CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

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To be cited as: *Chem. Eur. J.* 10.1002/chem.201905199

Link to VoR: http://dx.doi.org/10.1002/chem.201905199

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$AuCl_3$-Catalyzed Ring-Closing Carbonyl–Olefin Metathesis

Rui Wang,[+a] Yi Chen, [+a] Mao Shu,[+a] Wenwen Zhao,[a] Maoling Tao,[a] Chao Du,[a] Xiaoya Fu,[a] Ao Li,*[a] Zhihua Lin,*[a]

Abstract: Compared with the ripeness of olefin metathesis, exploration of the construction of carbon–carbon double bond through the catalytic carbonyl–olefin metathesis reaction remains stagnant and has received scant attention. Herein, a highly efficient $AuCl_3$-catalyzed intramolecular ring-colsing carbonyl−olefin metathesis reaction is described. This method features easily accessible starting materials, simple operation, good functional group tolerance and short reaction time, and provided target cyclopentenes, polycycles, benzocarbocycles, and N-heterocycles derivatives in good to excellent yields.

Carbon-carbon double bond formation is one of the useful and fundamental reactions in synthetic organic chemistry, particularly in the synthesis of complex natural products, bioactive molecules, synthetic drugs and functional organic materials.[1] Generally, conventional wisdom states that the construction of carbon-carbon double bond mostly relies on the olefination of carbonyl compounds and olefin metathesis. Since the pioneering work by Wittig, Horner and Emmons, the synthesis of alkenes by the olefination of carbonyl compounds has evolved as one of the most efficient methods, which use phosphorus, sulfur and silicon ylides as highly polarized nucleophilic components add to carbonyl derivatives.[2]Olefin metathesis is another more important approach to obtain olefins and has brought about a huge development of many applications in synthetic organic chemistry, since the discovery of second generation catalysts consisting of well-defined metal-carbene complexes, which mostly based on stable molybdenum or ruthenium.[3] Compared with the ripeness of olefin metathesis and Horner–Wadsworth–Emmons reactions, other double-bond metathesis reactions is much less developed,[4] but these metathesis reactions should hold great potential for complex molecular synthesis through one step synthetic transformation. Among them, the hitherto elusive carbonyl–olefin metathesis may be the most powerful alternative which are appeared in the some applications for the total synthesis of natural products and construction of complex molecules, usually, these molecules are difficult to synthesis by other methods.[5] However, the historical early reports based on photo-induced，stoichiometric amounts of transition-metal-promoted and even metal alkylidenes mediated carbonyl–olefin metathesis hampered the practicality because of limitations for substrates bearing chromophores, harsh reaction conditions, competing polymerization, high cost and environmental pollution.[6] The fundamental cause of the stagnancy about carbonyl-olefin metathesis lies in: 1) the difficulties in establishing a catalytic version due to the formation of a kinetically inert metal-oxo complex during the cycloreversion step; 2) potential side reactions such as polymerization, ene reaction, alkylation and Prins reaction etc.; 3) regeneration of starting carbonyl-olefin pairs.

Recently, the real breakthrough has begun to dawn because of strategies and catalysts, so called catalytic carbonyl–olefin metathesis reactions were demonstrated.[7] In a pioneering studies in 2012, Lambert established an organocatalytic [3+2]/retro [3+2]-cycloaddition approach to synthesis γ,δ-unsaturated aldehydes through carbonyl–olefin metathesis reactions, but the requirement of highly strained cyclopropenes as olefin components and the tedious preparation of the starting materials impeded its application (Scheme 1a).[8] Lambert has subsequently extended this strategy to the synthesis of 2H-chromenes. [8d]Transiently coordination of the Lewis acid to the carbonyl oxygen will promote cycloaddition and cycloreversion, obviating the formation of inert metaloxo-byproduct and making the bona fide catalytic carbonyl–olefin metathesis become true. Based on this, groups of Schindler and Li independently disclosed that $FeCl_3$ was a high efficient catalyst which allowed carbonyl–olefin metathesis reaction to proceed with [2+2]-cycloaddtion/[2+2]-cycloreversion efficiently, the substrate scope which went beyond previous work. Subsequently, Schindler extended this catalyst to the synthesis of the polycyclic aromatics, functionalized pyrrolines (Scheme 1b).[9] Nguyen and Franzén groups have demonstrated that carbocation could efficiently assist catalytic carbonyl–olefin metathesis reactions, shedding light on the potential of organic Lewis acid (Scheme 1c).[10] Very recently, benign supramolecule and molecular iodine catalysts were also uncovered.[11]Later on, exploratory work of catalytic ring-opening cross-metathesis and more clever reaction design were described which will offer new opportunities for carbonyl–olefin metathesis.[12]

Despite some achievements made in past three years, catalytic carbonyl–olefin metathesis reactions are still in the infancy status, and there are still many challenges and limitations, for instance: 1) to the best of our knowledge, catalytic carbonyl–olefin metathesis reaction promoted by Lewis acid only was limited to $FeCl_3$, $GaCl_3$ and organic Lewis acid to date, more diverse catalytic system should be discovered; 2) the catalytic aldehyde–olefin metathesis still remains stagnant,[10b], [12a], [13] an urgent need to expand the relatively narrow substrate scope of catalytic carbonyl–olefin metathesis reaction.

Along these lines, herein, we would like to report our recent efforts toward catalytic carbonyl–olefin metathesis via $AuCl_3$-catalyzed intramolecular cyclization providing the corresponding cyclic olefin, polycycles, benzocarbocycles, and N-heterocycles derivatives with good to excellent yields (Scheme 1d).

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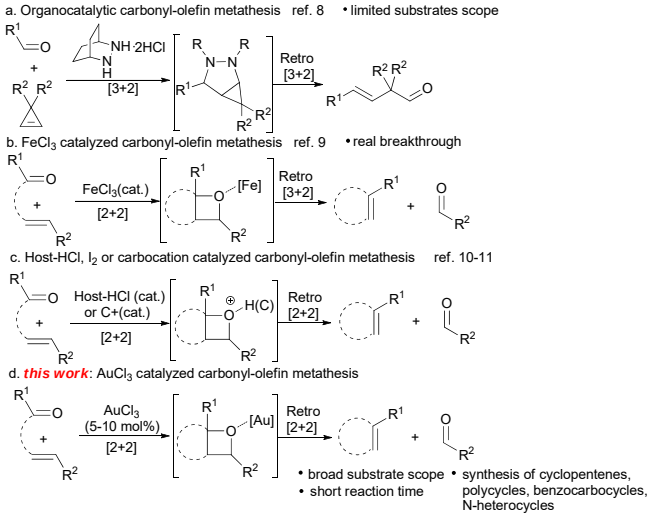
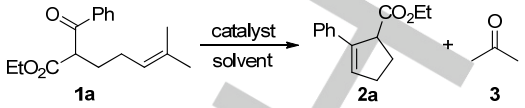


Scheme 1. Catalytic carbonyl–olefin metathesis.

Our study commenced by examining the intramolecular reactions of β-ketoesters bearing a pendant isoprenyl group **1a** in the presence of different Lewis acid, as summarized in Table 1. Except those transition metal catalysts such as Fe, In, Sc, Yb, Ti, Sn, Zn and B which have been investigated by Schindler and others we screened other many transition metal catalysts.[9] After elaborate screening experiments, it was delighted to find that when $AuCl_3$ was used as the catalyst, the desired ring-closing product **2a** was obtained in 99% isolated yield at 25°C for 24h (entry 1). Fortunately, potential competing side reactions were not observed, meanwhile, the reaction time could be reduced to 3 h without compromising the reaction yield (entry 1), obviously, $AuCl_3$ was found to be more efficiently than the $FeCl_3$, carbocation or host-HCl system. Furthermore, the LC-MS comparison of $AuCl_3$ vs $FeCl_3$ and NMR experiments can also confirm the efficacy of $AuCl_3$ (Figure S1 and S2). Additionally, no reaction occurred when using Mn, Co, Ni, Cu, and Ag salts as catalysts (entries 2-9). Further evaluation related to noble transition metal salts (entries 10-15) and salts of trifluoromethanesulfonic acid (entries 19-21) revealed that no desired product was detected except $In(OTf)_3$ which gave moderate yield, in these reaction we could discover small amounts of chlorinated or/and its subsequent alkylation product. Notably, $BiCl_3$ could also catalyze the reaction and the corresponding yield was enhanced up to 80%. While using $GaCl_3$ as catalyst, a substantial decrease in the yield of **2a** was observed (entries 16-18). Subsequently, various solvents were screened. As listed in entries 22-25, no product or inferior yield was observed in other solvents, and DCE appeared preferable with regard to reaction time and product yield. Unfortunately, decreasing the amount of catalyst diminished the efficiency (entry 26). Moreover, the purity of $AuCl_3$ and oxidation state of the gold catalyst also had great influence on the reaction, sublimed grade $AuCl_3$ (>99.9%) afforded quantitative yield of **2a** under anhydrous conditions and reagent grade $AuCl_3$ trihydrate was suitable catalyst but longer reaction time was needed (Table 1, entries 27-28), AuCl was not effective to catalyze this ring-closing reaction (Table 1, entry 29).

Table 1. Evaluation of reaction conditions[a]



1a **2a** **3**

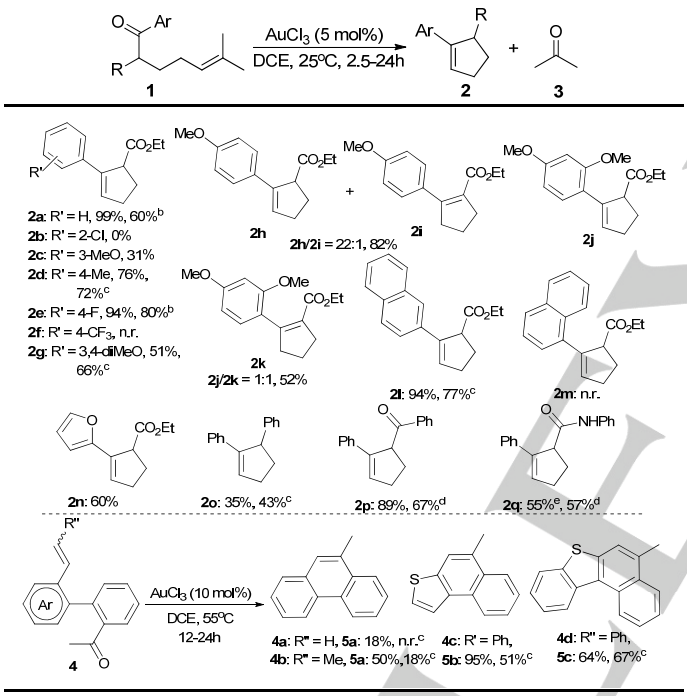
Entry	Catalyst (5 mol%)	Solvent	Yield [%][b]
1	$AuCl_3$	DCE	99/99[c]
2	$Mn(OAc)_3$	DCE	n.r.
3	$CoCl_2$	DCE	n.r.
4	$NiCl_2$	DCE	n.r.
5	$CuCl_2$	DCE	n.r.
6	$NbCl_5$	DCE	n.d.(<5)
7	$AgNO_3$	DCE	n.r.
8	Ag_2CO_3	DCE	n.r.
9	AgOTf	DCE	n.r.
10	$IrCl_3$	DCE	n.d.(<5)
11	$RuCl_3$	DCE	n.d.(<5)
12	$RhCl_3$	DCE	n.d.(<5)
13	$Rh(OAc)_2$	DCE	n.r.
14	$PdCl_2$	DCE	n.d.
15	Pd(TFA)	DCE	n.d.
16	$BiCl_3$	DCE	80
17	$GaCl_3$	DCE	55[d]
18	$CeCl_3$	DCE	n.r.
19	$Ni(OTf)_3$	DCE	n.r.
20	$Cu(OTf)_2$	DCE	n.r.
21	$In(OTf)_3$	DCE	43
22	$AuCl_3$	Dioxane/ Ether/THF	<5
23	$AuCl_3$	DCM/Toluene	84/n.r.
24	$AuCl_3$	DMF/ DMSO	n.r
25	$AuCl_3$	CH_3CN/ MeOH	n.d.
26[e]	$AuCl_3$	DCE	90
27[c,f]	$AuCl_3$	DCE	99
28[g]	$AuCl_3{\cdot}3H_2O$	DCE	35/96
29[h]	AuCl	DCE	<10

[a] Reaction conditions: **1a** (0.20 mmol), catalyst (0.02 mmol, 10 mol%), solvent (20 mL), 25°C, in a sealed tube, 24 h. [b] Isolated yield after column chromatograph, the yield values in parentheses were the conversion of side products. [c] 3 h. [d] see Ref [9d]. [e] $AuCl_3$ (2.5 mol%). [f] Sigma-Aldrich, sublimed grade, >99.9% trace metal basis. [g] yields of 3h and 24h, respectively. [h] Alfa, 99.99%. n.d.=not detected, n.r.=no reaction. DCE=1,2-dicholoroethane, DCM=dicholoromethane, DMF=N,N-dimethylformamide, DMSO = dimethyl sulfoxide.

With the optimal conditions established, the generality of the synthetic method for preparing cyclic olefin derivatives was subsequently investigated (Table 2). Gratifyingly, various substituted β-ketoesters bearing a pendant isoprenyl group could smoothly undergo annulation to furnish the desired cyclopentene derivatives in good to excellent yields. Firstly, the influence of the substituents on the benzene ring moiety was evaluated (**2a**-**2k**). Benzene ring backbones bearing electron-donating or -withdrawing groups were compatible with optimized protocol. When 4-methyl and 4-fulorophenyl substituted β-ketoesters were employed, the corresponding products were obtained in high to excellent yield (**2d** and **2e**). Slightly lower yields could be obtained when using the 3-methoxy, 3,4-dimethoxy and 2,4-dimethoxyphenyl substituted β-ketoesters as substrates (**2c**, **2g**, **2j** and **2k**). It was worth noting that the transformation of 4-methyoxyphenyl substituted β-ketoesters was more selective compared to the approach mediated by $FeCl_3$ or Host-HCl,[9a], [11a] the former afforded the higher selectivity of isomer **2h** probably due to quickly reaction catalyzed by $AuCl_3$, and decreased the generation of thermodynamically stable products. Furthermore, the isomers of

2j and **2k** were both individually isolated by column chromatograph. Switching the phenyl ring with β-naphthalene ring gave the corresponding cyclopentene derivatives **2l** in 94% yields which was far higher than 77% yield catalyzed by $FeCl_3$.[9a] In addition, Furan ring was tolerated and performed smoothly, furnishing the **2n** in 60% yield. Unfortunately, several groups remained as limitations to the current methods, the reaction did not take place with **2b**, **2f,** and **2m**, presumably contribute to the strong ability of enolization of ortho-chloro, the trifluoromethyl and steric hindrance of α-naphthalene nucleus (unreported substrates). We then surveyed the scope of β-substitutions, for instance, phenyl, benzoyl and benzamidyl motifs were all tolerated (**2o**-**2q**), with regard to benzoyl group the $AuCl_3$ was more appropriate choice of catalyst (**2p**, 89% vs 67%). Notably, the substrates **2p** and **2q** needed stoichiometric amounts of $FeCl_3$ for full conversion.[9a]

Table 2. Substrate scope for the synthesis of five-membered carbocycles and polycyclic aromatic compounds [a]

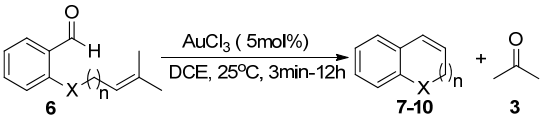


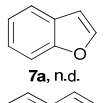
[a] Reaction conditions: all reactions were performed with **1** (or **4**, 0.2 mmol), $AuCl_3$ (0.02 mmol), and DCE (20 mL) at 25°C (or 55°C for **4**) for 2-24h, all yields refer to isolated yield. [b] 0.5 h. [c] 10 mol % $FeCl_3$. [d] Stoichiometric amount of $FeCl_3$, also see Ref [9a]. [e] At 55°C. Ratios were determined by ^1H NMR analysis. n.r. = no reaction.

Next, we questioned whether polycyclic aromatic compounds could be prepared by $AuCl_3$-catalyzed carbonyl−olefin metathesis approach, which are privileged structures in biologically active natural and unnatural products, and functional organic materials. [9c],[14] As expected, when R'' was hydrogen or methyl groups which is more atom economical and less environmental pollution than the substituents of phenyl groups since large amounts of benzaldehyde are generated as by-product (Table 2), formed the methyl phenanthrenes in 18% and 50% yields, respectively (**5a**).[9c] In the case of sulfur-containing heterocycles, higher yields of products were obtained compared with the catalyst of $FeCl_3$ (**5b**).

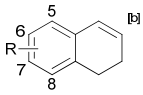
To further expand the scope of our protocol, we next focused on the synthesis of benzocarbocycles.[14] Initially, ethers and unprotected amines were unsuitable substrates due to the cleavage of carbon-oxygen and carbon-nitrogen bond promoted by $AuCl_3$ (Table 3, **7a**-**c**).[8d] This type of cabonyl–olefin metathesis involving aldehydes is essentially unknown.[10b],[12a],[13] To our delight, the generality of $AuCl_3$-catalyzed aldehyde−olefin metathesis reaction was further verified with benzocarbocycles backbones. It's indeed the case, as shown in Table 3, substituted 2-(4-methylpent-3-en-1-yl) benzaldehydes, which could be easily prepared by Sabitha's procedure,[15] were found to be superior substrates under the standard conditions, affording the corresponding dihydronaphthalene derivatives (**8a**-**8i**) in good to excellent yields. Generally, both electron-donating and -withdrawing groups at the benzene ring were compatible with the $AuCl_3$ catalytic system, and substituents at the different position did not influence the yields dramatically. It is particularly noteworthy that the most of the reactions could be accomplished within a few minutes, 5 mol% $AuCl_3$ was enough to initiate the reaction, delivering the corresponding 1,2-dihydronaphthalene products. This observation could be attributed to the suppression of a side reaction because of extremely quickly reaction. On the other hand, fluorine, chloride and bromide groups on different positions of the phenyl rings proceeded smoothly, providing the opportunity for downstream applications via classic cross-coupling reactions (**8e**-**8f**, **8h**-**8i**). Furthermore, of note, the strong electron-withdrawing groups such as CF_3 and NO_2 were not compatible under the standard conditions, probably the isomerization of double bond in substrates promoted by the strong electron-withdrawing groups. Encouraged by the above results, we extended this protocol to seven-membered and five-membered benzocarbocycles (**9a**-**9i** and **10a**-**10i**). As expected, the corresponding benzo[7]annulene derivatives were obtained in good to excellent yield from the annulations of substituted benzaldehydes. Notably, as far as indene derivatives were concerned, $BiCl_3$ was more suitable choice of catalyst than previously $AuCl_3$ catalyst. In general, their electronic properties were similar to dihydronaphthalenes, the synthesis of seven-membered benzocarbocycles mediated by $AuCl_3$ was more effective compared with the indene derivatives and the reduced reaction rate needed to be compensated by increasing the reaction time, and the diminished yields probably due to the partially decomposition of product. Additionally, the present method does not permit the construction of benzo[8]annulene.

Table 3. Substrate scope for $AuCl_3$ catalyzed aldehyde–olefin ring closing metathesis [a]

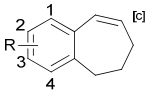




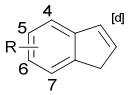
7a, n.d.



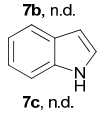
8a: R = H, 82%
8b: R = 5-Me,88%
8c: R = 6-MeO,83%
8d: R = 7-Me,94%
8e: R = 7-F, 92%
8f: R = 7-Cl, 90%
8g: R = 8-Me,78%
8h: R = 8-F,78%
8i: R = 8-Cl,96%



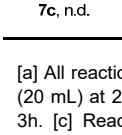
9a: R = H, 74%
9b: R = 1-Me, 83%
9c: R = 2-MeO, 72%
9d: R = 3-Me, 92%
9e: R = 3-F, 99%
9f: R = 3-Cl, 90%
9g: R = 4-Me, 86%
9h: R = 4-F, 88%
9i: R = 4-Cl, 75%



10a: R = H, 46%[e]
10b: R = 4-F, 60%
10c: R = 5-Me, 58%
10d: R = 5-MeO, 50%
10e: R = 5-Cl, 62%
10f: R = 6-Me, 60%
10g: R = 6-MeO, 55%
10h: R = 6-F, 65%
10i: R = 7-F, 62%



7b, n.d.



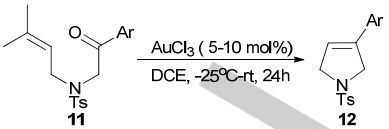
7c, n.d.

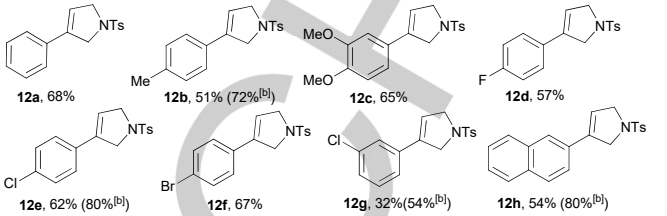
[a] All reactions were conducted with 6 (0.4 mmol), $AuCl_3$ (5 mol%), and DCE (20 mL) at 25°C, all yields refer to isolated yield. [b] Reaction time was 3min-3h. [c] Reaction time increased to 18-20h. [d] 10 mol% $BiCl_3$ as catalyst, reaction time increased to 12-20h. [e] When using 10 mol% of $AuCl_3$ and $FeCl_3$ as catalyst, only gave 20% and 0% yields, respectively.

Afterward, we turned our attention to evaluate the compatibility with five-membered N-heterocycles which are key scaffold in biological and medicinal chemistry. At present, the synthesis of dihydropyrrole based on iron (III)-catalyzed carbonyl-olefin metathesis primarily relies on the additive of excessive allyltrimethylsilane (5.0 equiv) or subtle adjusting of electron-deficient nitrogen protecting group, and lacking the straightforward approaches.[9b], [9e],[11b] and [16] We questioned if $AuCl_3$-catalyzed system could be applicable to the synthesis of dihydropyrrole. Disappointedly, an initial attempt found that the ring-closing metathesis of **11a** only afforded the deallylation product in 90% yield, and small amount of starting materials, while decreasing the temperature to -30°C completely recovered the starting materials. Obviously, reaction temperature played vital role in this transformation. After many trials and errors, we found that slowly gradual warming-procedure through simple temperature controlling was suitable for this transformation, more to the point, the desired dihydropyrrole derivatives were formed selectively and reaction background was clean. Under the optimized reaction conditions, we continued to investigate the substrate scope of various aroyl moieties of **11**. As shown in Table 4, both electron-deficient and electron-rich substituents on the aromatic ring reacted smoothly, affording the desired products in moderate to good yields. Substituents with methyl, methoxy, fuloro, chloro, bromo, and napthyl were well tolerated in our system, similar to the system of molecular iodine,[11b] substrates with the heteroaromatic furan, thiophene moieties failed to provide the metathesis products, being mostly recovered after 24h, perhaps a consequence of competitive binding to the substrates resulting in the inhibition of catalytic activity.[9e] Additionally, it is worth mentioning that the reactions of substrates with aliphatic ketones and steric hindrance ketones were sluggish under the standard conditions, and molecular iodine was also ineffective.

Encouraged by the aforementioned intramolecular carbonyl-olefin metathesis reaction, we extended the method to intermolecular and ring-opening carbonyl-olefin metathesis reaction. Disappointingly, the reaction only gave trace amount of product under standard reaction conditions.

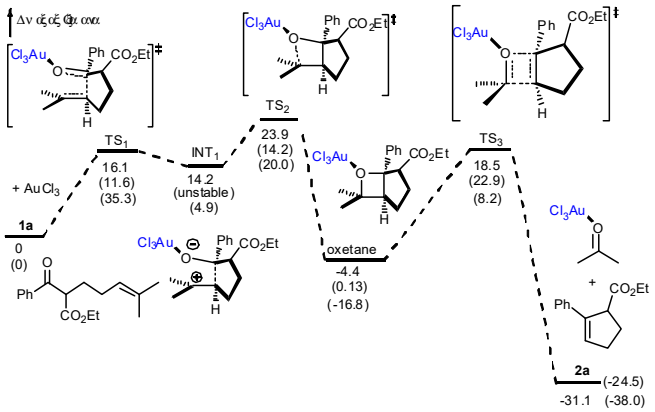
Table 4. Substrate scope for $AuCl_3$ catalyzed aldehyde–olefin ring closing metathesis [a]





[a] See page S18 in the ESI. [b] Yields are based on recovered starting material.

To gain mechanistic insight into this transformation, several control experiments were conducted (see the ESI for details). Attempts to trap the possible carbocationic species using MeOH failed to give any corresponding products, indicating that a carbocation intermediate may not be involved and this transformation doesn't contain a stepwise process. Furthermore, the by-product of acetone could be observed clearly in situ NMR experiments, similar to $FeCl_3$-catalyzed carbonyl−olefin metathesis. To further shed light on this transformation, the density functional theory (DFT) calculations were employed. Our studies show that, when using $AuCl_3$ as catalyst, the energy barrier for TS_1 is modest at 16.1kcal/mol, the formation of INT_1 is mildly exergonic ($TS_1 \rightarrow INT_1$). Notably, the formation of TS_2 is endergonic, and leads to the gold-bound oxetane intermediate in an exergonic fashion (-4.4 kcal/mol), the activation energy from oxetane to TS_3 requires 18.5 kcal/mol, and cycloreversion into the final adduct and actone is stongly exergonic. It is clear from the calculations that the reaction is significantly enhanced by $AuCl_3$, the rate-limiting step for this pathway is about 38 kcal/mol lower compared to the uncatalyzed pathway (TS_2: 23.9 vs 61.8 kcal/mol, see the ESI about uncatalyzed pathway). The computational comparison among the pathway of $AuCl_3$, $GaCl_3$, and $BiCl_3$ show that the energy barrier for TS_1 in the $BiCl_3$-catalyzed pathway is 19.4kcal/mol higher than that of $AuCl_3$, so the formation of the carbon–carbon bond need higher energy. Although the $GaCl_3$-catalyzed pathway own the lowest-barrier of TS_1 and TS_2, the TS_3 energy was found to be higher that of $AuCl_3$ (shown in the parentheses, Scheme 2). The catalyst of $GaCl_3$ is less effective, probably due to the competition of intramolecular side reactions (Table 1, entry 17, 55% yield). Generally, the calculations suggest that the reaction mechanism includes a concerted, asynchronous formation of the oxetane intermediate and concerted, asynchronous oxetane fragmentation two-stage process as shown in Scheme 2. These results indicated that this mechanism catalyzed by $AuCl_3$ is analogous to that of $FeCl_3$ described by Schlinder and co-workers.[9d]



Scheme 2. DFT calculations for metathesis reaction catalyzed by $AuCl_3$, the free energies in the parentheses are the pathway in the presence of $GaCl_3$ and $BiCl_3$, respectively.

In conclusion, we have successfully developed a mild $AuCl_3$-catalyzed intramolecuar ring-colsing carbonyl−olefin metathesis reaction providing target cyclopentenes, polycycles and N-heterocycles derivatives in good to excellent yields, especially this method offers a facile entry to benzocarbocycles through intramolecuar ring-colsing aldehyde–olefin metathesis. This method features easily accessible starting materials, simple operation, broad substrate scope, good functional group tolerance and short reaction time. All of these combined with the importance of target molecule make this new method a useful advancement for recent reports about carbonyl−olefin metathesis reaction and paradigms in retrosynthetic analysis of complex molecules. Further studies on extending the use of the methodology to macrocycles are underway.

Acknowledgements

We gratefully acknowledge support from CSTC (2015jcyjA90023, 2015jcyjBX0080), the Innovative Research Team Development Program in University of Chongqing (No. cxtdx201601031), and the Scientific and Technological Research Program of Chongqing Municipal Education Commission (KJ1600906, KJZD-K201801102) for financial support.

Keywords: Catalytic carbonyl–olefin Metathesis • gold catalysis• benzocarbocycles • heterocycles• aldehyde–olefin metathesis

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10.1002/chem.201905199

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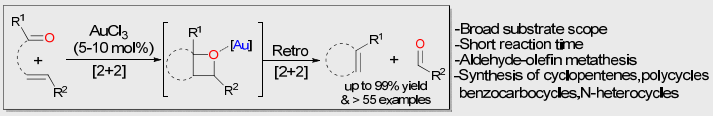

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$AuCl_3$-Catalyzed Ring-Closing Carbonyl–Olefin Metathesis

$AuCl_3$ could efficiently catalyze intramolecular ring-colsing carbonyl−olefin metathesis reaction providing target cyclopentenes, phenanthrenes, benzocarbocycles, and N-heterocycles derivatives in good to excellent yields. This method features easily accessible starting materials, simple operation, broad substrate scope, good functional group tolerance and short reaction time.