

The Principles of Gold-Catalyzed Molecular Gymnastics

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Resum. L'or(I) dirigeix el contorsionisme molecular mitjançant reaccions intramoleculars i intermoleculars d'enins per mitjà d'intermedis ciclopropil o carbens altament distorsionats. La síntesi de productes naturals com (+)-orientalol F i (-)-englerin A mostra l'estat d'art de la catàlisi de l'or(I) per a construir complexitat molecular.

Paraules clau: or · enins · ciclitzacions · reordenaments · síntesi total · processos en tàndem

Summary. Gold(I) orchestrates molecular gymnastics by intra- and intermolecular reaction of enynes via highly distorted cyclopropyl gold carbenes as intermediates. The synthesis of natural products such as (+)-orientalol F and (-)-englerin A illustrates the state of the art of gold (I) catalysis for the buildup of molecular complexity.

Keywords: Gold · enynes · cyclizations · rearrangements · total synthesis · tandem process

Introduction

Gold is certainly a rare element, but it is more abundant than palladium, platinum, rhodium, and many other precious metals. It is one of the few chemical elements that every adult has heard about. In nature it is encountered in elemental form because its low reactivity due to its highly positive normal potential for oxidation (Fig. 1).

Gold complexes catalyzed a bewildering array of transformations, triggered by the activation of unsaturated functional groups such as alkynes, allenes, and alkenes. The relativistic effects of gold explain this unique π -acidity, which reaches a maxi-

mum in the periodic table with gold [43,100–102, 108]. In particular, gold(I) salts and complexes show extraordinary affinity for alkynes (alkynophilicity) leading to their activation in the presence of many other functional groups. In a simplified form, the attack of nucleophiles to the alkynes occurs via π -complexes **1** to give *trans*-alkenyl-gold complexes of type **2** as reactive intermediates (Fig. 2) [32,35,42,46,52,72,81,83,86,87,89,96,110,124,127].

The alkynophilicity of gold(I) has been exploited for building up molecular complexity with great efficiency [52]. In the following, we review the basic reactivity principles for gold(I)-promoted activation of alkynes in simple 1,6-enynes, which have been used as a benchmark for the developing of new transformations in this area. We also present a selection of new transformations that highlight the potential of gold-catalysis for the construction of complex molecular architectures.



Fig. 1. Gold metal and a gold(I) catalyst.

Gold Complexes

Many reactions of relatively simple substrates can be catalyzed by commercially available gold salts such as AuCl, AuCl₃, or NaAuCl₄. However, for gold-catalyzed transformations of more functionalized substrates, the most convenient catalysts are cationic complexes [Au(S)(L)]X (L = phosphine ligand, S = sol-

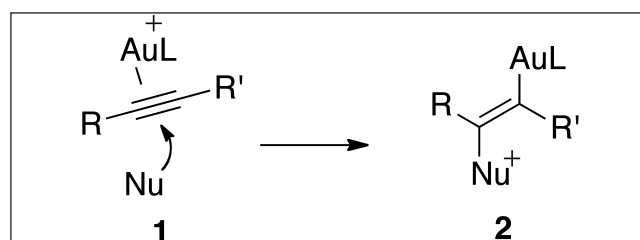


Fig. 2. Electrophilic activation of alkynes with AuL⁺.

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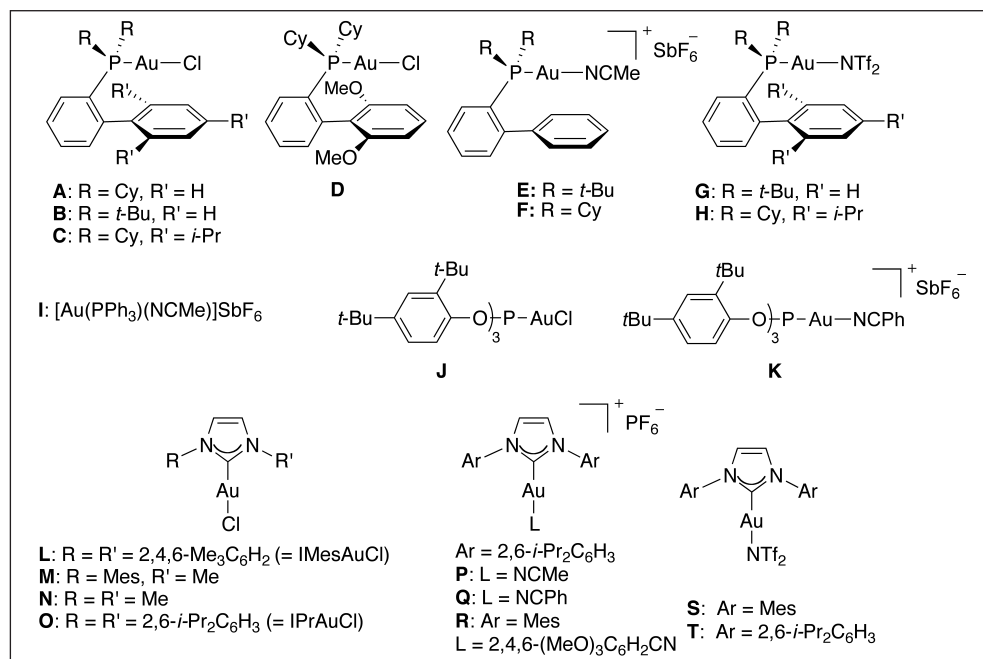


Fig. 3. Selected gold(I) catalysts.

vent molecule) that are formed in situ by chloride abstraction from [AuCl(L)] using an equivalent of a silver salt AgX with a non-coordinating anion [32,85,89]. Similarly, cationic gold(I) complexes can be generated by cleavage of the Au-alkyl bond in [AuMe(PPh₃)] with a protic acid [85,89,75,76,114]. Gold-oxo complex [(Ph₃PAu)₃O]BF₄ [80,126] has also been used as a catalyst in reactions of enynes [111]. Different types of gold(I) complexes **A-F** have been developed using bulky, biphenyl-based phosphines, which have been introduced as ligands for Pd-catalyzed reactions [4,5,55,113,122], lead to very active catalysts upon being mixed with Ag(I) salts [87] (Fig. 3). The cationic derivatives of these neutral complexes **E-F, K** and **P-R** [86,87] which are stable crystalline solids that can be handled under ordinary conditions, are more convenient since they are more reactive catalysts in a variety of transformations and silver salts can be avoided in the reaction [31,33,53,85]. The structures of **A-F**, and **J** have been confirmed by X-ray crystallography [44,97]. Related complexes **G-H** with weakly coordinated bis(trifluoromethanesulfonyl)amide NTf₂ (Tf = CF₃SO₂) have also been reported [71]. Gold(I) complexes **J** and **K** bearing tris(2,6-di-*tert*-butylphenyl)phosphite as ligand are one of the highest electrophilic cationic gold(I) catalysts [65,83]. Gold complexes with highly donating *N*-heterocyclic ligands (NHC) such as **L-O** are also good precatalysts [22,23,24,87,107]. Cationic complexes bearing NHC ligands such as **P-R**, which show moderate stability at room temperature [23], and those with NTf₂ ligand (**S-T**) have also been reported [63,104].

Cyclizations of enynes: Basic principles

Mechanistic studies on gold(I)-catalyzed cyclizations of 1,*n*-enynes (mainly 1,5-, 1,6- and 1,7-enynes) have led to the invention of new catalysts and new reactions [52]. In general, in the absence of external nucleophiles, simple 1,6-enynes **3** give dienes **4** by skeletal rearrangement (single *exo*-cleavage) or **5**

(double *exo*-cleavage) (Fig. 4) using gold(I) or other electrophilic metal catalysts [3,14,15,17,18,39–41,57,59,69,70,73,74,79,92,93,116–119].

Dienes **6** were also observed using cationic gold(I) catalysts with 1,6-enynes [12,89]. This corresponds to a third type of skeletal rearrangement (single *endo*-cleavage). Products of type **6** were later found in reactions catalyzed by InCl₃ [73], Fe(III) [86], or Ru(II) [28]. [2+2] Intramolecular cycloaddition processes leading to the formation of cyclobutenes were also observed starting from 1,6- [60], 1,7- [17,18,37,129], and 1,8-enynes [9,11]. Other type of cyclobutenes have also been obtained in the palladium- [118,119], platinum- [38], and gold-catalyzed cyclization of enynes [19,20,68,83,87].

Dienes **4** obtained by the single *exo*-cleavage rearrangement are identical to those formed by the transition metal-catalyzed metathesis of enynes [26,78]. However, it is important to note that the mechanism of the skeletal rearrangement, which is a fully intramolecular transformation, is very different from the metathesis of enynes [84,112]. For gold(I) catalysts, this rearrangement was proposed to proceed via cyclopropyl gold(I) carbenes **7** as intermediates (Fig. 5) [88]. On the other hand, the double-cleav-

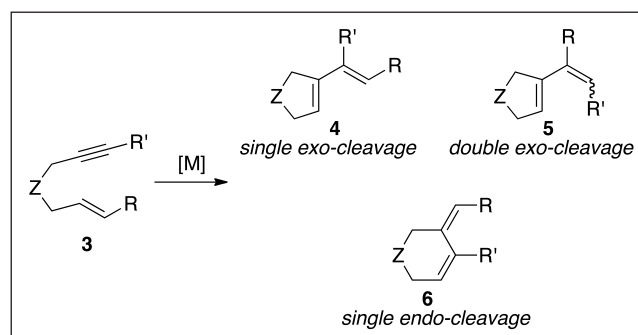


Fig. 4. Dienes obtained by metal-catalyzed skeletal rearrangement of 1,6-enynes.

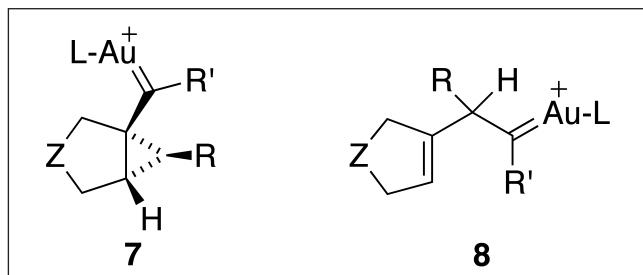


Fig. 5. Key intermediates in gold-catalyzed cyclization of 1,6-enynes.

age skeletal rearrangement usually leads to dienes **5** with predominant [1,2,52,59,119] or exclusive Z [94,95] configuration. For gold(I), products of type **5** are presumably obtained via rearranged carbene **8**, followed by 1,2-hydrogen shift and proto-demetalation. The involvement of intermediates of type **8** has been supported experimentally by their trapping with alkenes [65], in-doles, allyl silanes [1,2,115], and carbonyl compounds [105,106].

The dual character of intermediates **7** as metal carbenes and carbocationic species has been recently discussed by several groups [7,36,109]. These intermediates are often depicted for convenience as cyclopropyl gold carbenes **7**, although according to DFT calculations these species are distorted structures with a short C-C bond connecting the carbene and the cyclopropane C atoms, which correspond to intermediate structures between cyclopropyl gold carbenes and gold-stabilized homoallylic carbocations [12,29,30,112]. Intermediates of type **7** are involved in other processes such as nucleophilic additions of heteronucleophiles [6,9,12,52,62,81,89,100,101,124] inter- and intramolecular cyclopropanations [16,67,85], and intramolecular [4+2] cycloadditions of arylalkynes with alkenes [83,87], which are all stereospecific processes.

If the cyclization reactions would take place through open carbocations as reactive intermediates, rotation of the bond could occur losing the stereospecificity that is usually observed in these reactions. Indeed, in a few cases non-stereospecific transformations have been observed. Thus, whereas reaction of enyne *E*-**9a** in MeOH as solvent proceeds stereospecifically to lead the product of methoxycyclization **10** as a single *anti* isomer, according with the general behavior observed by other 1,6-enynes in similar reactions catalyzed by gold-[86,89] or platinum [69,70]. When the reaction was performed with a limited amount of MeOH, adduct **10** was obtained as an *anti/syn* mixture of stereoisomers (Fig. 6) [51]. In addition, substrates **11a-b** with strongly electron-donating substituents at the alkene react non-stereoselectively with cationic gold(I) catalysts **E** or **K** to give **12a-b** as *trans/cis* mixtures, although we have shown that the gold-catalyzed [4+2] cycloadditions of 1,6-enynes substituted at the alkyne with aryl groups occurs stereospecifically [83,87]. These results demonstrate that bond-rotation in the carbocationic intermediate is faster than intramolecular attack by methanol or cyclization with the aryl group. Loss of stereoselectivity was also observed in some ring-expansion/Prins cyclizations of 1,6-enynes bearing protected cyclopropanol groups at the alkyne [53].

We found that in contrast with the behavior of most enynes that react stereospecifically [52,72], the gold(I)-catalyzed skeletal

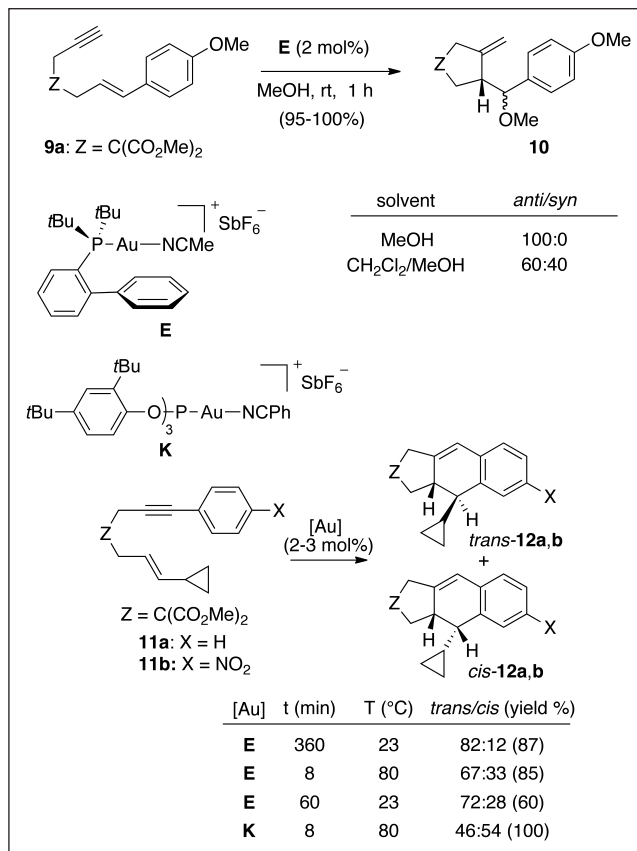


Fig. 6. Stereoselectivity in gold(I)-catalyzed reaction of 1,6-enynes with highly electron-donating groups at the alkene.

etal rearrangement of 1,6-enynes with strongly electron-donating groups at the alkene such as **9a-c**, **13** and **14** proceeds anomalously (Fig. 7) [51]. Substrates **9a-c**, **13** and **14** react with gold(I) catalyst **E** or a cationic Pt(II) complex to give **15a-d** and **16** with a Z-configuration. The Z-isomers of 1,6-enynes **9a** and **14** also give rise to Z-dienes with gold(I) catalysts.

These results suggest the involvement of open carbocations in these reactions as intermediates, which is supported by DFT

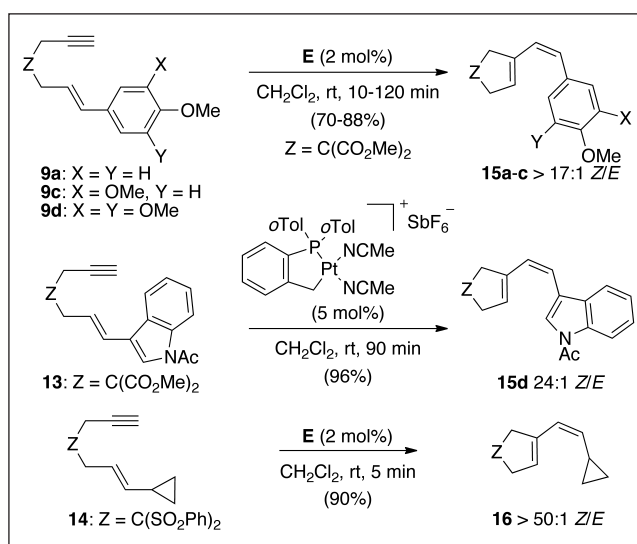
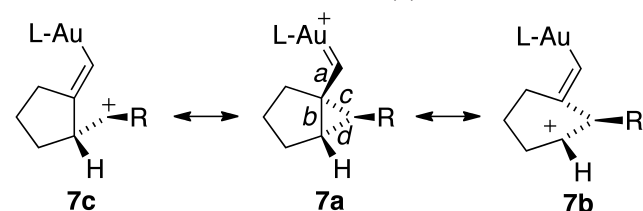


Fig. 7. *Cis*-Selective skeletal rearrangement of 1,6-enynes bearing strongly electron-donating groups at the alkene.

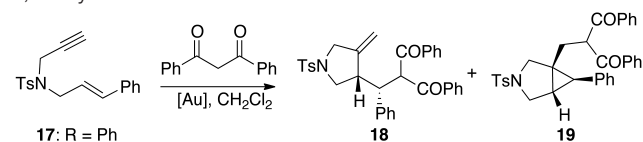
Table 1. Calculated bond distances (Å) for intermediates **7**^a

R	L	a	b	c
H	PH ₃	1.378	1.742	1.569
Me	PH ₃	1.372	1.720	1.622
<i>c</i> -C ₃ H ₅	Cl ⁻	1.401	1.621	1.606
<i>c</i> -C ₃ H ₅	PH ₃	1.356	1.586	1.987
<i>p</i> -MeOC ₆ H ₄	PH ₃	1.344	1.578	2.328

^aDFT calculations at the B3LYP/6-31G(d) (C,H,P), LANL2DZ (Au) level.

calculations (Table 1) [12,51,88]. Thus, whereas for cationic gold intermediates **7** where R = H or Me, the more relevant resonance structure is **7b** with a relatively long *b* bond, when R = *c*-C₃H₅ or *p*-MeOC₆H₄, the more relevant canonical structures correspond more closely to open carbocations **7c**, in which the long cyclopropane bond is now *c*. It is important to note that neutral intermediate **7** with the strongly electron-donating ligand L = Cl⁻ shows a more regular structure resembling **7a** with similarly elongated *b* and *c* bonds (Table 1) [51].

An experimental evidence of the strong effect of ligands on the structure of intermediates in gold-catalyzed cyclizations of 1,6-enynes was observed in the reaction of enyne **17** with dibenzoylmethane. In this reaction we obtained the expected adduct **18**, and the cyclopropyl derivative **19** (Table 2) [1]. Thus, **18** was the major product using highly electrophilic catalysts **K** or **J** / AgSbF₆ with a triarylphosphite as ligand (Table 2,

Table 2. Gold(I)-catalyzed addition of dibenzoylmethane to 1,6-enynes **17**^a

entry	[Au]	time (min)	18/19 (yield, %)
1	E	30	33:67 (85)
2	K	20	77:23 (83)
3 ^b	J / AgSbF ₆	30	95:5 (91)
4	L / AgSbF ₆	30	2:98 (99)
5	Q	20	<2:98 (87)
6	R	20	<1:99 (86)

^aReactions carried out at room temperature in CH₂Cl₂ with 5 mol% catalyst. ^bReaction carried out at -50 °C.

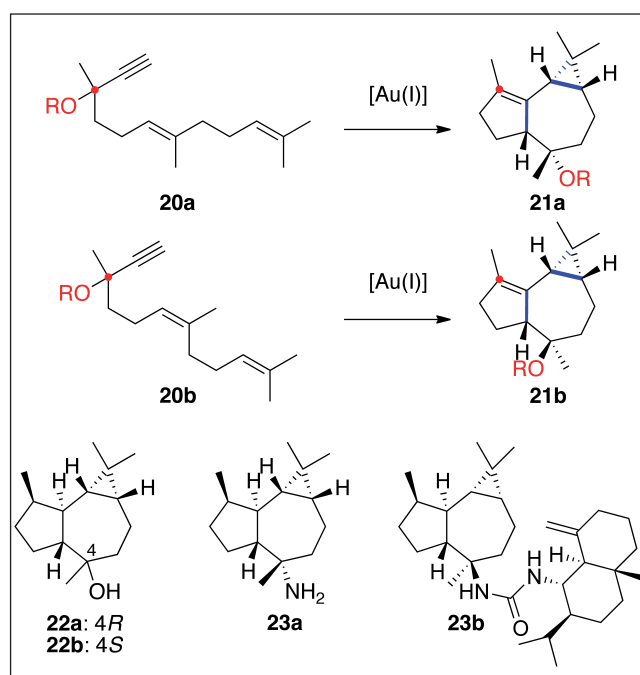
entries 2 and 3), whereas **19** was obtained almost exclusively when complexes **L, Q-R** with more donating NHC ligands were used (Table 2, entries 4–6). On the other hand, the site selectivity was lower with the gold(I)-phosphine complex **E**, which is a catalyst of intermediate electrophilicity (Table 2, entry 1).

Gold-catalyzed cascade cyclizations

When alcohols, ethers, and silyl ethers are present at the propargylic position of the 1,6-enynes a new gold(I)-catalyzed intramolecular migration of the OR groups takes place (Fig. 8) [50]. In the case of dienyne **20a-b**, this 1,5-migration leads to tricyclic compounds **21a-b** that are structurally related to the sesquiterpene globulol (**22a**), epiglobulol (**22b**) [13], and the amine halichonadin F (**23a**) [48]. Halichonadin F (**23a**) shows antimicrobial activity, whereas related natural product halichonadin E (**23b**) is cytotoxic against L1210 murine leukemia (IC₅₀, 3.0 mg/mL) and KB human epidermoid carcinoma cells (IC₅₀, 2.6 mg/mL) in vitro. Along with the *cis*-tricyclic products, compounds with a *trans*-bicyclo[5.1.0]octane skeleton were also obtained in these reactions as minor product [10,21,125].

Reaction of dienyne **20b** (Z configuration) in a 30:1 mixture of CH₂Cl₂/MeOH gave ether **21a** in addition to the expected **21b**. When this reaction was performed with CD₃OD, **21b** showed no deuterium incorporation, which confirms that the 1,5-migration is an intramolecular process (Fig. 9), whereas the methoxy group of **21a** was deuterated.

Formation of **21b** is consistent with the involvement of intermediate **24**, in which the OR group attacks the cationic center to form **27**. Opening of **27** then gives a *a,b*-unsaturated gold carbene/allyl gold carbocation **25a**, which undergoes an intramolecular cyclopropanation with the alkene at the side chain to give tricyclic compound **21b**. Formation of product **21a-d**₃

**Fig. 8.** Gold(I)-catalyzed 1,5-migration of OR groups in dienyne **20a-b**.

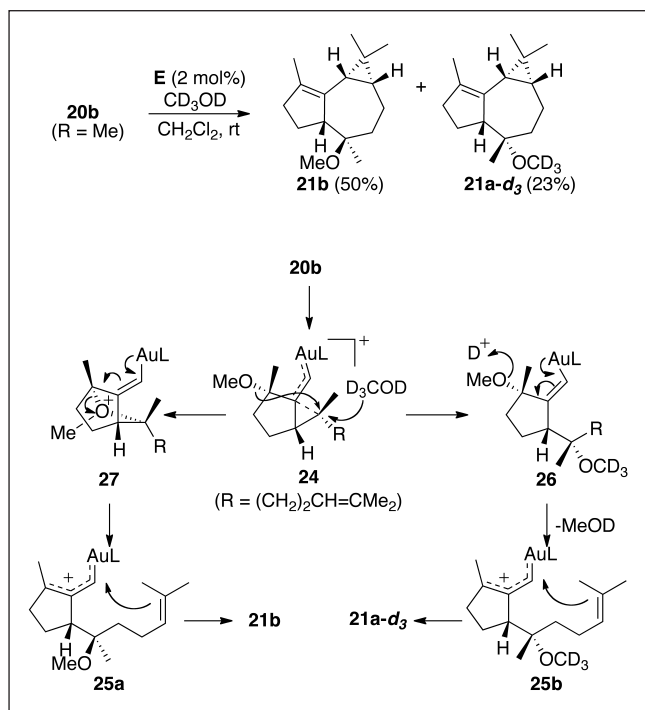


Fig. 9. 1,5-Migration of OR groups via allyl gold cations **24**.

can be explained by intermolecular nucleophilic addition of CD_3OD to **24** that gives **26**, which extrudes MeOD to form **25b** that finally form **21a-d₃** by intramolecular cyclopropanation.

The stereochemistry observed in the formation of **21a-d₃** from **20b** shows that, contrary to that suggested for related substrates [81,86], the cyclization is not concerted and proceeds through discrete intermediates such as **24**. The configuration shown in **21b** gives information about the nature of the intermediates: **24** cannot be an open carbocation since the original configuration at the alkene is preserved in these transformations that are stereospecific. Additionally, it is interesting that migration of the OR group is faster than the intramolecular trapping of the first intermediate **24** by the pendant alkene,

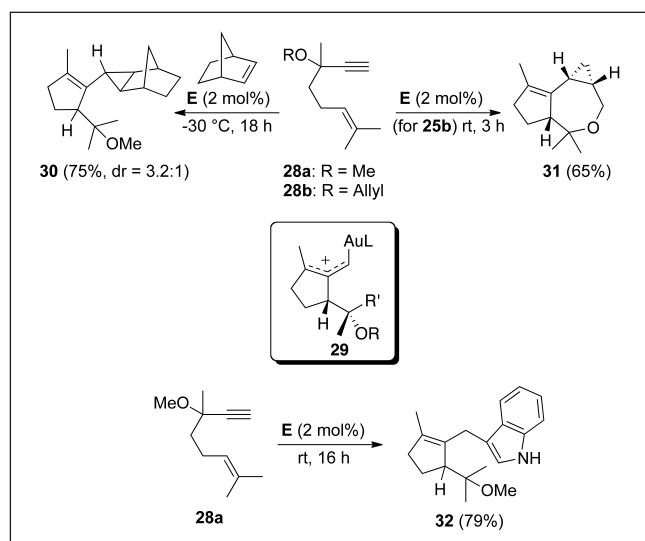


Fig. 10. Reactions of 1,6-enynes **28a-b** via 1,5-migration of OR groups.

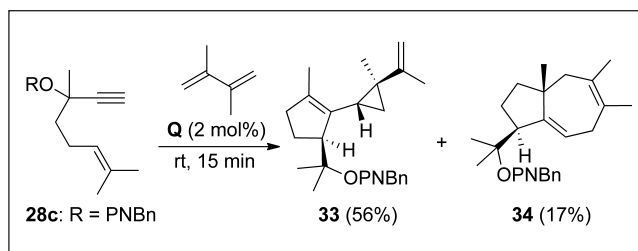


Fig. 11. Reaction of 1,6-enyne **28c** with 2,3-dimethylbutadiene via 1,5-migration of OR.

which have been previously shown to be a fast process in di-enynes leading to bicyclopropanation [72,85].

Gold(I)-catalyzed reactions of more simple enynes **28a-b** bearing different OR groups at the propargyl position also proceed via *a,b*-unsaturated gold carbenes/allyl-gold cations **29** which has been shown by different inter- and intramolecular cyclopropanation (Fig. 10). Thus, reaction of **28a** in the presence of norbornene gave cyclopropane **30**, whereas enyne **28b** with an allyloxy group gave stereoselectively **31** as a result of a 1,5-migration followed by an intramolecular trapping of the carbene intermediate. The 1,5-migration intermediate **29** formed in the cyclization of enyne **28a** also reacted with indole to give adduct **32**.

The intermolecular cyclopropanation also occurred with 1,3-dienes. Thus, reaction between **28c** and 2,3-dimethyl-1,3-butadiene with cationic catalyst **Q** with a bulky NHC ligand (Fig. 11) gave a 3.3:1 mixture of **33** and hexahydroazulene **34**, which is formed by a Cope rearrangement [54,56] of the *cis*-divinylcyclopropane diastereoisomer of product **33**. Interestingly, hexahydroazulene **34** has the same relative configuration and a similar carbon skeleton to that of several naturally-occurring sesquiterpenes and diterpenes [66,121].

Enynes **28c-e** react with catalyst **E** to give **35a-c** and **36a-c** by 1,5-migration followed by a formal C-H insertion (Fig. 12). Related formal C-H insertions have been observed in other reaction proceeding through Au or Pt carbenes [8,27,34,45,58, 61,90,91]. These results are consistent with a mechanism in which the intermediate *a,b*-unsaturated gold carbene/allyl-gold cation **37** abstracts a hydride from the ArCH_2O group to form a

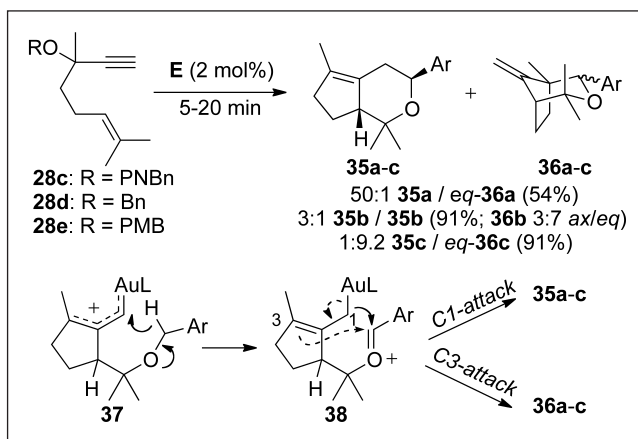


Fig. 12. 1,5-Migration of 3-benzyloxy-1,6-enynes **28c-e** followed by formal C-H insertion.

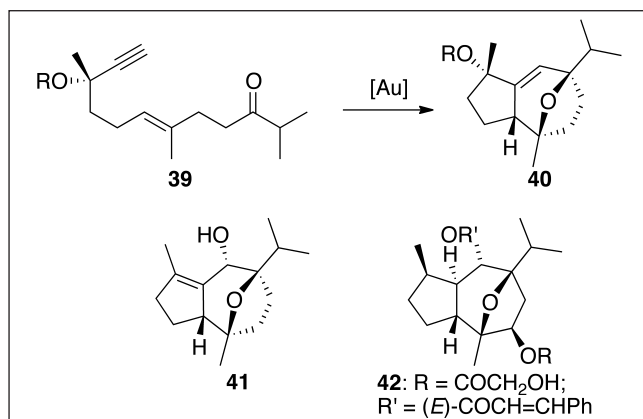


Fig. 13. Intramolecular [2+2+2] alkyne/alkene/carbonyl cycloaddition of ketoenynes.

n^1 -allyl-gold(I) **38** [99], which reacts at C-1 or C-3 with the oxonium cation to give products **35a-c** or **36a-c**, respectively.

The reactivity of oxonium cation with gold(I) intermediates has been studied in the inter-[27] and intramolecular [53] reaction of 1,6-enynes with aldehydes and ketones. 1,6-Enynes with propargyl alcohols, ethers, or silyl ethers and a carbonyl group at the alkenyl side chain do not react through 1,5-migration in the presence of gold(I) catalysts. Thus, oxatricyclic skeletons **40** were obtained by a domino process in which two C-C and one C-O bonds are assembled by a formal [2+2+2] alkyne/alkene/carbonyl cycloaddition (Fig. 13) [27]. We have recently applied this cyclization for the synthesis of orientalol F (**41**) [49], a sesquiterpene isolated from the rhizomes of the Chinese plant *Alisma orientalis* [98]. This natural product is structurally related to cytotoxic englerin A (**42**) [103,123].

The synthesis of (+)-orientalol F (**41**) was carried out starting with enyne **39**, readily available from farnesol in seven steps (Fig. 14). Gold catalyzed cyclization of enantiomerically enriched (*S*)-**39** (95:5 *er*) using catalyst **R** gave tricyclic derivative **40** in 65% yield. After desilylation, the allylic alcohol was treated with Collins reagent to give *syn*-epoxy alcohol **43**, which was deoxygenated

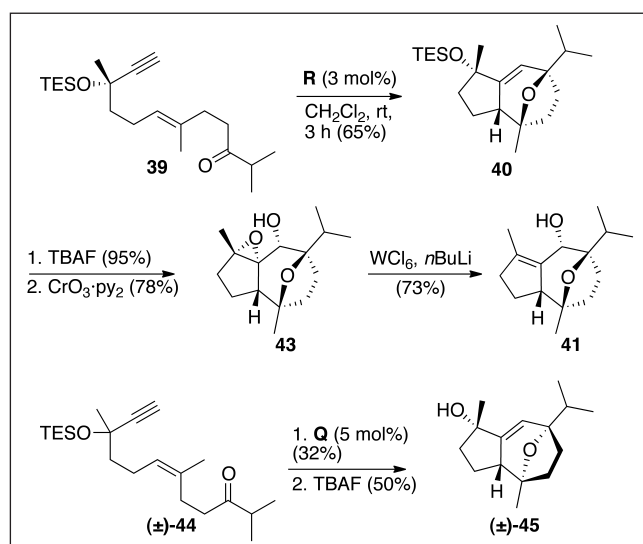


Fig. 14. Synthesis of orientalol F (**41**) and pubinernoid B (**45**) by gold-catalyzed [2+2+2] alkyne/alkene/carbonyl cycloaddition.

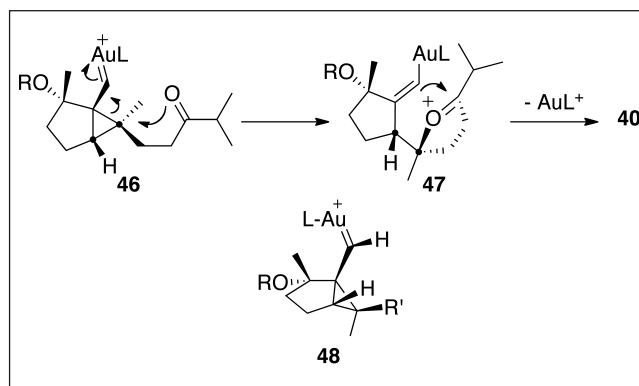


Fig. 15. Model for stereocontrol in the cyclization of enynes with propargyl OR substituents.

with WCl_6 and *n*-BuLi [120] to give (+)-orientalol F (**41**). The synthesis of pubinernoid B (**45**) [47] was similarly carried out from substrate **44** with the *Z*-configuration at the double bond.

The stereoselectivity observed in the cyclizations of substrates **39** and **44** can be explained by the control by the propargyl stereocenter in the formation of the three new stereocenters during the gold(I)-catalyzed cyclization. The reaction presumably proceeds via intermediates **46** and **47**, followed by an intramolecular Prins reaction and metal loss to form **40** (Fig. 15). All these results suggest that these reactions proceed through intermediate **48** in which the OR group and the gold carbene are *anti* oriented. Interestingly, attack of carbonyl groups to the cyclopropyl gold carbene via **46** is faster than the 1,5-migration of the OR groups.

Recently, our group completed the enantioselective total synthesis of (–)-englerin A (**51**) [77], a sesquiterpene that has been shown to selectively inhibit the growth of renal cancer cell lines at nanomolar level [82,103,128], using the cascade gold(I)-catalyzed reaction as the key step (Fig. 16).

Summary and outlook

Reactions of enynes catalyzed by highly electrophilic gold(I) complexes proceed through highly distorted cyclopropyl gold carbenes of type **7**. Although in a few cases the reactions proceed through open carbocations as intermediates, most transformations of substituted 1,6-enynes are stereospecific.

The synthesis of (+)-orientalol F (**41**) and (–)-englerin A (**51**) illustrates the potential of gold(I) catalysis for the stereoselective synthesis of complex natural products in a highly concise manner. Most of the reported synthetic applications are based on skeletal rearrangements, cycloadditions, and nucleophilic addition processes in which gold(I) orchestrates complex molecular gymnastics. C-H insertions, such as those shown in Fig. 12, could also be used for the additional build up of molecular complexity.

Much has been advanced in the understanding of the reactivity of alkynes with gold(I) catalysts in intermolecular processes in the last few years. However, the intermolecular reaction of alkynes with alkenes using gold(I) catalysts was an unknown process until the very recent discovery that, by using gold(I) catalysts with very bulky ligands, cyclobutenes are formed by

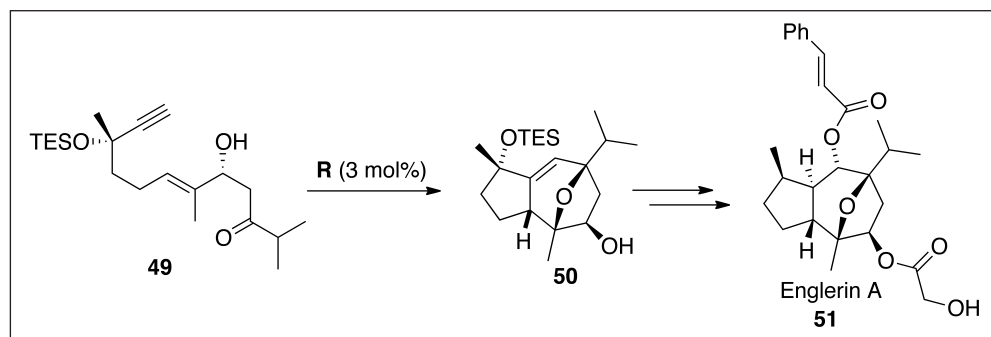


Fig. 16. Enantioselective total synthesis of (-)-englerin A (51).

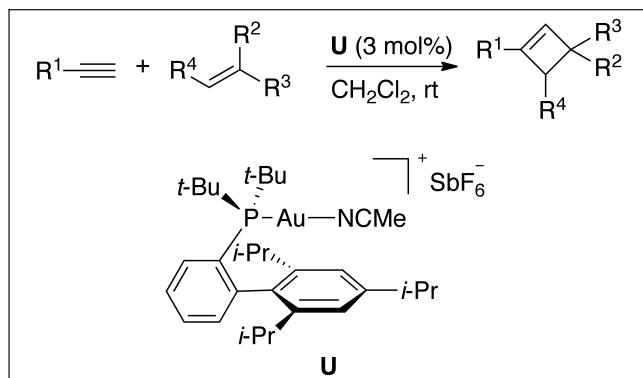


Fig. 17. [2+2]-Cycloaddition of alkynes with alkenes catalyzed by gold(I).

[2+2]-cycloaddition (Fig. 17) [64]. This new transformation opens new opportunities for the invention of related intermolecular gold(I)-catalyzed reactions.

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Antonio M. Echavarren studied in Barcelona and Madrid, and obtained in 1982 his Ph.D. at the Autonomous University of Madrid (UAM) with Prof. Francisco Fariña. After a postdoctoral stay in Boston College with Prof. T. Ross Kelly, he joined in UAM as an Assistant Professor (1984–86). Following a two years period as a NATO-fellow in the group of Prof. John K. Stille in Fort Collins (Colorado State University), he joined in the Institute of Organic Chemistry of the Spanish National Research Council (CSIC) in Madrid where he stayed until 1992. That year he returned to the UAM as a Professor of Organic Chemistry. He was

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