Gold-Catalyzed Rearrangements and Beyond
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CONSPECTUS

Cycloisomerizations of enynes are probably the most representative carbon–carbon bond forming reactions catalyzed by electrophilic metal complexes. These transformations are synthetically useful because chemists can use them to build complex architectures under mild conditions from readily assembled starting materials. However, these transformations can have complex mechanisms. In general, gold(I) activates alkynes in the presence of any other unsaturated functional group by forming an \( \eta^2\text{-alkyne} \)–gold complex. This species reacts readily with nucleophiles, including electron-rich alkenes. In this case, the reaction forms cyclopropyl gold(I) carbene-like intermediates. These can come from different pathways depending on the substitution pattern of the alkyne and the alkene. In the absence of external nucleophiles, 1,\( n \)-enynes can form products of skeletal rearrangement in fully intramolecular reactions, which are mechanistically very different from metathesis reactions initiated by the \([2 + 2]\) cycloaddition of a Grubbs-type carbene or other related metal carbenes.

In this Account, we discuss how cycloisomerization and addition reactions of substituted enynes, as well as intermolecular reactions between alkynes and alkenes, are best interpreted as proceeding through discrete cationic intermediates in which gold(I) plays a significant role in the stabilization of the positive charge. The most important intermediates are highly delocalized cationic species that some chemists describe as cyclopropyl gold(I) carbenes or gold(I)-stabilized cyclopropylmethy/cyclobutyl/homoallyl carbocations. However, we prefer the cyclopropyl gold(I) carbene formulation for its simplicity and mnemonic value, highlighting the tendency of these intermediates to undergo cyclopropanation reactions with alkenes.

We can add a variety of hetero- and carbonucleophiles to the enynes in the presence of gold(I) in intra- or intermolecular reactions, leading to the corresponding adducts with high stereoselectivity through stereospecific anti-additions. We have also developed stereospecific syn-additions, which probably occur through similar intermediates. The attack of carbonyl groups at the cyclopropyl carbons of the intermediate cyclopropyl gold(I) carbenes initiates a particularly interesting group of reactions. These trigger a cascade transformation that can lead to the formation of two C–C and one C–O bonds. In the fully intramolecular process, this stereospecific transformation has been applied for the synthesis of natural sesquiterpenoids such as \((\pm\)orientalol F and \((\pm\)-englerin A.

Intra- and intermolecular trapping of cyclopropyl gold(I) carbenes with alkenes leads to the formation of cyclopropanes with significant increase in the molecular complexity, particularly in cases in which this process combines with the migration of propargylic alkoxy and related OR groups. We have recently shown this in the stereoselective total synthesis of the antiviral sesquiterpene \((\pm\)-schisanwilsonene by a cyclization/1,5-acetoxy migration/intermolecular cyclopropanation. In this synthesis, the cyclization/1,5-acetoxy migration is faster than the alternative 1,2-acyloxy migration that would result in racemization.

1. Introduction
Cycloisomerizations of enynes proceed by mechanistically complex, multistep transformations and can lead to complex architectures by fully intramolecular processes. The pioneering work on the electrophilic activation of enynes was carried out by the group of Trost in the 1980s using palladium catalysts.\(^1\) These early studies were followed by several groups that examined other electrophilic metals, mainly ruthenium\(^2\) and platinum.\(^3–7\) The potential of gold catalysis in organic synthesis was demonstrated with the development of efficient additions of alcohols and water to alkynes under mild conditions by Teles\(^8\) and Tanaka,\(^9\) as
well as by the phenol synthesis discovered by Hashmi using gold(III). This synthesis of phenols by cyclization of furans with alkynes was shown to be mechanistically related to some metal-catalyzed cycloisomerization reactions. In 2004, our group and those of Fürstner and Toste reported that gold(I) complexes were the most active and selective catalysts for the cycloisomerization of enynes. A mechanistically related gold(I)-catalyzed Conia-ene reaction of β-ketoesters with alkynes was also reported by Toste in 2004. Henceforth, homogeneous gold(I) catalysis experienced an outburst leading to the discovery of a phenomenal amount of new synthetically useful transformations. In addition to the important synthetic achievements made in the past decade in this area, the nature of the gold—carbon bond in intermediates of type [AuCH=CHR]⁺, which are involved in many gold(I)-catalyzed transformations, has inspired certain debate on the role played by gold(I) in the stabilization of these carbocationic species.

Several reviews have covered synthetic and mechanistic aspects of homogeneous gold catalysis. In this Account, we focus on the developments of gold(I) catalytic transformations derived from our early studies on the cycloisomerization of simple enynes that have led to the discovery of complex cascade reactions.

2. Gold(I)-Catalyzed Cyclization of Enynes

Broadly, gold(I) selectively activates alkynes in the presence of alkenes and other functional groups. The high alkynephilicity of gold(I) does not reflect any thermodynamic preference for its coordination to alkynes, but it correlates with the higher reactivity of the resulting (η²-alkyne)—gold(I) complexes toward nucleophilic attack. In analogy to that shown in related cyclizations catalyzed by platinum(II), activation of the alkyno functionality by gold(I) forms an (η²-alkyne)—metal complex that reacts as an electrophile with the alkene to form cyclopropyl gold(I) carbene-like intermediates or by an anti-5-exo-dig or a 6-endo-dig cyclization, respectively (Scheme 1). Intermediates 2 can evolve to generate new rearranged carbenes by the formal insertion of the terminal alkene carbon into the alkyno carbons. These new carbenes undergo α-proton elimination to yield 1,3-dienes, the products of an overall double-cleavage rearrangement. In this process, both the alkyno and the alkene have been cleaved in an intramolecular transformation. Although products with both configurations have been observed in this rearrangement, often compounds are obtained. On the other hand, intermediates 3 of 6-endo-dig cyclization can lead to bicyclo[4.1.0]hept-2-ene derivatives by α-proton elimination. Alternatively, isomerization of 3 by ring expansion of the cyclopropane gives (η²-cyclobutene)—gold(I) complexes 7. The opening of these gold(I) complexes can form complexes 8, precursor of 1,3-dienes 9, in a transformation in which only the alkene has been cleaved. Highly strained bicyclo[3.2.0]hept-5-enes, which are the free ligands of 7, have been isolated only in a few cases. Less strained cyclobutenes resulting from a formal [2 + 2] cycloaddition have been obtained in the cyclization of 1,7- and 1,8-enynes. Intermediates 7 can also undergo isomerization to give bicyclo[3.2.0]hept-2-ene derivatives. Similarly, 1,5- and 1,7-enynes undergo rearrangements with gold(I) catalysts by somewhat related pathways.

According to DFT calculations, the syn-5-exo-dig cyclization via intermediates does not compete with the other two pathways. Exocyclic carbene intermediate 2, formed in the anti-5-exo-dig pathway, can also give rise to products of single-cleavage rearrangement 9 through transition state TS2 and intermediates 12. The pathway followed by a particular enyne is highly dependent on its substitution pattern. Thus, 1,6-enyne 13a

**SCHEME 1. General Pathways for the Gold(I)-Catalyzed Cycloisomerization of 1,6-Enynes**
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with a terminal alkyne and a disubstituted alkene reacts with a cationic catalyst formed in situ from [Au(PPh₃)Cl] and AgBF₄ to form exclusively single-cleavage rearrangement diene 14a (Scheme 2). An identical product 14a was obtained from 1,6-enyne 13b, with the methyl substituent at the alkyne, in an equally highly selective double-cleavage rearrangement. Although the gold(I)-catalyzed single-cleavage rearrangement is usually a stereospecific process in which the configuration of the alkene is retained, reaction of (E)-1,6-enynes such as 13c–f, bearing strongly electron-donating substituents at the terminal alkene carbon, react anomalously with cationic gold(I) catalyst 36,47,48 to give selectively Z-configured dienes 14b. The same Z-preference was observed with other highly electrophilic gold(I) or platinum(II) catalysts. The Z-isomers of enynes 13c and 13d also give rise to Z-dienes with gold(I) or platinum(II) catalysts.49 The stereochemically anomalous rearrangement remains mechanistically puzzling.

3. Gold(I)-Catalyzed Nucleophilic Additions to Enynes

In the presence of alcohols or water, gold(I) catalyzes the addition of these nucleophiles to the enynes leading to products of alkoxy- or hydroxycyclization (Scheme 3). The overall process is an anti addition of an electrophile (the (η²-alkyne)–gold(I) complex) and a heteronucleophile to an alkene. Therefore, this reaction is stereospecific, as illustrated in the methoxycyclizations of diastereomers 13g and 13h, which afford diastereomeric adducts 15a and 15b, respectively, by attack of MeOH to Intermediate 16a (Scheme 3). These processes follow the Markovnikov regiochemistry, which is further illustrated by the reaction of substrate 13i in MeOH to form six-membered ring 15c through intermediates of type 16b. Related additions to 1,5-enynes are also stereospecific.55–57 A few exceptions have been observed with the most polarized substrates. Thus, whereas reaction of enyne 13j in MeOH as solvent gives the product of methoxycyclization 15d as a single anti isomer, in agreement with the general behavior observed by other 1,6-enynes in similar reactions catalyzed by gold13,30 or platinum,6 when the reaction of 13j was performed with only 5 equiv of MeOH, adduct 15d was obtained as a 3:2 anti/syn mixture of stereoisomers (Scheme 3).49

Additions of carbon nucleophiles to enynes can also be carried out in the presence of gold(I). Thus, for example, reaction of 1,6-enyne 13k with indole, an electron-rich...
heteroarene, leads to adducts 17a and 17b by nucleophilic attack at the cyclopropyl or carbene carbons, respectively, of intermediate 18 (Scheme 4).58,59 Adduct 17a was favored using phosphine–gold(I) complex A, whereas complex B with an NHC ligand directed the nucleophilic attack at the carbene carbon, leading to adduct 17b. This result can be explained by the enhancement of the carbene-like character of the intermediate 18 by the highly donating NHC ligand. The 6-endo-dig cyclization pathway predominates in the case of the addition of indole to phenyl-substituted enyne 13l, which leads stereospecifically to adduct 19, while in the case of substrate 13m, the electron-rich arene attacks at the most substituted alkene carbon leading to 20.59 The addition of 1,3-dicarbonyl compounds and allyl silanes to 1,6-enynes, as well as similar additions of diverse carbon nucleophiles to 1,5-enynes are also catalyzed by cationic gold(I) catalysts.59

Related intramolecular arylation of 1,6-enynes,62,63 as well as additions of carboxylic acids to enynes,17 have been proposed to take place in a concerted manner following the Stork–Eschenmoser model for cyclizations of squalene and oxidosqualene. However, the results of Schemes 3 and 4 and other related studies64 are best accommodated if distorted cationic cyclopropyl gold(I) carbenes are involved as discrete intermediates. A similar type of intermediate is probably also involved in processes in which two carbon bonds are formed by electrophilic syn-addition to the alkene. An illustrative case is the intramolecular [4 + 2] cyclization of aryl alkynes with alkenes to form tricyclic derivatives (Scheme 5).36,38 This reaction of 1,6-enynes such as 13n is stereospecific and, according to DFT calculations, proceeds stepwise through intermediate 22, which evolves by a Friedel–Crafts-type reaction to form the final tricyclic derivative 21a.38 Similarly, 1-naphthyl substituted 1,6-enyne 13o gives tetracyclic derivative 21b, and a related 1,7-enyne 23 gives rise to 21c. Recently, we have obtained enantiomeric excesses up to 88% in the same [4 + 2] cycloadditions of aryl-substituted 1,6-enynes using chiral gold(I) phosphite complexes derived from 3,3′-bis(triphenylsilyl)-1,1′-bi-2-naphthol.65 Chiral biphosphine gold(I) catalysts had also been used for this type of [4 + 2] cycloadditions of aryl-substituted 1,6-enynes.66
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4. Gold(I)-Catalyzed Intermolecular Reactions of Alkynes with Alkenes

The parent intermolecular reaction between alkynes and alkenes catalyzed by gold(I) was a challenge since all the conceivable products are themselves substituted alkynes, which can compete with the initial alkyne leading to oligomerization products. In addition, electron-rich alkenes, which would be the best partners for this reaction, would coordinate preferentially with gold(I), thus reducing the concentration of the active \((\eta^2\text{-alkyne})/\text{gold(I)}\) complex. After much experimentation with different gold(I) complexes, cyclobutenes 27 were obtained as the products of this intermolecular reaction by using cationic gold(I) complex D with a very bulky phosphine (Scheme 6).

The observed regiochemistry of this \([2 + 2]\) cycloaddition is consistent with a reaction proceeding by electrophilic addition to the alkyne via \(\text{TS}_{28-29}\) to form a highly distorted cyclopropyl gold(I) carbene 29, which undergoes ring expansion through \(\text{TS}_{29-30}\) to give \((\eta^2\text{-cyclobutene})/\text{gold(I)}\) complex 30. Intermediate 29 was also trapped intramolecularly with an alkyne to form the corresponding cyclopropane.

Interestingly, the intermolecular reaction of propiolic acid with alkenes proceeds through regioisomeric cyclopropyl gold(I) carbene intermediates 35, in which gold bonds to the internal carbon of the alkyne (Scheme 8). Asymmetrically substituted alkynes, such as styrene, give lactones 33 by attack of the carboxylic acid to the most substituted carbon of the alkyne. On the other hand, alkenes with two identical, or very similar, substituents evolve by 1,3-migration to form stereospecifically 1,3-dienes 34.

It is interesting that a very similar transition state to \(\text{TS}_{34-35}\) for the formation of 1,3-dienes from propiolic acid had been also proposed in a seemingly different context. Electrophilic gold(I) catalysts promote the retro-Buchner reaction of 7-substituted 1,3,5-cycloheptatrienes,
generating substituted gold(I) carbenes and a molecule of benzene.\(^{70}\) This reaction proceeds by retrocyclopropanation of the norcaradienes, which are in tautomeric equilibrium with the cycloheptatrienes. Other related retrocyclopropanations have been observed in the presence of gold(I).\(^{71,72}\)

In the case of 7-cyclopropylcycloheptatriene \(36\), the reaction leads selectively to \(Z, Z\)-1,4-diphenyl-1,3-butadiene (\(Z, Z\)-37), whose formation can be rationalized by the evolution of cyclopropyl gold(I) carbene \(38\) through \(TS_{38-37}\) by 1,3-shift of a CHPh fragment (Scheme 9). This transition state is also very similar to that involved in the single cleavage rearrangement (\(TS_{2-12}\), Scheme 1). The ring expansion of \(38\) to form cyclobutene \(39\), which would have afforded \(E,E\)-37 by conrotatory opening, was not observed in this system.\(^{70}\)

### 5. Gold(I)-Catalyzed Cyclopropanation of Enynes

The carbenic-like character of the intermediates formed in metal-catalyzed cycloisomerizations is more clearly manifested in intra- and intermolecular cyclopropanation of alkenes.\(^{2,7,73}\) Thus, reaction of dienynes \(13p\) and \(13q\) with gold(I) leads stereoselectively to tetracyclic compounds \(40a\) and \(40b\) (Scheme 10). These cyclopropanations occur through intermediates such as \(41\) or \(42\) for intermolecular processes,\(^{74,75}\) in a concerted although highly asynchronous manner. Intramolecular cyclopropanations of 1,5-enynes proceed similarly through an \textit{endo}-carbene.\(^{53}\) However, cyclopropanation of 1,6-enynes occurs stepwise for more polarized alkenes such as styrenes, although the overall process is still stereospecific since formation of the second carbon–carbon bond occurred with a very small activation energy.\(^{75}\) Other theoretical calculations also suggest that the cyclopropanation of electron-rich alkenes by gold(I) carbenes proceeds by a stepwise mechanism.\(^{76}\)

Dienynes such as \(13r\) substituted with OR groups at the propargylic position react with gold(I) catalysts by...
intramolecular 1,5-migration of OR groups to form tricyclic compounds 43a,b, which are structurally related to the sesquiterpenes globulol and epiglobulol (Scheme 11).77 This result is consistent with a reaction occurring via intermediate 44, in which the OR group attacks the cationic center to form bridged system 45. Opening of 45 then leads to an α,β-unsaturated gold carbene/allyl-gold cation 46a, which undergoes intramolecular cyclopropanation with the alkene at the side chain to give 43a. In the presence of CD$_3$OD, intermolecular addition of this external nucleophile to 44 leads to 47, which then gives rise to 43b–d$_3$ via 46b.

Other 1,6-enynes bearing different OR groups at the propargylic position react similarly to form α,β-unsaturated gold carbenes/allyl-gold cations related to 46. Thus, enyne 13s with an allyloxy group gave stereoselectively tricyclic compound 48a by cyclization, 1,5-migration, and, finally, an intramolecular cyclopropanation (Scheme 12).79 Diene 53 was also obtained as a minor product. This reaction probably takes place by nucleophilic opening of the cyclopropane ring of intermediate 54 by the carbonyl group to form an oxonium cation 55, which gives 56 by a Prins-type intramolecular reaction closing a seven-membered ring. Intermediate 56 then gives oxatricyclic derivative 52a by metal elimination or diene 53 by a fragmentation process. The [2 + 2 + 2] cycloaddition of substrates 13w and 13x led to more functionalized tricyclic products 52b and 52c, which were transformed into the natural products (±)-orientalol F (57)80 and (−)-englerin A (58).81 Another total synthesis of 58 used a very similar gold(I) catalyzed reaction as the key step.82

6. Gold(I)-Catalyzed Cascade Reactions of Oxoynes

1,6-Enyne 13v with a carbonyl group at the alkenyl side chain reacts in the presence of gold(I) to give oxatricyclic derivative 52a by a cascade [2 + 2 + 2] alkyne/alkene/ carbonyl cycloaddition in which two C–C and one C–O bonds are formed (Scheme 13).79 Diene 53 was also obtained as a minor product. This reaction probably takes place by nucleophilic opening of the cyclopropane ring of intermediate 54 by the carbonyl group to form an oxonium cation 55, which gives 56 by a Prins-type intramolecular reaction closing a seven-membered ring. Intermediate 56 then gives oxatricyclic derivative 52a by metal elimination or diene 53 by a fragmentation process. The [2 + 2 + 2] cycloaddition of substrates 13w and 13x led to more functionalized tricyclic products 52b and 52c, which were transformed into the natural products (±)-orientalol F (57)80 and (−)-englerin A (58).81 Another total synthesis of 58 used a very similar gold(I) catalyzed reaction as the key step.82

The remarkable stereochemical control exerted by the propargylic stereocenter in the cyclizations of substrates 13w and 13x is identical to that observed in the cyclization proceeding via 1,5-OR migration through intermediate 44 (Scheme 11).77 Interestingly, attack of a carbonyl group to
the cyclopropyl gold carbene is faster than the 1,5-migration of the propargylic OR groups.

Intermolecular reactions of 1,6-enynes with carbonyl compounds in the presence of gold(I) catalysts lead to a variety of products depending on the substitution pattern of the alkene.83–85 Thus, for example, 1,6-enyne 13y reacts with 2,4,6-trimethylbenzaldehyde to give the product of formal [2 + 2 + 2] cycloaddition 59a, along with diene 60a, resulting from a metathesis-type reaction (Scheme 14).83 When the reaction was performed with 13z and 1-pyrene-carboxaldehyde, 1,3-diene 60b was obtained as the major compound. Formation of the [2 + 2 + 2] cycloaddition products of type 59 can be explained by attack of the aldehyde to cyclopropyl gold(I) intermediate 61 to give oxonium cation 62, followed by Prins cyclization to form tetrahydropyranyl cation 63 and metal elimination. Metathesis-type products 60 could be formed by a fragmentation of 63, analogous to that observed in the intramolecular gold(I)-catalyzed reaction of oxo-1,6-enynes (Scheme 13).79

Oxo-1,5-enynes such as E- and Z-64 also undergo gold(I)-catalyzed cyclization to form tricyclic derivatives 65a and 65b, respectively (Scheme 15).86 When gold(I) complexes with donating ligands are used as catalysts, the major cycloisomerization pathway proceeding through intermediates 66 and 67 is stereospecific. However, the stereoselectivity is only moderate in the case of E-64, which is consistent with the existence of two competitive pathways, supporting again the proposal for stepwise processes via discrete intermediates in gold(I) catalyzed cascade reactions.

The intermolecular gold(I)-catalyzed reaction of terminal alkynes with oxoalkenes of type 68 leads to 8-oxabicyclo-[3.2.1]oct-3-enes 69 by a similar [2 + 2 + 2] cycloaddition process through intermediates 70 in which two C–C and one C–O bonds are formed (Scheme 16).87

7. Concluding Remarks

Many reactions of 1,n-enynes and related substrates catalyzed by gold(I) bear certain resemblance with carbocationic processes promoted by Bronsted or Lewis acids. However, gold(I) catalysts orchestrate complex reactions with
exquisite regio- and stereocontrol, by stabilizing the key reactive cationic intermediates. Although in a few cases the reactions proceed through open carbocations, most transformations are stereospecific. The basic mechanistic pathways involved in the cyclosimerization of 1,7-enynes are reasonably well understood, although still the factors that control the many competitive pathways are still rather obscure, particularly in intermolecular reactions. Nevertheless, complex cascade transformations can now be designed based on relatively simple principles. This journey to gain mechanistic insight into this family of complex transformations has also led to the discovery of robust, yet highly reactive mechanistic insight into this family of complex transformations can now be designed based on relatively simple principles. This journey to gain mechanistic insight into this family of complex transformations has also led to the discovery of robust, yet highly reactive catalysts.

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BIOPGRAPHICAL INFORMATION

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FOOTNOTES

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The authors declare no competing financial interest.

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