Review

Gold-Catalyzed Organic Transformations

Zigang Li, Chad Brouwer, and Chuan He

Chem. Rev., **2008**, 108 (8), 3239-3265 • DOI: 10.1021/cr068434l • Publication Date (Web): 10 July 2008

Gold-Catalyzed Organic Transformations

Zigang Li, Chad Brouwer, and Chuan He*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received January 23, 2008

Contents

1. Introduction

Thanks to its unusual stability, metallic gold has been used for thousands of years in jewelry, currency, chinaware, and so forth. However, gold had not become the chemists' "precious metal" until very recently. In the past few years, reports on gold-catalyzed organic transformations have increased substantially. Thanks to gold-based catalysts, various organic transformations have been accessible under facile conditions with both high yields and chemoselectivity.

Although previous reviews have covered a broad scope of reactions on gold catalysis,[1] the high speed of publication on gold still demands an outlook on recent developments that are important to the synthetic community. We cover here literature published between the beginning of 2004 and the end of 2007 and focus on new organic reactions with gold as the active species. This review will be organized into several sections; each section contains similar reaction types or reaction mechanisms with discussion.

* To whom correspondence should be addressed. Phone: 773-702-5061. Fax: 773-702-0805. E-mail: chuanhe@uchicago.edu.

2. Gold-Catalyzed Nucleophilic Additions

2.1. Gold-Catalyzed Cyclizations with Olefins as Nucleophiles

Several groups reported on gold(I)-catalyzed cyclization of enynes in 2004,[2] with gold carbenes implicated as reactive intermediates.[3] Numerous transformations have been developed based on *in situ* gold carbene generation and most have already been reviewed in detail.[1] To avoid redundancy, only limited space will be devoted to this class of reactions.

Recent studies by Toste et al. have shown that propargylic acetates are rearranged by cationic gold(I) complexes. This report spurred further effort into these systems. It was shown that *in situ* generated gold carbenes are trapped by alkenes to form cyclopropane derivatives.[4] The reaction is highly *cis* selective, with diastereoselectivity greater than 20:1 in some cases. A screen identified Solvias' chiral (*R*)-DTBM-SEGPHOS as an effective ligand in enantioselective cyclopropanation, albeit with modest *ee* (Scheme 1).

In a different study reported by Echavarren et al. on gold carbenes generated in 1,6-enyne rearrangements,[5] olefins are trapped by cyclopropyl gold(I) carbenes before they have a chance to rearrange further. The use of a nitrogen-heterocycle-carbene (NHC) ligand over a phosphine one was crucial to suppressing side reactions. Interestingly, the ligand screen also revealed that comparable yields could be attained in the absence of any ligand (Scheme 2).

Gold(III) salts are less-frequently used in cyclizations than gold(I) salts, perhaps due to their propensity for increased byproducts generation as well as their relatively high oxidative potentials. Zhang et al. constructed substrates which can undergo acetoxy migration to an alkyne, where the resulting vinyl-gold(III) intermediate is trapped by a proximal allylic cation.[6] Typical gold(I) catalysts such as $Ph_3PAuSbF_6$ do not catalyze the reaction. Instead, the authors found that the bidentate 2-pyridine carboxylate to be an ideal ligand for the $AuCl_3$ promoted rearrangement. The benefits of this ligand were first demonstrated by Hashmi in the synthesis of tetrahydroisoquinolines[7] (Scheme 3).

Like alkynes, allenes are also promising synthons in gold-mediated rearrangements. Several groups have explored the 1,6-allenyne cycloisomerization reaction. The outcome of the reaction has a marked dependence on which catalyst was used. For example, while simple salts like $AuCl_3$ and AuCl furnish hydrindienes exclusively, $Ph_3PAuSbF_6$ gives solely Alder-ene products. Malacria et al. attribute this dramatic change in product distribution to the anions as opposed to the ligands, although the role of different ligands was not reported[8] (Scheme 4).

Afterward, Gagné et al. studied the isomerization of 1,6-allenenes.[9] Vinyl cyclohexenes are obtained in good yields

10.1021/cr068434l CCC: $71.00
Published on Web 07/10/2008

Zigang Li was born in 1978 in Hefei, China. He received his B.S. (2001) of neuroscience and biophysics from the University of Science and Technology of China, Hefei, China. He obtained his M.S. in organic chemistry under the guidance of Professor Chao-Jun Li from Tulane University in 2004. Then he moved to the University of Chicago to continue his Ph.D. study. His current research focuses on novel metal-mediated oxidation reactions, reaction mechanisms and activation mechanisms of virulence regulator proteins in *Staphylococcus aureus*. Besides science and history, he also likes travel, friends, and good food.

Chad Brouwer was born in Evergreen Park, IL, in 1977. After several years training as a drummer, he switched gears and studied chemistry at the University of Illinois at Chicago. There he studied under Prof. Vladimir Gevorgyan on novel methods for silylations of alkynes, which resulted in 1st place in UIC's Undergraduate Research Symposium. He was given the Reetz Award for the Outstanding Graduate in Chemistry as well as his B.S. in chemistry (high distinction) in 2003. He then spent a year with Lisheng Cai at the National Institutes of Mental Health on an intramural research training award where he helped develop ligands that bind β-amyloid plaques. In 2005, he began graduate studies at the University of Chicago's Chemistry Department with Prof. Chuan He. Here, he is developing novel gold-catalyzed methodologies. Hobbies include collecting vinyl records, cinema, and quiet walks on the beach.

and modest *ee* (up to 77% in one case) by employing (*R*)-3,5-xylyl-BINAP(AuOTf)$_2$ as the catalyst (Scheme 5).

Malacria et al. further expanded the substrate scope to include propargylic acetates, which are known to undergo [3,3]-sigma tropic shifts. Vinyl allene intermediates form if the starting substrates are conjugated enynes. Vinyl allenes can then undergo an aura-Nazarov rearrangement and are situated specifically to trap a pendant olefin, forming multiply fused carbocycles under mild conditions[10] (Scheme 6).

The generation and use of all-carbon 1,3-dipoles that can cyclize onto alkenes has recently been developed by Zhang et al.[11] This formal [3 + 2] cyclization is accessible only by using Hashmi's gold(III) catalyst, and the reaction is highly diastereoselective, suggesting that a concerted dipolar cy-

Chuan He was born in 1972 in P. R. China and graduated with a B.S. in chemistry in 1994 from the University of Science and Technology of China, Hefei, China. Then he moved to U.S. and obtained a Ph.D. in chemistry at Massachusetts Instituted of Technology in 2000 working with Professor Stephen J. Lippard. As a Damon-Runyon Cancer Research Foundation Postdoctoral Fellow, he worked in Professor Gregory L. Verdine's group at Harvard University on DNA repair proteins. Dr. He started his independent research at the University of Chicago in 2002 and is currently an Associate Professor in the Department of Chemistry. His research covers several different areas that include chemistry and catalysis with silver and gold, selective metal ion recognition in biology, regulation of virulence factors in pathogens, structure, function and mechanism of direct DNA repair proteins, and proteomics on DNA repair and DNA modification proteins. He is a Searle Scholar, a G&P Foundation of Cancer Research Young Investigator, a W. M. Keck Foundation Distinguished Young Investigator, an Arnold and Mabel Beckman Foundation Young Investigator, a Cottrell Scholar from the Research Corporation, a Camille Dreyfus Teacher Scholar, an Alfred P. Sloan Research Fellow, and a recipient of a Research Corporation Research Innovation Award and CACPA Distinguished Junior Faculty Award.

cloaddition occurs. The end product contains an all-carbon quaternary center. Toste et al. expanded the reaction scope by showing [2 + 2] that allenene cyclizations are also possible.[12] Enantioenriched products can be obtained using standard dinuclear biarylphosphines as ligands (Scheme 7).

These cyclizations in Scheme 7 suggest that vinyl allenes should also have the potential to undergo similar rearrangements. Indeed, Toste demonstrated that highly substituted pentadienes are obtained under mild conditions.[13] Enantioenriched substrates give completely racemic products, suggesting that the cyclization is not concerted (Scheme 8).

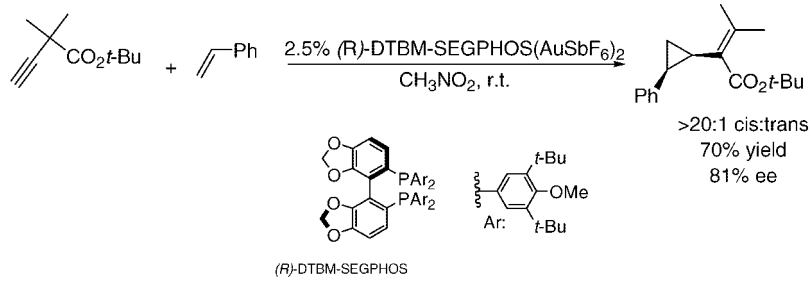
2.2. Gold-Catalyzed Nucleophilic Additions Using Nitrogen Nucleophiles

Both inter- and intramolecular hydroamination of alkynes catalyzed by both gold(I) and gold(III) have been reported earlier.[14] In the past few years, the scope of alkyne aminations has been significantly broadened with gold catalysts.[1]

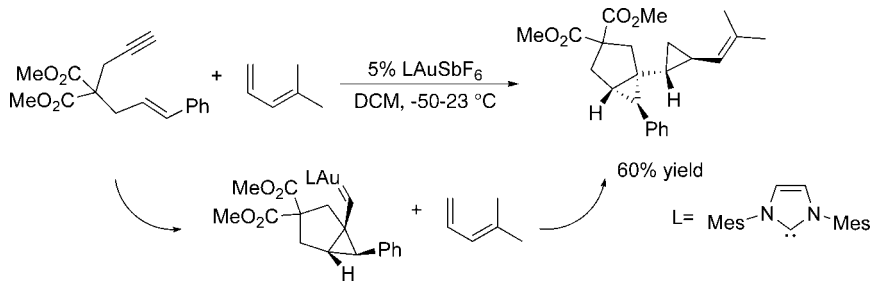
Ortho-alkynylanilines are known to be suitable substrates for gold-catalyzed indole syntheses. However, Li et al. showed that, in the presence of a terminal alkyne, the intermolecular hydroamination occurs first.[15] The resulting Schiff bases can then cyclize onto the pendant alkyne. Indole does not undergo hydroamination with terminal alkyne in a control experiment. $AuCl_3$ efficiently catalyzes this reaction with neat substrate, although addition of AgOTf gives higher yields under milder conditions (Scheme 9).

In another example of intramolecular hydroamination of alkynes with imine derivatives, Shin et al. reported that homopropargylic trichloroacetimidates can rapidly undergo

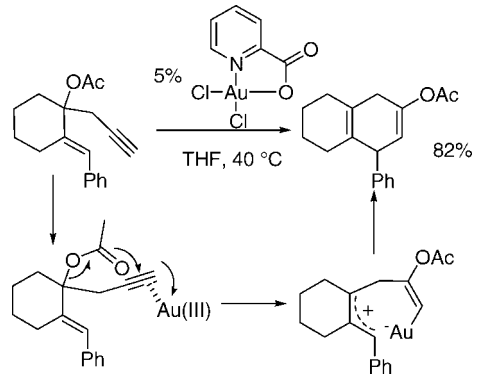
Scheme 1



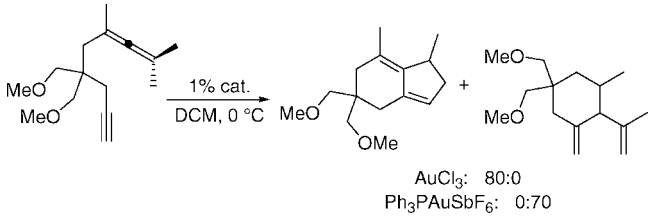
Scheme 2



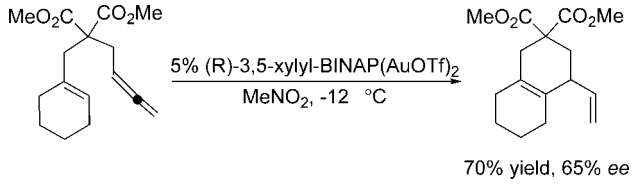
Scheme 3



Scheme 4



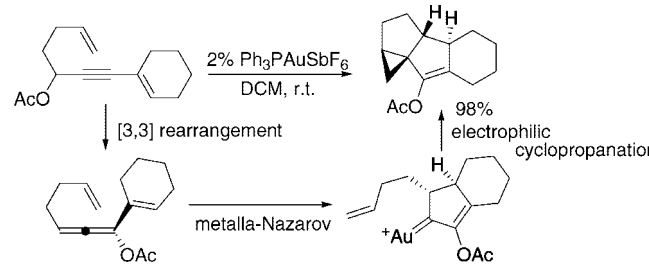
Scheme 5



6-*exo-trig* cyclizations in the presence of Ph_3PAuBF_4 under mild conditions ($T = 0$ °C).[16] They had success with both terminal and internal alkynes, and in all cases, the *anti*-addition product is obtained exclusively (Scheme 10).

Nakamura et al. showed that a similar reaction profile is accessible with *ortho*-alkynyl-tertiary-*N*-sulfonylanilines, where the sulfonyl group migrates during the amination.[17] $AuBr_3$ (as well as $InBr_3$) is the best catalyst for the synthesis of 3-sulfonylindoles. In several cases, sulfonyl migration is

Scheme 6



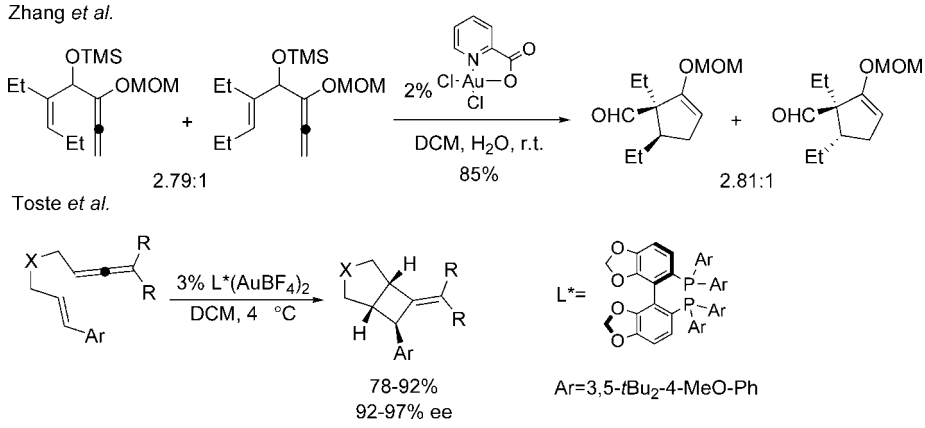
not limited to C3, yielding other isomers. A crossover experiment revealed that the formal aminosulfonylation occurs intramolecularly (Scheme 11).

Like tertiary anilines, pyridines also serve as nucleophiles for intramolecular additions. Gevorgyan's laboratory screened a plethora of metals, and most, including gold(I) and gold(III), are competent catalysts for this reaction.[18] With similar substrates, they demonstrated that main group functionalities containing silicon, tin, and germanium will undergo migration.[19] The germanium migration is the first-ever reported. The mechanism involves a cascade reaction *via* isomerization to a gold-vinylidene, followed by a hydride shift (Scheme 12).

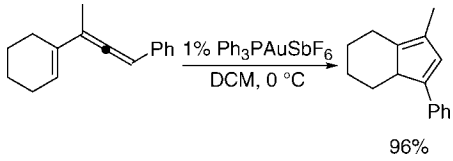
Toste et al. exploited gold(I)'s ability to act as a transition metal in conjunction with its π acidity in a variation of the Schmidt reaction, where a nucleophile with a latent leaving group attached can add intramolecularly to an unactivated alkyne.[20] At this point, rather than proto-deauration, gold backbonds electron density to the substrate, expelling N_2. A catalyst screen identified the dinuclear bisphosphine $(dppm)Au_2Cl_2$ activated by $AgSbF_6$ as the most effective combination for the pyrrole synthesis. If the propargylic carbon is tertiary, then the 1,2-hydride shift is replaced by an OTBS shift, or even a ring expansion product (MG = migrating group) (Scheme 13).

Allenes are fertile ground for new reactivity in intramolecular nucleophilic additions. Indeed, the 5-*endo-dig* cyclization of α-aminoallenes with $AuCl_3$ occurs under very mild conditions (0 °C to room temperature) in good to excellent yields (70−95%).[21] Surprisingly, the degree of

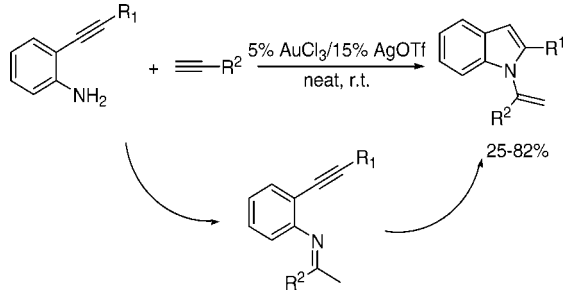
Scheme 7



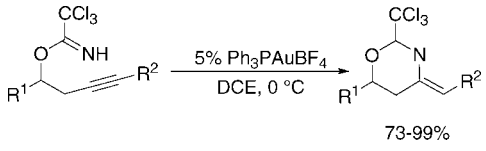
Scheme 8



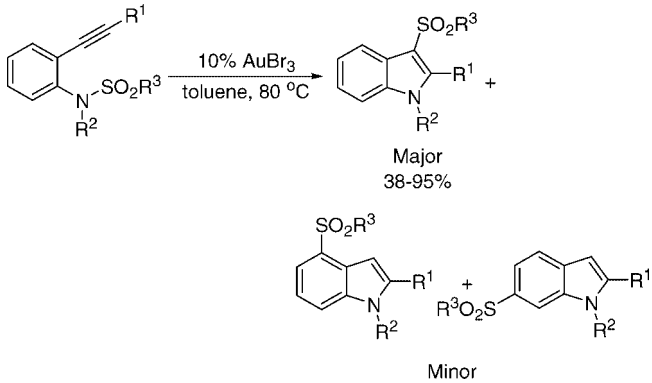
Scheme 9



Scheme 10

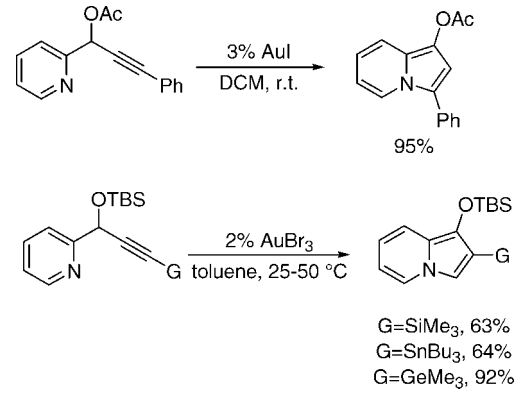


Scheme 11

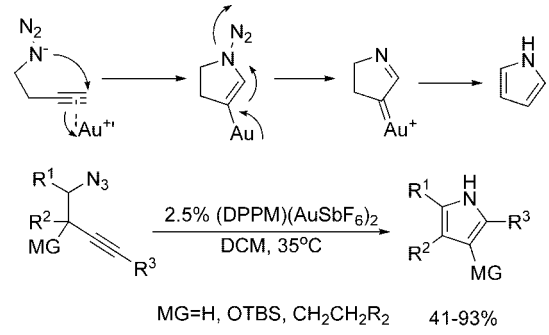


chirality transfer appears to have a dependence on the protecting group employed on the nitrogen, where the highest diastereoselectivity resulted in the absence of any protecting group. Of course, this high diastereoselectivity is achieved at the expense of longer reaction times. Widenhoefer et al. later reported similar results with not only nitrogen,[22] but also oxygen[23] and carbon nucleophiles.[24] Lee et al. showed

Scheme 12



Scheme 13

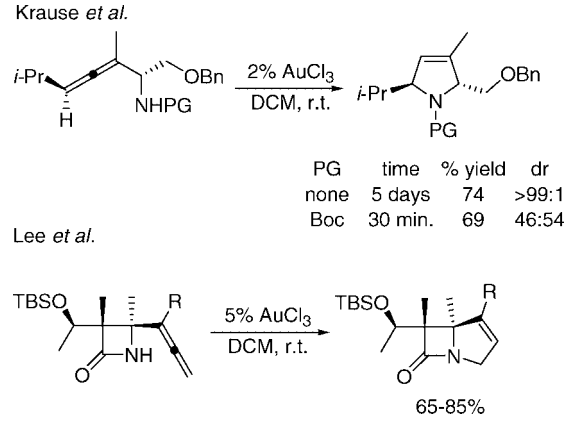


that the intramolecular hydroamination of secondary azetidinones onto terminal allenes is feasible under mild conditions, offering good isolated yields of bicyclic β-lactam products[25] (Scheme 14).

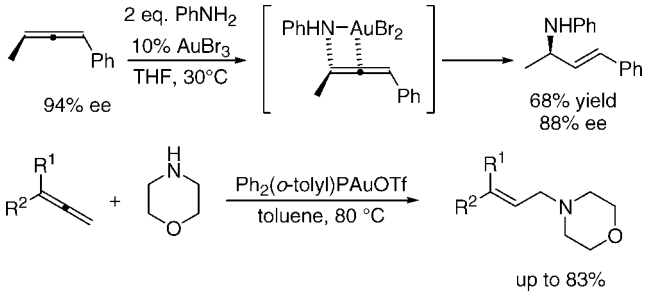
Yamamoto et al. reported the more challenging intermolecular hydroamination of allenes, proceeding with quite high chirality transfer.[26] They propose that the catalyst is not acting merely as a Lewis acid but is complexed to the amine prior to addition. Two equivalents of aniline was used which may explain why the chirality transfer is successful. Aniline was certainly also acting as a BrØnsted base/proton shuttle here. In a later report, the same group reported that cationic gold(I) catalyzes the same reaction between allenes and morpholine to give allylic amines. This is the first example of gold-catalyzed intermolecular hydroamination with aliphatic amines[27] (Scheme 15).

Toste et al. reported the enantioselective intramolecular hydroamination of allenes.[28] This is noteworthy as he was the first to show gold is competent in transmitting chiral

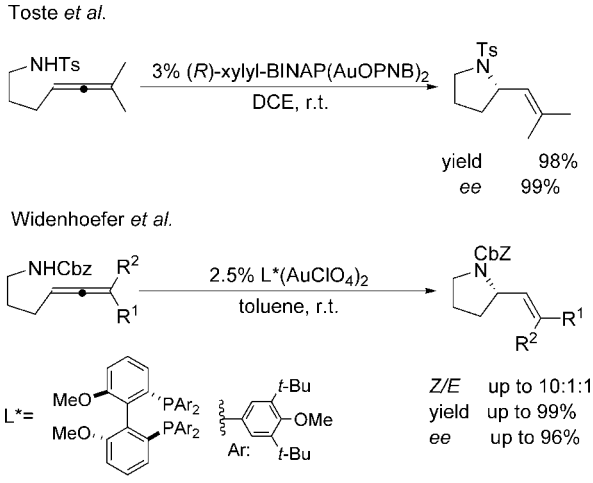
Scheme 14



Scheme 15



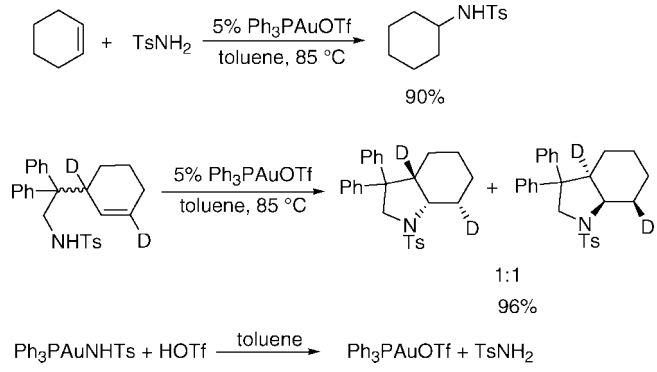
Scheme 16



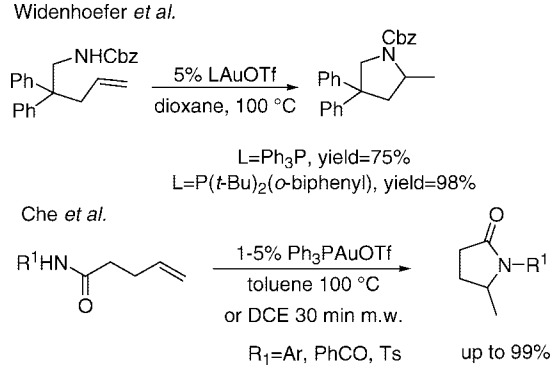
information to its substrates. The problem is inherently difficult for gold(I) since it strongly prefers a linear coordination geometry, which positions the substrate furthest from the ligand. Nonetheless, his group employed chiral bisphosphines and uncovered a strong counterion effect, both of which were crucial to achieving high enantioselectivity. Widenhoefer subsequently published similar results with carbamates and carboxamides.[22] He found that the relative size of R_1 to R_2 strongly influenced both enantio- and diastereoselectivity. Similarly sized substituents gave lower *ee* with concomitant higher *de* and *vice versa* when the substituents are increasingly different in sterics (Scheme 16).

He et al. first demonstrated that Au(I) promotes the hydroamination of alkenes.[29] With 5% $Ph_3PAuOTf$ at 85 °C, both inter- and intramolecular additions of tosylamide occur in good to excellent yields. A mechanistic analysis confirmed that a *trans*-addition mechanism is operative. Generally, most of the gold-catalyzed hydroamination of olefins could also

Scheme 17



Scheme 18

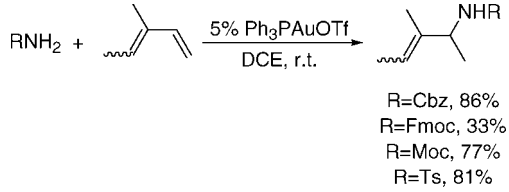


be catalyzed by catalytic amount of HOTf.[30,31] As a control experiment, they studied the ^{31}P NMR of $Ph_3PAuOTf$ at 85 °C and found that the $AuPPh_3^+$ species does not interact with $TsNH_2$ and indeed interacts with norbornene or cyclohexene. They further synthesized $Ph_3PAuNHTs$, which could not catalyze or undergo the olefin hydroamination reaction but did react with strong BrØnsted acids immediately to release $TsNH_2$.[30] However, a comprehensive understanding of the mechanism is still necessary (Scheme 17).

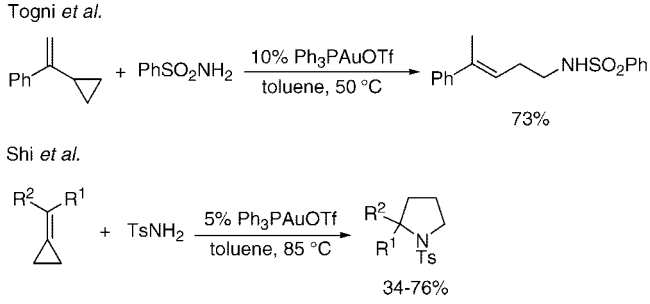
Widenhoefer, Che, and Shi largely extended the hydroamination reaction scope. Widenhoefer et al. found that the bulkier phosphine ligand P(*t*-Bu)$_2$(*o*-biphenyl) increases yields substantially using carbamates,[32] carboxamides,[33] and ureas.[34] Che et al. reported that both inter- and intramolecular hydroamination of olefins with sulfonamides, carbamates, and carboxamides occurs under microwave irradiation in only 30 min.[35] A remarkable reaction found by Che et al. showed that an intramolecular olefin addition occurs even in 90% water[36] (Scheme 18).

He's group also used conjugated dienes as substrates for hydroamination using the same catalyst.[30,37] Many commonly encountered carbamates as well as sulfonamides added at room temperature with good to very high yields. Although the reaction occurs *via* 1,2- and 1,4-addition, compounds that are symmetric about C3 give the same products. In early 2008, Ujaque et al. published DFT calculations on the intricate details of this reaction and unearthed some surprising results concerning its mechanism,[38] namely, the importance of the counteranion in subsequent steps. Their calculations found direct proton transfer from nitrogen to carbon to be enthalpic by 51.5 kcal/mol. However, a lower energy pathway was identified where triflate facilitates $H_2N-C{=}O$ to $HN{=}C-OH$ tautomerization followed by proton transfer from oxygen to carbon, with a global barrier at 26.2 kcal/mol (Scheme 19).

Scheme 19



Scheme 20



If the terminal olefin above is replaced with a cyclopropane, homoallylic amines can then be accessed through a ring opening process.[39] Hammett plots of the $Ph_3PAuOTf$ versus HOTf catalyzed processes yield similar ρ values ($\rho_{Au}^{+} = -2.1$ and $\rho_{H}^{+} = -1.8$) and demonstrates how alike Au^{+} and H^{+} are. In a similar reaction by Shi et al,[40] methylenecyclopropanes undergo a tandem ring-opening/intramolecular hydroamination at elevated temperatures. Pyrrolidines were synthesized in fair to good yields with $Ph_3PAuOTf$ (Scheme 20).

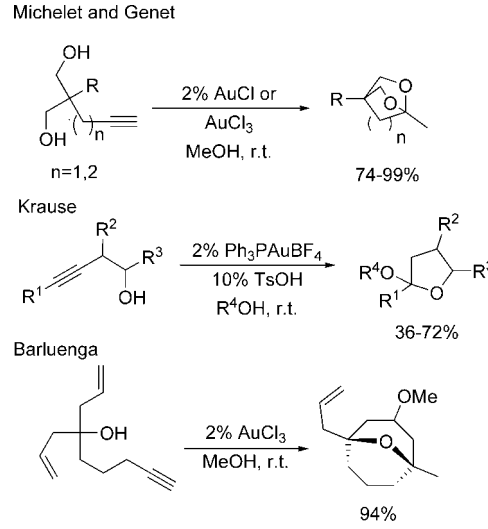
2.3. Gold-Catalyzed Nucleophilic Additions Using Oxygen and Sulfur Nucleophiles

Utimoto reported the first gold-catalyzed hydration and hydroalkoxylation of alkynes as early as 1991.[41] Since then, much effort has focused on exploiting this initial discovery.[1] It was found that a double intramolecular hydroxylation of alkynes can give high yields of bicyclic ketals under very mild conditions with either AuCl or $AuCl_3$.[42] Although Michelet and Genêt propose directing group assistance from one of the alcoholic side chains, it seems just as likely that the solvent (MeOH) could attack first, followed by an intramolecular displacement of a Lewis acid activated MeO-leaving group. Krause demonstrated that a tandem cycloisomerization-hydroalkoxylation is also possible when the substrate has only one OH group; [43] however, BrØnsted acid cocatalyst is required. Barluenga reported similar results. If the substrate contains a pendant olefin instead of an alcohol, the olefin can attack the oxonium intermediate, and itself be trapped by solvent, analogous to the Prins reaction[44] (Scheme 21).

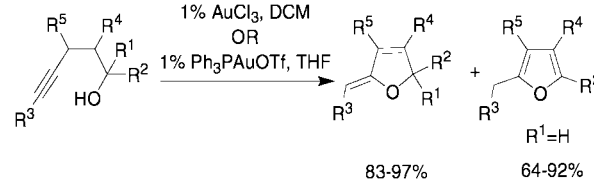
Inspired by a finding from Hashmi's laboratory, Liu et al. showed that a slew of fully substituted dihydrofurans and furans are accessible from (*Z*)-2-en-4-yn-1-ols in very good to excellent yields.[45] Very electron-deficient substrates and those containing amines are more challenging. Both $AuCl_3$ and $Ph_3PAuOTf$ enable reactivity and, in some cases, with as low as 0.1% catalyst loading (Scheme 22).

A considerable improvement to the Meyer-Schuster rearrangement of propargylic alcohols to α,β-unsaturated esters was discovered by Dudley et al.[46] The reaction is mild (5 min. at room temperature in many cases), but is wanting in stereoselectivity. One control reaction shows that TsOH could

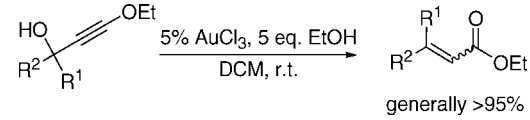
Scheme 21



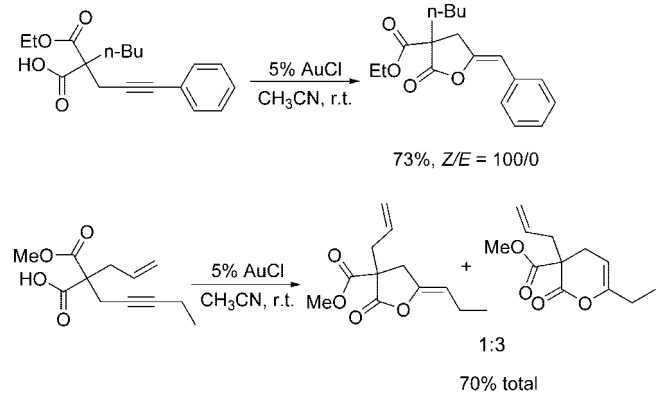
Scheme 22



Scheme 23



Scheme 24

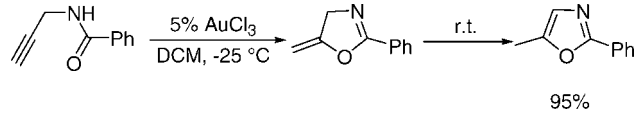


only give 15% product in 1 h, while $AuCl_3$ could give 86% product in less than 5 min, which highlights the advantage of gold for this particular example (Scheme 23).

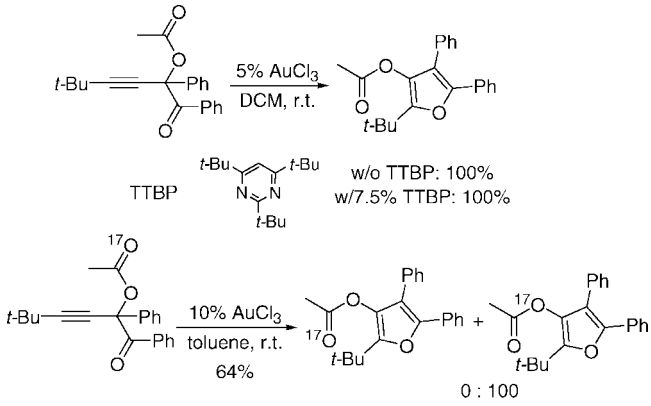
Genêt and Michelet showed that carboxylic acids also add to alkynes, in very good to excellent yields, despite their lower nucleophilicity.[47] Depending on the electronic nature of the alkynyl substituent, 5- or 6-membered lactones are formed. The 5-membered lactones can be generated with complete stereoselectivity (Scheme 24).

Hashmi et al. published work on the formation of oxazoles *via N*-propargylcarboxamide cyclization.[48] He was able to trap the methylene dihydrooxazole intermediate at lower temperatures. Isolated yields from room temperature examples were typically excellent (>95%) (Scheme 25).

Scheme 25



Scheme 26



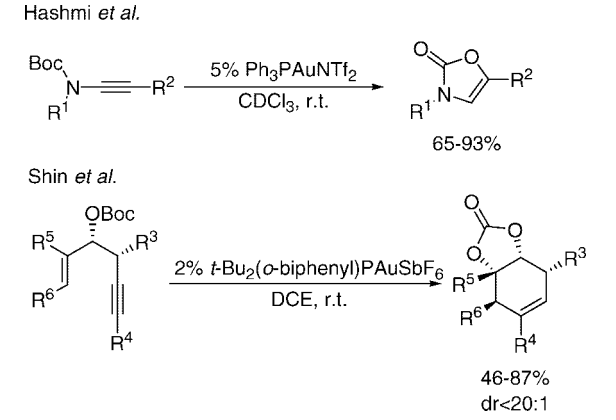
In an effort to differentiate gold from BrØnsted acid as the true catalyst, Gevorgyan employed the HOTf sponge, 2,4,6-tri-*tert*-butylpyrimidine (TTBP), a bulky base known to not coordinate to metals.[49] In a full investigation on propargylic acetate rearrangement/cyclization reactions, his group used a small excess of this base, and found no diminution to reactivity. This control demonstrated the true nature of the catalyst and could be a useful tool for future reports in gold catalysis which does not include a proton transfer process.[17] O-labeling studies on this reaction show conclusively that the carbonyl oxygen attacks first in a 1,2-shift, generating a gold carbenoid, which subsequently undergoes a cascade nucleophilic attack/cycloisomerization. This mechanism differs from one in which a [3,3]-sigmatrophic shift occurs, followed by 1,2-shift, all of which would change the outcome of the labeled oxygen. Similarly, propargylic carbonates give cyclic enol carbonates[50] (Scheme 26).

In the carbonyl addition to alkynes, Hashmi et al. employed Boc-protected alkynylamines to undergo similar cyclizations to produce oxazolinones, although the scope is limited to terminal or silyl-protected alkynes.[51] Shin reported highly diastereoselective cyclizations of 3-*O*-Boc-1,5-enynes.[52] *t*-Bu group serves as a leaving group, and this process leads to highly substituted cyclohexene-fused carbonates (Scheme 27).

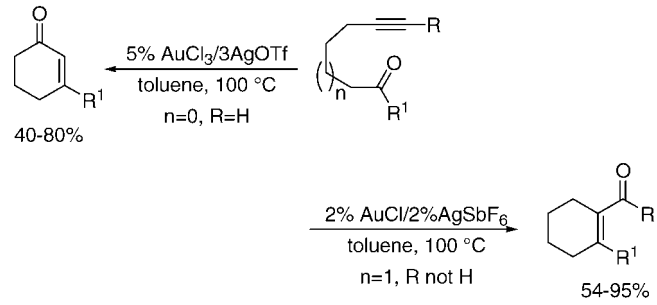
Since it has been established that ketones can add intramolecularly to alkynes, the reactivity of the intermediates generated has recently been under investigation. Yamamoto et al. hypothesized that an appropriate length tether between the alkyne and ketone could position the resultant cyclic oxonium to proceed through a [2 + 2] carbocyclization, yielding cyclic enones.[53] The fate of the carbonyl can be dictated by the use of terminal or internal alkynes, as well as the specific tether length (Scheme 28).

Similarly to carbonyls, epoxides are also nucleophiles for intramolecular alkyne attack. Hashmi et al. showed that the cyclization is induced with $AuCl_3$ in modest to good yields.[54] Free alcohols are tolerated and do not participate in the reaction. Shi et al. found when a three-carbon spacer is added between epoxide and alkyne functionalities, a highly regio- and diastereoselective cyclization of alkynyl epoxides will occur, followed by an intermolecular addition of another

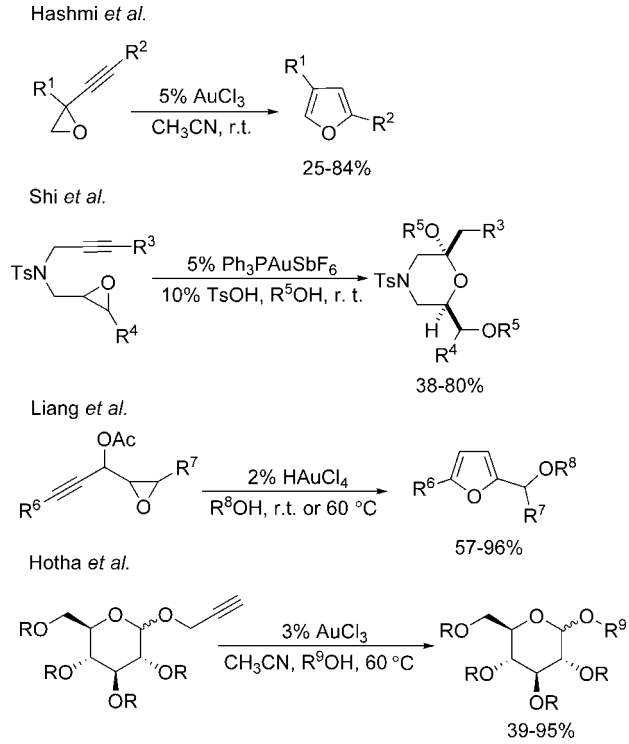
Scheme 27



Scheme 28



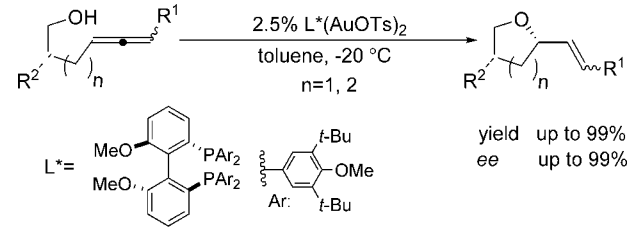
Scheme 29



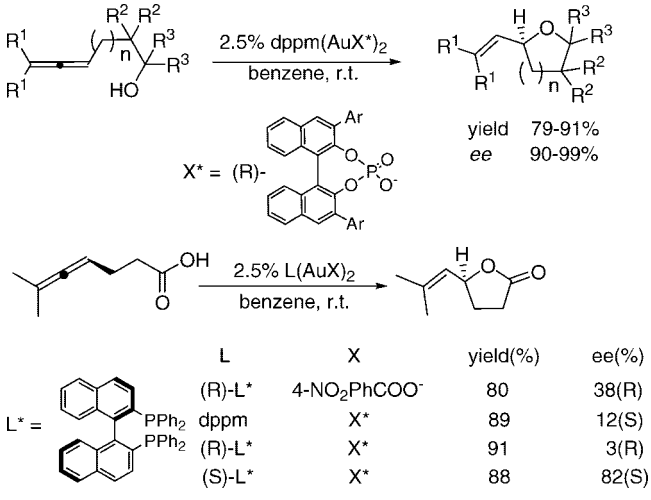
molecule of water or alcohol.[55] Meanwhile, Liang et al. reported a similar intermolecular alcohol addition to alkynyl epoxides, in which a one-carbon spacer with a leaving group was used to facilitate the formation of furan products.[56] Hotha et al. utilized propargyl as a leaving group to make different glycosides[57] (Scheme 29).

Widenhoefer's work on allene hydroaminations also demonstrated that alcohols could undergo the same reaction,[23] and soon thereafter, Krause showed that β-hydroxy-

Scheme 30



Scheme 31



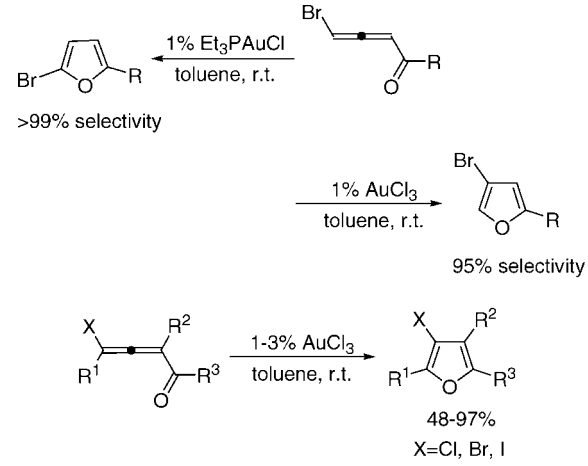
allenes undergo a similar 6-*endo-dig* cyclization to dihydropyrans.[58] When chiral BINAP type ligands were employed, Widenhoefer et al. were able to achieve high *ee*'s at −20 °C to give furan or pyran derivatives.[23] If enantioenriched allenes are used, perfect chirality transfer ensues (Scheme 30).

In their research on the intramolecular enantioselective hydroalkoxylation and hydroamination of allenes, Toste et al. proposed using chiral binaphthol-derived phosphate anions to boost enantioselectivity.[59] Notably, in some cases where neither ligand nor anion induce satisfactory enantioselectivity, they used a combination of both, significantly enhancing the reaction efficiency (Scheme 31).

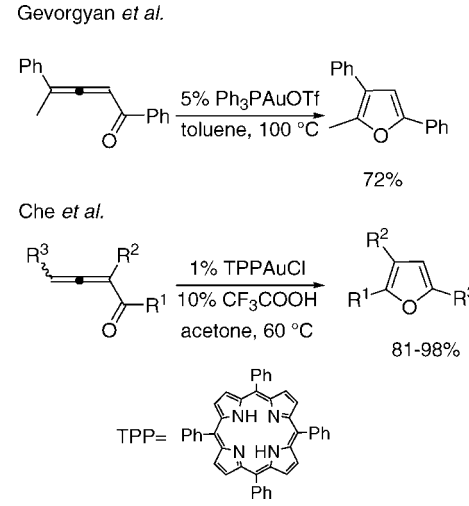
While most groups which work on gold-catalyzed rearrangements employ substrates that undergo proton, or carbon-based functional group, shifts, Gevorgyan's laboratory has shown that other members of the main group elements are prone to these sorts of migrations. Their first report on these processes showed that gold is ideal for mediating halogen shifts in haloallenyl ketone isomerizations.[60] The reaction profile is unique in that it furnishes halofurans regioselectively depending on the oxidation state of the metal. This is an excellent example of the regiodivergent role that gold's oxidation state can play on the reaction outcome. Because of the higher Lewis acidic nature of gold(III), binding to the substrate is thought to occur at oxygen, whereas the softer gold(I) preferentially binds the allene. A halirenium species is implicated as the intermediate. Substrates can contain iodide, bromide, and even chloride to a lesser extent, in yields ranging from 48−97% (Scheme 32).

The same group found if the halogen is replaced with two alkyl groups, an unprecedented 1,2-alkyl shift will take place, but harsher reaction conditions are necessary.[61] While optimization of the catalyst system identified $In(OTf)_3$ as the best catalyst, $Ph_3PAuOTf$ is also suitable. Che et al. reported that allenones react smoothly to give furan derivatives with

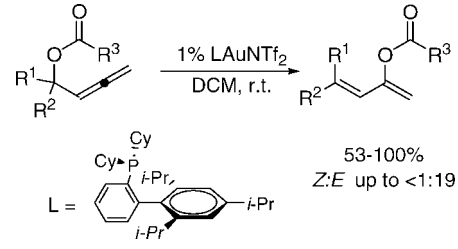
Scheme 32



Scheme 33



Scheme 34

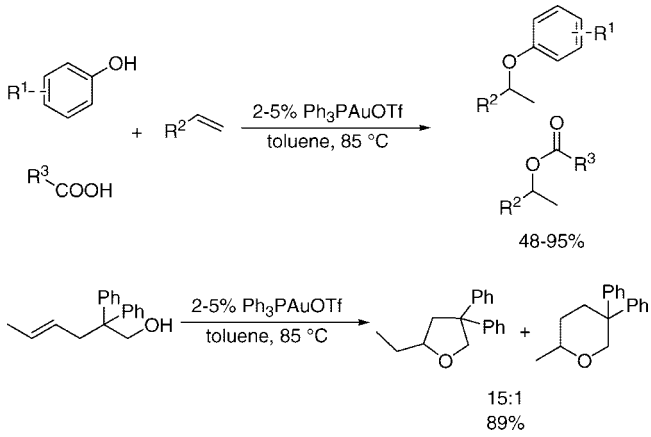


a gold(III) porphyrin complex. This catalyst is recyclable with TON up to 8300[62] (Scheme 33).

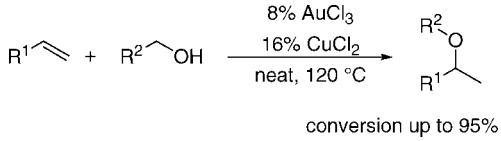
Gagosz's group worked on a similiar system with allenyl carbinol esters.[63] They used a bulky gold(I) catalyst in this system and, instead of cyclization, substrates undergo a 1,3-shift, yielding 1,3-butadien-2-ol esters. The reaction is generally stereoselective, favoring the *E*-isomer, which could possibly be attributed to 1,3-diaxial strain in the intermediate (Scheme 34).

He et al. first reported the intermolecular addition of both phenols and carboxylic acids to simple olefins with $Ph_3PAuOTf$ at 85 °C.[30,64] Some terminal olefins eventually migrate to an internal position to give mixed products, but further migration does not take place. Allylic benzenes, however, do not migrate to more stable styrenes. Different functional groups are tolerated (Scheme 35).

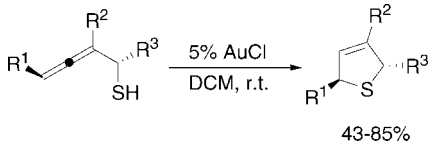
Scheme 35



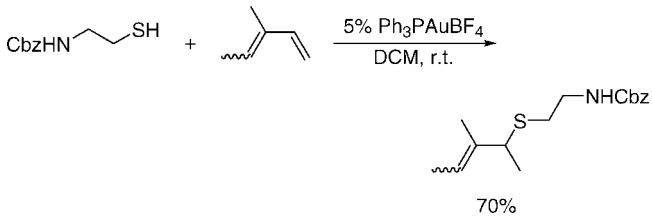
Scheme 36



Scheme 37



Scheme 38



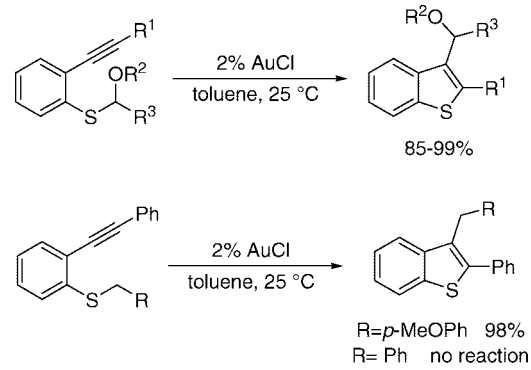
Corma et al. reported a gold(III)-catalyzed intermolecular addition of alcohols to alkenes.[65] Interestingly, a catalytic amount of copper(II) chloride significantly enhances the stability of gold(III) catalyst to increase the yields. Both styrenes and simple aliphatic olefins are reactive. The major side products include chlorination and oxidation of the olefins and dehydration of the alcohols (Scheme 36).

Despite the propensity for thiols to bind to gold, which would be expected to nullify its ability to act as a catalytic candidate, Krause et al. found that an intramolecular hydrothiolation of allenes takes place.[66] This is the first gold-catalyzed C−S bond formation. He posits that the gold−thiol complex should be the preferred species *in situ* with perfect chirality transfer observed. AuI is also efficient in some cases (Scheme 37).

He et al. found Ph_3PAuBF_4 to be a highly active catalyst for the addition of a wide variety of sulfur nucleophiles to conjugated dienes.[67] A number of functional groups are tolerated including OH, NO_2, and OMe. While NH_2 is not tolerated, it can be protected as Cbz to permit addition. Unfortunately, attempts to add simple thiols to simple olefins failed, even at 100 °C (Scheme 38).

Nakumura's group was able to employ Pd, Pt, and Au salts in the cyclization-isomerization of *o*-alkynylanilines as well as *o*-alkynylphenols, given that a suitable migratory group is available (e.g., allyl, acyl, etc.). The corresponding cyclizations for *o*-alkynylthiophenols are not feasible for Pd due to catalyst poisoning. They found that AuCl or $AuCl_3$, however, are ideal for promoting the cyclization, which is the first protocol for directly synthesizing 2,3-disubstituted benzothiophenes.[68] Similar candidate catalysts, such as $AuBr_3$, $PtCl_4$, and AgOTf do not support any reaction. Although the reaction is sensitive to the electronic requirements of the migrating group, it is remarkably tolerant of the sterics of the substrate. The catalyst loading is quite low, conditions mild, and all yields excellent (Scheme 39).

Scheme 39



The same group further studied the cyclization of (*ortho*-alkynylphenylthio)silanes into thiophene derivatives. They believe a vinyl gold species is the reaction intermediate which then subsequently undergoes 1,3-silyl-demetalation. They detected 1:1:1:1 crossover products by reacting two different (*ortho*-alkynylphenylthio)silanes together. *O*, *S*-acetal substrates gave crossover products only in trace amounts[69] (Scheme 40).

2.4. Gold-Catalyzed Nucleophilic Additions Using HX

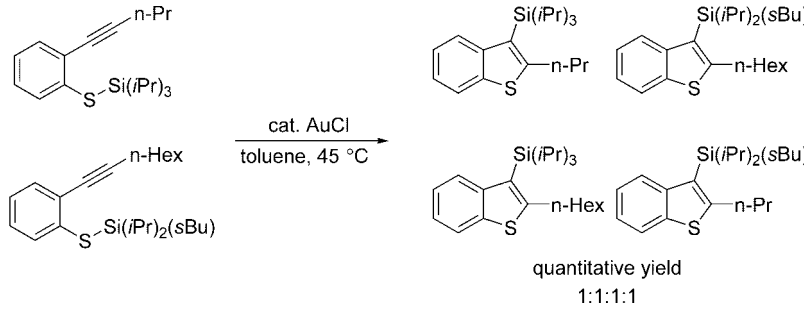
While the first gold-catalyzed hydrochlorination of alkynes was reported as early as 1976, [70] it was not until 2007 that the first hydrofluorination of alkynes appeared.[71] Sadighi et al. found that (NHC)gold(I) fluoride reversibly inserted into internal alkynes, demonstrating the first gold-mediated C−F bond formation. Replacing F^- with the less coordinating BF_4^- enables catalysis with $Et_3N \cdot 3HF$ as a source of HF to give good to very good yields of vinyl fluorides. Additions across the alkyne are always in an *anti* fashion, giving a mixture of regioisomers that depends on the electronic nature of R. It should be noted that $PhNMe_2 \cdot HOTf$ cocatalyst and $KHSO_4$ additive greatly increase yields (Scheme 41).

2.5. Gold-Catalyzed Nucleophilic Additions Using Carbon Nucleophiles

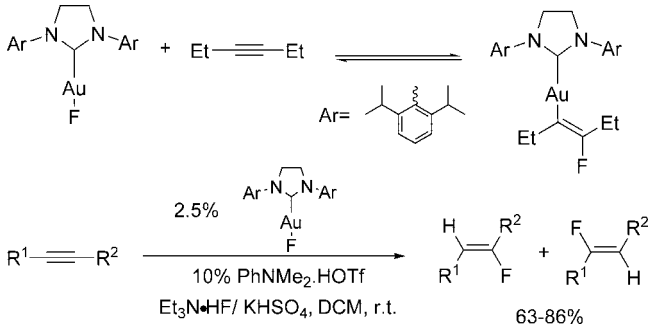
Generally, two types of carbon nucleophiles are commonly utilized in gold catalysis: electron-rich arenes and 1,3-dicarbonyl compounds. We will discuss the utilization of electron-rich arenes in a separate section and only cover 1,3-dicarbonyl nucleophiles in this section. Recently, gold catalysts were shown to efficiently catalyze the addition of 1,3-dicarbonyl compounds to carbon-carbon multiple bonds.

In 2004, Toste et al. reported a gold(I)-catalyzed Conia-ene reaction of β-ketoesters with tethered alkynes to give α-vinylated ketones in excellent yields. They proposed a

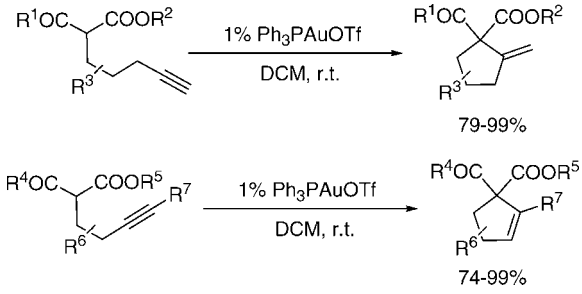
Scheme 40



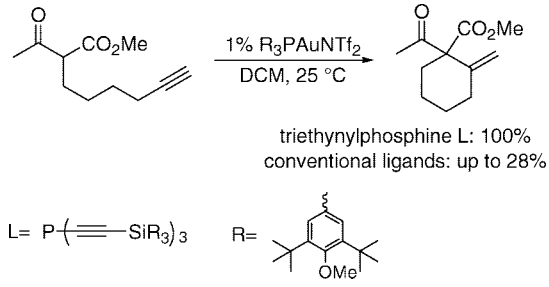
Scheme 41



Scheme 42



Scheme 43



mechanism involving attack of 1,3-dicarbonyl nucleophiles on a Au(I)−alkyne complex, which is supported by deuterium-labeling experiments. No reaction occurs with diesters and poor reactivity is observed with internal alkynes.[72] They also found that if the triple bond is moved one carbon closer, the reaction gives almost exclusive 5-*endo-dig* products in excellent yields under the same conditions[73] (Scheme 42).

Conventional $[AuPPh_3]^+$ did not show much reactivity in the 6-*exo-dig* cyclization of acetylenic keto esters. Sawamura et al. developed a novel triethynylphosphine−gold complex, which shows significantly higher reactivity in the 6-*exo-dig* cyclization of acetylenic keto esters.[74] They believe the bulky caps on the ethynyl ends create a catalytic pocket which is crucial for the reactivity (Scheme 43).

Echavarren et al. also reported that 1, 3-dicarbonyl compounds act as carbon nucleophiles in addition to propargyl carboxylates.[75] They found that Au[P(*t*-Bu)$_2$(*o*-biphenyl)]OTf is the best catalyst, giving enol carboxylates in high yields and chemoselectivity. The mechanism likely involves a gold(I)-carbene or gold(I)-allene (Scheme 44).

Li et al. reported a gold(III)-catalyzed intermolecular addition of 1,3-diketones to olefins.[76] Because of the high Lewis acidity of the $AuCl_3$/3AuOTf catalyst system, dimethyl malonate and β-ketoesters decompose and do not undergo the reaction. There is no detectable diasteroselectivity with the gold(III) system at room temperature. Shortly after, they found by lowering the reaction temperature to 0 °C, dienes, trienes, and cyclic enol ethers also react with diketones to give good yields.[77] Sterically hindered dienes give lower yields (Scheme 45).

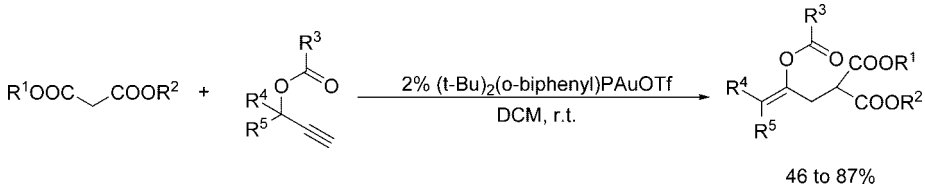
Much success has been achieved in the intramolecular addition of 1,3-dicarbonyls to unactivated olefins with palladium catalysts. However, most reactions go through a 6-*endo-trig* pathway. Che et al. reported that gold(I) is capable to catalyze the 5-*exo-trig* and 6-*exo-trig* cyclization of a variety of β-ketoamides to form 5- or 6-membered cyclic lactams in excellent yields.[36] Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl turned out to be the best catalyst, while gold(I) supported by less bulky phosphine ligands gave lower yields. Diastereoselectivities are as high as 4:1. Not surprisingly, they found β-esteramides and 1,3-diamides could not undergo the same reaction, maybe due to the decreased enol concentration. Notably, the reaction is still efficient in aqueous media. The water leveling effect ruled out the BrØnsted acid possibility and suggests the Lewis acidity of gold is still robust with a carefully chosen ligand and substrates (Scheme 46).

2.6. Gold-Catalyzed Tandem Nucleophilic Additions

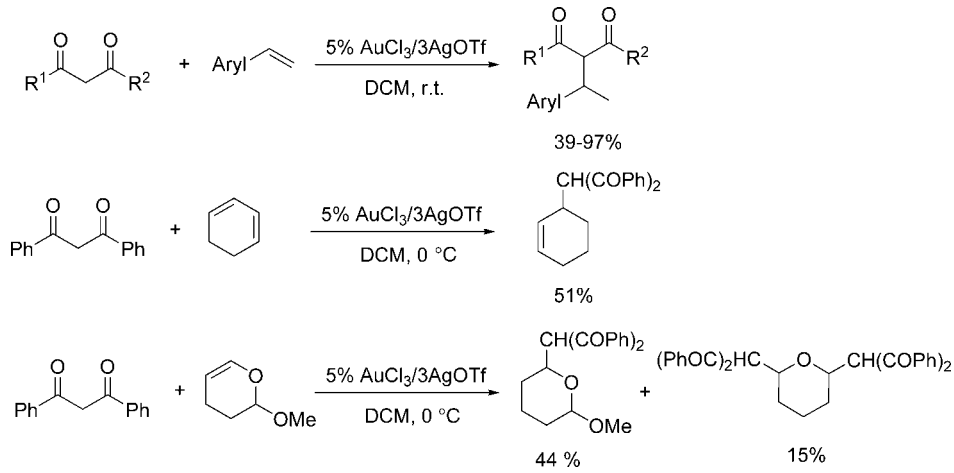
Kozmin et al. reported an efficient and diastereospecific tandem assembly of 1,5-enynes tethered with oxygen or nitrogen nucleophiles to give heterobicyclic systems, via an exclusive 6-*endo-dig* (or 5-*endo-dig*) cyclization.[78] Gold(III) and gold(I) catalysts could both be used for different substrates (Scheme 47).

Michelet and Genêt et al. reported a tandem enyne cyclization/intermolecular addition of nitrogen nucleophiles.[79] When 1,5-enynes undergo gold catalyzed cyclizations, the incipient carbocations generated have the potential to be trapped with nucleophiles. Sulfonamides, carbamates, and anilines are all suitable substrates for this reaction. Similarly, Gagosz et al. carried out a tandem 1,5-*endo*-enyne isomerization/alkoxylation.[80] A range of alcohols are suitable for addition including phenols, carboxylic acids, cyclohexanol, and even water (Scheme 48).

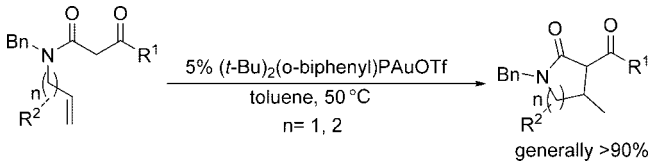
Scheme 44



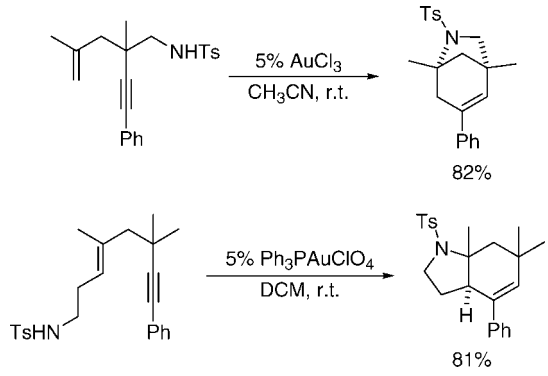
Scheme 45



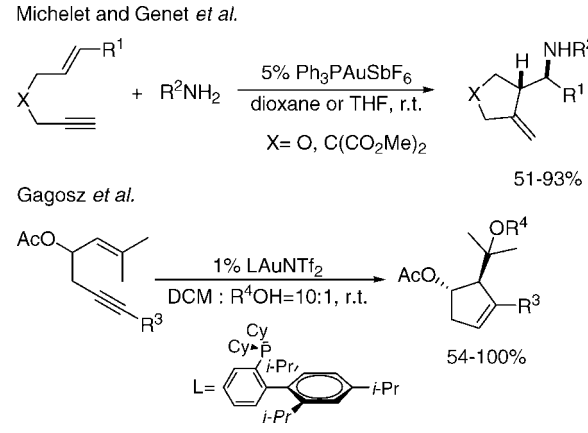
Scheme 46



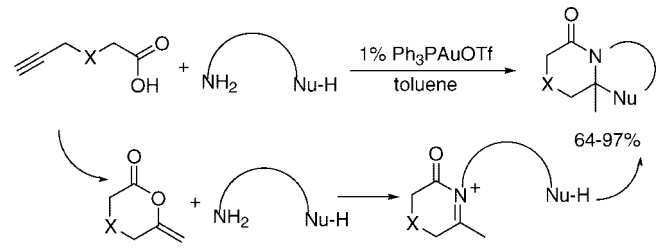
Scheme 47



Scheme 48



Scheme 49

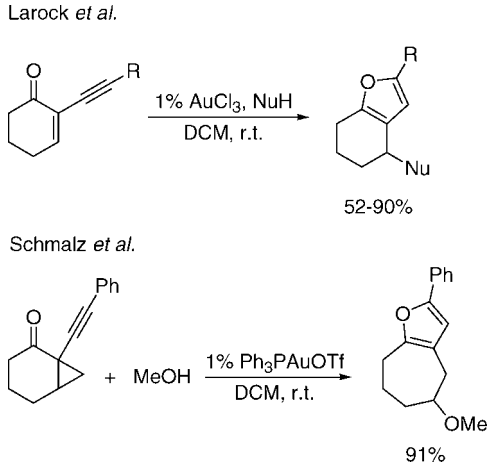


Dixon et al. reported an interesting gold(I)-catalyzed cascade of alkynoic acids and primary amines.[81] Multiring heterocyclic products are produced in good yields. They believe that the alkynoic acids will form enol lactone intermediates, which subsequently react with primary amines to form *N*-acyl iminium intermediates. The tethered electron-rich heterocycles then attack the iminium to yield multiring heterocyclic products. Terminal and internal alkynes are suitable for additions. To probe the nature of the active catalyst for the final two steps in the sequence, control experiments using a phosphorine base (BEMP) and/or HOTf confirmed that indeed a Lewis acid assisted BrØnsted acid is responsible for this part of the reaction (Scheme 49).

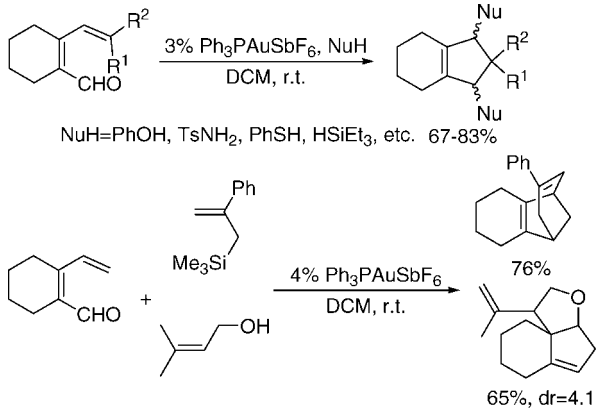
Larock et al. used conjugated alkynyl enones as substrates that undergo tandem intramolecular carbonyl addition/intermolecular nucleophilic attack to generate highly substituted furans.[82] Notably, a variety of different nucleophiles add successfully, including alcohols, β-diketones, indoles, and even arenes. Schmalz et al. later showed that substituting the olefin with cyclopropane leads to ring-expansion products.[83] Yields are quite good with a range of alcohols and some heterocycles acting as nucleophiles (Scheme 50).

Liu et al. demonstrated that two equivalents of nucleophile also add to dienals with concomitant loss of oxygenated byproducts.[84] Depending on the specific nucleophiles used, the regiochemistry of the product differs, with 1,4- and 1,2-additions acting as competing pathways. Substrates with

Scheme 50



Scheme 51



more than one nucleophilic center add twice to form more complex structures (Scheme 51).

In their study of the intramolecular hydroalkoxylation of alkynes, Hashmi et al. found interesting dimerization products which are produced through a gold-catalyzed benzylic C−H activation pathway.[85] From isotope labeling experiments, they found the ketone oxygen comes from the alcohol, which supports the ketone oxidation and benzylic C−H mechanism. His report agrees with He's simultaneous finding on benzylic C−H activation (Scheme 52).

3. Gold-Catalyzed Friedel−Crafts Reactions and C−H Activations

3.1. Friedel−Crafts Reactions via Arylgold

Gold(III) has been known for more than 70 years to activate aryl C−H groups to form aryl−gold(III) complexes.[86] This is achieved by simply mixing gold(III) chloride with benzene in hexanes. Aryl hydrazines are also oxidized by $(NBu_4)AuCl_4$ or $(NBu_4)AuBr_4$ into their corresponding aryl−gold(III) complexes.[87] After several quiet decades, utilizations of aryl−gold(III) species in organic transformations began to appear. Since Hashmi's first report in 2000,[88] gold-catalyzed hydroarylations have been explored with various substrates by several research groups. Because of the strong Lewis acidity of gold(III), it is difficult to ascertain the reaction mechanism that involves a C−H functionalization to form an aryl−gold(III) species versus a Friedel−Crafts-type reaction catalyzed by a gold Lewis acid.

Hashmi et al. first reported that 2-methylfuran efficiently adds to methyl vinyl ketones using $AuCl_3$ in CH_3CN.[88] They also discovered that if an alkyne group is tethered with the methyl vinyl ketone, a tandem reaction takes place to afford phenol products. In this process, five new bonds form in a domino process.[89] He et al. studied the reaction of heterocycles and electron-rich arenes with electron-deficient olefins or alkynes.[90] It was found that, when electron-deficient alkynes and heterocycles were used as substrates, dual-addition products of heterocycles to alkynes were the only product, which suggests electron-deficient olefins to be more reactive than corresponding alkynes in this reaction (Scheme 53).

Hashmi et al. also detected similar reactivity between 2-methylfuran and unactivated alkynes with 2.5% $[(Mes_3PAu)_2Cl]BF_4$ (Schmidbaur-Bayler salt).[91] Reports of direct hydroarylation of simple olefins by gold are rare. Liu et al. found that gold(III) can catalyze addition of protected indoles to vinyl arenes and trisubstituted olefins using the DNA-encoding and DNA-programed assembly of substrate pairs.[92] Most reactions could also be catalyzed by a catalytic amount of strong BrØnsted acids (Scheme 54).

Li et al. reported that a gold(III) catalyst system catalyzes an efficient annulation of phenols and dienes to give various benzofuran products.[93] Cationic $Ph_3PAuOTf$ shows no product formation, perhaps due to degradation of dienes by cationic gold(I). He et al. reported a similar process to form benzofurans through a $Ph_3PAuOTf$-catalyzed Claisen rearrangement of aryl allyl ethers. This is followed by a tandem phenol addition.[94] If 2,6-substituted aryl allyl ethers are used, a further [3, 3] rearrangement occurs to give the *para*-substituted product. Gold(III) is also capable of catalyzing this reaction with a lower efficiency. As shown by control reactions, gold(III) works better for mediating the Claisen rearrangement, while gold(I) is more efficient at catalyzing the phenol addition step (Scheme 55).

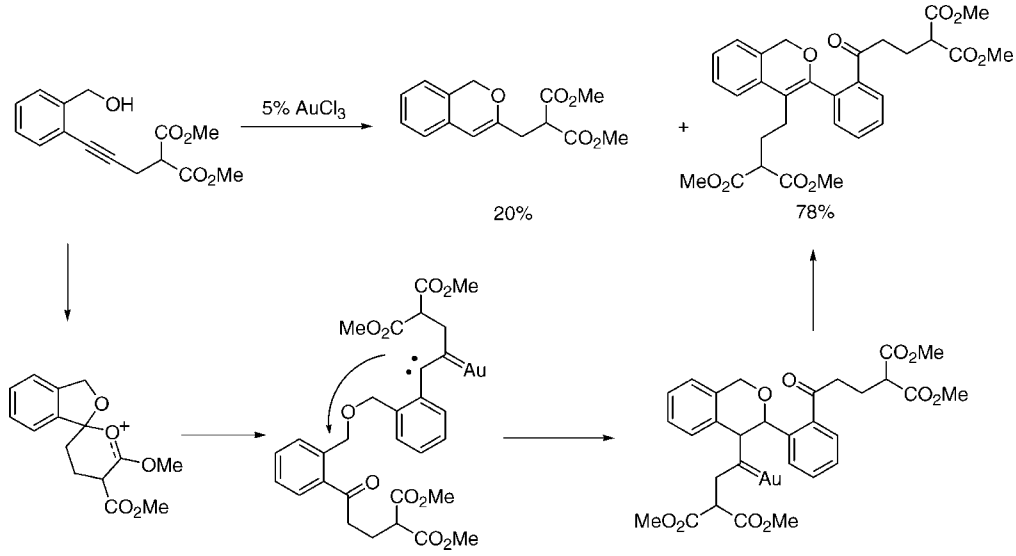
Arcadi et al. reported another tandem reaction using 2-alkynyl-phenylamines with α,β-enones that affords substituted indoles with a catalytic amount of $NaAuCl_4$ in ethanol.[95] When an ionic liquid is used as the solvent, similar results are obtained (Scheme 56).

In 2003 and 2004, Reetz and He reported a gold(III)-catalyzed hydroarylation of normal alkynes and electron-deficient alkynes, respectively.[96,97] In the latter case, this reaction was extended into an intramolecular version to give coumarin derivatives as products. It is noteworthy that the hydroarylation of electron-deficient alkynes is not catalyzed by strong BrØnsted acids (Scheme 57).

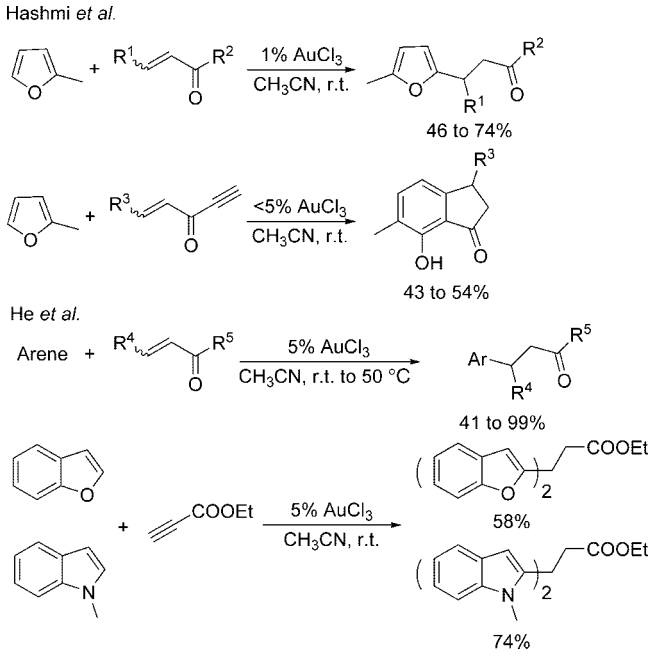
Shortly after, Echavarren et al. reported an interesting intramolecular reaction of indoles with tethered alkynes.[98] Gold(I) and gold(III) show 7-*exo-dig* and 8-*endo-dig* chemoselectivity to give 7- or 8-membered cyclic products, respectively. Bulkier $[P(t\text{-}Bu)_2(o\text{-biphenyl})]AuCl$ gives higher *exo* selectivity when compared to simple Ph_3PAuCl. In some cases, allenes are the major products and react further to afford tetracyclic products with the gold(I) catalyst[99] (Scheme 58).

Nolan et al. reported an intramolecular hydroarylation of propargylic acetates catalyzed by an NHC-gold(I) catalyst.[100] Propargylic acetates undergo a rearrangement into allenes with tandem hydroarylation to furnish substituted indenes. Notably, this reaction requires strictly anhydrous conditions; if water is present, the same substrates give conjugated enone

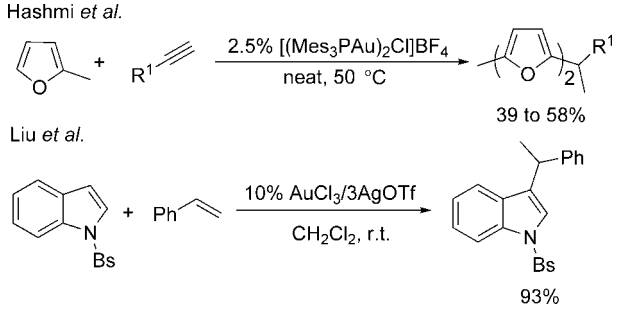
Scheme 52



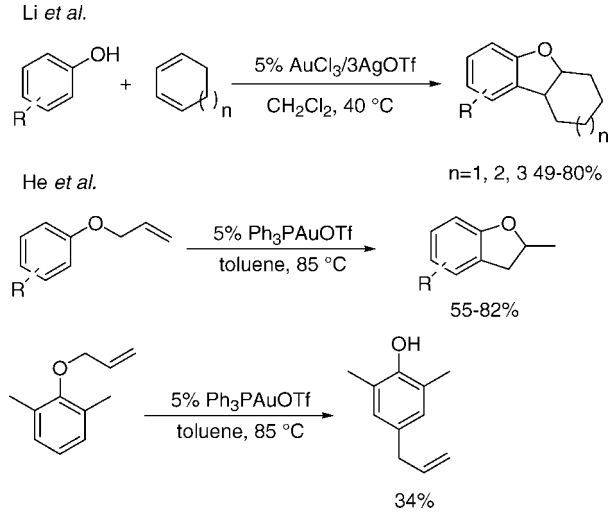
Scheme 53



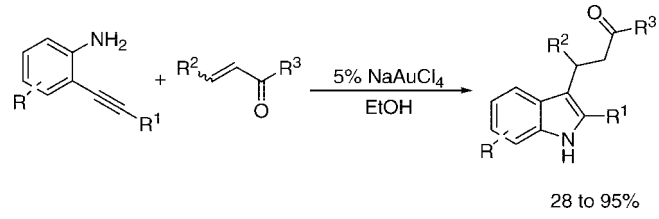
Scheme 54



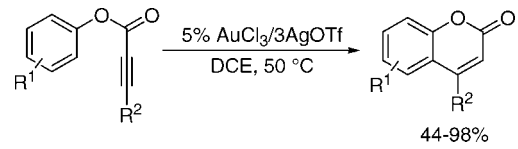
Scheme 55



Scheme 56



Scheme 57

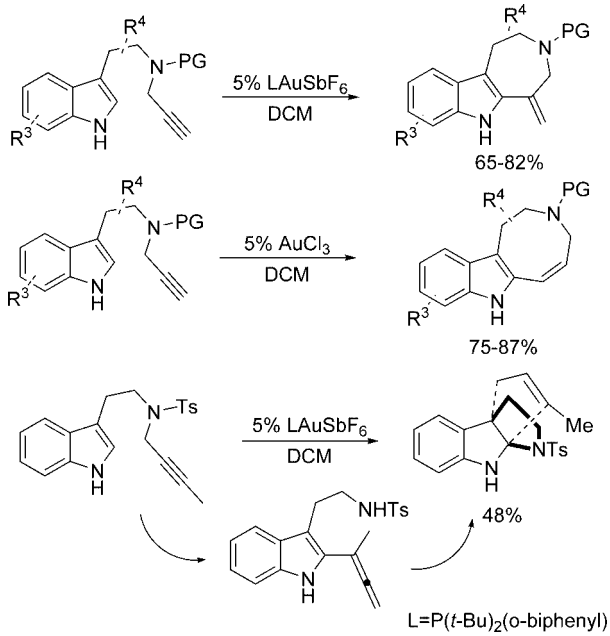


and enal products.[101] Higher temperatures or microwave assistance are required in the latter case (Scheme 59).

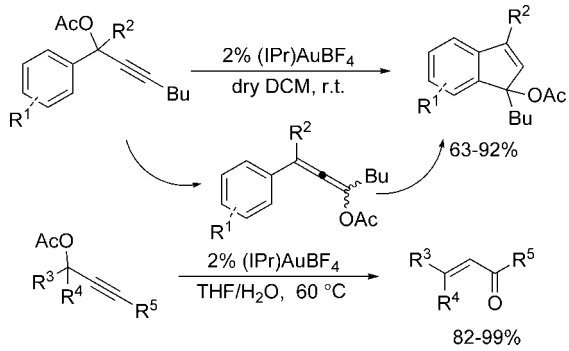
Wang et al. reported that propargylic sulfides and dithioacetals rearrange to give indenes as shown by Nolan et al.[100,102] A 1,3-nucleophilic attack of the thioether to the alkyne may be the first step to generate a putative gold-carbenoid intermediate (Scheme 60).

Toste et al. reported a synthesis of benzonorcaradienes catalyzed by gold(I) using a tandem cyclopropanation/hydroarylation strategy.[103] When styrenes and propargyl ester-containing diynes are the substrates, formation of three carbon−carbon bonds and two rings (3- and 6-membered) is achieved in one step. A supporting phosphine ligand is necessary; simple gold(I) and gold(III) chloride could only achieve the cyclopropanation step (Scheme 61).

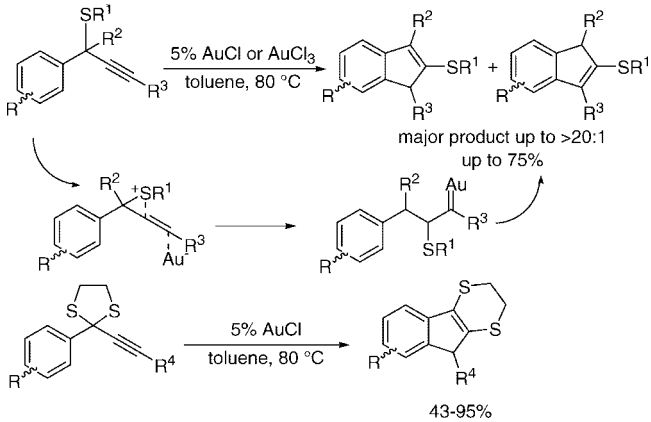
Scheme 58



Scheme 59



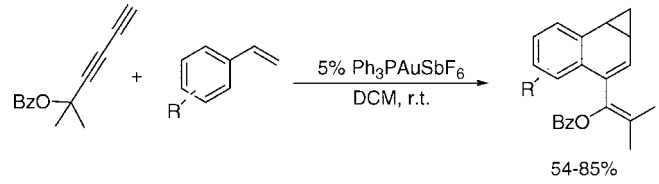
Scheme 60



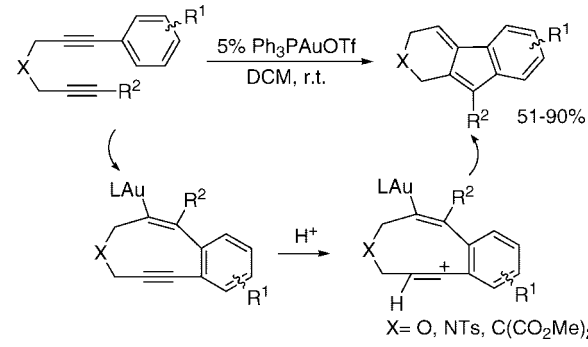
Liu et al. discovered a gold-catalyzed intramolecular cycloaddition of diynes with tethered arenes.[104] On the basis of deuterium-labeling, they believe the first reaction step is the intramolecular arylation of one alkyne to form vinylgold(I), which then undergoes either a 5-*exo-dig* addition or Nazazov cyclization to give the final product (Scheme 62).

A gold(I)-catalyzed tandem Friedel−Crafts addition/carbocyclization between enynes and electron-rich arenes was reported by Genêt and Michelet.[105] They believe the enyne cyclization occurs first to give a transient carbenic intermediate which is subsequently attacked by the electron-rich arene. A similar system was also reported almost simultaneously by Echavarren[106] (Scheme 63).

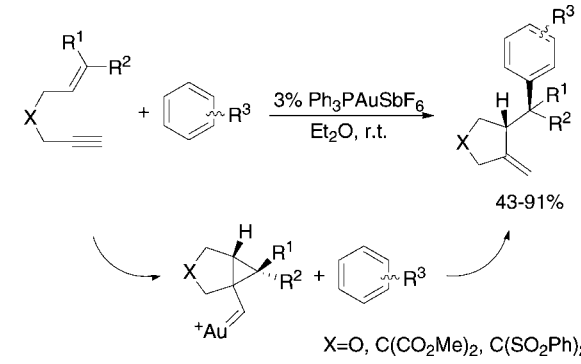
Scheme 61



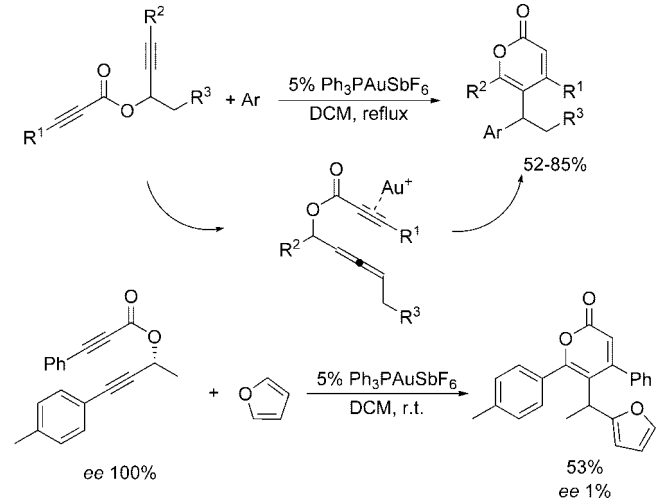
Scheme 62



Scheme 63

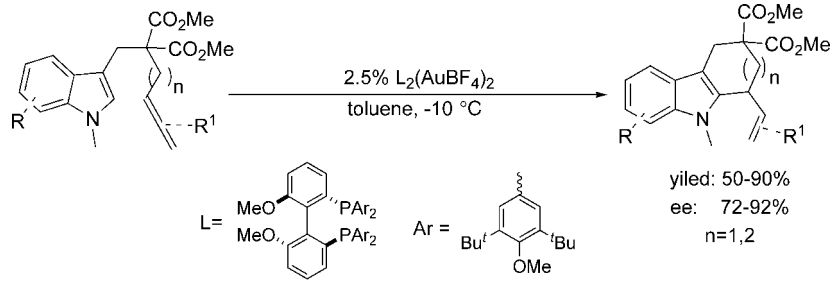


Scheme 64

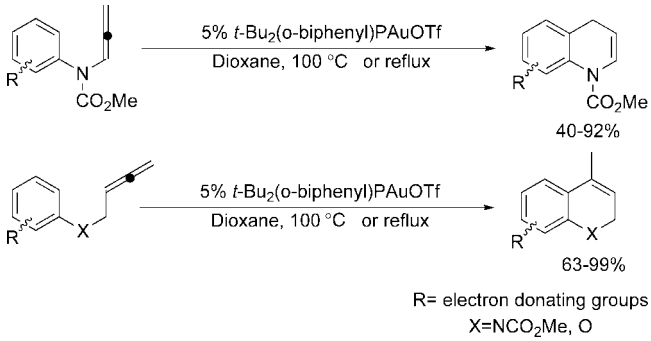


Very recently, Schreiber et al. reported the synthesis of α-pyrones from diynes and electron-rich arenes catalyzed by a gold(I) species.[107] The first step is proposed to be the rearrangement of the alkyne to an allene, which is supported by racemization of enantio-enriched substrates (Scheme 64)

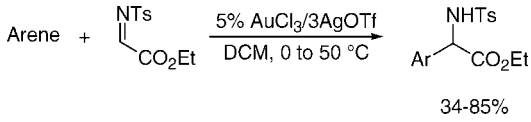
Scheme 65



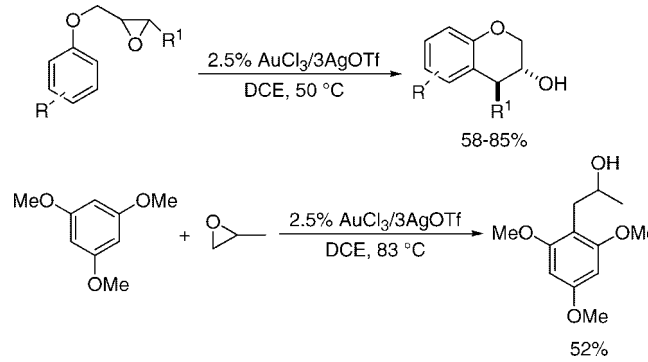
Scheme 66



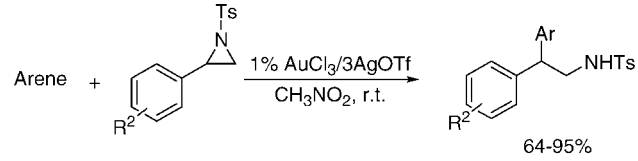
Scheme 67



Scheme 68



Scheme 69



Allenes have also been broadly utilized as hydroarylation substrates. Widenhoefer et al. reported an efficient intramolecular indole addition to tethered allenes.[24] Notably, if the axially chiral 2-allenylindole is used, almost exclusive *E*-alkene forms as the product. With one substitution at the C(2) position of the 4,5-hexadienyl chain, a 5:1 *cis*−*trans* diastereoselectivity is obtained. The asymmetric version of this reaction was also developed by the same group using a chiral bisphosphine ligand.[108] The same ligand was used in the asymmetric hydroalkoxylation/hydroamination reaction (Scheme 65).

In addition to indoles, Fujii, Ohno, and co-workers reported a gold(I)-catalyzed intramolecular addition of simple arenes to tethered allenes to produce quinolines and benzofurans. Electron-donating substitutions on the arene are required for the reaction which preferentially produces 6-membered rings[109] (Scheme 66).

In addition to hydroarylation of carbon−carbon multiple bonds, addition of arenes to C═O and C═N bonds are also interesting reactions. Direct hydroarylation of aldehydes or ketones are rare because the resulting alcohols react with another molecule of arene to give the condensation product.[110] Li et al. first reported the gold(III)-catalyzed direct addition of electron-rich arenes to imines.[111] They found that only electron-rich arenes (i.e., 1,3,5-trimethoxybenzene) react with unactivated imines (e.g., PhC═NTs). If the activated imine TsNH═CHCO$_2$Et is used, a much broader arene scope could be employed. Simple arenes, such as benzene and toluene, undergo the reaction smoothly to give products in 34−85% yields (Scheme 67).

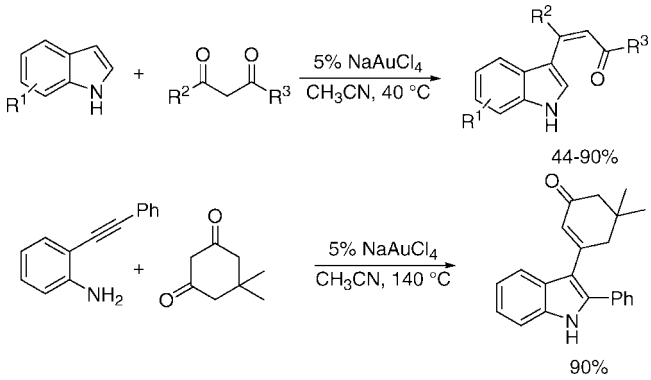
In 2004, He et al. reported an inter- and intramolecular hydroarylation of epoxides with AuCl$_3$/3AgOTf.[112] The intramolecular reaction is stereospecific. More importantly, an intermolecular reaction of 1,3,5-trimethoxybenzene with propylene oxide affords the addition only at the less hindered terminal carbon. This is in contrast to the well-known Lewis acid/BrØnsted acid catalyzed Friedel−Crafts reaction which forms C−C bonds at the more substituted carbon. The reaction most likely goes through an S_N2 mechanism, which involves an aryl−gold(III) species (Scheme 68).

Wu et al. reported an efficient addition of arenes to tosyl-protected aziridines.[113] This reaction may go through a Friedel−Crafts-type pathway as the arene attacks the more reactive benzylic carbon. Aliphatic aziridines fail to react (Scheme 69).

Arcadi et al. found that gold(III) can catalyze coupling reactions between N-containing heterocycles and 1,3-dicarbonyl compounds.[114] The enol form of the 1,3-dicarbonyl compounds seems to react with the heterocycles. A tandem process was also developed by using 2-alkynylphenylamines, which gives indoles with NaAuCl$_4$ (Scheme 70).

A gold(III)-catalyzed alkylation reaction of arenes using primary alcohol sulfonate esters was reported by He in 2004.[115] If a Friedel−Crafts mechanism is involved, one would expect secondary alkylation products due to a carbocation rearrangement. However, when pentamethylbenzene is used, almost exclusive primary alkylation product is observed, which suggests the formation of an aryl−gold(III) intermediate in a S_N2-type mechanism. When benzene is used, 90% of the product mixture is secondary alkylation product. The use of mesitylene decreases the secondary product to ∼50%. When 1,2,4,5-tetramethylbenzene is used, less than 5% secondary alkylation product is detected. With

Scheme 70



pentamethylbenzene and a primary alcohol sulfonate ester next to a secondary benzylic carbon, exclusive primary alkylation product is obtained. The chemoselectivity increases with methyl substitution, or with the increase of electron density on the ring. However, more electron-rich heterocycles could not undergo the same reaction; based on our knowledge, a heterocycle−gold(III) complex has yet to be reported in the literature (Scheme 71).

We propose that gold-catalyzed hydroarylation could go through either a Friedel−Crafts-type mechanism or an aryl−gold(III) intermediate. Heteroatoms in heterocycles are good ligands for gold(III), which prevents the formation of aryl−gold(III). Thus, reactions involving most heterocycles may go through a gold(III)-catalyzed Friedel−Crafts mechanism. When hydrocarbon arenes are employed, the reactivity of aryl−gold(III) species increases with the increased electron density of the ring. The Friedel−Crafts pathway may dominate with less electron-rich arenes, while the aryl−gold(III) pathway dominates with electron-rich arenes.

3.2. Activation of *sp*-C−H by Gold

Gold is known to react with alkynes in two different ways. It acts as a Lewis acid, which is the common case for internal alkynes. With terminal alkynes, gold can substitute the terminal position and form a gold-acetylide. Gold-acetylide species are believed to be stable and were not commonly utilized in organic synthesis until recently.

Li et al. first utilized an *in situ* formed gold-acetylide as an intermediate to react with different aldehydes, alkynes, and amines to afford propargyl amines with good yields in water.[116] Only a catalytic amount of gold is necessary and the reaction can also be catalyzed by copper and silver, both of which are well-known to form metal-acetylides.[117] Gold nanoparticles and layered double hydroxide-supported gold (LDH-$AuCl_4$) are also capable of catalyzing this reaction.[118] Che et al. further developed this reaction by using salen ligands on gold(III), which helps to lower the reaction temperature to 40 °C.[119] One additional benefit of the low reaction temperature is that cyclic chiral amines can be used as asymmetric auxiliaries. Good to excellent diastereoselectivities are achieved with bulkier auxiliaries on the amine. Shortly after, Liu et al. reported that, if pyridine-2-carboxaldehyde is used instead of a simple aldehyde, the pyridine lone pair attacks the neighboring alkyne intramolecularly to give functionalized indolizines *via* the proparygyl amine intermediates[120] (Scheme 72).

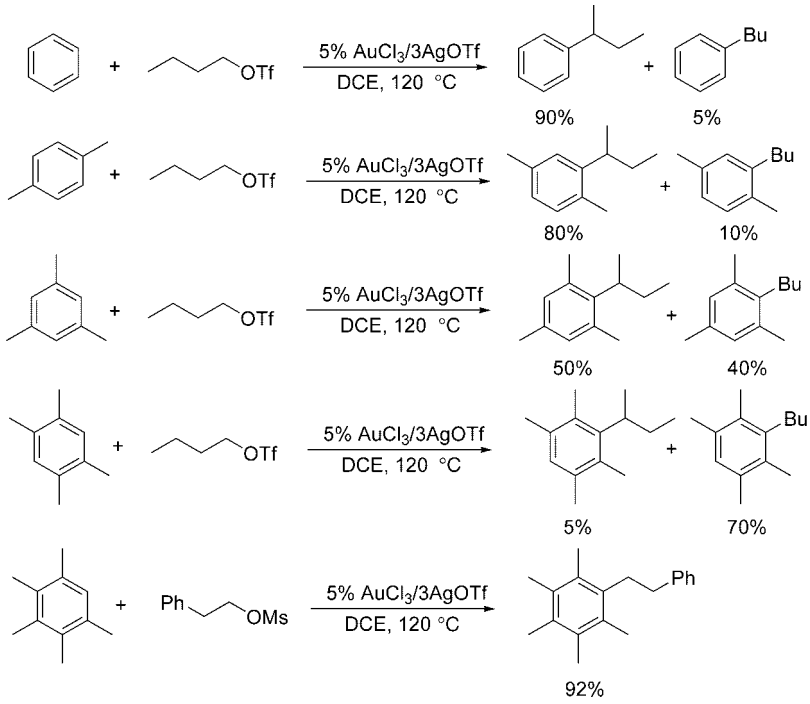
Cyclic (alkyl)(amino)carbenes (CAAC) are a new family of NHC ligands with one nitrogen in the traditional NHC ligand replaced with a carbon, which makes the ligand more electron-donating.[121] Bertrand et al. recently showed that a CAAC-supported gold(I) complex can catalyze the coupling between enamines and terminal alkynes to produce allenes in good yields.[122] They proposed that gold-acetylide species form together with 1 equiv of ammonium salt only when the enamines were added. The reaction then goes through a gold-carbene pathway as shown in Scheme 73.

Although gold-acetylide species are broadly utilized to prepare propargyl amines, there is no report on gold-catalyzed propargyl alcohol synthesis to our knowledge. Gold is relatively oxophilic and may irreversibly bind the propargyl alcohol, arresting the catalytic cycle. Li et al. reported that, by tethering an alkynyl group to the ortho position of an aryl aldehyde, the propargyl alcohol−gold complex is shown to undergo an intramolecular nucleophilic addition to give 1-alkynyl-1*H*-isochromenes.[123] Not surprisingly, simple aryl aldehydes do not succeed in this reaction. The chelation effect of the neighboring alkynyl group was proven to be crucial and the proposed intermediate is similar to the one Yamamoto and Asao proposed earlier.[124] The same group found that, if salicylaldehyde is used, the reaction goes through a completely different pathway to afford isoflavanones.[125] The chemoselectivity of the reaction is intriguing and the authors proposed that the carbonyl proton is activated by gold(I), which subsequently adds to the alkyne. A similar reaction with *o*-tosylaminobenzaldehyde gives azaflavanones in lower yields and only aromatic alkynes work in the reaction[126] (Scheme 74).

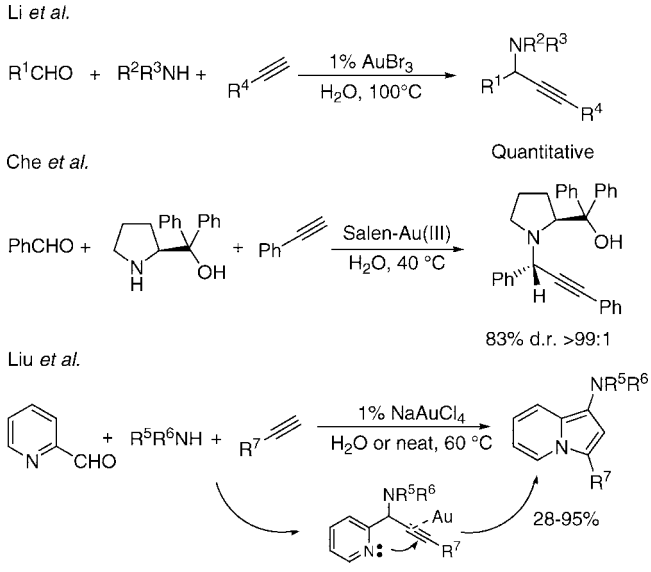
Recently, Che et al. discovered a gold(I)-catalyzed synthesis of dihydroquinoline and quinoline from aromatic amines and terminal alkynes.[127] Microwave irradiation facilitates the reaction in some cases. They proposed a mechanism in which a gold-catalyzed hydroamination of the alkyne gives an enamine intermediate, which tautomerizes to a ketimine. The ketimine intermediate then reacts with another molecule of alkyne to yield a propargylic amine, which then undergoes an intramolecular hydroarylation to yield the final dihydroquinoline product. Both primary and secondary aromatic amines give good yields in this reaction (Scheme 75).

Gold-mediated coupling reactions have also been studied. Fuchita et al. reported a Sonogashira type coupling reaction with terminal alkynes by using a stoichiometric amount of arylgold−lutidine complexes.[128] Corma et al. recently found that gold nanoparticles supported on CeO_2 are reusable catalysts for the Sonogashira coupling between terminal alkynes and iodobenzenes; however, homocoupling products from alkynes and iodobenzenes were also detected.[129] On the basis of X-ray photoelectron spectroscopy, gold nanoparticles supported on CeO_2 contain gold(0), gold(I), and gold(III) species. Gold(0), gold(I), and gold(III) complexes were prepared and tested with parallel control experiments with palladium catalysts. The results revealed that (a) gold(0) is not catalytically active; (b) gold(III) is responsible for the homocoupling products; (c) gold(I) shows good reactivity and selectivity for the Sonogashira reaction. The selectivity of the reaction is similar to the parallel controls conducted with palladium. Similarly, gold also catalyzes Suzuki-type coupling reactions; however, the reaction conditions and substrate scope need further improvements to be useful.[130]

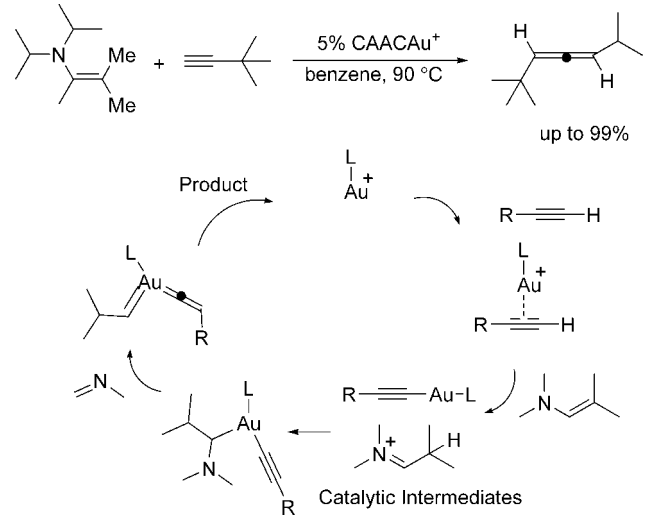
Scheme 71



Scheme 72



Scheme 73



4. Gold-Catalyzed Hydrogenations and Oxidations

4.1. Gold-Catalyzed Hydrogenations and Dehydrogenations

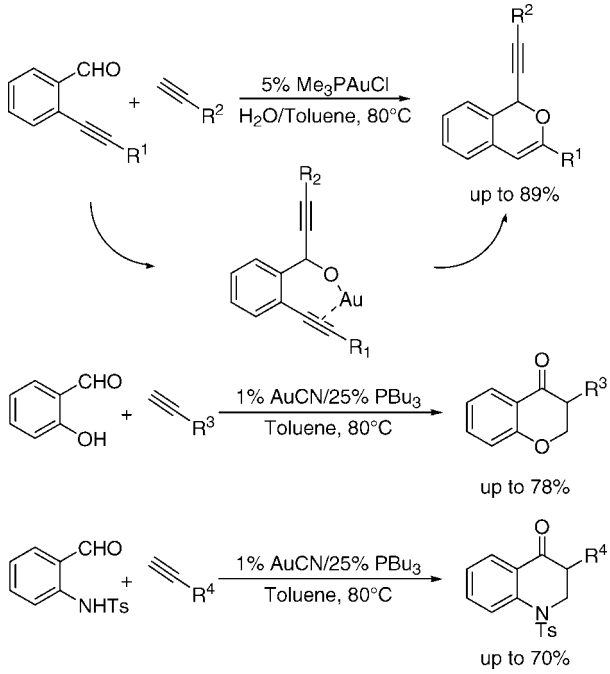
Hydrogenation of different organic substrates has been reported with various forms of gold for many decades.[1] Molecular hydrogen can be activated by various soluble gold species and gold surface.[131] In 2005, Xu et al. reported that isolated Au^{3+} ion could mediate the selective hydrogenation of 1,3-butadiene with a Au^{3+}/ZrO_2 catalyst.[132] A similar homogeneous hydrogenation system was also reported with gold(III).[133]

Gold selectively hydrogenates α,β-unsaturated carbonyl substrates into unsaturated alcohols, which then undergo isomerization and further hydrogenation into saturated alcohols.[134,135] Different metal oxide supports significantly impact both reactivity and selectivity. Milones et al. found that the nature of the iron oxide support influences the reaction more than the morphology of gold particles.[135] Electron transfer from the reduced support to produce negatively charged gold particles may help in generating the active reaction sites.

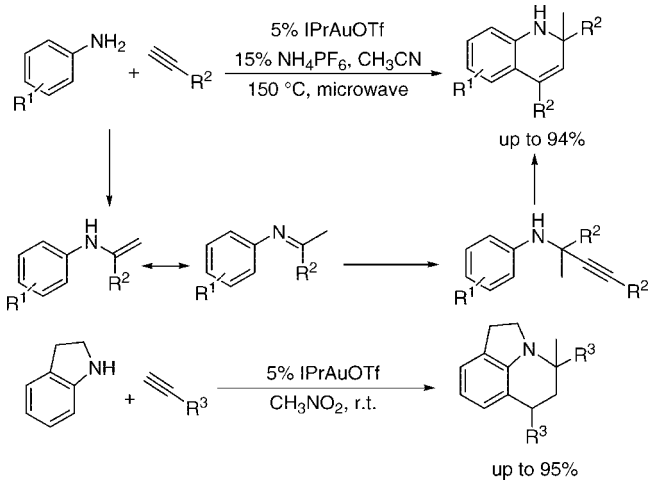
In 2006, Corma et al. discovered that metal-oxide supported gold could efficiently mediate selective hydrogenation of nitro complexes into their corresponding amino products.[136] The predominant selectivity toward hydrogenation of nitro groups (generally >90%) makes it a very valuable method to produce substituted anilines. Shortly thereafter, Corma et al. reported a further application of the supported gold catalyst to selectively hydrogenate α,β-unsaturated nitrocomplexes into corresponding oximes. Importantly, the catalyst remains highly selective even with another nitro group present in the substrate[137] (Scheme 76).

Homogenous hydrogenation catalyzed by ligand-supported gold was less explored than its heterogeneous counterpart.

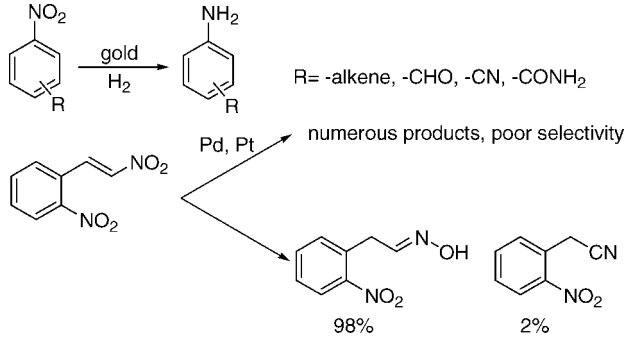
Scheme 74



Scheme 75

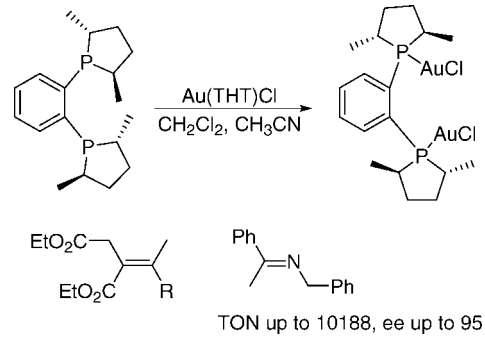


Scheme 76

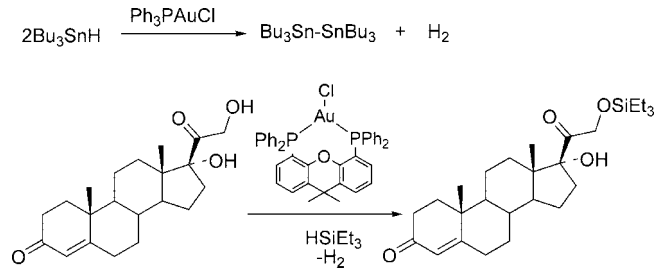


Corma et al. studied Schiff-base gold complexes (both homogeneous and heterogeneous) in hydrogenation reactions.[138] They showed that the nature of the solvent plays an important role in the homogeneous cleavage of H_2. The same group also reported the only currently known enantioselective hydrogenation, catalyzed by a gold−methyl-Duphos complex (Scheme 77).

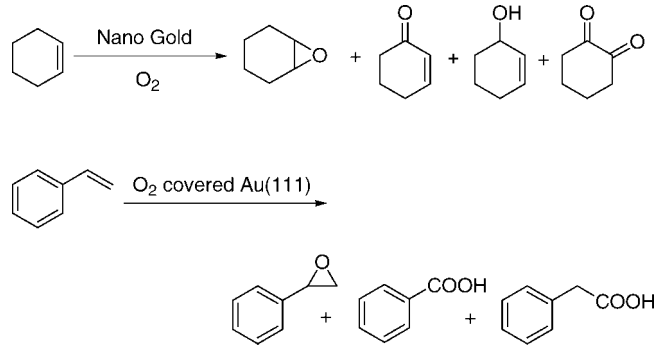
Scheme 77



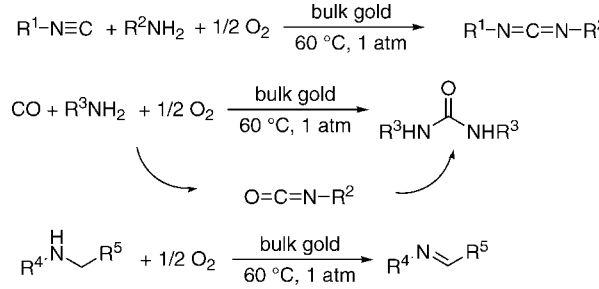
Scheme 78



Scheme 79

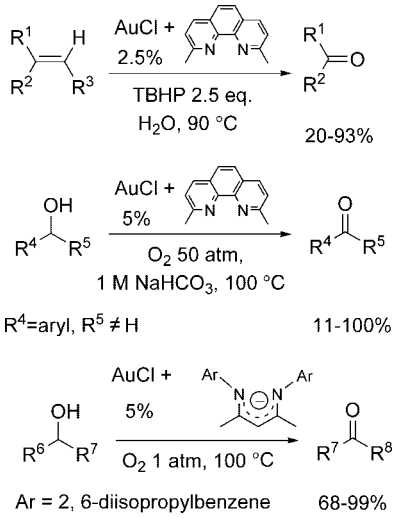


Scheme 80

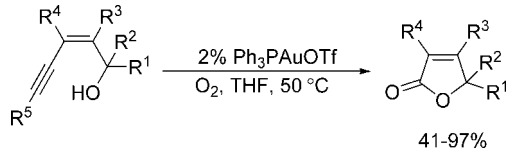


Metallic gold films mediate dehydrogenation of alkanes and alkenes at elevated temperatures.[139] In 1999, Hosomi et al. reported an interesting gold(I)-catalyzed dehydrogenative homocoupling of tributyltin hydride into hexabutyldistannane in very high yields. They noticed a color change in solution and release of hydrogen gas.[140] In 2003, Arcadi et al. reported a gold(III)-catalyzed pyridine synthesis.[141] Dehydrogenation is the last step; however, another equivalent of propargyl amine is required to absorb the released hydrogen. Ito and Sawamura reported the dehydrogenation of alcohols and silanes catalyzed by a gold(I)−xantphos complex.[142] Different functional groups are well-tolerated in this transformation. A gold-hydride mechanism cannot be confirmed (Scheme 78).

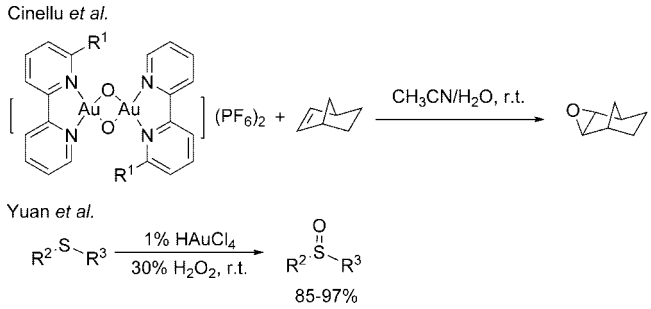
Scheme 81



Scheme 82



Scheme 83



4.2. Gold-Catalyzed Oxidations

Both heterogeneous and homogeneous gold-catalyzed oxidation chemistry have been explored recently and we will only briefly cover heterogeneous oxidations and focus more on the homogeneous gold catalysis.[1]

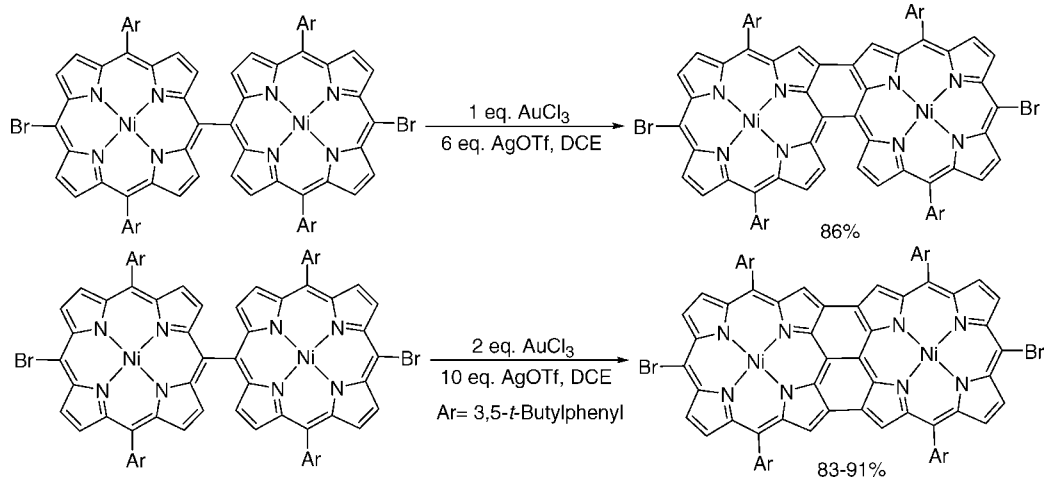
In 2005, Hutchings et al. reported an oxidation of alkenes with air over nanogold catalysts[143] (Scheme 79). Different oxidation products such as epoxides, ketones, and alcohols were detected. Meanwhile, Friend et al. reported a selective oxidation of styrene on an oxygen covered Au(111) surface to yield styrene epoxide, benzene acetic acid and benzoic acid with less than 20% complete combustion products.[144] Selective oxidation of alcohols into carbonylic compounds has been studied by Hutchings, Corma, Christensen, and others.[145]

In 2006, Friend et al. reported a method of adding NH_3 to styrene to yield aziridines.[146] Evidence shows that NH_3 reacts with the O_2-adsorbed Au(111) to give a reactive NH_x (x = 1, 2) species, which may be responsible for the reaction. Corma et al. also reported a gold-nanoparticle catalyzed homocoupling reaction of boronic acids.[147] They also demonstrated that homogeneous gold catalysts supported by salen ligands efficiently catalyze the homocoupling of various aryl-boronic acids.[148] Sakurai et al. reported that poly(*N*-vinyl-2-pyrrolidone) supported gold nanoparticles are capable of catalyzing the homocoupling of potassium aryltrifluoroborates under aerobic conditions.[149]

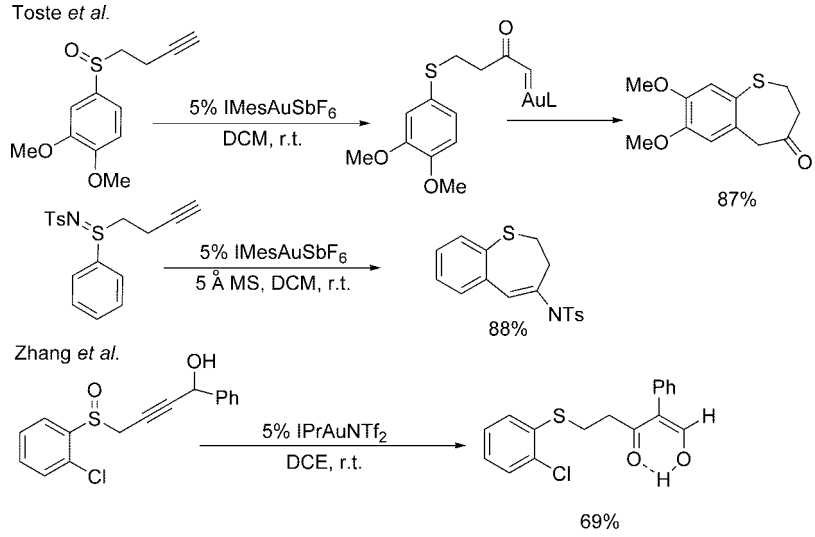
Bulk gold (~1000 nm) also exhibits catalytic abilities. Angelici et al. reported that bulk gold catalyzes a reaction between isocyanide, primary amine, and dioxygen to give carbodiimides, instead of formamidine, which would be more likely to form under homogeneous conditions.[150] If isocyanide is replaced by CO, ureas are the product with isocyanates as intermediates.[151] Secondary amines are effectively dehydrogenated into their corresponding imines under similar conditions in the presence of oxygen.[152] Notably, only 1 atm of oxygen is sufficient for all of these reactions (Scheme 80).

Oxidation reactions mediated by homogeneous gold catalysts have also been developed. In 2005, Shi et al. reported a gold(I) neocuproine system to oxidatively cleave carbon−carbon double bonds of different styrenes in water to afford carbonylic products.[153] TBHP is the oxidant which gives ketones in moderate to good yields. This system does not oxidize epoxides into ketones and the addition of TEMPO inhibits the reaction, which suggests that this reaction may not go through an epoxide-ketone pathway but rather involves a radical-based process. As a follow-up study, they found that the same gold system is also capable of catalyzing the oxidation of secondary benzylic alcohols into their corresponding ketones with dioxygen.[154] Primary benzylic alcohols give both aldehydes as well as carboxylic acids as products. The same group also reported a an anionic-AU(I)

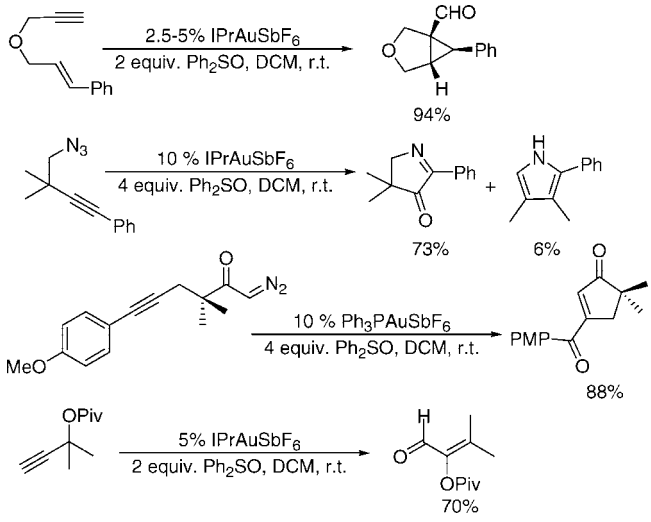
Scheme 84



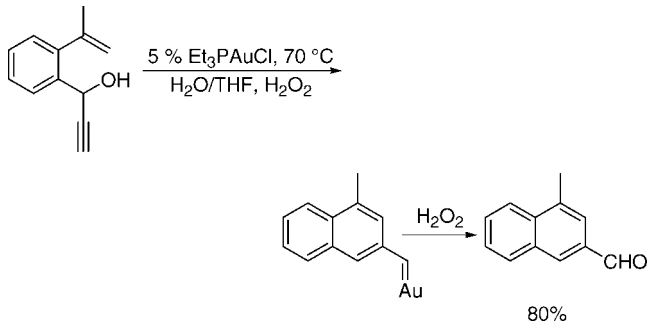
Scheme 85



Scheme 86



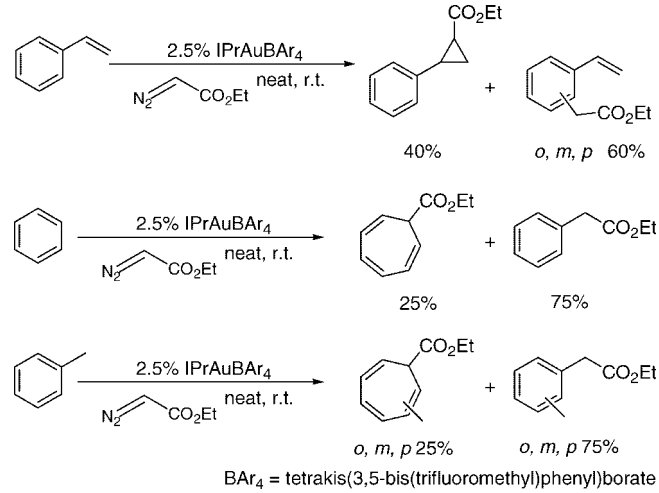
Scheme 87



diketimine system that selectively oxidizes benzylic and aliphatic alcohols into their corresponding carbonylic products.[155] Notably, primary alcohols give corresponding aldehydes as the major products. Dioxygen or air at 1 atm is sufficient as the oxidant (Scheme 81).

In the course of investigating cyclization of enynols with cationic PPh_3AuOTf, Liu et al. found that dioxygen could cleave the carbon−carbon double bond formed by the intramolecular addition of a hydroxyl group to a carbon−carbon triple bond.[156] Good yields are achieved in general and spirolactones are obtained in a few cases. Different phosphine-supported gold(I) catalysts are active; however, gold(III) chloride only gives 6% conversion. Enol ethers also undergo a similar cleavage reaction, while simple olefins do not. Addition of 2,6-di-*tert*-butyl-*p*-cresol or 4-hydroxy-TEMPO inhibits the reaction, suggesting a radical-based mechanism (Scheme 82).

Scheme 88

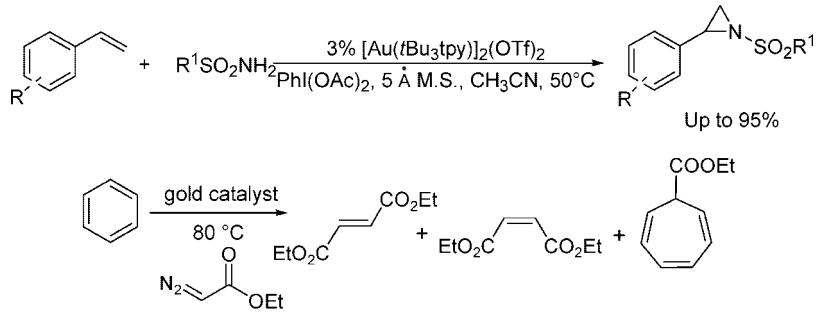


Olefin epoxidation mediated by homogeneous gold is much less developed. Cinellu et al. discovered that a Au(III)−oxo complex supported by bipyridine transfers the oxo group to cyclic alkenes such as norbornene.[157] However, a stoichiometric amount of gold(III)−oxo complex is necessary to facilitate this reaction. Yuan et al. reported a gold(III)-catalyzed oxidation of sulfides to sulfoxides with 30% hydrogen peroxide in good yields and chemoselectivities[158](Scheme 83).

Osuka et al. reported an interesting synthesis of brominated, directly fused diporphyrins in minutes by using stoichiometric amount of gold(III) chloride and an excess amount of silver triflate.[159] This method significantly improves the reaction yields if compared with the traditional methods using $Sc(OTf)_3$/DDQ (e.g., 9%)[160] (Scheme 84).

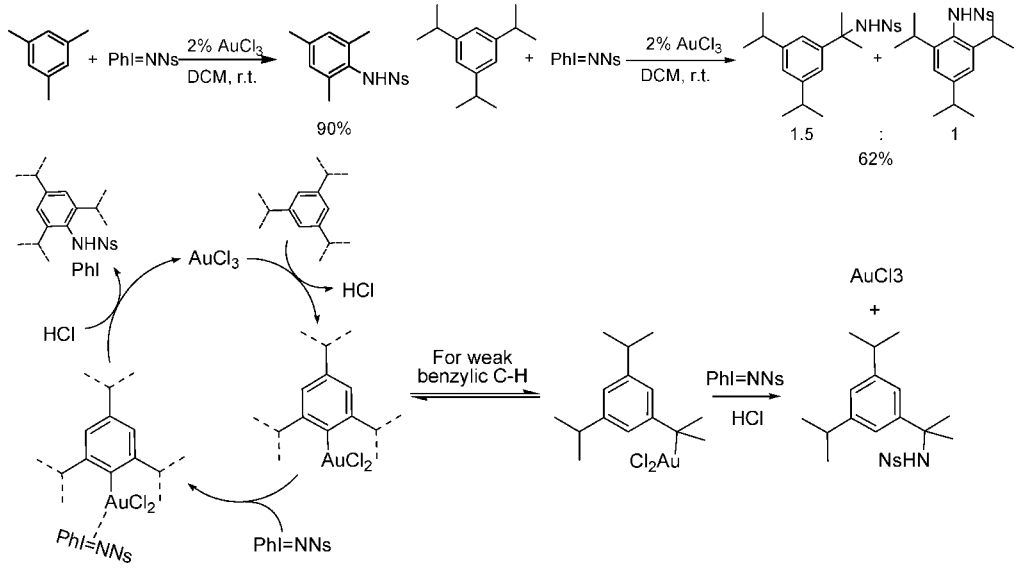
Toste et al. recently found that sulfoxides could serve as an oxygen donor to gold(I)-carbenoids to yield carbonylic products.[161] The intramolecular version of this oxo-transfer process involves an intramolecular alkynyl sulfoxide

Scheme 89

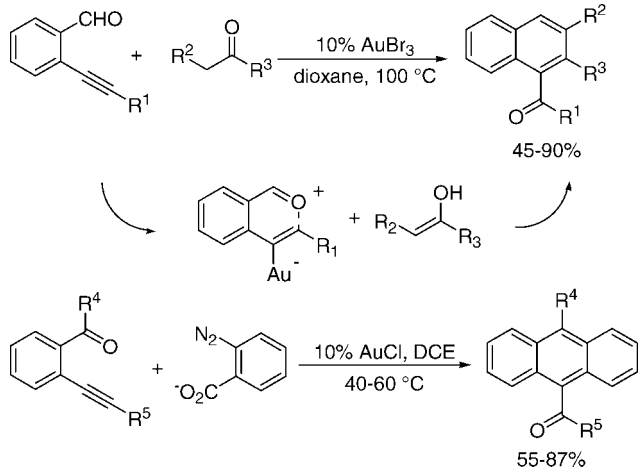


[Au*t*Bu$_3$tpy](OTf)	23	:	20	:	57
[Au*t*Bu$_2$bpy](OTf)	29	:	40	:	31
[Au(bathophenanthroline)](OTf)	23	:	23	:	54

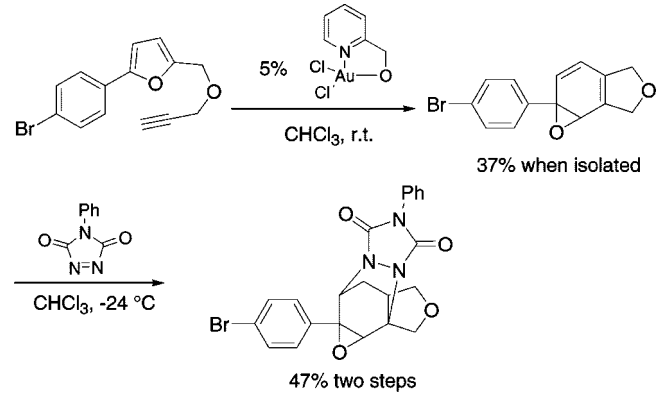
Scheme 90



Scheme 91



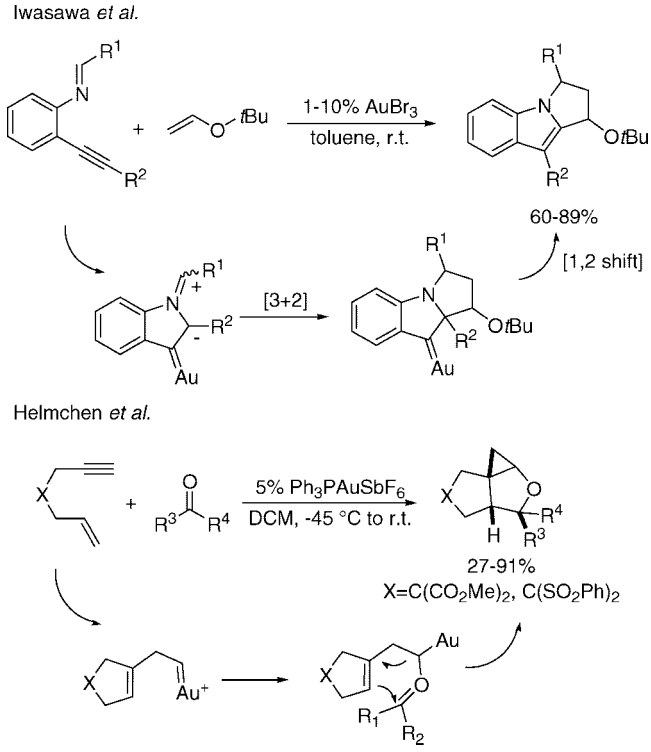
Scheme 92



rearrangement to give benzothiepinone products in good yields. Notably, sulfimines also undergo this transformation to form an enamine with good yields. Meanwhile, Zhang et al. reported a similar intramolecular redox system.[162] Instead of simple alkynes, they employed propargyl alcohols, which are further oxidized and rearrange into α,γ-diketones (Scheme 85).

Later, the intermolecular version was reported by Toste et al. using diphenylsulfoxide as the oxygen donor.[163] Different reactions involving gold(I)-carbenoids generated the carbonylic products in good to excellent yields. Different transition metals also catalyze the same reaction; however,

Scheme 93



the complex $IPrAu^+$ gives the best diastereoselectivity (Scheme 86).

Liu et al. reported a Et_3PAuCl-catalyzed oxidative cyclization of 2-ethenyl-1-(prop-2′-yn-1′-ol)benzenes into naphthyl aldehydes and ketones using H_2O_2 as the oxidant.[164] They also proposed a gold-carbene intermediate. One interesting note about this reaction is that silver cocatalyst is not necessary, which is crucial for many gold-catalyzed organic transformations. The leveling effect of the water/THF mixed solvent system might help explain this. When naphthyl alcohols are subjected to the same conditions, only a small amount of naphthyl aldehyde is formed, which supports gold-carbene as the intermediate. $PtCl_2$ also shows similar reactivity (Scheme 87).

In the first example of its kind, Nolan et al. reported that an NHC gold(I) complex activates diazo ethyl acetate and inserts the carbene group into N−H, O−H, and more interestingly, the aromatic C−H bonds.[165] When styrene was used as the substrate, the C−H insertion on the benzene ring was preferred over cyclopropanation. It is a unique reactivity known only to gold (Scheme 88).

Gold-catalyzed organic transformations involving nitrene intermediates are much less studied. He et al. showed that simple gold(I) salts and phosphine-supported gold(I) complexes are inefficient in mediating olefin aziridination. Nitrogen-based ligands, such as 4, 4′, 4″-tri-*tert*-butyl-2,2′:6′,2″terpyridine (tBu$_3$tpy) supported gold(I) efficiently catalyze olefin aziridination with the use of the commercially available oxidant $PhI(OAc)_2$ and sulfonamides.[166] Styrenes and sulfonamides bearing different functional groups are good substrates. Sulfonamide-tethered olefins and activated aliphatic olefins also undergo this reaction. This system also mediates carbene insertion into benzene (Scheme 89).

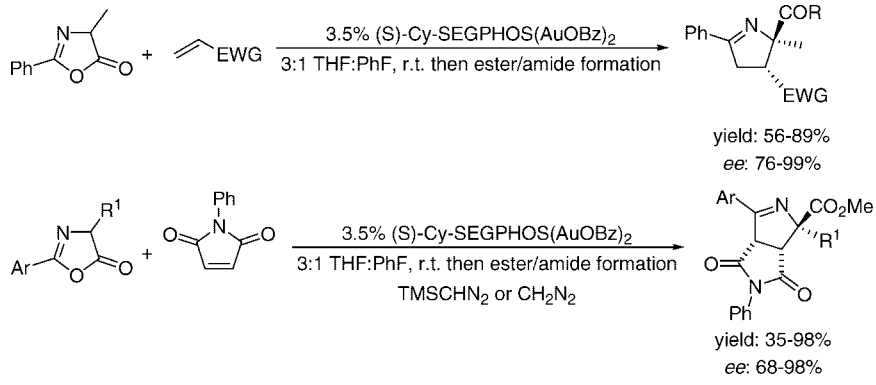
He et al. also found that simple gold(III) chloride has unique reactivity and catalyzes the reaction between electron-rich arenes and the nitrene precursor PhI=NNs (Ns = *p*-nitrosulfonyl) to give aromatic C−H insertion products.[167] A Friedel−Crafts-type process is not favored for two reasons: (i) heterocycles, which are the best substrates for Friedel−Crafts reactions, do not react; and (ii) if an activated benzylic C−H bond is present, the reaction occurs at both the aromatic and benzylic positions[168] (Scheme 90). An aryl−gold(III) species is probably generated from the reaction of $AuCl_3$ with the aromatic C−H bond in the first step, which further reacts with PhI=NNs. If a weak neighboring benzylic C−H is present, gold may shift to form the benzylic−gold species, which then further undergoes nitrene insertion. Further mechanistic study is required to support the hypothesis.

5. Other Reactions

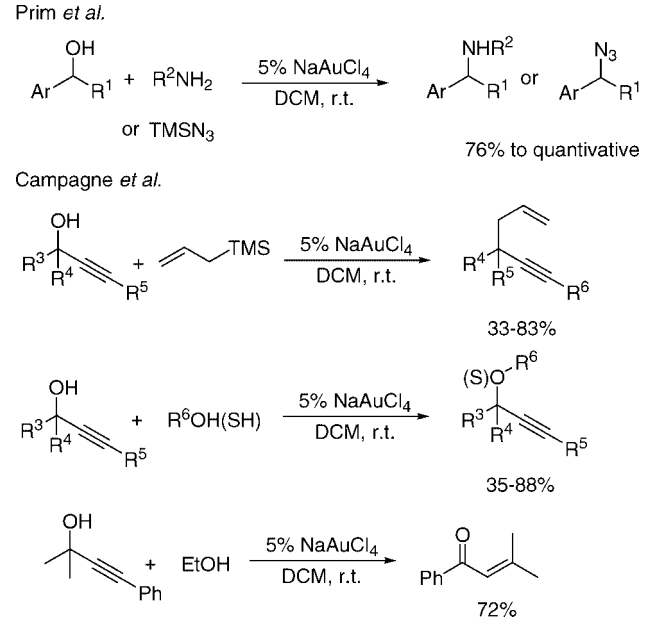
One of the most well-known gold-catalyzed Diels−Alder reactions is a benzannulation reported by Asao and Yamamoto.[124] Early examples include the benzannulation of enynals with alkynes and olefins both intra- and intermolecularly.[124] This method has been utilized in the total synthesis of (+)-ochromycinone and (+)-rubiginone B2, which will be discussed later.[169] They further developed the benzannulation reaction with enynal and enol, the mechanism of which involves an aurate intermediate that is formed by the nucleophilic attack of the carbonyl oxygen on the electron-deficient alkyne.[170] The ate intermediate that reacts with the enol form of the carbonyl substrate gives the benzannulation product. Recently, the same group reported a benzannulation reaction to make anthracene derivatives by utilizing benzenediazonium 2-carboxylate as the benzyne precursor[171] (Scheme 91).

Another important example is the phenol synthesis starting from furan substrates. Hashmi et al. first explored this field and largely broadened the reaction scope. This work has been reviewed recently.[1] In newer work, by furnishing the furan with a 2-ketal group, they could stabilize the reaction

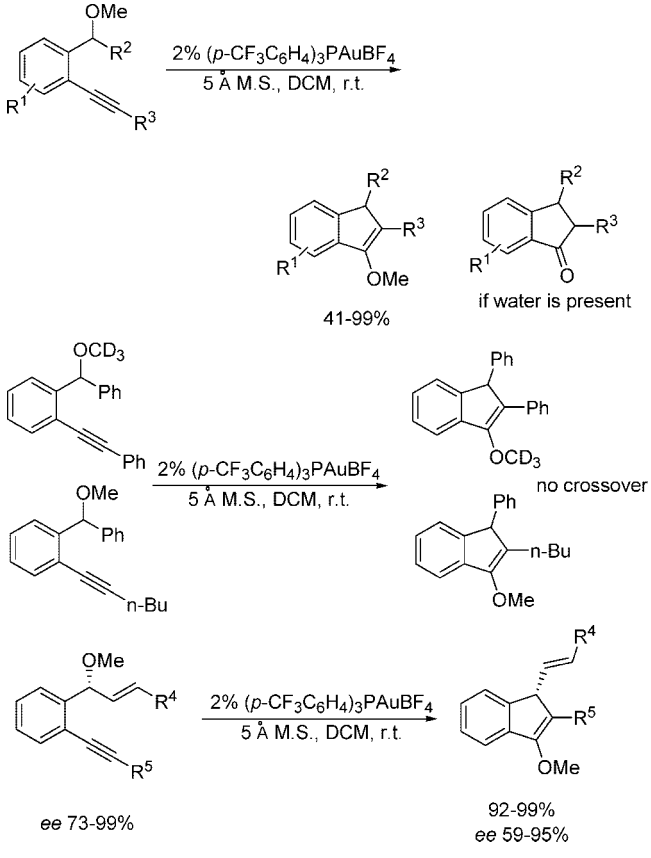
Scheme 94



Scheme 95



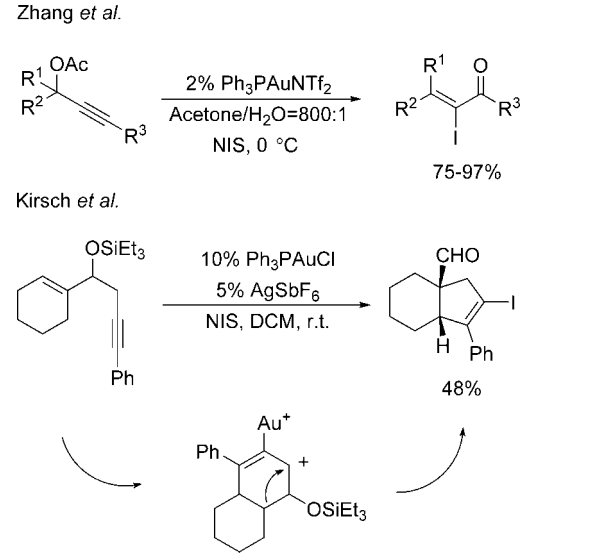
Scheme 96



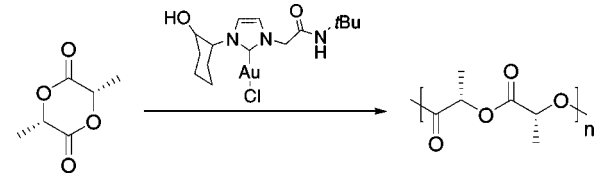
intermediate in the presence of gold(III), and a tandem Diels−Alder reaction with *N*-phenyltriazolindione occurs to give polycyclic products[172](Scheme 92).

Iwasawa et al. reported the [3 + 2] cycloaddition of *N*-(*o*-alkynylphenyl)imine, which proceeds via a metal-containing azomethine ylide *in situ* with olefins.[173] $PtCl_2$ and $AuBr_3$ show better catalytic reactivity compared to other metals. Helmchen et al. reported the intermolecular addition of aldehydes and ketones to 1,6-enynes to give polycyclic

Scheme 97



Scheme 98



products.[174] They believe the *in situ* generated gold-carbene attacks the carbonyl group to give the final product (Scheme 93).

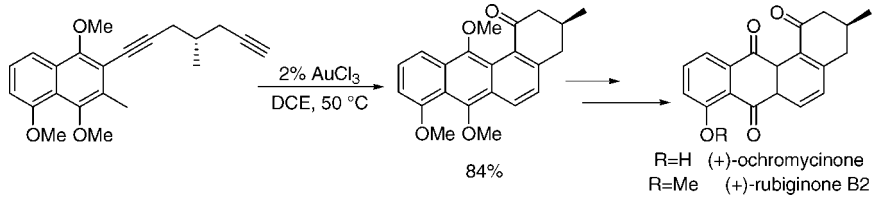
(*S*)-Cy-SEGPHOS(AuOBz)$_2$-catalyzed enantioselective cycloadditions of munchnones with electron-deficient alkenes was reported by Toste et al.[175] The reaction seems to go through a 1,3-dipolar addition pathway. Good to excellent *ee*'s are achieved along with good yields (Scheme 94).

Prim et al. reported that $NaAuCl_4$ catalyzes the amination and azidation of benzylic alcohols.[176] The same group developed another intriguing method to make enynes from propargyl alcohols with allyltrimethylsilane.[177] Various alcohols and thiols are also suitable nucleophiles. They found that propargyl alcohols readily undergo rearrangement into α,β-unsaturated ketones in a manner similar to propargyl alcohol esters and allyl alcohol esters. Enantioenriched propargyl alcohol only results in racemic product, suggesting a carbocation intermediate. Takai et al. reported a similar reaction using a rhenium/gold dual catalyst system, the details of which will not be covered in this review[178] (Scheme 95).

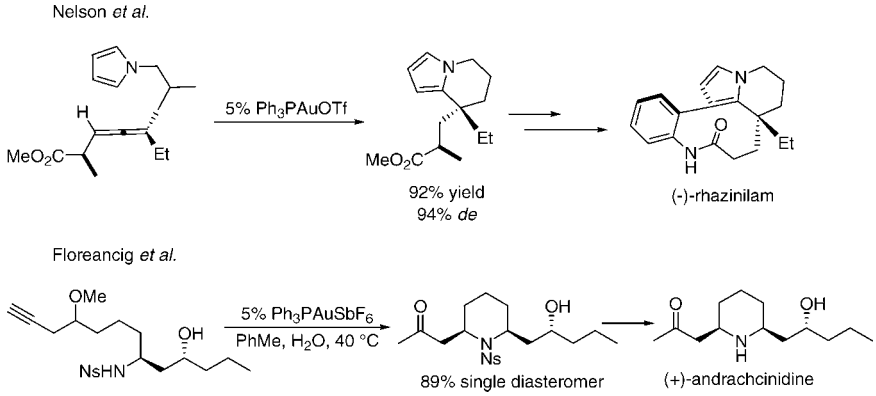
Toste et al. reported an intramolecular carboalkoxylation of alkynes including the shifting of a methoxide group.[179] If water is present, the enol ethers further hydrolyze into indanones, which can be prevented by adding molecular sieves. When two different substrates react in one pot, they do not detect any crossover product, suggesting that gold(I) activates the alkyne instead of an ionization of the benzylic ether. The possibility of a close ion pair cannot be completely excluded. Notably, if an enantio-enriched substrate is used, the chirality remains with only a small deterioration (Scheme 96).

Zhang reported a useful method to make α-iodoenones by utilizing the facile rearrangement of propargylic acetates catalyzed by gold(I) in the presence of NIS. With large aliphatic substitutions on the substrates, mainly *Z*-configu-

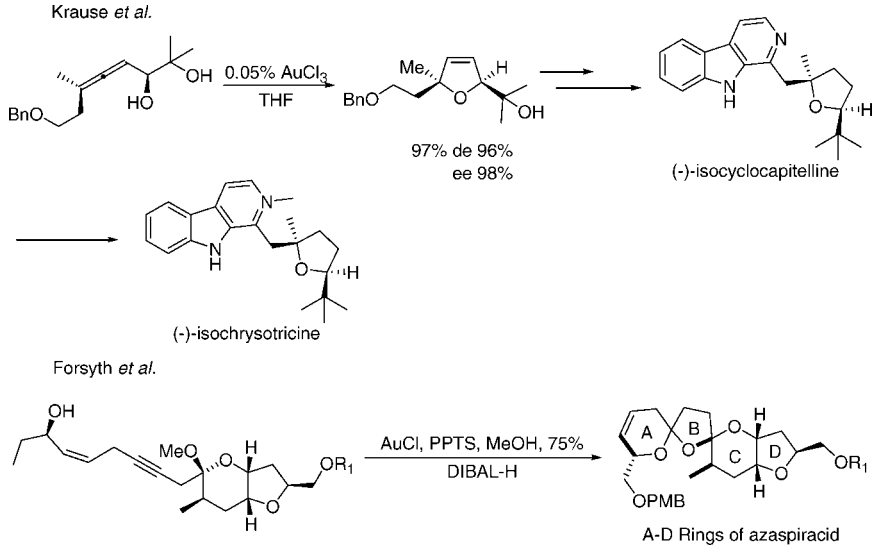
Scheme 99



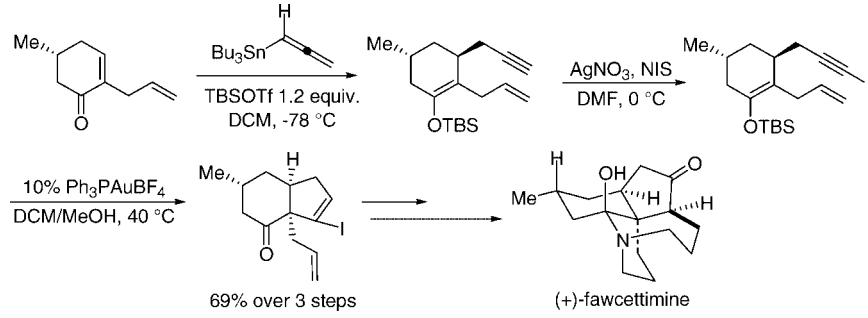
Scheme 100



Scheme 101



Scheme 102



ration products were generated, while aromatic substitutions diminish the selectivity. Meanwhile, Kirsch et al. utilized a similar strategy to make iodo-aldehydes in a tandem cyclization/pinacol rearrangement of 3-silyloxy-1,5-enynes catalyzed by gold(I)[181] (Scheme 97).

Catalysis is crucial for the polymerization of different organic substrates into functional materials. Only limited success has been achieved so far on gold-catalyzed polymerizations. In 2006, Ghosh et al. reported [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl catalyzes the ring-opening polymerization of L-lactide.[182] Under solvent-free melting conditions, low to moderate molecular weight polylactide polymers are produced with a narrow molecular weight distribution. Silver

with the same ligand could also catalyze the same reaction (Scheme 98).

To the best of our knowledge, direct polymerization of substrates with unsaturated bonds has not been reported. Rasika Dias et al. recently reported two intriguing gold(I) ethylene complexes, showing that gold(I) ethylene adducts have more covalent character than other metals.[183] This finding is helpful for further understanding and developing the gold-catalyzed insertion into olefins.

6. Applications of Gold Catalysis in Total Synthesis

Gold-catalyzed reactions have already been utilized in the total synthesis of various natural products. As an early example, Bachi et al. utilized the classic gold-catalyzed asymmetric aldol reaction with isocyanoacetate, originally reported by Hayashi in the enantioselective total synthesis of (−)-α-kainic acid.[184] In other cases, although the key steps catalyzed by gold are not enantioselective, the chirality is well-maintained from the enantio-enriched substrates under different reaction conditions.

Asao and Yamamoto et al. reported an enantioselective total synthesis of (+)-ochromycinone and (+)-rubiginone B2 by using the intramolecular version of the gold-catalyzed [4 + 2] benzannulation they developed previously.[169] Their report shows this method is suitable to construct complex 2,3-dihydrophenanthren-4(1*H*)-one skeleton, an important building block, in one facile step (Scheme 99).

Nelson et al. reported an enantioselective total synthesis of (−)-rhazinilam by utilizing a gold-catalyzed annulation of enantioenriched allenes with high yields and *de*.[185] Floreancig et al. reported the enantioselective total synthesis of (+)-andrachcinidine using a gold-catalyzed intramolecular nucleophilic substitution and hydration of enantio-enriched alkynyl ether tethered with an amine functional group[186] (Scheme 100).

Krause et al. reported the enantioselective total synthesis of (−)-isocyclocapitelline and (−)-isochrysotricine using gold-catalyzed allene cycloisomerization with enantioenriched allene substrates.[187] Similarly, Forsyth et al. reported the construction of the A-D rings of azaspiracid, which contains the trioxadispiroketal core structure, using a gold-catalyzed nucleophilic bis-spiroketalization[188] (Scheme 101).

Toste et al. utilized a key step of gold-catalyzed 5-*endo-dig* carbocyclization of enantioenriched iodoacetylene tethered silyl enol ethers in their total synthesis of (+)-fawcettimine.[189] Notably, the hydrindanone core and a quaternary center were installed in one facile step, and a 62% yield was achieved over three steps (Scheme 102).

7. Conclusion

It is obvious that currently gold catalysis is in a crucial developing stage. The discovery of new reaction categories that could be catalyzed by gold has slowed down, while gold(I)-catalyzed asymmetric organic transformations have accelerated. Satisfactory results have been reported in both yields and *ee*'s. Although currently the reaction scope is limited, the future of gold asymmetric catalysis remains bright.

On the other hand, the utilization of gold catalysts in total synthesis is intriguing. All the total syntheses described above involve using enantioenriched substrates and the chosen gold-catalyzed steps retain the chirality instead of installing the chirality. With the development of asymmetric gold catalysis, much more effort will probably be spent in the key steps of total synthesis in the near future.

8. Acknowledgments

We thank the University of Chicago for support and David A. Capretto for fruitful discussions and proofreading of this manuscript.

9. References

(1) (a) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896. (b) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271. (c) Furstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (d) Jimenez-Nunez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333. (e) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395. (f) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180. (g) Marion, N.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2750. (h) Hashmi, A. S. K. *Nature* **2007**, *449*, 292.
(2) (a) Luzung, M. R.; Markham, J. P.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 10858. (b) Mamane, V.; Gress, T.; Krause, H.; Füerstner, A. *J. Am. Chem. Soc.* **2004**, *126*, 8654. (c) Nieto-Oberhuber, C.; Munoz, M. P.; Bunuel, E.; Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402. (d) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 11806.
(3) Hintermann, L. *Nächr. Chem.* **2005**, *53*, 420.
(4) Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002.
(5) (a) Lopez, S. H.-G., E.; Perez-Galan, P.; Nieto-Oberhuber, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6029. ((b)) For another gold-catalyzed skeletal rearrangement, please see Tang, J.-M.; Bhunia, S.; Abu Sohel, S. M.; Lin, M.-Y.; Liao, H.-Y.; Datta, S.; Das, A.; Liu, R.-S. *J. Am. Chem. Soc.* **2007**, *129*, 15677.
(6) Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006**, *128*, 14274.
(7) Hashmi, A. S. K.; Weyrauch, J. P.; Rudolph, M.; Kurpejovic, E. *Angew. Chem., Int. Ed.* **2004**, *43*, 6545.
(8) Lemiere, G.; Gandon, V.; Agenet, N.; Goddard, J.-P.; de Kozak, A.; Aubert, C.; Fensterbank, L.; Malacria, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7596.
(9) Tarselli, M. A.; Chianese, A. R.; Lee, S. J.; Gagne, M. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6670.
(10) Lemiere, G.; Gandon, V.; Cariou, K.; Fukuyama, T.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *Org. Lett.* **2007**, *9*, 2207.
(11) Huang, X.; Zhang, L. *J. Am. Chem. Soc.* **2007**, *129*, 6398.
(12) Luzung, M. R.; Mauleon, P.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 12402.
(13) Lee, J. H.; Toste, F. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 912.
(14) (a) Mueller, T. E.; Grosche, M.; Herdtweck, E.; Pleier, A.-K.; Walter, E.; Yan, Y.-K. *Organometallics* **2000**, *19*, 170. (b) Mizushima, E.; Hayashi, T.; Tanaka, M. *Org. Lett.* **2003**, *5*, 3349.
(15) Zhang, Y.; Donahue, J. P.; Li, C.-J. *Org. Lett.* **2007**, *9*, 627.
(16) Kang, J.-E.; Kim, H.-B.; Lee, J.-W.; Shin, S. *Org. Lett.* **2006**, *8*, 3537.
(17) Nakamura, I.; Yamagishi, U.; Song, D.; Konta, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 2284.
(18) Seregin, I. V.; Schammel, A. W.; Gevorgyan, V. *Org. Lett.* **2007**, *9*, 3433.
(19) Seregin, I. V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2006**, *128*, 12050.
(20) Gorin, D. J.; Davis, N. R.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 11260.
(21) Morita, N.; Krause, N. *Org. Lett.* **2004**, *6*, 4121.
(22) Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *Org. Lett.* **2007**, *9*, 2887.
(23) Zhang, Z.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 283.
(24) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066.
(25) Lee, P. H.; Kim, H.; Lee, K.; Kim, M.; Noh, K.; Kim, H.; Seomoon, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 1840.
(26) Nishina, N.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3314.
(27) Nishina, N.; Yamamoto, Y. *Synlett* **2007**, 1767.
(28) LaLonde, R. L.; Sherry, B. D.; Kang, E. J.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 2452.
(29) Zhang, J.; Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2006**, *128*, 1798.
(30) Li, Z.; Zhang, J.; Brouwer, C.; Yang, C.-G.; Reich, N. W.; He, C. *Org. Lett.* **2006**, *8*, 4175.
(31) Rosenfeld, D. C.; Shekhar, S.; Takemiya, A.; Utsunomiya, M.; Hartwig, J. F. *Org. Lett.* **2006**, *8*, 4179.
(32) Han, X.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1747.
(33) Bender, C. F.; Widenhoefer, R. A. *Chem. Commun.* **2006**, 4143.

(34) Bender, C. F.; Widenhoefer, R. A. *Org. Lett.* **2006**, *8*, 5303.
(35) Liu, X.-Y.; Li, C.-H.; Che, C.-M. *Org. Lett.* **2006**, *8*, 2707.
(36) Zhou, C.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2007**, *129*, 5828.
(37) Brouwer, C.; He, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1744.
(38) Kovacs, G.; Ujaque, G.; Lledos, A. *J. Am. Chem. Soc.* **2008**, *130*, 853.
(39) Shi, W.-J.; Liu, Y.; Butti, P.; Togni, A. *Adv. Synth. Catal.* **2007**, *349*, 1619.
(40) Shi, M.; Liu, L.-P.; Tang, J. *Org. Lett.* **2006**, *8*, 4043.
(41) Fukuda, Y.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 3729.
(42) Antoniotti, S.; Genin, E.; Michelet, V.; Genet, J.-P. *J. Am. Chem. Soc.* **2005**, *127*, 9976.
(43) Belting, V.; Krause, N. *Org. Lett.* **2006**, *8*, 4489.
(44) Barluenga, J.; Dieguez, A.; Fernandez, A.; Rodriguez, F.; Fananas, F. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2091.
(45) Liu, Y.; Song, F.; Song, Z.; Liu, M.; Yan, B. *Org. Lett.* **2005**, *7*, 5409.
(46) Engel, D. A.; Dudley, G. B. *Org. Lett.* **2006**, *8*, 4027–4029.
(47) Genin, E.; Toullec, P. Y.; Antoniotti, S.; Brancour, C.; Genet, J.-P.; Michelet, V. *J. Am. Chem. Soc.* **2006**, *128*, 3112.
(48) Hashmi, A. S. K.; Weyrauch, J. P.; Frey, W.; Bats, J. W. *Org. Lett.* **2004**, *6*, 4391.
(49) Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 9868.
(50) (a) Buzas, A.; Gagosz, F. *Org. Lett.* **2006**, *8*, 515. (b) Buzas, A.; Gagosz, F. *Synlett* **2006**, 2727. (c) Kang, J.-E.; Shin, S. *Synlett* **2006**, 717.
(51) Hashmi, A. S. K.; Salathe, R.; Frey, W. *Synlett* **2007**, 1763.
(52) Lim, C.; Kang, J.-E.; Lee, J.-E.; Shin, S. *Org. Lett.* **2007**, *9*, 3539.
(53) Jin, T.; Yamamoto, Y. *Org. Lett.* **2007**, *9*, 5259.
(54) Hashmi, A. S. K.; Sinha, P. *Adv. Synth. Catal.* **2004**, *346*, 432.
(55) Dai, L.-Z.; Qi, M.-J.; Shi, Y.-L.; Liu, X.-G.; Shi, M. *Org. Lett.* **2007**, *9*, 3191.
(56) Shu, X.-Z.; Liu, X.-Y.; Xiao, H.-Q.; Ji, K.-G.; Guo, L.-N.; Qi, C.-Z.; Liang, Y.-M. *Adv. Synth. Catal.* **2007**, *349*, 2493.
(57) (a) Hotha, S.; Kashyap, S. *J. Am. Chem. Soc.* **2006**, *128*, 9620. (b) Asao, N.; Aikawa, H.; Tago, S.; Umetsu, K. *Org. Lett.* **2007**, *9*, 4299.
(58) Gockel, B.; Krause, N. *Org. Lett.* **2006**, *8*, 4485.
(59) Hamilton, G. L.; Kang, E. J.; Mba, M.; Toste, F. D. *Science* **2007**, *317*, 496.
(60) Sromek, A. W.; Rubina, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*, 10500.
(61) Dudnik, A. S.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2007**, *46*, 5195.
(62) Zhou, C.-Y.; Chan, P. W. H.; Che, C.-M. *Org. Lett.* **2006**, *8*, 325.
(63) Buzas, A. K.; Istrate, F. M.; Gagosz, F. *Org. Lett.* **2007**, *9*, 985.
(64) Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2005**, *127*, 6966.
(65) Zhang, X.; Corma, A. *Dalton Trans.* **2008**, 397.
(66) Morita, N.; Krause, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 1897.
(67) Brouwer, C.; Rahaman, R.; He, C. *Synlett* **2007**, 1785.
(68) Nakamura, I.; Sato, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 4473.
(69) Nakamura, I.; Sato, T.; Terada, M.; Yamamoto, Y. *Org. Lett.* **2007**, *9*, 4081.
(70) Norman, R. O. C.; Parr, W. J. E.; Thomas, C. B. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1983.
(71) Akana, J. A.; Bhattacharyya, K. X.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 7736.
(72) Kennedy-Smith, J.-J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 4526.
(73) Staben, S. T.; Kennedy-Smith, J. J.; Toste, F. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 5350.
(74) Ochida, A.; Ito, H.; Sawamura, M. *J. Am. Chem. Soc.* **2006**, *128*, 16486.
(75) Amijs, C. H. M.; Lopez-Carrillo, V.; Echavarren, A. M. *Org. Lett.* **2007**, *9*, 4021.
(76) Yao, X.-Q.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 6884.
(77) Nguyen, R.-V.; Yao, X.-Q.; Bohle, D. S.; Li, C.-J. *Org. Lett.* **2005**, *7*, 673.
(78) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 6962.
(79) Leseurre, L.; Toullec, P. Y.; Genet, J.-P.; Michelet, V. *Org. Lett.* **2007**, *9*, 4049.
(80) Buzas, A. K.; Istrate, F. M.; Gagosz, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1141.
(81) Yang, T.; Campbell, L.; Dixon, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 12070.
(82) Yao, T.; Zhang, X.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 7679.
(83) Zhang, J.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **2006**, *45*, 6704.
(84) Lin, C.-C.; Teng, T.-M.; Odedra, A.; Liu, R.-S. *J. Am. Chem. Soc.* **2007**, *129*, 3798.
(85) Hashmi, A. S. K.; Schafer, S.; Wolfle, M.; Diez Gil, C.; Fischer, P.; Laguna, A.; Blanco, M. C.; Gimeno, M. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 6184.
(86) Kharasch, M. S.; Isbell, H. S. *J. Am. Chem. Soc.* **1931**, *53*, 3053.
(87) (a) Braunstein, P. *J. Chem. Soc. Chem. Commun.* **1973**, 851. (b) Braunstein, P.; Clark, R. J. H. *Inorg. Chem.* **1974**, *13*, 2224.
(88) Hashmi, A. S. K.; Schwarz, L.; Choi, J.-H.; Frost, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2285.
(89) Hashmi, A. S. K.; Grundl, L. *Tetrahedron* **2005**, *61*, 6231.
(90) Li, Z.; Shi, Z.; He, C. *J. Organomet. Chem.* **2005**, *690*, 5049.
(91) (a) Hashmi, A. S. K.; Blanco, M. C. *Eur. J. Org. Chem.* **2006**, 4340. (b) Hashmi, A. S. K.; Salathe, R.; Frey, W. *Eur. J. Org. Chem.* **2007**, 1648.
(92) Rozenman, M. M.; Kanan, M. W.; Liu, D. R. *J. Am. Chem. Soc.* **2007**, *129*, 14933.
(93) Nguyen, R. V.; Yao, X.-Q.; Li, C.-J. *Org. Lett.* **2006**, *8*, 2397.
(94) Reich, N. W.; Yang, C.-G.; Shi, Z.; He, C. *Synlett* **2006**, 1278.
(95) (a) Alfonsi, M.; Arcadi, A.; Aschi, M.; Bianchi, G.; Marinelli, F. *J. Org. Chem.* **2005**, *70*, 2265. (b) Arcadi, A.; Cacchi, S.; Fabrizi, G.; Marinelli, F. *Synlett* **2007**, 1775.
(96) Shi, Z.; He, C. *J. Org. Chem.* **2004**, *69*, 3669.
(97) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485.
(98) Ferrer, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1105.
(99) Ferrer, C.; Amijs, C. H. M.; Echavarren, A. M. *Chem. Eur. J.* **2007**, *13*, 1358.
(100) Marion, N.; Diez-Gonzalez, S.; de Fremont, P.; Noble, A. R.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3647.
(101) Marion, N.; Carlqvist, P.; Gealageas, R.; de Fremont, P.; Maseras, F.; Nolan, S. P. *Chem.−Eur. J.* **2007**, *13*, 6437.
(102) Peng, L.; Zhang, X.; Zhang, S.; Wang, J. *J. Org. Chem.* **2007**, *72*, 1192.
(103) Gorin, D. J.; Dube, P.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 14480.
(104) Lian, J.-J.; Chen, P.-C.; Lin, Y.-P.; Ting, H.-C.; Liu, R.-S. *J. Am. Chem. Soc.* **2006**, *128*, 11372.
(105) Toullec, P. Y.; Genin, E.; Leseurre, L.; Genet, J.-P.; Michelet, V. *Angew. Chem., Int. Ed.* **2006**, *45*, 7427.
(106) Amijs, C. H. M.; Ferrer, C.; Echavarren, A. M. *Chem. Commun.* **2007**, 698.
(107) Luo, T.; Schreiber, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 8250.
(108) Liu, C.; Widenhoefer, R. A. *Org. Lett.* **2007**, *9*, 1935.
(109) Watanabe, T.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2007**, *9*, 4821.
(110) Hashmi, A. S. K.; Schwarz, L.; Rubenbauer, P.; Blanco, M. C. *Adv. Synth. Catal.* **2006**, *348*, 705.
(111) Luo, Y.; Li, C.-J. *Chem. Commun.* **2004**, 1930.
(112) Shi, Z.; He, C. *J. Am. Chem. Soc.* **2004**, *126*, 5964.
(113) Sun, X.; Sun, W.; Fan, R.; Wu, J. *Adv. Synth. Catal.* **2007**, *349*, 2151.
(114) Arcadi, A.; Alfonsi, M.; Bianchi, G.; Anniballe, G. D.; Marinellia, F. *Adv. Synth. Catal.* **2006**, *348*, 331.
(115) Shi, Z.; He, C. *J. Am. Chem. Soc.* **2004**, *126*, 13596.
(116) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2003**, *125*, 9584.
(117) (a) Wei, C.; Li, Z.; Li, C.-J. *Synlett* **2004**, 1472. (b) Huang, B.; Yao, X.-Q.; Li, C.-J. *Adv. Synth. Catal.* **2006**, *348*, 1528.
(118) (a) Kantam, M. L.; Prakash, B. V.; Reddy, C. R. V.; Sreedhar, B. *Synlett* **2005**, 2329. (b) Kidwai, M.; Bansal, V.; Kumarb, A.; Mozumdar, S. *Green Chem.* **2007**, *9*, 742.
(119) Lo, V. K.-Y.; Liu, Y.; Wong, M.-K.; Che, C.-M. *Org. Lett.* **2006**, *8*, 1529.
(120) Yan, B.; Liu, Y. *Org. Lett.* **2007**, *9*, 4323–4326.
(121) Lavallo, V.; Frey, G. D.; Kousar, S.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705.
(122) Lavallo, V.; Frey, G. D.; Kousar, S.; Donnadieu, B.; Bertrand, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 13569.
(123) Yao, X.-Q.; Li, C.-J. *Org. Lett.* **2006**, *8*, 1953.
(124) Asao, N. *Synlett* **2006**, 1645.
(125) Skouta, R.; Li, C.-J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1117.
(126) Skouta, R.; Li, C.-J. *Synlett* **2007**, 1759.
(127) Liu, X.-Y.; Ding, P.; Huang, J.-S.; Che, C.-M. *Org. Lett.* **2007**, *9*, 2645.
(128) Fuchita, Y.; Utsunomiya, Y.; Yasutake, M. *J. Chem. Soc., Dalton Trans.* **2001**, 2330.
(129) (a) Corma, A.; Puebl, G.; Iglesias, M.; Monge, A.; Pérez-Ferreras, S.; Sánchez, F. *Adv. Synth. Catal.* **2006**, *348*, 1899. (b) González-Arellano, C.; Abad, A.; Corma, A.; Garcia, H.; Iglesias, M.; Sanchez, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1536.
(130) (a) Gonzalez-Arellano, C.; Corma, A.; Iglesias, M.; Sanchez, F. *J. Catal.* **2006**, *238*, 497. (b) Corma, A.; González-Arellano, C.; Iglesias, M.; Perez-Ferreras, S.; Sanchez, F. *Synlett* **2007**, 1771.
(131) (a) Mikovsky, R. J.; Boudart, M.; Taylor, H. S. *J. Am. Chem. Soc.* **1954**, *76*, 3814. (b) Wise, H.; Sancier, K. M. *J. Catal.* **1963**, *2*, 149. (c) Cocco, G.; Enzo, S.; Fagherazzi, G.; Schiffini, L.; Bassi, I. W.; Vlaic, G.; Galvagno, S.; Parravano, G. *J. Phys. Chem.* **1979**, *83*, 2527. (d) Bond, G. C.; Sermon, P. A. *Gold Bull.* **1973**, *6*, 102. (e) Sermon, P. A.; Bond, G. C.; Wells, P. B. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 385. (f) Saito, A.; Tanimoto, M. *J. Chem. Soc., Chem. Commun.* **1988**, 832.

(132) Zhang, X.; Shi, H.; Xu, B.-X. *Angew. Chem., Int. Ed.* **2005**, *44*, 7132.
(133) Comas-Vives, A.; Gonzalez-Arellano, C.; Corma, A.; Iglesias, M.; Sanchez, F.; Ujaque, G. *J. Am. Chem. Soc.* **2006**, *128*, 4756.
(134) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852.
(135) Milone, C.; Crisafulli, C.; Ingoglia, R.; Schipilliti, L.; Galvagno, S. *Catal. Today* **2007**, *122*, 341.
(136) (a) Corma, A.; Serna, P. *Nat. Protocol* **2006**, *1*, 2590. (b) Corma, A.; Serna, P. *Science* **2006**, *313*, 332.
(137) Corma, A.; Serna, P.; Garcia, H. *J. Am. Chem. Soc.* **2007**, *129*, 6358.
(138) Gonzalez-Arellano, C.; Corma, A.; Iglesias, M.; Sanchez, F. *Chem. Commun.* **2005**, 3451.
(139) (a) Clark, C. H. D.; Toplet, B. *J. Phys. Chem.* **1928**, 121. (b) Sachtler, W. M. H.; deBoer, N. H. *J. Phys. Chem.* **1960**, *64*, 1579. (c) Kane, A. F.; Clarke, J. K. A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1640. (d) Parravano, G. *J. Catal.* **1970**, *18*, 320. (e) Galvagno, S.; Parravano, G. *J. Catal.* **1979**, *57*, 272.
(140) Ito, H.; Yajima, T.; Tateiwa, J.-i.; Hosomi, A. *Tetrahedron Lett.* **1999**, *40*, 7807.
(141) Abbiati, G.; Arcadi, A.; Bianchi, G.; Di Giuseppe, S.; Marinelli, F.; Rossi, E. *J. Org. Chem.* **2003**, *68*, 6959.
(142) Ito, H.; Takagi, K.; Miyahara, T.; Sawamura, M. *Org. Lett.* **2005**, *7*, 3001.
(143) (a) Haruta, M. *Nature* **2005**, *437*, 1098. (b) Hughes, M. D.; Xu, Y.-J.; Jenkins, P.; McMorn, P.; Landon, P.; Enache, D. I.; Carley, A. F.; Attard, G. A.; Hutchings, G. J.; King, F.; Stitt, E. H.; Johnston, P.; Griffin, K.; Kiely, C. J. *Nature* **2005**, *437*, 1132.
(144) Deng, X.; Friend, C. M. *J. Am. Chem. Soc.* **2005**, *127*, 17178.
(145) (a) Alexander Nijhuis, T.; Visser, T.; Weckhuysen, B. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1115. (b) Abad, A.; Almela, C.; Corma, A.; Garcia, H. *Chem. Commun.* **2006**, 3178. (c) Christensen, C.-H.; Jorgensen, B.; Rass-Hansen, J.; Egeblad, K.; Madsen, R.; Klitgaard, S. K.; Hansen, S. M.; Hansen, M. R.; Andersen, H. C.; Riisager, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4648. (d) Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanabe, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. *Science* **2006**, *311*, 362. (e) Comotti, M.; Pina, C. D.; Falletta, E.; Rossi, M. *Adv. Synth. Catal.* **2006**, *348*, 313. (f) Miyamura, H.; Matsubara, R.; Miyazaki, Y.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4151. (g) Nielsen, I. S.; Taarning, E.; Egeblad, K.; Madsen, R.; Christensen, C. H. *Catal. Lett.* **2007**, *116*, 35. (h) Alvaro, M.; Aprile, C.; Corma, A.; Ferrer, B.; Garcia, H. *J. Catal.* **2007**, *245*, 249. (i) Choudhary, V. R.; Jha, R.; Jana, P. *Green Chem.* **2007**, *9*, 267.
(146) Deng, X.; Baker, T. A.; Friend, C. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7075.
(147) Carrettin, S.; Guzman, J.; Corma, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2242.
(148) Gonzalez-Arellano, C.; Corma, A.; Iglesias, M.; Sanchez, F. *Chem. Commun.* **2005**, 1990.
(149) Sakurai, H.; Tsunoyama, H.; Tsukuda, T. *J. Organomet. Chem.* **2007**, *692*, 368.
(150) Lazar, M.; Angelici, R. J. *J. Am. Chem. Soc.* **2006**, *128*, 10613.
(151) Zhu, B.; Angelici, R. J. *J. Am. Chem. Soc.* **2006**, *128*, 14460.
(152) Zhu, B.; Angelici, R. J. *Chem. Commun.* **2007**, 2157.
(153) Xing, D.; Guan, B.; Cai, G.; Fang, Z.; Yang, L.; Shi, Z. *Org. Lett.* **2006**, *8*, 693.
(154) Li, H.; Guan, B.; Wang, W.; Xing, D.; Fang, Z.; Wan, X.; Yang, L.; Shi, Z. *Tetrahedron* **2007**, *63*, 8430.
(155) Guan, B.; Xing, D.; Cai, G.; Wan, X.; Yu, N.; Fang, Z.; Yang, L.; Shi, Z. *J. Am. Chem. Soc.* **2005**, *127*, 18004.
(156) Liu, y.; Song, F.; Guo, S. *J. Am. Chem. Soc.* **2006**, *128*, 11332.
(157) Cinellu, M. A.; Minghetti, G.; Cocco, F.; Stoccoro, S.; Zucca, A.; Manassero, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6892.
(158) Yuan, Y.; Bian, Y. *Tetrahedron Lett.* **2007**, *48*, 8518.
(159) Sahoo, A. K.; Nakamura, Y.; Aratani, N.; Kim, K. S.; Noh, S. B.; Shinokubo, H.; Kim, D.; Osuka, A. *Org. Lett.* **2006**, *8*, 4141.
(160) (a) Tsuda, A.; Furuta, H.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 10304. (b) Tsuda, A.; Nakamura, Y.; Osuka, A. *Chem. Commun.* **2003**, 1096.
(161) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 4160.
(162) Li, G.; Zhang, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 5156.
(163) Witham, C. A.; Mauleon, P.; Shapiro, N. D.; Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 5838.
(164) Taduri, B. P.; Abu Sohel, S. M.; Cheng, H.-M.; Lin, G.-Y.; Liu, R.-S. *Chem. Commun.* **2007**, 2530.
(165) Fructos, M. R.; Belderrain, T. R.; de Fremont, P.; Scott, N. M.; Nolan, S. P.; Diaz-Requejo, M. M.; Perez, P. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 5284.
(166) Li, Z.; Ding, X.; He, C. *J. Org. Chem.* **2006**, *71*, 5876.
(167) Li, Z.; Capretto, D. A.; Rahaman, R. O.; He, C. *J. Am. Chem. Soc.* **2007**, *129*, 12058.
(168) (a) Heyduk, A. F.; Driver, T. G.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 15034. (b) Driver, T. G.; Williams, T. J.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2007**, *26*, 294.
(169) Sato, K.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 8977.
(170) (a) Asao, N.; Aikawa, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 7458. (b) Asao, N.; Aikawa, H. *J. Org. Chem.* **2006**, *71*, 5249.
(171) Asao, N.; Sato, K. *Org. Lett.* **2006**, *8*, 5361.
(172) Hashmi, A. S. K.; Kurpejovic, E.; Wölfle, M.; Frey, W.; Bats, J. W. *Adv. Synth. Catal.* **2007**, *349*, 1743.
(173) Kusama, H.; Miyashita, Y.; Takaya, J.; Iwasawa, N. *Org. Lett.* **2006**, *8*, 289.
(174) Schelwies, M.; Dempwolff, A. L.; Rominger, F.; Helmchen, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5598.
(175) Melhado, A. D.; Luparia, M.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 12638.
(176) Terrasson, V.; Marque, S.; Georgy, M.; Campagne, J.-M.; Prim, D. *Adv. Synth. Catal.* **2006**, *348*, 2063.
(177) Georgy, M.; Boucard, V.; Campagne, J.-M. *J. Am. Chem. Soc.* **2005**, *127*, 14180.
(178) Kuninobu, Y.; Ishii, E.; Takai, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3296.
(179) Dube, P.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 12062.
(180) Yu, M.; Zhang, G.; Zhang, L. *Org. Lett.* **2007**, *9*, 2147.
(181) Kirsch, S. F.; Binder, J. T.; Crone, B.; Duschek, A.; Haug, T. T.; Libert, C.; Menz, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 2310.
(182) (a) Ray, L.; Katiyar, V.; Raihan, M. J.; Nanavati, H.; Shaikh, M. M.; Ghosh, P. *Eur. J. Inorg. Chem.* **2006**, 3724. (b) Ray, L.; Katiyar, V.; Barman, S.; Raihan, M. J.; Nanavati, H.; Shaikh, M. M.; Ghosh, P. *J. Organomet. Chem.* **2007**, *692*, 4259.
(183) (a) Rasika Dias, H. V.; Wu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 7814. (b) Rasika Dias, H. V.; Fianchini, M.; Cundari, T. R.; Campana, C. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 556.
(184) Bachi, M. D.; Melman, A. *J. Org. Chem.* **1997**, *62*, 1896.
(185) Liu, Z.; Wasmuth, A. S.; Nelson, S. G. *J. Am. Chem. Soc.* **2006**, *128*, 10352.
(186) Jung, H. H.; Floreancig, P. E. *J. Org. Chem.* **2007**, *72*, 7359.
(187) (a) Morita, N.; Krause, N. *Eur. J. Org. Chem.* **2006**, 4634. (b) Volz, F.; Krause, N. *Org. Biomol. Chem.* **2007**, *5*, 1519.
(188) Li, Y.; Zhou, F.; Forsyth, C. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 279.
(189) Linghu, X.; Kennedy-Smith, J. J.; Toste, F. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 7671.

CR068434L