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Intriguing mechanistic labyrinths in gold(I) catalysis

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Many mechanistically intriguing reactions have been developed in the last decade using gold(I) as catalyst. Here we review the main mechanistic proposals in gold-catalysed activation of alkynes and allenes, in which this metal plays a central role by stabilising a variety of complex cationic intermediates.

Introduction

For centuries, gold was considered a precious, purely decorative noble metal. It was not until 1998, in a groundbreaking report, that the hydration of alkynes catalysed by Au(I) complexes under homogeneous conditions was reported.[1,2] Henceforth, numerous transformations have been developed, nourishing the field of organic synthesis.[3] Gold salts and complexes emerged as powerful catalysts for the selective electrophilic activation of multiple bonds towards a variety of hetero- and carbonucleophiles under mild conditions. Cycloisomerizations and cycloadditions attracted particular attention for the construction of complex polycyclic structures present in diverse natural products.[4,5]

In most cases, reactions catalysed by gold under homogeneous conditions proceed by multistep pathways that are rather complex. Therefore, a mechanistic understanding has been based often on analogy and speculation. Although coherent mechanistic schemes have been advanced by means of DFT calculations, as well as labelling and kinetic experiments, isolation of key intermediates has proven to be challenging.[6] Here we present a critical outlook of the main mechanistic proposals in this area of homogeneous catalysis. This discussion is by no means comprehensive, but it centres on some of the best-studied gold-catalysed activation of alkynes and allenes with the aim of contributing to a more clear understanding of this intricate field of research.

Gold(I) catalysts

Although simple gold salts such as $NaAuCl_4$ or AuCl are active enough to catalyse many transformations, precatalysts LAuCl bearing phosphine or N-heterocyclic carbene as ligands have found

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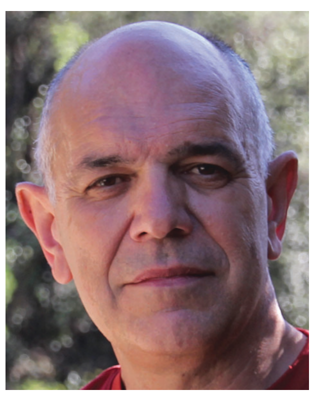


Antonio M. Echavarren

Antonio M. Echavarren obtained his PhD at the Universidad Autónoma de Madrid (UAM) in 1982. After postdoctoral stays in Boston College and Colorado State University, he joined the CSIC (Institute of Organic Chemistry) in Madrid. In 1992 he became Professor of Organic Chemistry at the UAM. He is also Professor of Research of the CSIC. In 2004 he moved to Tarragona as Group Leader at the Institute of Chemical Research of Catalonia (ICIQ). His research interests include the discovery of new catalytic methods based on the chemistry of transition metals as well as the synthesis of natural products and polyarenes.

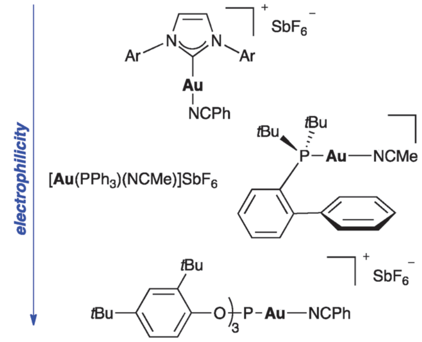


Fig. 1 Representative gold(I) cationic catalysts.

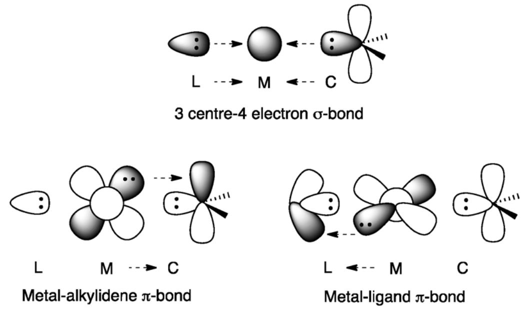


Fig. 2 Ligand–metal-substrate orbital interactions in gold–carbenes [L-Au=CR$_2$]$^+$.

more widespread applications.[7–9] (Fig. 1). The active species are often generated *in situ* by chloride abstraction using a silver salt with distinct anions. The innocence of silver in the reaction mixture has been recently questioned,[10] although this aspect merits additional scrutiny. The most convenient catalysts are gold complexes [AuLL′]X or [AuLX] with weakly coordinating neutral (L′)[11] or anionic ligands (X),[12] which could enter catalytic cycles by associative ligand exchange with the substrate.[13] The properties of the catalysts can be easily tuned sterically or electronically depending on the ligand. Thus, in general, complexes with phosphite and related ligands are more electrophilic than those bearing more donating N-heterocyclic carbenes, whereas with phosphines show intermediate electrophilicity.[3d] The use of chiral ligands has led to the development of efficient asymmetric processes.[14,15] Several studies have shown that the basicity and coordinating ability of the counteranion also play a significant role.[11b,14,16]

Activation of unsaturated substrates

Important structural features of gold are its aurophilicity, its linear geometry that limits the coordination potential, and the fact that it does not undergo spontaneous oxidative addition nor β-hydride elimination. Gold has the highest electronegativity among the transition metals, which is attributed to relativistic effects.[17–19] Hence, the contraction of the 6s orbital in gold is much more significant than for the rest of the transition metals, which leads to an expansion of the 5d orbital, decreasing its electron–electron repulsion. Furthermore, 5d electrons are too low in energy to experience a significant backbonding to anti-bonding orbitals but not to empty nonbonding orbitals. Thus, a 3 centre-4 electron σ-bond is proposed in gold(I)-carbenes [L-Au=CR$_2$]$^+$ accompanied by orthogonal weak π-backbonding from the metal to both the ligand and the substrate (Fig. 2).

Gold(I) forms stable monomeric two coordinate π-complexes with alkenes,[20–22] 1,3-dienes,[23] allenes,[24] and substituted alkynes.[19a,25,26] Variations of the bond lengths as well as the ligand–metal-substrate angle suggest that the alkene orientation is controlled largely by steric factors. Thus, terminal alkenes bind unsymmetrically with gold(I) resulting in longer bonds with the substituted carbon atom. The X-ray structure of isobutylene IPr–gold(I) complex **1a** revealed a 0.086 Å difference between the metal–carbon bonds, whereas for norbornene (**1b**)

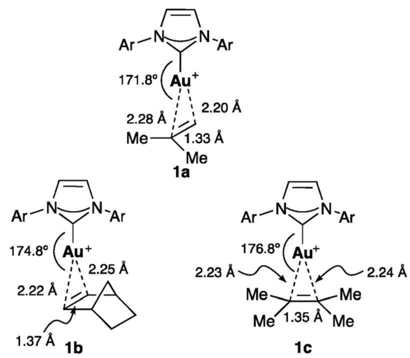


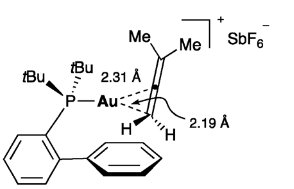
Fig. 3 Isobutylene (**1a**), norbornene (**1b**) and 2,3-dimethyl-2-butene (**1c**) IPr–Au(I) complexes (Ar = 2,6-iPr$_2$C$_6$H$_3$).[20b]

and 2,3-dimethyl-2-butene (**1c**), this difference is 0.024 Å and 0.009 Å, respectively (Fig. 3).[20b] The angle between the metal and the centroid of the alkene also increased with the bulkiness of the alkene: 171.8° (isobutylene), 174.8° (norbornene), and 176.8° (2,3-dimethyl-2-butene).

In the case of allenes, structural and solution analysis demonstrate that gold(I) preferentially binds to the less substituted C=C bond (Fig. 4).[24]

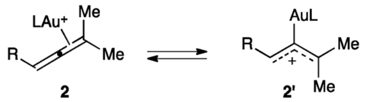
Although a theoretical study has proposed that π-coordinated gold(I) complexes **2** with model NHC or phosphite ligands could be in rapid equilibrium with η^1-allyl species **2′**, slightly favouring **2** (Scheme 1),[27] experimental results with gold(I) complexes bearing bulky phosphine ligands rule out the involvement of **2′** in the low energy ($\leq$10 kcal mol^{-1}) π-face exchange processes.[24]

Internal alkyne gold(I) complex **3a** shows the characteristic of almost symmetrical η^2-coordination (Fig. 5).[25e] The triple bond length is identical to that of a free alkyne, although there is significant bending back of the alkyl substituents.



2a

Fig. 4 3-Methylbuta-1,2-diene gold(I) complex **2a**.[24]



Scheme 1 Proposed equilibrium between η^2-allene (**2**) and η^1-allyl species (**2′**).[27]

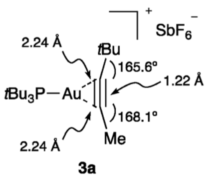


Fig. 5 Structure of η^2-alkyne Au(I) complex **3a**.[25e]

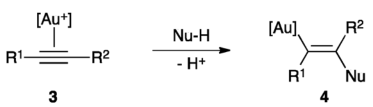
Nucleophilic attack

In general, attack of nucleophiles to η^2-alkyne Au(I) complexes **3** gives *trans*-alkenyl species **4** (Scheme 2).[3,28]

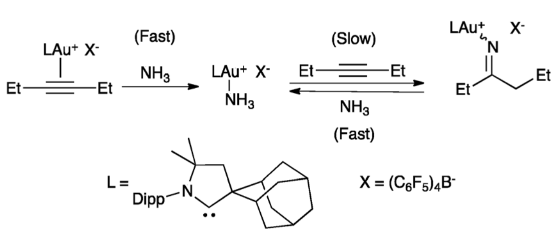
Although an outer-sphere mechanism is widely accepted and it has been verified many times in the stereoselectivity of gold(I)-catalysed reactions,[3] there are few exceptions. Although it is difficult to distinguish an outer-sphere attack from an insertion process, this type of mechanism was suggested in the gold(I)-catalysed hydroamination of alkynes and allenes with ammonia, since coordination to nitrogen was found to be preferred under catalytic conditions in the presence of an excess of alkyne (Scheme 3).[29,30] The *syn*-insertion of methyl propiolate into the Au–Si bond of a gold silyl complex has been recently demonstrated.[31]

A wide range of carbon and heteronucleophiles such as arenes,[32] heteroarenes,[33] alcohols,[34] amines,[35] imines,[36] sulfoxides,[37] *N*-oxides,[38] and thiols[39] have been used as nucleophiles in inter- or intramolecular processes. An early example is the gold(III)-catalysed cyclisation of α-hydroxyallenes that allows the straightforward synthesis of 2,5-dihydrofurans (Scheme 4).[40]

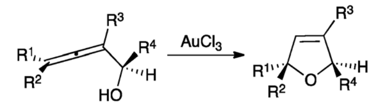
Noteworthy, the regioselectivity in the cyclization of halogenated allenones can be controlled depending on the oxidation state of the catalyst (Scheme 5).[41] Thus, gold(III) favours a mechanism in which the ketone is preferentially activated leading to cyclisation with concomitant 1,2-halogen migration through bromonium intermediate **5**, whereas gold(I) coordinates to the allene leading to cyclisation without halogen migration *via* **6**.



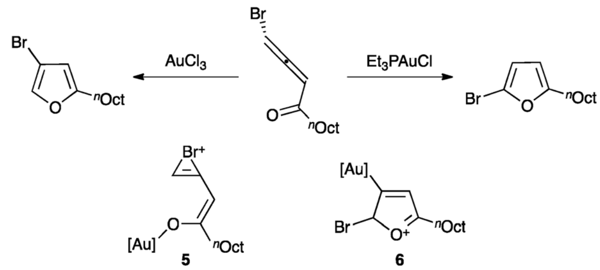
Scheme 2 Nucleophilic attack to a Au(I) π-activated alkyne **3**.



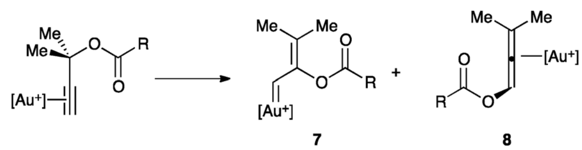
Scheme 3 Ligand exchange prior to reaction suggesting an insertion process.[29]



Scheme 4 Gold(III)-catalysed cyclization of α-hydroxyallenes.[40]



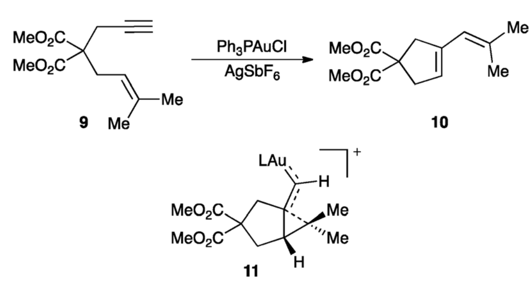
Scheme 5 Regioselective cyclization of halogenated allenones.[41]



Scheme 6 Key intermediates in the propargylic migrations.

The intramolecular nucleophilic addition deserves a special mention when the nucleophile is located at the propargylic position.[42] Thus, propargylic carboxylates can undergo 1,2- or 1,3-acyloxy migrations leading to the formation of vinyl gold(I) carbenoid species **7** or allene gold(I) complexes **8**, which could be in rapid equilibrium (Scheme 6).[43,44] A double 1,2-shift, which also leads to **8**, was found to be energetically more favoured than the direct 1,3-shift, although different substitution at the substrate could significantly influence this preference.

Cycloisomerisation of 1,*n*-enynes is a class of emblematic transformations in which an alkene acts as the nucleophile towards an alkyne activated by gold.[3,45] A diverse array of reactions are possible with a significant increase in molecular complexity and in a fully atom economic manner. A representative example is the single-cleavage rearrangement of 1,6-enynes **9** to form conjugated dienes **10**, which has been proposed to proceed through a cyclopropyl gold(I) carbene **11** that can also be viewed as an homoallyl carbocation (Scheme 7).[46,47]



Scheme 7 Single cleavage rearrangement of 1,6-enyne **9** to form **10** through key intermediate **11**.

Gold intermediates

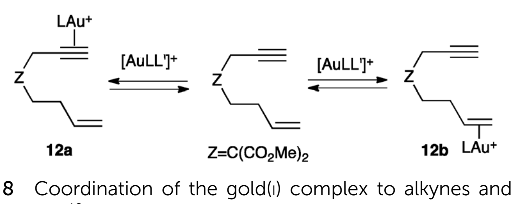
Although many gold intermediates are highly reactive to be readily isolated, some progress has been achieved in the observation of a few key species.[6]

In general, alkynes are selectively activated by gold(I) in the presence of alkenes. This high site-selectivity (alkynophilicity) of gold(I) is not directly related to a thermodynamic preference for the coordination to the alkynes, but to a higher reactivity of the η^2-alkyne gold(I) complexes towards nucleophilic attack.[48] Thus, NMR studies confirmed that both **12a** and **12b** coexist with free 1,7-enyne (Scheme 8), although this class of substrates exclusively reacts by intramolecular attack of the alkene to η^2-alkyne gold(I) species such as **12a**.[49]

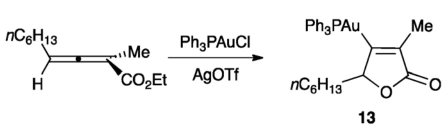
The first stable organogold(I) intermediate (**13**) was isolated in an intramolecular reaction between an allene and an ester (Scheme 9).[50,51] This result demonstrated the formation of vinyl gold(I) complexes by nucleophilic attack on allene–gold(I) complexes.

An interesting debate has been centred on the nature of the gold–carbon bond in complexes of type $[LAuCHR]^+$.[52,53] For the parent reaction between alkynes and alkenes, gold(I) carbenes (**14a**), gold(I) stabilized carbocations (**14b**), homoallyl (**14c**) or even cyclobutyl carbocations (**14d**) could be conceived (Scheme 10).[46] This transformation was realized intermolecularly between aryl alkynes and electron-rich alkenes using cationic gold(I) complexes bearing bulky phosphines (Scheme 10).[54] This reaction has also been applied for the synthesis of large macrocycles.[55] The observed regiochemistry as well as trapping experiments were consistent with a reaction proceeding through a highly distorted cyclopropyl gold(I) carbene **15**, intermediate between **14a–c**, which undergoes ring expansion to form cyclobutyl carbocation **16**. Related distorted cyclopropyl gold(I) carbenes **15** (Scheme 7) were also proposed in the reaction of propiolic acid with alkenes[56] as well as in the addition of nucleophiles to enynes.[46,47,57,58]

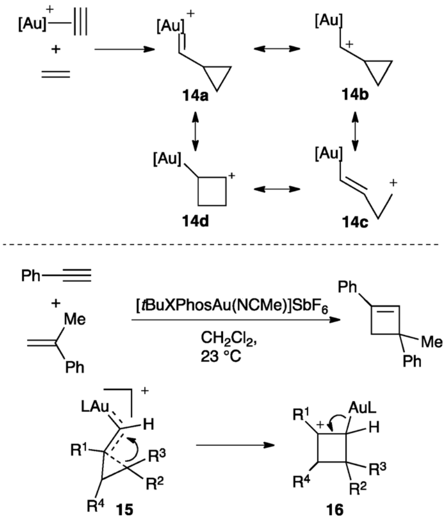
The regioselective cyclization of enynes **17** with a pending carboxylic acid forms selectively lactones **18** and/or **19** (Scheme 11).[59] Following the Stork–Eschenmoser model for cyclizations of squalene and oxidosqualene,[60] these types of cascade cyclizations were rationalized as proceeding through concerted transition states such as **20**, not involving cyclopropyl gold(I) carbenes as discrete intermediates.[61] Analogous reasoning was put forward in the asymmetric hydroarylation of 1,6-enynes[62] and in other related processes.[63]



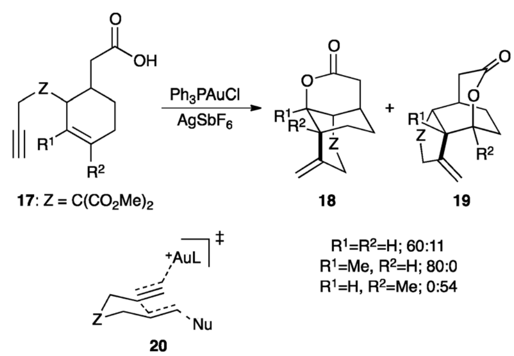
Scheme 8 Coordination of the gold(I) complex to alkynes and alkenes (L = JohnPhos).[48]



Scheme 9 Formation of the first isolated vinyl gold(I) complex in a gold(I)-catalysed cyclization.[50]



Scheme 10 Possible intermediates involved in the gold(I)-catalysed intermolecular [2+2] cycloaddition of alkynes with alkenes.

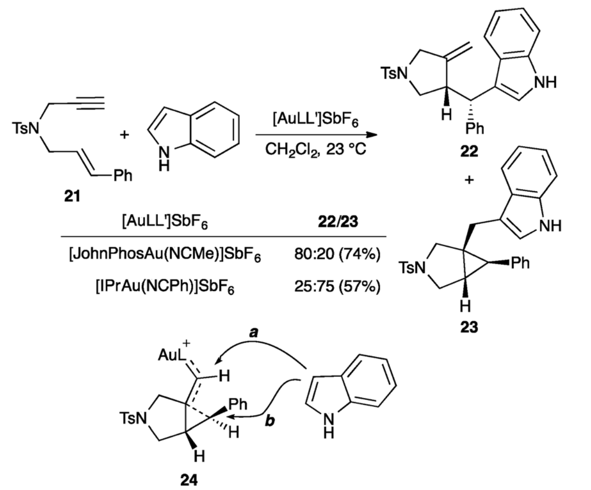


Scheme 11 Cascade cyclization of 1,6-enynes **17**.[59]

However, other studies strongly suggest that gold(I)-catalysed 1,*n*-enyne cyclizations occur step-wise involving cyclopropyl gold(I) carbenes (**11**) and related types of intermediates.[45–47,64] Thus, for example, reaction of 1,6-enyne **21** with indole leads to adducts **22** and **23** by nucleophilic attack at the cyclopropyl (b) or carbene (a) carbons of intermediate **24** (Scheme 12).[65] The use of complex $[IPrAu(NCPh)]SbF_6$ as the catalyst with a highly donating NHC ligand enhances the carbene-like nature of the intermediate, favouring nucleophilic attack at the carbene carbon leading to **23**.

Spectroscopic or structural data for carbene-like structures of relevance in homogeneous catalysis are lacking. The interesting earlier structure of gold(I) carbene **25** showed C–Au length within the range of a single bond between a sp^2 carbon atom and the metal while the C–N bond is shorter than a typical imine (Fig. 6).[66] However, this scaffold is far from the intermediates generated in a catalytic cycle.

Opening of cyclopropenone acetal **26** with gold(I) leads to ***Z*-27** that isomerises to ***E*-27** presumably through gold(I) carbene **28** (Scheme 13).[67] The spectroscopic data of ***Z*-27** and ***E*-27** revealed an oxocarbenium cationic structure.



Scheme 12 Nucleophilic addition to the gold(I) carbene position.[65]

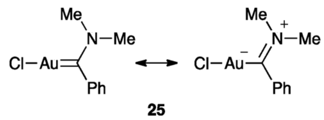
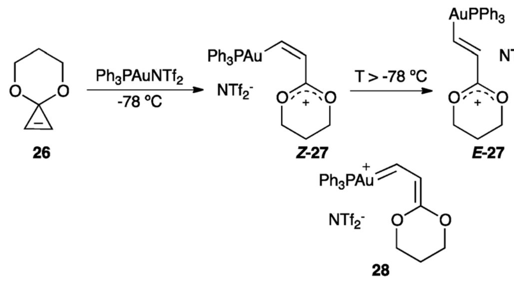


Fig. 6 Gold(I) carbene **25**.[66]



Scheme 13 Generation of carbocationic organogold(I) complexes.[67]

An in-depth theoretical analysis of the bond rotation energy for different carbocations demonstrates that AuL has a similar stabilizing effect as OMe on an allyl carbocation (Fig. 7).[52] Moreover, the bond length between gold and the carbene carbon decreased with strong σ-donating ligands such as chloride or N-heterocyclic carbenes, but it increases with less donating, π-acidic ligands such as phosphines or phosphites by reducing the back-donation to the substrate. This study concluded a continuum character of the organogold(I) species ranging from metal stabilized singlet carbene to metal coordinated carbocation depending on the substitution pattern and the ligand on gold.

Gold(I) allenylidenes such as **29** have been recently structurally characterized (Fig. 8).[68] Theoretical and experimental analysis suggested that the heteroatom stabilization favoured an Au-propargyl

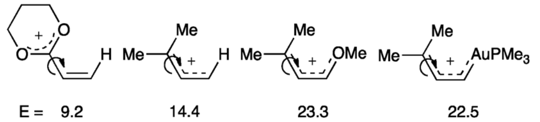


Fig. 7 Calculated rotation energies depending on the substituents (M06, kcal mol^{-1}).[52]

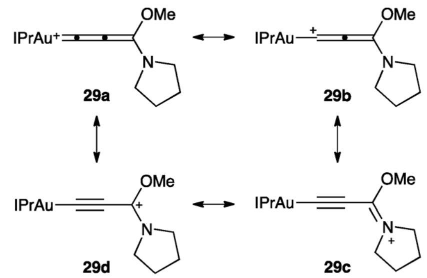


Fig. 8 Gold(I) allenylidene **29**.[68]

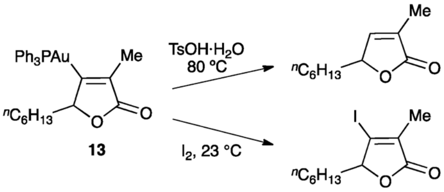
carbocation (**29c-d**). In contrast, without this stabilization provided by the heteroatoms, the structure depends on the ligand, ranging from gold(I)-propargyl carbocations to gold(I) allenylidenes. Gold(III) allenylidenes with similar substitution at the terminus carbon have also been structurally characterized.[69]

Evolution of the key gold intermediates

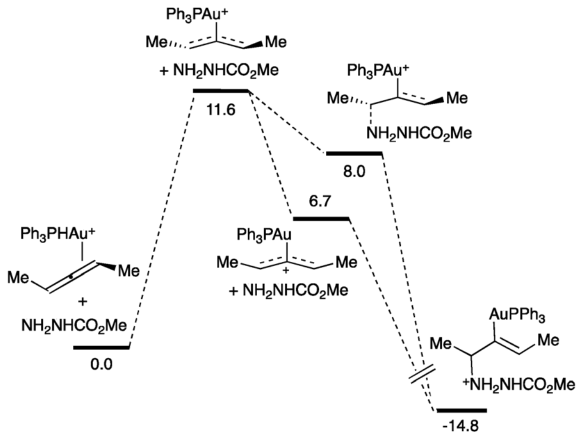
Subsequent to the gold activation of the unsaturated scaffold and its nucleophilic attack, the intermediates can evolve through many different pathways leading to a huge variety of complex products.[3] The simplest evolution of the alkenyl gold(I) intermediates is their reaction with an electrophile, most usually by protodeauration regenerating the active catalyst (Scheme 14).[6,50,51] Similarly, reaction with iodine and related electrophiles leads to the corresponding halo-derivatives.[50,70]

A mechanistic study of the intermolecular hydroamination of allenes by nucleophilic attack of a carbazate followed by protodeauration showed that the catalyst resting state was the η^2-allenegold(I) complex (Scheme 15).[71] Kinetic analysis showed zero order for the carbazate, suggesting that this nucleophile is not involved in the rate-determining step. DFT calculations predicted that the activation of the allene was the step with the highest activation energy, 11.6 kcal mol^{-1}. A two-step, no intermediate process followed by an irreversible protonation was proposed for this transformation.

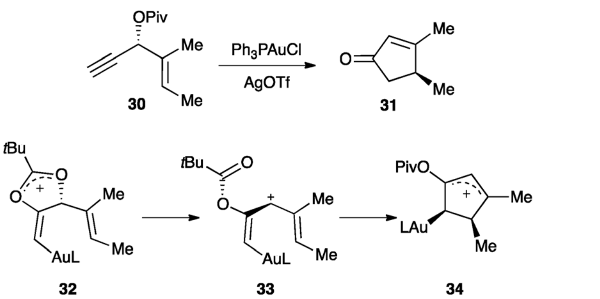
The alkenyl gold(I) intermediate could further react in a multistep process. As an important example, the enantioselective gold(I)-catalysed Rautenstrauch rearrangement of 1,4-enyne **30** with a propargylic pivaloyl group to form cyclopentenone **31** proceeded through 1,2-migration generating a vinyl gold(I) complex **32**, which underwent cyclisation with the alkene to form five-membered ring **34** (Scheme 16).[72] DFT calculations suggested that it is the helicity of the pentadienyl cation intermediate **33** that retains the chiral information.[73]



Scheme 14 Electrophilic attack to an alkenyl gold(I) complex.[50]



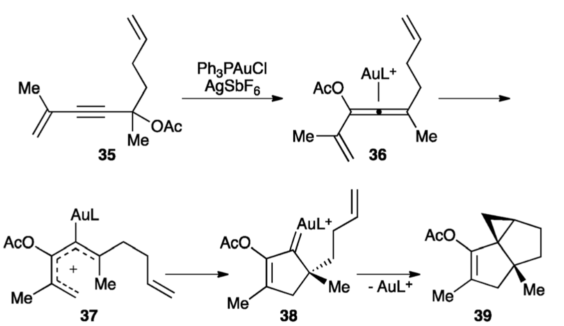
Scheme 15 Reaction coordinate for the hydroamination of allenes (kcal mol^{-1}).[71]



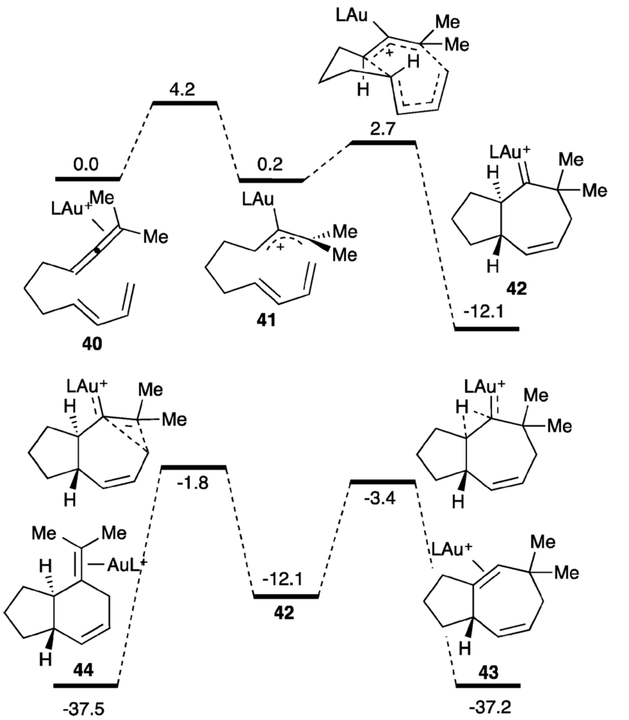
Scheme 16 Enantioselective gold(I)-catalysed Rautenstrauch rearrangement.[72,73]

Similarly, a gold(I)-catalysed 1,3-propargylic acetate migration of substrates such as **35** generates intermediate **36** that undergoes Nazarov-type electrocyclisation through **37** generating gold(I) carbene **38** (Scheme 17).[74] This intermediate can further react by intramolecular cyclopropanation to form tricyclic structure **39**.

An interesting cyclization of allenes with dienes proceeds by formal [4+3] and [4+2] cycloaddition forming seven or six-membered rings (Scheme 18).[27] The competitive cyclization processes are initiated by the selective activation of the allene with the gold(I) catalyst (**40**) to form the allyl cation **41** as the rate-determining step, which would rapidly lead to gold(I) carbene **42** in a concerted manner. This intermediate can then evolve through a 1,2-hydrogen shift leading to **43** or through a 1,2-alkyl shift resulting in a ring contraction forming **44**.



Scheme 17 Nazarov-type cyclization of substrates **35**.[74]



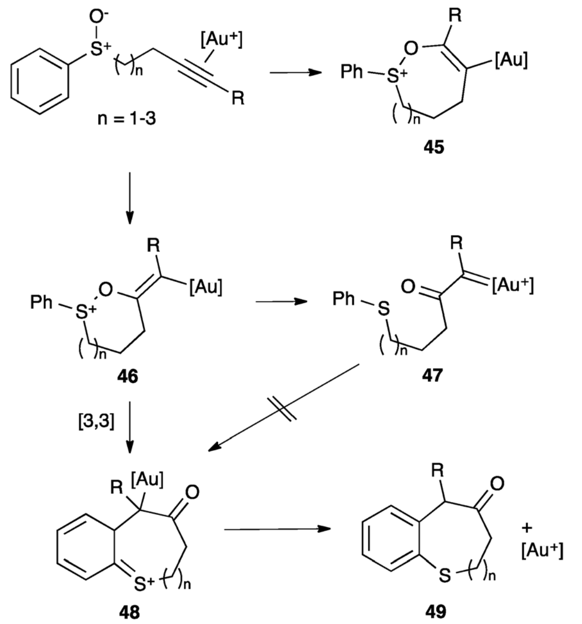
Scheme 18 Reaction coordinate of the cycloaddition between allenes and dienes (kcal mol^{-1}), L = P(OMe)$_3$.[27]

Gold(I) carbene **42** could be trapped by oxidation with diphenylsulfoxide forming a bicyclic ketone.[27a]

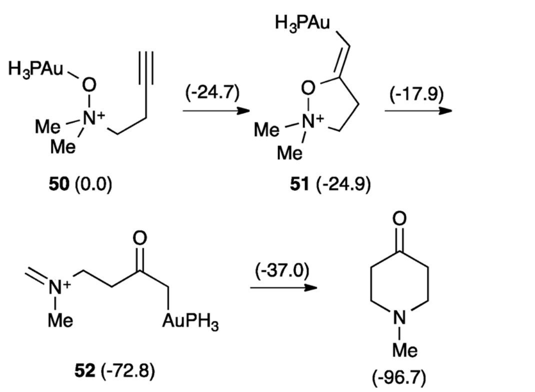
A different type of behaviour (push–pull reactivity) was suggested for certain alkenyl gold(I) complexes.[37a,75–77] An early example is the rearrangement of alkynyl sulfoxides.[78] In this case, the alkyne activation followed by *endo* or *exo* nucleophilic attack of the sulfoxide depending on R and formation of an alkenyl gold(I) intermediate (**45** or **46**, respectively) was initially proposed (Scheme 19). These species were proposed to evolve by retro-donating electron density from the metal and pushing the sulphide moiety forming a α-carbonyl gold(I) carbene **47** that underwent an intramolecular Friedel–Crafts reaction to give **48** and then **49**. However, recent studies supported theoretically and experimentally a completely different progression after the initial cyclization to **46**.[78c] Since the prepared α-carbonyl gold(I) carbene did not undergo the intramolecular Friedel–Crafts reaction, further DFT calculations were performed. Thus, a subtle change in the conformation of **46** allows a [3,3]-sigmatropic rearrangement to form **48**, which explains the observed results. Formation of α-carbonyl gold(I) carbenes has also been considered to be unlikely in other reactions of alkynes with sulfoxides.[37c]

The involvement of α-oxo gold(I) carbenes[38,79,80] was also questioned in the related reaction of alkynyl amine *N*-oxides.[76] This time DFT calculations revealed another completely different pathway (Scheme 20).[81] Hence, the gold-coordinated amine *N*-oxide **50** attacks the alkyne to form **51**, which evolves by 1,5-hydrogen shift to form iminium cation **52**, which undergoes an intramolecular Mannich reaction to form the final piperidinone.

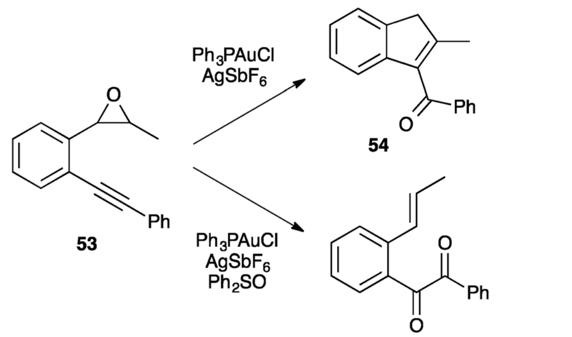
Nevertheless, a α-carbonyl gold(I) carbene was indeed trapped by oxidation with diphenylsulfoxide during the



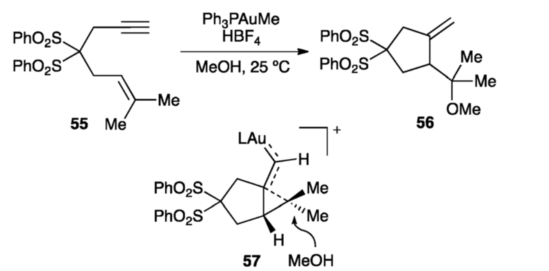
Scheme 19 Cyclization of alkynyl sulfoxides.[78c]



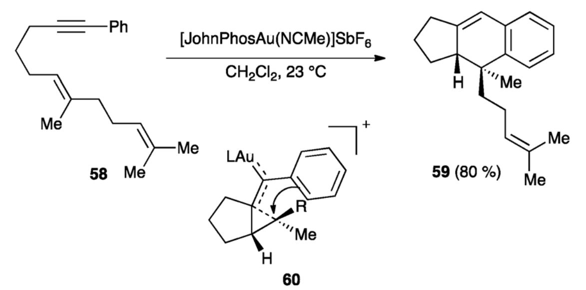
Scheme 20 Rearrangement of alkynyl amine *N*-oxides (kcal mol^{-1}).[81]



Scheme 21 Gold(I) carbene trapping in the cycloisomerization of epoxide-alkyne functionalities.



Scheme 22 Cyclopropane ring opening by nucleophilic attack (**57**).[46]



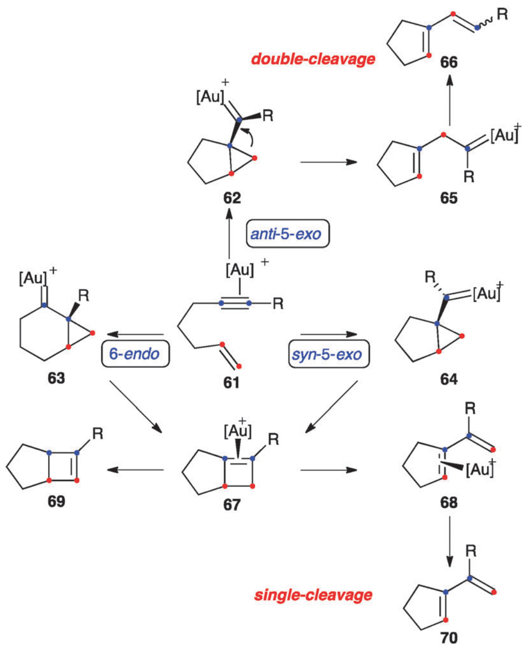
Scheme 23 [4+2] Cycloaddition of aryl substituted enynes.[83]

nucleophilic attack of an epoxide to an alkyne (**53**) in the cyclization to the α,β-unsaturated ketone **54** (Scheme 21).[75d]

1,*n*-Enynes react stereospecifically with a variety of nucleophiles.[46,47,57,58,65] As an illustrative example, 1,6-enyne **55** reacts with a gold(I) catalyst to form **56** as a result of the intermolecular *anti* attack of methanol on the cyclopropane-type ring of intermediate **57** (Scheme 22). Oxygen transfer to the carbene-like carbon of similar intermediates from diphenylsulfoxide, as a nucleophilic oxidant, leads to the corresponding aldehydes.[82]

Carbon nucleophiles react by similar mechanistic pathways.[65] A particular case is illustrated by the cycloaddition of aryl substituted enynes, such as **58**, which react readily with cationic gold(I) catalysts to form tricyclic derivatives **59** through intermediates of type **60** (Scheme 23).[83] This formal [4+2] cycloaddition is stereospecific and, according to DFT calculations, proceeds in a stepwise fashion in which formation of **60** is rate-determining.[83b]

In the absence of external or internal nucleophiles, enynes react with gold(I) by a series of fascinating rearrangements and related processes[3,46,84] These types of cycloisomerisations have also been observed with other metal catalysts,[85–90] although cationic gold(I) complexes are by far the most reactive and selective catalysts.[3,46] In the case of 1,6-enynes that bear an aryl substituted alkyne and a terminally unsubstituted alkene, which react sluggishly with electrophilic metal catalysts, the initial gold(I)-activated substrate **61** could evolve by three pathways: *anti*-5-*exo-dig* (*via* **62**), 6-*endo-dig* (*via* **63**), and *syn*-5-*exo-dig* (*via* **64**) (Scheme 24).[91] In general agreement with previous mechanistic work,[58,92] recent DFT calculations show that the *syn*-5-*exo-dig* cyclization does not compete with the other two pathways, whose relative preference depends on the substitution pattern of the enyne.[91] Products of double-cleavage rearrangement **66** could be formed through intermediate **65**, in which the methylene is formally inserted into the alkyne carbons. On the other hand, dienes **70** of single-cleavage rearrangement can be formed by expansion of the cyclopropane of **63** to form cyclobutene–Au(I) complex **67**, followed by cleavage to give diene–Au(I) complex **68**.

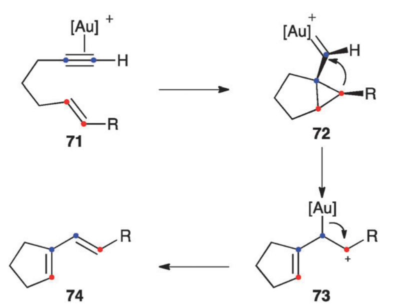


Scheme 24 General pathways for the skeletal rearrangement of [2+2] cycloaddition of 1,6-enynes.[91]

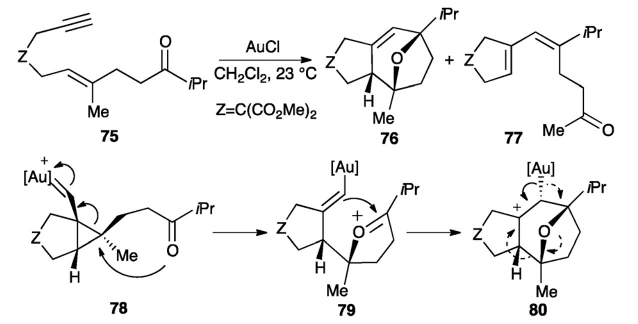
Intermediates **63** can also evolve to form bicyclo[4.1.0]hept-2-ene derivatives.[46,93]

Only a few examples of highly strained bicyclo[3.2.0]hept-5-enes have been reported in gold(I) catalysed isomerisations,[91,94,95] whereas products of formal [2+2] cycloaddition have been observed in the parent intermolecular reactions of alkynes with alkenes,[54] as well as in the cyclisation of 1,7-, 1,8-[46,96] and higher enynes.[55] Alternatively, **67** could give the product of alkene isomerisation **69**.[83] This type of isomerisation has been observed very recently by NMR at low temperature.[95]

1,6-Enynes substituted at the terminal carbon of the alkene (**71**) can directly give 1,3-dienes **74** of single-cleavage rearrangement by direct evolution of intermediates **72** formed in the *anti*-5-*exo-dig* pathway to form cations **73** (Scheme 25).[58] An endocyclic version of this rearrangement has also been documented.[46b,97] In general, this is a stereospecific process, although (*E*)-1,6-enynes bearing electron-donating R substituents at the alkene lead selectively to 1,3-dienes with the *Z* configuration.[98]



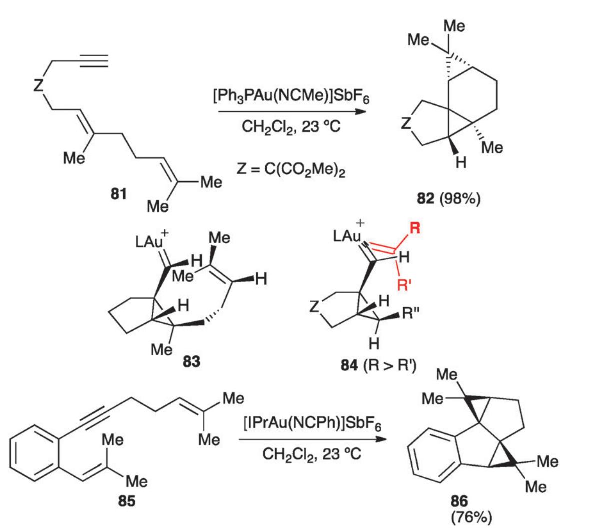
Scheme 25 Alternative mechanism for the single-cleavage skeletal rearrangement.[58]



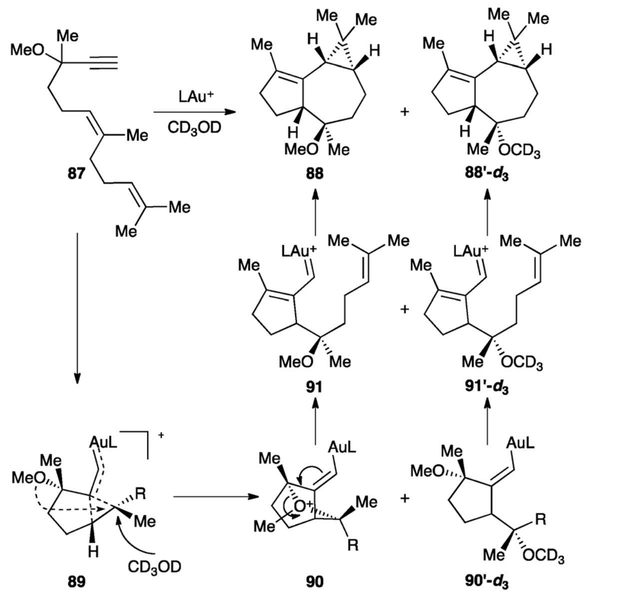
Scheme 26 Intramolecular [2+2+2] cycloaddition of oxoeynes.[101]

Cyclopropyl gold(I) carbene intermediates can also be trapped by carbonyl groups inter-[99,100] or intramolecularly.[101,102] Thus, oxo-1,6-enynes **75** undergo a [2+2+2] cycloaddition to form oxatricyclic compounds **76** (Scheme 26). As a side-reaction, diene **77** is also obtained. The reaction presumably proceeds through intermediate **78**, which evolves to form **79** that undergoes a Prins-type cyclization leading to tricyclic scaffold **80**. Cation **80** then furnishes oxatricyclic derivatives **76** by metal elimination or dienes **77** by fragmentation.

The carbene-like character of the intermediates generated by reaction of 1,*n*-enynes with gold(I) is more clearly revealed by their trapping with alkenes. Thus, for example, reaction of dienyne **81** leads stereoselectively to tetracyclic compound **82** (Scheme 27).[46] DFT calculations are consistent with a concerted, asynchronous cyclopropanation through intermediate **83**.[46] A similar model **84** was proposed for the intermolecular cyclopropanation of 1,6-enynes by alkenes.[103] The cyclopropanation was found to be concerted for symmetrical or less polarized alkenes, whereas styrenes react in a stepwise manner. Nevertheless, even in this case, the overall process is stereospecific since formation of the second carbon–carbon occurred with a very small energy. Similarly, double 1,5-enyne **85** furnished **86** by intramolecular cyclopropanation of the intermediate *endo*-carbene.[104] Gold(I) carbenes generated



Scheme 27 Intramolecular cyclopropanation of 1,6- and 1,5-enynes.[46,103,104]

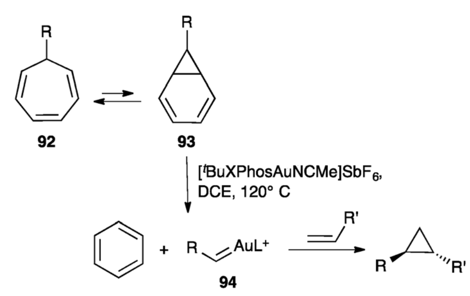


Scheme 28 1,5-Propargyl ether migration of a 1,6-enyne followed by intramolecular cyclopropanation (L = JohnPhos).[107]

through 1,2-migration of propargylic carboxylates were also trapped stereospecifically with alkenes.[105,106]

Dienynes such as **87** bearing an alkoxy group at the propargylic position react differently leading to tricyclic products **88** as a result of a cyclization cascade process that involves a formal 1,5-migration of the OR group (Scheme 28).[107] The reaction proceeds through intermediate **89**, which evolves by intramolecular attack of the OR at the electrophilic site of the cyclopropane to form **90**. α,β-Unsaturated gold(I) carbene **91**, generated by cleavage of the oxonium bridge, then undergoes cyclopropanation with the pending alkene. Intermediate **89** can also be trapped intermolecularly with an external nucleophile to generate the corresponding epimeric derivative.

Gold(I) carbene intermediates can also be generated by reaction of diazoacetates with gold(I) complexes.[108] The retro-Buchner reaction of 7-substituted cycloheptatrienes **92** also generates gold(I) carbenes (Scheme 29).[109] Cycloheptatrienes **92** react with gold(I) through norcaradienes **93** to give gold(I) carbenes **94**, which are trapped by alkenes leading to the corresponding cyclopropanes. A similar process was observed in the gas phase under electrospray ionization conditions.[110]



Scheme 29 Cyclopropanation of alkenes by retro-Buchner reaction of cycloheptatrienes.[109]

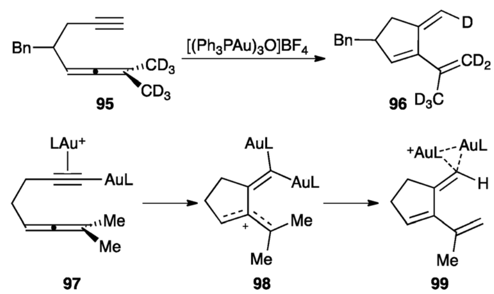
More recently, gold(I) catalysis has also been combined with strong oxidants,[111] organocatalysts,[112] palladium, nickel or rhodium,[113] and photoredox reactions[114] leading to a completely new set of interesting transformations.

Digold complexes

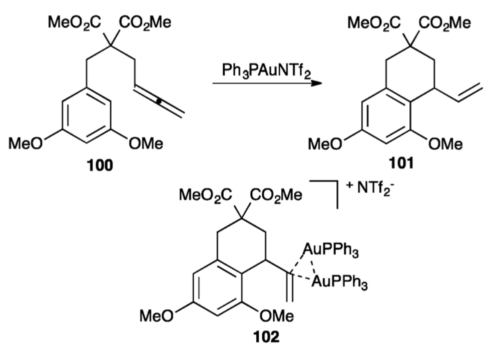
Digold(I) species were proposed to be involved as key intermediates in the cyclization of 1,5-allenynes such as **95**, which proceed by a stereospecific intramolecular hydrogen transfer from the allene to the alkyne (Scheme 30).[115] Accordingly, gold(I) coordinates with the alkyne making the proton more acidic, leading to an alkynyl gold(I) complex that reacts with a second equivalent of the catalyst to form **97**. Nucleophilic attack of the allene generates allyl stabilized carbocation **98** in the rate-determining step, which is followed by an intramolecular 1,5-hydrogen shift leading to **96** through diaurated species **99**.

Digold(I) complexes with the bridging 3-centre 2-electron bond related to **99** had been observed before in other contexts,[116] and were later found to play relevant roles in catalysis. Thus, for example, during the catalytic intramolecular hydroarylation of allenes **100** to give **101**, complex **102** was isolated as a catalyst resting state (Scheme 31).[117] Similar species were observed in the intramolecular allene hydroalkoxylation.[118]

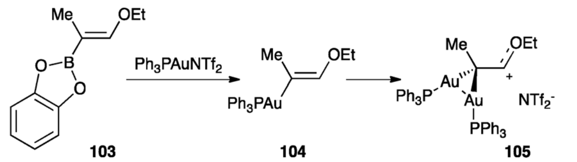
A species of this type was generated and fully characterized by gold–boron transmetalation from **103** (Scheme 32).[119] In this case, the monogold(I) complex **104** could not be observed. The analysis of the X-ray structure of **105** revealed an important stabilization from the oxygen atom and two almost regular carbon–gold σ-bonds.



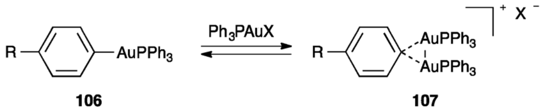
Scheme 30 Cycloisomerization of 1,5-allenynes.[115]



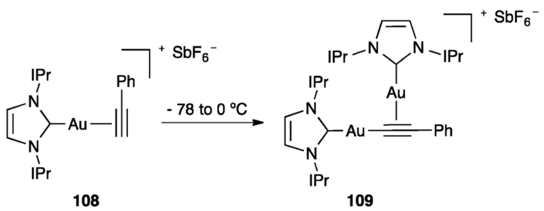
Scheme 31 Intramolecular hydroarylation of allenes.[117]



Scheme 32 Formation of digold(I) species by gold–boron transmetalation.[119]



Scheme 33 Equilibrium between mono- and digold(I) species.[120]

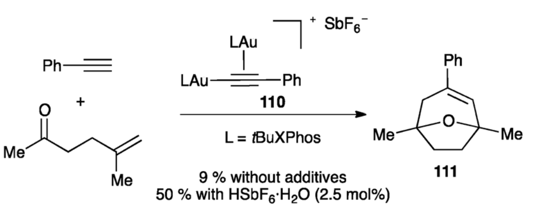


Scheme 34 Formation of alkynyl digold(I) complex **109**.[121]

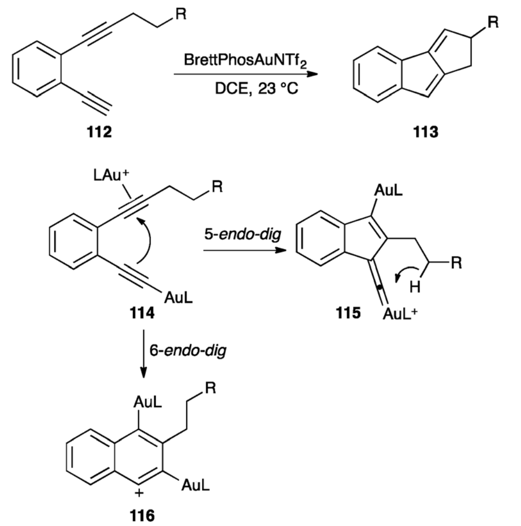
The nature of the 3-centre 2-electron interaction was also investigated by studying the equilibrium between aryl–gold **106** and digold(I) complexes **107** as a function of the electronic effects of the R substituents and the counteranions (Scheme 33).[120] Thus, it was found that formation of **107** was favoured with less coordinating counteranions as well as with more electron-rich substrates supporting the proposal of an electrodeficient Au_2C bond.

Alkynyl digold(I) complexes have been formed from terminal alkynes.[25e,121] At −78 °C complex **108** was formed, which then formed digold(I) complex **109** at higher temperatures (Scheme 34).[121]

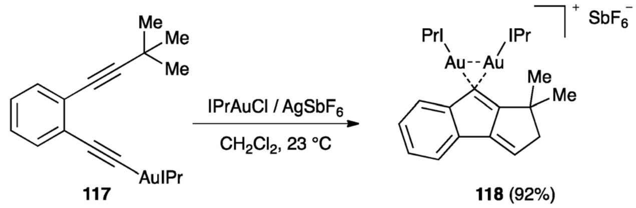
Similar digold(I) complexes with phosphine ligands were detected in the intermolecular [2+2] cycloaddition of alkynes with alkenes.[122] Complex **110** is also formed in the intermolecular [2+2+2] cycloaddition of alkynes with oxoalkenes, leading to oxatricyclic products **111** (Scheme 35),[123] a process mechanistically related to the intramolecular reaction of oxo-1,6-enynes (see Scheme 26). Although the digold(I) complex **110** was identified as the resting state of the catalytic cycle, only traces of product **111** were obtained when this complex was used as the catalyst. The catalytic activity was recovered in the presence of an acid, which cleaved the gold–acetylide bond. The results demonstrated that the reactive species is a π-coordinated monogold(I) complex, which was confirmed by DFT calculations.



Scheme 35 Digold(I) species **110** as a precatalyst.[123]



Scheme 36 Dual activation followed by C–H insertion.[125]



Scheme 37 Formation of digold(I) species **118** during the dual activation of diynes.[128]

The possible role of digold(I) complexes in cycloisomerization reactions of 1,6-enynes has also been examined.[124] Experimental and computational work suggested that these types of σ,π-digold(I) complexes are unreactive in the cycloisomerization process.

However, σ-alkynyl gold complexes react with alkynes in intramolecular transformations leading to a variety of interesting cyclic systems. Thus, diyne **112** was cyclised to form 1,2-dihydrocyclopenta[*a*]indene **113** (Scheme 36).[125] The reaction was proposed to proceed by formation of alkynyl gold(I) species **114**, which evolved by attack of the σ-alkynyl gold to the π-activated non-terminal alkyne in a 5-*endo-dig* cyclization. The resulting gold(I) vinylidene **115** could undergo a C–H insertion followed by protodeauration to form **113**. Theoretical work suggested that formation of **116** by 6-*endo-dig* cyclization could also be possible. A similar transformation has been applied for the synthesis of cyclopentapyridinones.[126]

In a parallel study, the reaction of **117** led to digold(I) complex **118** (Scheme 37).[127] Additionally, the intermolecular trapping of the vinylidene gold(I) complexes of type **115** with alkenes was found to give cyclobutane through a cyclopropanation reaction, followed by ring expansion.[128] Inter- and intramolecular reactions of vinylidene gold(I) complexes with arene rings have also been reported.[129] It is interesting that, in contrast to that found in the reactions between alkynes and alkenes, these types of diyne cyclizations are smoothly catalysed with σ,π-digold(I) alkyne complexes.[129–131]

Conclusions

Many reactions catalysed by gold, or by other electrophilic catalysts, closely resemble proton-initiated carbocationic processes. However, gold(I) very often provides exquisite control on these transformations, channeling the process towards the desired products by stabilising the key reactive intermediates. The basic mechanisms involved in the cycloisomerization of substrates containing alkynes and allenes are now better understood and have guided the discovery of synthetically useful cascade processes for the build up of complex molecular architectures. However, there are still some elusive aspects in this area, particularly in intermolecular reactions. Closer scrutiny of some early mechanistic proposals will certainly lead to the discovery of new types of reactivity. The recent outburst in digold catalysis, which suggests that more complex species are involved in certain cases, augurs well for the future discovery of yet more complex transformations.

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