Gold Catalysis

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Gold α-Oxo Carbenoids in Catalysis: Catalytic Oxygen-Atom Transfer to Alkynes

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alkynes · carbenoids · cycloaddition · gold · oxygen transfer

An overview of reactive gold α-oxo carbenoid intermediates in the gold-catalyzed functionalization of alkynes is presented. Such intermediates can be generated from inter- and intramolecular oxidation of alkynes by nucleophilic oxygen-atom donor groups, such as amine N-oxides, pyridine N-oxides, nitrones, nitro compounds, sulfoxides, and epoxides. These O-atom transfer processes occur by gold-mediated addition–elimination reactions. In catalytic systems, α-oxo carbenoids can undergo nucleophilic attack by imine, arene, and migrating hydride as well as alkyl groups, leading to cascade reactions and the construction of new skeletons. The facile construction of C–E (E = C, N, S, or O) bonds makes it an attractive step-economic approach to value-added molecules from readily available starting materials. The scope, mechanisms, and reactivity of such α-oxo carbenoid species are discussed. The remarkable diversity of structures accessible is demonstrated with various recent examples.

1. Introduction

Heterocycles are common core structures of various natural products and synthetic pharmaceuticals. Efficient, atom-economic, and selective constructions of novel heterocyles from readily available starting materials under mild conditions remain an important task in synthetic chemistry.[1] Catalytic cyclization of heteroatom-functionalized alkynes and alkenes is an important method in this context. Significantly, gold-mediated homogeneous catalysis is rapidly growing in popularity owing to its broad applications in the functionalization of alkynes and allenes, particularly in intramolecular fashion. Gold compounds are powerful soft Lewis acids that can activate alkynes toward N, O, and C nucleophiles, leading to cyclization, and recently this type of chemistry has been extensively reviewed.[2] The success of gold catalysis in catalyzing distinct and unusual organic transformations might result from the unique properties of Au^{I} and Au^{III} species that can promote two or more mechanistically distinct reactions in a tandem process. These cascade reactions circumvent the otherwise time-consuming, waste- and cost-intensive, and yield-reducing processes that require the isolation and purification of intermediates. Thus the unique ability of gold salts as soft, carbophilic Lewis acids enables activation of C–C multiple bonds towards nucleophilic attack, allowing for the formation of new C–C, C–O, C–N, and C–S bonds.

Although previous Reviews are comprehensive, most of them focused on the diversity of gold catalysts in mediating various coupling, particularly cycloisomerization reactions.[2] No Review covered these reactions from a perspective that focuses on a single, well-postulated key intermediate. In addition, most reports on gold catalysis after 2009 fall outside previous Reviews.[2] This Review focuses on the key role of important α-oxo carbenoid intermediates in recently developed oxygen-atom transfer reactions. We herein describe gold-catalyzed oxygen-atom transfer reactions between alkynes and N-oxides, sulfoxides, epoxides, and esters in both intramolecular and intermolecular reactions; reactions that enable the synthesis of useful complex structures.

2. Gold Carbenoids and Their Reactivity

Fully characterized gold complexes of Fischer-type carbenes, particularly N-heterocyclic carbenes (NHCs), are well established.[3] However, to our knowledge, the isolation of a well-characterized Schrock-type carbene complex has not

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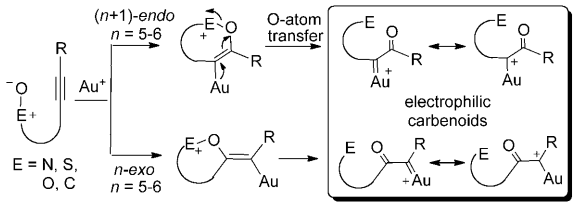
been reported. Even theoretical studies on the structure and reactivity of such carbene complexes are rather limited.[4] Toste and co-workers have recently examined the structures of a range of cationic carbene complexes of gold(I) using density functional theory (DFT) methods.[4e] Their DFT studies indicate that the gold–carbon bond in these species comprises varying degrees of both σ- and π-bonding character, depending on the *trans* ancillary ligand. However, the Au–C bond order is generally equal to or less than one. Thus, the character of these gold(I) carbene species ranges from gold-stabilized singlet carbenes to gold-stabilized carbocations. Structure–reactivity correlations of these gold carbene species were supported by gold-catalyzed cyclopropanation reactions, in which catalysts with ancillary ligands that favor carbene-like species provide higher catalytic reactivity.

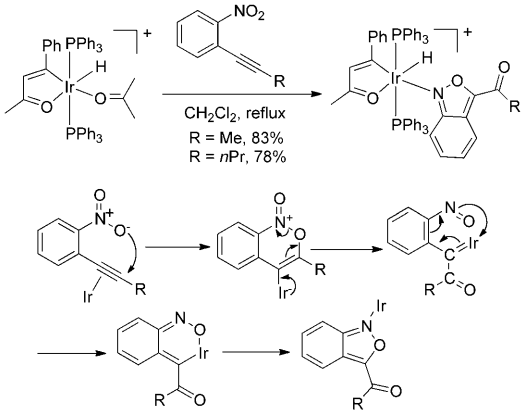
The carbene group in gold α-oxo carbene complexes (Scheme 1) should be even more electrophilic after the



Scheme 1. Generation of an α-oxo gold carbenoid by the intramolecular reaction of a gold alkyne complex with an oxygen-delivering oxidant.

introduction of a carbonyl group. Although no such complexes have been isolated or characterized, these species are widely proposed in the gold-catalyzed oxygen transfer of a nucleophilic oxygen atom to an alkyne group. Of the various nucleophiles that attack alkynes in reactions mediated by Au^{I} and Au^{III} species, the oxygen atoms in polar E–O bonds (E = N, S, and C) are special nucleophiles in that their attack at the alkyne is either *endo* or *exo* selective and gives gold vinyl[5] intermediates bearing positively charged electrophilic centers. A remarkable feature of this system is that this gold vinyl intermediate[6] can undergo ring opening and E–O bond cleavage to give a gold α-oxo carbenoid intermediate (Scheme 1). It should be noted that this α-oxo carbenoid intermediate could also be generated from denitrogenative reactions between α-diazoketones and Au^{I} species.[7] However, this alternative access requires explosive and hazardous diazoketones that are highly functionalized, and their synthesis is not trivial.

Interestingly, formation of this type of α-oxo carbenoid intermediate by addition–elimination process is not limited to gold-mediated reactions. Crabtree and co-workers observed iridium(III) hydride mediated intramolecular oxygen-atom transfer from a nitro group to the C≡C bond of *o*-RC≡C(C_6H_4)NO_2 (Scheme 2).[8] This reaction is proposed to



Scheme 2. Intramolecular oxygen-atom transfer from the nitro group to a C≡C bond, mediated by an iridium(III) complex.

involve an analogous addition–elimination process to give an oxo carbenoid, followed by 6e⁻ electrocyclization to afford an N-bound anthranil complex.[8] In this case the role of the iridium(III) center can be regarded as that of a Lewis acid.

In catalytic processes, these electrophilic carbenoids are known to participate in at least three types of elementary reactions (Scheme 3): a) attack by nucleophiles, such as N, O, arene, migrating hydride and alkyl groups, b) oxidation by sulfoxides,[9] and c) metalla Diels–Alder reactions with alkynes.[10] These reactivities enable extensive functionalization of alkynes.

The electrophilicity of such carbenoids is well established and they can participate in reactions that are typical for carbocations in classical organic chemistry. In these cases the introduction of an α-carbonyl group should further increase the electrophilicity of the carbenoid carbon. Thus, following the generation of the gold α-carbenoid intermediates, intra-

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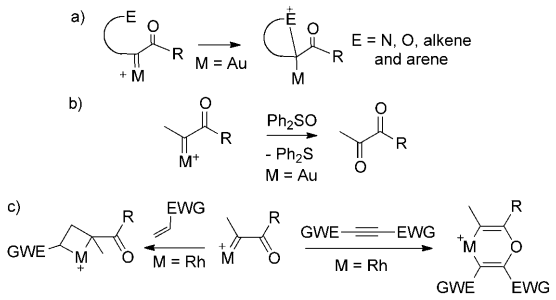


Scheme 3. The different reactions of α-oxo carbenoids, see text for details. EWG = electron withdrawing group.

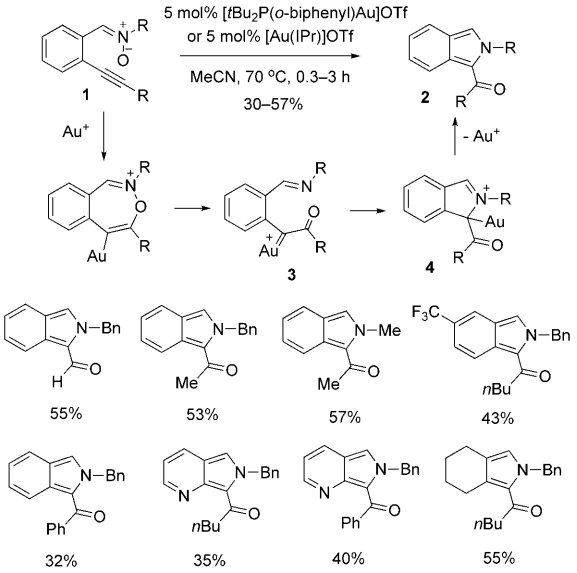
molecular nucleophiles, such as arene, imine groups, migrating hydride, and migrating alkyl groups can attack the carbenoid carbon to give a cyclic gold enolate, which allows for further manipulations of the skeleton.

2.1. N–O Groups as Oxidants

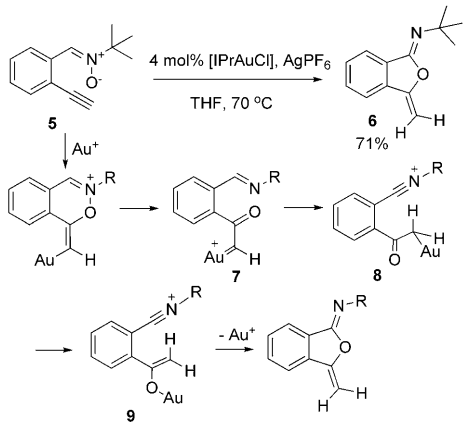
A particularly interesting class of substrate is an alkyne bearing a $R_3N^+–O^-$ group as in nitrone, nitro, and amine N-oxide compounds that are oxygen-atom donors. These polar N–O species, such as nitrones, have been shown to be interesting oxygen-bound ligands that can stabilize transition-metal centers.[11] They have also been used as oxidants in metal-mediated or metal-free reactions.[12] The combination of these two functions in concurrent tandem catalysis has been made possible by gold catalysts. Thus, the interactions between Au^I or Au^{III} catalysts and alkyne substrates bearing $R_3N–O$ groups lead to a reactive gold vinyl species as a result of the activation of the alkyne towards O attack. Subsequent N–O bond cleavage leads to α-oxo carbenoid species bearing a pendent R_3N group.

2.1.1. Oxygen-Atom Transfer from Nitrones

Nitrones are readily available starting materials, and the unique advantage of using nitrones as oxygen-atom donors is their facile synthesis from aldehydes and hydroxyamines. Nitrones are also undergo 1,3-dipolar addition reactions with alkenes.[13] Shin and co-workers developed a redox cyclization of nitrone-tethered simple alkynes **1** to give isoindoles **2** (Scheme 4).[14a] This selectivity suggests that 7-*endo* cyclization and subsequent internal oxygen transfer are involved. Attack of the imine nitrogen atom of **3** at the carbenoid carbon gives an azomethine intermediate **4** (Scheme 4), which in turn gives the isoindole product **2** upon deauration (R = Bn or Me, 30–57%). This method works well for both internal and terminal alkynes. On the other hand, the formation of this isoindole seems to be limited to nitrones bearing N–Bn and N–Me groups. Indeed, when the terminal-alkyne nitrone **5** bearing an N–*t*Bu group was treated with a commonly used [(IPr)AuCl]/$AgPF_6$ system, an imioester **6** with an *exo*-cyclic double bond was isolated as the sole isomer of the product (Scheme 5).[14b] In this case the selectivity of cyclization is switched to 6-*exo* as a result of steric and electronic effects of



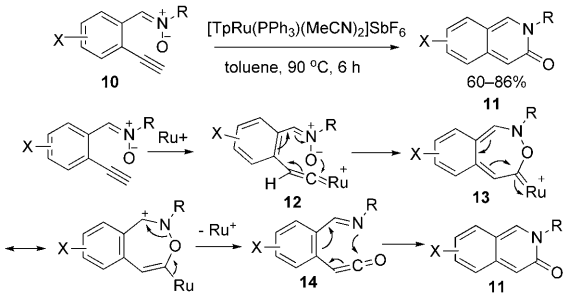
Scheme 4. Redox cyclization of nitrone-tethered simple alkynes.



Scheme 5. Formation of an iminoester from a nitrone-tethered alkyne. IPr = 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

the N-substituent. The resulting carbenoid **7** (Scheme 5) is preferentially attacked by a migrating hydride that originates from the imine unit in **8** to afford a gold enolate species **9** bearing an electrophilic nitrilium. Subsequent oxygen attack of the enolate at the nitrilium and demetalation affords the iminoester **6**. No analogous imine nitrogen attack was involved for steric reasons. Furthermore, electronically the competitive hydride migration is made more favorable by the donating nature of the *t*Bu group.

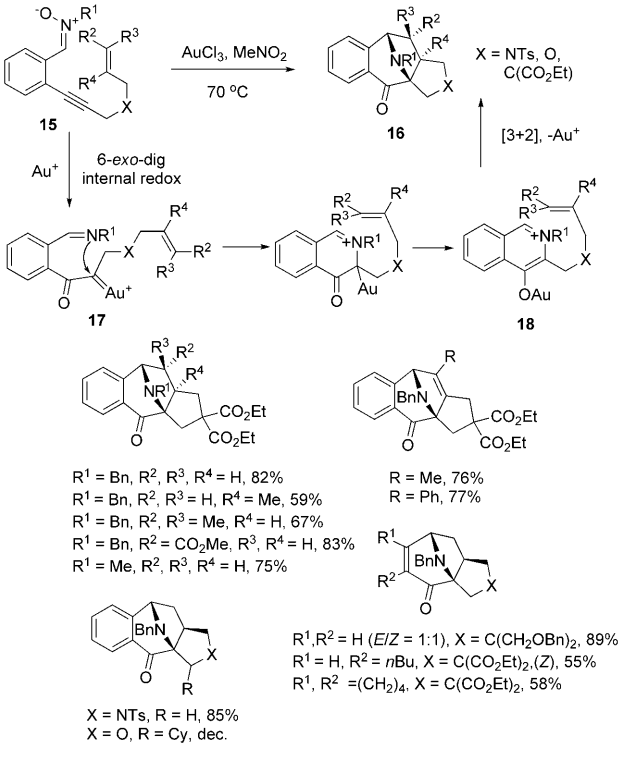
In sharp contrast to the results obtained with gold catalysts, products different from **2** and **6** were formed from essentially the same nitrone–alkyne substrates when [TpRu(PPh$_3$)(MeCN)$_2$]SbF_6 was used as a catalyst (Scheme 6).[15] The 3-isoquinolone products **11** were obtained in good yields, and this reaction also involved internal redox of the nitrone and alkyne groups. This reaction is proposed to involve the ruthenium(II)-mediated rearrangement of alkyne **10** to vinylidene **12**,[16] followed by the oxygen-atom attack at the α-carbon of **12** to give a ruthenium Fischer carbene inter-



Scheme 6. Ruthenium-catalyzed cycloisomerization of *o*-alkynylphenyl nitrones. Tp = tris(1-pyrazolyl)borate.

mediate **13**. Deruthenation affords ketene **14** bearing a nucleophilic imine group, which undergoes (uncatalyzed) 6π-electrocyclization to give the final product.

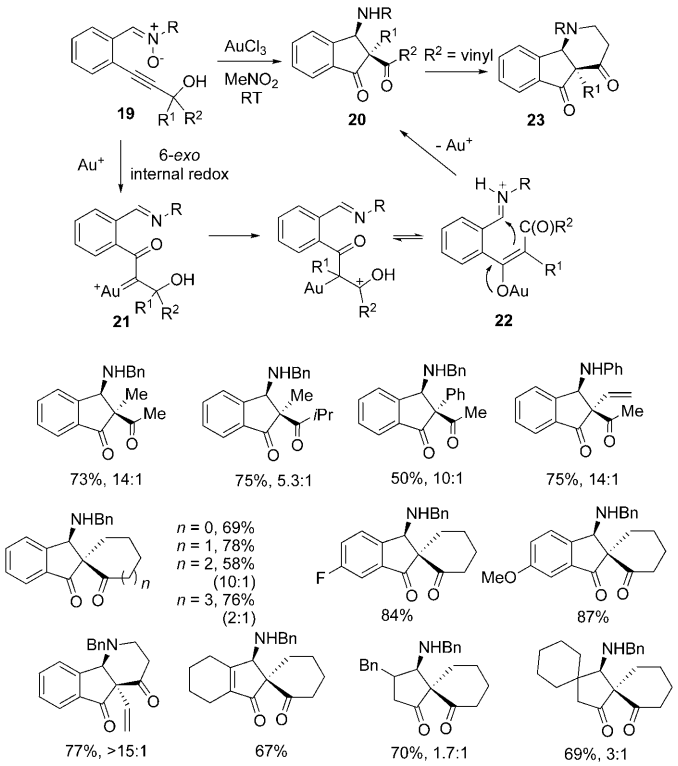
The catalytic cyclization of nitrone-functionalized enynes giving complimentary 6-*exo* selectivity did not occur in the cyclization of nitrone-tethered 1,6-enynes.[17] By attaching an alkene to the alkyne, versatile reactivity is achieved, leading to the construction of new skeletons. Thus cyclization of **15** gives tricyclic heterocycles **16** in good to high yields and high diasteroselectivity (Scheme 7). In contrast to the observed exclusive 7-*endo* cyclization for nitrone-tethered simple alkynes (Scheme 4), cyclization in this case gives 6-*exo* selectivity and the resulting α-oxo carbenoid species **17** is subject to intramolecular attack by the imine nitrogen atom to generate a gold enolate iminium intermediate **18**. This azomethine ylide and the alkene unit are proposed to undergo an intramolecular [3+2] dipolar cycloaddition cascade. It



Scheme 7. Internal redox/dipolar cycloaddition cascade reactions.

should be noted that in this system the 6-*exo* (leading to tricyclic products) and the 7-*endo* (leading to isoindoles) cyclization reactions are in competition when gold(I) catalysts are used. However, the 6-*exo* selectivity can be maximized when $AuCl_3$ is used. Competitive *endo* and *exo* cyclization has also been reported in the cyclization of nitro-functionalized alkynes.[18] General reactivity of metal Zwitterion complexes towards dipolar addition with alkenes have been reported for other electrophilic metals, such as Pt^{II}.[19]

Shin and co-workers further designed substrates of nitrone-tethered tertiary propargyl alcohols. The introduction of the tertiary alcohol moiety enables the construction of new skeletons with quaternary centers by a series of cascade reactions.[20] $AuCl_3$ was used to successfully catalyze the one-pot cyclization of **19** to β-aminodiketones **20** in high yield and moderate to high diastereoselectivity (Scheme 8). Analogous



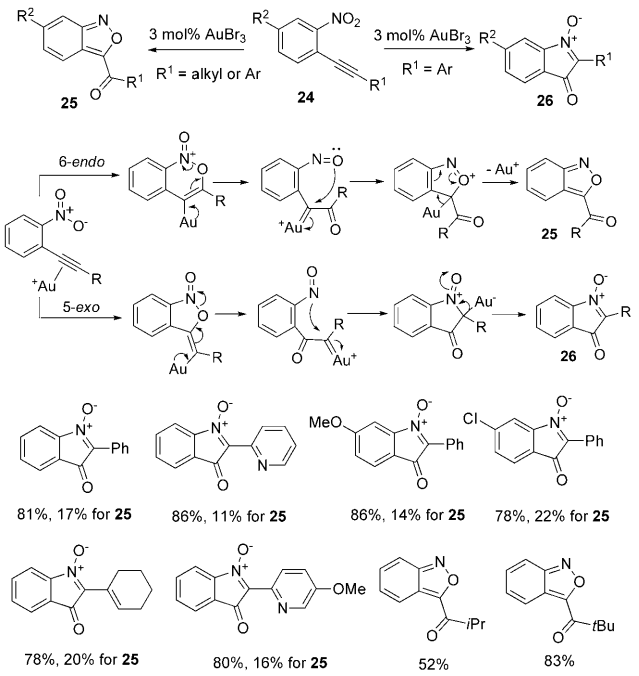
Scheme 8. Redox cyclization with pinacol rearrangement.

to the 6-*exo* cyclization of substrates **15** (scheme 7), a gold α-oxo carbenoid **21** is generated. However, the fate of the carbenoid is different. Instead of being attacked by the imine nitrogen atom, the α-R^1 group migrates to the carbenoid as in a classical pinacol rearrangement, leading to β-diketonate intermediate **22**. A subsequent cascade of Mannich additions gives the β-aminodiketone product **20**. Analysis of the product distributions obtained from the cyclization of non-symmetrically substituted alcohols indicates that the relative ease of migration for the alkyl groups depends on its steric bulk, in the order of Me > Et > *i*Pr. Furthermore, alkynyl, aryl, and vinyl groups preferably migrate over methyl group in acyclic alcohol substrates. Interestingly, when the spectator

group is a vinyl group, the initially obtained β-aminodiketones **20** can further undergo one-pot Michael addition between the N–H bond and the proximal enone to afford **23**, this addition is facilitated by treatment with silica gel. This novel pinacol–Mannich–Michael cascade utilizes reactive gold carbenoid imine intermediates to generate synthetically useful 5,6-fused azacycles starting from readily available nitrone compounds, which represents an atom-economic and step-economic approach.

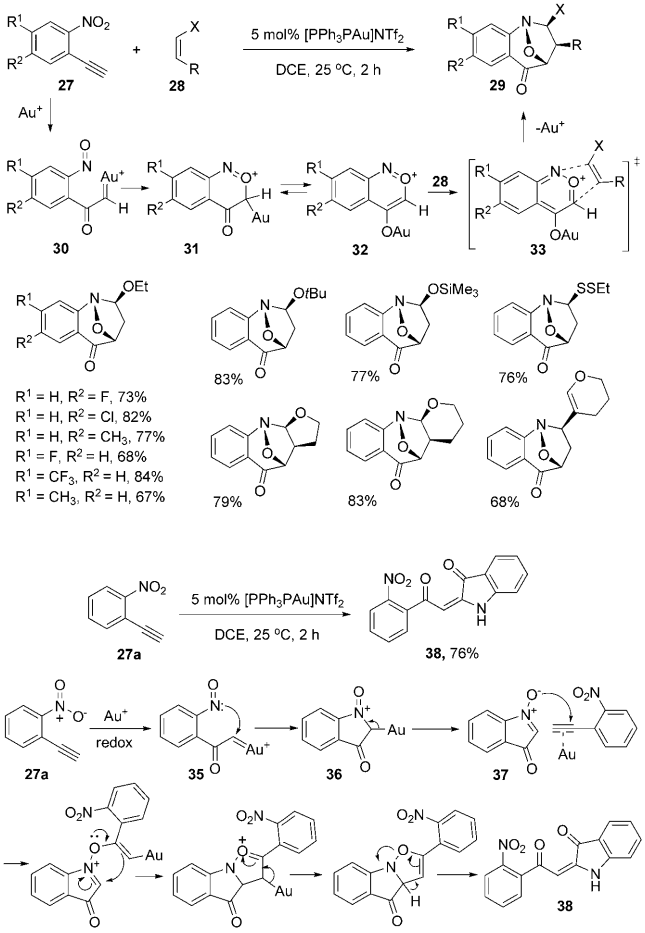
2.1.2. Oxygen-Atom Transfer from Nitro Compounds

Despite the fact that nitro groups are relatively less oxidizing and are also less weakly ligated to transition metals, Yamamoto and co-workers achieved the redox cyclization of *o*-alkynylnitrobenzenes catalyzed by $AuBr_3$ or $AuCl_3$.[18] In the case of *o*-(arylalkynyl)nitrobenzenes **24**, both anthranils **25** (minor) and isatogens **26** (major) were isolated (Scheme 9). These two types of products are proposed to originate from two competitive cyclization pathways with different regioselectivities, a scenario observed in the aforementioned cyclization of enynes (see Scheme 7). The similarity between the anthranil products **25** and the iridium anthranil complexes in Scheme 2 starting from the same nitro alkyne compounds suggests that they may follow the same type of mechanism.[21] Two key oxo carbenenoid intermediates are proposed and they undergo either N or O attack to give the corresponding five-membered-ring intermediates, and the final products were generated by deauration. Interestingly, only the anthranil products **25** (from 6-*endo* attack) were observed for the reaction of *o*-(alkylalkynyl)nitrobenzenes. These results highlight the rather large differences between alkyl and aryl substituents on the alkyne unit in terms of electronic and steric effects, and alkyl substituents on the C≡C bond favor the 6-*endo* cyclization selectivity.



Scheme 9. Redox cyclization of *o*-alkynylnitrobenzenes.

Recently, Liu and co-workers reported the gold-catalyzed stereoselective formation of azacyclic compounds **29** by a redox/[3+2] cycloaddition cascade starting from 1-ethynyl-2-nitrobenzenes **27** and alkenes **28** (Scheme 10).[22] The core structures of **29** are constructed through a formal [2+2+1] cycloaddition between α-carbonyl carbenoids, nitroso species, and external alkenes. A gold α-oxo carbenoid **30** was proposed to be generated from an internal redox process. Intramolecular oxygen attack on this gold carbenoid gave ketonyl oxonium **31**, which is proposed to tautomerize to the enol form **32** that undergoes a subsequent intermolecular [3+2] cycloaddition reaction with alkene in a concerted *exo* way via transition state **33** to give the observed products **29**. The scope of substrate covers diverse electron-rich alkenes (such as vinyl ethers, vinyl thioethers, and vinyl silyl ethers) and nitro alkyne substrates **27** bearing various substituents on the aryl ring. There seems to be some correlation between the reactivity and the electronic effects of the substituents *para* to the alkynyl or the nitro group in **27**, and electron-donating



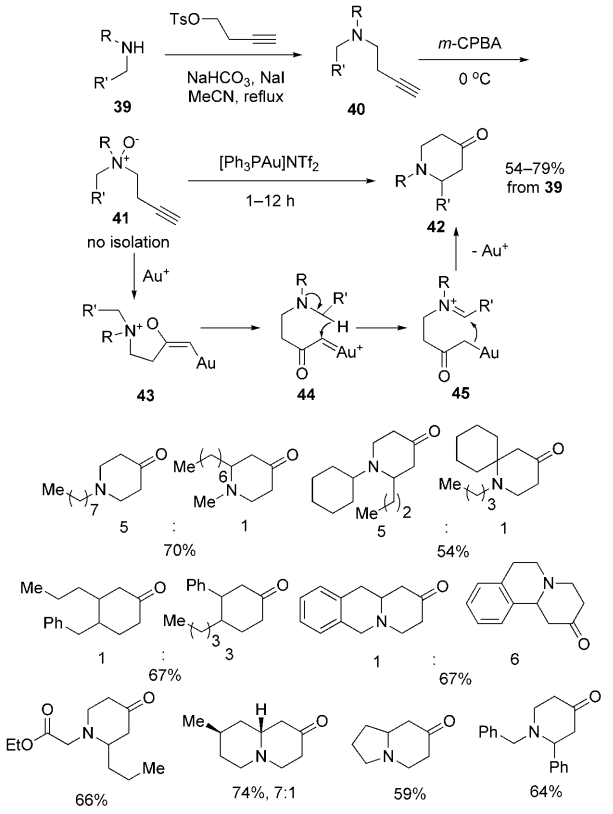
Scheme 10. Gold-catalyzed stereoselective synthesis of azacyclic compounds from 1-alkynyl-2-nitrobenzenes and alkenes. DCE = dichloroethane, NTf = trifluoromethylsulfonylamide.

groups (Me) tend to lower the reactivity. In fact, the introduction of methoxy groups at these two positions essentially suppressed this reaction because they tend to stabilize the nitro group and/or to reduce the electrophilicity of the alkyne. To fully understand the mechanism, control experiments and theoretical studies have been carried out. DFT studies indentified α-carbonyl carbenoid **30** as a key intermediate. It should be noted that alternative nitrogen attack on the carbenoid in intermediate **30** leading to nitrone occurs in the competitive dimerization reaction of **27a** to **38**. This process is believed to involve the formation of carbonyl carbenoid **35** from **27a**. Subsequent N attack at the carbenoid in **35** gives **36**, which undergoes deauration to afford nitrone **37**. The dimer product **38** was generated from nucleophilic attack of the nitrone oxygen atom on gold-activated alkynes followed by cyclization and ring opening. This competitive process, however, is suppressed in the presence of electron-rich alkene partners.

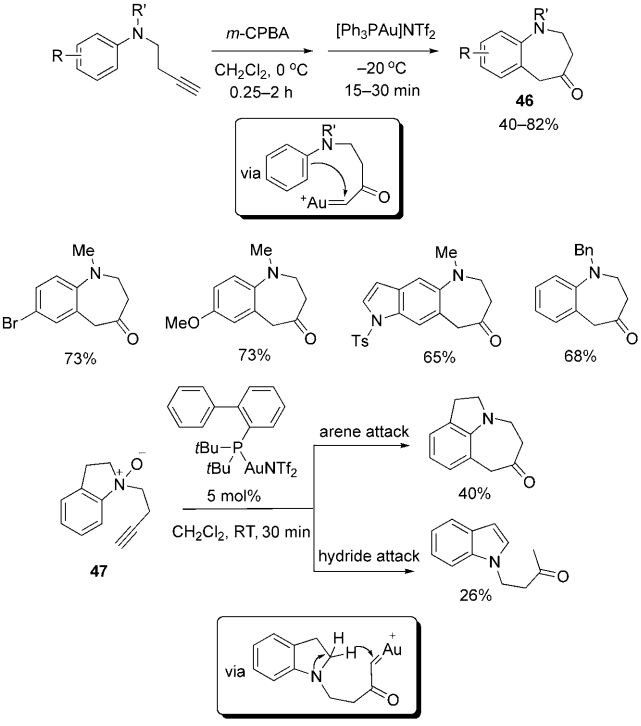
2.1.3. O-Atom Transfer from Amine N-oxides

Zhang and co-workers recently reported cyclization of amine N-oxides **41** which are synthesized from *m*-CPBA oxidation of homopropargyl amines **40**. One-pot cyclization was achieved upon treatment with a catalytic amount of $[Ph_3PAu]NTf_2$ to give piperidin-4-ones **42** (Scheme 11).[23a] A broad scope was defined for such amines bearing an N-methylene group and a terminal alkyne moiety, and the piperidin-4-one products **42** could be obtained in 54–79% yield starting from **39**. When two different N-methylene groups are available, the less-substituted one tends to be involved in the ring formation. In addition, cation-stabilizing groups (such as phenyl) also facilitate regioselective ring formation (Scheme 11). This method was successfully applied to the synthesis of racemic cermizine C in 63% yield starting from 4-methylpiperidine. The mechanism of this transformation is proposed to involve a 5-*exo*-*dig* cyclization to give **43** and the subsequent formation of a gold α-oxo carbenoid intermediate **44** with a pendent amine group. Intramolecular migration of the N-methylene hydrogen atom of **44** as a hydride to the carbenoid carbon gives intermediate **45** that contains a nucleophilic gold enolate and an electrophilic iminium. Subsequent Mannich-type cyclization of **45** affords the piperidin-4-one product **42**.

When one of the N-methylene groups (the source of hydride) is replaced by an aryl group, the resulting gold α-oxo carbenoid intermediate is preferentially attacked by the *ortho* carbon of an (electron-rich) aniline, leading to tetrahydrobenz[*b*]azepin-4-one product **46** via classical electrophilic aromatic substitution mechanism (Scheme 12).[23b] Thus $[Ph_3PAu]NTf_2$ can catalyze the cyclization of N-oxide-functionalized terminal alkynes in 40–82% yield. In most cases, the carbenoid carbon atom is preferentially attacked by the *ortho* carbon atom of the aniline rather than be possible migrating hydrides. However, when a short tether is installed between the N atom and the aryl ring as in **47** (Scheme 12), competitive nucleophilic attack by the aniline and the migrating hydride can be observed as a result of the partially restricted approach of the arene to the carbenoid.



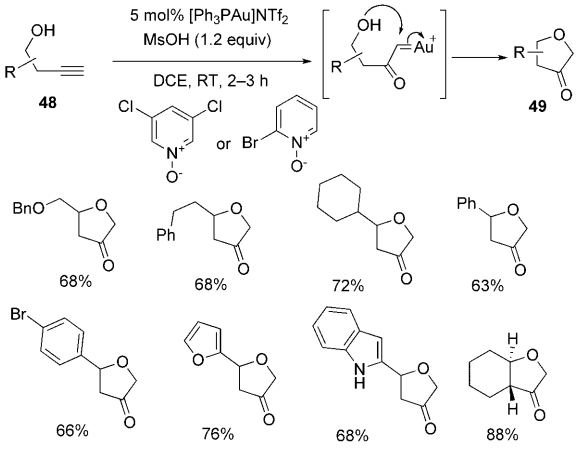
Scheme 11. Redox cyclization of amine N-oxides with hydride transfer. *m*-CPBA = *meta*-chloroperoxybenzoic acid.



Scheme 12. Redox cyclization of alkyne amine N-oxides. Ts = *p*-toluenesulfonyl.

2.1.4. Oxygen-Atom Transfer from Pyridine N-oxides

Pyridine N-oxides are commonly used in metal-mediated organic synthesis.[24] Their oxidizing character parallels that of amine N-oxides.[25] Significantly, Zhang and co-workers developed the intermolecular version of oxygen-atom transfer reactions between terminal alkynes and halopyridine N-oxides.[26a] To facilitate the subsequent nucleophilic attack on the gold α-oxo carbenoid intermediate, homopropargyl alcohols **48** were used as starting materials so that the proximal hydroxy group can efficiently trap the carbenoid, leading to cyclic ketones **49** (Scheme 13). Thus $[Ph_3PAu]NTf_2$ can catalyze the oxidative cyclization of various homopropargylic alcohols **48**. 4,5-Dichloropyridine *N*-oxide and 2-bromopyridine *N*-oxide proved to be the most suitable oxidants, and dihydrofuran-3-one products **49** were obtained in 55–88% yield when the reactions were conducted in the presence of MsOH (1.2 equiv), which is used to adjust the acidity of the reaction system.

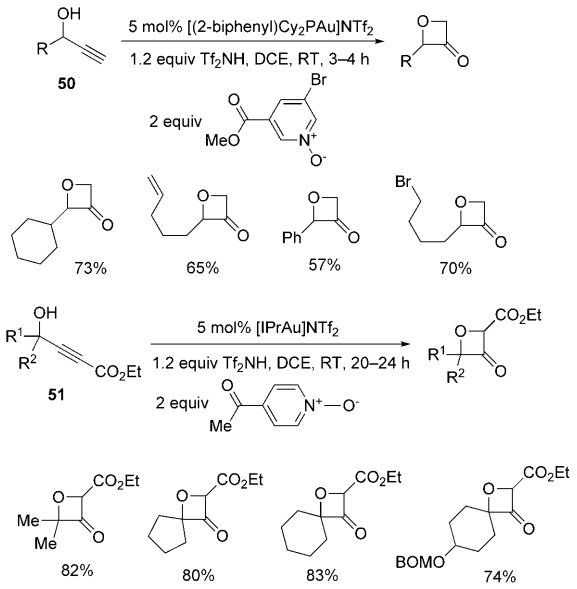


Scheme 13. Intermolecular redox cyclization of pyridine N-oxides. MsOH = methanesulfonic acid.

The same research group expanded the scope of this reaction to the synthesis of rather strained oxetan-3-ones starting from readily available propargylic alcohols.[26b] In general, earlier syntheses of oxetan-3-ones demand rather challenging steps starting from specially functionalized substrates.[27] In this reaction, $[(2\text{-biphenyl})Cy_2PAu]NTf_2$ turns out to be the most effective catalyst and Tf_2NH proves to be superior to MsOH as an acid additive. Various functionalized propargylic alcohols **50** (Scheme 14) can be tolerated. Importantly, the substrates can be extended to tertiary propargylic alcohols **51** bearing a carboxylate group (Scheme 14). These results indicate the important and unique roles of gold(I) catalysts in achieving the formation of strained rings via important α-oxo carbenoid intermediates.[26c]

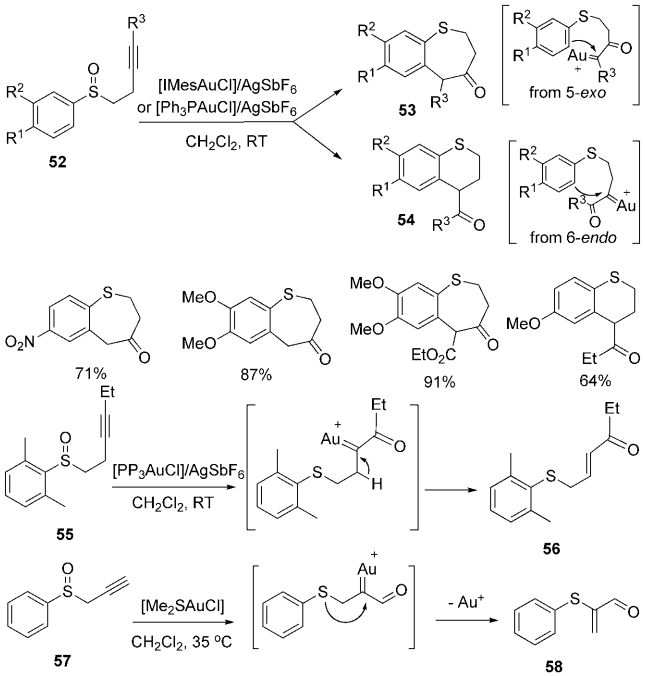
2.2. Oxygen-Atom Transfer from Sulfoxides

S=O bonds are also very polar and sulfoxides are often used as oxidants as in Swern oxidation reactions.[28] The



Scheme 14. Synthesis of oxetan-3-ones from propargylic alcohols.

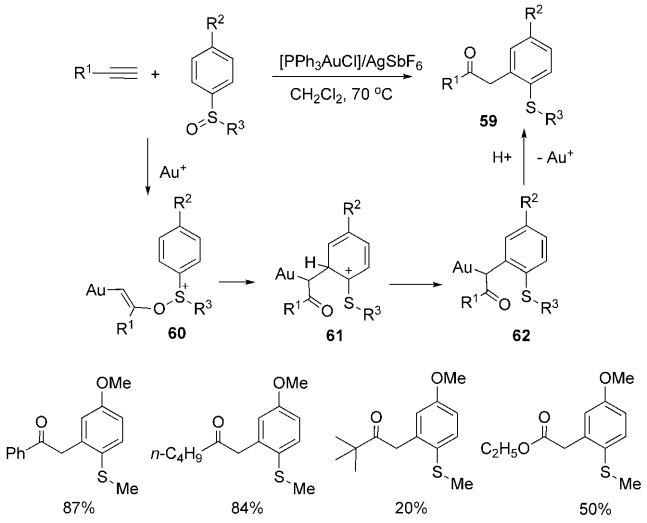
groups of Toste and Zhang independently reported gold-catalyzed intramolecular redox cyclization of alkynyl sulfoxides (Scheme 15).[29] $[(IMes)AuCl]/AgSbF_6$ (5 mol%) smoothly catalyzed the cyclization of substrates **52** to give benzothiepinones **53** and benzothiopine **54**.[29a] The regioselectivity of the oxygen nucleophilic attack seems directly dependent on the R^3 substituent of the alkyne unit. Thus terminal alkynes and alkynes bearing electron-withdrawing groups ($R^3 = CO_2Et$ or $p\text{-}NO_2C_6H_4$) afford the benzothiepinones as a result of the initial 5-*exo* cyclization. While for alkynes with alkyl groups, only the benzothiopine products



Scheme 15. Gold-catalyzed intramolecular redox reactions of sulfinyl alkynes. IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

were isolated. This selectivity was further supported by the gold-catalyzed isomerization of **55** (Scheme 15), in which the two *ortho*-substituents prevent any intramolecular Friedel–Crafts type alkylation. Instead, 1,2-H shift of the carbenoid intermediate occurred to give the enone product **56**. Interestingly, when the length of the tethering group between the sulfur and the alkyne is reduced to a methylene group such as in **57** (Scheme 15), no Friedel–Crafts type alkylation was observed either. The observed product **58** is a α-thioenone, and it is the sulfide group that undergoes 1,2-shift to attack the carbenoid to give product **58**.

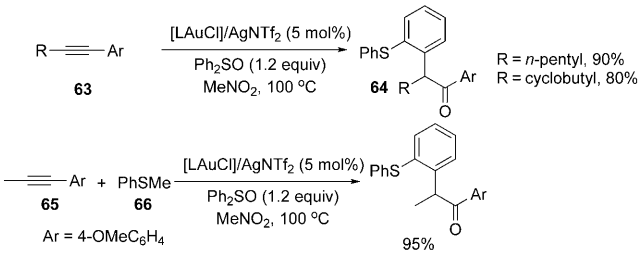
A formal intermolecular version of this coupling between terminal alkynes and sulfoxides were recently reported by Ujaque, Asensio, and co-workers.[30] (Scheme 16). Ketones **59**



Scheme 16. Gold(I)-catalyzed intermolecular oxyarylation of alkynes.

could be obtained in 20–87% yield. Although intermolecular version of the analogous reactions in Scheme 15 can be easily conceived, DFT studies were carried out in details using $[PH_3Au]^+$ as a model catalyst to gain deep insight into the mechanism. However, no formation of the α-oxo carbenoid together with a sulfide leaving group could be identified. Instead, in the lowest energy pathway, gold vinyl species (*E*)-**60** was identified as the key intermediate following the *anti* addition of the sulfoxide. DFT studies revealed that this intermediate undergoes [3,3′]-sigmatropic rearrangement via a six-membered transition state to give intermediate **61**. Next, a 1,2-hydride shift leads to the rearomatization of the π-system to afford **62**, which is followed by protodemetalation to complete the catalytic cycle. This proposed mechanism is different from those involving carbenoids, and it is preferred because the orientation of the arene and the gold vinyl is such that the [3,3′]-sigmatropic rearrangement proceeds with a low barrier.

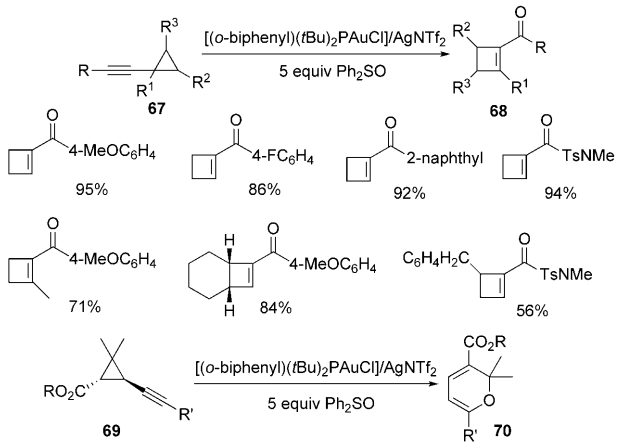
Liu and co-workers recently further explored this type of oxyarylation reaction and extended alkynes into internal ones.[31] Simple alkyl and aryl-substituted alkynes **63** undergo such reactions in the presence of Ph_2SO to afford products **64** (Scheme 17). Although generation of α-oxo carbenoids using



Scheme 17. Gold-catalyzed crossover experiment of internal alkynes with Ph_2SO.

Ph_2SO sometimes can be controversial, it is possible to use the experiment to probe the proposed mechanism. Importantly Liu and co-workers successfully used crossover experiments that involved alkyne **65**, an external sulfide **66**, and Ph_2SO to confirm that the external sulfide is not the reaction sources for the product, thus excluding the intermediacy of α-oxo carbenoids, which is consistent with the DFT studies by Asensio and co-workers.[30]

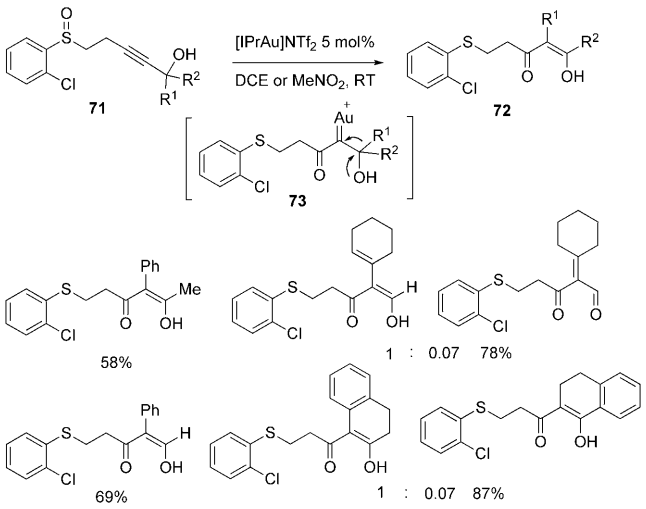
Significantly, Liu and co-workers also showed that when cyclopropyl-substituted internal alkynes were subjected to the same conditions, a novel gold-catalyzed oxidative ring-expansion of unactivated cyclopropylalkynes was achieved using Ph_2SO as an oxidant (Scheme 18).[31] Thus ring-expan-



Scheme 18. Gold-catalyzed oxidative ring expansions of alkynylcyclopropanes oxidized by diphenylsulfoxide.

sion of cyclopropane derivatives **67** under gold catalysis generated cyclobutene derivatives **68** in high yield. Such a ring-expansion process is further applied to the synthesis of 2*H*-pyrans **70** staring from **69** (Scheme 18), further showing the usefulness of this method.

Zhang and Li developed gold-catalyzed tandem reactions of sulfinyl-functionalized tertiary propargyl alcohols by combining an internal oxygen-atom transfer process with a pinnacol rearrangement.[29b] Thus $[IPrAu]NTf_2$ smoothly catalyzed the transformation of a series of propargyl alcohols **71** to β-dicarbonyl compounds **72** (Scheme 19). A proposed mechanism involves 5-*exo* attack of the O atom at the alkyne

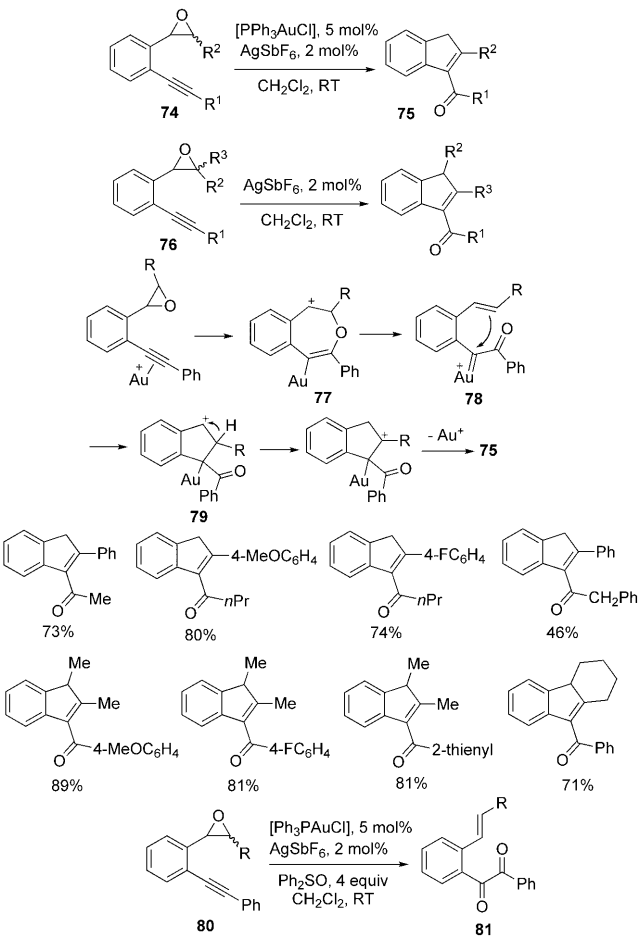


Scheme 19. The internal oxygen-atom transfer with pinnacol rearrangement.

followed by subsequent formation of a carbenoid intermediate **73**, which undergoes tandem pinnacol rearrangement to give the final product **72**. For non-symmetric alcohols bearing alkyl and aryl groups (R^1 and R^2), selective migration was observed, and aryl groups migrate preferentially. In the case of secondary alcohols bearing aryl or alkenyl groups, a high migration propensity was observed for such sp^2 groups, and no product derived from hydride migration was detected.

2.3. Oxygen-Atom Transfer from Epoxides

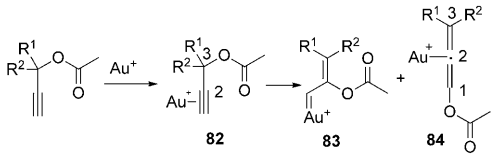
Despite the less polar character of C–O bonds in epoxides, oxygen-atom transfer from epoxides to alkynes was successfully achieved by the groups of Liu and Hashmi (Scheme 20).[32] In this case the release of the epoxide ring strain serves as a driving force. A combination of [Ph_3PAuCl] and $AgSbF_6$ can catalyze the isomerization of epoxide **74** to give ketone product **75**. In the case of epoxide **76**, the reaction can be simply catalyzed by $AgSbF_6$ (2 mol%). Apparently hydrogen or alkyl migration is involved in these reactions. The key α-oxo carbenoid intermediate is also proposed from an addition-elimination process. The proposed mechanism involves the oxygen attack at the alkyne in a 7-*endo* fashion, which gives a stabilized benzylic cabocation **77** (Scheme 20). Intramolecular elimination of the alkene group affords α-oxo carbenoid intermediate **78**. Nucleophilic attack of the alkene at the carbenoid affords **79** with a five-membered-ring framework, and subsequent 1,2-H shift is the key step leading to the final product **75**. The intermediacy of this carbenoid was supported by the formation of an α-diketone product **81** when **80** was treated with Ph_2SO (4 equiv); this carbenoid was trapped by an nucleophilic O-atom donor Ph_2SO (Scheme 20). In addition, this 1,2-hydide shift process was further confirmed by the preferential migration of aryl group as in the cyclization of **74**, which is consistent with the chemistry of sulfoxide alkynes, although the reaction conditions are different.



Scheme 20. Gold-catalyzed cycloisomerization of epoxide alkynes.

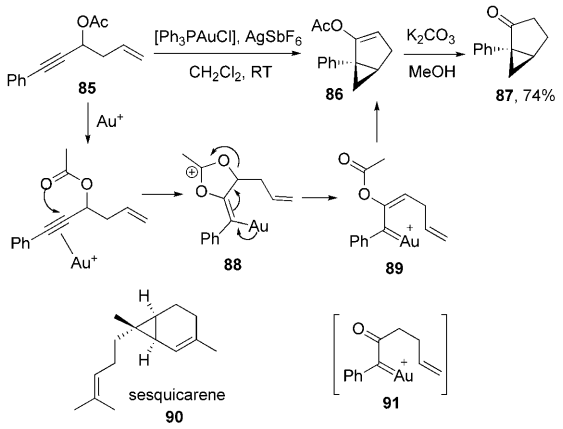
2.4. Oxygen-Atom Transfer from Esters

Among the most versatile substrates, the synthetic utility of easily accessible propargylic esters has also been investigated by several groups (Scheme 21).[33] Although esters are



Scheme 21. 1,2- or 1,3-acyloxy migration of propargylic esters.

not oxygen-atom donors, propargyl acetates can undergo analogous oxygen attack at an alkyne to give a vinyl species, which can further undergo formal 1,2-tranfer of the acetate group. It is established that gold propargylic esters species **82** can undergo 1,2- or 1,3-acyloxy migration to form a gold vinyl carbenoid species **83** or a gold allene species **84**,[34] which can be further trapped by other functional groups to allow for the synthesis of diverse organic products. For instance, Fürstner and co-workers reported the formation of bicyclo-[3.1.0]hexanone **87** by gold-catalyzed skeletal rearrangement



Scheme 22. Gold-catalyzed 1,2-transfer of acetate.

of propargylic acetate **85** (Scheme 22).[34a] The intramolecular nucleophilic attack of the carbonyl oxygen atom of the ester group on the alkyne affords a cationic gold vinyl intermediate **88**. Cleavage of the C–O bond in **88** gives a carbenoid intermediate **89**, followed by intramolecular cyclopropanation to give bicyclic vinylic ester **86**, in which the acetate has migrated. Treatment of **86** with a base provides bicyclo-[3.1.0]hexanone **87**, which is present in a large number of terpenes. This method has been used as a key step for the diastereoselective total synthesis of the natural product sesquicarene **90**.[35] In this case the overall process of 1,2-acetate transfer and subsequent base treatment is equivalent to an alpha-oxo carbenoid synthon **91**.

3. Conclusion

We have presented an overview of active gold α-oxo carbenoids that are generated in gold-mediated addition–elimination reactions between alkynes and E–O bonds in amine N-oxides, pyridine N-oxides, nitrones, nitros, sulfoxides, and epoxides. These polar N–O bonds act as both nucleophiles and oxygen-atom donors. The α-oxo carbenoids can undergo nucleophilic attack by imines, arenes, and migrating hydrides and alkyls leading to cascade reactions. The facile construction of C–E (E = C, N, O, or S) bonds and skeleton manipulation make it an attractive step-economic approach to access value-added molecules from readily available starting materials. While many novel catalytic processes have been uncovered in the past several years, we expect that many additional important reactions will be explored in the next decade, and the development of these reactions should be grounded on the previous mechanistic studies. We believe other rich synthetic methods will be developed on the basis of the intrinsic reactivity of such carbenoid intermediates. These new methods should serve to take up the challenge posed by the molecular complexity found in natural products and desired in synthetic chemistry.

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[1] For selected Reviews, see: a) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067; b) B. M. Trost, M. J. Krische, *Synlett* **1998**, 1; c) G. C. Lloyd-Jones, *Org. Biomol. Chem.* **2003**, *1*, 215; d) C. Aubert, O. Buisine, M. Malacria, *Chem. Rev.* **2002**, *102*, 813; e) B. M. Trost, *Chem. Eur. J.* **1998**, *4*, 2405; f) I. Ojima, M. Tzamarioudaki, Z. Y. Li, R. J. Donovan, *Chem. Rev.* **1996**, *96*, 635; g) B. Jiang, T. Rajale, W. Wever, S. Tu, G. Li, *Chem. Asian J.* **2010**, *5*, 2318; h) C. A. Carson, M. A. Kerr, *Chem. Soc. Rev.* **2009**, *38*, 3051; i) M. Zhang, *Adv. Synth. Catal.* **2009**, *351*, 2243; j) G. Zeni, R. C. Larock, *Chem. Rev.* **2004**, *104*, 2285.

[2] For Reviews on gold catalysis, see: a) N. Bongers, N. Krause, *Angew. Chem.* **2008**, *120*, 2208; *Angew. Chem. Int. Ed.* **2008**, *47*, 2178; b) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351; c) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326; d) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239; e) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266; f) J. Muzart, *Tetrahedron* **2008**, *64*, 5815; g) H. C. Shen, *Tetrahedron* **2008**, *64*, 7847; h) H. C. Shen, *Tetrahedron* **2008**, *64*, 3885; i) R. A. Widenhoefer, *Chem. Eur. J.* **2008**, *14*, 5382; j) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395; k) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410; l) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Commun.* **2007**, 333; m) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; n) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271; o) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896; p) A. Hoffmann-Röder, N. Krause, *Org. Biomol. Chem.* **2005**, *3*, 387; q) A. S. K. Hashmi, *Gold Bull.* **2004**, *37*, 51; r) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766; s) A. S. K. Hashmi, M. Bührle, *Alrdichim. Acta* **2010**, *43*, 27; t) N. D. Shapiro, F. D. Toste, *Synlett* **2010**, 675; u) S. Sengupta, X. Shi, *ChemCatChem* **2010**, *2*, 609; v) M. Bandini, *Chem. Soc. Rev.* **2011**, *40*, 1358; w) T. C. Boorman, I. Larrosa, *Chem. Soc. Rev.* **2011**, *40*, 1910.

[3] For a Review on gold N-heterocyclic carbenes, see: a) S. P. Nolan, *Acc. Chem. Res.* **2011**, *44*, 91. For selected examples on Fischer-type carbene complexes of gold, see: b) H. G. Raubenheimer, M. W. Esterhuysen, A. Timoshkin, Y. Chen, G. Frenking, *Organometallics* **2002**, *21*, 3173; c) U. Schubert, K. Ackermann, R. Aumann, *Cryst. Struct. Comm.* **1982**, *11*, 591; d) M. Fañanás-Mastral, F. Aznar, *Organometallics* **2009**, *28*, 666.

[4] For recent examples: see: a) K. Ando, *J. Org. Chem.* **2010**, *75*, 8516; b) A. S. Dudnik, Y. Xia, Y. Li, V. Gevorgyan, *J. Am. Chem. Soc.* **2010**, *132*, 7645; c) Y. Liu, D. Zhang, S. Bi, *J. Phys. Chem. A* **2010**, *114*, 12893; < lit d > D. Garayalde, E. Gómez-Bengoa, X. Huang, A. Goeke, C. Nevado, *J. Am. Chem. Soc.* **2010**, *132*, 4720; e) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482.

[5] a) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642; b) D. Weber, M. A. Tarselli, M. R. Gagne, *Angew. Chem.* **2009**, *121*, 5843; *Angew. Chem. Int. Ed.* **2009**, *48*, 5733; c) A. S. K. Hashmi, A. Schuster, F. Rominger, *Angew. Chem.* **2009**, *121*, 8396; *Angew. Chem. Int. Ed.* **2009**, *48*, 8247; d) A. S. K. Hashmi, *Gold Bull.* **2009**, *42*, 275.

[6] For a Review on mechanisms and intermediates in gold catalysis, see: A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232.

[7] C. A. Witham, P. Mauleón, N. D. Shapiro, B. D. Sherry, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 5838.

[8] X. Li, C. D. Incarvito, T. Vogel, R. H. Crabtree, *Organometallics* **2005**, *24*, 3066.

[9] A. S. K. Hashmi, *Angew. Chem.* **2008**, *120*, 6856; *Angew. Chem. Int. Ed.* **2008**, *47*, 6754.

[10] Y. Shibata, K. Noguchi, K. Tanaka, *J. Am. Chem. Soc.* **2010**, *132*, 7896.

[11] a) Q. Yao, M. Zabawa, J. Woo, C. Zheng, *J. Am. Chem. Soc.* **2007**, *129*, 3088; b) Y. Zhang, G. Song, G. Ma, J. Zhao, C. L. Pan, X. Li, *Organometallics* **2009**, *28*, 3233.

[12] For Reviews, see: a) S. Youssif, *ARKIVOC* **2001**, 242; b) A. V. Ryzhakov, L. L. Rodina, *Heterocycles* **2008**, *75*, 2367; c) S. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis* **1994**, 639. For some examples, see: d) J. Pool, B. Scott, J. Kiplinger, *J. Am. Chem. Soc.* **2005**, *127*, 1338.

[13] For Reviews, see: a) A. Banerji, P. Sengupta, *J. Indian Inst. Sci.* **2001**, *81*, 313; b) K. V. Gothelf, K. A. Jørgensen, *Chem. Rev.* **1998**, *98*, 863; c) K. V. Gothelf, K. A. Jørgensen, *Chem. Commun.* **2000**, 1449; d) H. Pellissier, *Tetrahedron* **2007**, *63*, 3235; e) K. V. Gothelf in *Cycloaddition Reactions in Organic Synthesis* (Eds.: S. Kobayashi, K. A. Jørgensen), Wiley-VCH, Weinheim, **2002**, chap. 6, p. 211; f) S. Kanemasa in *Cycloaddition Reactions in Organic Synthesis* (Eds.: S. Kobayashi, K. A. Jørgensen, Wiley-VCH, Weinheim, **2002**, chap. 7, p. 249.

[14] a) H. S. Yeom, Y. Lee, J. E. Lee, S. Shin, *Org. Biomol. Chem.* **2009**, *7*, 4744; b) D. Chen, X. Li, unpublished results.

[15] K. Pati, R. S. Liu, *Chem. Commun.* **2009**, 5233.

[16] a) C. Bruneau, P. H. Dixneuf, *Angew. Chem.* **2006**, *118*, 2232; *Angew. Chem. Int. Ed.* **2006**, *45*, 2176; b) X. Li, T. Vogel, C. D. Incarvito, R. H. Crabtree, *Organometallics* **2005**, *24*, 62.

[17] H. S. Yeom, J. E. Lee, S. Shin, *Angew. Chem.* **2008**, *120*, 7148; *Angew. Chem. Int. Ed.* **2008**, *47*, 7040.

[18] N. Asao, K. Sato, Y. Yamamoto, *Tetrahedron Lett.* **2003**, *44*, 5675.

[19] H. Zheng, J. Zheng, B. Yu, Q. Chen, X. Wang, Y. He, Z. Yang, X. She, *J. Am. Chem. Soc.* **2010**, *132*, 1788.

[20] H. Yeom, Y. Lee, J. Jeong, E. So, S. Hwang, J. Lee, S. Lee, and S. Shin, *Angew. Chem.* **2010**, *122*, 1655; *Angew. Chem. Int. Ed.* **2010**, *49*, 1611.

[21] Failure of the Ir^{III}-catalyzed synthesis of anthranil is ascribed to product inhibition.

[22] A. M. Jadhav, S. Bhunia, H. Y. Liao, R. S. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 1769.

[23] a) L. Cui, Y. Peng, L. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 8394; b) L. Cui, G. Zhang, Y. Peng, L. Zhang, *Org. Lett.* **2009**, *11*, 1225.

[24] a) L. C. Campeau, S. Rousseaux, K. Fagnou, *J. Am. Chem. Soc.* **2005**, *127*, 18020; b) L. C. Campeau, D. J. Schipper, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 3266; c) L. C. Campeau, D. R. Stuart, J.-P. Leclerc, M. Bertrand-Laperle, E. Villemure, H. Y. Sun, S. Lasserre, N. Guimond, M. Lecavallier, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 3291; d) J. P. Leclerc, K. Fagnou, *Angew. Chem.* **2006**, *118*, 7945; *Angew. Chem. Int. Ed.* **2006**, *45*, 7781; e) M. P. Huestis, K. Fagnou, *Org. Lett.* **2009**, *11*, 1357; f) S. H. Cho, S. J. Hwang, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 9254; g) P. Xi, F. Yang, S. Qin, D. Zhao, J. Lan, G. Gao, C. Hu, J. You, *J. Am. Chem. Soc.* **2010**, *132*, 1822.

[25] J. Wu, X. Cui, L. Chen, G. Jiang, Y. Wu, *J. Am. Chem. Soc.* **2009**, *131*, 13888.

[26] a) L. Ye, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 3258; b) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8550; after submission of this manuscript Zhang and co-workers reported gold catalyzed intermolecular alkyne oxidation with nitriles via a gold α-oxo carbenoid intermediate: c) W. He, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8482.

[27] For a Review, see: a) Y. Dejaegher, N. M. Kuz'menok, A. M. Zvonok, N. De Kimpe, *Chem. Rev.* **2002**, *102*, 29. For individual examples, see: b) A. P. Kozikowski, A. H. Fauq, *Synlett* **1991**, *1991*, 783; c) P. J. Hamzik, J. D. Brubaker, *Org. Lett.* **2010**, *12*, 1116; d) G. Wuitschik, M. Rogers-Evans, K. Müller, H. Fischer, B. Wagner, F. Schuler, L. Polonchuk, E. M. Carreira, *Angew. Chem.* **2006**, *118*, 7900; *Angew. Chem. Int. Ed.* **2006**, *45*, 7736.

[28] a) A. J. Mancuso, D. Swern, *Synthesis* **1981**, 165; b) T. T. Tidwell, *Org. React.* **1990**, *39*, 297; c) T. T. Tidwell, *Synthesis* **1990**, 857; d) W. W. Epstein, F. W. Sweat, *Chem. Rev.* **1967**, *67*, 247.

[29] a) N. D. Shapiro, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 4160; b) G. Li, L. M. Zhang, *Angew. Chem.* **2007**, *119*, 5248; *Angew. Chem. Int. Ed.* **2007**, *46*, 5156.

[30] A. B. Cuenca, S. Montserrat, K. M. Hossain, G. Mancha, A. Lledós, M. Medio-Simón, G. Ujaque, G. Asensio, *Org. Lett.* **2009**, *11*, 4906.

[31] C.-W. Li, K. Pati, G.-Y. Lin, H.-H. Hung, R.-S. Liu, *Angew. Chem.* **2010**, *122*, 10087; *Angew. Chem. Int. Ed.* **2010**, *49*, 9891.

[32] a) G. Y. Lin, C. W. Li, S. H. Hung, R. S. Liu, *Org. Lett.* **2008**, *10*, 5059; b) A. S. K. Hashmi, M. Bührle, R. Salathé, J. W. Bats, *Adv. Synth. Catal.* **2008**, *350*, 2059.

[33] For Reviews of propargylic esters in Pt and Au catalysis, see: a) N. Marion, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 2806; *Angew. Chem. Int. Ed.* **2007**, *46*, 2750; b) J. Marco-Contelles, E. Soriano, *Chem. Eur. J.* **2007**, *13*, 1350; c) D. J. Gorin, I. D. G. Watson, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 3736; d) N. D. Shapiro, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 9244; e) N. D. Shapiro, Y. Shi, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 11654; f) A. Correa, N. Marion, L. Fensterbank, M. Malacria, S. P. Nolan, L. Cavallo, *Angew. Chem.* **2008**, *120*, 730; *Angew. Chem. Int. Ed.* **2008**, *47*, 718; g) G. Lemière, V. Gandon, K. Cariou, T. Fukuyama, A. L. Dhimane, L. Fensterbank, M. Malacria, *Org. Lett.* **2007**, *9*, 2207; h) N. Marion, P. Carlqvist, R. Gealageas, P. De Frémont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437. For Pt-catalyzed intermolecular cycloaddition reactions using propargyl esters, see: i) J. Barluenga, L. Riesgo, R. Vicente, L. A. López, M. Tomás, *J. Am. Chem. Soc.* **2007**, *129*, 7772; j) J. K. D. Brabander, B. Liu, M. Qian, *Org. Lett.* **2008**, *10*, 2533; k) L. Lu, X.-Y. Liu, X.-Z. Shu, K. Yang, K. G. Ji, Y.-M. Liang, *J. Org. Chem.* **2009**, *74*, 474. For Ruthenium-catalyzed cyclopropanation of alkenes using propargylic carboxylates as precursors of vinylcarbenoids, see: l) K. Miki, K. Ohe, S. Uemura, *Tetrahedron Lett.* **2003**, *44*, 2019; m) K. Miki, K. Ohe, S. Uemura, *J. Org. Chem.* **2003**, *68*, 8505.

[34] For Au-mediated 1,2-shift of propargylic esters, see: a) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654; b) X. Shi, D. J. Gorin, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 5802; c) M. J. Johansson, D. J. Gorin, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 18002; d) D. J. Gorin, P. Dubé, F. D. Toste, *J. Am. Chem. Soc.* **2006**, *128*, 14480; e) N. Marion, P. de Frémont, G. Lemière, E. D. Stevens, L. Fensterbank, M. Malacria, S. P. Nolan, *Chem. Commun.* **2006**, 2048. For examples of Au-mediated 1,3-shifts of propargylic esters, see: f) C. H. Oh, A. Kim, W. Park, D. I. Park, N. Kim, *Synlett* **2006**, 2781; g) A. Buzas, F. Gagosz, *J. Am. Chem. Soc.* **2006**, *128*, 12614; h) S. Wang, L. Zhang, *J. Am. Chem. Soc.* **2006**, *128*, 14274; i) H. S. Yeom, S. J. Yoon, S. Shin, *Tetrahedron Lett.* **2007**, *48*, 4817; j) G. Lemière, V. Gandon, K. Cariou, T. Fukuyama, A. L. Dhimane, L. Fensterbank, M. Malacria, *Org. Lett.* **2007**, *9*, 2207.

[35] A. Fürstner, P. Hannen, *Chem. Commun.* **2004**, 2546.

