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Silver and Gold Catalysis for Cycloisomerization Reactions

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Dedicated to Dr. Jean-Pierre Vigneron

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We have focused our attention on cycloisomerization reactions involving silver- and gold-based homogeneous catalysis. This topic is divided into two parts: one relating to cycloisomerization with an allene group and the other with an alkyne group. In each case we have then studied different partners such as carbonyl/carboxy groups, imines, amides or alkenes. Reactions involving allene and alkyne systems as partners are also briefly reported, along with miscellaneous transformations. Our purpose is also to stimulate some discussion by setting together the contributions of different authors to each type of cycloisomerization reaction. Meanwhile, we have outlined when necessary the impact of the choice of counterion or metal (silver vs. gold) in the course of the reaction. Finally, some mechanistic discussion and reaction intermediates are also mentioned if available.

Introduction

Silver and gold are part of the magic triad with copper known as "coinage metals", and their growing relevance in the field of organometallic chemistry has recently been thoroughly reviewed.[1–27] The theme of this review is the study of recent developments in silver- and gold-based catalysis in cycloisomerization reactions, and so heterocyclization reactions in which heteroatoms are involved (alcohols, phenols, acids, amines …), without an isomerization process, are not covered.[28–34] This review does not aim to be exhaustive but intends to present some insights into cycloisomerization reactions catalysed by silver or gold salts. Counterion effects are taken into account, especially with regard to silver-mediated anion metathesis for cationic gold chemistry. Cycloisomerization reactions under gold or silver catalysis conditions essentially involve activation of allenes or alkynes, giving rise to subsequent isomerization reactions with various partners such as alkenes, carbonyl groups/imines, ketones or amides. Also of interest is the presence in

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Philippe Belmont was born in Paris in 1970, grew up in the French Caribbean and in 1990 moved to the Université Joseph Fourier (Grenoble, France) where in 1996 he obtained a PhD in Organic Chemistry under the guidance of Dr. M. Demeunynck and Prof. Jean Lhomme. He then moved successively as a post-doctoral fellow to Case Western Reserve University (Prof. A. J. Pearson, Cleveland, USA) and to the Collège de France (Prof. J.-M. Lehn and Dr. J.-P. Vigneron, Paris, France). In 2000 he joined the group of Prof. M. A. Ciufolini (Université de Lyon, France) as a Researcher for the Centre National de la Recherche Scientifique (CNRS). Finally, in 2004 he obtained the habilitation diploma and since then has managed a research group investigating organometallic chemistry (Rh, Au, Ag, Co) for the synthesis of nitrogen- and oxygen-containing heterocyclic compounds, with interest in their biological properties. In 2009 he is moving to the Institut Curie in Paris.

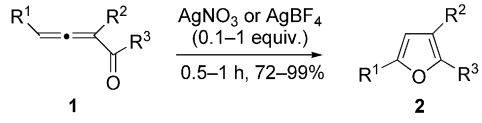
Evelyne (Poerava) Parker was born in 1983 in French Polynesia. She underwent her undergraduate studies (BS degree) at the Université de Rennes I and the Université de Lyon (France) where she majored in organic chemistry in 2006. After successfully obtaining her Master degree in 2007, working on the synthesis of kinase inhibitors in the team of Dr. Philippe Belmont, she is now working on her PhD in the same group, focusing on cycloisomerization reactions catalysed by silver and gold species for access to various heterocycles with antitumor and antimalaria properties.

the nearby environment of other functional groups (esters, epoxides or cyclopropenes) that may participate in the reaction, leading to more complex polycyclic structures.

Cycloisomerization Reactions with Allenes

Reactions with Carbonyl or Carboxy Groups as Partners

In 1990, following previous observations on allenyl alcohols,[35–37] seminal work by Marshall et al.[38] conducted on allenyl ketones or allenyl aldehydes **1** (Scheme 1), leading to the synthesis of substituted furans **2**, paved the way for further silver-based cycloisomerization reactions. Although it was first discovered under Rh^I catalysis, this transformation was further developed with stoichiometric quantities of Ag^I salts such as $AgNO_3$ and $AgBF_4$ (Scheme 1). Catalytic conditions (0.1–0.2 equiv.) were then used[39] and allowed access to furanocyclic natural products.[40,41]



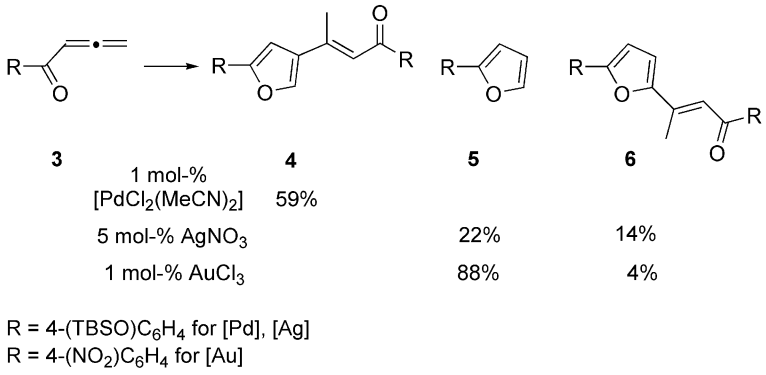
Scheme 1. Marshall's furan synthesis.[38,39]

Hashmi et al. later showed that under palladium catalysis conditions the allenyl ketones **3** could undergo an efficient cycloisomerization/dimerization process (cycloisomerization product **5** and dimerization products **4** or **6**; Scheme 2).[42] In 2000, Hashmi's group[43] was looking for new catalyst systems for this transformation and came up with $AuCl_3$ as an efficient species. The reactions occurred at different rates depending on the metallic component (Scheme 2), with gold catalysis being the best in terms both of kinetics and of catalyst loading, allowing one to go down to 0.1 mol-% catalyst without any loss in efficiency.

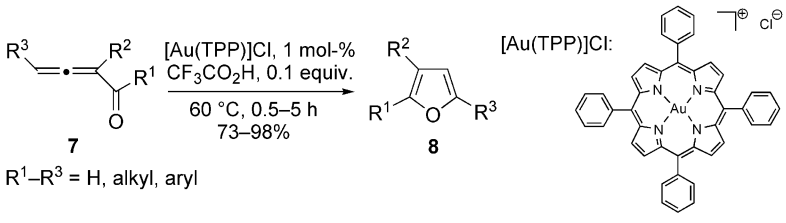
Che et al.[44] used [Au(TPP)]Cl, a (porphyrin)Au^{III}-based catalyst, for cycloisomerization of mono-, di- and even trisubstituted allenones (**7**, Scheme 3). The presence of CF_3CO_2H as an additive (0.1 equiv.) seemed to be essential for the demetallation step. Moreover, when used alone CF_3CO_2H gave only poor yields of the desired furans **8**.

The boundary with the following chapter on alkynes is indistinct here, so in this chapter we also consider reactions in which the allenyl unit is a constitutive part of the starting material or has been proposed as the reactive intermediate (sometimes isolated) leading to the cycloisomerization reaction. Gevorgyan's group[45] extensively studied the formation of furan rings **11** [Scheme 4, Equation (1)] generated from alkynyl ketones **9** through allenyl ketone intermediates **10** by a proposed [3,3]-shift/1,2-migration/cycloisomerization sequence under $AgBF_4$ catalysis conditions (5 mol-%). Depending on the migrating group (acyloxy, phosphatyloxy or sulfonyloxy on **9**), the allenyl ketone intermediates **10** were characterizable by NMR spectroscopy or could even be isolated. This cascade reaction is a powerful method, because it yields tri- and tetrasubstituted furans **11** (Scheme 4). This transformation is also efficiently catalysed by the cationic Au^I complex [$Au(PPh_3)$]OTf, with catalyst loads down to 1 mol-% [**12** → **13**, Scheme 4, Equation (2)].[46]

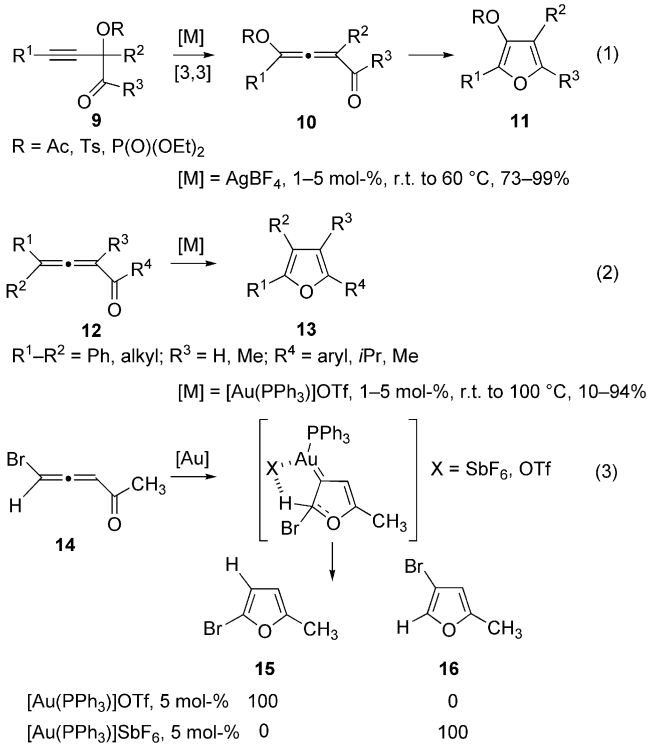
Mechanistic aspects of this reaction have been thoroughly studied[48,49] by ^{17}O-labelling[48] of compounds **9** (R group, Scheme 4), which has indicated that the nature of the



Scheme 2. Hashmi's Pd-, Ag- and Au-based furan synthesis.[42,43]



Scheme 3. Che's furan synthesis.[44]



Scheme 4. Gevorgyan's furan synthesis.[45–47]

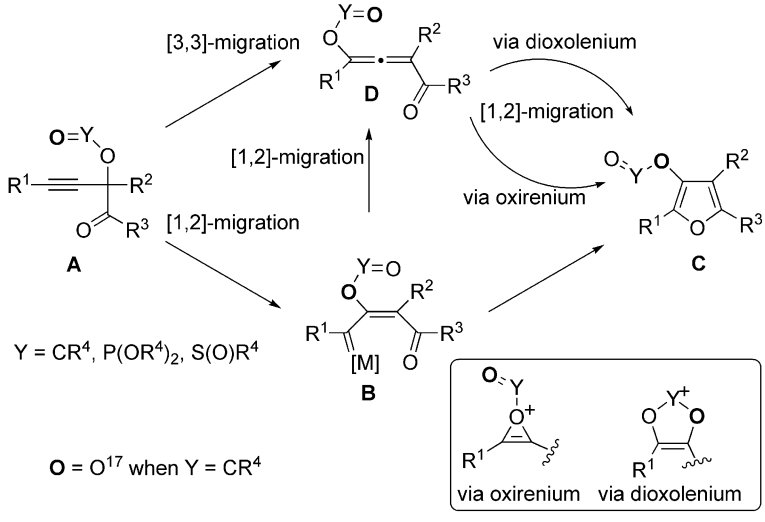
migrating group is important. The proposed 1,2-migration mechanism (**A** → **B**, Scheme 5) was confirmed for the migration of the acyloxy group. Two alternative mechanisms are therefore proposed: (i) direct trapping of the carbenoid (**B**, Scheme 5) by the carbonyl ester group can yield the furan ring **C**, or (ii) the desired furan ring **C** can also be reached after a second 1,2-migration mechanism, producing the allenyl intermediate **D**, and two competing oxirenium/dioxolenium pathways. Interestingly, the same research group[47] determined that for cycloisomerization of the bromoallenyl ketones **14** [Scheme 4, Equation (3)] the counterion-assisted H-shift (vs. 1,2-Br migration), showing a remarkable counterion effect, was the major process governing the regioselectivity (**15** or **16**). In this case, DFT calculations revealed that an OTf^--assisted 1,2-H shift required an activation energy of only 9.6 kcal mol^{-1}, versus a much higher value for SbF_6^- (29 kcal mol^{-1}), therefore explaining the observed regioselectivity.

Shin et al.[50] described a [3,3]-sigmatropic rearrangement under Au[tBu$_2$P(o-biphenyl)]OTf catalysis conditions, as in Gevorgyan's work,[45] followed by a cycloisomerization reaction. The propargyl esters **17** may therefore rearrange to *O*-acetyl allenes **18** and produce various spirocyclic dihydrofurans **19** [Scheme 6, Equation (1)]. Addition of alkenyl groups to give substrates such as **20** allowed Gagosz's group[51] to obtain, through allenes **21**, bicyclo[3.1.0]hexenes **22** under Au^{I} catalysis conditions [Scheme 6, Equation (2)].

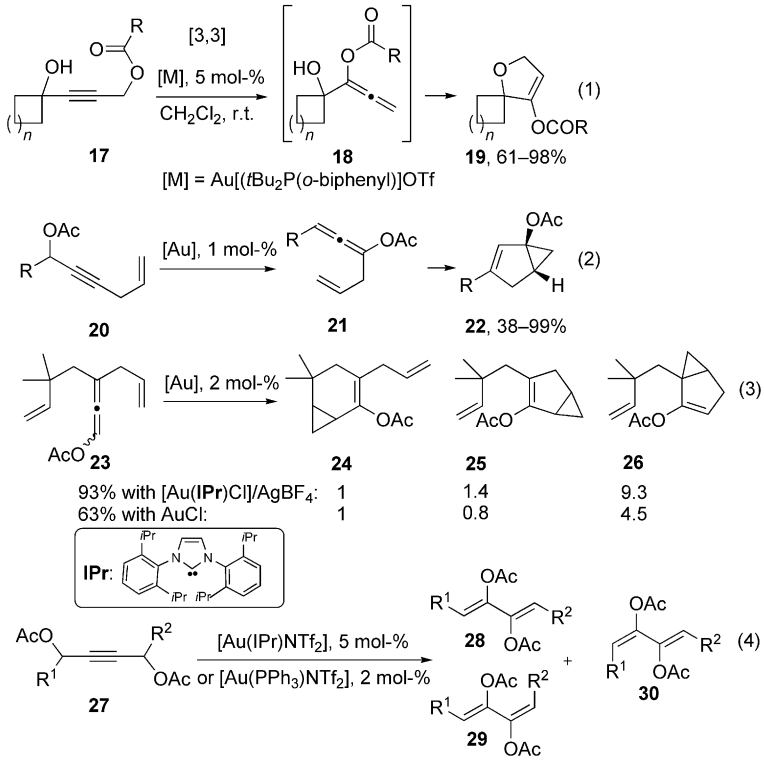
Cavallo, Fensterbank, Malacria and Nolan[52] published a detailed experimental and theoretical study in which allenyl esters **23** were used to produce complex structures, among them the bicyclo[3.1.0]hexene **26** [Scheme 6, Equation (3)], with the aid of the *N*-heterocyclic carbene (NHC) complex [Au(IPr)Cl]/AgBF$_4$ (2 mol-%). AuCl catalysis gave poorer selectivity and therefore larger amounts of bicycles **24** and **25**. Toste's group[53] also achieved some new mechanistic insights into related propargyl vinyl esters/ethers. The behaviour of the 1,4-propargyl diacetates **27** was also investigated recently by Nevado's group; under gold catalysis conditions they afforded various isomeric 2,3-diacetoxy-1,3-dienes **28**, **29** or **30** [Scheme 6, Equation (4)].

Reactions with Amides as Partners

Brandsma et al.[54] reported that the cycloisomerization of 2,3-dienamides (allenylamides) **31** [Scheme 7, Equation (1)] could yield the 2(5*H*)-furanylidenamines **32** and/or the 1,5-dihydro-2*H*-pyrrol-2-ones **33**, depending on whether the reaction proceeded through an *N*- or *O*-cyclization process. The nature of the counterion is also of importance here, because the reaction is efficient under AgOAc catalysis



Scheme 5. Mechanistic insights.[48,49]

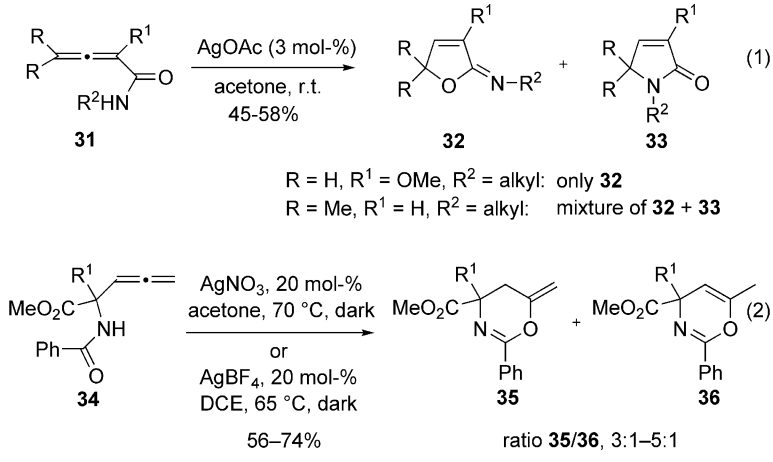


Scheme 6. Polycycle and diene synthesis.[50–53]

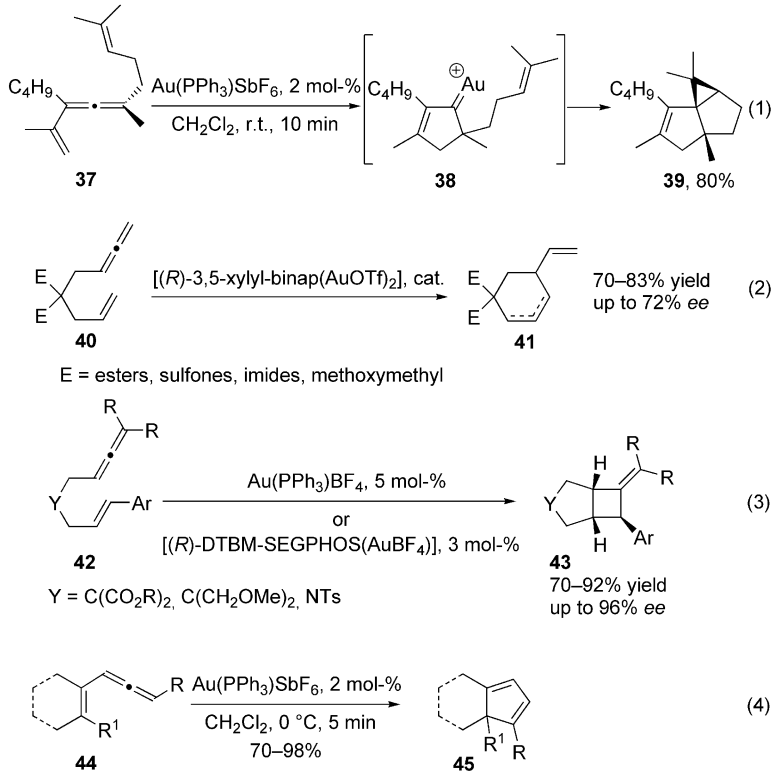
conditions (3 mol-%), to a lesser extent with $AgNO_3$ and ineffective with AgCN and AgBr. The formation of furanylidenamines **32** as the sole product, or in mixtures with various amounts of pyrrol-2-ones **33**, is directed by the natures of the substituents on the 2,3-dienamides **31**. Similar work was published by Brummond et al.,[55] who used the amino-acid-derived allenes **34** [Scheme 7, Equation (2)] under $AgBF_4$ or $AgNO_3$ catalysis conditions (20 mol-%). Oxazines **35** were obtained along with some minor isomers **36**.

Reactions with Alkenes as Partners

Combined theoretical and experimental studies from work by Gandon, Fensterbank and Malacria[56,57] gave insights into the cycloisomerization mechanisms of vinylallenes such as **37**. As one example, vinylallene **37** produced cyclopentene **39** via the proposed (cyclopentenylidene)gold intermediate **38** [Scheme 8, Equation (1)] under [Au(PPh_3)Cl]/$AgSbF_6$ catalysis conditions (2 mol-%).



Scheme 7. Brandsma's[54] and Brummond's[55] work on allenecarboxamides.



Scheme 8. Syntheses of cyclopentenes,[56] cyclohexenes[58] and bicycles.[59,60]

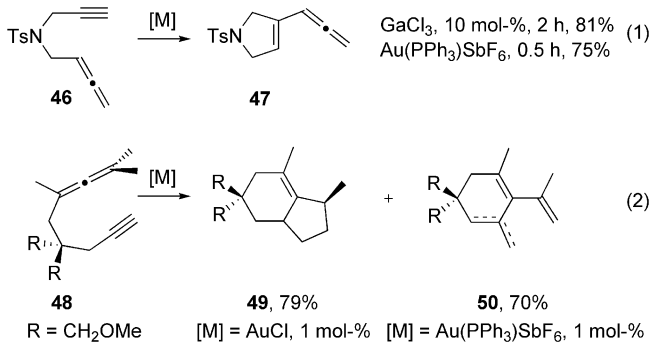
Gagné et al.[58] used the chiral gold complex (*R*)-3,5-xylyl-binap(AuCl)$_2$ with AgOTf additives (in excess) on the 1,6-ene–allenes **40** to yield the vinylcyclohexenes **41** [Scheme 8, Equation (2)]. The complex as generated in situ gave reproducible results and good enantioselectivities (up to 72% *ee*), whereas work with the isolated (*R*)-3,5-xylyl-binap(AuOTf)$_2$ resulted in slow reactions and low enantiomeric excesses (*ee*s), so a role for Ag^+ in the reaction mixture cannot be ruled out. DFT studies have also recently been performed, and some investigations into $[Au(PPh_3)]^+$-catalysed cycloisomerization of allenic arenes predicted diaurated intermediates in the course of the reaction.[61]

In the same year, Toste et al.[59] developed [2+2] cycloadditions of 1,6-ene–allenes **42** [Scheme 8, Equation (3)] in the presence of Au(PPh$_3$)BF$_4$ (formed in situ, 5 mol-%), producing the bicyclo[3.2.0] structures **43**. An enantioselective version, with *ee*s of up to 96%, with a (biarylphosphane)-Au^I complex has also been reported. The same group, working on the vinylallenes (1,3-ene–allenes) **44**, obtained various functionalized cyclopentadienes **45** [Scheme 8, Equation (4)].[60]

Miscellaneous

This part is a link to the next section, because here we consider cycloisomerization reactions between alkyne and allene partners.

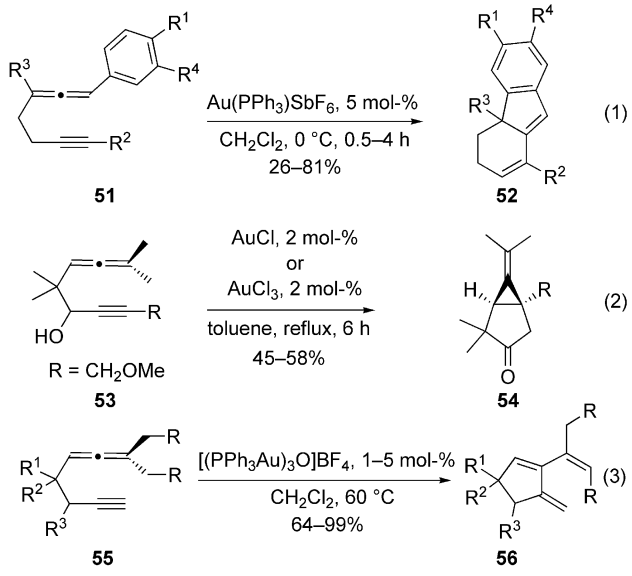
Cycloisomerization of 1,6-allenynes to vinylallenes under GaCl$_3$ catalysis (10 mol-%) conditions was described by Chung et al.,[62] but during the optimization process they also found that Au(PPh$_3$)SbF$_6$ (5 mol-%) was rather efficient for the generation of the allenene **47** from the linear derivative **46** [Scheme 9, Equation (1)]. Aubert, Fensterbank and Malacria[63] also worked on 1,6-allenynes and found an amazing chloride effect: treatment of compounds **48** with AuCl$_3$, NaAuCl$_4$ or AuCl (1 mol-%) exclusively gave the bicyclo[4.3.0]nonadienes **49** in high yields, whereas with Au(PPh$_3$)SbF$_6$ and Au(PPh$_3$)NTf$_2$ the vinylhexene/hexadienes **50** (Alder-ene product) were produced [Scheme 9, Equation (2)]. DFT calculations provided insights into that chloride effect, because the formation of bicyclo[4.3.0]nonadiene derivatives presumably proceeds through the elimination of HCl.



Scheme 9. Reactivity of 1,6-allenynes.[62,63]

The polycyclic structures **52** [Scheme 10, Equation (1)], related to **49**, were obtained by Liu from the starting vinyl-1,5-allenynes **51** in the presence of Au(PPh$_3$)SbF$_6$ (5 mol-

%),[64] whereas the Aubert, Fensterbank and Malacria group[65] used the hydroxy-1,5-allenynes **53** to yield the bicyclic ketones **54** under AuCl and $AuCl_3$ catalysis conditions [Scheme 10, Equation (2)]. Note that the use of $Au(PPh_3)SbF_6$ exclusively gave the cycloaddition product resulting from alcohol attack on the gold-activated allene moiety. Modification of the number of methylene units linking the allene moiety to the alkynyl part in compounds **51** [Scheme 10, Equation (1)] was recently examined, along with theoretical calculations, by Liu and Liao's group,[66] who were able to obtain a variety of cyclopropane/cyclopropene derivatives.



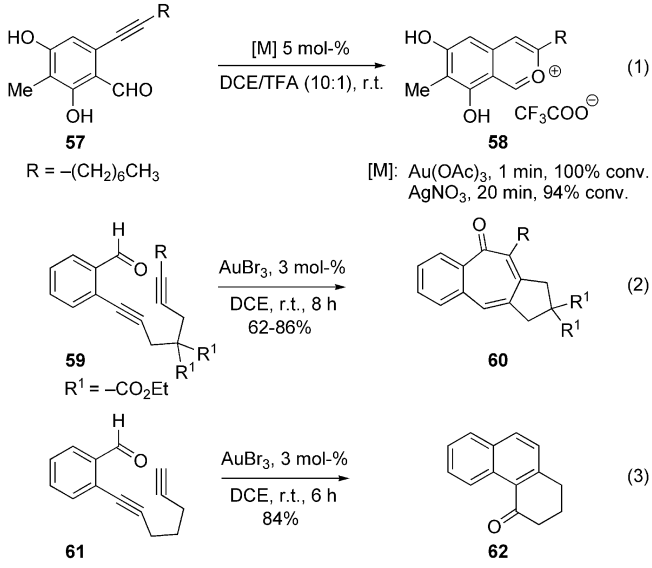
Scheme 10. Reactivity of 1,5-allenynes.[64,65,67]

Houk and Toste[67] conducted theoretical and experimental studies on the cycloisomerization of the 1,5-allenynes **55** in the presence of the tris[(phosphane)gold]oxonium complex $[(PPh_3Au)_3O]BF_4$, obtaining the cross-conjugated trienes **56**.

Cycloisomerization Reactions with Alkynes

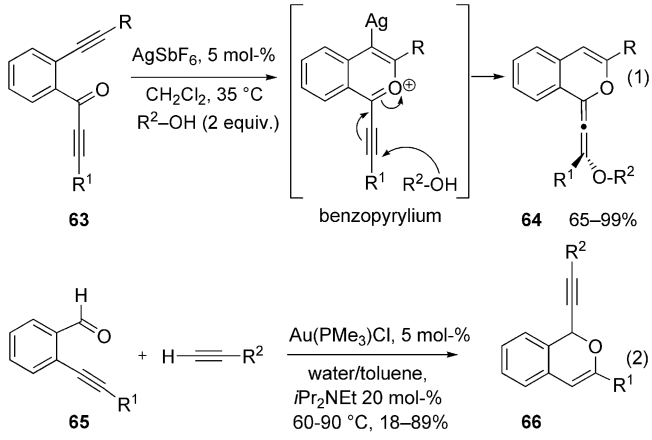
Reactions with Carbonyl Systems as Partners

Porco et al.[68] were able to isolate the benzopyrylium salts **58** from the *o*-alkynylbenzaldehydes **57** under silver or gold catalysis conditions [Scheme 11, Equation (1)]. Oh's group[69] later reported Au^{III}-catalysed cycloisomerizations of the *o*-alkynylbenzaldehydes **59** with pendant alkynyl systems directing the reactions towards the formation of tricyclic compounds **60** through a [3+2] cycloaddition process [Scheme 11, Equation (2)]. Interestingly, without the *gem*-ester group separating the diyne portion (compound **61**), the reaction turned in favour of the formation of the dihydrophenanthrenone **62** through a [4+2] benzannulation reaction [Scheme 11, Equation (3)].



Scheme 11. Porco's and Oh's work.[68,69]

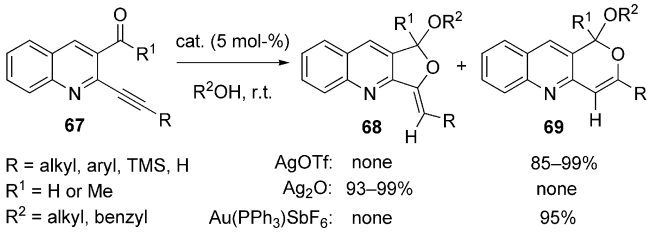
In 2005, Yamamoto's group[70] achieved the synthesis of the 1-allenylchromenes **64** from the alkynyl ketone units **63** under silver catalysis conditions, thanks to cascade cyclizations presumably involving addition of alcohols to preformed benzopyrylium intermediates [Scheme 12, Equation (1)]. Also, working on the *o*-alkynylaryl aldehydes **65**, Li's group[71] developed tandem alkynylation/cyclization reactions of terminal alkynes, producing the 1-alkynyl-1*H*-isochromenes **66** [Scheme 12, Equation (2)] with the aid of the (phosphane)gold complex $Au(PMe_3)Cl$ (5 mol-%). Note that use of related silver complexes led only to trace amounts of the desired products. Later on, Wu et al.[72] extended this work with unusual nucleophiles such as diethyl phosphites.



Scheme 12. Synthesis of isochromenes.[70,71]

Belmont's group[73] used the cationic gold catalyst $Au(PPh_3)SbF_6$ for tandem cycloisomerization/acetalization reactions with alcohol nucleophiles to give the pyrano[4,3-*b*]-quinoline scaffold **69** (Scheme 13). Control reactions with

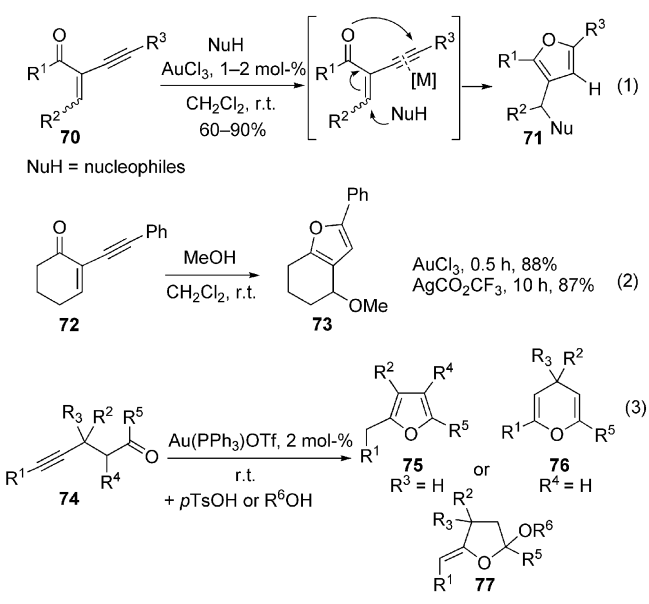
the silver salt needed for the anion metathesis ($AgSbF_6$) made it clear that silver and gold catalysis were both efficient for such a transformation.



Scheme 13. Belmont's work.[73]

Versatile reaction behaviour based on the *o*-alkynyl carbonyl compounds **67** and a range of silver salts was discovered. Two groups of silver salts were defined, depending on the natures of their counterions: with AgOTf as catalyst the pyrano[4,3-*b*]quinolines **69** could be formed, whereas with Ag_2O the furo[3,4-*b*]quinolines **68** were obtained. These products were the results of regioselective 6-*endo*-dig or 5-*exo*-dig cyclization processes, respectively (Scheme 13).

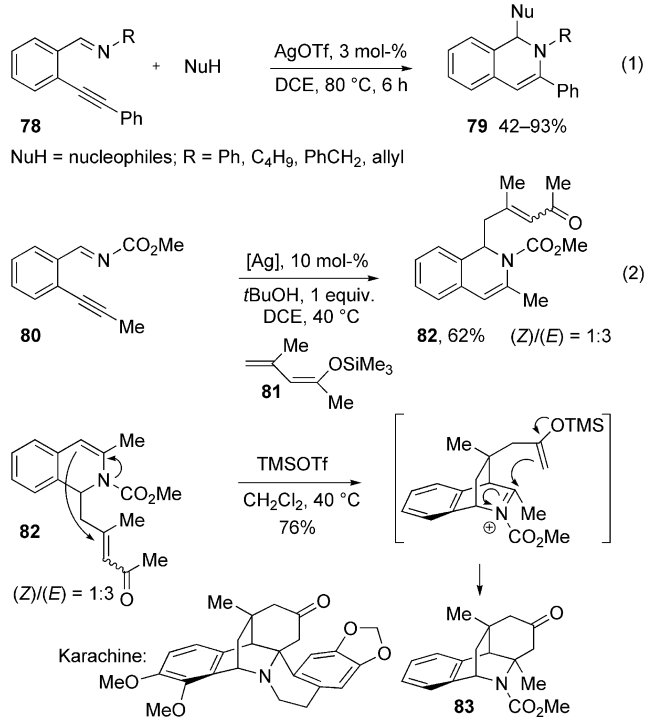
In 2004, Larock et al.[74] reported the use of the 2-(1-alkynyl)-2-alken-1-ones **70** for the synthesis of the highly substituted furans **71** [Scheme 14, Equation (1)]. During optimization work with 2-(phenylethynyl)cyclohex-2-en-1-one (**72**) and methanol [Scheme 14, Equation (2)], the gold catalysis proved to be more efficient ($AuCl_3$, 0.5 h, **73**, 88%) than the silver one ($AgCO_2CF_3$, 10 h, **73**, 87%). Finally, Krause et al.[75] transformed the 1,4-alkynones **74** variously into the furans **75**, the 4*H*-pyrans **76** or the tetrahydrofuranyl ethers **77** – depending on the substitution pattern, solvent and reaction conditions – with the aid of $Au(PPh_3)OTf$ (2 mol-%) as catalyst [Scheme 14, Equation (3)].



Scheme 14. Larock's and Krause's work.[74,75]

Reactions with Imines as Partners

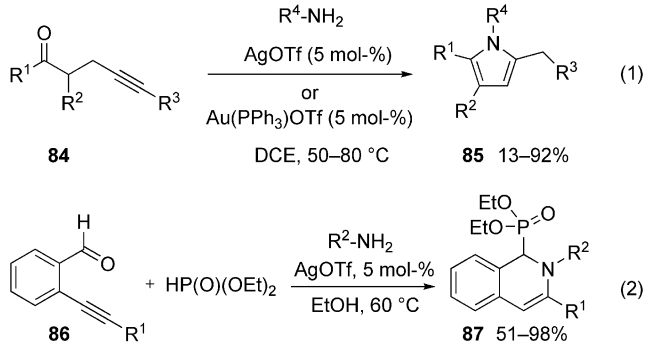
In 2005, Asao et al.[76] reported outstanding direct Mannich reactions on non-activated imines. These reactions were developed with the *o*-alkynylaryl aldimines **78** [Scheme 15, Equation (1)], yielding the dihydroisoquinolines **79**, and nucleophiles such as nitromethane, terminal alkynes or activated methylene species (malonate type). AgOTf catalysed these reactions efficiently, whereas AuCl catalysis was useless. With related substrates but with the activated imines **80** [Scheme 15, Equation (2)], Porco et al.[77] carried out the reactions under $AgSbF_6$ (10 mol-%) catalysis conditions. As in Asao's case,[76] activated methylene species were used, but more interestingly, bis(2,4,6-trimethylpyridine)silver(I) hexafluorophosphate (10 mol-%) proved to be a more powerful catalyst for challenging nucleophiles such as the substituted silyl enol ethers **81**, leading to the dihydroisoquinoline **82**. After a tandem Michael addition/Mannich reaction sequence, they accessed **83** [Scheme 15, Equation (2)], possessing the main structural features of karachine, a berberine alkaloid. The same group also accessed the pyrroloisoquinoline core after dipolar additions of activated alkynes to isoquinoline ylide intermediates.[78]



Scheme 15. Asao's and Porco's work.[76,77]

Dake's group[79] with the β-alkynyl ketones **84** and primary amines provided various substituted pyrroles **85**, through imine formation and cycloisomerization, in the presence of 5 mol-% of AgOTf or $Au(PPh_3)OTf$ (formed in situ with [AuCl, AgOTf, PPh_3]) [Scheme 16, Equation (1)].

The different methods above were augmented by Wu's team,[80] who developed multicomponent reactions with the *o*-alkynylbenzaldehydes **86** and diethyl phosphite, used as a nucleophile, to afford the dihydroisoquinolin-1-ylphos-

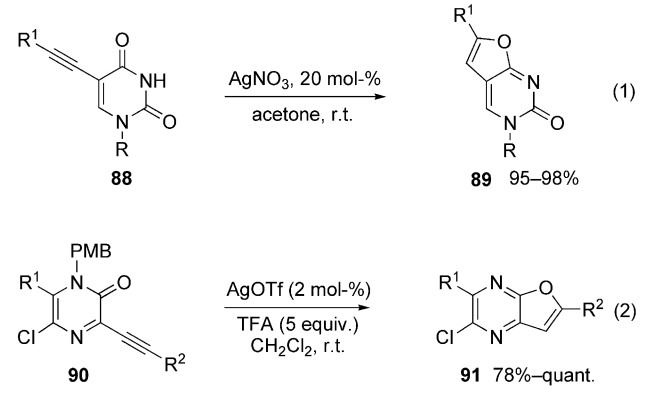


Scheme 16. Dake's and Wu's work.[79,80]

phonate derivatives **87** [Scheme 16, Equation (2)]. A different approach with enolizable ketones and proline, thus mixing organocatalysis and silver catalysis, also led to the synthesis of dihydroisoquinoline derivatives.[81]

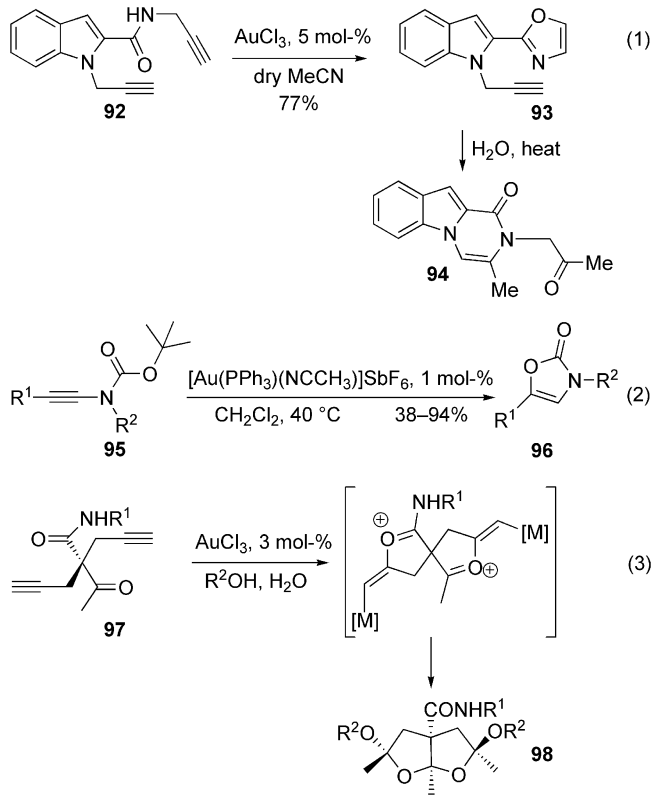
Reactions with Amides as Partners

Agrofoglio et al.[82] constructed the furo[2,3-*d*]pyrimidine nucleosides **89** from the alkynyl-uridines **88** [Scheme 17, Equation (1)]. The reactions operated through a 5-*endo*-dig cyclization mode and were catalysed by $AgNO_3$ (20 mol-%) in acetone. The related furo[2,3-*d*]pyrazine structures **91** [Scheme 17, Equation (2)], were obtained by Van der Eycken's team[83a] from the *p*-methoxybenzyl-protected 3-alkynyl-5-chloropyrazines **90**. Indeed, with a dual mixture of AgOTf (2 mol-%) and trifluoroacetic acid (TFA, 5 equiv.) in CH_2Cl_2, compounds **90** could undergo cyclization and also PMB deprotection. It was shown that without TFA the reactions proceeded slowly (15 h instead of 5 min!) and that $AgNO_3$ gave lower yields, probably due to its poor solubility in CH_2Cl_2. The role of proton-catalysis in gold and silver chemistry has already been discussed.[83b,83c]



Scheme 17. Synthesis of furo[2,3-*d*]heterocycles.[82,83]

Padwa's group[84] studied the behaviour of substituted *N*-propargylamides in the presence of gold (catalysis) or silver (in stoichiometric quantities). During their research, cyclization of the enol forms of some derivatives along with direct *N*-alkylation of amide structures was found. More interestingly for our present concern, however, an indole ring bearing the *N*-propargylamide unit [compound **92**, Scheme 18, Equation (1)] could cycloisomerize to yield the oxazole-tethered indole **93** under $AuCl_3$ catalysis conditions. Thereafter, simple heating of **93** in aqueous acetonitrile gave the 2*H*-pyrazino[1,2-*a*]indolone **94**.



Scheme 18. Syntheses of oxazolones and bicyclic ketals.[84–86]

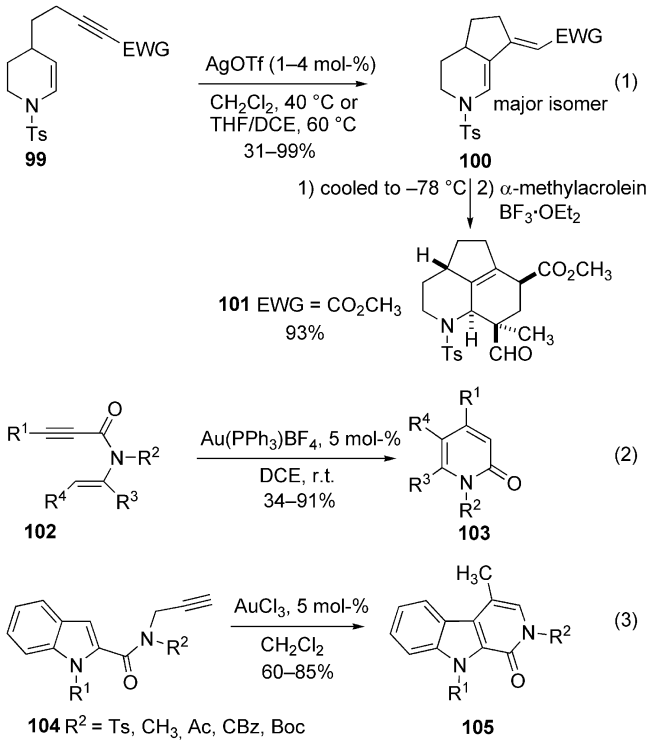
Similarly, the oxazolones **96** [Scheme 18, Equation (2)] were obtained by Gagosz et al.[85] from the *N*-alkynyl *tert*-butoxycarbonylcarbamates **95** with the optimized gold catalyst system $[Au(PPh_3)(NCCH_3)]SbF_6$ (1 mol-%). Finally, Liu's group[86] used the 4-acyl-/amidyl-1,6-diynes **97**, which afforded the bicyclic ketals **98** in a cyclization/hydrolysis/tandem addition process [Scheme 18, Equation (3)].

Reactions with Alkenes as Partners

Overall, the main field of interest in gold-catalysed cycloisomerization is with alkenes or alkynes as partners,[87] silver catalysis being less developed in this area. The alkene and alkyne units can be either "nude" or functionalized: the alkenyl group, for instance, can be either an enol ether or an enamine group, and the alkynyl part can be an ynamide group. Oxo functionalities or alkyl groups/carbocycles can also be placed near the reactive centres and may participate in the reaction mechanism.[88]

In 2004, Dake's group[89] reported Pt^{II}- and Ag^{I}-catalysed cyclizations of enesulfonamides **99**, containing tethered alkyne systems bearing electron-withdrawing groups

[Scheme 19, Equation (1)]. The produced bicyclic compounds **100** [Scheme 19, Equation (1)] were able to undergo tandem Diels–Alder reactions giving the tricyclic structures **101**.

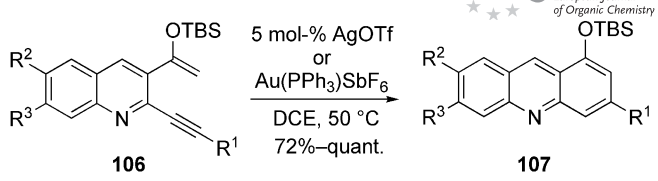


Scheme 19. "Enamine" addition onto alkynes.[89–91]

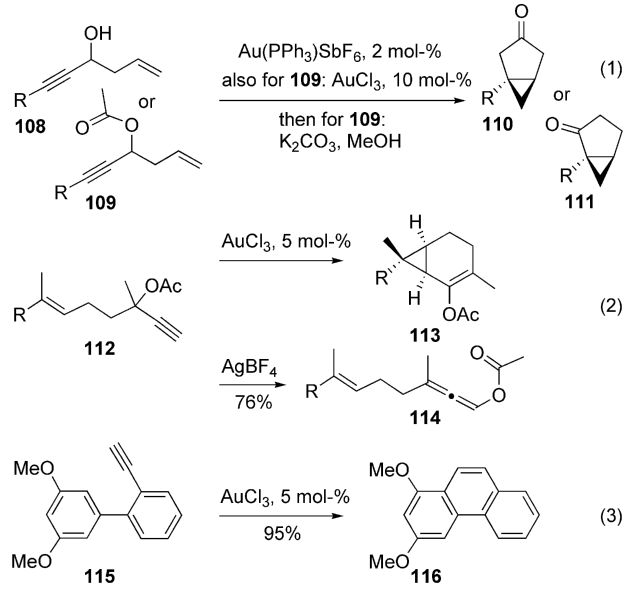
Tanaka et al.[90] exploited the *N*-alkenylalkynylamides **102** as substrates [Scheme 19, Equation (2)] to form a variety of substituted 2-pyridones **103** under [Au(PPh$_3$)Cl]/AgBF$_4$ catalysis conditions (5 mol-%). A test reaction run with AgBF$_4$ (5 mol-%) as catalyst gave a lower yield (52% vs. 82% for activated gold) and longer reaction time (5 h instead of 0.5 h). Padwa's group[91] [Scheme 19, Equation (3)] were able to generate the β-carbolinones **105** efficiently from the *N*-propargylindole-2-carboxamides **104** with AuCl$_3$ (5 mol-%) as catalyst.

Belmont's team[92] recently reported access to a large variety of polysubstituted acridines **107** (Scheme 20) from the 2-alkynyl-3-(silyl enol ether)quinoline derivatives **106**, through a benzannulation process. These reactions were efficient with the silver-activated gold species Au(PPh$_3$)SbF$_6$, along with various silver salts used alone (AgSbF$_6$, AgPF$_6$, AgOTf, AgNO$_3$ and AgCO$_2$CF$_3$) but interestingly could not be run with other silver salts such as AgF, AgOAc, Ag$_2$CO$_3$ and Ag$_2$O. This could be explained by the intrinsic properties of these salts in comparison with the previous ones.[73,93] This work is also connected to preliminary results from Dankwardt,[94] but in this case stoichiometric quantities of Ag(CO$_2$CF$_3$) (in nitromethane) were required for the transformations.

Fürstner et al.[95,96] used the hydroxy or acetyloxy ene–yne systems **108** or **109** [Scheme 21, Equation (1)] to produce the regioisomeric bicyclic ketones **110** or **111**, respectively, in a cycloisomerization process with gold catalysts Au(PPh$_3$)SbF$_6$ or AuCl$_3$.[97,98] Interestingly, in the case of the dienylpropargylic acetate **112** [Scheme 21, Equation (2)], AuCl$_3$ catalysis gave the expected bicyclic structure **113**, whereas AgBF$_4$ catalysis afforded the allene moiety **114**.[98] Note that the same research group[99] was able to synthesize the phenanthrenes **116** and related heterocyclic structures from the alkynylated biphenyls **115** with AuCl$_3$ (5 mol-%) as catalyst [Scheme 21, Equation (3)].



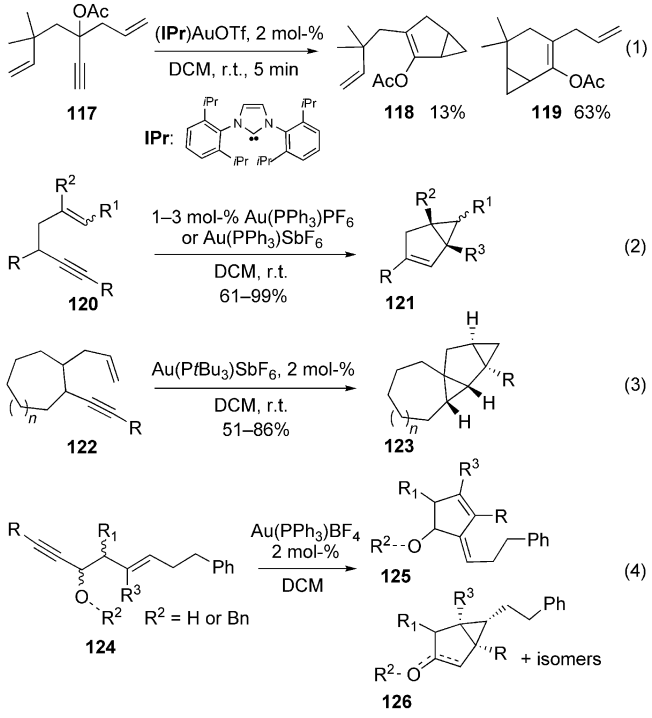
Scheme 20. Synthesis of acridines.[92]



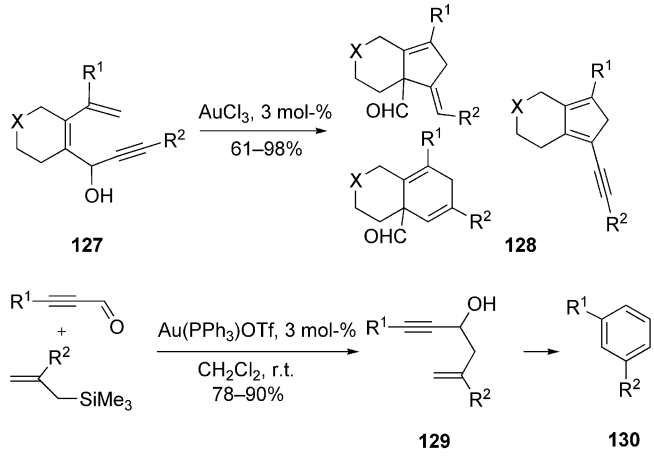
Scheme 21. Fürstner's synthesis of carbocycles.[95–99]

The 1,5-enyne systems **117**, containing propargylic acetate units [Scheme 22, Equation (1)], developed by Nolan[100] and by Fensterbank and Malacria,[101,102] allowed the formation of the bicyclo[3.1.0]hexene and bicyclo[4.1.0]-heptene scaffolds **118** and **119** with the aid of (NHC)Au complexes. Application of this method to 1,6-enynes gave cyclopropyl-containing carbocycles, and the reactions could also be amenable to ionic liquid conditions.[101,102] In connection with the previously discussed work by Fürstner[95,96,98] and by Nolan,[100] Fehr et al.[103] were able to synthesize (–)-cubebol from 1,5-enyne systems.

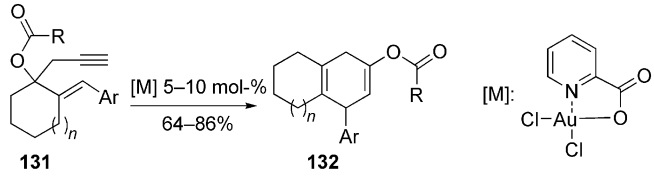
The 1,5-enyne structures **120** [Scheme 22, Equation (2)] were studied by Toste's group;[104] in the presence of Au(PPh$_3$)SbF$_6$ or Au(PPh$_3$)PF$_6$ (1–3 mol-%) they yielded the bicyclo[3.1.0]hexene systems **121**. Applied to propargylic esters, this process also allowed access to fluorenes and styrenes[105] along with medium-sized rings.[106] Horino and Toste have also recently shown that cycloisomerizations



Scheme 22. Transformations of 1,5-enynes.[100–102,104,107–109]



Scheme 23. Bicyclic and benzannulated products.[111,112]



Scheme 24. Cycloisomerizations of 1,5-enynes.[113]

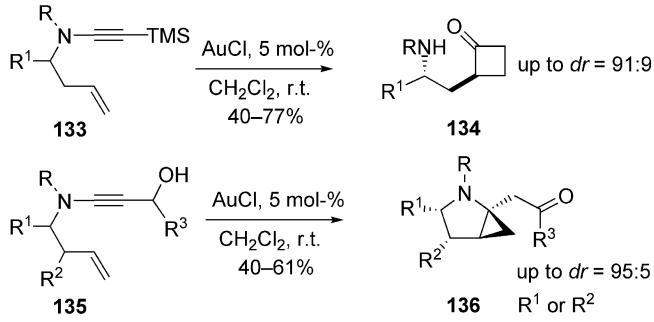
of the 1,5-enynes **122** [Scheme 22, Equation (3)] in the presence of Au(P*t*Bu$_3$)SbF$_6$ (2 mol-%) could end in a C–H insertion process, therefore affording the bis(cyclopropane)-carbocycles **123**.[107]

In addition, Gagosz et al.[108,109] studied cycloisomerization processes of the 3-hydroxylated 1,5-enynes **124** in the presence of Au(PPh$_3$)BF$_4$ (2 mol-%) [Scheme 22, Equation (4)]; these led to various products such as the alkylidenecyclopentenes **125** along with the bicyclo[3.1.0]hexenes **126**. Note that cyclobutene intermediates have been isolated when the reactions were carried out with 1,8-enyne systems.[110]

Liu's team,[111] using the *cis*-4,6-dien-1-yn-3-ol derivatives **127** (Scheme 23) under gold catalysis conditions, were able to obtain a variety of bicyclic structures (compounds **128**), along with some benzannulated derivatives. In addition, the 1,5-enynes **129** bearing propargylic alcohol groups, formed in situ (Scheme 23), could in turn lead to the benzene derivatives **130** through tandem allylation/benzannulation reaction sequences.[112]

Zhang et al.,[113] this time using homopropargylic esters on 1,5-enyne systems (compounds **131**, Scheme 24), were able to obtain the 1-carboxycyclohexa-1,4-diene scaffolds **132** with the aid of a dichloro(pyridine-2-carboxylato)-gold(III) complex (5 mol-%) and in some cases with KAuCl$_4$ additives. Moreover, cyclopropanation[114] or dienyl systems[115] could be achieved by some other groups.

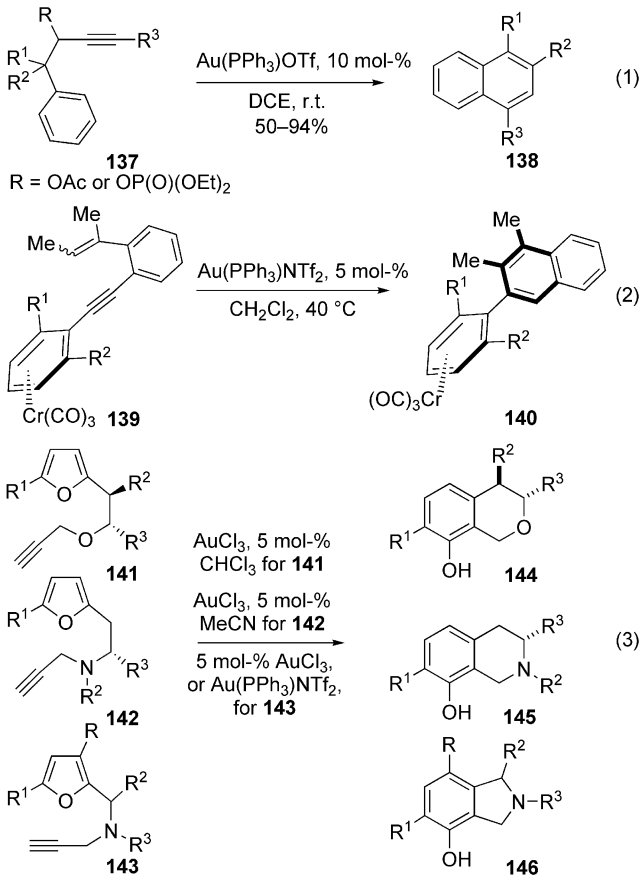
Cossy and Meyer,[116,117] using a variety of 1,6-enynamides such as **133** (Scheme 25) under AuCl catalysis conditions, obtained the cyclobutanones **134** with high levels of diastereoselectivity. Under the same conditions, the enynamides **135**, bearing propargylic alcohol groups, afforded carbonyl derivatives **136**, tethering 2-azabicyclo[3.1.0]-hexane structures.



Scheme 25. Cycloisomerizations of 1,6-enynamides.[116,117]

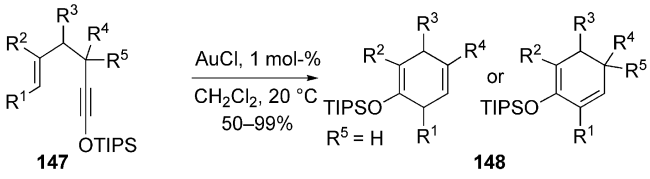
Gevorgyan's group[118,119] developed a double migration/benzannulation cascade reaction sequence. From the starting benzyl-substituted propargyl esters **137** [Scheme 26, Equation (1)], presumably through the formation of 1,3-diene intermediates, the naphthalene systems **138** could be formed in the presence of Au(PPh$_3$)OTf (10 mol-%). Similarly, Uemura's team[120,121] were able to cycloisomerize the enyne systems **139**, bearing enantiomerically pure (arene)-chromium complexes, with Au(PPh$_3$)NTf$_2$ (5 mol-%) as catalyst [Scheme 26, Equation (2)], thereby producing the axially chiral biaryl units **140**. Hashmi et al.[122–126] were able to synthesize various phenol derivatives thanks to AuCl$_3$ or Au(PPh$_3$)NTf$_2$ catalysis. Indeed, depending on the natures of the tethers linking together the furan and the alkynyl

units in **141**–**143** [Scheme 26, Equation (3)], one could obtain the isochromanes **144**, the tetrahydroisoquinolines **145** or the dihydroisoindoles **146**, respectively.



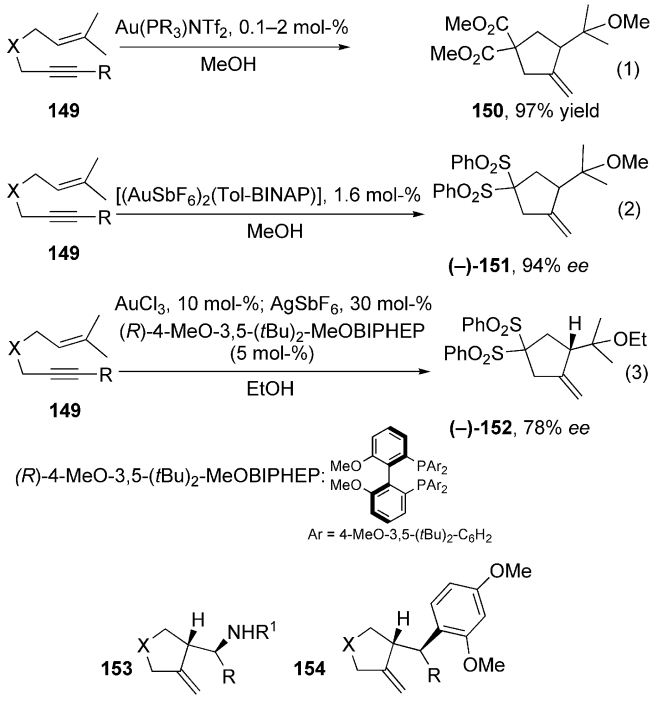
Scheme 26. Benzannulation reactions.[118–126]

Kozmin's team[127,128] performed transformations of the siloxy-1,5-enynes **147** (Scheme 27) into the cyclohexadiene derivatives **148** with AuCl (1 mol-%) as catalyst.



Scheme 27. Synthesis of cyclohexadienes.[127,128]

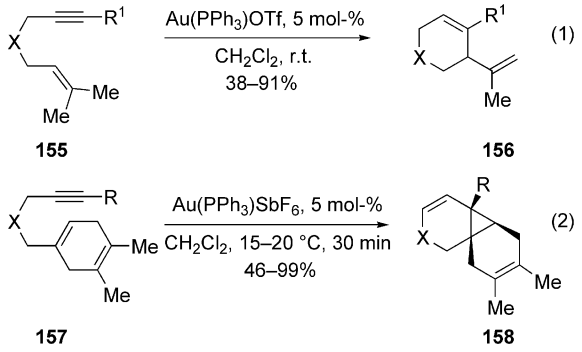
Alkoxycyclization with the enyne systems **149** (Scheme 28) has mostly been studied by the Echavarren,[129–132] Genêt/Michelet[133–135] and Gagosz groups.[109] Gagosz's team,[109] building on previous work by Echavarren,[129] used (L)AuNTf$_2$, in which various phosphanes (L) were studied for the reaction process, but simple Au(PPh$_3$)SbF$_6$ (2 mol-%) efficiently catalysed the transformation to the methylenecyclopentane system **150** [Scheme 28, Equation (1)]. Echavarren and co-workers[129,130] studied the enantioselectivity of this reaction with various chiral gold complexes: [(AuCl)$_2$(Tol-BINAP)]/AgSbF$_6$ was the best, with enantiomeric excesses of up to 94% being reached for the formation of the methylenecyclopentane system (–)-**151** [Scheme 28, Equation (2)]. Michelet et al.[133–135] extended their first alkoxycyclization results obtained with platinum salts[136] to chiral gold(III) catalysts.[135] The best results (up to 78% *ee*) were obtained with (*R*)-4-MeO-3,5-(*t*Bu)$_2$-MeOBIPHEP as ligand, giving the methylenecyclopentane system (–)-**152** [Scheme 28, Equation (3)]. Michelet's group also studied hydroamination/cycloisomerization[133] and Friedel–Crafts-type/cycloisomerization reaction[134] sequences with success, obtaining access to the methylenecyclopentane systems **153** and **154**, respectively.



Scheme 28. Alkoxycyclizations and related reactions.[109,129,130,133–135]

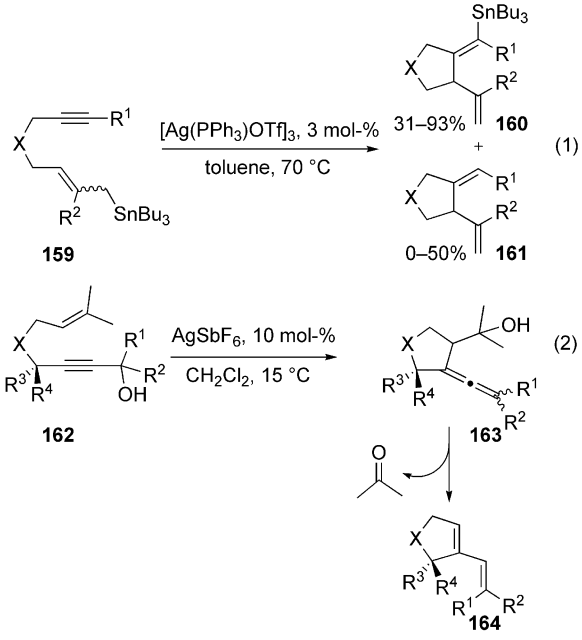
Following the seminal work of Echavarren,[131,132] Chung et al.[137–139] described the reactions of the 1,6-enynes **155** [Scheme 29, Equation (1)] under Au(PPh$_3$)OTf catalysis (5 mol-%) conditions, obtaining the 1,4-dienes **156**. Some enantioselectivity was achieved (up to 22%) in preliminary results with (*R*)-BINAP as ligand.[138] With systems **157**, bearing a cyclic olefin group [Scheme 29, Equation (2)], the polycyclic dienyl systems **158** were generated. Furthermore, (NHC)gold catalysts have also been successfully used,[139] and Chung's group in association with Kang[140] reported cycloisomerization reactions and DFT studies with 1,5-bis(allenes).

Interestingly, Echavarren[141] developed silver-catalysed transformations of the 1,6-enynes **159** bearing allylstannane systems [Scheme 30, Equation (1)], leading to the vinylstannanes **160** accompanied by the tin-free compounds **161**. With use of the catalyst [(AgOTf)$_2$(Tol-BINAP)] (5 mol-%), enantioselective cyclization could be performed with *ee*s of up to 78%. Liang's group,[142] working on the 1,6-enynes



Scheme 29. Cycloisomerizations of 1,6-enynes.[137–139,141]

162 [Scheme 30, Equation (2)], developed the synthesis of the isolable allene alcohols **163**, which could easily be transformed into the 1,3-dienes **164** through isomerization and loss of acetone.



Scheme 30. Cycloisomerizations of 1,6-enynes.[137–139,141,142]

Miscellaneous

Other chemical functionalities have also been brought together thanks to silver or gold catalysis. We can cite the work of Gevorgyan et al.[143,144] with propargyl-containing heterocycles, in which $AgBF_4$ catalysis (3 mol-%) was efficient in their transformation into a variety of fused heterocycles such as indolizines, pyrroloquinoxalines and pyrrolothiazoles. Note that gold catalysis was less efficient ($AuCl_3$) or needed longer reaction times (AuI, 3 h instead of 30 min for $AgBF_4$).

In addition, cycloisomerizations of oxirane moieties onto alkynyl groups, leading to 2,5-disubstituted furans, have been developed by Liang's group.[145,146] The Au^{III} catalysts $AuCl_3$ and $HAuCl_4{\cdot}4H_2O$ gave the best results, whereas $AgSbF_6$ was inefficient in these reactions. Shi's group,[147,148] using (homo)propargylic alcohols with oxiranes, obtained ketal and spiroketal moieties constructed on morpholino scaffolds under gold(I) catalysis conditions, whereas Liu's team[149,150] were able to form carbocycle and heterocycle scaffolds on *ortho*-substituted benzene with oxirane and alkyne units. Silver and gold catalysis were both efficient but interestingly did not always lead to the same reaction product.[149] Furthermore, Pale's group[151] working on alk-1-ynyloxiranes with AgOTf catalysis, produced trisubstituted furans. Note that *p*-toluenesulfonic acid and methanol were needed for such transformations.

Wu et al.[152] were able to generate benzothiazine cores from simple alkynylbenzamines, through the intermediate formation of thiourea moieties.

Finally, by bridging the ene and yne reactive sites through cyclopropane units, Toste[153] and Wang, Nevado and Goeke[154] found routes to the total synthesis of the angular triquinane ventricosene[153] and to five-, six- and seven-membered carbocycles.[154]

Conclusions

Gold-catalysed reactions have attracted increasing interest in the past ten years, and their overall impact and roles in carbocycle and heterocycle synthesis, through cycloisomerization reactions, are impressive. Although ligand effects are known in homogeneous gold catalysis, we have also stressed the impact of the counterions, because these have a profound influence on the conversion rates of cycloisomerization reactions. Silver has been intensively used to activate gold catalysts, through anion metathesis (counterion exchange), but here we have also reported silver catalysts' involvement in cycloisomerization reactions. Although seminal work was conducted in the early 1990s, efforts to develop the uses of silver in cycloisomerization reactions still need to be made. In particular, progress in enantioselective reactions is still needed, both through variation of ligands and also through the use of the concept of counterion chirality recently elucidated for gold chemistry by Toste[155,156] and found to be efficient for highly enantioselective heterocyclization reactions[157] or for ring expansions.[158,159]

Acknowledgments

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