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Gold as a catalyst. Part III. Addition to double bonds

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This publication is a continuation of the series of reviews devoted to the state of the art of gold catalysis in organic chemistry. The third review covers gold-catalyzed reactions of compounds containing double bonds. The reactions of alkenes, cumulated and conjugated dienes and enynes with different types of nucleophiles, including those with heteroatoms (oxygen, nitrogen and sulfur), are considered.
The bibliography includes 355 references.

Contents

1. Introduction 492
2. Nucleophilic addition to alkenes 492
   2.1. Hydroamination of alkenes 493
      2.1.1. Intermolecular hydroamination of activated alkenes 493
      2.1.2. Hydroamination of unactivated alkenes 495
   2.2. Addition of oxygen nucleophiles to the double bond 500
      2.2.1. Intramolecular addition to unactivated alkenes 500
      2.2.2. Intermolecular addition to unactivated alkenes 501
   2.3. Preparation of oxiranes 503
   2.4. Oxidative cleavage of double bonds 504
   2.5. Hydrothiolation of alkenes 504
   2.6. Formation of carbon – carbon bonds 505
   2.7. Cyclopropane synthesis 507
3. Conjugated dienes and styrenes 508
   3.1. Hydroamination 508
      3.1.1. Intramolecular reactions 508
      3.1.2. Intermolecular reactions 509
   3.2. Intermolecular addition of oxygen nucleophiles 509
   3.3. Formation of C – C bonds. Enol addition 509
   3.4. Hydrothiolation 510
4. Addition to allenes 510
   4.1. Hydroamination of allenes 510
      4.1.1. Intramolecular reactions 510
      4.1.2. Intermolecular reactions 514
   4.2. Addition of oxygen nucleophiles to allenes 516
      4.2.1. Intramolecular reactions 516
      4.2.2. Intermolecular reactions 522
   4.3. Hydrothiolation 524
   4.4. (Het)arenes as nucleophiles 524
   4.5. Hydrosilylation of allenes 525
5. Nucleophilic addition to enynes 525
   5.1. Addition of heteronucleophiles 525
   5.2. Addition of carbon nucleophiles, cycloisomerization reactions 526
6. Tandem reactions of methylene- and vinylenecyclopropanes 527
7. Conclusion 531

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1. Introduction

As recently as a few years ago, it was a sensation that gold — a noble and precious metal, chemically inert in the elemental state — can be an efficient catalyst for organic reactions when used as salts, complexes or nanoparticles. However, over the past years, catalysis by gold (and its derivatives) was exceptionally fruitful for a variety of processes and the number of publications devoted to this subject is constantly increasing. This is due to the fact that many gold-catalyzed reactions proceed under milder conditions and with higher selectivity than without gold or in the presence of other catalysts. For example, the use of Au^{I} or Au^{III}, a softer or harder Lewis acid, as a catalyst can change the site of attack by a nucleophile in a enone molecule (the double bond or the carbonyl group). In addition, there are reactions in which the original result is dictated particularly by the nature of the metal and the ability of gold to form unusual intermediates. Gold catalysis gave rise to new synthetic methods, which are already used to prepare heterocycles and biologically active and natural compounds.

We are presenting the third part of the review on gold catalysis (for previous Parts, see Refs 1 and 2), devoted to the use of gold-containing catalysts in modern organic chemistry. This Part covers gold-catalyzed addition to double bonds present in alkenes, cumulated and conjugated dienes and other organic compounds. We hope that this paper will be interesting and useful for researchers in organic synthesis.

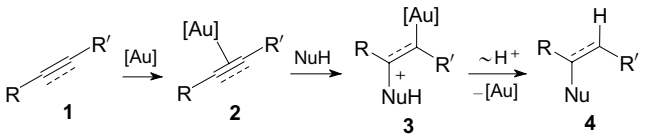
The following abbreviations are used:

ACP — alkylidenecyclopropane,
Ad — adamantyl,
AIBN — azobis(isobutyronitrile),
BINAP — 2,2′-bis(diphenylphosphino)-1,1′- binaphthyl,
BMIM — 1-n-butyl-3-methylimidazolium,
Boc — *tert*-butyloxycarbonyl,
bpy — 4,4′-bipyridine,
Bs — benzenesulfonyl,
Cbz — benzyloxycarbonyl,
Cy — cyclohexyl,
DBU — 1,8-diazabicyclo[5.4.0]undec-7-ene,
DCE — 1,2-dichloroethane,
DCM — dichloromethane,
DFT — density functional theory,
DIPAMP — 1,2-bis[(*o*-anisyl)phenylphosphino]ethane,
dppm — bis(diphenylphosphino)methane,
dr — diastereomeric ratio,
DTBM-SEGPhos — (*R*)-(−)-5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi(1,3-benzodioxole),
ee — enantiomeric excess,
EWG — electron-withdrawing group,
IBu^{t} — 1,3-bis(2,6-di-*tert*-butylphenyl)imidazol-2-ylidene,
IPr — 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene,
JohnPhos — 2-(di-*tert*-butylphosphino)biphenyl,
MCP — methylenecyclopropane,
Ms — methanesulfonyl (mesyl),
MS — molecular sieves,
MW — microwave radiation,
Naph — naphthyl,
NHC — *N*-heterocyclic carbene,
NIS — *N*-iodosuccinimide,
NP — nanoparticles,
Ns — *p*-nitrobenzenesulfonyl (nosyl),
NuH — nucleophile,
PG — protecting group,
Phth — phthalimido,
PMB — 4-methoxybenzyl,
PVP — poly(*N*-vinyl-2-pyrrolidone),
rt — room temperature,
SEM — 2-(trimethylsilyl)ethoxymethyl,
SIMes — 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene,
Solv — solvent,
TBHP — *tert*-butylhydroperoxide,
TBS — *tert*-butyldimethylsilyl,
TCE — tetrachloroethane,
Tf — trifluoromethanesulfonyl (triflyl),
Th — thienyl,
THP — tetrahydropyran-2-yl,
TMS — trimethylsilyl,
Ts — *p*-toluenesulfonyl (tosyl),
VDCP — vinylidenecyclopropanes.

2. Nucleophilic addition to alkenes

As has been indicated in Part I of the review,[1] the carbon–carbon multiple bond of alkenes, allenes and alkynes can be coordinated to gold complexes, being thus activated towards the attack by nucleophiles. In other words, gold interacts with the π-electron system of substrate **1** to give intermediate **2**, which is subjected to the nucleophilic attack (Scheme 1).

Scheme 1



NuH is nucleophile

It was confirmed experimentally that the nucleophile adds to the *anti* position relative to the metal. Then intermediate **3** is protodemetallated to be converted to product **4**, releasing the gold-containing catalyst.

The metal-catalyzed addition of a nucleophile to a carbon–carbon triple bond is more efficient than similar addition to a C=C double bond, which is due to the formation of a much weaker π-bond between the metal of the catalyst and the alkyne, compared to such bond for alkenes.[3,4] Strong π-coordination of the metal in the transition complex results in inhibition. Recently, it was shown [5] that under basic conditions (for example, in the presence of

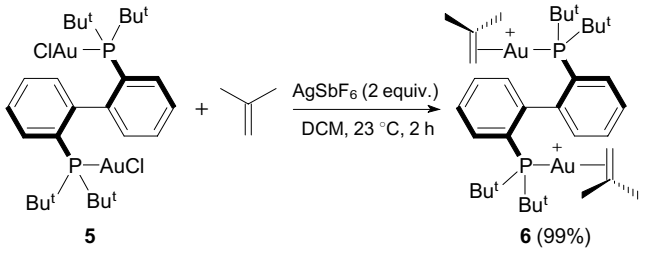
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Translation: Z.P.Svitanko

triethylamine), the π-activation of alkenes by gold is more efficient.

Owing to strong π-coordination, it is possible to isolate gold complexes with alkenes. For example, Savjani *et al.*[6] reported results of studying gold(III) complexes with alkenes and characteristics for isolated complexes of this type. Brooner and Widenhoefer[7] synthesized a binuclear gold π-complex with isobutylene in a high yield from substrate **5** (Scheme 2). The structure of complex **6** was determined by NMR spectroscopy and X-ray crystallography.

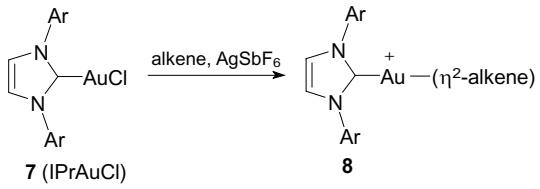
Scheme 2



DCM is dichloromethane

York[8] reported a quantum chemical study of the Au^{I}–alkene bond in the $[(NHC)Au(alkene)]^{+}$ complex, where NHC (N-heterocyclic carbene) is 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene or its analogues. Previously, complexes of this type were prepared from the compound IPrAuCl (**7**) [IPr is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] and appropriate alkenes (Scheme 3).[9]

Scheme 3



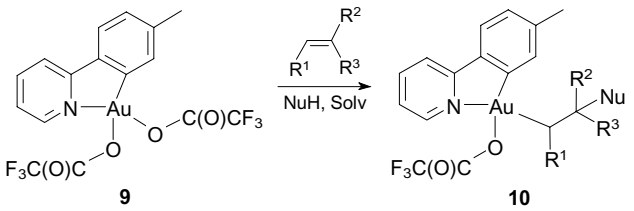
Ar = 2,6-$Pr^{i}_{2}C_6H_3$

Cationic complexes **8a**–**g** are formed in relatively high yields.

A large series of gold(III) complexes with alkenes and nucleophiles was prepared[10] on the basis of trifluoroacetate **9**. Complexes **10** were isolated in a pure state and characterized by physicochemical analysis. In all cases, *anti*-addition of gold to the double bond according to Markovnikov's rule took place (Scheme 4).

Relatively recently, it was found[11,12] that gold(I) complexes are not sufficiently electrophilic to activate the carbon–carbon double bond towards the attack of some nucleophiles; however, gold compounds catalyze these transformations. This suggests that in this case, nucleophilic addition to double bonds follows a different mechanism, possibly, involving activation of the nucleophile or generation of a more potent electrophile, a proton.[13]

Scheme 4



R^1, R^2, R^3 = H, Alk, Ar; NuH = CF_3CO_2H, AcOH, MeOH, EtOH, $Pr^{i}OH$, $Bu^{t}OH$, H_2O; Solv is solvent

2.1. Hydroamination of alkenes

Development of a mild and efficient method for hydroamination of unactivated alkenes is a challenging problem of modern organic chemistry. The reason is the competition between alkenes, weakly coordinated to transition metals, and strongly coordinated aliphatic amines. This results in the preferable formation of a transition metal complex with amine, with the alkene remaining unactivated. The use of Au^{I}-based catalysts offers new prospects for addressing this problem. In recent years, numerous studies have been devoted to the application of various metals as catalysts for hydroamination of unsaturated organic compounds: in particular, the use of silver for hydroamination of alkenes and dienes,[14–16] the use of copper for diamination,[17–19] carboamination[20–22] and hydroamination,[23–29] and also the use of gold for intermolecular and intramolecular hydroamination of alkenes,[30–42] allenes[43–68] and dienes.[35,37,40,69–75]

It is noteworthy that most hydroamination reactions of terminal alkenes in the presence of transition metal-based catalysts result in the formation of Markovnikov addition products.[34,76–78] Meanwhile, the anti-Markovnikov hydroamination is a fairly complicated synthetic task[79] and is much more rarely encountered.[80–83]

The interest in the hydroamination of alkenes has been permanently increasing during the last decades, since this reaction has a huge potential for the synthesis of natural compounds and pharmaceutical agents.[84–87]

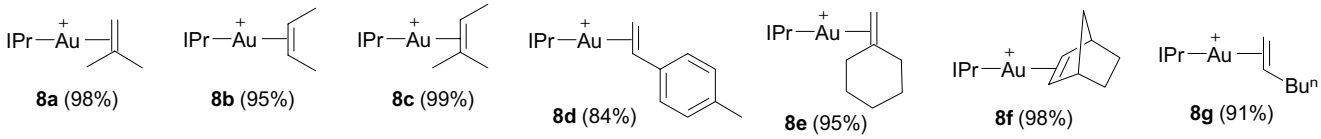
2.1.1. Intermolecular hydroamination of activated alkenes

The aza-Michael reaction was studied rather extensively,[88–95] but the use of gold catalysis of this reaction started relatively recently. Scheme 5 shows an example of reaction of enones **11** with carbamates **12**[88] catalyzed by the gold chlorides. The yield of products **13** is nearly quantitative.

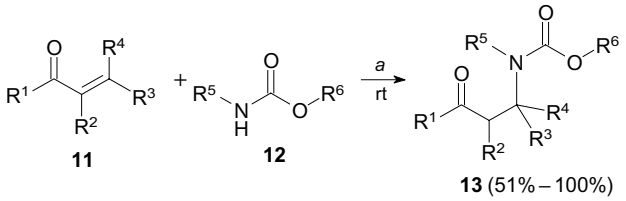
This reaction can also be catalyzed by $PtCl_4$, $IrCl_4$ and $ReCl_5$; however, the highest activity was found for $AuCl_3$.[88]

A classical combination of the gold chloride complex IPrAuCl (**7**) and the silver salt AgOTf [where Tf is trifluoro-

Structures 8



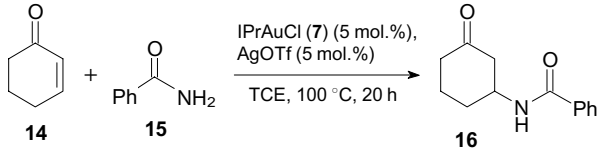
Scheme 5



(*a*) $AuCl_3$ or AuCl (10 mol.%), DCM, rt; R^1 = Alk, Ar; R^2, R^3, R^4, R^5 = H, Alk; R^3 = Alk, Bn

methanesulfonyl (triflyl)] was used to catalyze the intermolecular hydroamination of activated alkenes, for example, cyclohex-2-en-1-one (**14**), with benzamide (**15**) (Scheme 6).[96]

Scheme 6



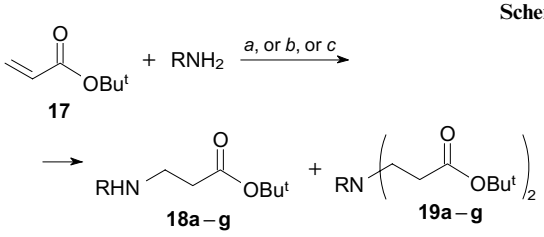
TCE is tetrachloroethane

This reaction is carried out in the presence of catalysts based on both Au^I and Au^{III} (Ref. 96). It was shown that the complex IPrAuCl (**7**) does not catalyze this reaction. For the preparation of the active catalyst, IPrAuOTf,[97] an equimolar amount of AgOTf should be added to the reaction mixture. The degree of conversion of the starting compounds to product **16** increases when Au^I complexes with electron-rich phosphines or NHC ligands [*e.g.*, IBu^tAuCl, IBu^t is 1,3-bis(2,6-di-*tert*-butylphenyl)imidazol-2-ylidene] are used as precatalysts. The Au^{III}-based catalysts showed much lower activity. No changes in the catalyst activity were noted if the catalyst was prepared *in situ* rather than isolated in advance.

In this reaction, no influence of silver ions on the catalytic activity of gold was observed,[98] as confirmed by retention of catalytic activity of the complex IPrAuOTf filtered through the Celite™ diatomite.[97] The complex IPrAuOTf proved to be less active than catalysts based on other metals, which catalyzed this reaction at room or even lower temperature. However, this complex can be isolated from the reaction mixture as IPrAuOH, regenerated and reused.

One more example of gold-catalyzed addition of amines to activated alkenes was reported by Pirovano *et al.*[99] In some cases, hydroamination product **18**, formed from *tert*-butyl acrylate (**17**), is further converted to tertiary amine **19** (Scheme 7, Table 1).

Scheme 7



(*a*) IPrAuCl (**7**) (5 mol.%), AgOTf (5 mol.%), PhMe, 100 °C; (*b*) PhMe, 100 °C; (*c*) PhMe, 30 °C

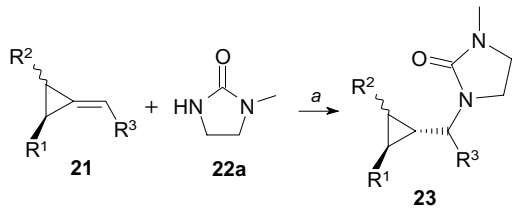
Table 1. Hydroamination of *tert*-butyl acrylate in the presence of the Au catalyst (see Scheme 7).[99]

Compound	R	Time /h	Yield of **18** + **19** (%)		
			conditions *a*	conditions *b*	conditions *c*
a	Pr^i	40	0 + 70	37 + 38	8 + 0
b	Bn	20	17 + 82	53 + 47	25 + 0
c	Cy	30	39 + 60	100 + 0	23 + 0
d	Ph	70	65 + 0	0	See [a]
e	Bu^n	20	0 + 97	0 + 90	44 + 0
f	Bu^t	20	28 + 0	32 + 0	0
g	BzNH	20	0 + 100	0 + 100	0 + 5

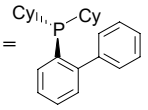
[a] The reaction was not carried out.

Widenhoefer and co-workers [100] demonstrated that the use of a gold complex with ligand **20** to catalyze the hydroamination of alkylidenecyclopropanes (ACP) **21** with 1-methylimidazolidin-2-one (**22a**) results in the formation of the anti-Markovnikov hydroamination product **23** (Scheme 8). The reaction is characterized by high chemo-, regio- and diastereoselectivity.

Scheme 8

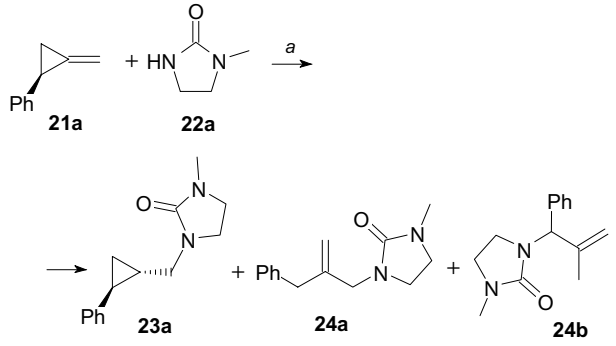


(*a*) [(**20**)AuNCMe]SbF_6 (5 mol.%), 1,4-dioxane, 80 °C, 18 h; R^1 = Alk, Ph, CO_2Alk; R^2 = H, Alk, CO_2Alk; R^3 = H, Me;

20 =  ; Cy is cyclohexyl

This is, perhaps, the first example of gold-catalyzed hydroamination of alkenes, resulting in the anti-Markovnikov addition product. As has already been noted, this process has high chemoselectivity; the yield of the alkene hydroamination product (for example, compound **23a**) is 1.5 times higher than the total yields of products **24a**,**b**

Scheme 9



(*a*) [(**20**)AuNCMe]SbF_6 (5 mol.%), 1,4-dioxane, 80 °C, 18 h

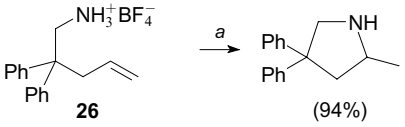
formed upon cyclopropane ring cleavage (with substrate conversion of > 98%) (Scheme 9).

In addition, this reaction has high diastereoselectivity (*anti*-hydroamination predominates over formation of the *syn*-product). This set of features makes this reaction valuable for modern organic synthesis. Relying on analysis of NMR spectroscopy data, Widenhoefer and co-workers [100] suggested that high regioselectivity is associated with partial sp-hybridization of the internal carbon atom. A detailed quantum chemical investigation of this reaction using density functional theory (DFT) method was reported by Wang *et al.*[79]

2.1.2. Hydroamination of unactivated alkenes

Intramolecular reactions. The first example of gold-catalyzed hydroamination of unactivated alkene was reported by Bender and Widenhoefer.[36] In the presence of a gold complex with ligand **25**, ammonium salt **26** participates in the reaction (Scheme 10).

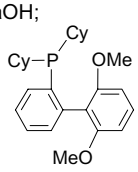
Scheme 10



26 (94%)

(*a*) 1) (**25**)AuCl (5 mol.%), AgOTf (5 mol.%), PhMe, 80 °C, 18 h; 2) NaOH;

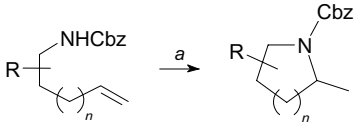
25 =



Gold nanoclusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (PVP) can be used as efficient catalysts for intramolecular hydroamination of unactivated alkenes.[32] This catalyst is stable to moisture and air. A high catalytic activity was found for gold-based bimetallic nanoparticles [101] Au – M, where M = Pt, Pd, Cu, Ni. In this case, hydroamination follows Markovnikov's rule.

In 2006, the research team headed by Widenhoefer [102] reported an example of intramolecular hydroamidation of alkenylcarbamates **27**. The reaction proceeded even for labile carbamates. In the presence of a gold complex with the JohnPhos ligand (**28**) [JohnPhos is 2-(di-*tert*-butylphosphino)biphenyl], product **29** was also formed according to Markovnikov's rule (Scheme 11).

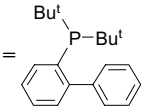
Scheme 11



27 **29** (59% – 97%, 15 examples)

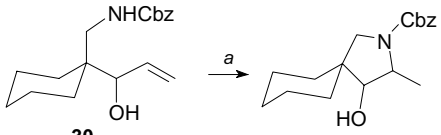
(*a*) (**28**)AuCl (5 mol.%), AgOTf (5 mol.%), 1,4-dioxane, 60 – 100 °C, 16 – 68 h; R = OH, OAc, Ar, Alk; *n* = 1, 2; Cbz is benzyloxycarbonyl;

28 =



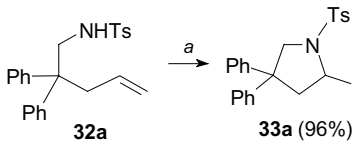
More intramolecular hydroamidation reactions of unactivated alkenes were reported in other publications.[39, 42, 102 – 104] For example, alkene **30** cyclizes to give substituted pyrrolidine **31**, while alkene **32a** is converted to derivative **33a** (Scheme 12).

Scheme 12



30 **31** (91%, *dr* = 3.6 : 1)

(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), 1,4-dioxane, 60 °C; *dr* is diastereomeric ratio



32a **33a** (96%)

(*a*) [Ph_3PAu]OTf (5 mol.%), PhMe, 85 °C, 17 h; Ts is *p*-toluenesulfonyl (tosyl)

The hydroamidation reaction similar to those described above was also accomplished under aerobic conditions in the presence of a base. Gold clusters supported on polyvinylpyrrolidone, Au-PVP, were used as the catalyst (Scheme 13).[31, 32, 105] During the reaction, oxygen was adsorbed on gold clusters, which finally resulted in the formation of cationic centres on their surface. Experiments with isotopically labelled compounds demonstrated that solvent (ethanol) participates in the protonolysis of the C – Au bond.

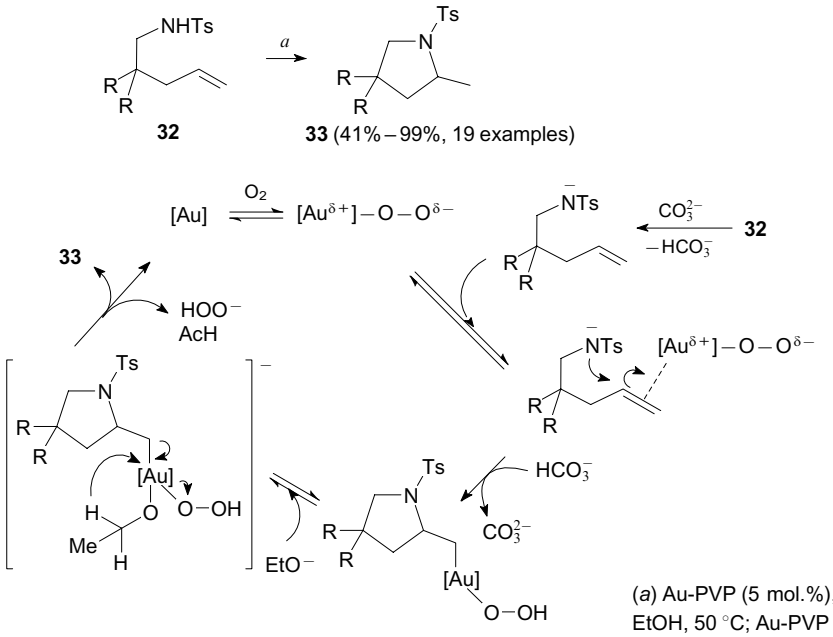
Binuclear gold complex **34** with a chiral phosphoric acid makes it possible to perform the enantioselective intramolecular hydroamidation of *N*-alkenylurea **35**.[30] It should be noted that the enantiomeric excess (*ee*) of product **36** is moderate (Scheme 14). It was shown that binuclear gold complex **34** substantially accelerates the cyclization by means of proximal and bimetallic activation of both reaction counterparts — the double bond and the nitrogen atom of urea.

Toste and co-workers [78] converted substrate **37** to gold(I) alkyl complexes **38** by Au^I-catalyzed intramolecular addition of various nucleophilic amide groups to a double bond. The use of deuterium-labeled compounds and X-ray crystallography confirmed the *anti*-addition of the nucleophile to the gold-activated double bond. The protonolysis of the $C(sp^2)$ – Au bond was the fastest and the most efficient step.[106, 107] However, attempts at the protodeauration of complex **38** resulted in the formation of the initial alkene **37**.[108] Nevertheless, the Alk – Au^I bond is cleaved under reduction conditions, thus yielding 2-methylpyrrolidine derivative **39** (Scheme 15).

Terminal alkenes **40** containing tosylamide (R = Ts, X = CH_2) [41] or carbamate (X = O) [39] groups undergo an intramolecular reaction catalyzed by the Au^I – Ag^I system to be converted to the corresponding cyclic lactams or carbamates **41** in moderate to good yields (Scheme 16).

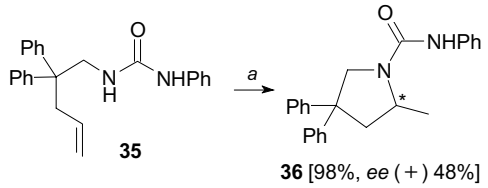
Zhu *et al.*[109] reported an example of intramolecular hydroamidation of alkenes **32**, **42** and **43** accompanied by

Scheme 13



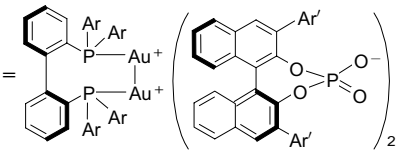
(*a*) Au-PVP (5 mol.%), Cs_2CO_3 (300 mol.%), EtOH, 50 °C; Au-PVP = [Au]

Scheme 14



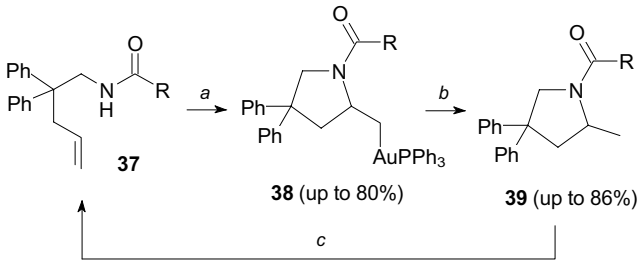
(*a*) **34** (5 mol.%), 1,4-dioxane, rt, 3 h;

34 =



Ar = 3,5-$Me_2C_6H_3$, Ar′ = 4-(2-Naph)C_6H_4; Naph is naphthyl

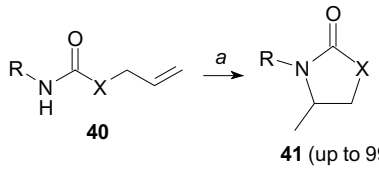
Scheme 15



(*a*) $[(Ph_3PAu)_3O]BF_4$ (0.4 equiv.), Et_3N (2 equiv.), $CDCl_3$; (*b*) $NaBH_4$, EtOH; (*c*) TsOH, $CDCl_3$; R = $NHBu^t$, OPh, OBu^t

arylation, which is catalyzed by the carbene gold complexes with the NHC ligands, for example, SIMesAuCl (**44**) [SIMes is 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]. The reaction, which proceeds in the presence of Selectfluor®, includes oxidative cross-coupling with arylboronic acids and gives rise to arylmethyl-substituted pyrrolidines **33** and their analogues **45** and **46** (Scheme 17).

Scheme 16



(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), PhMe, 60 – 100 °C, 24 – 30 h; X = CH_2, O; R = Ph, 4-ClC_6H_4, Bz, Ts

The mechanism proposed for this reaction[109,110] is depicted in Scheme 18 in relation to the conversion of substrate **32b**.

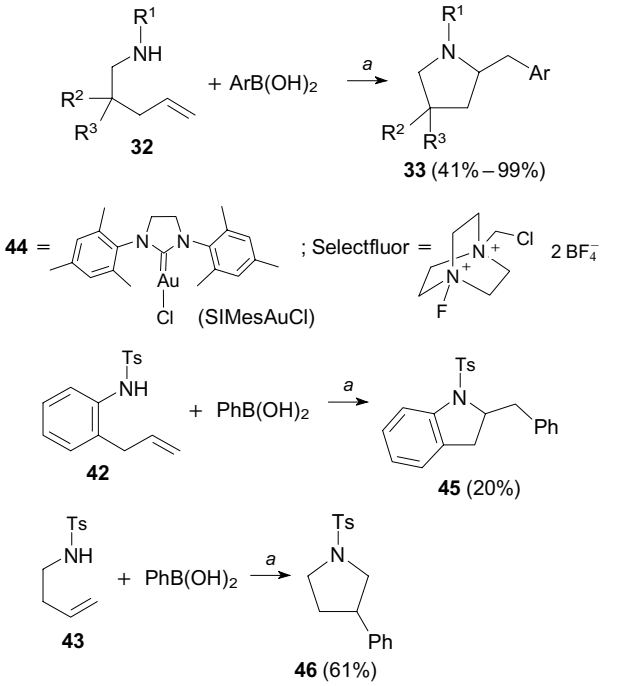
A similar reaction was described earlier,[111–113] but in these cases, gold(I) mono- and bis-phosphine complexes were used as catalysts.

Under the hydroamidation – oxidative cross-coupling conditions indicated above, ureas **47** also undergo cyclization to give cyclic products **48** (Scheme 19).[109] In the case of compound **47** containing a benzyl-substituted amino group, the yields of products are much higher (66% – 88%) than in the case of the tosyl derivative (12% – 40%).

The application of the Au^I/Au^{III} catalytic cycle allowed Iglesias and Muñiz[33] to carry out intramolecular double hydroamination of alkene **49** and thus to obtain annulated imidazolinones **50** in high yields (Scheme 20). Among several catalysts tested in this reaction, the highest activity was found for the gold triphenylphosphine complex. The reaction was carried out in the presence of $PhI(OAc)_2$ and sodium acetate.

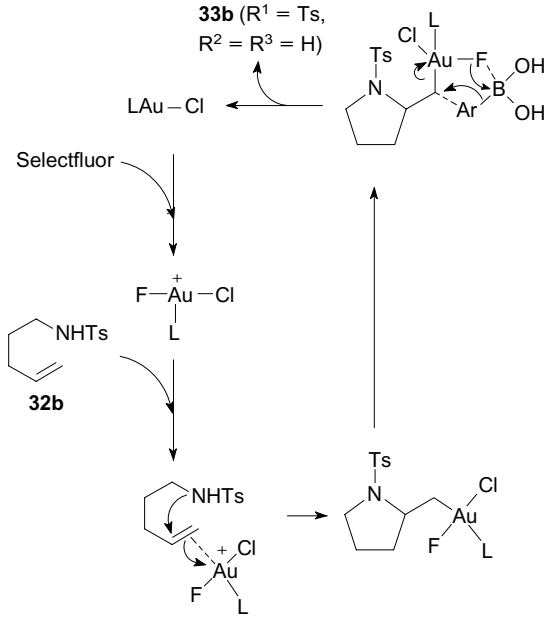
By using deuterium-labelled substrate **49a** and studying the stoichiometry of this reaction with isolated model gold complexes, the authors proposed the mechanism presented in Scheme 21. Diamination proceeds *via anti*-aminoauration to give alkyl gold(I) complex **A**, which is oxidized to gold(III) complex **B**. The anionic complex **C** undergoes intramolecular nucleophilic substitution with inversion of

Scheme 17

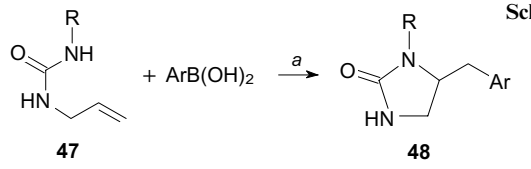


(*a*) SIMesAuCl (**44**) (5 mol.%), Selectfluor (1.5 equiv.), MeCN, 80 °C; R^1 = Ts, Ms, Ns; R^2 = H, Ph; R^3 = H, Me, Ph; Ar = 4-XC_6H_4 (X = H, Me, Bu^t, Br, Cl, F, CF_3); Ms is methanesulfonyl (mesyl), Ns is *p*-nitrobenzenesulfonyl (nosyl)

Scheme 18

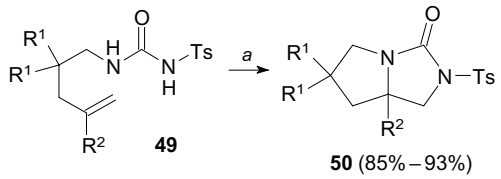


Scheme 19



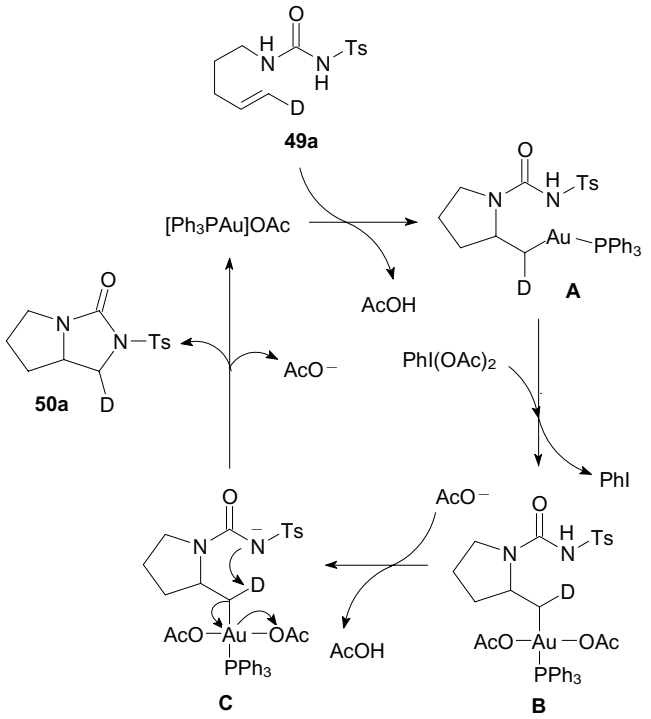
(*a*) SIMesAuCl (**44**) (5 mol.%), Selectfluor (1.5 equiv.), MeCN, 80 °C, 24 h; R = Bn, Ts; Ar = 4-XC_6H_4 (X = H, Me, Bu^t, Br, Cl, F, CF_3)

Scheme 20



(*a*) [Ph_3PAu]OAc (7.5 mol.%), $PhI(OAc)_2$ (1.2 equiv.), NaOAc (0.5 equiv.), DCE, 55 °C, 10 h; R^1, R^2 = H, Me, Ph; $R^1 – R^1$ = $(CH_2)_2$; DCE is 1,2-dichloroethane

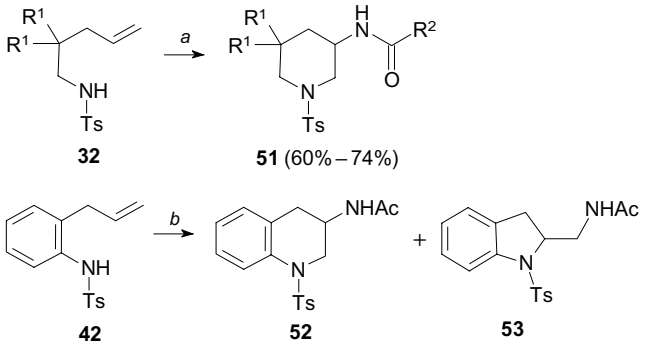
Scheme 21



configuration at the carbon centre to give product **50a** and the reduced gold(I) complex.

De Haro and Nevado [114] accomplished oxidative difunctionalization of alkenes including intra- and intermolecular

Scheme 22



(*a*) R^2CN, H_2O (2 equiv.), [Ph_3PAu]SbF_6 (5 mol.%), Selectfluor (2 equiv.), $NaHCO_3$ (1 equiv.), 80 °C, 1.5 h; R^1 = H, Me, Ph; R^2 = Me, Et, Pr^n; $R^1 – R^1$ = $(CH_2)_5$;
(*b*) MeCN, H_2O (2 equiv.), [Ph_3PAu]SbF_6 (5 mol.%), Selectfluor (2 equiv.), $NaHCO_3$ (1 equiv.), 80 °C, 1.5 h

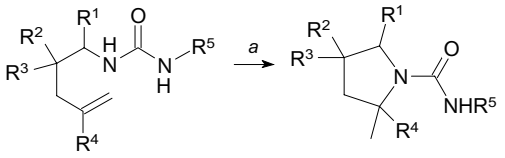
aminoamidation of *N*-tosylpent-4-enes **32** (Scheme 22). The reaction also includes the Au^{I}/Au^{III} catalytic cycle. The cationic gold(I) complex $[(Ph_3P)Au]SbF_6$ is used as the catalyst and Selectfluor serves as the oxidant. Substrates **32** undergo 6-*endo*-*trig*-cyclization to give *N*-piperidin-3-ylcarboxamides **51** in high yields. Nitriles serve as solvents. Some nitriles such as acetonitrile, propionitrile and butyronitrile function as external nucleophiles. The reaction takes place only for terminal alkenes. A similar transformation occurs for *o*-allylaniline **42**, which is converted to an equimolecular mixture of products **52** and **53** in a total yield of 70%. The diamination reaction has a great synthetic value, because it can serve for the synthesis of products different from those obtained in a similar reaction catalyzed by the Pd^{II}/Pd^{IV} system, which is characterized by 5-*exo*-selectivity.[115]

De Haro and Nevado[114] suggested that diamination proceeds, in this case, along different pathways, as shown in Scheme 23 for substrate **32b**. The major pathway includes gold(I)-catalyzed 6-*endo*-*trans*-aminoauration of the substrate to give intermediate **54**, which is oxidized with Selectfluor to give the corresponding Alk-Au^{III} complex **55**. The displacement of fluorine by acetonitrile, hydrolysis of the activated ligand and the subsequent reductive elimination afford the major aminoamidation product **51a**. The formation of five-membered amines, for example, compound **56** (see also product **53** in Scheme 22) can be interpreted as resulting from the 5-*exo* pathway, which includes the formation of intermediates **57** and **58**. It was also noted that diamination may proceed by an alternative mechanism in which the common bicyclic aziridinium cation **59**,[116,117] formed upon the intramolecular reductive elimination of intermediates **55** and/or **58**, undergoes the Ritter reaction[118] with the solvent (nitrile) yielding the final products **51a** and/or **56**. Feige *et al.*[119] reported further studies of this type of reaction.

In 2011, Hong's research team[120] employed the acyclic aminooxycarbene gold(I) complex **60** as an efficient catalyst for the hydroamidation of alkenylureas **61** to give substituted pyrrolidines **62** in good yields (Scheme 24).

Intermolecular reactions. Examples of intermolecular amine addition to unactivated double bonds are shown in

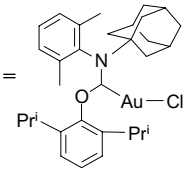
Scheme 24



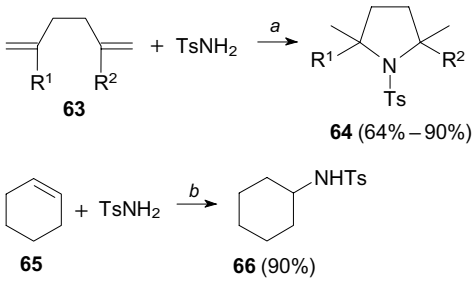
61 **62** (49% – 99%)

(*a*) **60** (5 mol.% – 10 mol.%), AgOTf (5 mol.% – 10 mol.%);
R^1 = H, Ph; R^2, R^3 = H, Alk, Ph; R^4 = H, Me; R^5 = Ph, Bn;

60 =



Scheme 25



63 **64** (64% – 90%)

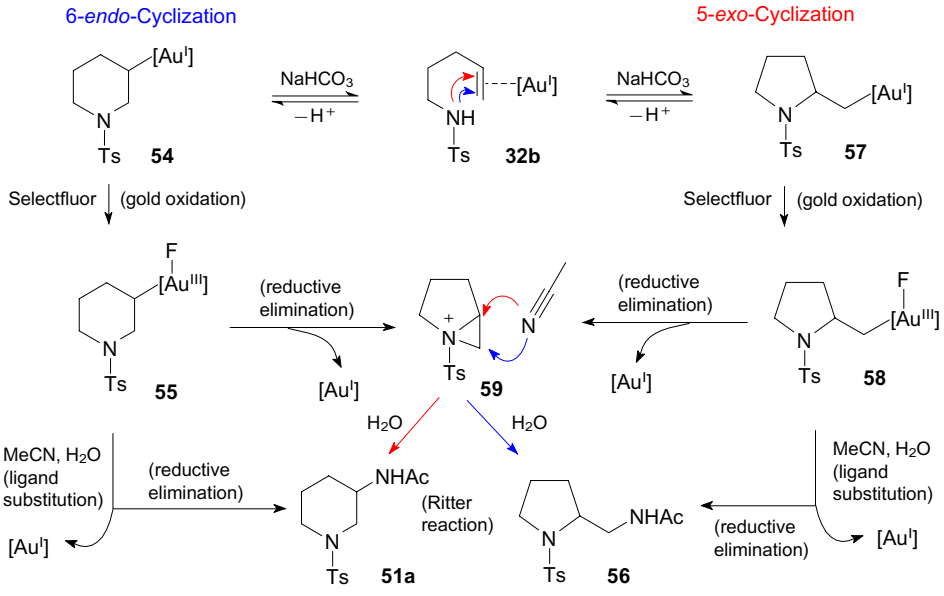
65 **66** (90%)

(*a*) $[Ph_3PAu]OTf$ (5 mol.%), PhMe, 95 °C; R^1, R^2 = H, Alk;
(*b*) $[Ph_3PAu]OTf$ (5 mol.%), PhMe, 85 °C, 15 h

Scheme 25. The reaction proceeds with tosylamide (in the case of the Cbz group, only an intramolecular reaction is possible, as noted above). Using isotope labelling, *anti*-addition of amine and gold was demonstrated.[39] The cited paper describes the addition of amine to nonconjugated dienes **63** to give pyrrolidines **64** and to a cyclic alkene, cyclohexene (**65**), to give protected cyclohexylamine **66**.

Mono-, 1,1-di- and trisubstituted alkenes can also participate in the intermolecular hydroamination, which usu-

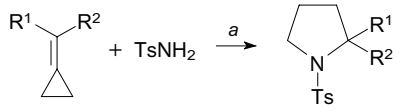
Scheme 23



ally results in the formation of the Markovnikov product, most often, with a good selectivity.

Nitrogen-containing saturated heterocyclic systems are of great importance in organic synthesis, largely due to the fact that they are fragments of important biologically active molecules. It was found that pyrrolidine derivatives are formed in good yields from methylenecyclopropane and $TsNH_2$ in the presence of gold(I) salts, soft Lewis acids, as catalysts.[3, 121 – 138] Shi *et al.*[38] described a domino reaction of this type. The hydroamination of methylenecyclopropanes **67** with tosylamide in the presence of the $Au^I – Ag^I$ system furnishes pyrrolidines **68** in moderate to good yields (Scheme 26).

Scheme 26

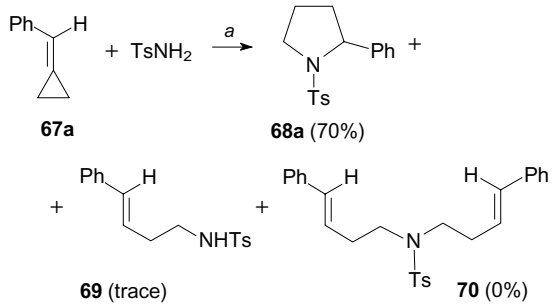


67 **68** (34% – 76%)

(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), PhMe, 85 °C, 4 – 24 h; R^1 = Bu^n, n-C_7H_{15}, XC_6H_4 (X = H, 2-Me, 3-Me, 4-Me, 4-Cl, 3-Br, 2-OMe, 4-OEt), 1-Naph; R^2 = H, Me, Bu^n; $R^1 – R^2$ = $(CH_2)_5$, $(CH_2)_2CHPh(CH_2)_3$

N-Tosyl-2-phenylpyrrolidine (**68a**) was isolated in 70% yield. Analysis of the reaction mixture showed the presence of a trace of product **69**, while no dialkylated derivative **70** was detected in this case (Scheme 27).

Scheme 27



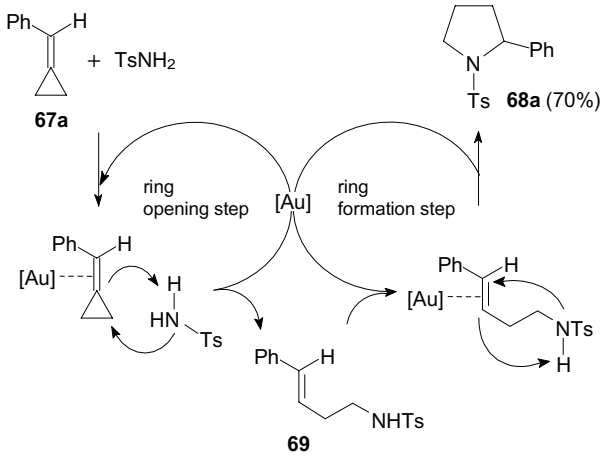
(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), PhMe, 85 °C

The reaction mechanism proposed by Shi *et al.*[38] is presented in Scheme 28.

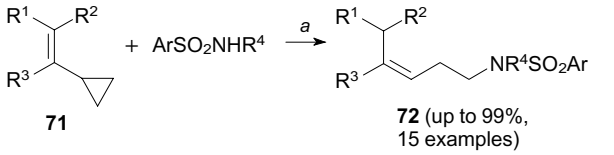
The use of other Lewis acids such as $Sn(OTf)_2$, $In(OTf)_3$, $Yb(OTf)_3$, $Sc(OTf)_3$ and $BF_3 \cdot Et_2O$ in this reaction gives, in most cases, only product **69** with a minor amount of dialkylated derivative **70**. Electron-donating substituents in the aromatic ring promote the formation of pyrrolidine derivatives **68** in a higher yield over a shorter period of time. Electron-withdrawing groups decrease the yield of the cyclic product, while the reaction time increases.

Hydroamidation of vinylcyclopropanes **71** with arenesulfonamides in the presence of $[Ph_3PAu]OTf$ results in the formation of homoallylic amides **72**.[139] The reaction is accompanied by regioselective opening of the three-membered ring. Products **72** usually have a *Z* configuration at the double bond; only in the case of α-phenyl-substituted

Scheme 28



Scheme 29



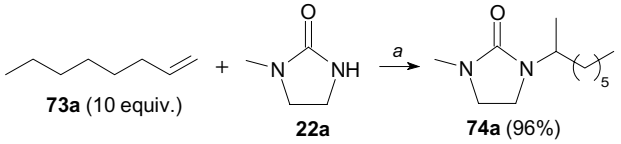
(*a*) $[Ph_3PAu]OTf$ (10 mol.%), PhMe, 50 °C, 24 h; R^1 = H, Me, Ph; R^2, R^4 = H, Me; R^3 = Alk, Ar

vinylcyclopropanes, was an *E* configuration established for the products (Scheme 29).

A drawback of the methods described above is the need to use sulfonamides as nitrogen-containing nucleophiles.

In 2009, Widenhoefer's group reported[34] the application of a cationic gold(I) complex to catalyze the intermolecular hydroamidation of unactivated alkenes. A number of unactivated terminal alkenes, including ethylene, were converted to the corresponding Markovnikov hydroamidation products. The reaction was conducted at temperatures of 100 °C and lower and gives excellent yields of products. Drawbacks of this reaction include the necessity of using a 10-fold excess of alkene (in order to attain good yields of products) and only cyclic ureas, for example, compound **22a**, as the amide substrate. For example, oct-1-ene (**73a**) was converted to imidazolinone **74a** in a quantitative yield (Scheme 30).

Scheme 30

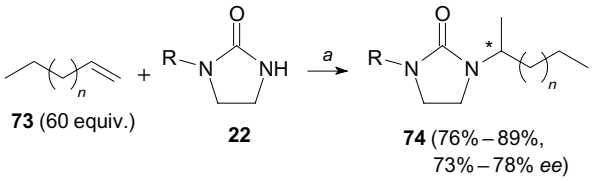


(*a*) (**28**)AuCl (5 mol.%), $AgSbF_6$ (5 mol.%), 1,4-dioxane, 100 °C, 24 h

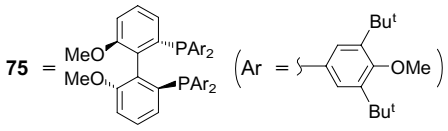
In the presence of chiral bis-phosphine ligand **75**, the reaction can follow an asymmetric pathway with good enantioselectivity (Scheme 31).[34]

Couce-Rios *et al.*[140] performed quantum chemical DFT calculations for the gold(I)-catalyzed hydroamination of terminal alkenes. The reaction mechanism and regioselectivity were discussed.

Scheme 31



(*a*) (**75**)AuCl (5 mol.%), $AgSbF_6$ (5 mol.%), 1,4-dioxane, 100 °C, 24 h; R = Alk, Ar; *n* = 4 – 8

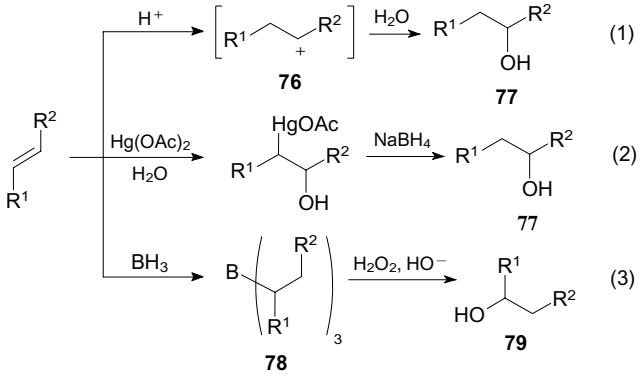


2.2. Addition of oxygen nucleophiles to the double bond

The direct addition of the O – H group to the C=C bond has a high synthetic value, since it offers a route to alcohols, ethers and esters over a smaller number of steps.[141] Traditionally, three methods are used to convert alkenes to alcohols.

1. Protonation of the C=C bond gives the carbocation intermediate **76**, which then reacts with water to form alcohol **77** [reaction (1) in Scheme 32]. The selective formation of thermodynamically more stable carbocation gives the Markovnikov addition product. This process is not widely used in organic synthesis due to drastic reaction conditions. The presence of a strong acid and high temperature bring about numerous side reactions, for example, isomerization of the carbocation. Furthermore, the reverse reaction, dehydration, may prove to be thermodynamically preferable.

Scheme 32

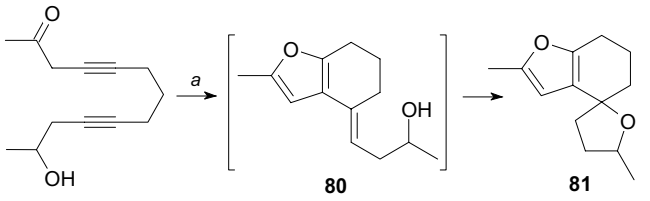


2. Oxymercuration results in the formation of products **77** corresponding to Markovnikov's rule under mild conditions [reaction (2)]. This approach avoids the formation of a carbocationic intermediate and, hence, precludes isomerization producing by-products.[142] The main drawback of the method is the involvement of highly toxic mercury.

3. Hydroboration of the C=C bond followed by oxidative cleavage of the trialkylborane intermediate **78** opens up the route towards the selective formation of anti-Markovnikov addition products, alcohols **79**, under mild conditions. This approach is extensively used in organic synthesis, in particular, in the asymmetric synthesis involving chiral boranes[143] or chiral transition metal complexes.[144] As drawbacks of the method, note the need for a stoichiometric amount of borane and the sensitivity of some functional groups to the oxidant used in the reaction.

In 2000, Hashmi *et al.*[145] reported the first example of gold-catalyzed intramolecular addition of the hydroxyl group to activated alkene in intermediate **80** *via* a domino process, resulting in spirocyclic compound **81** (Scheme 33).

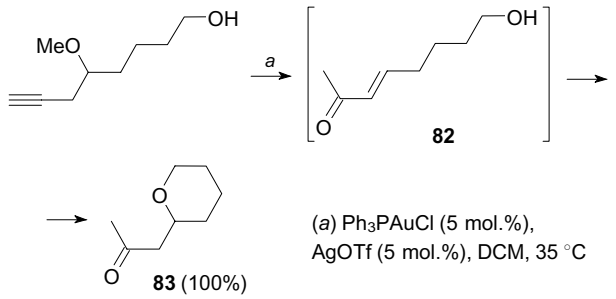
Scheme 33



(*a*) $AuCl_3$ (1 mol.%), MeCN

One more example of intramolecular addition of the hydroxy group to the double bond in intermediate **82** was reported by Jung and Floreansig.[128] In this case, the double bond is activated and product **83** is formed in a quantitative yield (Scheme 34).

Scheme 34



Quantum chemical simulation [13] leads to the conclusion that the actual catalyst of the gold-catalyzed hydroxyarylation and hydroacylation is a Brønsted acid, the proton, which is locally formed with the participation of the gold complex, which is a Lewis acid. The addition of oxygen nucleophiles to double bonds is the subject of several reviews, for example, Kaur *et al.*[146] considered the gold-catalyzed formation of C – O bonds for the synthesis of six-membered oxygen-containing heterocyclic compounds.

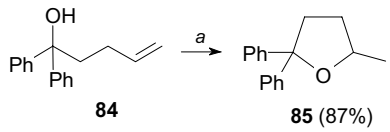
2.2.1. Intramolecular addition to unactivated alkenes

The cyclization of ω-alkenols affords five- or six-membered oxygen-containing heterocycles. The reaction is usually catalyzed by strong Brønsted acids (*e.g.*, TfOH) and conducted in polar solvents at elevated temperatures (~100 °C).[147]

The heterogeneous Au-PVP catalyst was used for the efficient cyclization of γ-alkenol **84** under aerobic conditions at 50 °C (Scheme 35).[148] It is noteworthy that this reaction proceeds in a basic medium and gives 2-methyl-5,5-diphenyltetrahydrofuran (**85**) in a high yield.

The application of the Ph_3PAuCl – AgOTf catalytic system for the cyclization of monoallylic diols **86** – **89** makes it possible to prepare tetrahydrofuran **90** and tetrahydropyrans **91** – **93**.[149] The reactions are carried out in dichloromethane in the presence of 4 Å molecular sieves

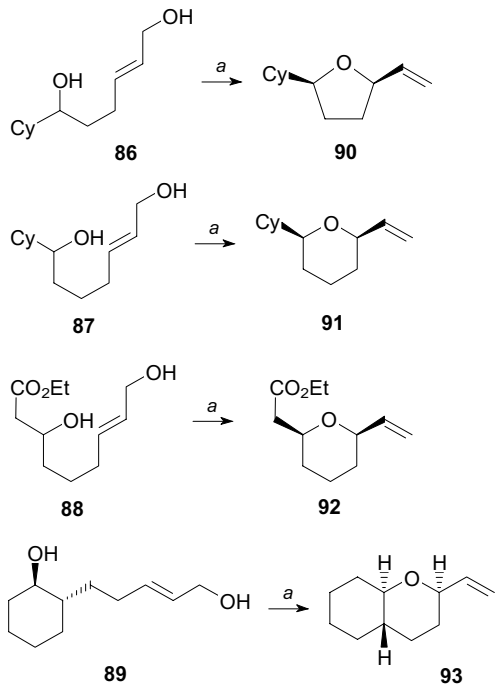
Scheme 35



84 **85** (87%)

(*a*) Au-PVP, DBU (200 mol.%), H_2O, DMF, 50 °C, 16 h; DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene

Scheme 36



(*a*) Ph_3PAuCl (1 mol.%), AgOTf (1 mol.%), DCM, 4 Å MS

Table 2. Cyclization of monoallylic diols in the presence of the Au catalyst (see Scheme 36).[149]

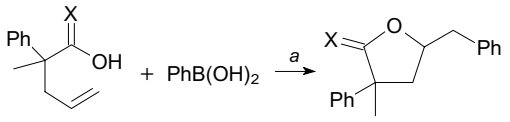
Product	Time /h	Temperature /°C	Yield (%)	*dr*
90	0.5	rt	89	5 : 1
	10	−50	79	7 : 1
91	0.3	rt	95	11 : 1
	8	−50	80	> 25 : 1
92	0.5	rt	96	6 : 1
	9	−10	99	12 : 1
	21	rt	80	5 : 1
93	0.3	rt	87	4 : 1
	10	−50	76	5 : 1
	10	−78	79	10 : 1

(MS) at temperatures from −78 °C to room temperature using 1 mol.% of the catalyst. The product yields vary from 79% to 99% (Scheme 36, Table 2).

It can be seen in Scheme 36 that the reaction is insensitive to the structural features of the substrate over rather broad limits and in the case of 2,6-disubstituted tetrahydropyrans, the reaction is highly diastereoselective and results in the formation of 2,6-*cis*-products. The product yields increase with increasing reaction temperature, while the diastereoselectivity increases with decreasing temperature. Later, transfer of chirality was demonstrated for gold-catalyzed cyclization of monoallylic diols.[150] The formation of a particular enantiomer in this reaction is dictated by the geometry of the starting alkene.

Zhu *et al.*[109] reported the intramolecular addition of a hydroxy group to the terminal double bond of compounds **94** accompanied by arylation as a result of simultaneous cross-coupling with phenylboronic acid (Scheme 37). The reaction is accompanied by a gold redox cycle and affords products **95** as mixtures of *cis* and *trans* isomers.

Scheme 37

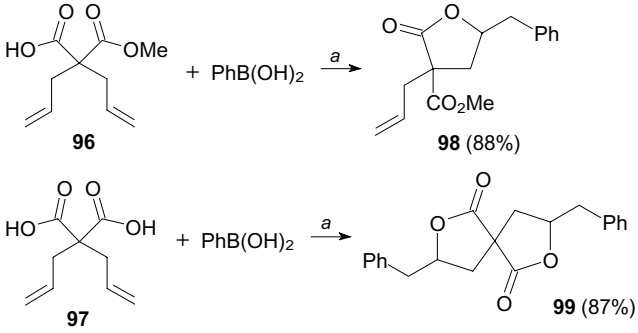


94 **95**

(*a*) SIMesAuCl (**44**) (5 mol.%), Selectfluor (1.5 equiv.), MeCN, 80 °C, 24 h; X = 2 H (94%, *cis* : *trans* = 45 : 55), O (92%, *cis* : *trans* = 43 : 57)

A similar cyclization of diallyl-substituted malonic monoester **96** and diacid **97** affords dihydrofuranones **98** and **99** in *cis* to *trans* ratios of 44 : 56 and 30 : 70, respectively (Scheme 38).

Scheme 38



(*a*) SIMesAuCl (**44**) (5 mol.%), Selectfluor (1.5 equiv.), MeCN, 80 °C, 24 h

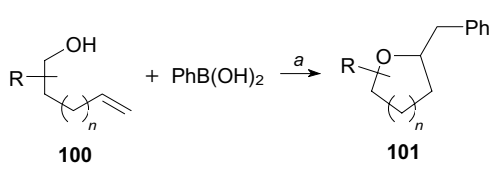
Unsaturated alcohols **100** were allowed to react with 2 equiv. of phenylboronic acid under the same conditions[111] to give a number of tetrahydrofurans **101** (Scheme 39); the structures and yields of some products (compounds **101a**–**g**) are depicted below.

A new, highly efficient process was proposed for hydroxy- and aminoarylation of alkenols **102**, conducted in the presence of gold and a photoredox dual catalyst on exposure to visible light, which resulted in the synthesis of heterocyclic compounds **103** in good yields and with high diastereoselectivity.[151] Unlike the classical gold-catalyzed hydroxyarylation of alkenes,[111–114] the dual catalysis can be implemented at room temperature without using a stoichiometric amount of a strong external oxidant (Scheme 40).

2.2.2. Intermolecular addition to unactivated alkenes

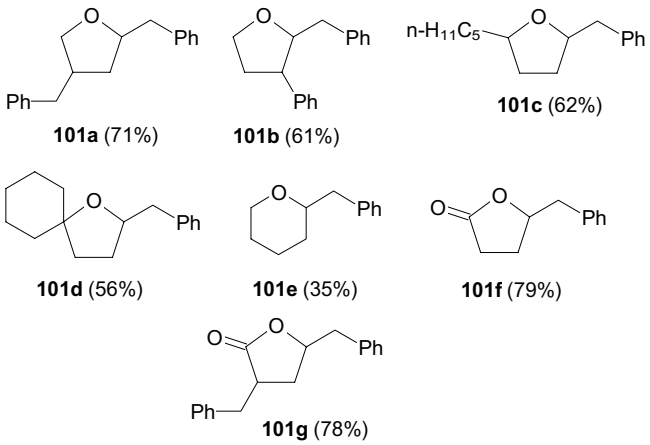
In 2005, the first example of addition of phenols and carboxylic acids to simple alkenes under relatively mild conditions using an Au^I catalyst was reported (Fig. 1).[152]

Scheme 39



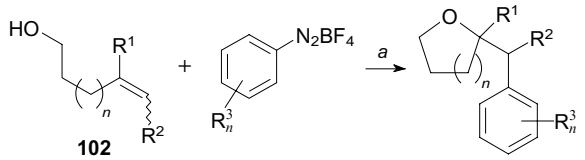
100 **101**

(*a*) Ph_3PAuCl (5 mol.%), Selectfluor (2 equiv.), MeCN, 60 °C, 2 – 8 h; n = 1, 2



101a (71%) **101b** (61%) **101c** (62%) **101d** (56%) **101e** (35%) **101f** (79%) **101g** (78%)

Scheme 40



102 **103** (32% – 83%)

(*a*) $Ph_3PAuNTf_2$ (10 mol.%), $Ru(bpy)_3(PF_6)_2$ (2.5 mol.%), 23 W fluorescent lamp, degassed MeOH, rt, 4 – 16 h; n = 1, 2; R^1 = H, Me, Ph; R^2 = H, Me; R^3_n = H, 4-Me, 4-Ph, 4-F, 4-Br, 4-CO_2Et, 3-Me-5-CF_3, 2-Br-4-Cl; bpy is 4,4′-bipyridine

The reaction products corresponded to Markovnikov's rule. The authors used 4 equiv. of alkene, which could be recovered at the end of the reaction; the Ph_3PAuCl – AgOTf system (2 mol.% – 5 mol.%) served as the catalyst, and toluene was employed as the solvent. At a temperature of 85 °C, the reaction took 14 to 18 h.

For some substrates, for example, for compound **104**, the formation of ether **105** was accompanied by the formation of product **106** (80% total yield), which was due to the ability of gold to catalyze alkene isomerization under the reaction conditions (Scheme 41). Later, it was shown that trifluoromethanesulfonic acid catalyzes the same reactions under milder conditions, which prevents decomposition and isomerization of compounds.[153]

Hydroalkoxylation of unactivated alkenes with $HOCH_2CH_2X$ (where X is halogen or alkoxy group) was implemented using the $(C_6F_5)_3PAuCl$ – AgOTf catalytic system.[154] Their addition to oct-1-ene was reversible; ethanol and other unsubstituted aliphatic alcohols did not react.

The addition of alcohols and phenols to alkenes catalyzed by a combination of Au^{III} and Cu^{II} was reported by Zhang and Corma.[155] The reaction proceeded as the Markovnikov addition to give product **107** (Scheme 42, conditions *a*). When the Au^{III} salt alone was used, it was rapidly reduced. Other Au^{III} salts were also employed as co-catalysts. However, in the presence of the Au^{I} complex (**108**) as the catalyst and acrylonitrile as the alkene, alcohol addition

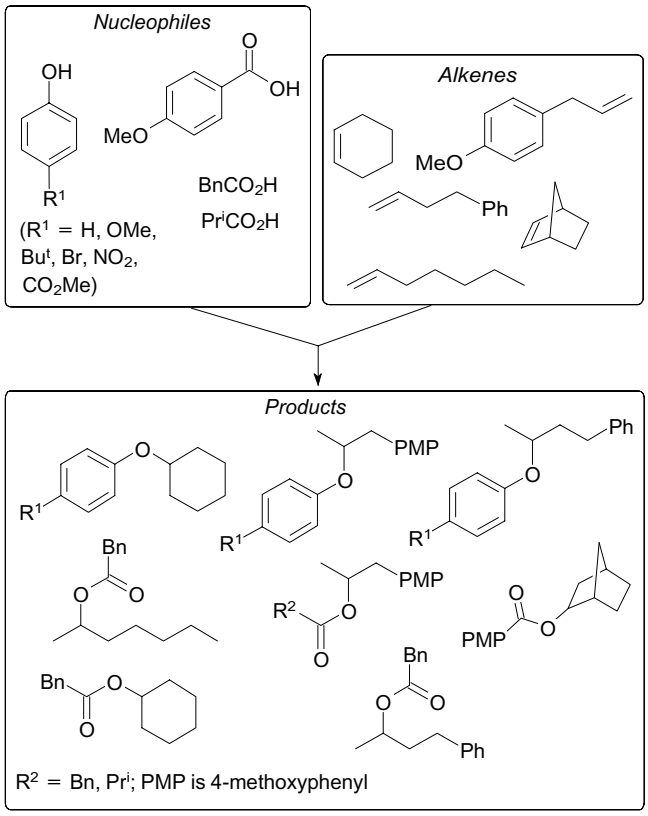
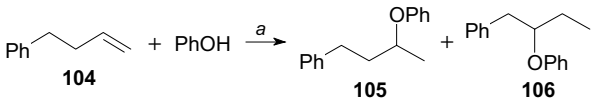


Figure 1. Product of addition of phenols and carboxylic acids to simple alkenes with Au^{I} catalyst.[152]

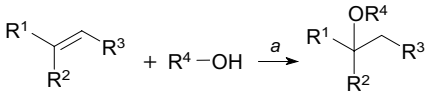
Scheme 41



104 **105** **106**

(*a*) Ph_3PAuCl (2 mol.%), AgOTf (2 mol.%), PhMe, 85 °C

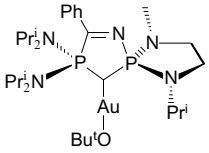
Scheme 42



107

(*a*) $AuCl_3$ (8 mol.%), $CuCl_2$ (16 mol.%), PhMe, 120 °C (for R^1, R^2, R^3 = H, Alk, Ar; R^4 = Alk, Ar; 35% – 90% yield); (*b*) **108** (5.5 mol.%), C_6D_6, rt (for R^1 = R^2 = H, R^3 = CN: R^4 = Alk, Ar; 10% – 60% yield);

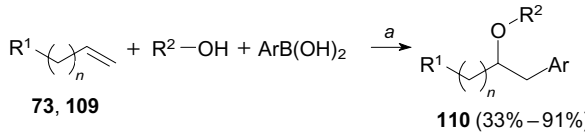
108 =



occurred against Markovnikov's rule[156] (see Scheme 42, conditions *b*).

Gold(III)-catalyzed three-component oxidative oxyarylation of terminal alkenes **73** (R^1 = H, Me) and their functionalized analogues **109** was reported by Melhado *et al.*[112] The reaction includes a two-electron redox cycle of gold. Nucleophiles are represented by alcohols (primary, secondary and even tertiary ones; in the last-mentioned case, however, the product yields are moderate), carboxylic acids or even water (Scheme 43).

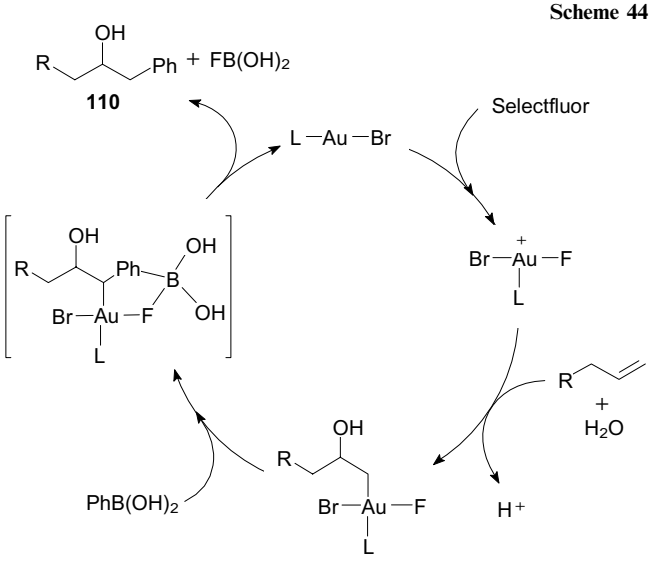
Scheme 43



(*a*) dppm(AuBr)$_2$ (5 mol.%), Selectfluor (2 equiv.), MeCN, 50 °C;
R^1 = H, Me, CH(Ph)CH_2NHC(O)CF_3, C_6H_4Br-2, OC_6H_4CN-2, OC(O)$C_6H_4NO_2$-4, Phth, N(Ts)All; R^2 = H, Me, Et, Pr^i, Bu^t, CH_2Bu^t cyclo-C_5H_9, $(CH_2)_2$OMe, CH(Me)CH_2OMe, Ac, C(O)Et, C(O)Pr^i, Bz; Ar = C_6H_4X (X = 4-Me, 4-Br, 3-F, 2-CO_2Me); *n* = 1 – 10;
dppm is bis(diphenylphosphino)methane, Phth is phthalimido

When water is used as the nucleophile, secondary alcohols **110** are formed in good yields.[112] In this case, a fairly broad range of substituents is possible for substrate **109**. The reaction mechanism proposed by the authors is presented in Scheme 44.

Scheme 44

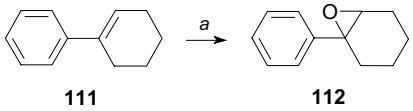


2.3. Preparation of oxiranes

The synthesis of epoxides from alkenes is usually heterogeneously catalyzed by gold.[157] One of the few examples of homogeneous catalysis was reported by Corma *et al.*,[158] who converted 1-phenylcyclohexene (**111**) to epoxide **112** with chiral gold complex **113** as a homogeneous catalyst (Scheme 45). Other alkenes also react in the presence of this catalyst, giving products in moderate yields (53% – 66%) and with moderate enantioselectivity (10% – 32% *ee*).

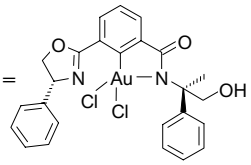
Heterogeneous catalysis using supported gold catalysts is applied more often to prepare epoxides **114a** – **g** from

Scheme 45



(*a*) **113** (0.5 mol.%), O_2, PhIO or $NaClO_4$, rt;

113 =



Scheme 46



Table 3. Synthesis of oxiranes from alkenes in the presence of a heterogeneous Au catalyst (see Scheme 46).

Compound **114**	R^1	R^2	Possible catalyst	Ref.
a	H	H	Au/TiO_2	159 – 166
b	Me	H	Au/TiO_2	167 – 184
c	Et	H	Au/(TiO_2 + TS-1 zeolite)	185
d	n-C_6H_{13}	H	Au/(CeO_2 + Ti-MCM-41)	186
e	$(CH_2)_6$		Au/graphite or Au/SiNWs	187 – 190
f	Ph	H	Au on various supports	191 – 201
g	Ph	Ph	Au/SiO_2 or Au/TiO_2	202 – 205

Note. MCM-41 are mesoporous molecular sieves, SiNWs are silicon nanowires.

alkenes. Propene, styrene, stilbene and other alkenes are applicable as substrates for this reaction (Scheme 46, Table 3).

Quite a few patent applications[159 – 166] on gold-catalyzed epoxidation of alkenes were submitted. Substituents at the double bond reduce the selectivity of epoxidation. This is observable even for propene. Haruta's group[167] used the Au/TiO_2 catalyst to obtain propylene oxide **114b** and carried out the first epoxidation in the presence of hydrogen, which allowed for oxygen activation under mild conditions.[168] The supports utilized for gold include titanium compounds: TiO_2,[169 – 172] Ti-SBA-15,[169, 173] titanium-containing hexagonal mesoporous silica Ti-HMS,[174] titanosilicate TS,[175 – 178] and a mixture of titania and silica ($TiO_2 – SiO_2$)[179] also Al_2O_3 films.[180] Hydrogen in the $O_2 + H_2$ combination as the oxidant can be replaced, in some cases, by water.[170, 180, 181] This replacement has a high practical value for chemical industry. Haruta's research team[181] showed, in particular, that the use of gold clusters with < 2 nm size and an $O_2 + H_2O$ mixture as the oxidant results in a more efficient epoxidation of propene compared to catalytic systems based on silver and copper. Although the yield of product **114b** remains low, gold catalysis makes it possible to attain selectivity of more than 50%. Air[179] and N_2O[172] were also employed as oxidants. The role of gold nanoparticles in the synthesis of oxiranes from alkenes was studied in considerable detail. Spectroscopic evidence for propene adsorption on gold nanoparticles during epox-

idation has been reported.[182] Experimental and theoretical studies of the catalytic activity of subnanometre Au_6-Au_{10} gold clusters were described by Lee *et al.*[180] and the model calculations for oxidation on the Au(111) surface were reported by Torres and co-workers.[183, 184]

A combination of two catalysts, Au/TiO_2 and TS-1 zeolite, was applied for epoxidation of but-1-ene giving oxirane **114c** (see Scheme 46) with molecular oxygen in aqueous solution under very mild conditions.[185] Carbon monoxide served for oxygen activation (sacrificial reductant).

One-pot epoxidation of oct-1-ene was accomplished with a catalyst comprising a mixture of gold nanoparticles supported on CeO_2 and Ti-MCM-41 in the presence of hydrocarbons and azobis(isobutyronitrile) (AIBN) as the activator.[186] Product **114d** was isolated in a moderate yield with high selectivity.

The selective epoxidation of cyclooctene to give oxirane **114e** was catalyzed by supported gold and proceeded without a solvent.[187] Air was used as the oxidant, while *tert*-butyl hydroperoxide (TBHP) functioned as the peroxide initiator of the reaction. The catalyst activity depended on the nature of the support, decreasing in the order graphite > SiO_2 > TiO_2. The catalyst was prepared by the sol immobilization method,[188] which considerably increased the catalyst activity, while maintaining the selectivity. The use of a hydroperoxide initiator for the oxidation of alkenes with oxygen was first described in 2005.[189]

Gold-modified silicon nanowires (SiNWs) demonstrated excellent catalytic activity towards selective oxidation of *cis*-cyclooctene to epoxycyclooctane **114e**, which was formed with high selectivity (90%) and in moderate yield (38%).[190] Air served as the oxidant.

A wide range of supports was used for styrene epoxidation catalyzed by gold nanoparticles. Among them are alkaline earth metal oxides,[191, 192] Group IIIa metal oxides, transition and rare earth metal oxides,[192] boron nitride, SiO_2 and carbon,[193] carbon nanotubes,[194] the silicas SBA-12[195] and SBA-15,[196] hybrid mesoporous silica gel,[197] Au(111) surface,[198] a manganese porphyrin complex[199] and ionic liquids.[200] Turner *et al.*[193] showed that the 55-atom gold cluster (~1.4 nm size) supported on an inert material is an efficient catalyst for selective oxidation of styrene with oxygen. Meanwhile, gold nanoparticles of 2 nm and larger size are inactive. Quantum chemical modelling of styrene oxidation (DFT method) leads to the conclusion that the minimum size of gold clusters that catalyze the epoxidation is 38 atoms.[201]

Trans-stilbene was converted to stilbene oxide **114g** under aerobic conditions in methylcyclohexane, the reaction being initiated by *tert*-butyl hydroperoxide.[202] Gold nanoparticles of 1.8 nm size supported on passivated silica gel (containing no OH groups) served as the catalyst. They were prepared by controlled functionalization of the silica gel surface by Au^I complexes and their subsequent reduction with hydrogen under mild conditions. The selectivity of *trans*-stilbene epoxidation is 80%, with substrate conversion being almost complete. For aerobic oxidation of stilbene, gold nanoparticles supported on titania (AuNPs/TiO_2)[203, 204] and on hybrid nanocrystalline titania[205] were used.

2.4. Oxidative cleavage of double bonds

Xing *et al.*[206] reported the oxidation of the carbon – carbon double bond in alkenes homogeneously catalyzed by gold(I)

Scheme 47

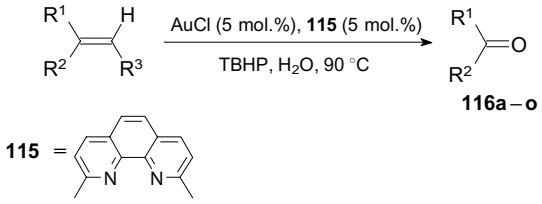


Table 4. Oxidative cleavage of the double bond in alkenes in the presence of a Au catalyst (see Scheme 47).[206]

Compound **116**	R^1	R^2	R^3	Time /h	Yield (%)
a	Ph	Ph	H	3	**93**
b	Ph	4-MeC_6H_4	H	3	**84**
c	Ph	4-$MeOC_6H_4$	H	3	70
d	Ph	2-MeC_6H_4	H	18	**89**
e	Ph	1-Naph	H	24	56
f	Ph	4-FC_6H_4	H	3	62
g	Ph	4-BrC_6H_4	H	6	**86**
h	Ph	2-MeO-5-ClC_6H_3	H	3	44
i	Ph	2-Th	H	24	53
j	Ph	Me	H	36	39
k	Ph	H	Me	36	66
l	Ph	H	H	36	56
m	4-$AcOCH_2C_6H_4$	H	H	24	62
n	2-Naph	H	H	24	52
o	4-$MeO_2CC_6H_4$	H	H	36	20

Note. Th is thienyl. The highest product yields are given in bold.

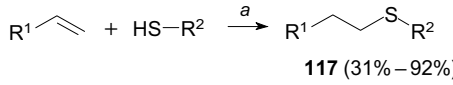
in the presence of ligand **115** to give carbonyl compounds **116a – o** (Scheme 47, Table 4).

Double bond oxidation yielding two carbonyl compounds is an important synthetic approach. Usually, it is implemented as ozonation followed by reduction[207] or as dihydroxylation followed by oxidation.[208] With gold(I) catalysts, TBHP is used as the oxidant and the reaction proceeds under mild conditions in water and tolerates a broad range of substituents in the substrate.

2.5. Hydrothiolation of alkenes

The addition of sulfur nucleophiles to alkenes catalyzed by transition metals is a challenging task for a variety of reasons. First, as has already been noted in this review, alkenes have a low coordination ability, especially in comparison with alkynes. Second, organosulfur compounds are catalyst poisons, which deactivate transition metal-based catalysts.[209] As a result, a few publications have been devoted to the addition of organosulfur compounds to alkenes in the last two decades; among them, papers by Mitamura *et al.*[210] and Ogawa[211] deserve attention. Like in many other processes described, in particular, in our previous reviews,[1, 2] these problems were overcome by using gold-based catalysts. For example, Tamai *et al.*[212] reported the regioselective anti-Markovnikov hydrothiolation of internal alkenes catalyzed by the classical gold complex $Ph_3PAuNTf_2$ (Scheme 48). The reaction is carried out under mild conditions with an excess of thiol. This results in the synthesis of sulfides **117** in moderate to good yields.

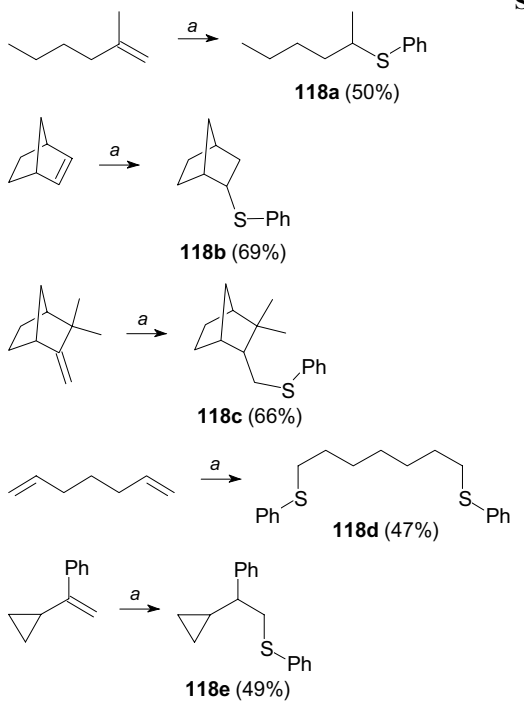
Scheme 48



117 (31% – 92%)

(*a*) $Ph_3PAuNTf_2$ (2 mol.%), THF, 45 °C, 20 h;
R^1 = n-C_8H_{17}, $NC(CH_2)_2$, $HO(CH_2)_3$, $Cl(CH_2)_4$, Ph, Bn, PhO;
R^2 = n-$C_{12}H_{25}$, Bn, 4-XC_6H_4 (X = H, Me, F, Cl)

Scheme 49



118a (50%)

118b (69%)

118c (66%)

118d (47%)

118e (49%)

(*a*) PhSH, $Ph_3PAuNTf_2$ (2 mol.%), THF, 45 °C, 20 h

According to a ^{31}P NMR study of the reaction mixture,[212] the gold ion coordination changed after the addition of thiol into a solution of the starting gold complex. The formed complex was isolated in a pure state and studied by X-ray crystallography. Thus, it was found that the hydrothiolation of alkenes involves the tetranuclear gold complex $[(PPh_3)_4Au_4(SPh)_2](NTf_2)_2$, in which the gold ions occur in one plane, at the corners of a square, linked to one another and to the ligands.

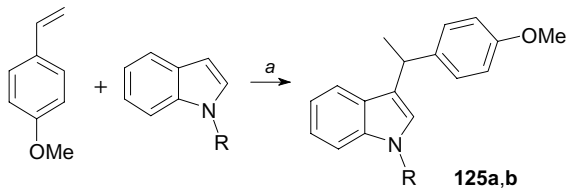
It is noteworthy that benzenethiol, reacts with not only monosubstituted (see Scheme 48), but also disubstituted ethylenes and nonconjugated alkadienes, as shown in Scheme 49 in relation to the synthesis of sulfides **118a** – **e**.

2.6. Formation of carbon – carbon bonds

An interesting situation arises when indoles react with 3,3-disubstituted cyclopropenes **119**. Depending on the conditions, gold(I)-catalyzed addition affords products **120** – **122** (Scheme 50).[213] In addition, the product nature depends on the substituents present in cyclopropene: with increasing size of substituents, bis(indolyl)alkenes **120** and epoxides **121** are predominantly formed. In the presence of complex **123**, either monoaddition (product **122**) or diaddition (product **120**) takes place, depending on the reaction temperature and duration and on whether 2 or 2.2 equivalents of indole are used.

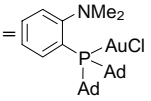
Gold complex **124** with a chelating ligand proved to be an efficient catalyst for intermolecular hydrohetarylation of alkenes, as shown in Scheme 51.[214] Products **125a**,**b** were obtained in high yields.

Scheme 51

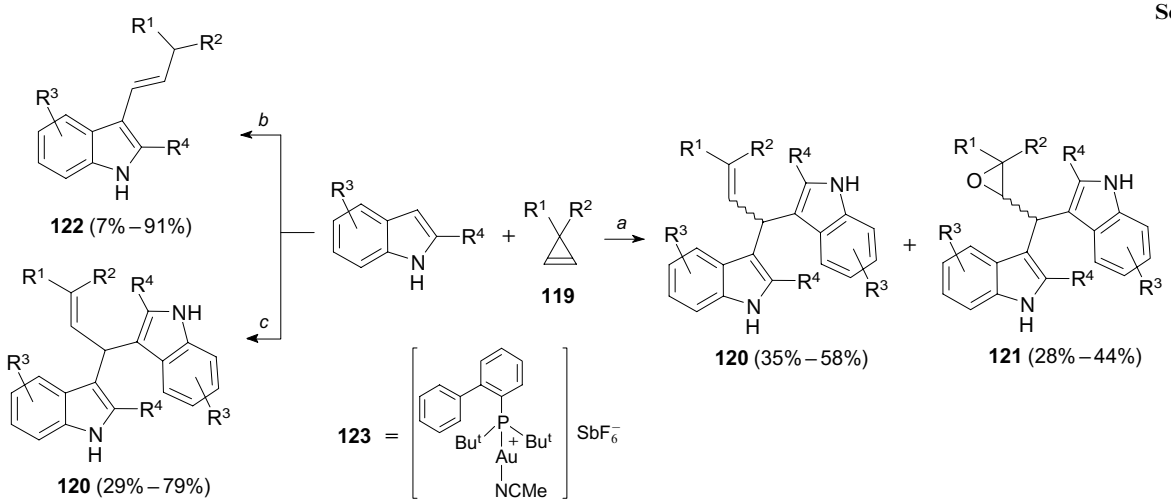


(*a*) **124** – $KB(C_6F_5)_4$ (5 mol.%), $CHCl_3$, 135 °C, 8 h;
R = H (**a**, 93%), Me (**b**, 99%);

124 =



Scheme 50



122 (7% – 91%)

120 (29% – 79%)

119

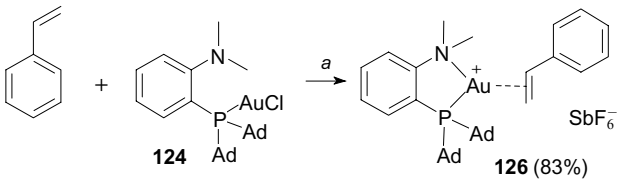
120 (35% – 58%)

121 (28% – 44%)

123 =

(*a*) $Ph_3PAuNTf_2$ (2 mol.%), DCM, rt, 12 h; (*b*) **123** (5 mol.%), DCM, 0 °C, 3 – 9 h; (*c*) **123** (5 mol.%), DCM, Δ, 42 h; **120**, **121** (conditions *a*):
R^1 = R^2 = Cy; R^3 = H, 5-OMe, 5-F; R^4 = H; **120** (conditions *c*): R^1 = Me, Bn, Cy; R^2 = Pr^i, n-C_9H_{19}, Cy, Bn, CH_2Bn, Ph, 1-Ad; R^3 = H, 5-OMe, 5-F, 5-Cl, 6-Cl, 7-Et; R^4 = H, Me; **122**: R^1 = Me, Cy; R^2 = Pr^i, n-C_9H_{19}, Cy, Bn, CH_2Bn, Ph, 1-Ad; R^3 = H, 5-OMe, 5-F, 5-Cl, 6-Cl, 7-Et; R^4 = H;
Ad is adamantyl

Scheme 52

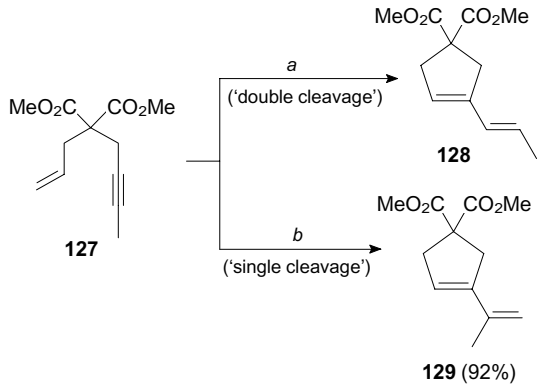


(*a*) $AgSbF_6$, DCM, from −30 to 0 °C, 0.5 h

At low temperature, three-coordinate gold complex with alkene **126** was isolated in a pure state in a high yield (Scheme 52).

The formation of a new carbon – carbon bond in the enyne system **127** proceeds *via* triple bond activation by gold, which was considered in sufficient detail in Part II of our review.[2] Here we would like to draw attention to only one reaction the route of which depends on the gold catalyst (Scheme 53).

Scheme 53



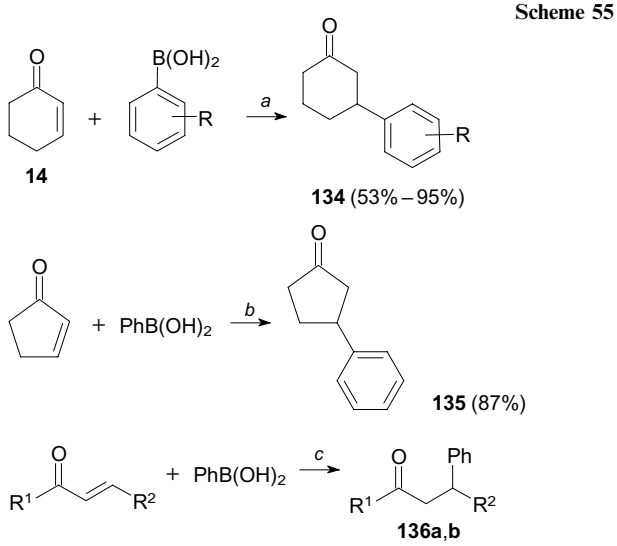
(*a*) Ph_3PAuCl; (*b*) Au/TiO_2, DCE, 70 °C, 4 days

When a cationic gold(I) complex is used as the catalyst [homogeneous catalysis by gold(I)], cyclization of 1,6-enyne **127** gives only product **128** *via* a double cleavage process.[132] However, with TiO_2-supported gold nanoparticles, the reaction gives compound **129**, formed *via* a single cleavage process, as the only product.[215]

The two alternative mechanisms proposed for the reaction of 2-methylfuran with vinyl methyl ketone (but-3-en-2-one) to give ketone **130** (Scheme 54) involve the formation of gold complexes **131** – **133**.[145] Organogold compounds like **131** were reported previously,[216, 217] which confirms the concept of direct auration of electron-rich hetarenes. A similar reaction of pyrroles, which are more nucleophilic, is non-selective. However, indoles or their 7-aza analogues undergo selective monohydroarylation under these conditions.[218 – 221]

Gold supported on TiO_2-UVM-7 is a highly active and selective heterogeneous catalyst, which allows 1,4-addition of various functionalized arylboronic acids to cyclohex-2-en-1-one (**14**) (55% – 98% conversion) and other enones.[222] The reaction is carried out in toluene, products **134** – **136** are formed in high yields and the catalyst can be recovered and reused (Scheme 55).

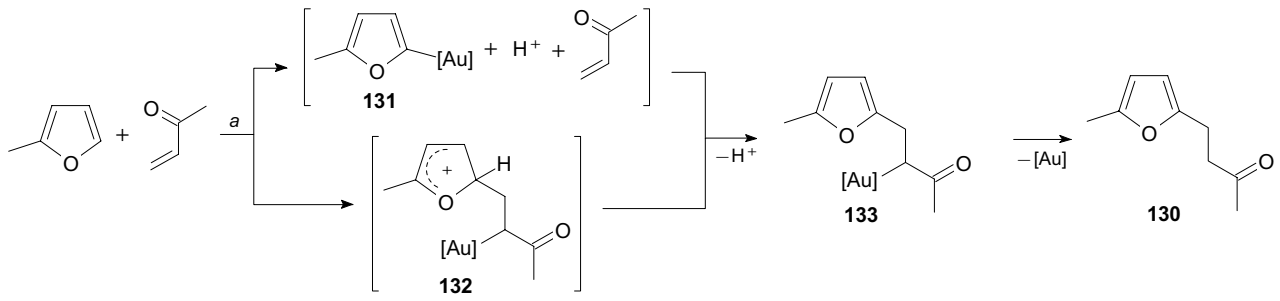
Scheme 55



(*a*) Au/TiO_2-UVM-7, Na_2CO_3, PhMe, 80 °C, 16 h; R = H, 4-OMe, 4-CF_3, 3-Cl, 3-Br, 3-CF_3, 2-Me;
(*b*) Au/TiO_2-UVM-7, Na_2CO_3, PhMe, 80 °C, 8 h;
(*c*) Au/TiO_2-UVM-7, Na_2CO_3, PhMe, 80 °C, 24 h; R^1 = Me, R^2 = n-C_5H_{11} (**a**, 91%); R^1 = R^2 = Ph (**b**, 86%)

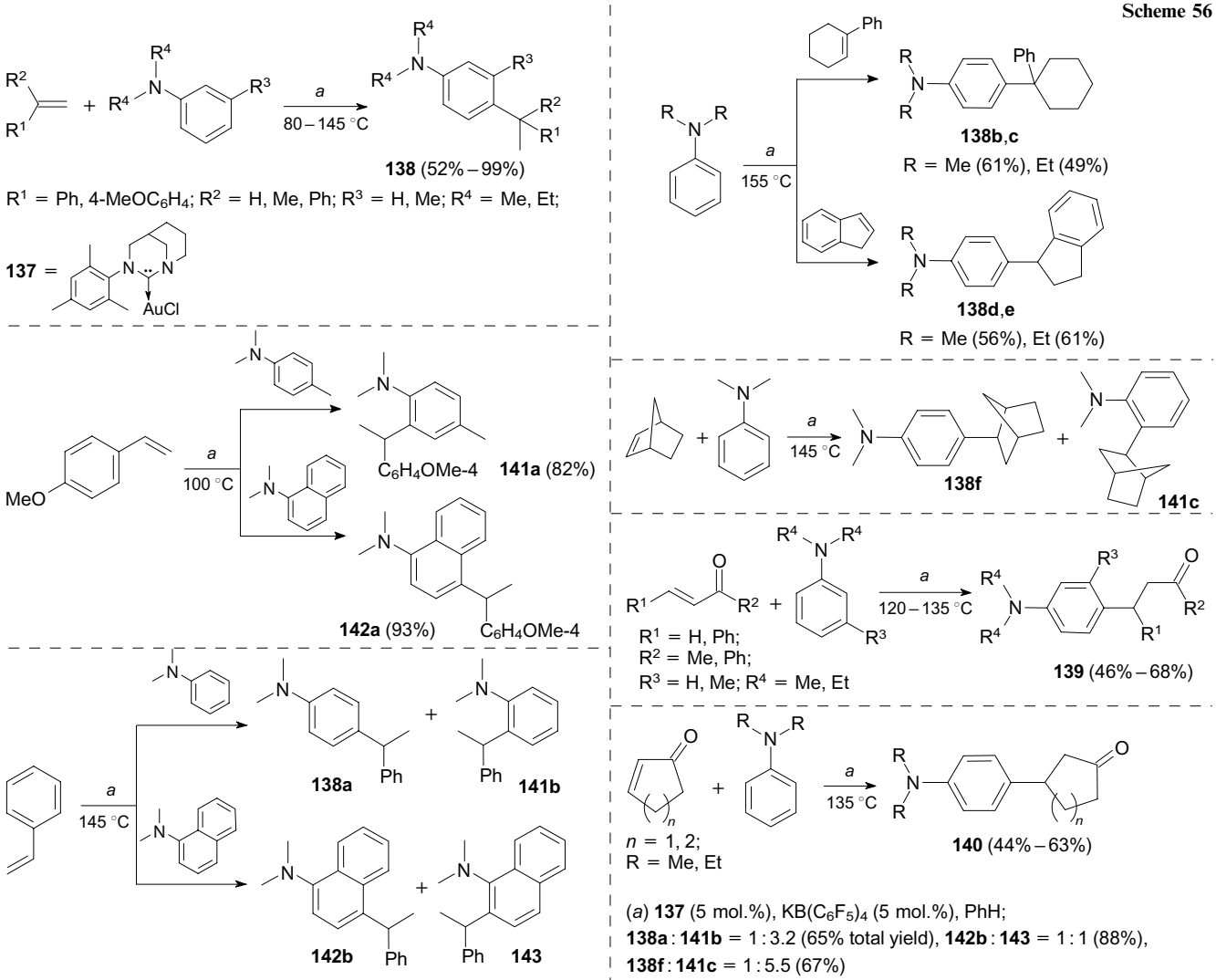
The Friedel – Crafts reaction is an important method for addition of a carbon group to an aromatic system.[223] A large success was attained in this reaction with neutral arenes (such as toluene, anisole and their homologues).[224] In the case of arenes containing an amino group, considerable complications arise, because of coordination of the amino group to the strong Lewis acid used as the catalyst and the proton capture during the C – H activation.[225] The recently prepared complexes of gold(I) with anti-Bredt cyclic diaminocarbenes (for example, compound **137**) proved to be highly efficient catalysts for the Friedel – Crafts reaction involving alkenes and *N*,*N*-dialkylanilines.[226] In this case, hydroarylation follows Markovnikov's

Scheme 54



(*a*) $AuCl_3$ (1 mol.%), MeCN, 20 °C

Scheme 56



rule. The *para*- and/or *ortho*-substitution in the aromatic ring is preferred (Scheme 56). This method was applied to prepare *para*- (**138** – **140**) and *ortho*-substituted anilines (**141**) and analogous aminonaphthalene derivatives **142**, **143**.

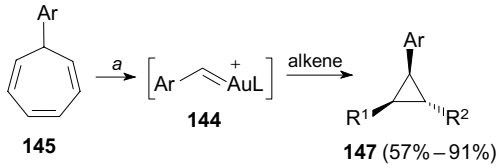
2.7. Cyclopropane synthesis

In 2011, Echavarren's research team [227, 228] proposed a route for the cyclopropanation of styrenes and stilbenes *via* the gold(I)-catalyzed formation of carbenes **144** from 7-arylcyclohepta-1,3,5-trienes **145** in the retro-Buchner reaction (Scheme 57). Complex **146** was used as the catalyst. Substrates **145** and alkenes may contain a rather broad range of substituents. This method allows for the synthesis of 1,2,3-trisubstituted cyclopropanes **147**, which cannot be easily prepared by alternative methods. In the case of styrenes, *cis*-products are predominantly formed (up to 15 : 1).

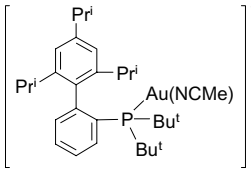
One more example of the synthesis of cyclopropanes **148** by the retro-Buchner reaction *via* generation of gold(I) carbene was reported by Herlé *et al.*[229] and is shown in Scheme 58.

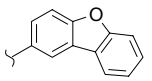
In this reaction, *cis*-vinylcyclopropanes **148** are formed as the major products (the isomer ratio often exceeds 20 : 1).

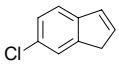
Scheme 57



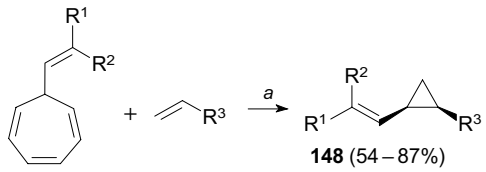
(*a*) **146** (5 mol.%), DCE, 120 °C (– PhH);

146 =  SbF_6^-;

Ar = 4-XC_6H_4 (X = H, F, Cl, Br, OMe), ;

alkene = R^1  R^2 [R^1 = H, Ph; R^2 = YC_6H_4 (Y = H, 4-Me, 4-Bu^t, 4-OMe, 3-NO_2)] or 

Scheme 58



(*a*) **123** (5 mol.%), EtOAc, 75 °C (−PhH); R^1 = Me, 4-XC_6H_4 (X = H, Ac, CF_3, Br); R^2 = H, Me; R^1CR^2 = ; R^3 = YC_6H_4 (Y = H, 4-CF_3, 4-OMe, 4-CO_2Me, 3-Me), Phth

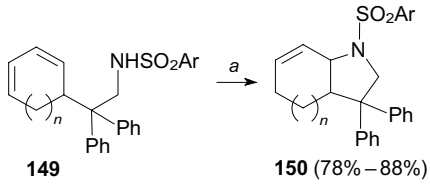
3. Conjugated dienes and styrenes

3.1. Hydroamination

3.1.1. Intramolecular reactions

The cationic gold complex Ph_3PAuCl shows a high catalytic activity towards the intramolecular hydroamidation of cyclic 1,3-diene **149** (Scheme 59).[35]

Scheme 59

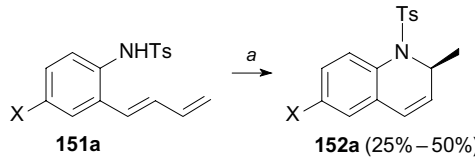


(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), PhMe, 85 °C, 18 h; *n* = 1, 2

Gold species are coordinated to 1,3-diene **149** at the double bond proximal to the sulfonamide group to give the η^2-complex involving the double bond and gold. The *anti*-attack by the sulfonamide group on the terminal carbon atom converts the diene system to a bicyclic fused system with a new C−Au bond in the allylic position. The reaction product **150** is formed upon the successive allylic rearrangement of the η^1-AlAu complex and protodemetallation.

The same catalytic system was used to accomplish the intramolecular cyclization of aniline derivatives **151a** (Scheme 60).[74] When the N-substituent is tosyl, the reaction proceeds selectively by an intramolecular pathway to give Markovnikov products **152a**.

Scheme 60

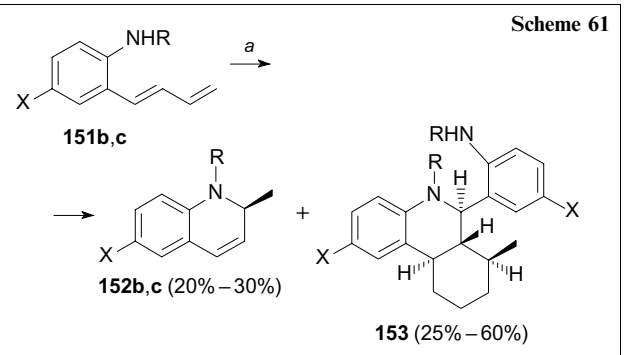


(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), PhMe, 100 °C; X = H, Cl, Br, OMe, CO_2Me

In the case where R is an acyl or ester group (**151b**,**c**), the reaction is no longer selective. The major product in this case is heterocycle **153**, resulting from a reaction sequence of intermolecular hydroamidation of 1,3-diene and [4 + 2]-cycloaddition (Scheme 61).

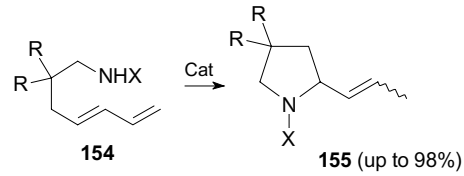
Various transition metals were used to catalyze the intramolecular hydroamination of conjugated acyclic aminodienes **154**. Among the tested catalysts, mention may be made of silver triflate, cationic gold complexes, $FeCl_3$, $InBr_3$ and BINAP−$Cu(OTf)_2$ system [BINAP is 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]. In addition, iodine (Lewis acid) and TfOH (Brønsted acid) were utilized as catalysts (Scheme 62).[15,84] The best results were demonstrated by the cationic gold complex $[(PhO)_3PAu]OTf$ and trifluoromethanesulfonic acid.

Scheme 61



(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), PhMe, 100 °C; R = Ac (**b**), CO_2Et (**c**); X = H, Cl, Br, OMe, CO_2Me

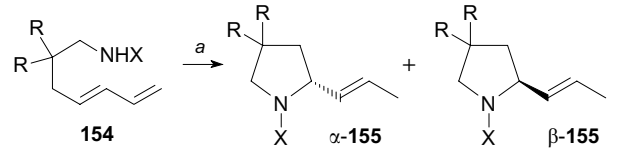
Scheme 62



R = H, Me, Ph; R−R = $(CH_2)_5$; X = Ts, Cbz; Cat = AgOTf, $[(PhO)_3PAu]OTf$, $FeCl_3 \cdot 6H_2O$, [(*R*/*S*)-BINAP]$Cu(OTf)_2$, TfOH

The asymmetric intramolecular hydroamidation of 1,3-dienes **154** was described by Toste's research team.[71] The authors used a binuclear gold complex as the catalyst. The rate and selectivity of the transformation were improved by addition of a potential Brønsted acid, (−)-menthol, which resulted in a total yield of products α-**155** and β-**155** reaching 99%, with their ratio being 9 : 1, while the enantioselectivity was 98% (Scheme 63).

Scheme 63



(*a*) (*R*)-DTBM-SEGPhos$(AuCl)_2$ (3 mol.%), $AgBF_4$ (6 mol.%), (−)-menthol, DCM, rt; R = H, Alk, Ph; X = Ts, Ms; (*R*)-DTBM-SEGPhos is (*R*)-(−)-5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi(1,3-benzodioxole)

Control experiments showed that two stereoisomers are formed by two different mechanisms. In one case, gold is coordinated to the diene, and this is followed by intramolecular nucleophilic addition. The protodeauration of the complex formed upon the nucleophilic addition gives product β-**155**. In the second case, gold is coordinated to menthol, which increases the Brønsted acidity of the alco-

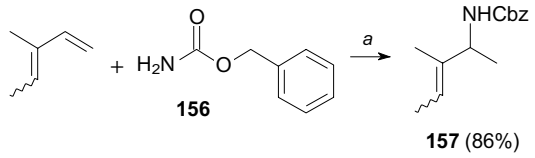
hol. This is followed by protonation of the diene and subsequent cyclization with a nucleophilic moiety to give product α-**155**.

Wang *et al.*[230] reported the results of studying gold complexes and ligands for enantioselective catalysis.

3.1.2. Intermolecular reactions

Conjugated dienes and allens are, most often, more reactive towards transition metal complexes than simple alkenes. An example of intermolecular hydroamidation is provided by the reaction of 3-methylpenta-1,3-diene with benzylcarbamate (**156**), resulting in the formation of enamine **157** (Scheme 64).[40]

Scheme 64



156

157 (86%)

(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), DCE, 25 °C

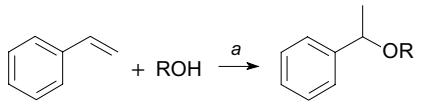
Sulfonamides can participate in this reaction instead of carbamates. Analysis of the reaction mixture by ^{13}C and ^{31}P NMR spectroscopy demonstrated that the diene component rather than carbamate is complexed with gold. The reaction of 1,3-dienes with sulfonamides is efficiently catalyzed by a $[(PhO)_3P]AuCl-AgOTf$ mixture at room temperature, the catalyst amount being 0.1 mol.%.[37] The reaction can be catalyzed by AgOTf alone at 85 °C.[16]

3.2. Intermolecular addition of oxygen nucleophiles

The hydroalkoxylation of a conjugated C=C double bond has not yet found extensive use in organic synthesis, since this reaction is significantly complicated by polymerization of the starting diene.

The addition of alcohols and phenols to styrene was described by Zhang and Corma.[155,231] Reactions of this type afford Markovnikov products **158** and are conducted with the $Au^{III}-Cu^{II}$ system at 120 °C (Scheme 65).

Scheme 65



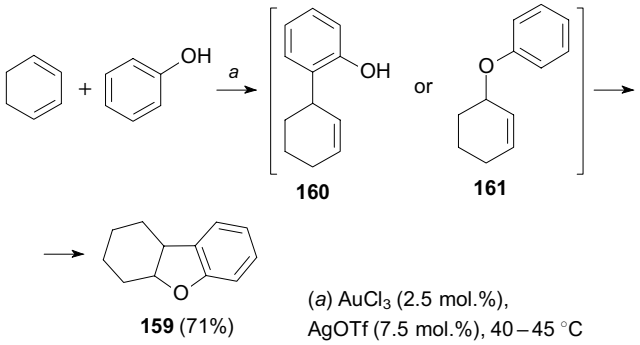
158 (50% – 87%)

(*a*) $AuCl_3$ (8 mol.%), $CuCl_2$ (16 mol.%) or Amberlyst 15, PhMe or without a solvent; R = Alk, Ar

The hydroalkoxylation of styrene can also be implemented with Brønsted acid catalysis under the same conditions. Amberlyst 15, a heterogeneous cation exchange resin in the H^+-form, was used as the acid.[232–235]

The reaction of cyclohexa-1,3-diene with phenol affords two diastereomers **159** with the *syn*:*anti* ratio of 3:1.[130] It remains unknown which bond, C–C (intermediate **160**) or C–O (intermediate **161**), is the first to be formed (Scheme 66).

Scheme 66



160 **161**

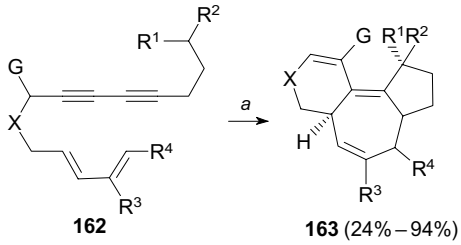
159 (71%)

(*a*) $AuCl_3$ (2.5 mol.%), AgOTf (7.5 mol.%), 40 – 45 °C

3.3. Formation of C – C bonds. Enol addition

The formation reactions of carbon – carbon bonds involving multiple carbon – carbon bonds were covered in considerable detail in our previous review.[2] Here we present only one example of polycyclization involving 1,3-diene system **162**, resulting in polycyclic system **163**, which contains a seven-membered ring (Scheme 67). [236]

Scheme 67



162

163 (24% – 94%)

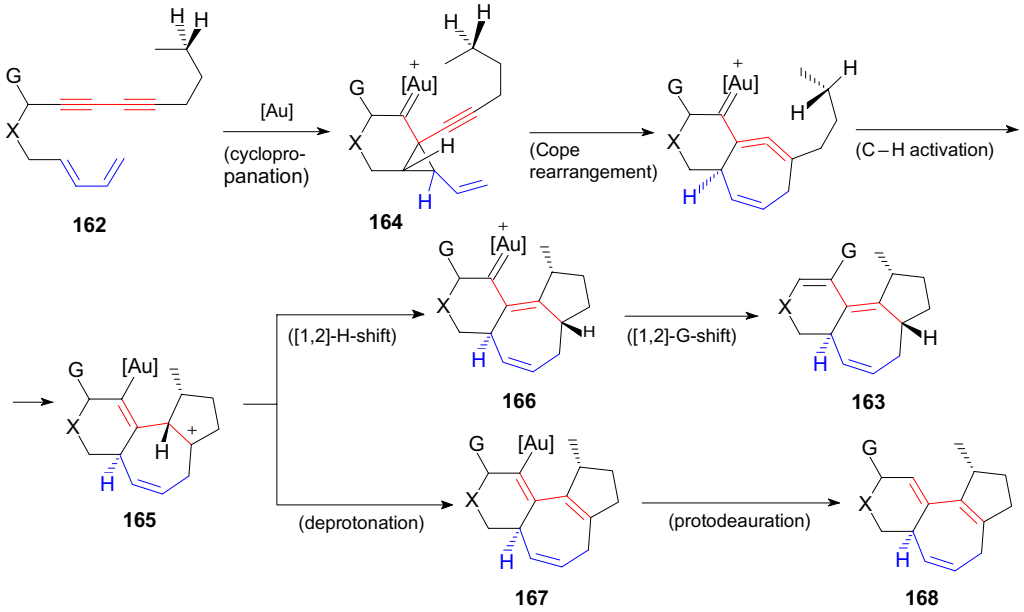
(*a*) **123** (10 mol.%), DCE, rt, 0.5 – 24 h; X = NTs, O, CH_2; G = H, OAc; R^1 = H, Me, Et, n-C_6H_{11}, CH_2OTBS, Ph; R^2, R^3, R^4 = H, Me; TBS is *tert*-butyldimethylsilyl

The starting linear dienediynes **162** can be readily synthesized and the ratio of the target diastereomers varies from 3:1 to >20:1.[236] The reaction mechanism is depicted in Scheme 68 (for R^1 = Me, R^2-R^4 = H) and includes C–H activation in the aliphatic moiety of the molecule to form intermediate **164**. (The participation of gold in C–H activation processes will be the subject of a separate review.)

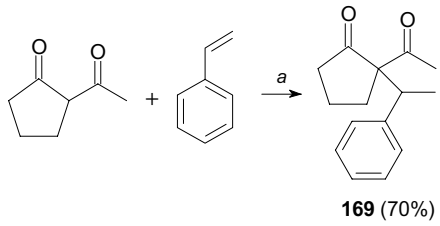
Cai *et al.*[236] considered a sequence of the [1,2]-H- and [1,2]-G-shifts (giving intermediates **165** → **166**) as the major transformation pathway (in the case of both G = OAc and G = H). This mechanism was confirmed by the results of DFT calculations. Meanwhile, carbocation **165** can be deprotonated, which gives rise to intermediate **167**. The latter is protodeaurated to be converted to product **168**. Water and triflate anion present in the reaction medium would facilitate the deprotonation of intermediate **165** and, in turn, would be favourable for the formation of large amounts of product **168**.

1,3-Dicarbonyl compounds (for example, 2-acetylcyclopentanone) can react with activated alkenes (*e.g.*, styrene), norbornene and enol ethers.[237,238] The reaction proceeds *via* the formation of the enol form and gives an equimolar mixture of diastereomers **169** (Scheme 69).

Scheme 68



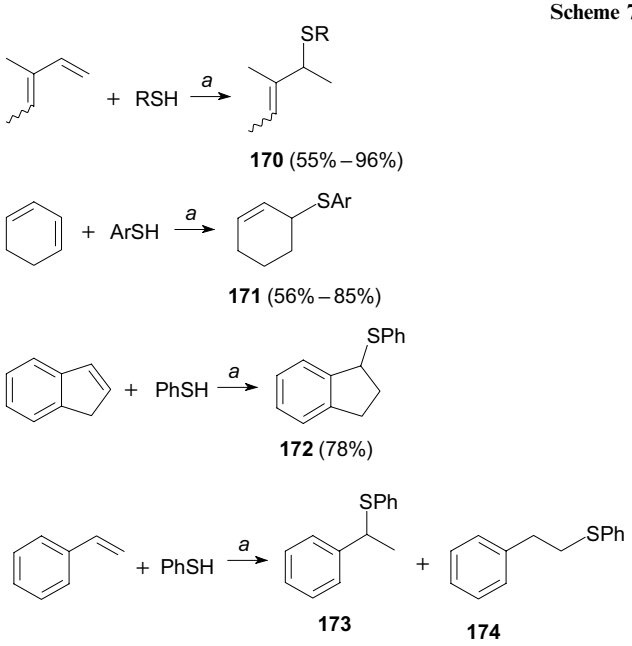
Scheme 69



169 (70%)

(*a*) Ph_3PAuCl (15 mol.%), AgOTf (15 mol.%), $MeNO_2$, Δ

Scheme 70



(*a*) $[Ph_3PAu]OTf$ (5 mol.%), DCE, N_2, rt, 12 h; R = Pr^n, Bu^t, Bn, Ph, Mes, Ac, Bz, $P(S)Ph_2$, $(CH_2)_2TMS$, $(CH_2)_2OH$, $(CH_2)_2NHCbz$; Ar = XC_6H_4 (X = 3-Cl, 3-NO_2, 4-OMe); TMS is trimethylsilyl

3.4. Hydrothiolation

The Au^I-catalyzed hydrothiolation of conjugated alkenes was reported by Brouwer *et al.*[239] (Scheme 70). The reaction proceeds under mild conditions (at room temperature). Quite a number of sulfides **170** were prepared in this way from a variety of thiols [except for $H_2N(CH_2)_2SH$]. Substituted arenethiols react with cyclohexa-1,3-diene to give products **171** in moderate yields. Sulfide **172** was synthesized by the addition of benzenethiol to indene, while in the case of BzSH, polymerization of the substrate took place. As can be seen from reactions presented in Scheme 70, the addition generally follows Markovnikov's rule. Only in the reaction of styrene with benzenethiol, was a 9 : 1 mixture of isomers **173** and **174** formed in a total yield of 86%.

4. Addition to allenes

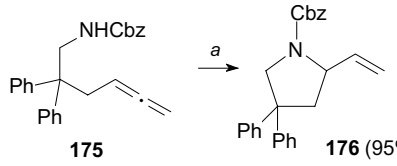
In the case of allenes (1,2-dienes), there is a problem of low selectivity of nucleophilic addition.[240] However, in some cases, this problem can be efficiently overcome using gold catalysis; several examples of controlled selectivity of nucleophilic addition to allenes are described below.

4.1. Hydroamination of allenes

4.1.1. Intramolecular reactions

Usually allenes are more reactive towards transition metals than alkenes.[241] For example, intramolecular *exo*-hydroamination of *N*-allenylpropylcarbamates **175** in dioxane at room temperature, catalyzed by a sterically hindered Au(I) phosphine complex with ligand **28** and AgOTf as the co-catalyst, gives pyrrolidine **176** in a high yield over a period of 45 min (Scheme 71).[67]

Scheme 71

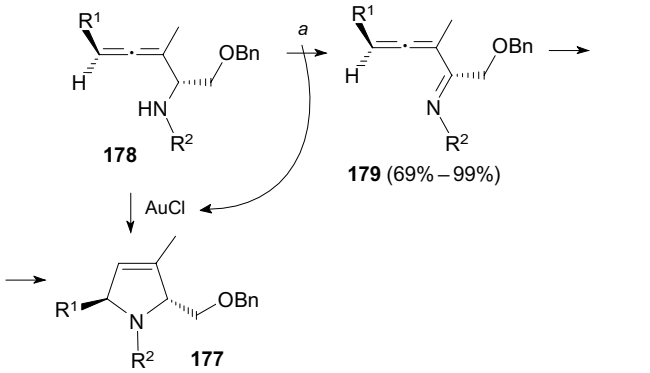


(*a*) (**28**)AuCl (5 mol.%), AgOTf (5 mol.%), 1,4-dioxane, rt, 45 min

The reaction tolerates various substituents in the alkyl chain of *N*-allenylpropylcarbamates and is equally efficient for internal and terminal allenyl derivatives.

The $AuCl_3$-catalyzed intramolecular *endo*-hydroamination (*endo*-hydroamidation) was reported by Morita and Krause [242] in 2004. The authors obtained the corresponding 3-pyrrolines **177** in good to high yields (Scheme 72; the yields and *dr* values for products **177a – e** with $R^1 = Pr^i$ are given).

Scheme 72



(*a*) $AuCl_3$ (2 mol.%), DCM, rt; R^1 = Alk, Ph; R^2 = H, Ms, Ts, Ac, Boc; Boc is *tert*-butyloxycarbonyl

Compound **177**	R^2	Time /h	Yield (%)	*dr*
a	H	120	74	> 99 : 1
b	Ms	0.5	77	94 : 6
c	Ts	0.5	93	95 : 5
d	Ac	0.5	80	70 : 30
e	Boc	0.5	69	46 : 54

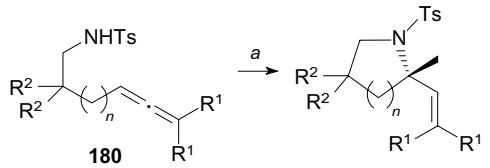
The amine protecting group considerably affects the reaction rate and stereoselectivity. Indeed, in the case of unprotected primary α-aminoallenes **178** (R^2 = H), the duration of the reaction substantially increases. When the same amino derivatives are used with the protected amino group, the reaction time is shortened; however, this is often accompanied by decreasing diastereoselectivity. The applicable solvents are dichloromethane or THF; the reaction is carried out at temperatures ranging from room temperature to 80 °C.

It is of interest that, according to earlier studies,[242] $AuCl_3$ is a good catalyst for this reaction, whereas cationic Au^I complexes were inefficient. Nevertheless, Krause's research team [243] discovered that in the case of unprotected α-aminoallenes **178** (R^2 = H), the use of AuCl instead of $AuCl_3$ can markedly increase the reaction rate. Moreover, even in the case of $AuCl_3$, the catalytically active species are Au^I species generated upon gold reduction in the reaction mixture with substrate **178**, which is converted to imine **179** (see Scheme 72). Later, it was shown [244] that the micellar catalyst, $AuBr_3$, is able to catalyze the reaction shown in Scheme 72 at room temperature in water. The catalyst has a high activity and can be reused.

The proposed synthetic method offers new opportunities for the synthesis of functionalized pyrrolines and pyrrolidines with a broad range of biological activities.[245 – 248] It was shown that sulfonamides cyclize on treatment with potassium carbonate in DMF without any catalyst.[249]

The first example of asymmetric hydroamidation of allenes **180** giving vinyl-substituted saturated heterocycles **181** was reported in 2007.[63] The binuclear gold(I) complex catalyzes the enantioselective synthesis of vinyl pyrrolidine and piperidine derivatives (Scheme 73). Subsequently, this method was further developed.[44, 50, 62, 65]

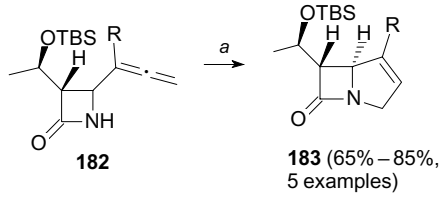
Scheme 73



(*a*) $L(AuOPNB)_2$ (3 mol.% – 5 mol.%), DCE, rt; L = xylylBINAP, SEGPhos, ClMeOBIPHEP; R^1 = H, Alk; R^2 = H, Alk, Ar; *n* = 1, 2; OBNP is 4-nitrobenzoate; xylylBINAP is 2,2′-bis[bis(3,5-dimethylphenyl)phosphino]-1,1′-binaphthyl; ClMeOBIPHEP is 2,2′-dimethoxy-6,6′-bis(diphenylphosphino)-3,3′-dichlorobiphenyl

Lee *et al.*[250] proposed highly efficient intramolecular hydroamination of 4-allenylazetidin-2-one **182** catalyzed by $AuCl_3$ and furnishing the corresponding bicyclic β-lactams **183** (Scheme 74).

Scheme 74

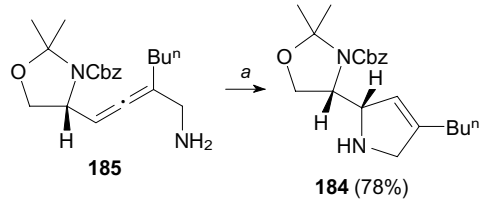


(*a*) $AuCl_3$ (5 mol.%), DCM, rt, 15 – 60 min; R = Me, Bu^n, Ph, 2-Naph, CH_2OTHP; THP is tetrahydropyran-2-yl

In 2013, Jorg and Krause [251] demonstrated that imidazole can be used as a stabilizing ligand. For example, dihydropyrrole **184**, which is a key intermediate in the synthesis of biologically active (α*S*,2*R*)-(2,5-dihydro-1*H*-pyrrol-2-yl)glycine, was prepared in a good yield from allene **185** in the presence of the AuCl catalyst stabilized by imidazole (Scheme 75).

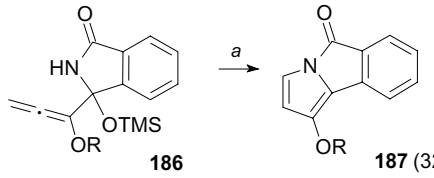
Alkoxyallenes **186** with a trimethylsilyloxy substituent form pyrroles **187** upon the intramolecular addition of the amino group (Scheme 76).[252]

Scheme 75



(*a*) AuCl (10 mol.%), imidazole (10 mol.%), PhMe, 80 °C, 12 h

Scheme 76

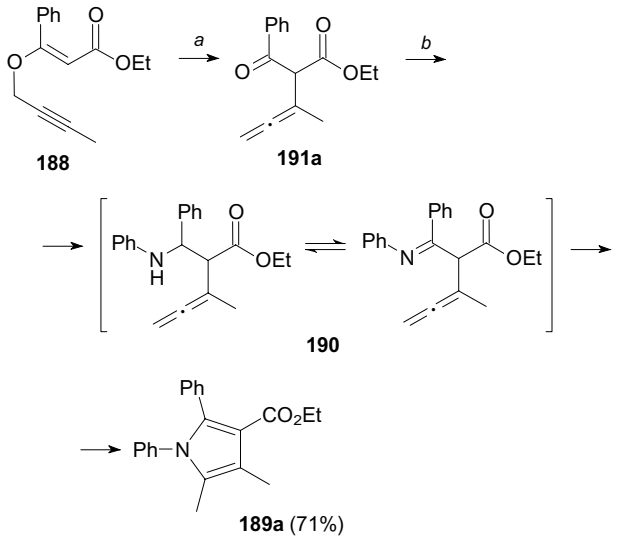


186 **187** (32% – 40%)

(*a*) $AuCl_3$ (5 mol.%), DCM, 0 °C → rt, 30 min; R = Me, Bn, SEM; SEM is 2-(trimethylsilyl)ethoxymethyl

The rearrangement – condensation – cyclization sequence starting from propargyl vinyl ether **188** affords pyrrole **189a** (Scheme 77).[253] The final transformation step is the Au^I-catalyzed *endo*-hydroamination of allene **190**.

Scheme 77



188 **191a** **190** **189a** (71%)

(*a*) $AgSbF_6$ (5 mol.%), DCM, 23 °C; (*b*) 1) $PhNH_2$ (1.5 equiv.); 2) Ph_3PAuCl (5 mol.%), DCM, 38 °C, 30 min

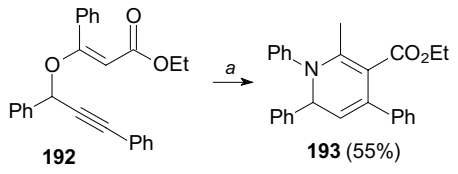
The salt $AgSbF_6$ not only catalyzes the conversion of alkyne **188** to allene **191a** (Claisen rearrangement), but also participates in the gold activation at the subsequent conversion of **191a** to product **190**. In the absence of $AgSbF_6$, the complex Ph_3PAuCl does not catalyze the transformation of allene **191a**, prepared in advance by another method, to pyrrole **190**. The reaction proceeds with various aromatic, but not with aliphatic amines. A substitution in the propargyl position considerably decreases the reaction efficiency; therefore, this method is best suited for the synthesis of 5-methylpyrroles. 5-Methylpyrroles obtained in this way can be easily converted to 5-formylpyrroles by treatment with 2-iodoxybenzoic acid.

It is noteworthy that vinyl propargyl ethers substituted in the propargyl position (*e.g.*, with the ethyl or phenyl group, as in substrate **192**) undergo successive rearrangement – condensation – cyclization reactions to form substituted dihydropyridine **193** in a moderate yield (Scheme 78).[253]

The formation of the six-membered ring of piperidine **194** *via* intramolecular 6-*exo*-*trig*-hydroamidation of compound **195** was reported by Zhang *et al.*[67] (Scheme 79).

The 5-*exo*-*trig*- and 6-*exo*-*trig*-hydroamidation of allene amides **196** and **197** resulted in the synthesis of 2-vinyl-

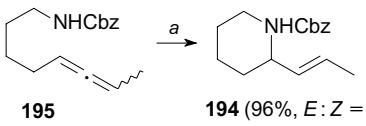
Scheme 78



192 **193** (55%)

(*a*) 1) $AgSbF_6$ (5 mol.%); 2) $PhNH_2$ (1.5 equiv.); 3) Ph_3PAuCl (5 mol.%), DCM, 23 – 38 °C

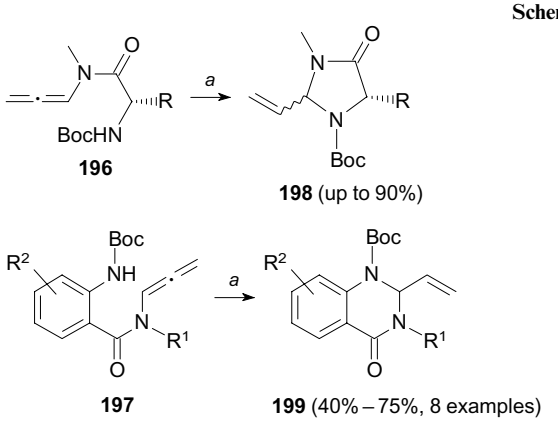
Scheme 79



195 **194** (96%, *E* : *Z* = > 50 : 1)

(*a*) (**28**)AuCl (5 mol.%), AgOTf (5 mol.%), 1,4-dioxane, rt, 30 min

Scheme 80



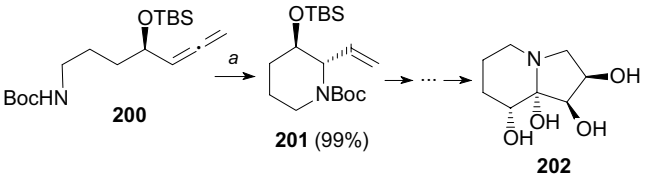
196 **198** (up to 90%) **197** **199** (40% – 75%, 8 examples)

(*a*) $AuCl_3$ (5 mol.%), MeCN, Δ; R = Me, Et, Pr^i, Bu^t, Bn, Ph; R^1 = Alk: R^2 = H, Cl, NO_2 (in various positions)

imidazolidin-4-ones **198** [56] and 2,3-dihydrquinazolin-4(1*H*)-ones **199**, respectively (Scheme 80).[254] The reactions were conducted in refluxing acetonitrile and catalyzed by $AuCl_3$.

The gold-catalyzed intramolecular hydroamidation of allene **200** giving piperidine **201** was successfully used in the stereoselective multistep synthesis of a natural compound, swainsonine (**202**),[255] which is a potential mannosidase inhibitor (Scheme 81).

Scheme 81



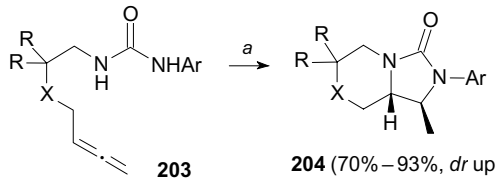
200 **201** (99%) **202**

(*a*) $AuCl_3$ (5 mol.%), $CaCO_3$ (1 equiv.), DCM, rt

Li and Widenhoefer[256] used Au^I catalysis for the cyclization of *N*-δ-allenylureas **203**, which led to highly efficient diastereoselective synthesis of bicyclic imidazolidinones **204** and analogous systems (Scheme 82).

In this case, the cyclization is catalyzed by a mixture of a gold(I) complex with a *N*-heterocyclic carbene ligand (com-

Scheme 82



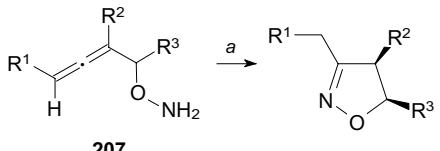
203 **204** (70% – 93%, *dr* up to > 50 : 1)

(*a*) IPrAuCl (**7**) (5 mol.%), $AgPF_6$ (5 mol.%), DCM, rt, 2 – 60 h;
R = H, Me, Ph; X = CH_2, O, NTs; Ar = Bn, 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$

pound **7**) and $AgPF_6$ at room temperature. The reaction is tolerant to a broad range of N-substituents in urea and to various heteroatoms in the heptadienyl chain of the substrate and, hence, it can be used, for example, for the synthesis of morpholine (X = O) and piperazine (X = NTs) fused systems **204**. The reaction includes two steps: allene hydroamidation and subsequent hydroamidation of the gold alkenyl species formed *in situ*.

Highly regio- and stereoselective synthesis of chiral heterocycles such as 4,5-dihydroisoxazole **205** and 3,6-dihydro-1,2-oxazine **206** by cyclization of hydroxylamino allene derivatives **207** and **208** was reported by Winter and Krause [257] (Scheme 83).

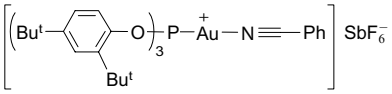
Scheme 83

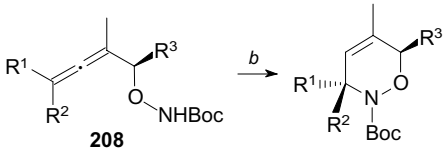


207 **205** (72% – 86%)

(*a*) **209** (5 mol.%), DCM, rt, 15 min – 2 h; R^1 = H, Me, Bu^n;
R^2 = H, Me; R^3 = Me, CH_2OBn;

209 =





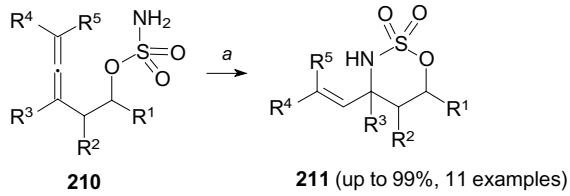
208 **206** (75% – 82%)

(*b*) AuCl (5 mol.%), DCM, rt, 10 min – 1.5 h; R^1 = Me, Pr^i, Bu^n;
R^2 = H, Me; R^3 = CH_2OMe, CH_2OBn

In this case, the nitrogen atom acts as a nucleophile, attacking the allene group. The reaction follows two pathways: 5-*endo*- and 6-*endo*-cyclizations. In the case of hydroxylamines **207**, the reaction can be directed towards the formation of dihydrooxazole **205** in the presence of catalyst **209**. For the synthesis of dihydrooxazine **206**, *N*-Boc-protected precursor **208** is used in the reaction. (One more intramolecular cyclization reaction involving N,O-dinucleophiles is considered in Section 6).

In the first reported example of hydroamidation of allenes **210** involving a sulfonamide group,[258] the intramolecular reaction gives six-membered cyclic derivative **211** containing an *N*-substituted quaternary carbon atom (Scheme 84).

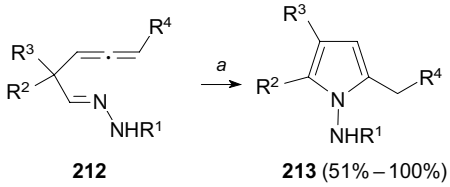
Scheme 84



210 **211** (up to 99%, 11 examples)

(*a*) $Ph_3PAuNTf_2$ (5 mol.%), DCM or DCE, 25 – 40 °C;
R^1, R^2, R^3, R^4, R^5 = H, Alk

Scheme 85



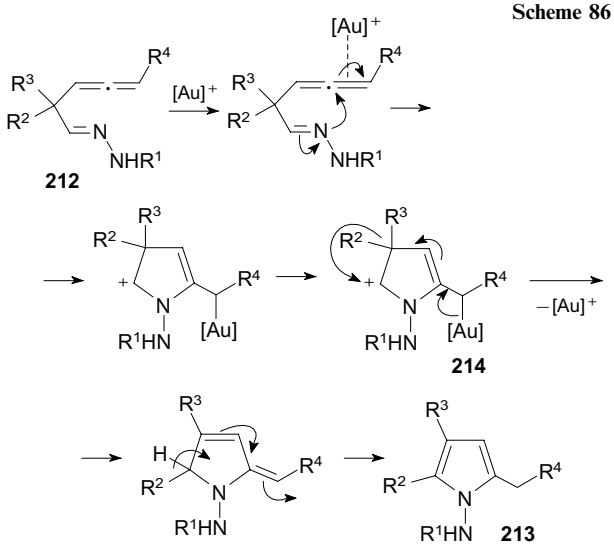
212 **213** (51% – 100%)

(*a*) $Ph_3PAuNTf_2 \cdot 0.5$ PhMe (5 mol.%), DCE, MW, 100 °C, 20 min;
R^1 = Ts, 2,4-$(O_2N)_2C_6H_3$, MeO_2C; R^2 = Me, Ph; R^3 = Me, Et, Ph;
$R^2 – R^3$ = $(CH_2)_4$, $(CH_2)_5$; R^4 = Me, Bu^n, Ph, 4-BrC_6H_4

The cycloisomerization of β-allenylhydrazones **212** was proposed as a simple and efficient method for the synthesis of functionalized pyrroles **213** under microwave irradiation (MW) (Scheme 85).[259]

The reaction involves a selective intramolecular 1,2-shift of the alkyl or aryl group (see the structure of intermediate **214** in Scheme 86).

Scheme 86

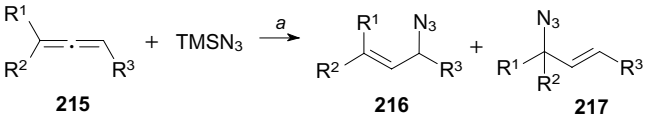


212 **214** **213**

Gold complexes **123** and $[Ph_3PAu]NTf_2 \cdot 0.5$ PhMe showed the highest activity in this reaction.

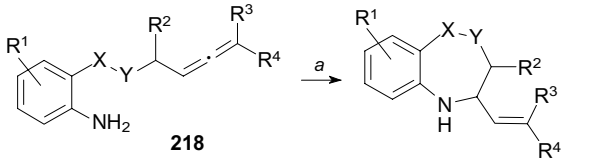
The addition of trimethylsilyl azide to allenes **215** giving allyl azide derivatives **216** and **217** was carried out in the presence of trifluoroacetic acid, which protodeaurated the vinyl – gold complex [260] (Scheme 87). The total yields of products were 38% – 100%, while the **216** to **217** isomer ratio varied from 1 : 1.3 to 1 : 0 (16 compounds were prepared).

Scheme 87



(*a*) $(PhO)_3PAuCl$ (5 mol.%), AgOTf (5 mol.%), CF_3CO_2H (3 equiv.), H_2O (5 equiv.), DCM, rt, 14 – 22 h; R^1 = Alk, Ar; R^2, R^3 = Alk

Scheme 88



219 (67% – 89%, 16 examples)

(*a*) IPrAuCl (**7**) (3 mol.%), AgOTf (3 mol.%), 1,4-dioxane, 80 °C; R^1 = H, Me, OMe, CN, CO_2Me, CF_3; R^1 = H, Alk; R^3, R^4 = Alk; X = O, Y = CH_2 or X = CH_2, Y = NTs

Aniline derivatives **218** containing an allene moiety undergo 7-*exo-trig*-cyclization catalyzed by IPrAu to be converted to synthetically valuable products: 1,5-benzoxazepines **219** (X = O, Y = CH_2) and 1,4-benzodiazepines **219** (X = CH_2, Y = NTs) in good yields (Scheme 88).[261]

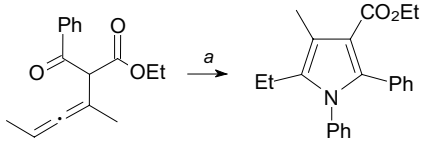
Joyce *et al.*[262] described reactions of β-aminoallene **220** resulting in pyrrolines **221** and **222** and tetrahydropyridine **223** in a total yield of up to 70%. The authors used both Au^I and Ag^I as catalysts for this reaction (Scheme 89, Table 5). In the presence of Au^I, 5-*endo-dig*-cyclization takes place (the formed compound **222** rapidly isomerizes to a compound with an endocyclic double bond) and in the case of Ag^I, 6-*endo-trig*-cyclization takes place.

To summarize the discussion of the intramolecular hydroamination of allenes, we would like to note that this reaction offers broad opportunities for efficient preparation of nitrogen heterocycles. Depending on the nature of the substrate, the reaction gives saturated, partly unsaturated and aromatic five-, six- and even seven-membered heterocyclic derivatives. Schemes 72 – 74 and 90 show examples of intramolecular hydroamination of an allene double bond catalyzed by gold salts and complexes, which give heterocycles valuable for practical purposes.[66, 68, 242, 250, 253]

Scheme 89



Scheme 90



(*a*) 1) $PhNH_2$; 2) Ph_3PAuCl (5 mol.%), DCM

4.1.2. Intermolecular reactions

Gold(III)-based catalysts make it possible to perform intermolecular hydroamination of allenes with aromatic amines, giving rise to allylamines.[66] For example, the treatment of a mixture of propa-1,2-dienylbenzene (**224a**) and aniline (1 : 2 ratio) with a catalytic amount of $AuBr_3$ in THF at 30 °C affords the allene hydroamination product, compound **225a** (Scheme 91). Similarly, allenes **224b – d** are converted to substituted anilines **225b – d**.

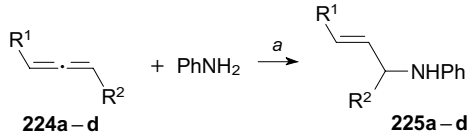
This reaction can be performed for monosubstituted arylallenes and alkylallenes and also 1,3-disubstituted

Table 5. Cyclization of β-aminoallenes in the presence of a Au catalyst (see Scheme 89).[262]

Catalyst	Amount (mol.%)	Conditions	Yield (%)	Product ratio **221** : **222** : **223**
$Ph_3PAuCl – AgBF_4$	10	DCM, rt, 46 h	55	1 : 1.7 : 0
AuCl	10	DCM, Δ, 5 days	19	1 : 0 : 0
$Ph_3PAuCl – AgBF_4$	20	DCE, Δ, 24 h	10	1 : 0 : 0
IPrAuCl (**7**) – $AgBF_4$	10	DCE, rt, 24 h	47	1 : 3.2 : 0
IPrAuCl (**7**) – $AgBF_4$	10	DCE, Δ, 8 h	57	1 : 1.05 : traces
$Ph_3PAuCl – AgBF_4$	10	PhMe, rt, 3 days	0	–
$Ph_3PAuCl – AgBF_4$	10	MeCN, rt, 30 min	70	1.5 : 1 : 0
$Ph_3PAuCl – AgBF_4$	10	THF, rt, 38 h	65	1 : 1 : 0
$AgNO_3$	10	Me_2CO, rt, 32 h; then 60 °C, 43 h	5	0 : 0 : 1
$AgBF_4$	10	DCM, rt, 30 h	56	0 : 0 : 1
Ag_2O	10	Me_2CO, rt, 28 h	61	1 : 2.8 : 0
$KOBu^t$	120	THF, 40 °C, 3 days; then Δ, 56 h	58	4 : 1 : 0
$AgBF_4$	10	PhMe, rt, 22 h	68	1 : 9.1 : 0
$AgBF_4$	10	MeCN, rt, 15 h	0	–
$AgBF_4$	10	THF, rt, 30 min	0	–
$AgBF_4$	10	Et_2O, rt, 21 h	44	0 : 0 : 1

Note. Dash means that the reaction does not proceed.

Scheme 91



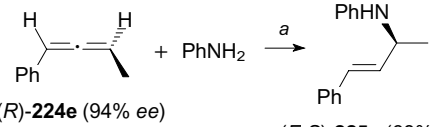
224a – d **225a – d**

(*a*) $AuBr_3$ (10 mol.%), THF, 30 °C, 1 – 5 h; R^2 = H: R^1 = Ph (**a**, 78%), n-C_8H_{17} (**b**, 70%); R^1 = Ph, R^2 = Me (**c**, 68%); R^1 = R^2 = n-C_5H_{11} (**d**, 80%)

allenes. Meanwhile, 1,1-disubstituted allenes virtually do not react with aniline.

The intermolecular hydroamination of axially chiral 1,3-disubstituted allenes is accompanied by selective transfer of chirality. For example, hydroamination of enantiomerically enriched buta-1,2-dienylbenzene **224e** with aniline gives allylamine (*E*,*S*)-**225e** in 68% yield and with 88% *ee* (Scheme 92).

Scheme 92

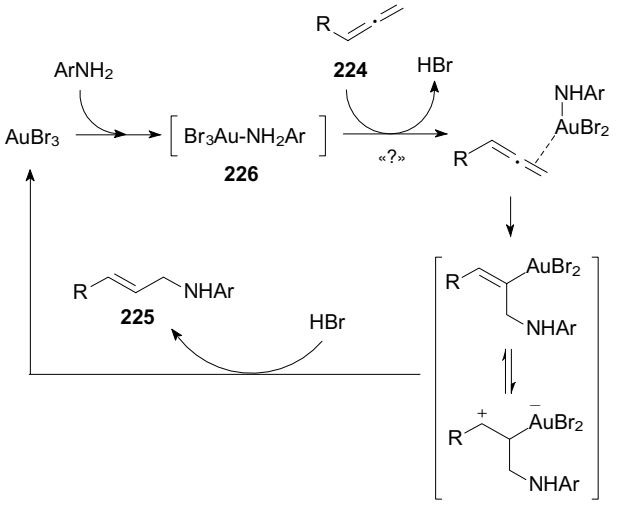


(*R*)-**224e** (94% *ee*) (*E*,*S*)-**225e** (68%, 88% *ee*)

(*a*) $AuBr_3$ (10 mol.%), THF, 30 °C

The gold – aniline complex [Br_3Au-NH_2Ph] (**226**) acts as the reactive species, which reacts with allene.[66] It was assumed that the reaction starts with coordination of the allene to complex **226**, while the subsequent insertion of allene and protodeauration give product **225** (Scheme 93).

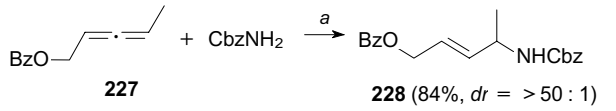
Scheme 93



However, in 2013, Bergman and co-workers[263] found that the gold – amide intermediates (for example, complex **226**) are inactive towards π-bonds, which implies that hydroamination follows some other (outer-sphere) mechanism.

The intermolecular reaction of allene **227** with benzylcarbamate in the presence of a Au complex with an NHC ligand gives product **228** in a good yield and with a high regioselectivity (Scheme 94).[61]

Scheme 94

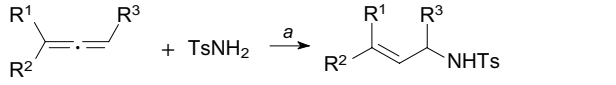


227 **228** (84%, *dr* = > 50 : 1)

(*a*) (NHC)AuCl (5 mol.%), AgOTf (5 mol.%), 1,4-dioxane, rt, 5 h

A reaction of the same type was reported by Zhang *et al.*,[264] who used a cationic gold complex as the catalyst and a sulfonamide (tosylamine) as the amino derivative. The reaction was highly regioselective for both 1,1- (**229**) or 1,3-disubstituted allenes (**224**) and trisubstituted allenes **215**. This resulted in the synthesis of *N*-allylamides **230** in moderate to good yields (Scheme 95).

Scheme 95

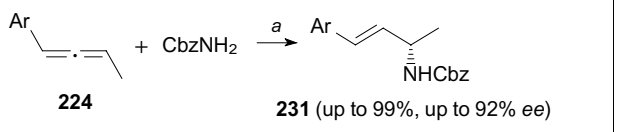


215, **224**, **229** **230** (31% – 91%, 14 examples)

(*a*) Ph_3PAuCl (5 mol.%), AgOTf (8 mol.%), 1,4-dioxane, rt, 16 h; R^1, R^3 = H, Alk, Ph; R^2 = Ar

Widenhoefer and co-workers[43] developed an asymmetric version of hydroamination of allenes **224** (R^1 = Ar, R^3 = Me) with *N*-unsubstituted carbamates (*e.g.*, benzylcarbamate). A binuclear gold complex with ligand **75** in the presence of a silver salt was used to catalyze the reaction. Protected asymmetric allylamines **231** were isolated in excellent yields and with high stereoselectivity (Scheme 96).

Scheme 96



224 **231** (up to 99%, up to 92% *ee*)

(*a*) (**75**)$(AuCl)_2$ (2.5 mol.%), $AgBF_4$ (5 mol.%), 1,4-dioxane, rt, 24 h

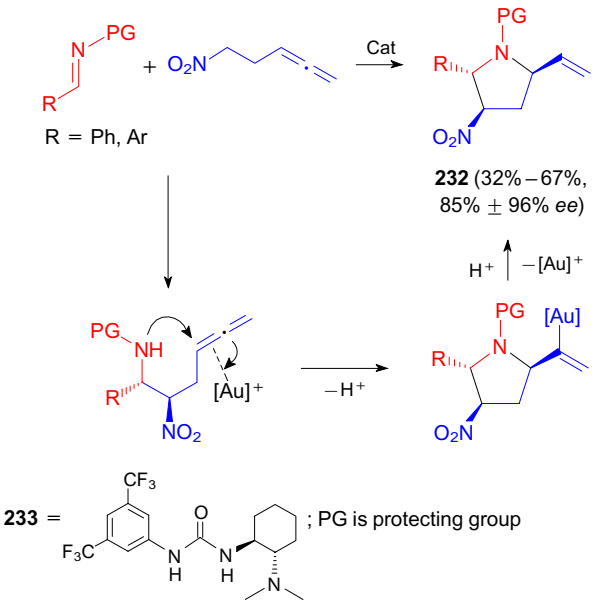
Trisubstituted pyrrolidines **232** can be obtained by an intermolecular nitro-Mannich and hydroamination cascade reactions, which combine an organocatalytic asymmetric reaction and the subsequent gold-catalyzed intramolecular hydroamination (Scheme 97).[265] The first reaction was catalyzed by urea **233**, while in the second one, the $Ph_3PAuCl-AgBF_4$ catalytic system was used.

Reactions similar to those described above can often be catalyzed by silver.[266] In addition, it was shown that allene sulfonamides cyclize with potassium carbonate in DMF in the absence of any transition metal.[249]

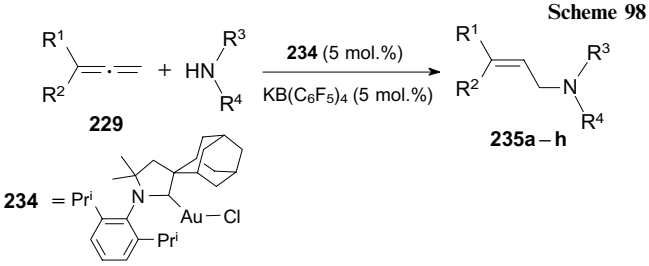
Gold catalysis of aminocyclization of allenes was also employed to prepare bicyclic β-lactams.[250]

The application of Au^I complex **234** and $KB(C_6F_5)_4$ as the catalyst boosts highly efficient intermolecular hydroamination of terminal allenes **229** on treatment with a broad range of primary and secondary amines (Scheme 98).[55] This procedure was used to prepare enamines **235a – h**.

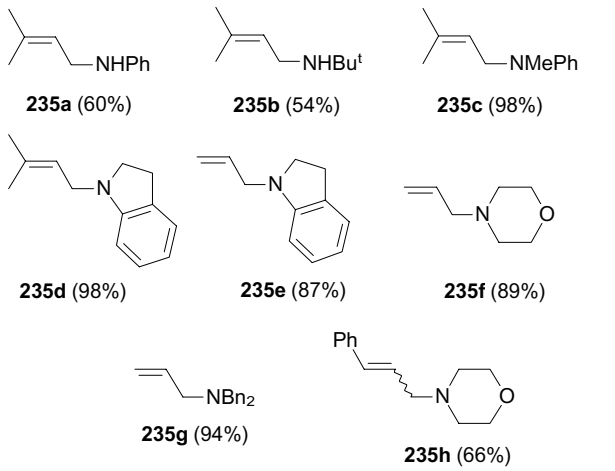
Scheme 97



Scheme 98



Structures 235

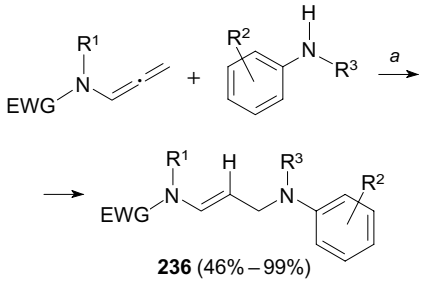


The intermolecular reaction of terminal allene amides containing an electron-withdrawing group (EWG) at the nitrogen atom with arylamines in the presence of a cationic gold complex is an efficient synthetic route to (*E*)-enamides **236** (Scheme 99).[52]

4.2. Addition of oxygen nucleophiles to allenes

Allenes are very complex substrates for nucleophilic and electrophilic addition, because even in the case of simple allenes, products with various chemo-, regio- and stereoselectivity can be formed. The use of gold-containing catalysts helps to significantly overcome these complications.[267]

Scheme 99

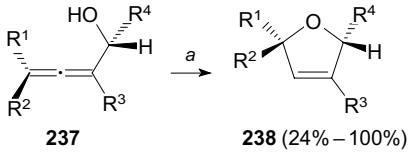


(*a*) $[Ph_3PAu]OTf$ (5 mol.%), DCM, rt; R^1 = H, Me; R^2 = Me, OMe, F, Br, I, CO_2Et, NO_2 (in various positions); R^3 = Alk; EWG – N – R^1 moiety may be a part of the heterocycle

4.2.1. Intramolecular reactions

Addition of hydroxy group. The nucleophilic intramolecular addition of a hydroxy group to the diene system of allenes gives heterocycles as a result of cycloisomerization. The intramolecular 5-*endo*-cyclization – hydroalkoxylation reactions of functionalized α-allenols **237** furnished 2,5-dihydrofurans **238** (Scheme 100).[268, 269]

Scheme 100

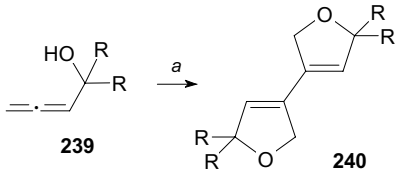


(*a*) $AuCl_3$ (10 mol.%), DCM, rt; R^1 = H, Alk; R^2 = H, Bu^t, CH_2All; R^3 = H, Me; R^4 = CH_2OH, CH_2OMe, CH_2OTBS, CO_2Me, CO_2Et

This reaction can proceed under acidic conditions, but in the case of acid-sensitive substrates, $AuCl_3$ catalysis is preferable. The use of $AuBr_3$ in ionic liquid $[BMIM]PF_6$ (BMIM is 1-n-butyl-3-methylimidazolium) as the catalytic system provides the synthesis of the target products with various alkyl- or aryl-substituted α-allenols.[270] This reaction in water is catalyzed by $HAuCl_4$ in the presence of LiCl.[271]

In the reactions of this type, $AuCl_3$ can be reduced *in situ*;[272] as a result, 1,1-disubstituted allenylcarbinols **239** are converted to oxidative dimerization products **240** in the absence of other oxidants in amounts comparable with the amounts of $AuCl_3$ used (Scheme 101).

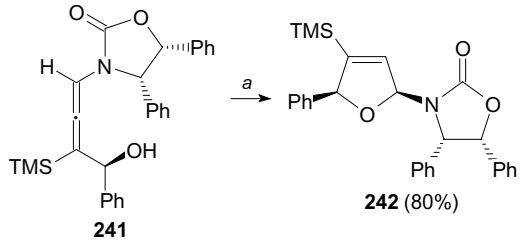
Scheme 101



(*a*) $AuCl_3$, MeCN, rt; R = Alk, Ar

Subsequently, it was found that Au^I-based catalysts are more efficient in these reactions;[273] an example is provided by cyclization of compound **241** to product **242** (Scheme 102).

Scheme 102

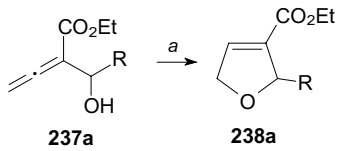


241 **242** (80%)

(*a*) Ph_3PAuCl (5 mol.%), $AgBF_4$ (5 mol.%), DCM

In most cases, the use of silver as a co-catalyst significantly increases the efficiency of catalysis. In particular, a series of 2,5-dihydrofuran-3-carboxylates **238a** were prepared in good yields[274] by cyclization of functionalized α-allenols **237a** in the presence of the $Ph_3PAuCl – AgOTf$ system at room temperature over a period of 1 h. In the absence of the Ag co-catalyst, the reaction gave only 15% yield of the product over a period of 15 h (Scheme 103).

Scheme 103

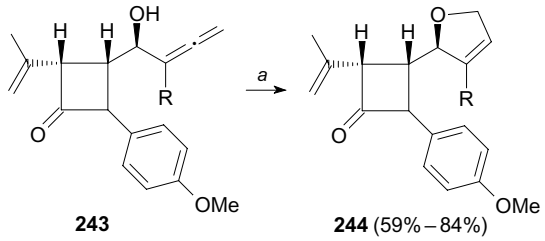


237a **238a**

(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), DCM, rt, 1 h; R = H, Alk, Ar

When the allene and alkene groups occur in the same substrate (see, for example, compound **243** in Scheme 104), the use of the $AuCl_3$ catalyst leads to dihydrofuran derivative **244** *via* selective activation of the allene moiety.

Scheme 104



243 **244** (59% – 84%)

(*a*) $AuCl_3$ (5 mol.%), DCM, rt; R = Me, Ph

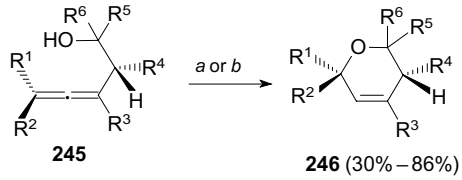
This reaction can also be catalyzed by $AgNO_3$, but in this case, a stoichiometric amount of the salt and heating are required.

The cyclization of the next member of the homologous series of allene alcohols, β-hydroxyallenes **245**, yields six-membered heterocycles **246** (Scheme 105).[275]

The possible catalysts include both a gold salt, AuCl, with pyridine or 2,2′-bipyridine as a co-catalyst in DCM or $AuCl_3$ in toluene and the $Au^I – Ag^I$ system. No 5-*exo*-isomer was detected among the products.

A similar result was obtained upon the cyclization of α-diesters **247**, which afforded β,γ-unsaturated δ-lactones **248** in high yields (Scheme 106).[276]

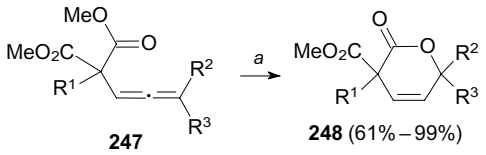
Scheme 105



245 **246** (30% – 86%)

(*a*) $AuCl_3$ (5 mol.%), PhMe, rt; (*b*) Ph_3PAuCl (5 mol.%), $AgBF_4$ (5 mol.%), DCM, rt; R^1, R^2, R^3 = H, Alk; R^4 = H, CO_2Et, Ac; R^5, R^6 = H, Me

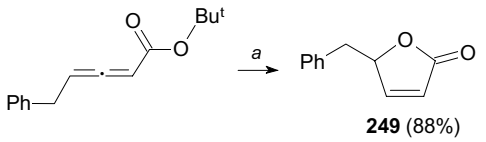
Scheme 106



247 **248** (61% – 99%)

(*a*) $AuCl_3$ (5 mol.%), $AgSbF_6$ (15 mol.%), AcOH, 70 °C, 4 – 6 h; R^1, R^2, R^3 = H, Alk

Scheme 107



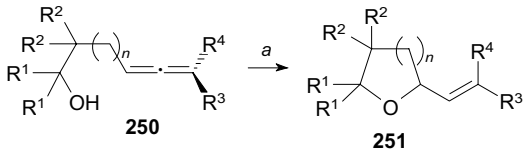
249 (88%)

(*a*) $AuCl_3$ (5 mol.%), DCM, 80°C

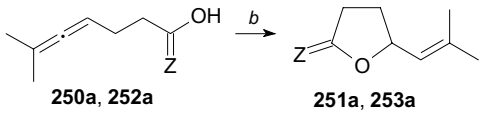
One more example of intramolecular hydroacylation of allenes[277] is provided by the synthesis of compound **249** (Scheme 107).

The *exo*-cyclization of γ- and δ-allenols **250** in toluene affords vinyl-substituted tetrahydrofurans and tetrahydropyrans **251** in good yields.[67] A mixture of the complex

Scheme 108

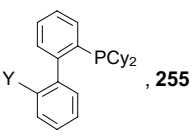
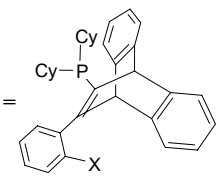


250 **251** (1)



250a, **252a** **251a**, **253a** (2)

(*a*) [(**28**)AuCl], AgOTs, PhMe, 25 °C; 5 – 75 min; (*b*) $LAuNTf_2$ (0.05 mol.% – 0.5 mol.%), C_6D_6, rt; *n* = 1, 2; Z = 2H (**250a**, **251a**); O (**252a**, **253a**); L = **28**, **254a**,**b**, **255a**,**b**; $R^1 – R^4$ = Alk, Ar;

254 =  , **255** = 

254: Y = NMe_2 (**a**, DavePhos), H (**b**, cyclohexylJohnPhos);
255: X = H (**a**, H-KITPHOS), OMe (**b**, OMe-KITPHOS)

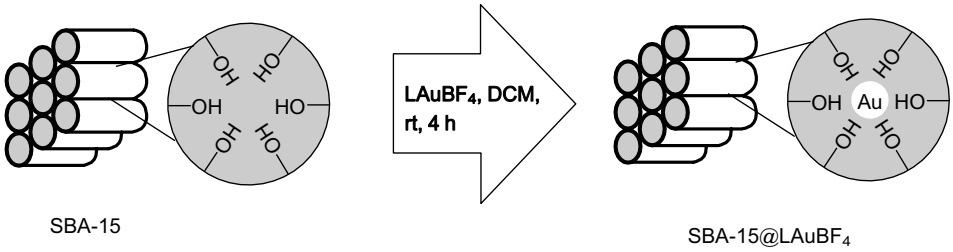


Figure 2. Formation of the complex SBA-15@$LAuBF_4$ (L = Ph_3P).[280]

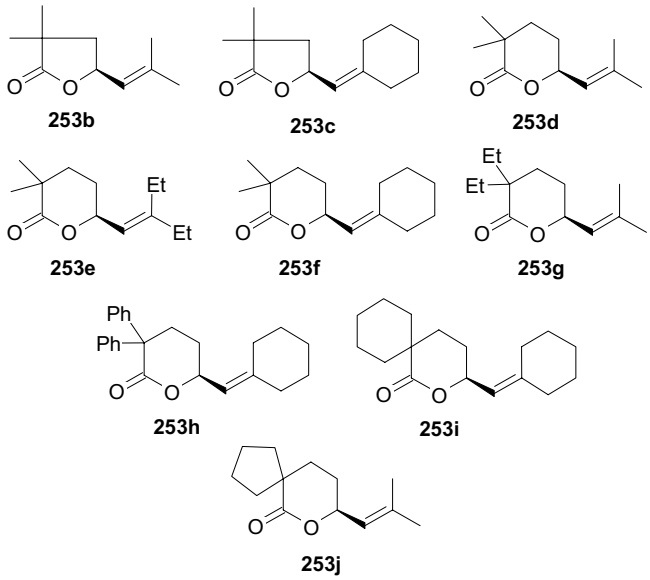
[(**28**)AuCl] with the JohnPhos ligand and AgOTs in 1 : 1 ratio is used as the catalyst [reaction (1) in Scheme 108].

The cyclization of γ-allenol **250a** and allenolic acid (**252a**) affords the corresponding hydrogenated furans **251a** and **253a** in the presence of Au^I-based helicene catalysts[278] or biphenyl- (**254a**,**b**) and 9,10-dihydro-9,10-ethenoanthracenephosphine catalysts (**255a**,**b**) [reaction (2), see Scheme 108].[279]

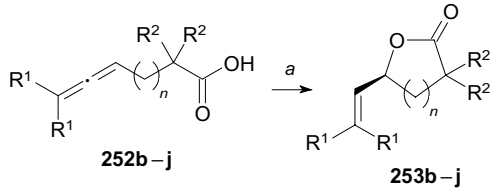
The cationic gold(I) complex supported on silica gel as a heterogeneous catalyst provides high regio- and enantioselective lactonization.[280] The molecular gold complex is confined in mesopores of silica gel (Fig. 2). A synergistic effect was observed between the acidic silica gel surface and gold, which was manifested as a considerable increase in the catalytic activity of gold and in the regio- and enantioselectivity of intramolecular reactions of allenes and alkynes. The gold-based heterogeneous catalyst was obtained by stirring the SBA-15 silica in a solution of Ph_3PAuBF_4 in CH_2Cl_2 at room temperature for 4 h. Scheme 109 shows a number of examples of efficient lactonization of allenolic acids, while Table 6 gives a comparison of the efficiency of homogeneous and heterogeneous catalysis.

The mechanism of 5-*exo*-*trig*-cyclization was studied by NMR spectroscopy in relation to 2,2-diphenylhexa-4,5-dien-1-ol (**250b**).[281] A stoichiometric mixture of acyclic substrate **250b**, complex (**28**)AuCl with the JohnPhos ligand, AgOTs and Et_3N in toluene reacts to give stable vinyl mono-gold complex **256**, which was isolated and fully characterized (Scheme 110). The addition of 1 equiv. of (**28**)AuCl with the JohnPhos ligand to complex **256** gives

Structures 253



Scheme 109

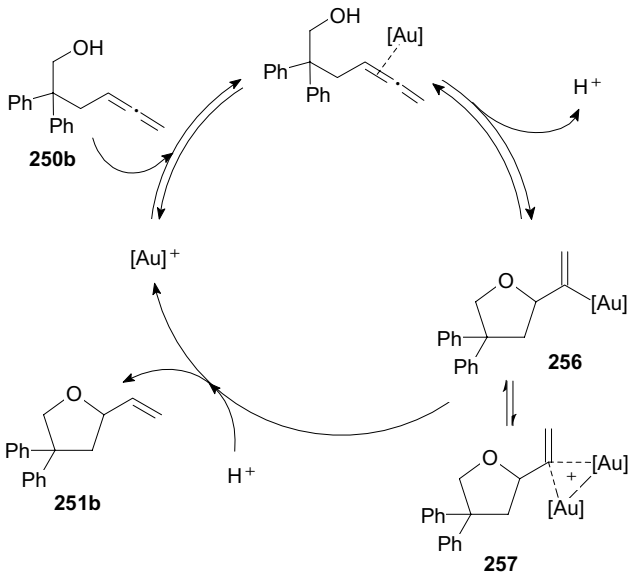


(*a*) SBA-15@ $Ph_3P(AuBF_4)_2$ (2 mol.%), DCM, rt; *n* = 1, 2

Table 6. Lactonization of allenolic acids in the presence of a Au catalyst (see Schemes **108** and **109**).[278 – 280]

Product **253**	Heterogeneous catalysis		Homogeneous catalysis	
	yield (%)	*ee* (%)	yield (%)	*ee* (%)
b	86	87	98	5
c	90	81	91	4
d	84	95	90	0
e	79	84	77	1
f	92	93	89	0
g	81	92	92	0
h	92	93	89	0
i	88	91	23	3
j	91	94	87	21

Scheme 110



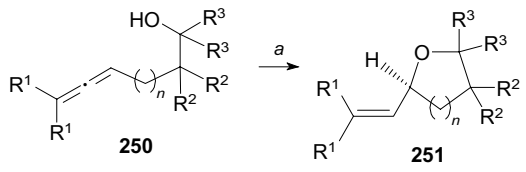
thermally unstable vinyl bis-gold complex **257**. After studying the reactivity of these two gold complexes towards acids, it was shown that the formation of complex **256** under the reaction conditions is fast and reversible, whereas complex **257** is beyond the catalytic cycle, functioning as a metal reservoir.

A highly enantioselective hydroalkoxylation catalyzed by the chiral diphosphane gold complex $[Au_2(P-P)Cl_2]$ [where P–P = 2,2′-bis(diarylphosphanyl)biphenyl] was reported.[282] The use of AgOTs as a co-catalyst at low temperature (−2 °C) and high dilution provides an enantioselectivity of >99% for the cyclization of the axially chiral γ-allenols; the reaction is relatively insensitive to dialkyl and diaryl substituents in the alkyl chain. This system was also efficient for the cyclization of achiral and chiral δ-allenols giving substituted tetrahydropyrans. The application of NAC ligands (NAC are nitrogen acyclic carbenes) in this reaction was described; however, the stereocontrol is lower in this case.[283]

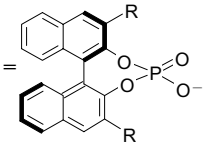
In recent years, the use of chiral anions for the control over the stereochemistry of hydroalkoxylation of allenols has been the subject of active studies.[284, 285]

In the presence of the binuclear gold complex with the achiral diphosphine dppm ligand in combination with a silver salt and chiral phosphate **258**, products **251** are formed with enantioselectivity of up to 97% (Scheme 111).

Scheme 111



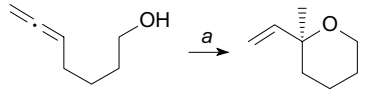
(*a*) [(dppm)$(AuCl)_2$ (2.5 mol.%), [(*R*)-**258**]Ag (5 mol.%), PhH, 23 °C; n = 1, 2; R^1, R^2, R^3 = Alk, Ar;

(*R*)-**258** =  (R = 2,4,6-$Pr^i_3C_6H_2$)

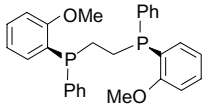
The use of chiral 1,2-bis[(*o*-anisyl)phenylphosphino]-ethane (DIPAMP, **259**) as a ligand for a gold complex and a chiral counter-ion in a silver salt results in the synthesis of the allenol cyclization product with excellent enantioselectivity even in the case of unsubstituted γ-allenol **250c** (Scheme 112).

The chiral anion strategy was also used for the enantioselective hydroalkoxylation of *N*-substituted hydroxylamines **260**, which gave vinylisoxazolidines and vinyloxazines **261** (n = 1 and 2, respectively) (Scheme 113).[48]

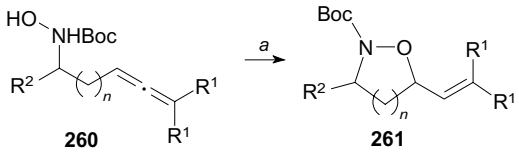
Scheme 112



(*a*) [(**259**)$(AuCl)_2$] (2.5 mol.%), [(*R*)-**258**]Ag (5 mol.%), PhH, 23 °C;

259 =  [(*S*,*S*)-DIPAMP]

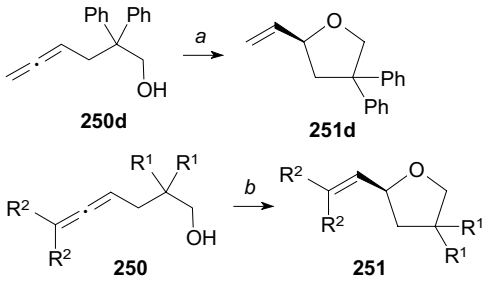
Scheme 113



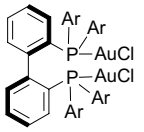
(*a*) [(**259**)$(AuCl)_2$] (2.5 mol.%), [(*R*)-**258**]Ag (5 mol.%), PhH, 23 °C; n = 1, 2

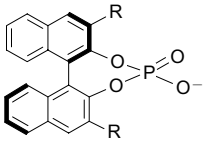
A synergistic effect of enantiomerically pure gold complex **262** and chiral phosphate anions **263**, **264** was found [286, 287] (Scheme 114).

Scheme 114



(*a*) **262** (2.5 mol.%); [(*S*)-**263**]Ag (5 mol.%) (75%, 75% *ee*) or [(*S*)-**263**]Ag (2.5 mol.%) (86%, 83% *ee*);
(*b*) **262** (2.5 mol.%); [(*S*)-**264**]Ag (2.5 mol.%);

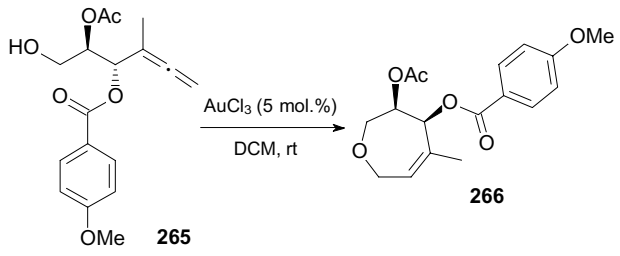
262 =  (Ar = 3,5-$Me_2C_6H_3$),

 {R = 4-PhC_6H_4 [(*S*)-**263**], 4-(4-$Bu^tC_6H_4$)C_6H_4 [(*S*)-**264**]}

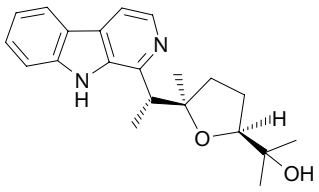
The coordination of the asymmetric anion to gold and participation of the complex thus formed in the catalytic cycle were demonstrated.[288]

Alcaide *et al.*[289] showed the possibility to prepare seven-membered oxygen-containing heterocycles. For example, the regioselective 7-*endo*-*trig*-cyclization of γ-allenol **265** in the presence of $AuCl_3$ affords tetrahydrooxepine **266** (Scheme 115).

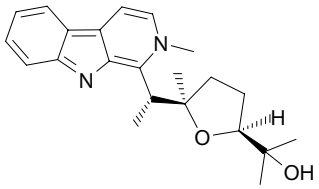
Scheme 115



Structures 267, 268



267 [(−)-Isocyclocapitelline]

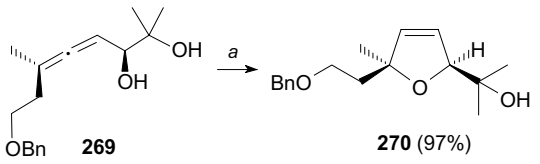


268 [(−)-Isochrysotricine]

The achievements of homogeneous gold catalysis in the series of allenes opened up the route to various five- and six-membered heterocyclic compounds,[290] which made it an available tool for stereoselective synthesis of complex natural products.[291–294] In particular, β -carboline alkaloids **267** and **268** were synthesized.

The cyclization of α-allenol **269** requires the use of only 0.05 mol.% $AuCl_3$; this gives highly functionalized dihydrofuran **270** in a high yield (Scheme 116). The reaction proceeds over a period of 10 min at room temperature, with the catalyst turnover number (TON) being 1900 (for loading of 2 g).[295, 296]

Scheme 116



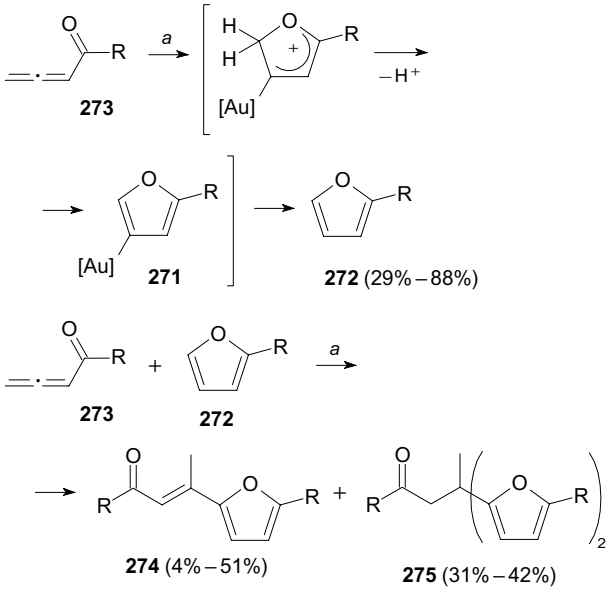
(*a*) $AuCl_3$ (0.05 mol.%), THF, rt, 10 min

Carbonyl group as a nucleophile. The carbonyl oxygen atom can act as a nucleophile. The elimination of gold from intermediate **271** as a result of protodeauration gives an aromatic compound, monosubstituted furan **272**.[145] The latter can react with substrate **273** to give mono- (**274**) and diaddition (**275**) products (Scheme 117).

Another approach to the synthesis of furans *via* a gold-catalyzed reaction was proposed by Zhou *et al.*[297] In the presence of a gold(III) complex with porphyrin, [Au(TPP)]Cl (**276**), cycloisomerization of allenones **273** may furnish the corresponding furans in high yields (Scheme 118, Table 7).

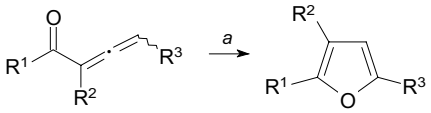
It was found that cycloisomerization of allenones in the presence of Au^{III} porphyrin catalyst **276** proceeds to a quantitative conversion of the substrate. More than 8300 products were obtained with this catalytic system.[297] Complex **276** is also active towards hydroamination and hydration. The mechanism of catalysis is not entirely clear, because there is no room for substrate coordination in the usual planar gold complex with tetradentate porphyrin; however the authors proposed the mechanism shown in Scheme 119.

Scheme 117



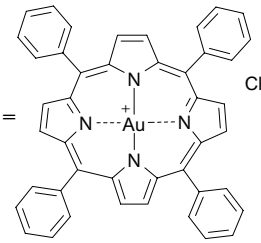
(*a*) $AuCl_3$ (0.1 mol.%), MeCN, rt; R = Alk, Ar

Scheme 118



(*a*) [Au(TPP)]Cl (**276**) (1 mol.%), CF_3CO_2H (10 mol.%), Me_2CO, 60 °C, 0.5 – 5 h; R^1, R^2, R^3 = H, Alk, Ar

276 =

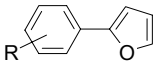
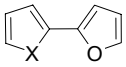
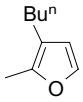
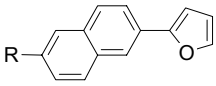
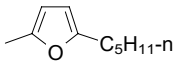
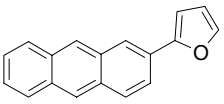
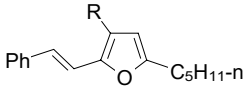
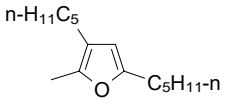
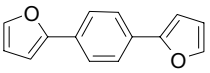


([Au(TPP)]Cl)

Study of the cycloisomerization of 4-$XC_6H_4C(O)CH{=}C{=}CH_2$ derivatives [**273**: X = H (**a**), Me (**b**), OMe (**c**), Br (**d**) and Cl (**g**)] showed that the reactivity of allenones with electron-donating groups (**273b**,**c**) is higher than the reactivity of unsubstituted substrate **273a**, whereas the presence of electron-withdrawing groups (**273d**,**g**) reduces the substrate reactivity. Using least squares fitting, a good correlation was found between log k_X/k_H (k_X, k_H are the reaction rate constants) and the Hammett constants (σ^+) (with the correlation coefficient $R = 0.998$), with the mean square deviation being $\rho^+ = -0.36$ (Fig. 3). A small negative value of ρ^+ indicates a minor positive charge arising on the allenone substrate and the electrophilic nature of the Au^{III} active species. In the opinion of the authors,[297] this means that the reaction is rate-limited by the formation of intermediate **277** and accounts for the increase in the reaction time for substrates containing electron-withdrawing groups. Table 7 presents examples of the obtained products **272**.

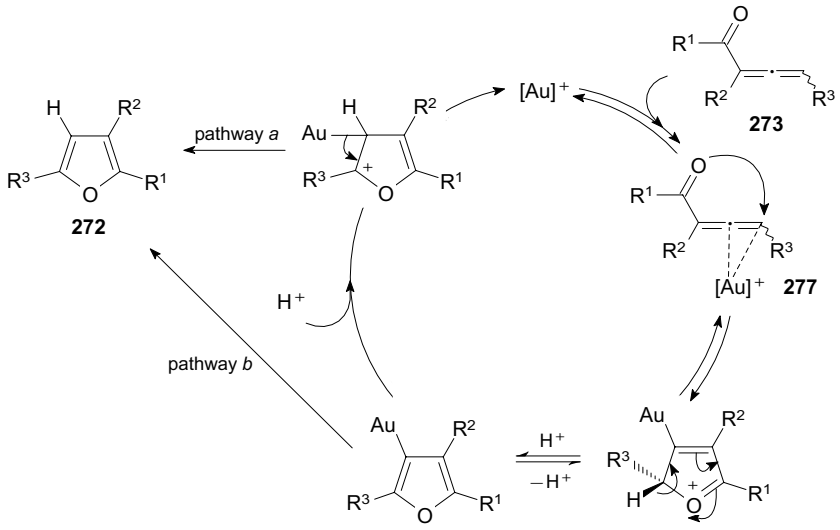
Since the hardness of Au^+ and Au^{3+} as Lewis acids differs, the cycloisomerization of bromo derivative **278** gives

Table 7. Cycloisomerization of allenones in the presence of a Au catalyst (see Scheme 118).[297]

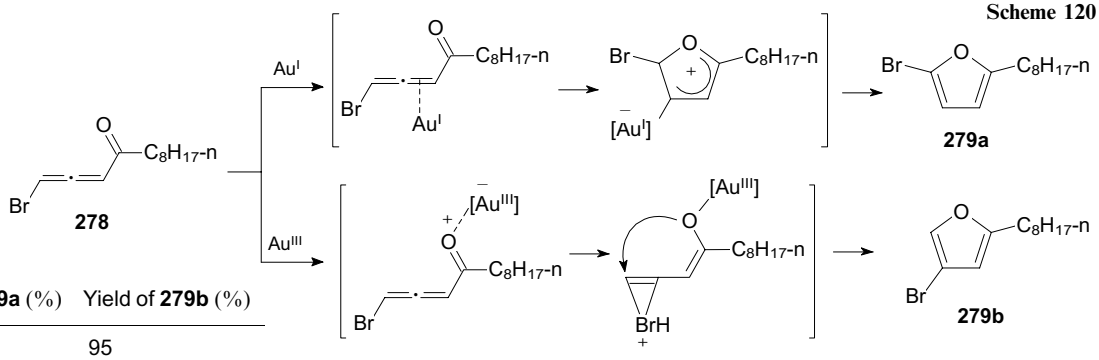
Product **272**	Compound	R or X	Yield (%)	Product **272**	Compound	R or X	Yield (%)
	**a**	H	88		**o**	O	82
	b	4-Me	84		**p**	S	78
	c	4-OMe	81				
	d	4-Br	85		**q**	Me	89
	e	3-Br	87		**r**	Bu^n	92
	f	2-Br	98				
	g	4-Cl	86		**s**	–	90
	h	4-CO_2Me	92				
	i	4-NO_2	91				
	**j**	H	80		**t**	–	97
	k	Br	85				
	l	CO_2Me	88				
					u	H	95
	**m**	–	84		**v**	Bu^n	93
					**w**	–	90
	**n**	–	73 (see [a])				

[a] Prepared from *p*-di(allylcarbonyl)benzene.

Scheme 119



Scheme 120



	Yield of **279a** (%)	Yield of **279b** (%)
$AuCl_3$	5	95
$(Et_3P)AuCl$	99	1

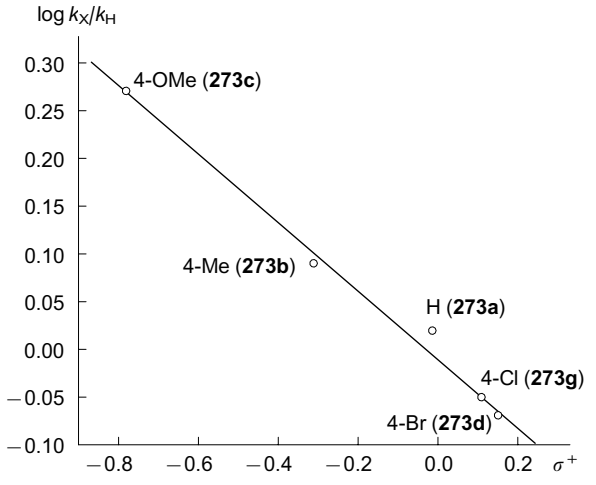
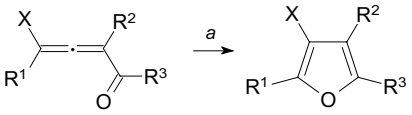


Figure 3. Correlation between log k_X/k_H and σ^+ for compounds **273**.[297]

different major products depending on the type of catalyst: bromofurans **279a** or **279b** (Scheme 120).[298] The Au^+ ion behaves as a carbophile (soft Lewis acid), while the Au^{3+} ion behaves as an oxophile (hard Lewis acid).

Gevorgyan and co-workers[299] studied the Au^{III} salt-catalyzed cyclization of substrates **280** accompanied by 1,2-shift of the halogen atom in the allene system (the mechanism is depicted in Scheme 120). The reaction produces halo-substituted furans **281** in moderate to high yields (Scheme 121).

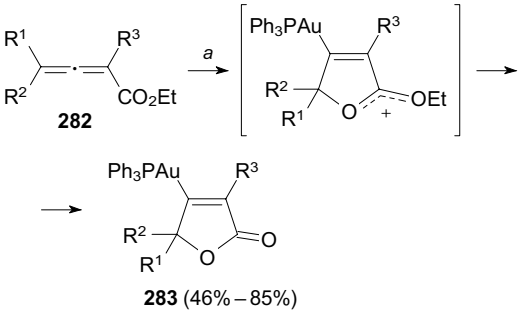
Scheme 121



(*a*) $AuCl_3$ (1 mol.%), PhMe, rt; X = Cl, Br; R^1 = H, Alk, $(CH_2)_2OTBS$; R^2, R^3 = H, Alk, Ph

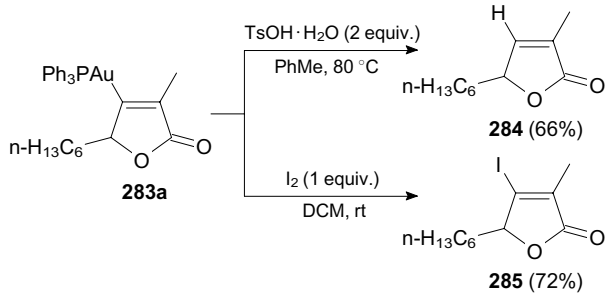
Allenoates **282** react with an equimolar amount of the cationic gold complex giving vinyl – gold complexes **283** (Scheme 122). The reaction is carried out at room temperature in air. Complexes **283** are stable; they were isolated in a pure state and some of them were studied by X-ray crystallography.[111, 300]

Scheme 122



(*a*) [Ph_3PAu]OTf; R^1, R^3 = H, Me; R^2 = Me, Pr^i, n-C_6H_{13}, Bn

Scheme 123



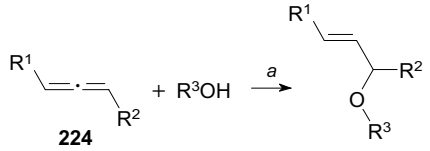
Complexes **283** can participate in the subsequent transformations (see, for example, the synthesis of compounds **284** and **285** in Scheme 123). It was assumed[300] that complexes of this type are formed as intermediates in gold-catalyzed reactions.

Studies of vinyl gold derivatives were continued and form a separate subject for discussion; currently, quite a few studies along this line have been reported (see, for example, Ref. 301).

4.2.2. Intermolecular reactions

A highly regio- and stereoselective synthesis of allylic ethers **286** from asymmetric allenes **224** and alcohols was developed by Cui *et al.*[302] The reaction was catalyzed by a mixture of Ph_3PAuNO_3 with sulfuric acid (Scheme 124).

Scheme 124

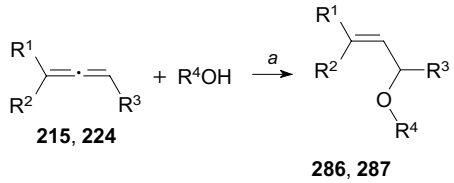


(*a*) Ph_3PAuNO_3 (2 mol.%), H_2SO_4 (2 mol.%), 40 °C, 4 h;
R^1 = Ar: R^2 = H, Me; R^3 = Alk, Bn, cyclo-Alk

Nishina and Yamamoto[60] proposed a highly efficient method for hydroalkoxylation of allenes **215** and **224** in the absence of a solvent with a gold complex as a catalyst. In the case of trisubstituted allenes **215**, the alkoxy group adds to the least substituted carbon atom (product **287**), which is apparently due to the steric effects of the reactants (Scheme 125).

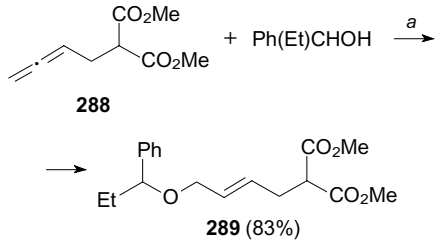
Widenhoefer's research team[303] demonstrated the applicability of a Au^I complex with the NHC ligand in combination with AgOTf as catalysts for regio- and stereo-

Scheme 125



(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), without a solvent, 30 °C;
R^1 = Alk, cyclo-Alk, Bn, Ar; R^3 = Alk; R^4 = Alk, All, Bn;
R^2 = H (**224**, **286**), Alk (**215**, **287**)

Scheme 126

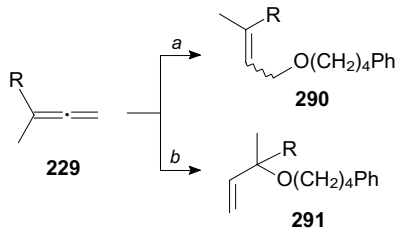


(*a*) IPrAuCl (**7**) (5 mol.%), AgOTf (5 mol.%), PhMe, 23 °C, 4 h

selective hydroalkoxylation of allene **288** to ether **289** (Scheme 126).

Three research teams (headed by Widenhoefer, Yamamoto and Zhang) demonstrated that Au^I-catalyzed intermolecular hydroalkoxylation of allene **229a** (R = Me) results in the predominant formation of sterically least hindered primary allylic ethers **290** (Scheme 127).[58, 60, 302 – 306]

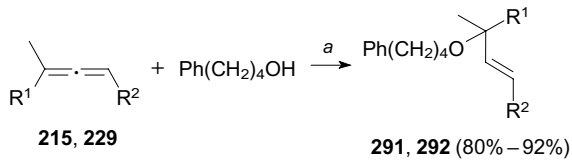
Scheme 127



(*a*) $Ph(CH_2)_4OH$, Au^I; (*b*) $Ph(CH_2)_4OH$ (excess), Au^I, DMF;
R = Me, n-C_9H_{19}, Bn, $BnCH_2$, Ph

Quantum chemical calculations by the DFT method carried out by Paton and Maseras[307] for model substrates, dimethylallene (**229a**) and methanol, demonstrated a high probability of fast rearrangement of the gold – allene transition complex with alcohol into thermodynamically stable primary allylic ether. However, soon after that, Hadfield and Lee[308] experimentally showed the possibility of preparing tertiary allylic ethers **291**, **292** (which are kinetic products) by using a 10-fold excess of alcohol. High regioselectivity (> 99 : 1) was attained by preventing isomerization, which produces the primary allylic ether, by using excess alcohol (Scheme 128).

Scheme 128

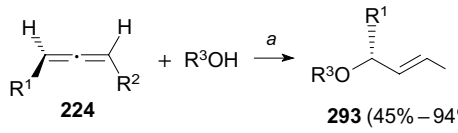


(*a*) IPrAuCl (**7**) (10 mol.%), AgOTf (10 mol.%), DMF, 0 °C, 24 h;
R^1 = Me, n-C_9H_{19}, Bn, $BnCH_2$, Ph; R^2 = H (**229**, **291**), $(CH_2)_2OTBS$ (**215**, **292**)

Thus, currently both products of alcohol addition to allene, that is, primary and tertiary allylic ethers, can be obtained using Au^I catalysts (see Scheme 127).

The transfer of chirality involved in the intermolecular gold(I)-catalyzed hydroalkoxylation of less studied 1,3-disubstituted allenes **224** was reported in 2016[309] (Scheme 129). It was shown in control experiments that the nature (especially the inductive effect *I*) of substituents in the substrate is the decisive factor for regioselectivity of the formation of products **293**.

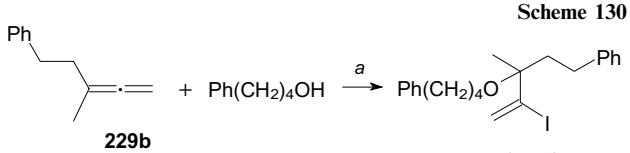
Scheme 129



(*a*) IPrAuCl (**7**) (10 mol.%), AgOTf (10 mol.%), DMF, 0 °C, 24 h;
R^1 = H, Alk, Cy; R^2 = Ph, $(CH_2)_2Ph$, CH_2CO_2Et, CH_2OBn, CH_2OBz, CH_2OCy; R^3 = Me, Bn, PMB; PMB is 4-methoxybenzyl

Lee's research team[310] ascertained that gold(I)-catalyzed intermolecular iodoalkoxylation of allenes (for example, compound **229b**) on treatment with *N*-iodosuccinimide (NIS) as the electrophilic agent in the presence of a 10-fold excess of alcohol follows a regio- and stereoselective pathway giving rise to α-iodo-*tert*-allylic ether **294** (Scheme 130).

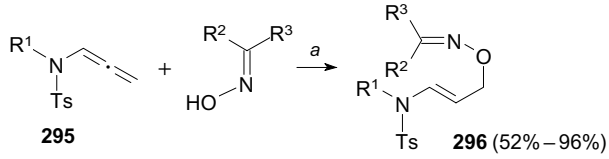
Scheme 130



(*a*) NIS (1.05 equiv.), IPrAuCl (**7**) (10 mol.%), AgOTf (10 mol.%), DMF, 0 °C, 24 h

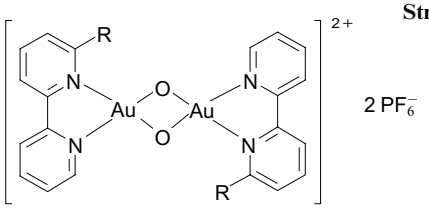
The [(**28**)Au^I]SbF_6 complex with the JohnPhos ligand catalyzes the regioselective addition of electron-rich aldoximes or ketoximes to the terminal allene carbon atom of *N*-allenylsulfonamides **295** to give allyloximino-(*E*)-enesulfonamides **296** (Scheme 131).[311]

Scheme 131



(*a*) [(**28**)Au^I]SbF_6 (5 mol.%), DCM, rt; R^1 = Alk, Ar, Bn;
R^3 = Ph: R^2 = H, Me; $R^2 – R^3$ = $(CH_2)_4$

Structures 297

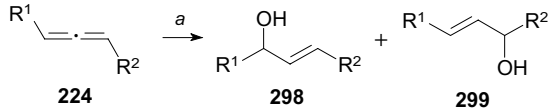


R = Me, Pr^i, neo-C_5H_{11}, 2,6-$Me_2C_6H_3$

Gold complex **297** catalyzes the addition of water to alkenes under mild conditions to give epoxides.[312]

The hydration of allenes **224** gives rise to a mixture of allylic alcohols **298** and **299** in moderate yields (25% – 72%) and with moderate regioselectivity (Scheme 132).[313]

Scheme 132

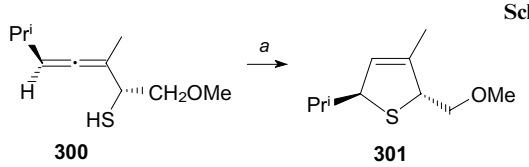


(*a*) H_2O (1.5 equiv.), AuCl (5 mol.%), AgOTf (5 mol.%), 1,4-dioxane, 23 °C; R^1, R^2 = Alk

4.3. Hydrothiolation

Morita and Krause[314] reported the first example of C–S bond formation upon gold-catalyzed cyclization of α-thioallene **300**. This reaction affords 2,5-dihydrothiophene **301** with the transfer of chirality[315] (axial to central chirality) (Scheme 133).

Scheme 133

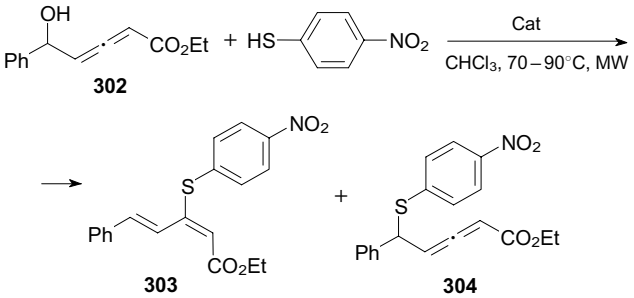


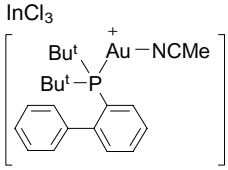
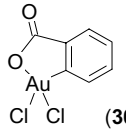
(*a*) AuCl (5 mol.%), DCM, 20 °C

It is well-known that organosulfur compounds (thiols, sulfides and disulfides) are capable of strong coordination to transition metals, in particular, gold.[316] Hence, the use of gold as a catalyst in the presence of these functional groups is rather unexpected. The mechanism of reaction presented in Scheme 133 was studied by quantum chemical calculations (B3LYP/6-31G*, SDD pseudopotential for Au).[317] The calculations revealed an effect of the solvent (dichloromethane) on the decrease in the activation energy and stabilization of the transition state.

The attempts at using gold complexes for dehydrative thiolation of allenol **302** were not quite successful:[318] products **303** and **304** were formed in relatively low yields and with low regioselectivity (Scheme 134). In this case, indium(III) chloride proved to be a more efficient catalyst, which in some cases provided the synthesis of compound **303** in a moderate yield, whereas in the presence of catalyst **305**, no reaction took place at all.

Scheme 134



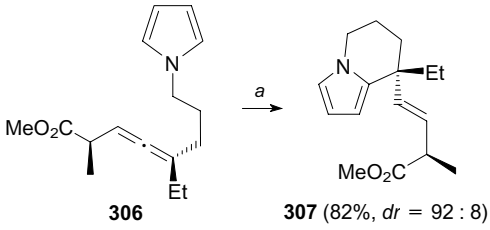
Cat	Yield of **303** (%)	Yield of **304** (%)
$InCl_3$	47	0
 (SbF_6^-) (**123**)	25	30
 (**305**)	0	0

4.4. (Het)arenes as nucleophiles

It was shown above that the reaction of allenyl ketones **273** with furans gives furan-containing α,β-unsaturated ketones **274** (see Scheme 117).[145] The yields of these products are moderate, as further furan addition takes place giving bis-products **275**.

Electron-rich pyrroles such as compound **306** can also act as nucleophiles and add to allenes in the presence of gold(I) and silver salts. This reaction was utilized by Nelson and co-workers[319] to prepare (–)-rhazinilam (Scheme 135). The complex $PdCl_2(MeCN)_2$ used in this reaction provides the synthesis of product **307** in the same yield; however, the diastereoselectivity of the reaction substantially decreases.

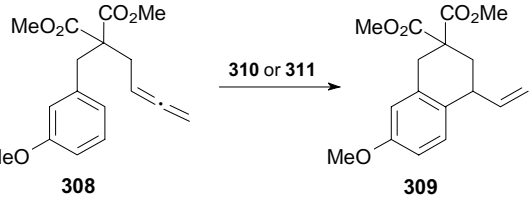
Scheme 135



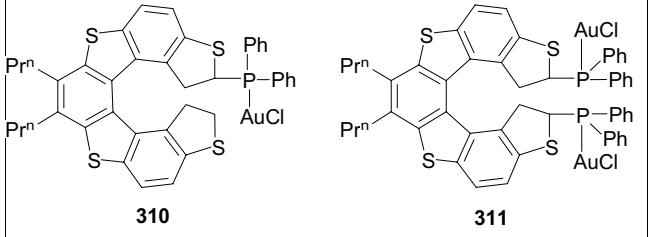
(*a*) AuCl (5 mol.%), AgOTf (20 mol.%)

An aryl group containing electron-donating substituents can also act as a nucleophile: for example, allene **308** is converted to product **309** under the action of helicene catalysts **310** or **311** (Scheme 136). [278]

Scheme 136



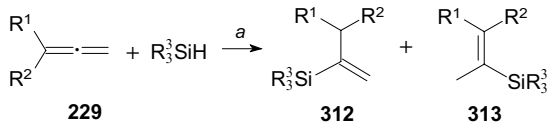
Structures 310, 311



4.5. Hydrosilylation of allenes

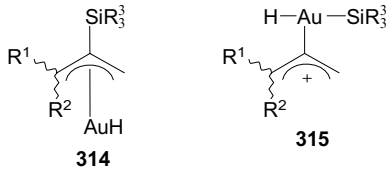
Gold nanoparticles (Au-NP) stabilized on the titania surface were used [320, 321] as recyclable and many times reusable catalysts for hydrosilylation of allenes **229** with trialkylsilanes (Scheme 137). The reaction is highly regioselective, with the trialkylsilyl group adding to the more substituted double bond of the allenyl system (the ratio of the major, or in some cases, the only, internal addition product **312** to the minor product **313** varies from 82 : 18 to 99 : 1). This Markovnikov regioselectivity is attributable to steric factors and to electron density distribution in the substrate molecule. Two possible reaction mechanisms were proposed [321] for this reaction, one implying the formation of π-allyl – gold(I) intermediate **314**, while the other one proceeding *via* σ-bonded η^1-complex **315**. Both mechanisms can interpret the formation of **312** as the major product.[321]

Scheme 137



(*a*) Au-NP/TiO_2 (1 mol.%); R^1 = H, Me, CH_2CO_2Et; R^2 = Me, Ph, CH_2CO_2Et, MeO, 4-XC_6H_4 (X = H, Me, OMe, F, Br); $R^1 – R^2 = (CH_2)_5$; R^3_3Si = Et_3Si, $PhMe_2Si$, Ph_2MeSi, HMe_2SiOMe_2Si, Me_3SiOMe_2Si

Structures 314, 315



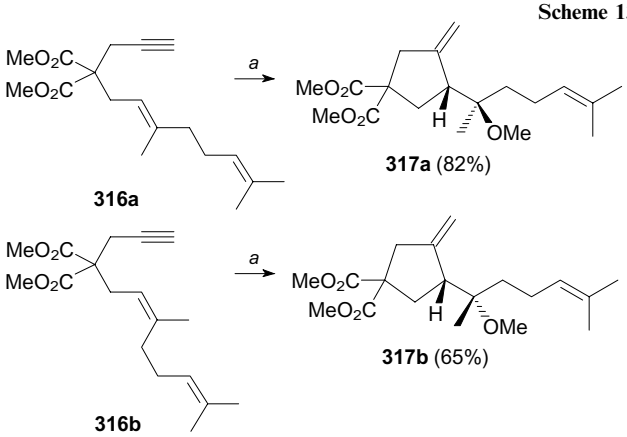
5. Nucleophilic addition to enynes

5.1. Addition of heteronucleophiles

In the presence of alcohols or water, gold(I) compounds catalyze the addition of heteronucleophiles to enynes to give alkoxy- or hydroxycyclization products.[132, 322] The process as a whole is stereospecific and includes *anti*-addition of the electrophile to give the (η^2-alkyne) – Au^I complex and heteronucleophile addition to the alkene. Scheme 138 presents the methoxycyclization of geometric isomers **316a**,**b**, which results in the formation of diastereomeric products **317a**,**b** *via* the attack by methanol on intermediate **318**.

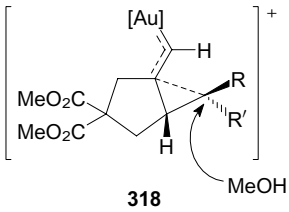
In this reaction, the catalyst is generated by protonolysis of the $Au^I – C$ bond in the Ph_3PAuMe precatalyst by strong Brønsted acid. The reaction obeys Markovnikov regioselectivity rule, which also illustrates the conversion of substrate

Scheme 138



(*a*) MeOH, Ph_3PAuMe (1 mol.%), HBF_4 (6 mol.%), 23 °C

Structure 318

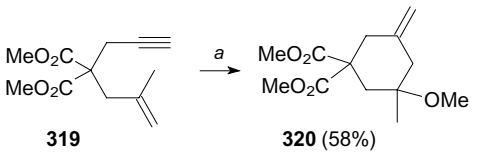


319 to six-membered ring **320** through intermediate **321** (Scheme 139).

The addition of heteronucleophiles to 1,5-enynes is also stereospecific.[138, 323, 324]

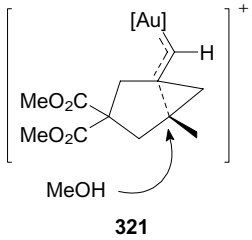
A number of highly polarizable substrates can be converted to mixtures of products in high yields (95% – 100%) depending on the reaction conditions. For example, sub-

Scheme 139

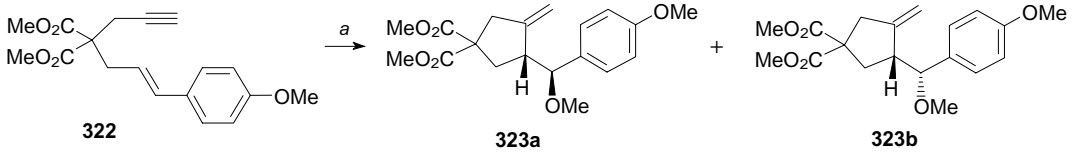


(*a*) MeOH, Ph_3PAuMe (3 mol.%), $AgSbF_6$ (3 mol.%), 23 °C

Structure 321



Scheme 140



(*a*) MeOH, [Au] (2 mol.%), Solv, 23 °C

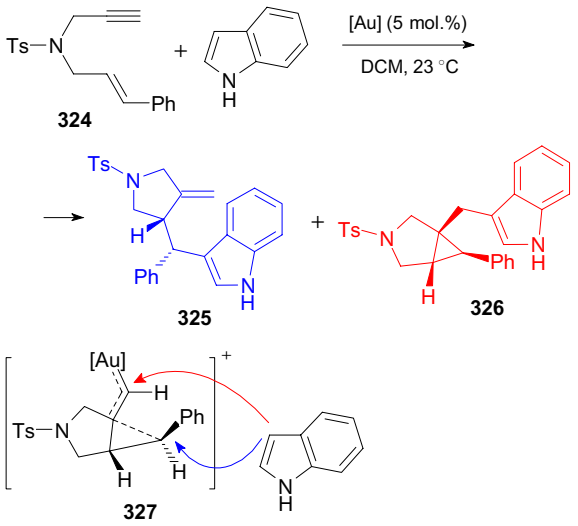
strate **322** reacts with 5 equiv. of MeOH in dichloromethane to give a mixture of *anti*- and *syn*-stereoisomers **323a**,**b** in 3 : 2 ratio, whereas in pure methanol the reaction gives only product **323a** (Scheme 140).[325]

5.2. Addition of carbon nucleophiles, cycloisomerization reactions

The gold-catalyzed reactions of enynes were considered in Part II of our review,[2] while cycloisomerization reactions will be discussed in detail in a subsequent part. It should be noted that a relatively recent review [326] is devoted to gold-catalyzed cycloisomerization reactions. However, this rather extensive research area is being constantly supplemented by new data; therefore, we will try to reflect as fully as possible the current state of research, including, whenever possible, all of the data available by the time of review preparation. In this Section, we will consider only some reactions of formation of new carbon – carbon bonds involving a double bond or a system of double bonds as illustrative examples.

Gold(I) catalysis is also possible for the addition of carbon nucleophiles to enynes.[323, 327 – 329] For example, 1,6-enyne **324** reacts with electron-rich heteroarene (indole) to give products **325** and **326** *via* nucleophilic attack on the cyclopropyl or carbene carbon atom in intermediate **327** (Scheme 141).[327, 328]

Scheme 141

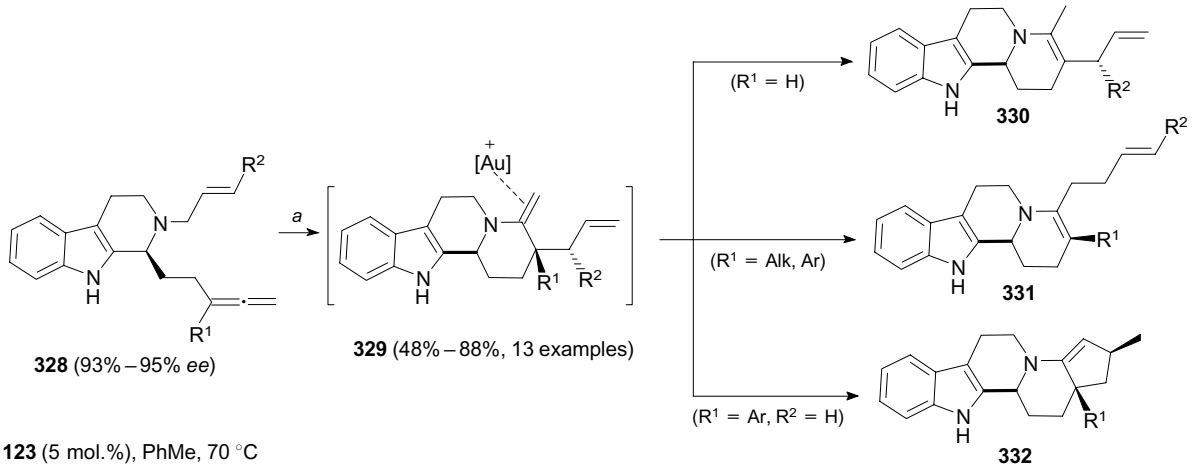


[Au]	Yield (%)	Ratio **325** : **326**
[(28) Au^{I}**]**SbF_6	74	80 : 20
[IPrAu(NCPh)]SbF_6	57	25 : 75

The addition of 1,3-dicarbonyl compounds, like the addition of allylsilanes, to 1,6-enynes and 1,5-enynes is also catalyzed by cationic Au^{I} catalysts.[328] The participation of allenes and their derivatives in the formal cycloaddition reactions catalyzed by gold and platinum were considered in detail in a review.[330]

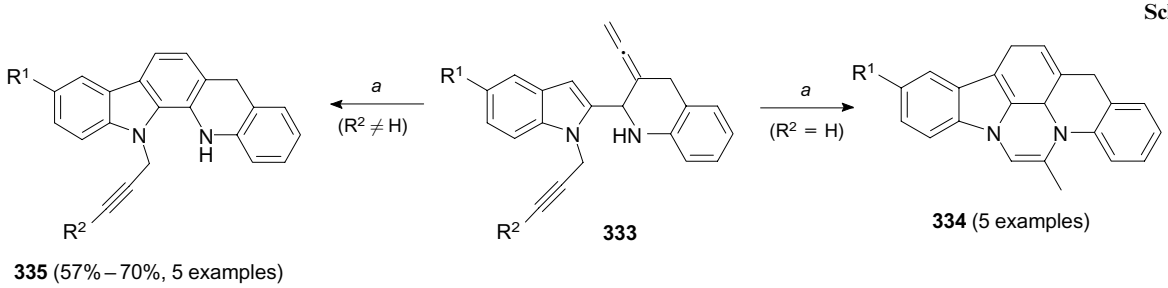
In 2018, an efficient method was proposed for the cyclization of enantioenriched *N*(2)-allylcarboline **328**.[331] A gold complex is used as the catalyst. The initial gold(I) activation of the allene moiety of substrate **328** triggers the tandem process consisting of 6-*exo*-*dig*-cyclization and aza-Cope reaction and leading to intermediate **329**. The nature of substituents R^1 and R^2 determines the transformation pathways of the intermediate, resulting in various indolo[2,3-*a*]quinazolines **330** – **332** (Scheme 142). When R^1 = H, isomerization of the exocyclic carbon – carbon

Scheme 142



(*a*) **123** (5 mol.%), PhMe, 70 °C

Scheme 143



(*a*) IPrAuCl (**7**) (5 mol.%), $AgSbF_6$ (5 mol.%), DCE, rt

double bond takes place to give product **330**. If the substituent R^1 is an alkyl or aryl group, 3,3-sigmatropic rearrangement takes place to afford product **331**. In a specific case (R^1 = Ar, R^2 = H), pentacyclic compounds **332** were isolated.

Allenynes **333**, containing an indole system and a secondary amine moiety, are converted under gold catalysis to fused heterocyclic compounds **334** and **335** (Scheme 143).[332] The cationic complex $[IPrAu]^+$ activates the allene group towards 6-*endo*-carboauration at the C(3) atom of the indole ring. If the alkyne moiety is terminal, the second cyclization *via* hydroamination of the alkyne triple bond is possible.

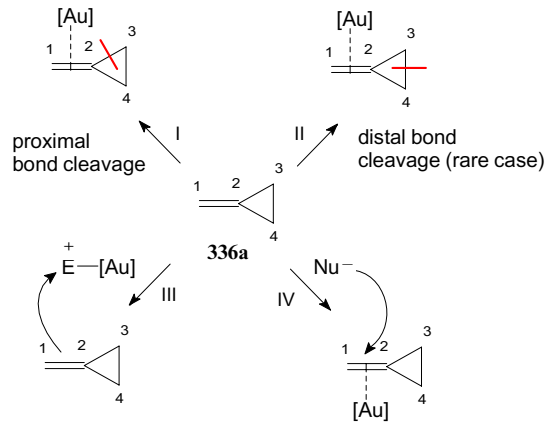
6. Tandem reactions of methylene- and vinylenecyclopropanes

Gold salts and complexes act as efficient soft Lewis acids in the electrophilic activation of carbon – carbon multiple bonds towards reactions with various nucleophiles, which are based on the interaction between the Au catalyst and the alkene, alkyne or allene π-bond. Transformations of this type are also inherent in highly strained methylene- (MCPs) and vinylidenecyclopropanes (VDCPs), accessible building blocks of modern organic synthesis.[333 – 335]

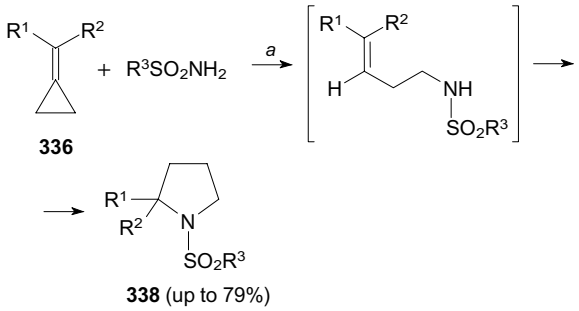
Methylene- and vinylidenecyclopropanes possess amphiphilic properties. Upon gold activation, MCPs or VDCPs can be nucleophilically attacked by another reagent, in some cases, with opening of the three-membered ring. The carbon – carbon double bond in such compounds can also act as a nucleophile, for example, when some more electrophilic gold-activated reagent is present in the system. In this case, subsequent cascade reactions are possible.[336] The cyclopropane moiety increases the s-character of the carbon – carbon double bond and is simultaneously an excellent π-donor moiety. Substituents in the three-membered ring or at the double bond have a considerable effect on the reaction mechanism.

The gold-catalyzed reactions of methylenecyclopropane (**336a**) can be divided into four groups (I – IV in Scheme 144).[336] The first group, characterized by initial cleavage of the C(2) – C(3) bond of MCP, includes hydroamidation (domino ring opening and closure reactions) (Scheme 145)[38] and intramolecular hydroamination of compound **337** (Scheme 146).[337] These transformations resulted in the synthesis of pyrrolidines **338** and isoxazolidines **339**.

Scheme 144

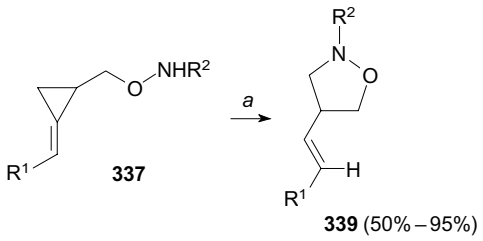


Scheme 145



(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), PhMe, 85 °C; R^1, R^2 = H, Alk, Ar; R^3 = Ar

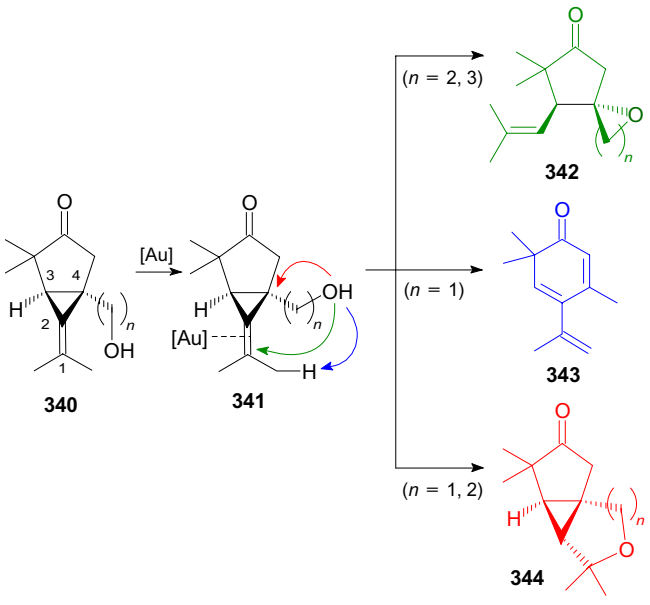
Scheme 146



(*a*) Ph_3PAuCl (10 mol.%), AgOTf (10 mol.%), DCE, 80 °C; R^1 = Ar; R^2 = Ts, Bs, Ns; Bs is benzenesulfonyl

One more interesting example of reactions of this type was reported by Zriba *et al.*[338] (Scheme 147). Gold(I)-catalyzed cycloisomerization of compound **340** affords different products or product mixtures depending on the size of the linker bearing the hydroxyl group. In the case where n = 2 or 3, the C(2) – C(3) bond cleavage of intermediate **341** takes place to give spirocyclic oxetanes and tetrahydrofurans **342**. However, when n = 1, the C(3) – C(4) bond is cleaved yielding cyclohexadienone **343**. The formation of tricyclic products **344** is also detected. For n = 1, the

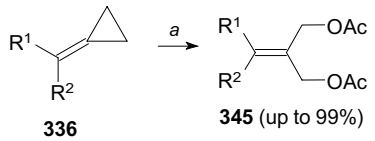
Scheme 147



343 : **344** product ratio is 54 : 38, while for $n = 2$, the **344** : **342** ratio is 42 : 30.

One more example of C(3)–C(4) bond cleavage of MCPs is represented by diacetylation of compounds **336**, which is catalyzed by Au^{I} and Au^{III} complexes and results in the formation of products **345** in high yield (Scheme 148).[339]

Scheme 148



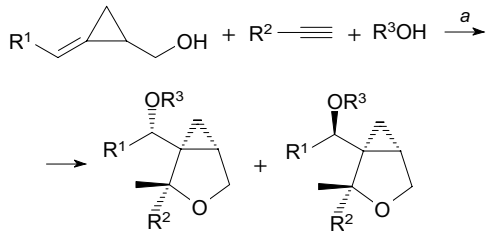
336 **345** (up to 99%)

(*a*) $PhI(OAc)_2$, Me_3PAuCl, AcOH, 60 °C; R^1, R^2 = H, Ar

A gold-catalyzed three-component intermolecular domino reaction was reported by Tian and Shi [340] (Scheme 149). During this reaction, the alkyne is subjected to double nucleophilic attack and protodemetallation (Scheme 150); as a result, a mixture of diastereomeric products **346a**,**b** is formed in 95% yield with a ratio of up to 3 : 1.

The enyne cycloisomerization is an important reaction, which allows the synthesis of functionalized cyclic

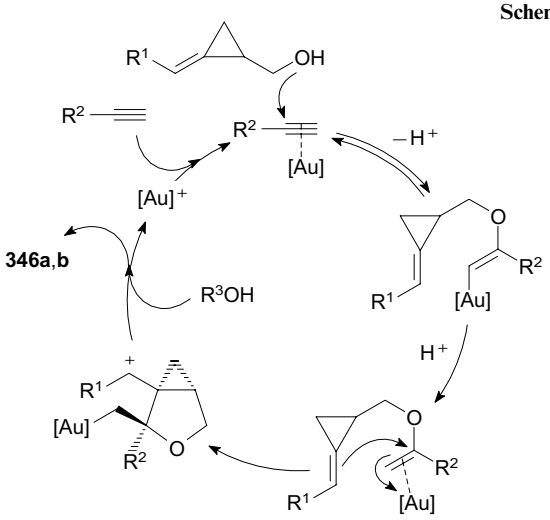
Scheme 149



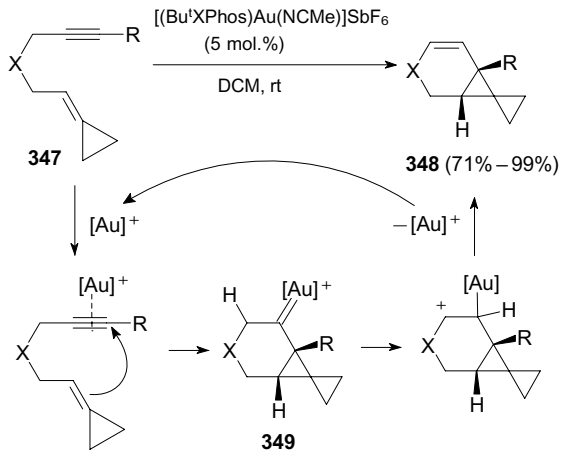
346a **346b**

(*a*) Ph_3PAuCl (3 mol.%), AgOTf (3 mol.%), DCM, 35 °C; R^1, R^2 = Ar; R^3 = Alk

Scheme 150



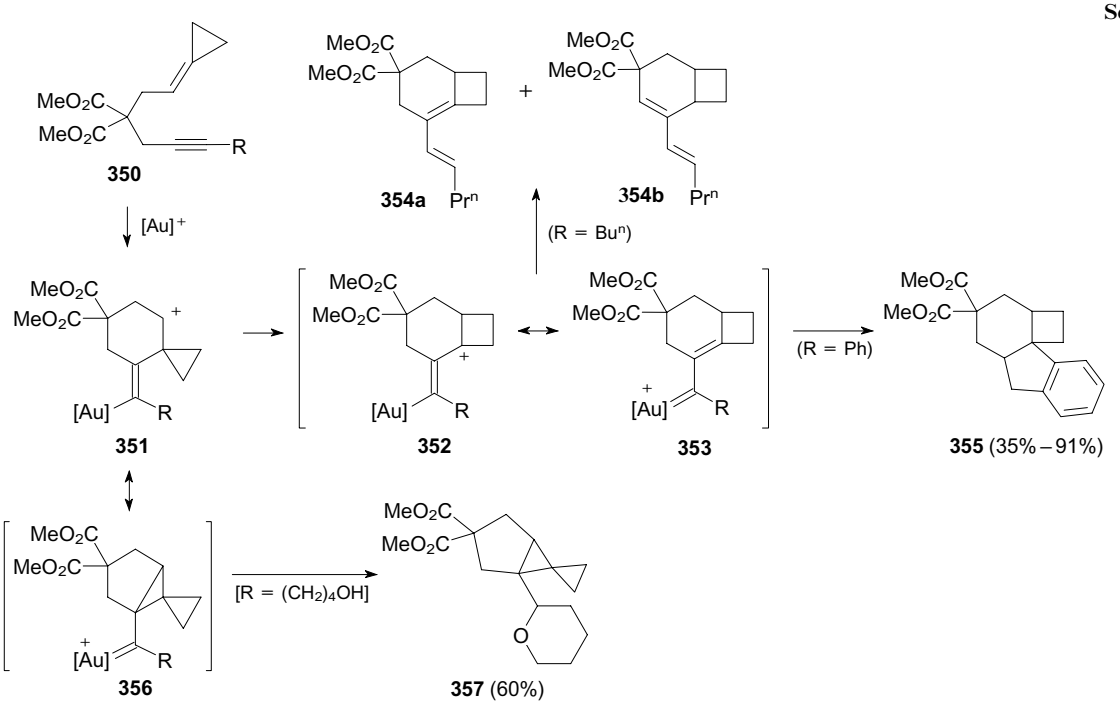
Scheme 151



347 **348** (71% – 99%) **349**

X = NTs, NBs, NNs, O; R = Ar, Alk; ButXPhos is 2-di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl

Scheme 152



structures.[341 – 343] Oxygen or nitrogen atom-bridged enynes are used for the synthesis of heterocyclic compounds. The gold(I)-catalyzed cycloisomerization of enynes **347**, containing a cyclopropane moiety and a nitrogen or oxygen bridge, gives tricyclic heterocycles **348** in high yields under mild conditions.[344] This reaction belongs to type IV reactions of MCPs (see Scheme 144) and comprises 6-*endo*-*dig*-cyclization, giving rise to intermediate **349** (Scheme 151).

Another example of the synthesis of complex polycyclic systems was reported by Sethofer *et al.*[345] In the first step, MCP **350** undergoes 6-*exo*-*dig*-addition to afford intermediate **351**, which is converted to cyclobutane intermediate **352** or intermediate Au carbene complex **353** upon expansion of the three-membered ring. The subsequent transformations depend of the nature of the substituent R and afford products **354a**,**b** and **355**. When the reaction time is 1 h, compounds **354a** and **354b** are formed in 92% yield and in 9 : 1 ratio, while after 15 h, the product ratio changes in favour of isomer **354b** (> 20 : 1), with the high total yield of the mixture (93%) being retained (Scheme 152).

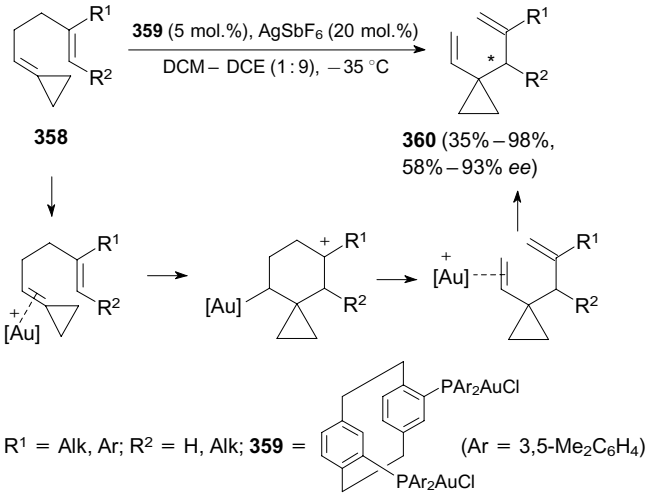
In the case where R = $(CH_2)_4OH$, intermediate **351** is converted to gold-stabilized cation **356** and then to pyran **357** in a moderate yield.

The enantioselective sigmatropic Cope rearrangement of alkenyl-substituted MCP **358** in the presence of chiral Au^I catalyst **359** proceeds at low temperature and affords vinylcyclopropanes **360** in high yields[346] (Scheme 153).

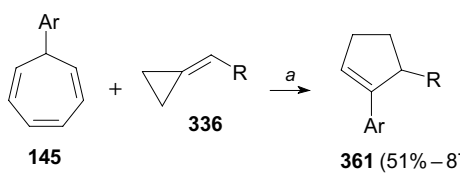
In 2014, Enchavarren's research team[347] demonstrated the possibility of the gold-catalyzed reaction between 7-arylcyclohepta-1,3,5-trienes **145** and methylenecyclopropanes **336** (R^1 = H), resulting in arylcyclopentenes **361** (Scheme 154). The gold – carbene intermediate is generated *via* gold-catalyzed retro-Buchner reaction of cycloheptatriene. Later, it was shown that the gold – carbene intermediate can be formed upon dehydrocarbonization of stable cyclopropanes.[348]

A known intramolecular version of this reaction is transformation of cycloheptatriene **145a** into tetracycle **362** (Scheme 155).[347]

Scheme 153

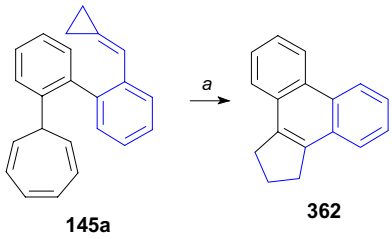


Scheme 154



(*a*) **123** (5 mol.%), DCE, 120 °C, 2 h (–PhH); Ar = 2-$PhOC_6H_4$, 2-(cyclo-C_3H_5)C_6H_4, 1-Naph; R = cyclo-C_3H_5, Cy, XC_6H_4 (X = H, 3-Cl, 4-Br, 4-Bu^t)

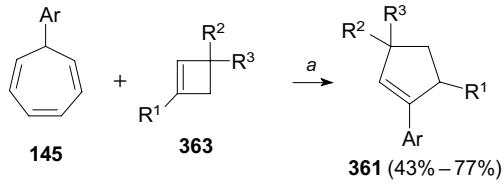
Scheme 155



(*a*) [IPrAu(NCPh)]SbF_6 (5 mol.%), DCE, 120 °C (–PhH)

In the reactions shown in Schemes 154 and 155, cyclobutene is formed from methylenecyclopropane as an intermediate. This is confirmed, in particular, by the fact that the use of cyclobutenes **363** under the same reaction conditions gives analogous cyclopentene derivatives **361** (Scheme 156).[347]

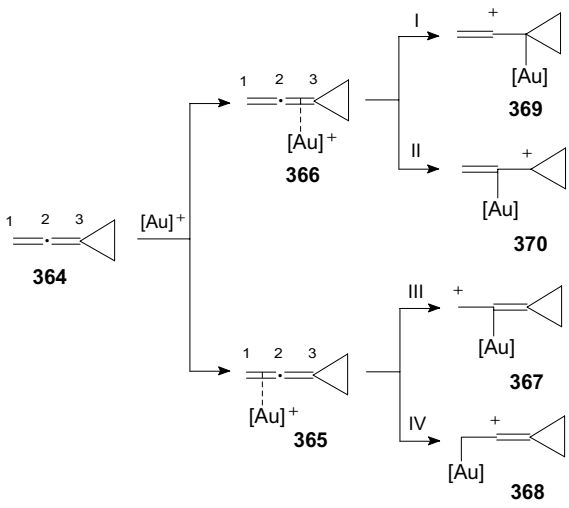
Scheme 156



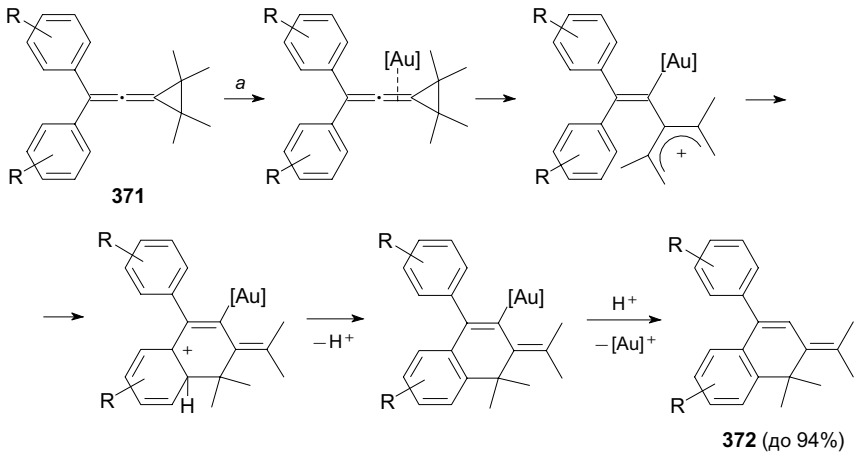
(*a*) **123** (5 mol.%), DCE, 120 °C, 3 h (–PhH); Ar = XC_6H_4 (X = H, 4-Cl, 2-OPh), 1-Naph; R^1 = YC_6H_4 (Y = H, 3-OH, 4-Br, 4-Bu^t, 4-OMe); R^2 = R^3 = H, Et; R^2–R^3 = $(CH_2)_5$

Gold-catalyzed reactions of vinylidenecyclopropanes **364** can also be divided into four groups (I – IV), which are presented in Scheme 157.

Scheme 157

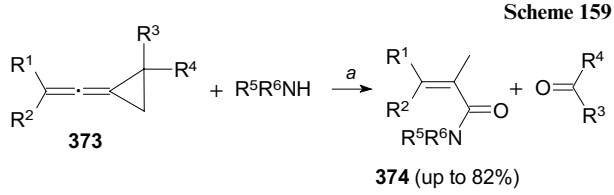


Scheme 158



(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), $MeNO_2$ – DCM (1 : 1) or $MeNO_2$, rt; R = H, Cl, OMe, F (in various positions)

Scheme 159



(*a*) O_2 (1 atm), Ph_3PAuCl (10 mol.%), TCE – DCE or PhMe, 50 °C; R^1, R^2, R^3 = Ar; R^4 = Me, Ar; R^5, R^6 = Alk

Depending on which of the allene double bonds is coordinated to gold, the reaction can give intermediates **365** or **366**, which are then converted to ions **367** – **370**. Note that no transformations of cation **368** have been described so far.[336]

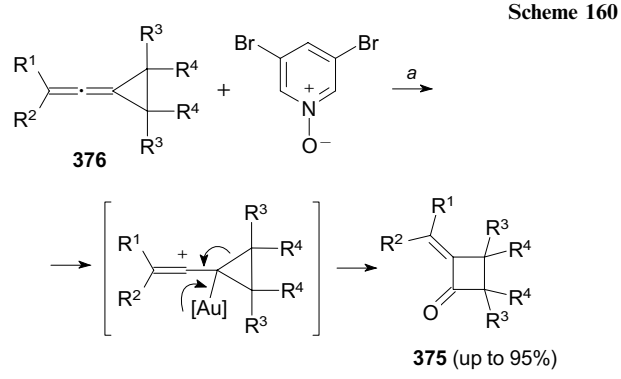
An example of reactions involving intermediates of type **366** and **370** is the gold-catalyzed transformation of VDCPs **371**, resulting in the formation of 1,2-dihydronaphthalene derivative **372** in high yield (Scheme 158).[349]

Another example of formation of intermediates **366** and **370** is provided by oxidative amination of VDCPs **373** with various secondary amines,[350] which gives fully substituted acrylamides **374** in good yields (Scheme 159).

Alkylidenecyclobutanones **375** are formed in good yields upon the oxidation of VDCPs **376** with 3,5-dibromopyridine *N*-oxide in the presence of the Ph_3PAuCl – $AgSbF_6$ catalytic system *via* intermediates of types **366** and **369** (Scheme 160). [351]

The mechanism of transformations of VDCPs functionalized by nucleophilic groups often differs from that presented in Scheme 157. For example, allene-containing tetrahydropyran **377** can be formed in a reaction the possible mechanisms of which are shown in Scheme 161.[352]

Scheme 160

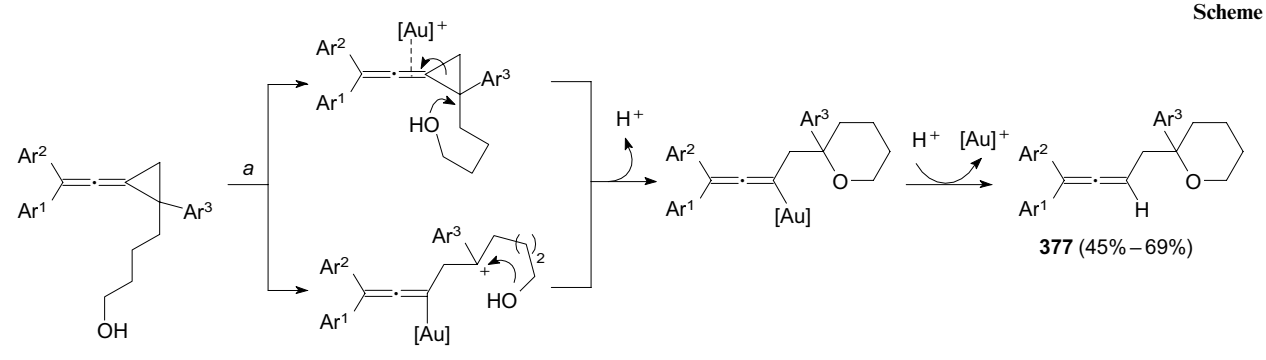


(*a*) Ph_3PAuCl (5 mol.%), $AgSbF_6$ (10 mol.%), DCE, rt, 1 h; R^1, R^2 = Alk, Ar; R^3, R^4 = Me, Cy

Another example, the intramolecular rearrangement of VDCPs **378** with a nucleophilic group in the three-membered ring to dienone **379** *via* the formation of complex **380**,[353] is shown in Scheme 162.

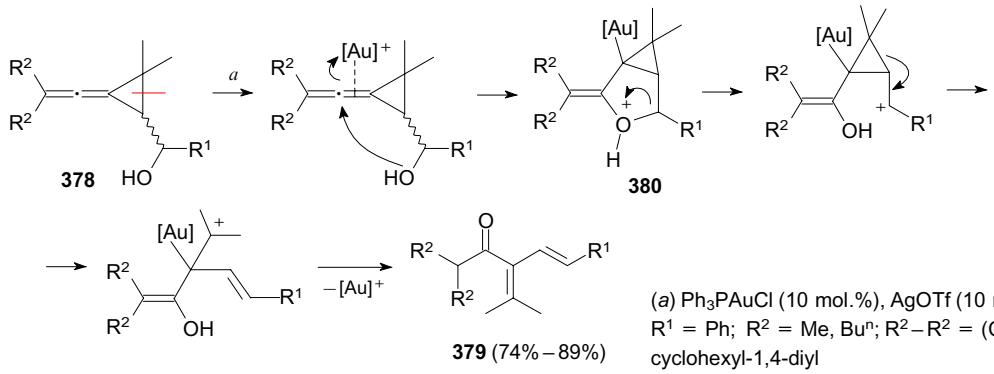
An interesting example is the domino reaction comprising intramolecular hydroamination and ring opening of compound **381** (Scheme 163).[354] Product **382** can be obtained in two ways: directly from substrate **381** with gold(I) catalysis in the presence of 1 equiv. of water or *via* the ytterbium(III) triflate-catalyzed formation of intermediate alkyne **383** followed by gold(I)-catalyzed hydration.

Scheme 161



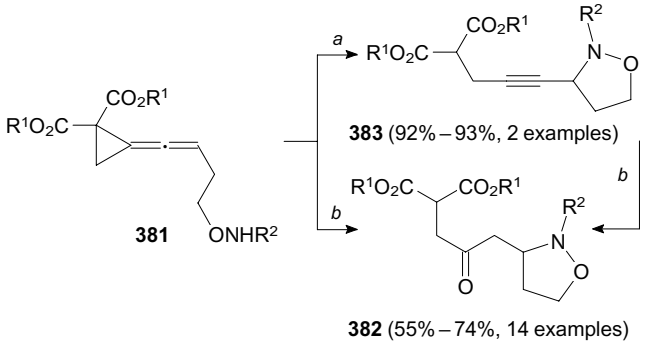
(*a*) $[(Ph_3PAu)_3]BF_4$ (4 mol.%), AgOTf (4 mol.%), 1,4-dioxane, 60 °C

Scheme 162



(*a*) Ph_3PAuCl (10 mol.%), AgOTf (10 mol.%), PhMe, 40 °C, 6 h;
R^1 = Ph; R^2 = Me, Bu^n; $R^2 – R^2$ = $(CH_2)_4$, $(CH_2)_6$, 2,6-dimethylcyclohexyl-1,4-diyl

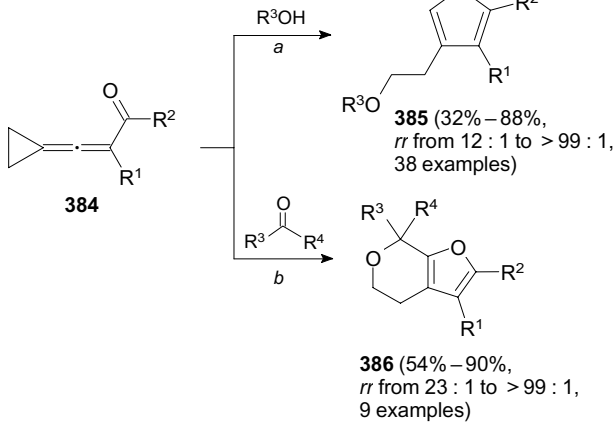
Scheme 163



(*a*) $Yb(OTf)_3$ (10 mol.%), PhMe, rt, 2 days; (*b*) H_2O (1 equiv.), Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), PhMe, rt, 1 day;
R^1 = Me, Et, Bn; R^2 = SO_2Ar, Bz

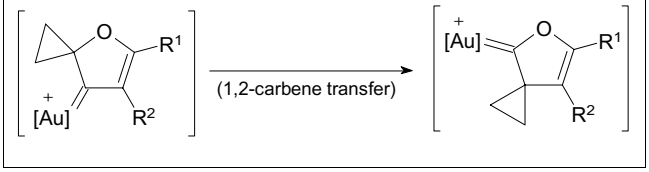
Miao *et al.*[355] described gold-catalyzed cycloisomerization – ring opening cascade reactions involving allenyl ketones **384** containing a cyclopropane moiety and a large set of alcohols and ketones (Scheme 164). The reaction includes regioselective 1,2-transfer of gold carbene

Scheme 164



(*a*) Au_2(*rac*-BINAP)Cl_2 (2.5 mol.%), $AgSbF_6$ (10 mol.%), DCM, rt;
(*b*) Au_2(*rac*-BINAP)Cl_2 (2.5 mol.%), $AgSbF_6$ (5 mol.%), rt or Δ;
385: R^1 = R^2 = Ph; R^3 = Me, Et, Pr^i, Bu^t, Bn, Cy, 1-Ad;
R^3OH = L-menthol, cholesterol, *etc.*;
386: R^1 = Ph, 1-Naph; R^2 = Pr^i, 4-XC_6H_4 (X = H, I, OMe); R^3 = Me, CD_3, $AcCH_2$; R^4 = Me, CD_3; $R^3 – R^4$ = $(CH_2)_4$, $(CH_2)_5$

Scheme 165



(Scheme 165) and gives tri- (**385**) and tetrasubstituted (**386**) furans in moderate to high yields.

7. Conclusion

The use of gold as a catalyst enables various modifications (which are often rather complicated and occur in one step) of double-bonded molecules with a broad range of possible substituents under mild conditions, giving high yields of target products, usually with high chemo- and stereoselectivity.

The main limitation of the use of gold catalysts is their high cost. Therefore, on an industrial scale, from the standpoint of production cost, it is more appropriate in some cases to use less efficient, but less expensive catalysts. Currently, solution of this problem is closely associated with gold complexes or nanoparticles immobilized on a support. This opens the way for not only multiple reuse of the catalyst, but also operation according to the green chemistry principles. Examples of such reactions were given in this review (as well as in the preceding parts [1, 2] of the review) and, beyond doubt, they deserve special consideration.

Much as we would like, we did not completely succeed in covering the diversity of gold-catalyzed transformations of alkenes, dienes and allenes. Some new publications appeared as the manuscript was prepared for the publication. We would like to apologize, in advance, to the authors whose papers were not cited here, which, in some cases, was purely for technical reasons.

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