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Cite this: *Chem. Commun.*, 2012, **48**, 10271–10279

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FEATURE ARTICLE

Transition metal-catalyzed carbocyclization of nitrogen and oxygen-tethered 1,*n*-enynes and diynes: synthesis of five or six-membered heterocyclic compounds

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Received 3rd July 2012, Accepted 31st July 2012
DOI: 10.1039/c2cc34739c

Cycloisomerization of 1,*n*-enynes and diynes is a powerful method in organic synthesis to access heterocyclic compounds and has drawn increasing attention from organic chemists. In this paper, we attempted to summarize our recent results on the transition metal-catalyzed cycloisomerization to synthesize five or six-membered heterocyclic compounds using 1,*n*-enynes and diynes having a propargylic ester moiety. First, we will describe the synthesis of 2,3-disubstituted 3-pyrrolines *via* gold catalyzed cycloisomerization of 1,6-diynes. In addition, we will also disclose a novel silver catalyzed tandem 1,3-acyloxy migration/Mannich-type addition/elimination of the sulfonyl group of *N*-sulfonylhydrazone-propargylic esters to 5,6-dihydropyridazin-4-one derivatives. Furthermore, we will introduce three interesting examples of the synthesis of bicyclic compounds *via* titanium or rhodium catalyzed carbocyclization of enynes. In this context, we have presented that 1,*n*-enynes and diynes containing propargylic esters are highly reactive and useful starting materials for the cycloisomerization catalyzed by a transition metal catalyst.

1. Introduction

Heterocyclic compounds are worth our attention for their biological properties, and many drugs are heterocycles.[1] Although a tremendous number of synthetic methods to approach heterocyclic compounds have been known, the development of newer and more efficient protocols remains an area of ongoing interest in organic synthesis.[2] Transition metal-catalyzed reactions are some of the most attractive methodologies for synthesizing heterocyclic compounds,[3] since a transition metal-catalyzed reaction can directly construct complicated molecules from readily accessible starting materials under mild conditions.[4] As Nakamura and Yamamoto proposed,[3d] the construction of heterocyclic skeletons is classified into two major processes: (1) C–C bond formation from the corresponding acyclic precursors; (2) C–Y bond formation from the corresponding acyclic precursors (Scheme 1). The synthesis of heterocycles *via* the cycloisomerization of enynes belongs to category 1.

The transition metal-catalyzed enyne cycloisomerization is among the most important strategies for the synthesis of

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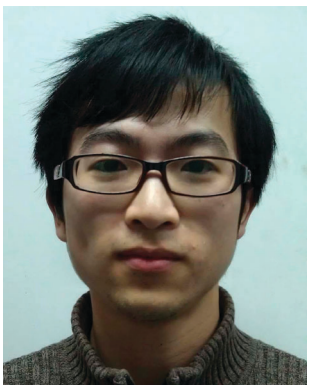

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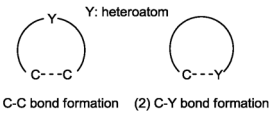


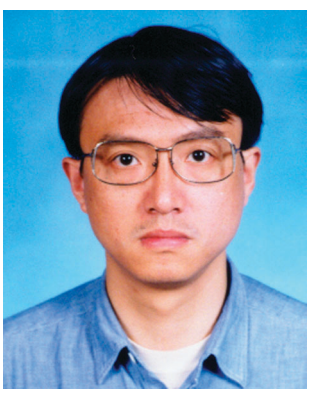
Scheme 1 Two major processes of heterocycle synthesis.

functionalized cyclic structures.[5] The chemical behavior of enynes may be influenced by other functional groups, such as alcohols, aldehydes, ethers, alkenes, or alkynes, thus enhancing the molecular complexity of the synthesized products. In recent years, propargylic esters have received extensive attention for their rich reactivities and easy availabilities,[6,7] and have been transformed into various synthetically valuable products *via* three routes: 1,2-acyloxy migration,[8] 1,3-acyloxy migration[9] and nucleophilic substitution[10] (Scheme 2). Herein, we wish to summarize our efforts on the synthesis of five or six-membered heterocyclic compounds during the recent years, and report some novel transition metal-catalyzed cycloisomerizations of 1,*n*-enynes and diynes containing a propargylic ester moiety.

2. Synthesis of five or six-membered heterocyclic compounds

2.1 Synthesis of 2,3-disubstituted 3-pyrrolines by a gold(I) catalyst

Homogeneous catalysis by gold complexes has received considerable attention in recent years.[11] Among these interesting reactions, gold-catalyzed cycloisomerization of 1,6-enynes and 1,6-diynes[12] is one of the most important strategies for the construction of functionalized cyclic structures. In the context of our ongoing efforts to develop gold-catalyzed tandem reactions, we realized that gold-catalyzed cascade transformation of 1,6-diynes into abnormal five-membered cycloadducts has been less explored. Thus far, only one example has been reported for the gold–phosphine catalyzed cycloisomerization of terminal 1,6-diynes to give cyclopentene products in less than 43% yield.[12o] Hence, we reported a novel C–C bond formation along with cycloisomerization from 1,6-diyne containing



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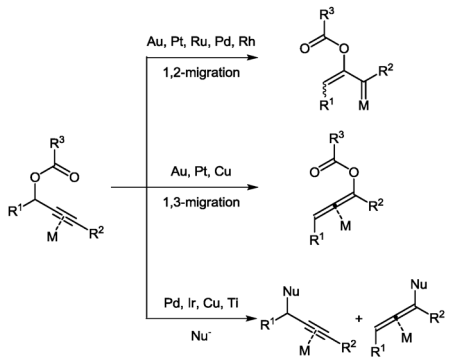
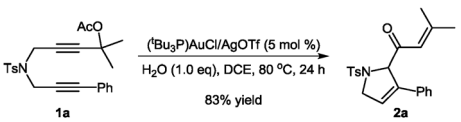
Dr Min Shi was born in 1963 in Shanghai, China. He received his BS in 1984 (Institute of Chemical Engineering of East China) and PhD in 1991 (Osaka University, Japan). He had his postdoctoral research experience with Prof. Kenneth M. Nicholas at University of Oklahoma (1995–1996) and worked as an ERATO Researcher in Japan Science and Technology Corporation (JST) (1996–1998). He is currently a group leader of the State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry (SIOC).



Scheme 2 Transition metal-catalyzed reactions of propargylic esters.



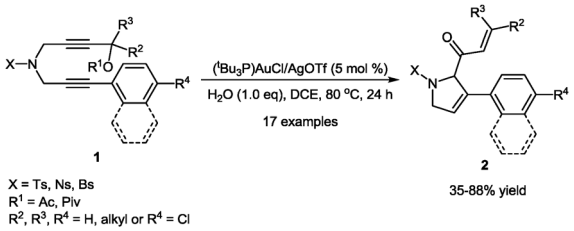
Scheme 3 Optimal reaction conditions for gold(I)-catalyzed intramolecular cyclization.

propargylic ester and arenyne toward nitrogen-containing five-membered heterocyclic rings, such as 2,3-disubstituted 3-pyrrolines,[6k] which have been extensively used as synthetic building blocks in organic synthesis and appear as structural motifs in many natural products, exhibiting interesting biological activities.[13]

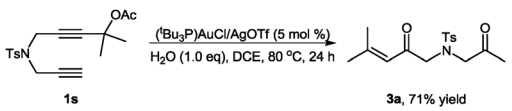
Initial studies using propargylic acetate-arenyne **1a** (0.2 mmol) as the substrate were aimed at determining the reaction outcome and subsequently optimizing the reaction conditions. As shown in Scheme 3, the optimal reaction conditions have been identified to carry out the reaction in DCE at 80 °C using (^{t}Bu$_3$P)AuCl/AgOTf (5 mol%) as the catalyst in the presence of H_2O (1.0 equiv.). We next examined the substrate generality of the reaction under the optimized conditions and the results are shown in Scheme 4. All of the reactions proceeded smoothly to afford the corresponding cycloadducts **2** in 35–88% yields.

When the terminal of an alkyne moiety is a hydrogen atom (**1s**), the corresponding enone **3a** could be formed in 71% yield rather than the cyclized product (Scheme 5).

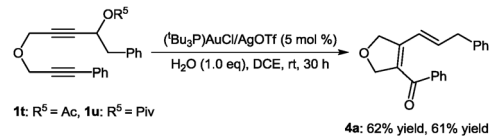
On the other hand, in the case of oxygen-tethered 1,6-diynes containing propargylic ester and arenyne such as substrates **1t**



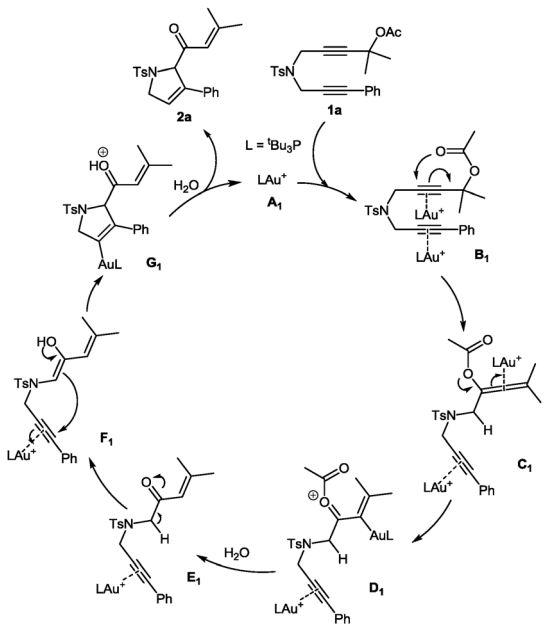
Scheme 4 Gold(I)-catalyzed cycloisomerization of 1,6-diynes **1**.



Scheme 5 Gold(I)-catalyzed cycloisomerization of **1s**.



Scheme 6 Gold(I)-catalyzed cycloisomerization of **1t** and **1u**. Piv = pivaloyl, Tf = triflate.



Scheme 7 A plausible reaction mechanism for the formation of **2a**.

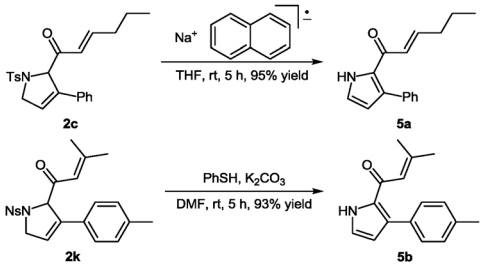
and **1u**, the reactions produced the corresponding 2,5-dihydrofuran derivative **4a** (normal cyclization) in 62% and 61% yield at room temperature (20 °C), respectively (Scheme 6).

A plausible mechanism for this reaction is outlined in Scheme 7 on the basis of above control experiments. Two cationic Au(I) complexes $\mathbf{A_1}$ first coordinate to the two alkyne moieties of **1a**, respectively, affording intermediate $\mathbf{B_1}$, which undergoes a Au-catalyzed 3,3-sigmatropic rearrangement to give carboxyallene intermediates $\mathbf{C_1}$. The resulting oxonium intermediate $\mathbf{D_1}$ undergoes hydrolysis to give enone $\mathbf{E_1}$. The enone $\mathbf{E_1}$ undergoes a Lewis acid-catalyzed enolization to give intermediate $\mathbf{F_1}$. Activation of the remaining alkyne moiety by the gold complex induces a 5-*endo*-dig cycloaddition to give intermediate $\mathbf{G_1}$. The hydrolysis of intermediate $\mathbf{G_1}$ produces cycloadduct **2a** and regenerates Au(I) complex $\mathbf{A_1}$ to complete the catalytic cycle.

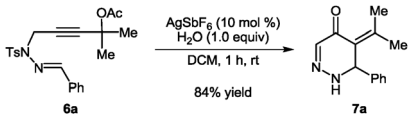
A study on the aromatization of products **2** has been undertaken to synthesize 2,3-disubstituted pyrrole derivatives. The results are shown in Scheme 8. The benzenesulfonyl group and the 4-nitrobenzenesulfonyl group could be easily removed by treatment with sodium naphthalene[14] or thiophenol in the presence of K_2CO_3,[15] respectively, giving the corresponding pyrrole derivatives **5a** and **5b** in good yields.

2.2 Synthesis of 5,6-dihydropyridazin-4-ones by a silver(I) catalyst

The addition of nucleophiles to C=N bonds offers a highly efficient synthetic strategy for accessing nitrogen-containing molecules.[16] In the well-developed addition reactions, such as the



Scheme 8 The aromatization of products **2c** and **2k**.



Scheme 9 Optimal reaction conditions for the formation of **7a**.

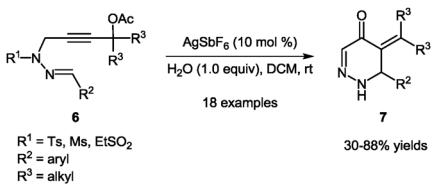
highly efficient Mannich reaction, various C–H bond activated compounds including carboxylic acid derivatives, nitroalkanes and terminal alkynes have been applied as nucleophiles to achieve different classes of amines.[17] However, employing novel nucleophiles without activated C–H bonds such as internal alkynes and allenic esters is limited when using metal catalysts.[18] Hence, we reported a novel addition of allenic esters to C=N bonds initiated by a silver catalyzed 1,3-migration of propargylic esters.[19]

Initially, we started the optimization of the reaction conditions by using (*E*)-5-(2-benzylidene-1-tosylhydrazinyl)-2-methylpent-3-yn-2-yl acetate **6a**. As shown in Scheme 9, the use of $AgSbF_6$ (10 mol%) as the catalyst and water (1.0 equiv.) as an additive in dry dichloromethane at room temperature have been identified as the optimal reaction conditions.

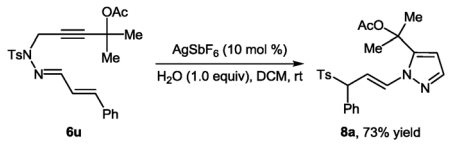
Under the optimized conditions, we next investigated the tolerance of silver(I)-catalyzed tandem cyclization of various hydrazones **6** and the results are shown in Scheme 10. All of the reactions proceeded smoothly to afford the corresponding products **7** in 30–88% yields.

On the other hand, for styrenyl hydrazone **6u**, the pyrazole **8a** was formed in 73% yield without the formation of the 5,6-dihydropyridazin-4-one product (Scheme 11).[20]

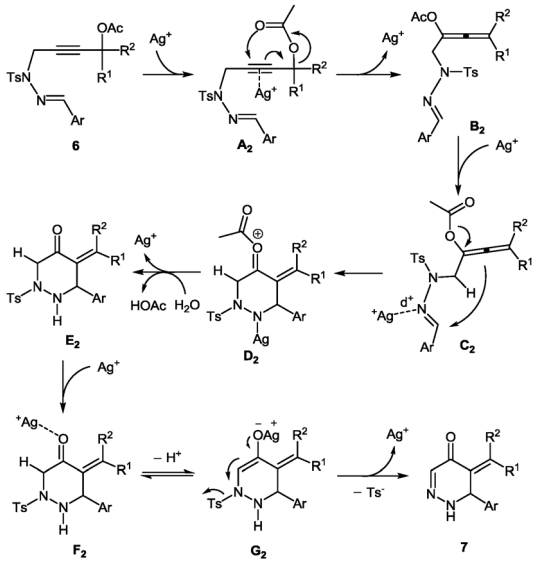
A plausible reaction mechanism is outlined in Scheme 12. The cationic silver(I) first coordinates to the alkyne moiety of **6** to afford intermediate $\mathbf{A_2}$, which undergoes a 3,3-sigmatropic



Scheme 10 Substrate scope of the silver-catalyzed tandem reaction.



Scheme 11 Silver-catalyzed tandem reaction **6u**.



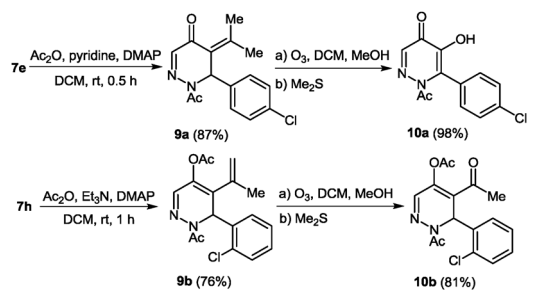
Scheme 12 A plausible reaction mechanism for the formation of **7**.

rearrangement to give carboxyallene intermediate $\mathbf{B_2}$. Activation of the hydrazone sp^2 nitrogen atom of $\mathbf{B_2}$ by silver(I) produces intermediate $\mathbf{C_2}$, which induces a Mannich-type addition of the allenic acetate to the C=N bond to give intermediate $\mathbf{D_2}$. In the presence of water, intermediate $\mathbf{D_2}$ undergoes hydrolysis to give intermediate $\mathbf{E_2}$ and regenerates the silver(I) catalyst. Then the carbonyl group of intermediate $\mathbf{E_2}$ is activated by cationic silver(I), affording intermediate $\mathbf{F_2}$ which undergoes a soft enolization to give intermediate $\mathbf{G_2}$. An elimination of tolylsulfinate of $\mathbf{G_2}$ produces product **7**.

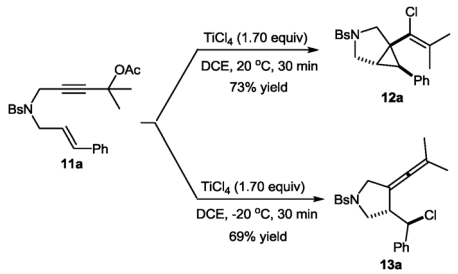
The transformation of the product 5,6-dihydropyridazin-4-one **7** into other pyridazin derivatives was briefly examined (Scheme 13). Compound **7e** was readily converted to *N*-acetylated product **9a** in the presence of acetic anhydride when pyridine was used as the base. However, when triethylamine was used instead of pyridine, the base could deprotonate the C–H bond of the methyl group and then enolization occurred which underwent acetylation to form product **9b**. By a conventional O_3 oxidation procedure, compound **9a** could be readily converted to 5-hydroxypyridazin-4-one **10a** and compound **9b** could be easily transformed into 1,6-dihydropyridazin **10b**, respectively.

2.3 Synthesis of 3-azabicyclo[3.1.0]hexanes and functionalized allenes by a titanium(IV) complex

$TiCl_4$ has been widely used in many carbon–carbon bond-forming reactions,[21] to the best of our knowledge, no investigation of



Scheme 13 The transformation of **7** into pyridazin derivatives **9** and **10**.



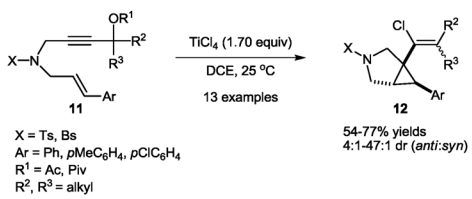
Scheme 14 Optimal reaction conditions for the formation of **12a** and **13a**.

cyclization of enynes has been carried out using $TiCl_4$ as a promoter. Only one notable example is the $TiCl_4$–Et_3N mediated intramolecular carbocyclization of active methine compounds with unactivated alkyne groups.[22] Herein, we reported a novel carbocyclization of 1,6-enynes in which easily available and inexpensive metal halides can serve as effective promoters to achieve the selective synthesis of 3-azabicyclo[3.1.0]hexanes and functionalized allenes by controlling the reaction temperature.[23] These 3-azabicyclo[3.1.0]hexanes are core structures of a variety of biologically active natural products[24] and the examples of direct transformation of enynes into allenes accompanied with ring formation are rare.[25]

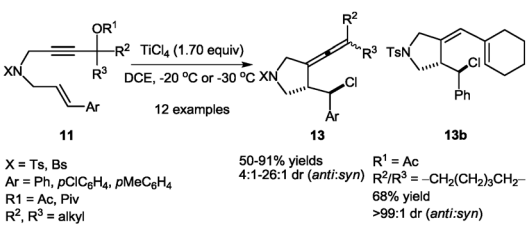
Initially, we tested the carbocyclization of enyne **11a** using various Lewis acids such as $BiCl_3$, $TiCl_4$, BCl_3 and $TiBr_4$. We found that only $TiCl_4$ gave good results, affording **12a** in 73% yield within 20 minutes at room temperature (25 °C). However, it was found that allene **13a** could be obtained in 69% yield at −20 °C after 30 minutes in the presence of 1.70 equiv. $TiCl_4$ (Scheme 14).

With these optimized conditions in hand, we next investigated the tolerance of $TiCl_4$-mediated carbocyclization with various enynes **11** to construct the corresponding 3-azabicyclo[3.1.0]-hexanes. As depicted in Scheme 15, all of the reactions proceeded smoothly to give the desired products **12** in 54–77% yields along with excellent diastereoselectivities (4 : 1 to 47 : 1) at 25 °C.

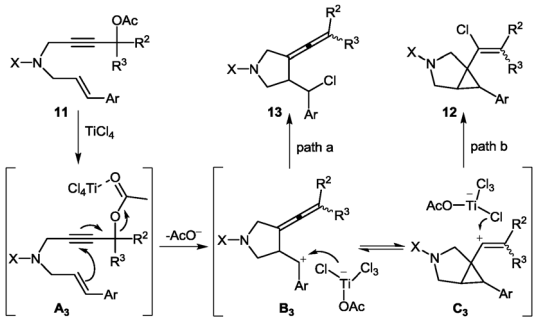
To obtain allene derivatives **13**, the reaction should be conducted at lower temperature (−20 or −30 °C) and the results are shown in Scheme 16. For various alkyl groups substituted **11**,



Scheme 15 $TiCl_4$-mediated synthesis of 3-azabicyclo[3.1.0]hexanes **12**.



Scheme 16 $TiCl_4$-mediated synthesis of allenes **13**.



Scheme 17 A plausible reaction mechanism for the formation of **12** and **13**.

the corresponding allene derivatives **13** could be obtained in 50–91% yields along with good diastereoselectivities (4 : 1 to 26 : 1). In the case of substrate **11b** with a cyclohexyl group, the product (*E*)-3-(chloro(phenyl)methyl)-4-(cyclohexenylmethylene)-1-tosylpyrrolidine **13b** was obtained in 68% yield without the formation of the corresponding allene derivative.

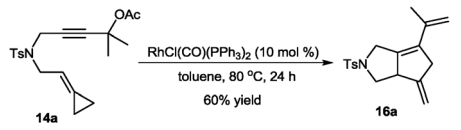
We proposed a mechanism for the $TiCl_4$-mediated carbocyclization in Scheme 17. Coordination of the ester group to $TiCl_4$ gives intermediate $\mathbf{A_3}$. The nucleophilic intramolecular addition of the pendant olefin to the alkyne along with leaving of the acyloxy group affords carbocation $\mathbf{B_3}$, which contains a vinylidene moiety. At low temperature, the chloride ion from the metal is transferred to an incipient benzylic carbocation to produce chlorinated allene **13** (path a). Due to the stability of the benzylic cation, the intermediate $\mathbf{B_3}$ could be isomerized to vinyl cation $\mathbf{C_3}$ at elevated temperature, which then undergoes chloride ion transfer from the metal to generate the chlorinated 3-azabicyclo[3.1.0]hexane **12** (path b).

2.4 Synthesis of 3-azabicyclo[3.3.0]octenes by a rhodium(I) catalyst

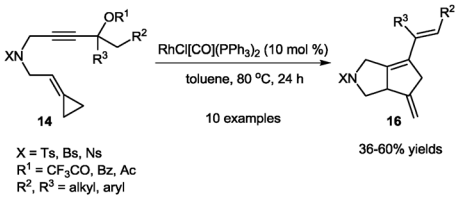
Methylenecyclopropanes (MCPs) and alkylidenecyclopropanes (ACPs), containing a coordinating double bond and a strained carbocycle, can undergo a number of interesting metal-assisted transformations.[26] Rhodium,[27] nickel,[28] ruthenium,[29] as well as palladium,[30] all can catalyze intermolecular and intramolecular cycloaddition of alkene- or alkyne-tethered ACPs, constructing a variety of interesting bicycles or tricycles, which are useful building blocks for the synthesis of natural products and medicinally important substances. Although the intermolecular rhodium(I)-catalyzed [3 + 2 + 2] carbocyclization reaction of ACPs with activated alkynes has been reported,[27] the corresponding intramolecular carbocyclization of ACPs is not forthcoming. Hence, we discovered the first intramolecular rhodium(I)-catalyzed [3 + 2] cycloaddition of ACPs containing propargylic esters, for the construction of the bicyclo[3.3.0]-octene derivatives.[31,32]

Initial studies using alkylidenecyclopropane-propargylic ester **14a** as the substrate were aimed at determining the reaction outcomes and subsequently optimizing the reaction conditions. As shown in Scheme 18, the optimal reaction conditions were identified to carry out the reaction in toluene (0.025 M) at 80 °C using $RhCl(CO)(PPh_3)_2$ (10 mol%) as the catalyst.

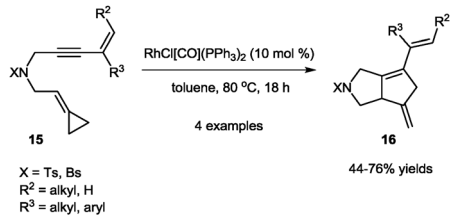
We next examined the substrate generality of the reaction under the optimized conditions. As can be seen from Scheme 19,



Scheme 18 Optimal reaction conditions for the formation of **16a**.



Scheme 19 Rhodium(I)-catalyzed [3 + 2] intramolecular cycloaddition of alkylidenecyclopropane-propargylic esters.



Scheme 20 Rhodium(I)-catalyzed [3 + 2] intramolecular cycloaddition of alkylidenecyclopropane-enyne.

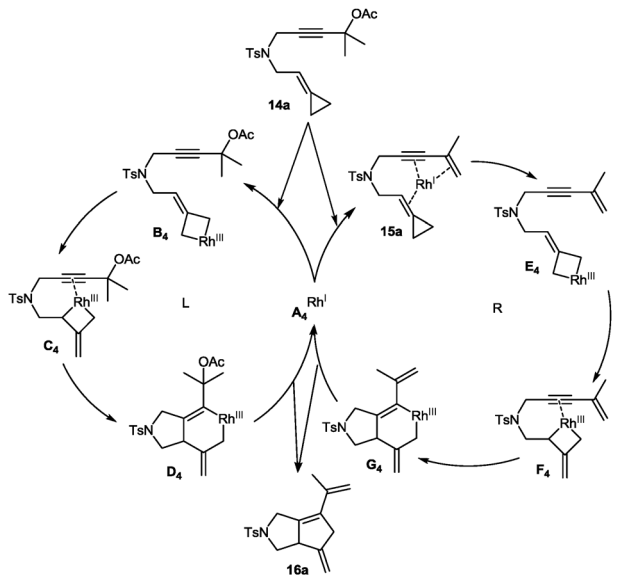
all of the reactions proceeded smoothly to give the corresponding cycloadducts **16** in 36–60% yields.

On the other hand, we found that alkylidenecyclopropane-enyne **15** can also produce the corresponding bicyclo[3.3.0]-octene derivatives **16** in moderate to good yields under similar conditions, and the results are summarized in Scheme 20.

A plausible mechanism for the formation of these bicyclo-[3.3.0]octene derivatives **16** is tentatively outlined in Scheme 21. *Cycle* ***L*** involves initial insertion of the metal at the distal position of the alkylidenecyclopropane **14a** to give metallacyclobutene $\mathbf{B_4}$, followed by isomerization to intermediate $\mathbf{C_4}$ through a TMM-like transition state and carbometalation to afford intermediate $\mathbf{D_4}$. Reductive elimination of intermediate $\mathbf{D_4}$ provides the final adduct **16a** along with the release of HOAc. In *Cycle* ***R***, propargylic ester **14a** produces enyne **15a** in the presence of Rh^I complex $\mathbf{A_4}$. Oxidative addition into the distal bond of the cyclopropane should afford the metallacyclobutene $\mathbf{E_4}$, which can presumably rearrange to intermediate $\mathbf{F_4}$. Intermediate $\mathbf{F_4}$ undergoes a carbometalation to give intermediate $\mathbf{G_4}$. Reductive elimination of intermediate $\mathbf{G_4}$ produces the corresponding cycloadduct **16a** and regenerates the Rh^I complex $\mathbf{A_4}$ to complete the catalytic cycle.

2.5 Synthesis of bicyclo[4.2.0]oct-5-enes by a titanium(IV) complex

Gold, platinum or palladium-catalyzed intramolecular cycloisomerization of propargylic esters is an efficient route to synthesize a variety of bicyclo[*n*.1.0]enol esters in good yields.[33] More recently, we have found that titanium(IV) chloride and bismuth(III) chloride can serve as effective promoters to achieve the synthesis of chlorinated 3-azabicyclo[3.1.0]hexanes from the

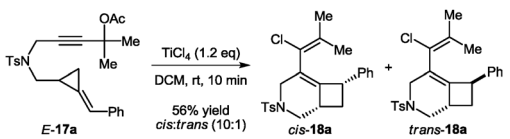


Scheme 21 A plausible reaction mechanism for the formation of **16a**.

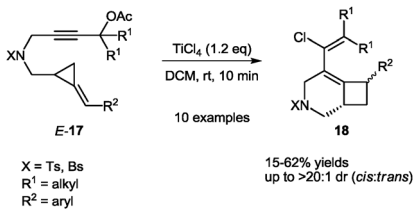
corresponding easily available propargylic esters under mild conditions.[23] These intriguing results promote us to examine other novel intramolecular carbocyclization processes to access other interesting bicyclic ring skeletons. Hence, we reported an efficient route to accomplish the synthesis of bicyclo[4.2.0]oct-5-ene derivatives[34] which have been only synthesized by heating allenenes at high temperature in dioxane or DMF through thermal-induced intramolecular [2 + 2] cycloaddition reactions.[35]

Initially, we started the optimization of the reaction conditions by using *E*-**17a**. As shown in Scheme 22, the optimal reaction conditions were identified to carry out the reaction in dichloromethane at room temperature using $TiCl_4$ (1.2 equiv.) as a Lewis acid promoter, and under these conditions, cycloisomerization product **18a** was formed in 56% yield along with 10 : 1 diastereoselectivity (*cis* : *trans*).

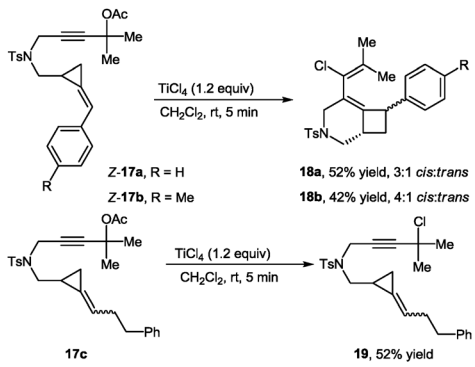
Next, with the optimized conditions in hand, we investigated the substrate scope of this $TiCl_4$-mediated carbocyclization with various methylenecyclopropanes *E*-**17** in the synthesis of 3-azabicyclo[4.2.0]oct-5-enes **18**. As can be seen from Scheme 23, all of the reactions proceeded smoothly to give



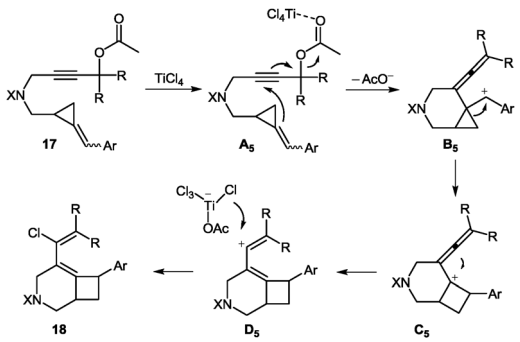
Scheme 22 Optimal reaction conditions for the formation of *cis*- and *trans*-**18a**.



Scheme 23 $TiCl_4$-mediated synthesis of bicyclo[4 2.0]oct-5-enes.



Scheme 24 The transformation of Z-**17a–c**.



Scheme 25 A plausible reaction mechanism for the formation of **18**.

the desired products **18** in moderate yields along with good diastereoselectivities.

To gain more insight into this $TiCl_4$-mediated transformation of **17** into **18**, we investigated the stereochemical course of ring enlargement of methylenecyclopropanes (MCPs) using *Z*-**17a** and *Z*-**17b** as the substrates under the standard conditions and found that the products **18a** and **18b** were obtained in 52% yield and 42% yield, respectively (Scheme 24). Substrate **17c** having an alkyl group substituted methylenecyclopropane was also tested in this reaction, but the corresponding nucleophilic displacement product **19** was afforded in 52% yield without the formation of 3-azabicyclo[4.2.0]oct-5-ene under the standard conditions (Scheme 24).

We proposed a plausible reaction mechanism for this $TiCl_4$-mediated carbocyclization in Scheme 25. Coordination of the ester group to $TiCl_4$ gives intermediate $\mathbf{A_5}$. The nucleophilic intramolecular addition of the pendant methylenecyclopropane to the alkyne moiety along with the release of an acyloxy group affords carbocation $\mathbf{B_5}$, which contains a vinylidene moiety. Subsequently, carbocationic intermediate $\mathbf{B_5}$ undergoes intramolecular ring enlargement of cyclopropane *via* 1,2-carbon migration giving intermediate $\mathbf{C_5}$ which can give vinyl cationic intermediate $\mathbf{D_5}$ through isomerization. Then a chloride ion is transferred to a vinyl cation from the *in situ* generated metal complex, affording the corresponding chlorinated bicyclo[4.2.0]oct-5-ene **18**. It should be also noted that carbocation $\mathbf{B_5}$ could be stabilized by the neighboring aryl unit which can serve as a driving force for this transformation. While alkyl group substituted methylenecyclopropane could not afford the stabilized intermediate $\mathbf{B_5}$, only produces the corresponding chlorinated nucleophilic displacement compound **19**.

3. Conclusion

For a long time, carbocyclization of 1,*n*-enynes and diynes is a powerful method in organic synthesis to access carbo- or heterocyclic rings which are important structural motifs found in many natural and pharmaceutical materials. Various transition metal catalysts, such as gold, rhodium, silver, and titanium, have been identified as effective promoters in these transformations to a variety of valuable substances. The control experiments have indicated that the other metal catalysts are totally ineffective in the corresponding transformation. Our group has made much more efforts for the synthesis of five or six-membered heterocyclic compounds, and reported some novel transition metal-catalyzed cycloisomerizations of 1,*n*-enynes and diynes containing a propargylic ester moiety. Further applications of transition metal catalysts and the more detailed investigation of the related reactions are underway in our laboratory.

Acknowledgements

We thank the Shanghai Municipal Committee of Science and Technology (11JC1402600), National Basic Research Program of China (973)-2009CB825300, the Fundamental Research Funds for the Central Universities and the National Natural Science Foundation of China for financial support (21072206, 20472096, 20872162, 20672127, 21121062 and 20732008).

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