. *5.2.2.1. Azepine, Oxepine, and Oxazepine and Derivatives.* A gold(I)-catalyzed cyclization of 1,4-diynes **444** has been developed by using cationic gold complexes. The cyclization occurs exclusively in an endo fashion under mild conditions and provides access to dihydrodioxepines and tetrahydrooxazepines **445** (Scheme 143).[577a]

In addition to this, cyclizations of diynamides with sulfonamide protecting groups and optically active gold complexes allowed the preparation of enantiomerically enriched *N*-protected tetrahydrooxazepines **446**.

Au(I) and Au(III) complexes catalyzed the synthesis of azepan-4-ones and azepines, respectively, via the [5 + 2] and [4 + 3] annulations of simple readily available starting materials.[577b,577c]

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The [4 + 3] cycloadditions highlight the generation and subsequent electrophilic trapping of an allylgold intermediate from gold stabilized vinylcarbenoid.[577b] On the other hand, the [5 + 2] annulation is sensitive to steric differences and can in general be highly regioselective. This sequence might involve a gold carbene intermediate via a gold-catalyzed intramolecular alkyne oxidation and require favoring a challenging formal 1,7-C(sp_3)-H insertion by carbene over a seemingly more feasible formal 1,5-C(sp_3)-H insertion in the ring formation step. The detailed mechanism of this surprising reaction is currently probed.[577c]

A three-component example for construction of a new type of oxazepine-based 5/7 bicyclic heterocyles has been developed through a novel diastereoselective Au(III)- or Cu-catalyzed tandem cycloisomerization/formal [4 + 3] cycloaddition of 1-(1-alkynyl) cyclopropyl ketones and nitrones.[578a]

Other benzazepine derivatives and tetrahydrobenz[*b*]azepin-4-ones are obtained by means of two different sequential processes from gold-catalyzed reactions of *N*-allenylamides and tertiary aniline substrates, respectively.[320,578b,c]

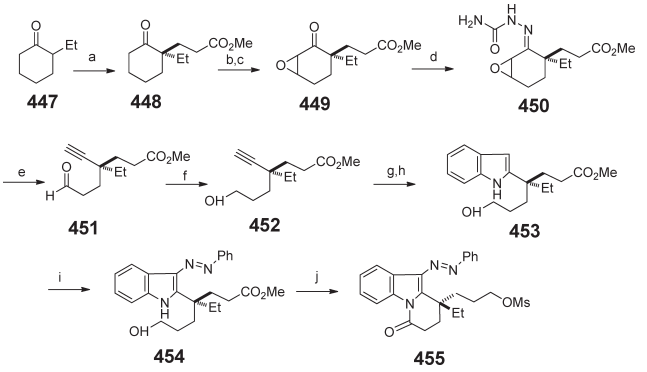
Recently, the simultaneous formation of a C−O and C−N bond has been reported in the novel cationic Au(I)-catalyzed tandem reaction to afford highly substituted furo[3,4-*c*]azepines from the simple readily available 2-(1-alkynyl)-2-alken-1-ones and heterodienes.[579]

5.3. Application to Total Synthesis

The use of gold catalysis in total synthesis is based in carbon−nitrogen disconnection. The gold-catalyzed C−N formation retrosynthetic disconnections include formation of an indole structure. For instance, the total synthesis of (−)-mersicarpine was achieved in 10 steps from the known keto ester **448** (Scheme 144).[580]

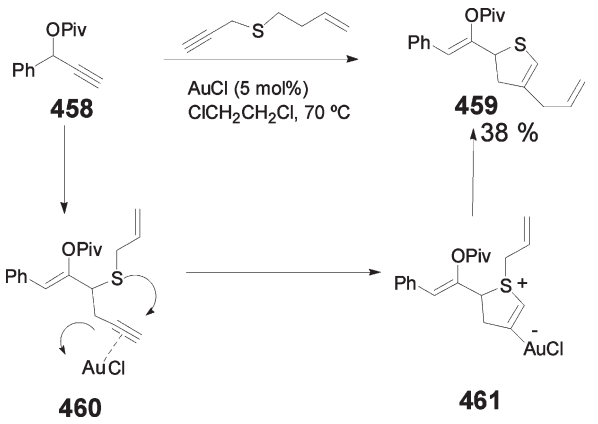
The oxidation of **448** with IBX followed by epoxidation of the resulting enone afforded epoxy ketone **449** that could react with semicarbazide to form semicarbazone **450**. This was oxidized with lead tetracetate to form the 1,3,4-oxadiazoline intermediate, which underwent an Eschenmoser−Tanabe-type fragmentation to furnish **451** in 60% yield. This compound was reduced with $NaBH_4$ to afford alcohol **452**. Sonogashira coupling of **452** with 2-iodoaniline proceed uneventfully to give the alkynylaniline, which was cyclized with a gold(III) catalyst to afford indole **453** in good yield. Reaction of **453** with benzenediazonium chloride proceeded cleanly to furnish **454**, and subsequent lactam formation by treatment with sodium hydride followed by mesylation of the primary alcohol afforded **455** (Scheme 144).

Scheme 144



Reagents and conditions: (a) See ref 580; (b) IBX, DMSO, 85 °C, 72%; (c) H_2O_2, NaOH, H_2O−MeOH, 0 °C, 88%; (d) $NH_2CONHNH_2 \cdot HCl$, NaOAc, H_2O−EtOH, rt, 89%; (e) $Pb(OAc)_4$, CH_2Cl_2, −10 °C, 60%; (f) $NaBH_4$, MeOH, 0 °C, 87%; (g) *o*-iodoaniline, $Pd(PPh_3)_4$, CuI, DMF−Et_3N, 80 °C, 78%; (h) $NaAuCl_4 \cdot 2H_2O$, EtOH, rt, 78%; (i) PhN_2Cl, NaOAc, *i*-PrOH−H_2O−1,4-dioxane, 0 °C, 97%; (j) NaH, MS4A, toluene, rt; MsCl, Et_3N, 0 °C, 77%; (k) H_2, Pd−C, *i*-PrOH−CH_2Cl_2, rt; (l) $NaHCO_3$, *i*-PrOH−CH_2Cl_2 (degassed), reflux; (m) autoxidation, Me_2S.

Scheme 145



Overall, this process involves three key stages: gold-catalyzed rearrangement, ylide formation and rearrangement, and gold-catalyzed cycloisomerization (Scheme 145).[581]

The same group showed that a simple and robust alkyne functionality can be used as a direct precursor to a sulfur ylide using gold or platinum catalysis. An internal redox combination strategy bypasses the need to employ sacrificial functionality to access sulfur ylide chemistry and enables nonstandard retrosynthetic approaches to be used. A range of functionalized sulfur heterocycles have been synthetized by novel cycloisomerization reactions of readily prepared sulfoxide tethered enynes **462**. The following scheme illustrates the formation of a fused heterocycle **463** using the complex dichloro(pyridine-2-carboxylate)gold-(III) **464** (Scheme 146).[582]

In this case, when the electronic bias on the alkyne group increased by substitution with an ester moiety, the isothiochroman-4-one product **463** was formed exclusively under gold catalysis.

6. FORMATION OF CARBON−SULFUR BONDS

There are few reports on gold-catalyzed C−S bond formation, and for the most part, this work is concerned with intramolecular reactions or a combination of inter- and intramolecular attack of the *S*- nucleophile to afford five- or six-membered *S*-heterocycles.

Davies et al. showed that the use of gold-catalyzed isomerizations to access reactive sulfur ylide intermediates is a viable intermolecular strategy.[581] A highly efficient rearrangement−coupling−rearrangement process has been developed that utilizes simple and readily constructed precursors to access highly functionalized materials under mild conditions. This study demonstrates that the gold carbenoids derived from propargylic carboxylates can show a complementary mode of reactivity to carbenoids derived from α-diazo carbonyl compounds, with the propargylic carboxylate reacting as an overall 1,3-dipolar synthon rather than a 1,1-dipolar species.

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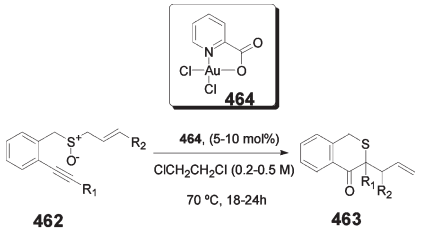
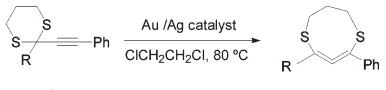
Scheme 146

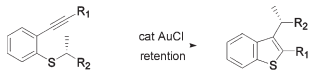


Scheme 147



R = *p*-Br-C_6H_4 60 %
R = *m*-Br-C_6H_4 76 %
R = *p*-Cl-C_6H_4 60 %
R = *p*-MeOC_6H_4 90 %

Scheme 148



		chirality transfer %
R_1 = p-anisyl, R_2 = Ph, **467a** (97 % ee)	98 % (88 %ee)	91
R_1 = p-anisyl, R_2 =p-ClC_6H_4 , **467b** (98 % ee)	97 % (79 %ee)	81

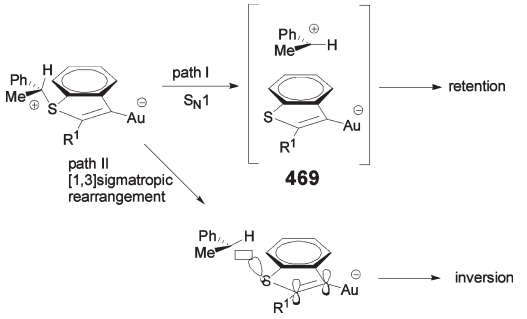
It has been reported that $AuBr_3$ catalyzes the regiospecific intermolecular hydrothiolation of aromatic allenes and aromatic thiols to afford the corresponding dithioacetals in good yields.[583a] Similarly, the Au(I)/Ag system catalyzed the transformation of alkynes into cyclic acetals and thioacetals at a much higher rate than Brønsted acids. The reaction appeared to be general for a range of alkynes and diols or dithiols, which were efficiently transformed with high selectivities. One of the salient features of this reaction process was the high reactivity of the enol ether or enol thioether intermediate, which underwent a rapid transformation to afford the cyclic thioacetal, so that isolation or subsequent activation processes were not required.[230]

In close connection to this, it has been reported that the $AuPPh_3Cl/AgSbF_6$ system catalyzes a novel rearrangement where propargylic 1,3-dithiane leads to the formation of eight-membered dithiosubstituted cyclic allenes with good yields and remarkable stability (Scheme 147).[583b]

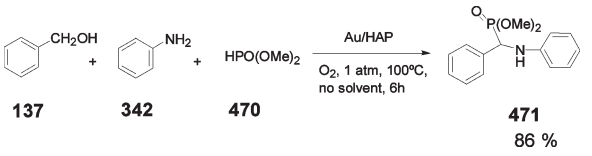
It was found that chirality transfer in gold-catalyzed carbothiolations of *o*-alkynylphenyl 1-arylethyl sulfides **467** proceeds with retention of the configuration at the 1-arylethyl group (Scheme 148).[584a]

The retention of the stereocenter suggested that the [1,3] migration of the α-phenethyl group in the present chirality transfer reaction took place through generation of the contact ion pair **469** followed by C−C bond formation before racemization of the stereocenter, as shown in path I (Scheme 149).

Scheme 149



Scheme 150



Thiophenes were also efficiently prepared by gold-catalyzed dehydrative cyclizations of readily available heteroatom-substituted propargylic alcohol. The reaction was rapid, high yielding, and procedurally simple, giving essentially pure aromatic heterocyles in minutes under open-flask conditions with catalyst loadings as low as 0.05 mol %.[137]

o-Alkynylbenzoic acid alkyl esters acted as alkylating agents of thiol derivatives with PPh_3AuCl in combination with AgOTf in 1,2-dichloromethane at 80 °C. The corresponding sulfide compounds were obtained in good to excellent yields.[584b]

7. FORMATION OF CARBON−PHOSPHORUS BONDS

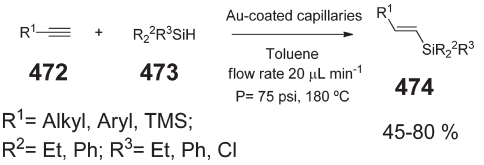
7.1. Heterogeneous Catalysis for Formation of Carbon−Phosphorus Bonds

A one-pot three-component approach has been designed as an alternative catalytic route for the tandem synthesis of α-aminophosphonates.[585] These compounds are currently obtained by a number of multistep synthetic approaches involving nucleophilic addition of phosphites to imines (Scheme 150).[586,587]

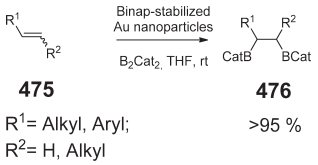
8. FORMATION OF CARBON−SILICON BONDS

The more direct and environmentally benign pathway to obtain C−Si bonds is the addition of silanes to unsaturated C−C bonds, particularly alkenes and alkynes.[588] Gold-catalyzed hydrosilylation of alkynes has been reported during this period and earlier.[589] The reaction can be run either homogeneously or heterogeneously. For instance, Caporusso and co-workers[589] have used gold nanoparticles, supported by means of the metal vapor synthesis technique on different metal oxides and carbon, as catalysts for the hydrosilylation of 1-hexyne, achieving the *E*-isomer with high selectivity. Similarly, Iglesias, Sánchez, and co-workers[590] have supported an *O,N,N*-tridentate pincer-type gold(III) complex onto ordered mesoporous silica MCM-41, which acts as heterogeneous catalyst for the hydrosilylation reaction. The single gold(III) complex was also studied as catalyst in homogeneous phase. However, when the heterogeneous version is efficient, several issues make it more convenient. For instance,

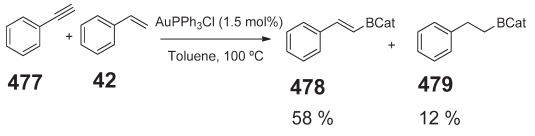
Scheme 151



Scheme 152



Scheme 153



Organ and Shore[591] have designed a gold-film-catalyzed hydrosilylation of alkynes by microwave-assisted, continuous-flow organic synthesis (MACOS, Scheme 151). This methodology is similar to that used by the same authors to obtain ketones (see Scheme 62).[310]

E-Vinylsilanes **474** were obtained in good yields and selectivities from the corresponding alkynes **472** and silanes **473**, the Au-film being reusable several times. However, other approaches to obtain new C−Si bonds rather than hydrosilylation of alkynes have been accomplished using gold catalysis. These approaches rely on the intramolecular migration of a silicon or a carbon atom. Thus, Gevorgyan and co-workers[592a] observed that the 1,2-shift of a silyl group occurred concomitantly to an alkyne−vinylidene isomerization during the $AuBr_3$-catalyzed synthesis of 1,2-disubstituted-*N*-fused pyrrole-containing heterocycles. The same group expanded their work to the Au-catalyzed synthesis of silylfurans via 1,2-Si or 1,2-H migrations, aided by DFT calculations.[592b] Murakami and co-workers[593] have reported the intramolecular transallylsilylation of silaenynes to form 3-allyl-1-silaindenes in good yields, using Au(I) complex **232** (see Scheme 88) as catalyst of choice.

9. FORMATION OF CARBON−BORON BONDS

The direct boration of unsaturated C−C bonds is the preferred method to obtain a new C−B bond, particularly the hydroboration reaction.[594−597] These reactions can be catalyzed by many metals, but prior to 2008, only one example with gold as catalyst was reported: Baker and co-workers[598] reported the gold(I)-catalyzed diboration of vinylarenes. In that work, surprisingly, the use of different coinage metals as catalysts led to different products when using bis(catecholate)diboron as reagent: if gold(I) was used, exclusively the corresponding diboration product was formed; however, if rhodium was used, a mixture of products including hydroboration products was encountered. Recently, two different gold-catalyzed C−B forming reactions have been accomplished: the diboration of alkenes[599] and the hydroboration of alkynes.[590] On one hand, Fernández and co-workers[599] have described BINAP-stabilized gold(0) nanoparticles, generated in situ, as catalysts for the conversion of alkenes **475**, either *E* or *Z*, to the corresponding 1,2-bis(boronate) esters **476** in high yields and with complete chemoselectivity (Scheme 152).

On the other hand, Corma and co-workers[600] have reported a chemoselective hydroboration of alkynes in the presence of alkenes using different Au(I) or Au(III) salts and complexes as catalysts (Scheme 153). Kinetics experiments corroborated the isolated yields of **478** and **479**, and the procedure was also applied to enynes.

10. CONCLUSIONS AND FUTURE TRENDS

We have seen the work on gold catalysis to increase exponentially in the last few years. This is specifically true for homogeneous gold(I) and some gold(III) catalysts. Despite further expansion of gold catalysts to form C−O and C−N bonds, new developments are now starting for selective formation of C−S and, especially, C−P, C−Si, and C−B bonds. This is a field that may offer new possibilities for gold catalysis.

From the catalytic point of view, there are still limitations in catalyst stability for homogeneous gold, which tends to precipitate inactive metallic gold with time. This also has the handicap of catalyst recovery.

The large variety of reactivity and good, and even unique, selectivities achieved with gold will expand its use for multistep catalyzed reactions, by means of the preparation of multisite catalysts. This may involve multimetal transition-metal complexes, dendrimers, or even hybrid organic−inorganic catalysts. The last one could be prepared by directly anchoring or intercalating the active phase on solid catalysts or by one-pot synthesis of high surface area solid hybrid materials such as, for instance, MOF catalysts.[601] With these types of material, one could still maintain the metal functionality of the homogeneous phase but in a solid catalyst. In other words, these methodologies should be able to establish a bridge between homogeneous and heterogeneous catalysis.[601a,602]

We have seen along this review that most of the reactions and reactivity features have been achieved with cationic (Lewis acid) gold, and only very few have made use of redox Au(I) ⇄ Au(III) properties of gold. Further possibilities to achieve high turnover numbers with the redox functionality remain to be explored.

Again, most of the catalytic advantages of cationic gold have been achieved with homogeneous gold catalysts, and relatively few results have been obtained with gold nanoparticles. In the later case, and despite efforts to stabilize cationic gold in supported nanoparticles,[603] the relatively small number of cationic sites on supported nanoparticles has limited its use for the reactions described in this review. We believe it should be possible to increase the number of accessible cationic sites by stabilizing still smaller nanoparticles (0.8−1.0 nm). Furthermore, if achieved, their electronic properties could be tuned by controlled surface adsorption of organic molecules, such as, for instance, phosphines.

Finally, we expect the possibilities of gold catalysts to be expanded by preparing multifunctional acid−metal, base−metal, acid−base−metal, and metal−metal catalysts that will be able to

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perform one-pot multistep reactions in an efficient and enviromenntally friendly way.

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BIOGRAPHIES

Avelino Corma was born in Moncófar, Spain, in 1951. He studied Chemistry at the Universidad de Valencia (1967−1973) and received his Ph.D. at the Universidad Complutense de Madrid in 1976. He was Postdoctoral in the Department of chemical engineering at the Queen's University (Canada, 1977−1979). He is director of the Instituto de Tecnología Química (UPV-CSIC) at the Universidad Politécnica de Valencia since 1990. His current research field is catalysis, covering aspects of synthesis, characterization, and reactivity in acid−base and redox catalysis. Avelino Corma is coauthor of more than 700 articles and 100 patents on these subjects.

Antonio Leyva-Pérez was born in Sevilla, Spain, in 1974. He received a graduate degree in Chemistry by the Universidad de Valencia in 2000 and a Ph.D. degree with honors by the Universidad Politécnica de Valencia in 2005, working in palladium-supported catalysis under the guidance of Prof. Hermenegildo García. During this period, he did a short stay in the group of Prof. Stephen L. Buchwald at M.I.T. in Cambridge, Massachusetts, USA. After this, he moved for post-doctoral studies to the group of Prof. Steven V. Ley at The University of Cambridge, U.K., working in the total synthesis of natural products. In 2008, he joined the group of Prof. Avelino Corma at the Instituto de Tecnología Química (ITQ) in Valencia. His current research involves the development of solid-supported or not metal catalysts for organic synthesis.

Maria Jose Sabater obtained her degree in Pharmacy from Universidad de Valencia (Spain) in 1987 and her Ph.D. in Organic Chemistry from the same University in 1991. After completing her doctorate, she joined the group of Prof. Waldemar Adam at the Würzburg University (Germany) as a post doctoral fellow of the Alexander von Humboldt Foundation (Germany), working on Photochemistry (1993−1994). Thereafter, she moved to Poitiers University (France) for a second postdoctoral stay under the supervision of Prof. Michel Guisnet (1995). This time, her research was focused on heterogeneous catalysis for fine chemicals. In early 1996, she returned to Spain and joined the group of Prof. A. Corma at the Instituto de Tecnología Química (UPV-CSIC) at the Universidad Politécnica de Valencia, where she was appointed Tenured Scientist from 2002. Since then, she pursued her research activities in the field of catalysis and synthesis of microporous materials.

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