Synthetic Methods

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Ruthenium-Triggered Ring Opening of Ethynylcyclopropanes: [3+2] Cycloaddition with Aldehydes and Aldimines Involving Metal Allenylidene Intermediates**

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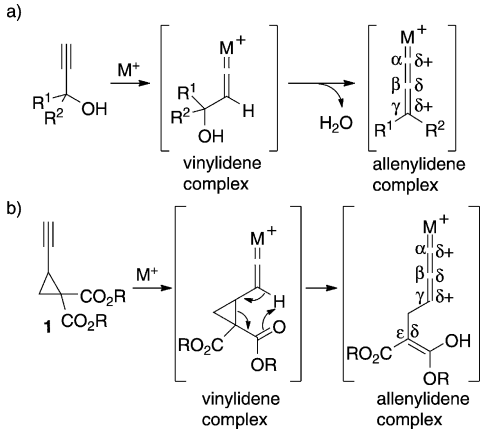
Transition metal allenylidene complexes have attracted considerable attention as versatile organometallic species for carbon-rich architecture, material science, and reactive intermediates in various organic transformations.[1–3] Since the first discovery of metal allenylidene complexes,[4] their structures, electronic properties, and stoichiometric reactivities have been studied extensively owing to the discovery of general method of access to metal allenylidene complexes by simple activation of propargylic alcohols (Scheme 1 a).[5] Although



Scheme 1. Approach to formation of metal allenylidene complexes.

the involvement of transition metal allenylidene complexes in catalytic reactions was reported for the first time in 1992,[6] significant progress has not been made until recently. Since our finding of the ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols with nucleophiles,[7] we have continuously studied a variety of unique catalytic transformations[8–11] involving ruthenium allenylidene complexes as key and common intermediates together with their enantioselective versions. Furthermore, other research groups have also developed a variety of catalytic reactions involving metal allenylidene complexes as key intermediates.[1,12–15] However, readily accessible precursors for formation of allenylidene complexes are limited only to propargylic alcohols and their derivatives. We have now designed an ethynylcyclopropane bearing two carboxy groups at the homopropargylic position as a new accessible precursor for a metal allenylidene complex. The isomerization of a cyclopropyl vinylidene complex can lead to the corresponding metal allenylidene complex, which is expected to serve as a 1,3-dipolar synthon at the γ and ε positions (Scheme 1 b). In fact, we report herein the ruthenium-catalyzed [3+2] cycloaddition of ethynylcyclopropanes with aldehydes and aldimines, where ruthenium allenylidene complexes serve as reactive intermediates. The scope and limitations of the catalytic [3+2] cycloaddition are described together with the density functional theory (DFT) calculations on the proposed reaction pathway, including the generation of ruthenium allenylidene complexes.

Treatment of **1a** with benzaldehyde (**2a**; 5 equiv) and $BF_3{\cdot}OEt_2$ (5 equiv) in the presence of 5 mol% of the methanethiolato-bridged diruthenium complex $[\{Cp^*RuCl(\mu_2\text{-}SMe)\}_2]$[9,16] (**3a**; $Cp^* = \eta^5\text{-}C_5Me_5$) in $ClCH_2CH_2Cl$ at room temperature for 15 hours afforded dimethyl 5-ethynyl-2-phenyltetrahydrofuran-3,3-dicarboxylate (**4a**) in 88% yield (Table 1, entry 1). The reaction of **1a** with 3 equivalents of **2a** proceeded smoothly, but a lower yield (67%) of **4a** was observed (Table 1, entry 2). When the amount of $BF_3{\cdot}OEt_2$ was reduced to 3 equivalents relative to **1a**, the yield of **4a** decreased slightly (Table 1, entry 3). We confirmed that no formation of **4a** was observed in either the absence of $BF_3{\cdot}OEt_2$ or **3a**, thus indicating that use of both $BF_3{\cdot}OEt_2$ and **3a** is necessary for producing **4a**. Other diruthenium complexes such as the complex bearing the sterically more demanding S*i*Pr moiety $[\{Cp^*RuCl(\mu_2\text{-}S\textit{i}Pr)\}_2]$ (**3b**) and the cationic diruthenium complex $[Cp^*RuCl(\mu_2\text{-}SMe)RuCp^*(OH_2)][OTf]$ (**3c**; $OTf = OSO_2CF_3$) exhibited a lower catalytic activity (Table 1, entries 4 and 5). Noteworthy is that only diruthenium complexes work as effective catalysts to promote the cycloaddition reaction. In fact, mononuclear ruthenium complexes such as $[TpRu(PPh_3)(CH_3CN)_2][PF_6]$ (Tp = tris(1-pyrazolyl)borate), $[CpRuCl(PPh_3)_2]$ ($Cp = \eta^5\text{-}C_5H_5$), and $[(\eta^5\text{-}C_9H_7)Ru(dppe)][PF_6]$ (dppe = 1,2-bis(diphenylphosphino)ethane) did not promote this cycloaddition at all.

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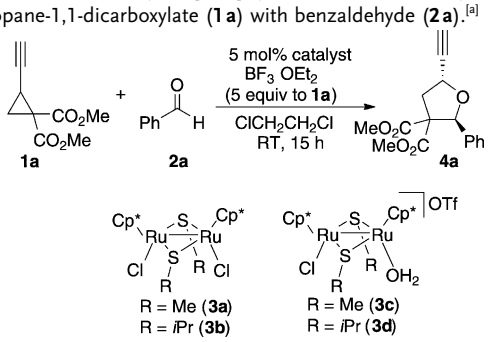
Table 1: Ruthenium-catalyzed [3+2] cycloaddition of dimethyl 2-ethynylcyclopropane-1,1-dicarboxylate (**1a**) with benzaldehyde (**2a**).[a]



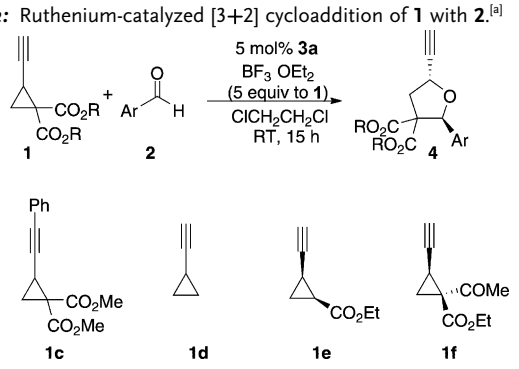
Entry	Catalyst	**2a** (equiv)[b]	**4a** yield [%][c] (*trans*/*cis*)[d]
1	**3a**	5	88 (2:1)
2	**3a**	3	67 (2:1)
3[e]	**3a**	5	74 (2:1)
4	**3b**	5	73 (2:1)
5	**3c**	5	51 (2:1)

[a] All reactions of **1a** (0.30 mmol) with **2a** and $BF_3{\cdot}OEt_2$ (1.5 mmol) were carried out in the presence of catalyst (0.015 mmol) in $ClCH_2CH_2Cl$ (6 mL) at room temperature for 15 h. [b] Equivalents relative to **1a**. [c] Yield of isolated product. [d] Determined by ^1H NMR spectroscopy. [e] $BF_3{\cdot}OEt_2$ (0.90 mmol; 3 equiv relative to **1a**) was used.

Other reactions of **1** with a variety of aldehydes (**2**) were investigated by using **3a** as the catalyst. Typical results are shown in Table 2. The introduction of a substituent such as methoxy, methyl, chloro, or fluoro groups at the *para* position of the benzene ring of **2** did not have much of an effect on the yield of **4** (Table 2, entries 2, 3, 6, and 7). The reaction of 3-methylbenzaldehyde (**2d**) and 2-naphthaldehyde (**2j**) took place smoothly to give the corresponding products **4d** and **4j** in high yields (Table 2, entries 4 and 10), while that of *p*-nitrobenzaldehyde (**2h**) and sterically hindered aldehydes such as *o*-tolylcarboaldehyde (**2e**) and 1-naphthylcarboaldehyde (**2i**) afforded a slightly lower product yield (Table 2, entries 5, 8, and 9). Unfortunately, no reaction of **1a** with cyclohexanecaboxaldehyde, benzophenone, and acetone occurred at all under the same reaction conditions. When diethyl 2-ethynylcyclopropane-1,1-dicarboxylate (**1b**) was used in place of **1a**, the cycloaddition products **4k**, **4l**, and **4m** were obtained in similar yields (Table 2, entries 11–13). The reaction of dimethyl 2-(2-phenylethynyl)cyclopropane-1,1-dicarboxylate (**1c**), bearing an internal alkyne moiety, with **2a** did not give the corresponding cycloaddition product; **1c** was recovered in 63% (see Scheme S1a in the Supporting Information).[18] In addition, no formation of the corresponding product was observed when either **1d** or **1e** was used in place of **1a**, whereas the reaction of **1f** proceeded under similar reaction conditions, but only a small amount of the product was obtained (Scheme S1b-d).[18] These results clearly indicate that use of 2-ethynylcyclopropane bearing two carboxy groups is necessary to promote the cycloaddition.

This methodology for the preparation of **4** can be applied to the formation of ethynylpyrrolidines (**6**). Typical results are shown in Table 3. Treatment of **1a** with *N*-benzylidene-4-methylbenzenesulfonamide (**5a**; 5 equiv) and $Sc(OTf)_3$

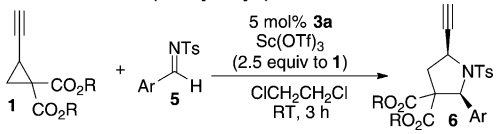
Table 2: Ruthenium-catalyzed [3+2] cycloaddition of **1** with **2**.[a]



Entry	R	Ar	Yield [%][b] (*trans*/*cis*)[c]
1	Me (**1a**)	Ph (**2a**)	88 (**4a**; 2:1)
2	Me (**1a**)	4-$MeOC_6H_4$ (**2b**)	87 (**4b**; 2:1)
3	Me (**1a**)	4-MeC_6H_4 (**2c**)	81 (**4c**; 2:1)
4	Me (**1a**)	3-MeC_6H_4 (**2d**)	80 (**4d**; 2:1)
5	Me (**1a**)	2-MeC_6H_4 (**2e**)	61 (**4e**; 1:1)
6	Me (**1a**)	4-ClC_6H_4 (**2f**)	76 (**4f**; 2:1)
7	Me (**1a**)	4-FC_6H_4 (**2g**)	75 (**4g**; 2:1)
8[d]	Me (**1a**)	4-$NO_2C_6H_4$ (**2h**)	56 (**4h**; 2:1)
9[e]	Me (**1a**)	1-naphthyl (**2i**)	40 (**4i**; 1:1)
10[f]	Me (**1a**)	2-naphthyl (**2j**)	72 (**4j**; 2:1)
11	Et (**1b**)	Ph (**2a**)	74 (**4k**; 2:1)
12	Et (**1b**)	4-$MeOC_6H_4$ (**2b**)	70 (**4l**; 2:1)
13	Et (**1b**)	4-MeC_6H_4 (**2c**)	72 (**4m**; 3:2)

[a] All reactions of **1** (0.30 mmol) with **2** (1.5 mmol) and $BF_3{\cdot}OEt_2$ (1.5 mmol) were carried out in the presence of **3a** (0.015 mmol) in $ClCH_2CH_2Cl$ (6 mL) at room temperature for 15 h. [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy. [d] For 38 h. [e] For 18 h. [f] For 20 h.

Table 3: Ruthenium-catalyzed [3+2] cycloaddition of **1** with **5**.[a]

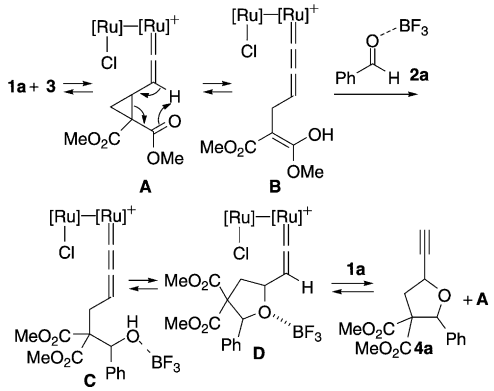


Entry	R	Ar	Yield [%][b] (*trans*/*cis*)[c]
1	Me (**1a**)	Ph (**5a**)	88 (**6a**; 1:50)
2[d]	Me (**1a**)	Ph (**5a**)	12[e] (**6a**; –)
3[f]	Me (**1a**)	Ph (**5a**)	0 (**6a**)
4[g]	Me (**1a**)	Ph (**5a**)	0 (**6a**)
5[h]	Me (**1a**)	Ph (**5a**)	70 (**6a**; 1:50)
6	Me (**1a**)	4-$MeOC_6H_4$ (**5b**)	52 (**6b**; 1:8)
7	Me (**1a**)	4-MeC_6H_4 (**5c**)	63 (**6c**; 1:20)
8	Me (**1a**)	3-MeC_6H_4 (**5d**)	80 (**6d**; 1:30)
9	Me (**1a**)	4-ClC_6H_4 (**5e**)	98 (**6e**; 1:50)
10	Me (**1a**)	4-FC_6H_4 (**5f**)	86 (**6f**; 1:50)
11	Me (**1a**)	2-naphthyl (**5g**)	76 (**6g**; 1:50)
12	Et (**1b**)	Ph (**5a**)	77 (**6h**; 1:50)
13	Et (**1b**)	4-ClC_6H_4 (**5e**)	90 (**6i**; 1:50)
14	Et (**1b**)	4-FC_6H_4 (**5f**)	93 (**6j**; 1:50)

[a] All reactions of **1** (0.30 mmol) with **5** (1.5 mmol) and $Sc(OTf)_3$ (0.75 mmol) were carried out in the presence of **3a** (0.015 mmol) in $ClCH_2CH_2Cl$ (6 mL) at room temperature for 3 h. [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy. [d] $BF_3{\cdot}OEt_2$ (1.50 mmol; 5 equiv to **1a**) was used in place of $Sc(OTf)_3$. [e] Yield determined by ^1H NMR spectroscopy. [f] In the absence of **3a**. [g] In the absence of $Sc(OTf)_3$. [h] **5a** (0.75 mmol; 2.5 equiv to **1a**) was used.

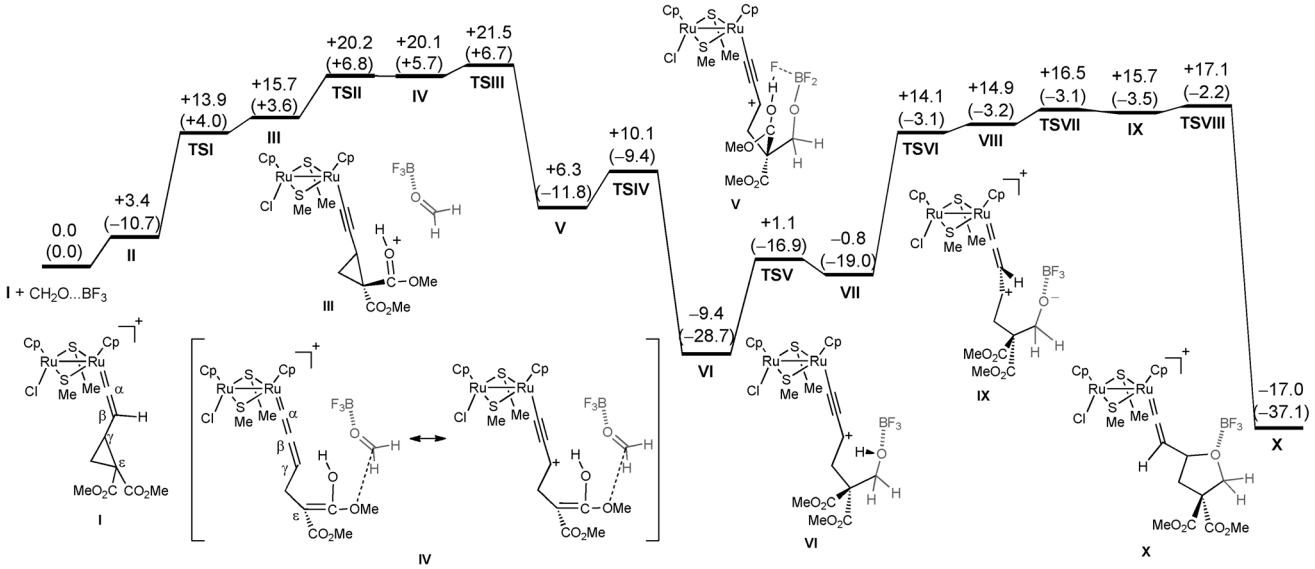
(2.5 equiv) in the presence of 5 mol% of **3a** afforded dimethyl 5-ethynyl-2-phenyl-1-tosylpyrrolidine-3,3-dicarboxylate (**6a**) in 88% yield as a mixture of two stereoisomers, with the *cis* isomer being predominant (Table 3, entry 1). When $BF_3{\cdot}OEt_2$ was used in place of $Sc(OTf)_3$, the yield of **6a** decreased dramatically (Table 3, entry 2). This decrease is due to the difference in the coordination ability of BF_3 versus that of $Sc(OTf)_3$. We confirmed that use of both $Sc(OTf)_3$ and **3a** is necessary for producing **6a** (Table 3, entries 3 and 4). The reaction of **1a** with 2.5 equivalents of **5a** under the same reaction conditions gave **6a** in 70% yield with a similar *cis* selectivity (Table 3, entry 5). Other reactions of **1** with a variety of *N*-tosylaldimines (**5**) proceeded smoothly to give the corresponding ethynylpyrrolidines (**6**) in high to excellent yields with an excellent selectivity for *cis* isomers (Table 3, entries 6–14).[19,20]

A plausible reaction pathway is shown in Scheme 2. The initial step is the formation of the ruthenium vinylidene complex **A** by the reaction of **1a** with **3**. Isomerization of **A** results in the formation of an allenylidene complex **B**, bearing an enol moiety. Nucleophilic attack of **B** on **2a**, which is activated by $BF_3{\cdot}OEt_2$, proceeds to afford a new allenylidene complex (**C**) with subsequent intramolecular cyclization to give a vinylidene complex **D**. Finally, a ligand exchange reaction between **D** and another **1a** occurs to give the corresponding cycloaddition product **4a** accompanied by regeneration of **A**. We believe that the synergistic effect[21] of the two ruthenium centers in the diruthenium complexes is also quite important for promotion of this catalytic reaction smoothly. Unfortunately, we have not yet observed the formation of the allenylidene complex **B** as a reactive species as it is considered to be too reactive to be isolated as an intermediate, but the formation of vinylidene complexes **A** and **D** can be confirmed by ^1H NMR analysis of the reaction mixture.[18]



Scheme 2. Proposed reaction pathway leading to cycloaddition product.

To gain insight into the reaction pathway, we carried out the DFT calculations using the B3LYP hybrid functional with Gaussian 03 and 09 programs (LANL2DZ for Ru atom and 6-31G* for other atoms)[18] for the model reaction of the ruthenium vinylidene complex $[CpRuCl(\mu_2\text{-}SMe)_2RuCp(=C=CHCHCH_2C(COOMe)_2)]^+$ (**I**), which forms through the reaction of the diruthenium complex $[CpRuCl(\mu_2\text{-}SMe)_2RuCp]^+$ with **1a**, and the BF_3-coordinated formaldehyde.[21] The Gibbs free-energy diagram is shown in Scheme 3. Detailed reaction pathway and optimized structures are shown in Figures S2 and S3, respectively, in the Supporting Information.[18] The complexation between **I** and the BF_3-coordinated formaldehyde gives a weak reactant complex (**II**) because of the electrostatic interaction between the cationic system **I** and the electronegative fluorine atoms at BF_3. The free energy (ΔG) of **II** relative to the initial state (**I** + BF_3-coordinated formaldehyde), is $+3.4$ kcal mol^{-1}. The transfer of the hydrogen atom from the β-carbon atom to the oxygen atom in the ester group gives the complex **III** ($\Delta G = +15.7$ kcal mol^{-1}) via the transition state **TSI**, and bond

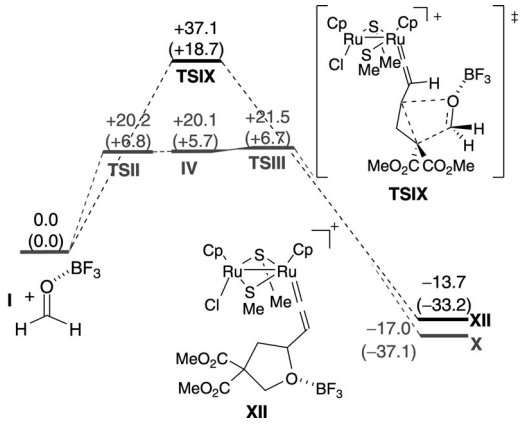


Scheme 3. Relative Gibbs free-energy diagrams (kcal mol^{-1}) for the model reactions in the gas phase at 298.15 K. Values in parentheses are relative energies.

cleavage between the γ-carbon atom and the ε-carbon atom subsequently occurs via **TSII** to afford the allenylidene complex **IV** ($\Delta G = +20.1$ kcal mol^{-1}). Then the nucleophilic attack of the ε-carbon atom in **IV** onto the carbonyl carbon atom of formaldehyde, the electrophilicity of which is strengthened by the coordination with the Lewis acid BF_3, occurs along with the interaction between the hydrogen atom in the ester group and the fluorine atom in BF_3 (**TSIII**) to afford the complex **V** ($\Delta G = +6.3$ kcal mol^{-1}). The carbonyl carbon atom of formaldehyde, which interacts with the oxygen atom of the ester group in **IV**, now binds to the ε-carbon atom in **V**. The hydrogen atom in the ester group which interacts tightly with the fluorine atom is easily transferred onto the oxygen atom derived from formaldehyde (**TSIV**) to afford the complex **VI** ($\Delta G = -9.4$ kcal mol^{-1}). Another conformational structure (**VII**) with respect to **VI** forms through **TSV**. Again the hydrogen atom which is attached to the oxygen atom derived from formaldehyde is transferred back to the β-carbon atom via **TSVI** to give the complex **VIII**. In **VIII**, the weak interaction between the hydrogen atom and the oxygen atom derived from formaldehyde still remains and is diminished through the transition-state **TSVII** to form the complex **IX**. Finally, the oxygen atom derived from formaldehyde attacks the γ-carbon atom (**TSVIII**) to afford the vinylidene complex **X**. The ΔG of **X** is -17.0 kcal mol^{-1}, which is much more stable than the initial state. Thus the proposed pathway involving the ruthenium allenylidene complex proceeds smoothly.

We also examined the concerted cycloaddition pathway in which the BF_3-coordinated formaldehyde directly attacks the cyclopropane ring in the ruthenium vinylidene complex **I** (Scheme 4).[18] The ΔG of the transition state for the concerted pathway is $+37.1$ kcal mol^{-1}, which is much larger than that of the transition states in the reaction pathway which proceeds through the ruthenium allenylidene complex. Therefore, the reaction pathway shown in Scheme 3 is preferred to the concerted pathway.

In summary, we have found that the ruthenium-catalyzed [3+2] cycloaddition of ethynylcyclopropanes, bearing two carboxy groups at the homopropargylic position, with aldehydes and aldimines leads to the corresponding 2-ethynyltetrahydrofurans and pyrrolidines in high to excellent yields.[22,23] The DFT calculations support the reaction pathway which involves the ruthenium allenylidene complex as a key intermediate. It is noted that the ruthenium allenylidene reaction pathway differs from the pathway which has been reported for the Lewis acid catalyzed cycloaddition of aldehydes with donor–acceptor cyclopropanes.[24–27] We believe that this finding will open up a new aspect of the chemistry of metal allenylidene complexes which can be accessed by a new approach, which differs from known methods using propargylic alcohols and its derivatives.



Scheme 4. Relative Gibbs free-energy diagrams (kcal mol^{-1}) for the model reactions in the gas phase at 298.15 K (**I**–**TSII**–**IV**–**TSIII**–**X** (gray line): pathway via ruthenium allenylidene intermediate; **I**–**TSIX**–**XII** (black line): concerted pathway). Values in parentheses are relative energies.

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Communications

Synthetic Methods

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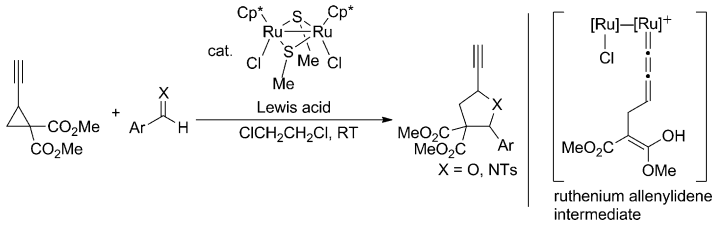
Ruthenium-Triggered Ring Opening of Ethynylcyclopropanes: [3+2] Cycloaddition with Aldehydes and Aldimines Involving Metal Allenylidene Intermediates



It's complex: Ruthenium-catalyzed [3+2] cycloaddition of ethynylcyclopropanes with aldehydes and aldimines has been found to give the corresponding 2-ethynyltetrahydrofurans or -pyrrolidines in high to excellent yields. In both cases, the formation of a ruthenium allenylidene complex as a key reactive intermediate is supported by density functional theory calculations. Cp* = η^5-C_5Me_5.

