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Gold(I)- and Yb(OTf)$_3$-Cocatalyzed Rearrangements of Epoxy Alkynes: Transfer of a Carbonyl Group in a Five-Membered Carbocycle

Lun-Zhi Dai and Min Shi*[a]

Abstract: We report here the intramolecular reactions between α,β-epoxy ketones and alkynes cocatalyzed by gold(I) and Yb(OTf)$_3$. This new catalytic system based on a combination of gold(I) and Yb(OTf)$_3$ allows facile transformation of epoxy alkynes to give novel indene derivatives in moderate to good yields under mild conditions. Moreover, we describe here the first observation of a transfer of a carbonyl group in a five-membered carbocycle during gold-catalyzed reactions. This proposed mechanism is corroborated by isotope-labeling experiments (D and ^{13}C). Furthermore, the probable role of each catalyst in this interesting domino reaction has been examined by ^{31}P NMR experiments. The utilization of gold catalysts combined with rare-earth metal salts offers a new concept for the design of catalyst combinations for domino or cascade reactions.

Keywords: epoxy alkynes · domino reactions · gold · heterocycles · indene derivatives · epoxy ketones

Introduction

Gold-catalyzed domino reactions are powerful tools in organic synthesis to access complex molecular frameworks.[1] Counter anions present in the Au^I solution are very important factors with respect to the catalytic activity. The combination of [LAuHal] (L = ligand, Hal = Cl, Br, etc) with silver salts is the most common method used to increase the catalytic abilities of gold catalysts.[2] In addition to silver salts, the Lewis acid $BF_3 \cdot Et_2O$ has also been used to activate the gold complexes.[3] However, the utilization of rare-earth metal salts as cocatalysts in gold-catalyzed reactions has never been reported before as far as we know.

Molecules bearing both an epoxy group and an alkynyl group can probably be transformed to complex and useful structures in the presence of suitable catalysts. Although there is growing interest in the gold-catalyzed domino isomerization of epoxy alkynes,[4] successful precedents using epoxides bearing an electron-withdrawing substituent are rare. Moreover, the rearrangement of α,β-epoxy ketones catalyzed by a Lewis acid was reported by House and Ryerson in the early 1960s;[5a] the products normally consist of a mixture of 1,2- and 1,3-diketones, which result from either hydride or acyl migration, respectively. Thus, if 1,3-diketones are formed from the epoxy alkynes, the resulting 1,3-diketone might react further with alkynes to give more interesting products. In addition to the In-,[6] Pd-,[7] and Zn-catalyzed[8] addition of 1,3-diketones to alkynes, which have been well described before, Toste[9] and co-workers have reported an efficient gold-catalyzed intramolecular addition of β-ketoesters to inactivated alkynes, providing the cyclization products derived from the carbon nucleophiles. More recently, Sawamura et al.[10] reported a similar reaction assisted by holey phosphine to give six- or seven-membered rings under similar conditions. Moreover, some other groups have also reported the nucleophilic addition of 1,3-dicarbonyl compounds to propargyl carboxylates and unactivated olefins catalyzed by gold to give the corresponding adducts in good yields under mild conditions.[11]

Based on the above results, two reaction models could be proposed.[12] We envisaged that the ketone-substituted epoxides **1** in the presence of acid might undergo isomerization to give 1,3-diketones **1’** (Scheme 1, step I). Subsequent intramolecular cyclization could occur via two pathways: 1) nucleophilic addition of an oxygen atom to the alkyne to give **2** (Scheme 1, step II, path a); 2) cyclization employing a carbon nucleophile to give **3**, in a way similar to that reported by Toste et al. and Sawamura et al. (Scheme 1, step II, path b).

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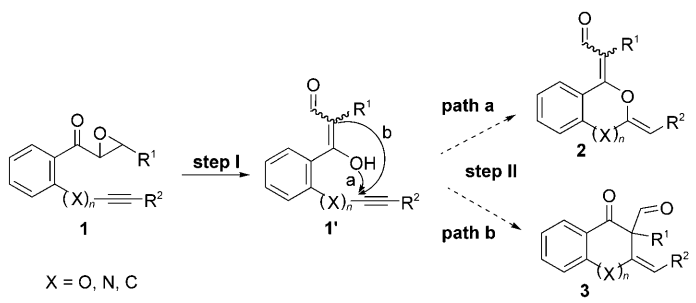
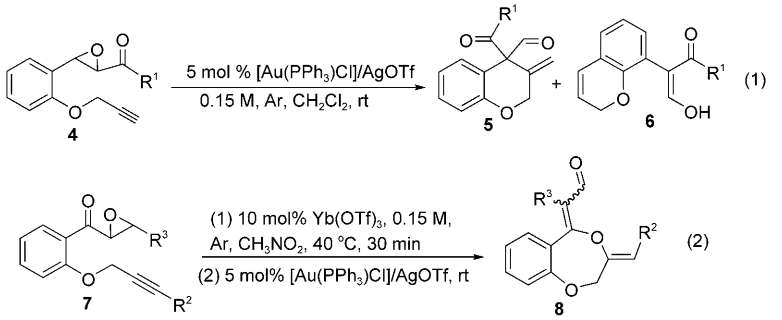


Scheme 1. Hypotheses for the one-pot conversion of epoxy alkynes.

The substrates **4** and **7** were prepared according to procedures reported previously.[13] A systematic examination of the reaction outcomes revealed that the type of cyclization was dependent on the structure of the substrates (Scheme 2). When substrate **4**, which bears four atoms between the epoxy and alkynyl groups, was catalyzed by 5 mol % [Au(PPh$_3$)Cl]/AgOTf, six-membered product **5** was formed in moderate yield along with by-product **6** (Scheme 2, [Eq. (1)]). However, seven-membered heterocycle **8** was afforded in an efficient one-pot, two-step route using substrate **7** as the starting material catalyzed by 10 mol % Yb(OTf)$_3$ and then 5 mol % [Au(PPh$_3$)Cl]/AgOTf (Scheme 2, [Eq. (2)]).[12]



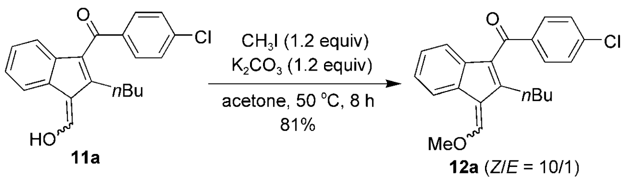
Scheme 2. Substrate-dependent selective cyclizations.

In the context of our ongoing efforts to develop cascade reactions using epoxy alkynes as substrates,[4b,12,14] herein, we report a novel combination of a gold complex and Yb(OTf)$_3$ that catalyzes the rearrangements of epoxy alkynes **9**, affording interesting functionalized indene derivatives in good yields. The significance of this reaction lies in the first observation of the transfer of a carbonyl group in the five-membered carbocycle.

Results and Discussion

Optimization of the reaction conditions: Preliminary experiments directed towards optimizing the reaction conditions of the transformation were carried out with epoxy alkyne **9a** in the presence of [Au(PMe$_3$)Cl] and AgOTf in nitromethane (CH$_3$NO$_2$) at 50 °C. We found that an interesting functionalized indene derivative **11a** was formed in 59 % yield (Table 1, entry 1). The structure of compound **11a** was confirmed by X-ray diffraction. Replacing AgOTf (5 mol %) with Yb(OTf)$_3$ (10 mol %) led to the formation of **11a** in 87 % yield (Table 1, entry 2). Control experiments indicated that using Yb(OTf)$_3$ alone as the catalyst gave the 1,2-acyl transfer product **10a** rather than **11a**, and that using [Au(PMe$_3$)Cl] alone as the catalyst, no reaction occurred (Table 1, entries 3 and 4). Changing the ligand on the gold complex to PPh$_3$ resulted in the formation of **11a** in 79 % yield (Table 1, entry 5). Using Sc(OTf)$_3$ or In(OTf)$_3$ (10 mol %) as a cocatalyst decreased the yield of **11a** (Table 1, entries 6 and 7). Performing the reaction under an O$_2$ atmosphere did not affect the reaction outcome significantly (Table 1, entry 8). Carrying out the reaction in tetrahydrofuran (THF) resulted in a sharp decrease of the yield (Table 1, entry 9). When 1,2-dichroloethane (DCE) was used as a solvent, there was no improvement in the yield compared with the result under identical reaction conditions when CH$_3$NO$_2$ was used as a solvent (Table 1, entry 10). Further screening of the amount of cocatalyst Yb(OTf)$_3$ applied, revealed that 5 mol % of Yb(OTf)$_3$ was the best choice for the reaction (Table 1, entries 11 and 12). Reducing the temperature to 30 °C or elevating the temperature to 70 °C did not improve the reaction outcome, although a clear cut in the reaction time could be observed at 70 °C (Table 1, entries 13 and 14). Traces of compound **11a′**, an isomer of **11a**, could be observed in all above cases.

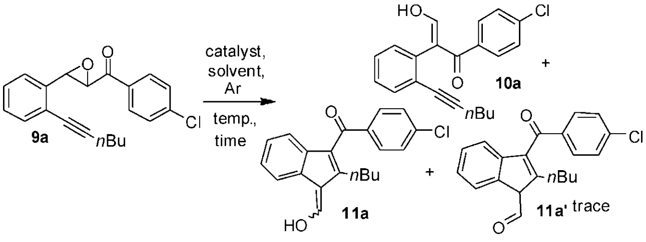
Due to the poor solubility of product **11a** in many organic solvents, the characterization of **11a** was performed by converting it to **12a** by further methylation using iodomethane in the presence of potassium carbonate (Scheme 3).



Scheme 3. Methylation of product **11a**.

Scope of the reaction: Under the optimized conditions, it was found that when R^2 was an alkyl group and R^1 was an aryl group, the reaction proceeded smoothly to give the desired products **12** in moderate yields after two steps

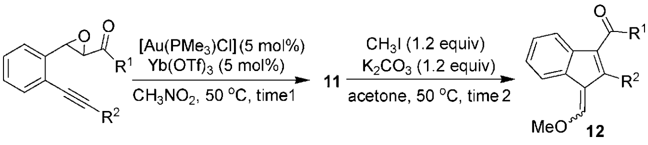
Table 1. Domino rearrangement of epoxy alkynes.



Entry	Catalyst (mol %)	Solvent	Temp.	Time [h]	Yield **10a** [%][a]	Yield **11a** [%][a]
1	$Au(PMe_3)Cl$ (5)/ AgOTf (5)	CH_3NO_2	50	22	trace	59
2	$Au(PMe_3)Cl$ (5)/ $Yb(OTf)_3$ (10)	CH_3NO_2	50	10	–	87
3	$Yb(OTf)_3$ (10)	CH_3NO_2	50	0.5	75	–
4	$Au(PMe_3)Cl$ (5)	CH_3NO_2	50	16	–	–
5	$Au(PPh_3)Cl$ (5)/ $Yb(OTf)_3$ (10)	CH_3NO_2	50	10	–	79
6	$Au(PMe_3)Cl$ (5)/ $Sc(OTf)_3$ (10)	CH_3NO_2	50	11.5	–	53
7	$Au(PMe_3)Cl$ (5)/ $In(OTf)_3$ (10)	CH_3NO_2	50	5	–	64
8[b]	$Au(PMe_3)Cl$ (5)/ $Yb(OTf)_3$ (10)	CH_3NO_2	50	13	–	84
9	$Au(PMe_3)Cl$ (5)/ $Yb(OTf)_3$ (10)	THF	50	64	–	11
10	$Au(PMe_3)Cl$ (5)/ $Yb(OTf)_3$ (10)	DCE	50	9	–	76
11	$Au(PMe_3)Cl$ (5)/ $Yb(OTf)_3$ (2.5)	CH_3NO_2	50	12	–	80
12[c]	$Au(PMe_3)Cl$ (5)/ $Yb(OTf)_3$ (5)	CH_3NO_2	50	11	–	87
13	$Au(PMe_3)Cl$ (5)/ $Yb(OTf)_3$ (5)	CH_3NO_2	50	23	–	76
14	$Au(PMe_3)Cl$ (5)/ $Yb(OTf)_3$ (5)	CH_3NO_2	70	4	–	70

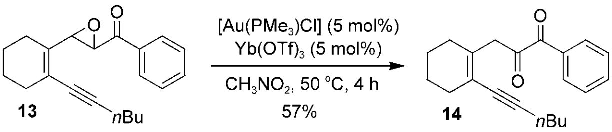
[a] Isolated yields. [b] Under an O_2 atmosphere. [c] The ratio of *Z*-**11a** to *E*-**11a** is 2.5:1.

Table 2. Reaction scope.



Entry	R^1	R^2	Time 1 [h]	Time 2 [h]	Yield [%][a] (*Z*/*E*) **12**
1	**9a**: p-ClC_6H_5	*n*Bu	11	8	**12a**: 70 (10:1)
2	**9b**: p-FC_6H_4	*n*Bu	12	6	**12b**: 60 (3.4:1)
3	**9c**: p-BrC_6H_4	*n*Bu	17	6	**12c**: 51 (2.3:1)
4	**9d**: m-BrC_6H_4	*n*-hexyl	20	7	**12d**: 60 (10.5:1)
5	**9e**: 2-naphthalenyl	*n*Bu	11	6	**12e**: 52 (1.9:1)
6	**9f**: p-MeC_6H_4	*n*-hexyl	24	6	**12f**: 46 (1.1:1)
7	**9g**: p-MeC_6H_4	*n*Bu	16	6	**12g**: 52 (1.4:1)
8[b]	**9h**: p-$MeOC_6H_4$	*n*-hexyl	18	6.5	**12h**: 45 (1.1:1)
9	**9i**: C_6H_5	*n*Bu	18	6	**12i**: 67 (1.5:1)
10[b]	**9j**: C_6H_5	C_6H_5	12	–	**12j**: –
11	**9k**: Me	*n*Bu	11	5.5	**12k**: 43 (4.4:1)

[a] Isolated overall yields for two steps. [b] The complex product mixture was obtained.



Scheme 4. Application of the method to the nonaromatic substrate **13**.

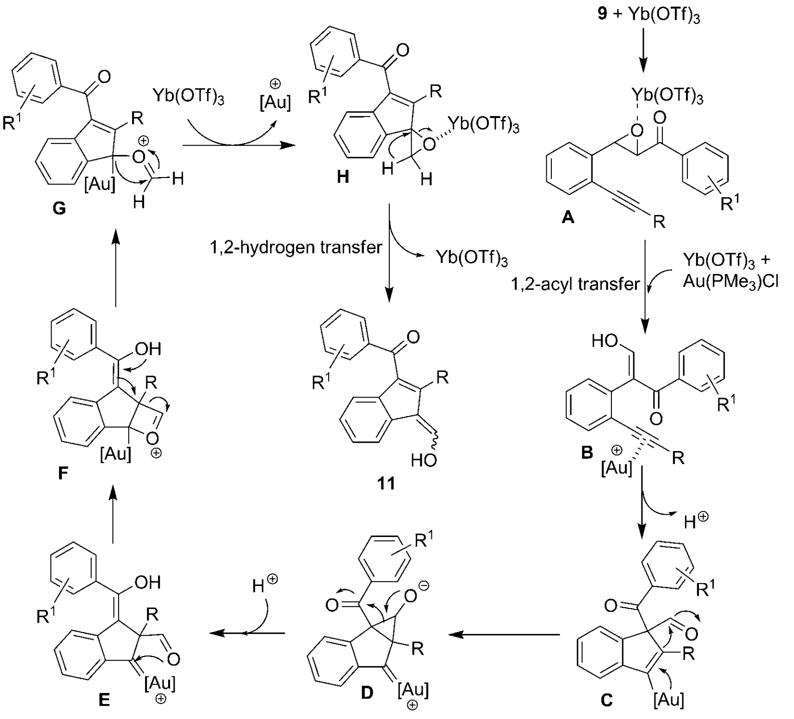
(Table 2, entries 1–9). However, when both R^2 and R^1 were aromatic groups, the reaction afforded a complex product mixture (Table 2, entry 10). Further examination of the substrate **9k** (R^1=Me, R^2=*n*Bu) revealed that the desired indene derivative **12k** was formed in 43% yield, indicating a broad substrate scope (Table 2, entry 11).

The combination of [$Au(PMe_3)Cl$] and $Yb(OTf)_3$ was also applied to nonaromatic substrate **13** under the standard conditions. The product **14** was obtained in 57% yield via an oxirane rearrangement (Scheme 4).

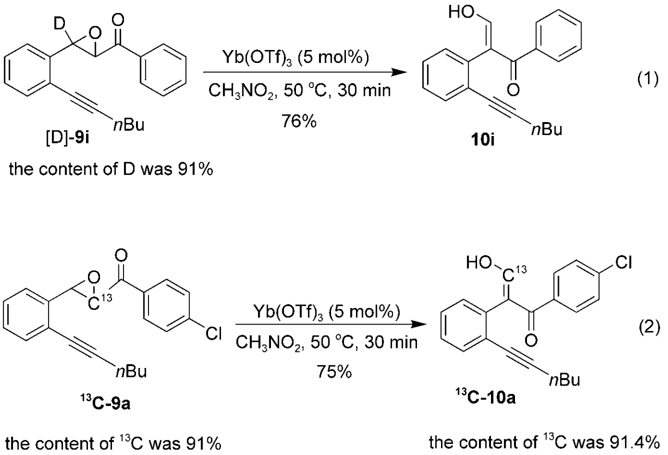
Overall reaction mechanism: A tentative reaction mechanism is proposed in Scheme 5. The mechanism initially involves the $Yb(OTf)_3$-catalyzed rearrangement of the epoxy group to give 1,3-diketone **10** via 1,2-acyl group transfer from intermediate **A**. Subsequent five-membered annulation[15] of **10** via intermediate **B** results in intermediate **C**. Gold-assisted nucleophilic addition of a carbonyl group by a double bond gives the gold(I)-carbenoid intermediate **D**,[16] which transforms to intermediate **E** automatically through the ring-opening of the cyclopropyl alcohol.[17] Subsequent nucleophilic addition of the aldehyde oxygen atom generates intermediate **F** that undergoes rearrangement with the assistance of the hydroxyl group to give oxonium **G**.[18] Intramolecular nucleophilic addition of the oxonium by a carbon–gold bond gives epoxy intermediate **H**, which transforms to product **11** catalyzed by $Yb(OTf)_3$. Interestingly, we find that the carbonyl group in intermediate **B** walks along a five-membered carbocycle (Scheme 5).

Recalling the reaction when [$Au(PMe_3)Cl$] and AgOTf were used as cocatalysts (Table 1, entry 1), we thought that [$Au(PMe_3)$]OTf acted as a catalyst to promote the rearrangement of the epoxide in the absence of $Yb(OTf)_3$.[19b] The remaining silver salt could also be an effective catalyst during the rearrangement of epoxides.[19b]

To verify the proposed reaction mechanism, a series of experiments was carried out. First of all, the process by which intermediate **B** was formed from intermediate **A** via 1,2-acyl migration was demonstrated by performing a deuterium-labeling experiment. Reaction of [D]-**9i** under the optimized conditions gave compound **10i**, which contains no deuterium label, in 76% yield (Scheme 6, [Eq. (1)]). This confirms the occurrence of an intramolecular 1,2-acyl migration and excludes an 1,2-aryl migration. The resulting active deuterium on the hydroxyl group was exchanged with the proton source during the workup process. A subsequent ^{13}C-labeling experiment also supported the 1,2-acyl migration with the observation of a strong signal at $\delta = 185.6$ ppm in the



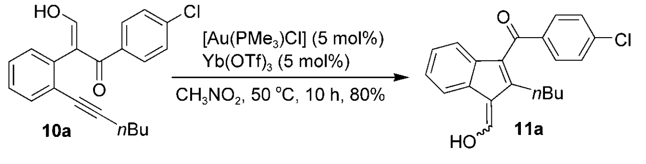
Scheme 5. Proposed mechanism.



Scheme 6. Isotope-labeling experiments using [D]-**9i** and ^{13}C-**9a**.

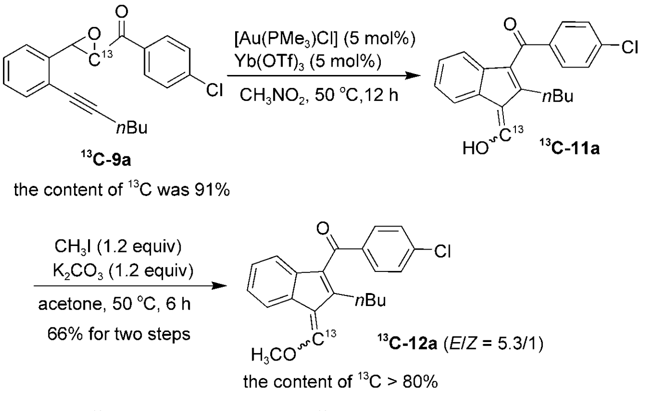
^{13}C NMR spectrum under identical conditions (Scheme 6, [Eq. (2)], see the Supporting Information).

The isolated product **10a** was further subjected to the optimized conditions, and it was found that **11a** was formed in 80 % yield, indicating that **10a** might be an intermediate in this transformation (Scheme 7). Moreover, this experiment also excluded the direct nucleophilic attack of an alkyne–gold complex by an epoxide oxygen.[3a,14b,19]



Scheme 7. A control experiment using **10a**.

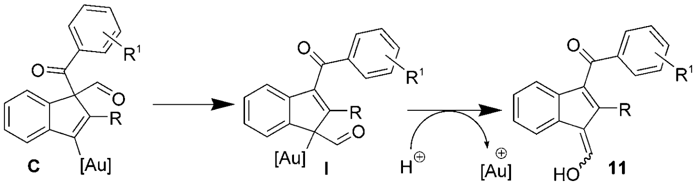
In line with the situation described in Scheme 1, the annulation of **10a** probably could also adopt two pathways.[12] If the annulation employed an oxygen nucleophile, a six- or seven-membered heterocycle would be produced as an intermediate. However, the transformation of the supposed heterocycle to the final product **11a** could not be explained. If the annulation employed a carbon nucleophile, in line with the proposed mechanism in Scheme 5, double transfer of the carbonyl group in the five-membered carbocycle might be involved in the reaction. We therefore prepared the ^{13}C-labeled derivative of **9a** to verify the reaction pathway (see the Supporting Information). Treatment of ^{13}C-**9a** under the optimized conditions resulted in ^{13}C-**11a**, which subsequently gave ^{13}C-**12a** in 60 % yield after methylation (^{13}C content >80 %; Scheme 8). This ^{13}C-labeling experiment clearly demonstrated the involvement of a double transfer of the carbonyl group in the five-membered carbocycle as shown in Scheme 5.



Scheme 8. ^{13}C-labeling studies using ^{13}C-**9a**.

A direct intramolecular [1,3]-migration of the acyl group from intermediate **C** to product **11** via intermediate **I**, as described by Yamamoto et al., could also account for the observations (Scheme 9).[20]

Roles of the catalysts: The functions of both catalysts were examined in this cocatalytic system. In Table 1, we described



Scheme 9. Intramolecular [1,3]-migration of the acyl moiety.

that using $[Au(PMe_3)Cl]$ alone as the catalyst, no reaction occurred, and using $Yb(OTf)_3$ alone as the catalyst, the 1,3-diketone **10a** was obtained in 75% yield. Further examination of the reaction outcome revealed that no final product was formed starting from the 1,3-diketone **10a** in the presence of $[Au(PMe_3)Cl]$, presumably due to the fact that $[Au(PMe_3)Cl]$ was not active enough to activate the alkynyl bond. Thus, both $[Au(PMe_3)Cl]$ and $Yb(OTf)_3$ are necessary catalysts for the transformation of the intermediate **10a** to the final product **11a** in this reaction. As shown in entry 1 of Table 1, using the combination of $[Au(PMe_3)Cl]$ and AgOTf afforded **11a** in 59% yield, suggesting that $[Au(PMe_3)]OTf$ is a real active species in this reaction. The combination of $[Au(PMe_3)Cl]$ and $Yb(OTf)_3$ probably plays a similar role as that of $[Au(PMe_3)]OTf$, but they are more effective than $[Au(PMe_3)]OTf$ alone under the standard reaction conditions.

Moreover, several ^{31}P NMR experiments were conducted to test the catalytic roles of $[Au(PMe_3)Cl]$ and $Yb(OTf)_3$.[3b] The ^{31}P NMR spectrum of a sample of $[Au(PMe_3)Cl]$ (1.0 equiv) and $Yb(OTf)_3$ (1.0 equiv) in CH_3NO_2 at 50°C shows a sharp signal at $\delta = -7.16$ ppm (Figure 1, c) that is almost identical to that of the pure gold complex (a signal at $\delta = -7.32$ ppm; Figure 1, a). The ^{31}P NMR signal for $[Au(PMe_3)]OTf$ is at $\delta = 10.19$ ppm in CH_3NO_2 at 50°C (some of the AgOTf decomposed when AgOTf was put into the tube or in CH_3NO_2, and $[Au(PMe_3)Cl]$ was still detected; Figure 1, b). The ^{31}P NMR spectrum of a sample of $[Au(PMe_3)Cl]$ (1.0 equiv) and $Yb(OTf)_3$ (1.0 equiv) in CH_3NO_2 at 50°C changes in the presence of substrate **9a** (2.0 equiv); two signals are observed at $\delta = -6.85$ and 10.29 ppm (Figure 1, f). This might be due to the fact that there is an equilibrium between the intermediate **15a** and the intermediate **16a** (Scheme 10). When $Yb(OTf)_3$ is added, these two species are in an equilibrium that slightly favors the later species, and which results in the reaction to form the indene derivative (Scheme 10). In contrast, the ^{31}P NMR experiment in which **9a** (Figure 1, d) is mixed with $[Au(PMe_3)Cl]$ or that in which **10a** is mixed with $[Au(PMe_3)Cl]$ (Figure 1, e) under otherwise identical conditions revealed a sharp signal at $\delta = -7.16$ ppm.

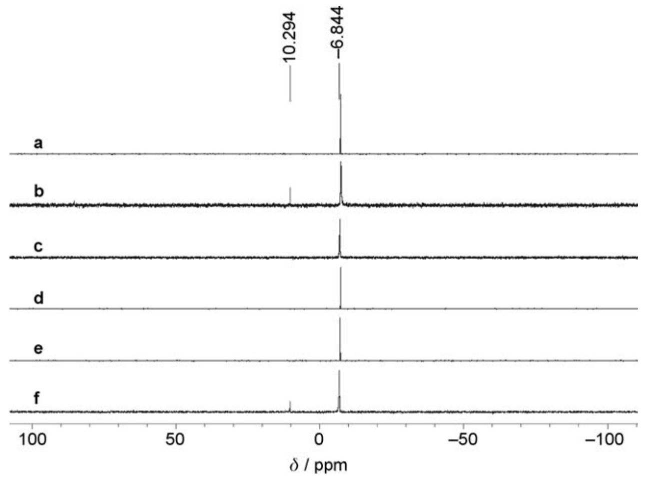
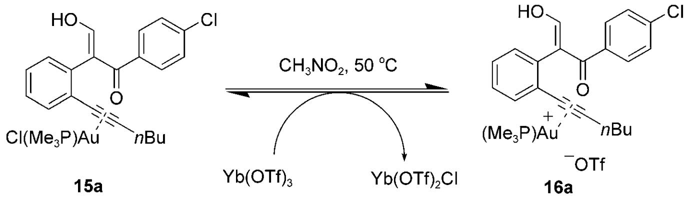


Figure 1. ^{31}P NMR spectra of experiments to determine the role of the catalysts: a) $[Au(PMe_3)Cl]$ in CH_3NO_2; b) $[Au(PMe_3)Cl]$ (1.0 equiv) and AgOTf (1.0 equiv) in CH_3NO_2; c) $[Au(PMe_3)Cl]$ (1.0 equiv) and $Yb(OTf)_3$ (1.0 equiv) in CH_3NO_2; d) a mixture of $[Au(PMe_3)Cl]$ (1.0 equiv) and substrate **9a** (2.0 equiv) in CH_3NO_2; e) a mixture of $[Au(PMe_3)Cl]$ (1.0 equiv) and substrate **10a** (2.0 equiv) in CH_3NO_2; f) a mixture of $[Au(PMe_3)Cl]$ (1.0 equiv), $Yb(OTf)_3$ (1.0 equiv), and substrate **9a** (2.0 equiv) in CH_3NO_2.



Scheme 10. Equilibrium between intermediate **15a** and intermediate **16a**.

Conclusions

A novel combination of $[Au(PMe_3)Cl]$ and $Yb(OTf)_3$ catalyzes the domino isomerization of epoxy alkynes to give functionalized indene derivatives in good yields under mild conditions.[21] Control experiments demonstrate that both $[Au(PMe_3)Cl]$ and $Yb(OTf)_3$ are necessary catalysts for the transformation of intermediate **10** to the final product **11**. $Yb(OTf)_3$ plays an important role in the reaction by promoting the rearrangement of epoxides, and by activating the alkyne–gold complex during the reaction.

Double transfer of a carbonyl group in a five-membered carbocycle or intramolecular [1,3]-migration of an acyl group might be involved in this process. Although the cleavage of carbon–heteroatom and heteroatom–heteroatom bonds along with a migration of a certain group in the presence of gold catalysts or platinum catalysts has been reported recently,[20,22] the cleavage of carbon–carbon bonds along with the migration of a certain group in gold-catalyzed reactions is rare due to the lack of reactivity and is still considered as a challenging subject. In this reaction, the cleavage of the carbon–carbon bond along with the migration of a carbonyl group is involved in the process based on the results of ^{13}C-labeling experiments.

Overall, the alkynyl α,β-epoxy ketones can be easily transformed to heterocycles and indene derivatives in the presence of gold complexes. This kind of reaction usually proceeds through two steps: isomerization of α,β-epoxy ketones to 1,3-dicarbonyl compounds followed by nucleophilic addition of 1,3-dicarbonyl compounds to the alkynyl group by employing an oxygen or carbon nucleophile. The reaction pathways are highly dependent on the structure of the employed substrates.

Experimental Section

General information: Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded in CDCl$_3$ with tetramethylsilane (TMS) as internal standard on Bruker AM-300 or AM-400 spectrometers; J values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF$_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

General procedure for the preparation of 11a: [Au(PMe$_3$)Cl] (5.1 mg, 0.015 mmol) and Yb(OTf)$_3$ (9.3 mg, 0.015 mmol) under argon were added to a solution of **9a** (101.4 mg, 0.3 mmol) in freshly distilled nitromethane (3.0 mL) at 50 °C. The reaction mixture was stirred for 11 h and was monitored by TLC plates. When the reaction was complete, the mixture was diluted with EtOAc, evaporated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, EtOAc/PE = 1:50). Compound **11a** (87.2 mg) was isolated in 87 % yield (containing some impurities). Compound **11a**: a yellow solid; IR (NaCl): $\tilde{\nu}$ = 3061, 2956, 2927, 2858, 1652, 1586, 1557, 1504, 1486, 1456, 1401, 1373, 1293, 1262, 1236, 1203, 1172, 1142, 1088, 1014 cm^{-1}; since the product **11a** exists in several forms (**11a** (Z or E) and **11a'**), the ^{1}H NMR and ^{13}C NMR spectra of **11a** are very complicated and are not presented here; MS (EI): m/z (%): 75 [M^+−263] (10.6), 111 [M^+−227] (30.7), 113 [M^+−225] (11.1), 139 [M^+−199] (100.0), 141 [M^+−197] (34.8), 338 [M]$^+$ (7.8); HRMS: m/z: calcd for $C_{21}H_{19}ClO_2$: 338.1074, found 338.1077. CCDC-715870 (**11a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] For selected very recent reviews on gold-catalyzed reactions, see: a) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; b) N. Bongers, N. Krause, *Angew. Chem.* **2008**, *120*, 2208–2211; *Angew. Chem. Int. Ed.* **2008**, *47*, 2178–2181; c) H. C. Shen, *Tetrahedron* **2008**, *64*, 3885–3903; d) H. C. Shen, *Tetrahedron* **2008**, *64*, 7847–7870; e) J. Muzart, *Tetrahedron* **2008**, *64*, 5815–5849; f) R. Skouta, C.-J. Li, *Tetrahedron* **2008**, *64*, 4917–4938; g) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; h) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; i) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; j) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; k) N. T. Patil, Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 3395–3442; l) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766–1775; m) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776–1782.

[2] G. Kovács, G. Ujaque, A. Lledós, *J. Am. Chem. Soc.* **2008**, *130*, 853–864.

[3] a) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem.* **1998**, *110*, 1475–1478; *Angew. Chem. Int. Ed.* **1998**, *37*, 1415–1418; b) M. T. Reetz, K. Sommer, *Eur. J. Org. Chem.* **2003**, 3485.

[4] a) A. S. K. Hashmi, P. Sinba, *Adv. Synth. Catal.* **2004**, *346*, 432–438; b) L.-Z. Dai, M.-J. Qi, Y.-L. Shi, X.-G. Liu, M. Shi, *Org. Lett.* **2007**, *9*, 3191–3194; c) X.-Z. Shu, X.-Y. Liu, H.-Q. Xiao, K.-G. Ji, L.-N. Guo, C.-Z. Qi, Y.-M. Liang, *Adv. Synth. Catal.* **2007**, *349*, 2493–2498; d) M.-C. Cordonnier, A. Blanc, P. Pale, *Org. Lett.* **2008**, *10*, 1569–1572.

[5] a) H. O. House, G. D. Ryerson, *J. Am. Chem. Soc.* **1961**, *83*, 979–983; b) R. C. Klix, R. D. Bach, *J. Org. Chem.* **1987**, *52*, 580–586; c) R. D. Bach, R. C. Klix, *J. Org. Chem.* **1985**, *50*, 5438–5440; d) R. D. Bach, J. M. Domagala, *J. Org. Chem.* **1984**, *49*, 4181–4188; e) R. D. Bach, R. C. Klix, *Tetrahedron Lett.* **1985**, *26*, 985–988.

[6] a) M. Nakamura, K. Endo, E. Nakamura, *J. Am. Chem. Soc.* **2003**, *125*, 13002–13003; b) K. Endo, T. Hatakeyama, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2007**, *129*, 5264–5271; c) T. Fujimoto, K. Endo, H. Tsuji, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2008**, *130*, 4492–4496; d) Y. Itoh, H. Tsuji, K. Yamagata, K. Endo, I. Tanaka, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2008**, *130*, 17161–17167.

[7] B. K. Corkey, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 17168–17169.

[8] M. Nakamura, T. Fujimoto, K. Endo, E. Nakamura, *Org. Lett.* **2004**, *6*, 4837–4840.

[9] a) J. J. Kennedy-Smith, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2004**, *126*, 4526–4527; b) S. T. Staben, J. J. Kennedy-Smith, F. D. Toste, *Angew. Chem.* **2004**, *116*, 5464–5466; *Angew. Chem. Int. Ed.* **2004**, *43*, 5350–5352.

[10] a) A. Ochida, H. Ito, M. Sawamura, *J. Am. Chem. Soc.* **2006**, *128*, 16486–16487; b) H. Ito, Y. Makida, A. Ochida, H. Ohmiya, M. Sawamura, *Org. Lett.* **2008**, *10*, 5051–5054.

[11] a) C. H. M. Amijs, V. López-Carrillo, A. M. Echavarren, *Org. Lett.* **2007**, *9*, 4021–4024; b) X.-Q. Yao, C.-J. Li, *J. Am. Chem. Soc.* **2004**, *126*, 6884–6885; c) R.-V. Nguyen, X.-Q. Yao, D. S. Bohle, C.-J. Li, *Org. Lett.* **2005**, *7*, 673–675; d) C.-Y. Zhou, C.-M. Che, *J. Am. Chem. Soc.* **2007**, *129*, 5828–5829; e) C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer, A. M. Echavarren, *J. Org. Chem.* **2008**, *73*, 7721–7730.

[12] L.-Z. Dai, M. Shi, *Eur. J. Org. Chem.* **2009**, 3129–3133.

[13] L.-Z. Dai, M. Shi, *Tetrahedron Lett.* **2009**, *50*, 651–655.

[14] a) L.-Z. Dai, M. Shi, *Chem. Eur. J.* **2008**, *14*, 7011–7018; b) L.-Z. Dai, M. Shi, *Tetrahedron Lett.* **2008**, *49*, 6437–6439.

[15] J.-H. Pan, M. Yang, Q. Gao, N.-Y. Zhu, D. Yang, *Synthesis* **2007**, 2539–2544.

[16] For reactions of Au–carbenoid intermediates, see: a) C. Nieto-Oberhuber, M. P. Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 2456–2460; *Angew. Chem. Int. Ed.* **2004**, *43*, 2402–2406; b) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654–8655; c) A. Fürstner, P. Hannen, *Chem. Commun.* **2004**, 2546–2547; d) M. R. Luzung, J. P. Markham, F. D. Toste, *J. Am. Chem. Soc.* **2004**, *126*, 10858–10859; e) I. D. G. Watson, S. Ritter, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 2056–2057; f) H.-S. Yeom, J.-E. Lee, S. Shin, *Angew. Chem.* **2008**, *120*, 7148–7151; *Angew. Chem. Int. Ed.* **2008**, *47*, 7040–7043; g) Y.-C. Hsu, C.-M. Ting, R.-S. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 2090–2091; h) L. Zhang, S. Wang, *J. Am. Chem. Soc.* **2006**, *128*, 1442–1443; i) G. Li, L. Zhang, *Angew. Chem.* **2007**, *119*, 5248–5251; *Angew. Chem. Int. Ed.* **2007**, *46*, 5156–5159; j) L. Peng, X. Zhang, S. Zhang, J. Wang, *J. Org. Chem.* **2007**, *72*, 1192–1197; k) C. H. Oh, S. J. Lee, J. H. Lee, Y. J. Na, *Chem. Commun.* **2008**, 5794–5796; l) A. S. K. Hashmi, M. Rudolph, J. P. Weyrauch, M. Wölfle, W. Frey, J. W. Bats, *Angew. Chem.* **2005**, *117*, 2858–2861; *Angew. Chem. Int. Ed.* **2005**, *44*, 2798–2801; m) M. R. Fructos, T. R. Belderrain, P. de Frémont, N. M. Scott, S. P. Nolan, M. M. Díaz-Requejo, P. J Pérez, *Angew. Chem.* **2005**, *117*, 5418–5422; *Angew. Chem. Int. Ed.* **2005**, *44*, 5284–5288.

[17] J. P. Markham, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 9708–9709.

[18] For gold-catalyzed reactions involving oxonium, see: a) N. Asao, K. Takahashi, S. Lee, T. Kasahara, Y. Yamamoto, *J. Am. Chem. Soc.* **2002**, *124*, 12650–12651; b) E. Jiménez-Núñez, C. K. Claverie, C. Nieto-Oberhuber, A. M. Echavarren, *Angew. Chem.* **2006**, *118*, 5578–5581; *Angew. Chem. Int. Ed.* **2006**, *45*, 5452–5455; c) M. Schelwies, A. L. Dempwolff, F. Rominger, G. Helmchen, *Angew. Chem.* **2007**, *119*, 5694–5697; *Angew. Chem. Int. Ed.* **2007**, *46*, 5598–5601.

[19] Examples of the direct nucleophilic attack of alkyne–gold complexes by epoxide oxygen atoms, see: a) A. S. K. Hashmi, M. Bührle, R. Salathé, J. W. Bats, *Adv. Synth. Catal.* **2008**, *350*, 2059–2064; b) G.-Y. Lin, C.-W. Li, S.-H. Hung, R.-S. Liu, *Org. Lett.* **2008**, *10*, 5059–5062; c) X.-Z. Shu, X.-Y. Liu, K.-G. Ji, H.-Q. Xiao, Y.-M. Liang, *Chem. Eur. J.* **2008**, *14*, 5282–5289.

[20] For a $PtCl_2$-catalyzed intramolecular [1,3]-migration of an acyl moiety, see: T. Shimada, I. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 10546–10547.

[21] For reports on indene synthesis by gold catalysis, see: a) N. Marion, S. Díez-González, P. de Frémont, A. R. Noble, S. P. Nolan, *Angew. Chem.* **2006**, *118*, 3729–3732; *Angew. Chem. Int. Ed.* **2006**, *45*, 3647–3650; b) C. M. Grisé, E. M. Rodrigue, L. Barriault, *Tetrahedron* **2008**, *64*, 797–808; c) J. T. Bauer, M. S. Hadfield, A.-L. Lee, *Chem. Commun.* **2008**, 6405–6407; d) Z.-B. Zhu, M. Shi, *Chem. Eur. J.* **2008**, *14*, 10219–10222.

[22] Migration of allyl groups: a) S. Cacchi, G. Fabrizi, P. Pace, *J. Org. Chem.* **1998**, *63*, 1001–1011; b) A. Fürstner, P. W. Davies, *J. Am. Chem. Soc.* **2005**, *127*, 15024–15025; propargyl groups: c) S. Cacchi, G. Fabrizi, L. Moro, *Tetrahedron Lett.* **1998**, *39*, 5101–5104; allyl groups: d) A. Arcadi, S. Cacchi, M. D. Rosario, G. Fabrizi, F. Marinelli, *J. Org. Chem.* **1996**, *61*, 9280–9288; e) S. Cacchi, G. Fabrizi, L. Moro, *Synlett* **1998**, 741–745; f) N. Monteiro, G. Balme, *Synlett* **1998**, 746–747; g) A. Fürstner, H. Szillat, F. Stelzer, *J. Am. Chem. Soc.* **2000**, *122*, 6785–6786; h) A. Fürstner, F. Stelzer, H. Szillat, *J. Am. Chem. Soc.* **2001**, *123*, 11863–11869; α-alkoxyalkyl groups: i) I. Nakamura, Y. Mizushima, Y. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 15022–15023; sulfonyl group: j) I. Nakamura, U. Yamagishi, D. Song, S. Konta, Y. Yamamoto, *Angew. Chem.* **2007**, *119*, 2334–2337; *Angew. Chem. Int. Ed.* **2007**, *46*, 2284–2287.

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