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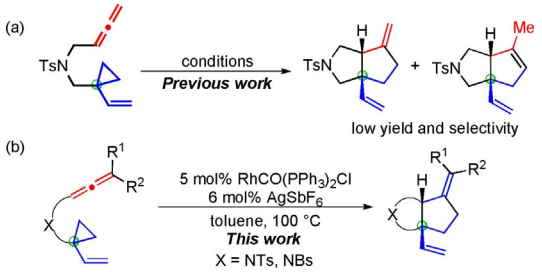
[3+2] Cycloadditions

Rh^{I}-Catalyzed Intramolecular [3+2] Cycloaddition of 1-Allene-vinylcyclopropanes

Cheng-Hang Liu, Feng Li, Yuan Yuan, Meng Dou, and Zhi-Xiang Yu*[a]

Abstract: A rhodium-catalyzed intramolecular [3+2] cycloaddition of 1-allene-vinylcyclopropanes (1-allene-VCPs) to construct cyclopentane-embedded bicyclic structures with quaternary stereocenters at the bridgehead position has been developed with good to excellent yields. In addition, this transformation could also be conducted on a large scale with reduced catalyst loading, which could be useful for further derivatizations and applications.



Scheme 1. Rh^{I}-catalyzed intramolecular [3+2] cycloaddition of 1-allene-VCPs.

Transition metal-catalyzed carbon-carbon bond activation of small rings with high strains provides unique opportunities to develop various intriguing transformations.[1] For example, the oxidative addition of transition metal into C–C bonds of cyclopropanes, followed by insertion of a 2π-component, has been established and developed by many groups to construct the ubiquitous five-membered carbocyclic skeletons in organic molecules.[2–5] Activating groups, such as electron-withdrawing groups[6] or directing groups,[7,8] are usually required for cycloaddition reactions involving cyclopropanes, by facilitating ring-opening and stabilizing the ring-opened intermediates. Our group found that vinylcyclopropane (VCP) derivatives without activating groups,[9] which can be either 5C- or 3C-synthons, can directly be applied in cycloadditions (Scheme 1).[10,11]

For example, our group developed a Rh^{I}-catalyzed intramolecular [3+2] cycloaddition reaction of 1-ene/yne-VCPs, affording cyclopentane- and cyclopentene-embedded bicyclic structures with quaternary stereocenter at the bridgehead position.[10b] While using terminally unsubstituted 1-allene-VCP as substrate, a mixture of cycloadducts with *exo* and *endo* C=C bonds was obtained in a moderate yield. We hypothesized that substituents on the allene moiety could stabilize the forming *exo* C=C bond and avoid the isomerization of [3+2] products, which could then become a valuable approach to synthesize widely found 5/5 and 6/5 skeletons with challenging bridgehead quaternary carbon centers. If this reaction is successful and generally applicable, it can also provide a good approach toward five-membered carbocycles with different substituents, which can complement the previous [3+2] reaction of 1-ene-VCPs, which did not tolerate any substituents at the 2C ene part.[10b] Herein we report our endeavors towards the development of intramolecular [3+2] cycloaddition of 1-allene-VCPs.

We began our investigation by using dimethyl-substituted allene-VCP substrate **1a** (Table 1). Our first experiment was conducted by using 5 mol% $[Rh(CO)_2Cl]_2$ as catalyst. To our delight, the proposed bicyclic cycloadduct **2a** could be achieved in a moderate yield, albeit accompanied by small amount of β-hydrogen elimination byproduct **3a** (Table 1, entry 1). We then tested other Rh^{I} catalysts with either C_2H_4 or norbornadiene (NBD) ligand, finding that a new eight-membered ring product **4a** was generated as the major product (Table 1, entries 2–3). The structure of compound **4a** was further confirmed by X-ray crystallographic analysis of its chemical derivative **6**, which was synthesized by a Diels–Alder reaction with 1-phenyl-1*H*-pyrrole-2,5-dione (see the Supporting Information). Further screening of catalysts showed that cationic rhodium catalysts were efficient for the transformation, and best yield and selectivity (74%, **2a**/**3a** = 95:5) were achieved when $Rh(CO)(PPh_3)_2Cl/AgSbF_6$ was used as the catalyst (Table 1, entries 5–7). Interestingly, spiro product **5a**, generated by oxidative cyclometalation pathway, was isolated in 34% yield from the reaction system when replacing the rhodium catalysts by an iridium catalyst (Table 1, entry 8).

Next, we screened other solvents such as 1,4-dioxane and DME, finding that both solvents gave lower yields and selectivities, compared to those reactions conducted in toluene (Table 1, entries 9–10). We increased the temperature of the [3+2] reaction to 100 °C, discovering that the reaction was finished within 4 h and the yield was slightly decreased to 72%

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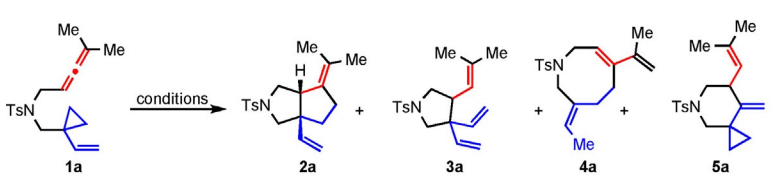
Table 1. Optimization of reaction conditions for the [3+2] reaction.[a]



Entry	Catalyst[b]	Additive[c]	Solvent	Temp [°C]	Time [h]	Yield [%][d]	2a/3a/4a[e,f]
1	$[Rh(CO)_2Cl]_2$	–	toluene	80	22	48	77:23:0
2	$[Rh(C_2H_4)_2Cl]_2$	–	toluene	80	17	57	32:21:47[g]
3	$[Rh(NBD)Cl]_2$	–	toluene	80	26	55	28:24:48[g]
4	$Rh(PPh_3)_3Cl$	–	toluene	80	17	complex mixture	–
5	$RhCO(PPh_3)_2Cl$	$AgSbF_6$	toluene	80	16	74	95:5:0
6	$Rh(PPh_3)_3Cl$	$AgSbF_6$	toluene	80	17	81	74:26:0
7	$[Rh(COD)_2]BF_4$	–	toluene	80	17	27	93:7:0
8	$[Ir(COD)Cl]_2$	–	toluene	80	18	34 (**5a**)	–
9	$RhCO(PPh_3)_2Cl$	$AgSbF_6$	1,4-dioxane	80	16	67	91:9:0
10	$RhCO(PPh_3)_2Cl$	$AgSbF_6$	DME	80	16	70	95:5:0
11	$RhCO(PPh_3)_2Cl$	$AgSbF_6$	toluene	100	4	72	>95:5:0
12[h]	**$RhCO(PPh_3)_2Cl$**	$AgSbF_6$	**toluene**	**100**	**4**	**90**[i]	**>95:5:0**
13[j]	$RhCO(PPh_3)_2Cl$	$AgSbF_6$	toluene	100	3	69	>95:5:0

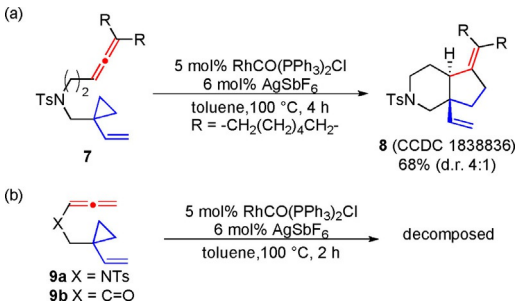
[a] Reactions were performed on a 0.1 mmol scale. [b] 5 mol%. [c] 6 mol%. [d] Isolated yield of **2a**, **3a** and **4a**. [e] Determined by ^{1}H NMR. [f] Pure **3a** could not be isolated and the structure was proposed by analyzing the ^{1}H NMR spectrum of the crude reaction mixture. [g] With unidentified byproduct. [h] **1a** was added slowly by syringe pump within 1 h. [i] Average yield of two runs. [j] Under 0.2 atm CO. NBD = norbornadiene, COD = 1,5-cyclooctadiene, DME = 1,2-dimethoxyethane, Ts = *p*-toluenesulfonyl.

(Table 1 entry 11). Furthermore, when the substrate was added slowly to the reaction solution by syringe pump, the yield of **2a** can be increased to 90% and trace β-hydrogen elimination product **3a** could be observed by ^{1}H NMR spectroscopy (Table 1, entry 12). Finally, we carried out the reaction under the atmosphere of CO, hoping to achieve the [3+2+1] product.[7,12,13] However, no CO insertion product was detected and the [3+2] cycloadduct **2a** was obtained in 69% yield (Table 1, entry 13). Therefore, we chose the conditions in entry 12 of Table 1 as optimal conditions to further study the scope of the present [3+2] cycloaddition.

Various 1-allene-VCP substrates were synthesized and submitted to the optimal reaction conditions of [3+2] reaction (Table 2). Firstly, terminally disubstituted allenes were found to be good substrates (Table 2, entries 1–5) and the desired fused bicyclic products **2a–e** were isolated in excellent yields. For substrate **1e** which had two different substituted groups, the corresponding cycloadduct **2e** was obtained in 88% yield, albeit with a low *Z*/*E* selectivity (Table 2, entry 5). Substrate **1f** with terminally mono-substituted allene was also synthesized and submitted to the optimal reaction conditions. A slightly lower yield was obtained with a *Z*/*E* ratio of 3.2:1 for substrate **1f**.

We also changed the NTs tether in substrate to NBs tether and the corresponding substrate **1g** delivered the [3+2] cycloadduct **2g** in 89% yield (Table 2, entry 7). Unfortunately, C-tethered substrate **2h** could not be converted into the desired bicyclic product and the starting material decomposed very slowly after long-time heating (Table 2, entry 8). For O-tethered substrate **2i**, a mixture containing both the [3+2] cycloadduct and β-hydride elimination byproduct was generated under the standard reaction conditions and the desired [3+2] cycloadduct could not be isolated as a pure form because both products had similar polarities. In addition, substrates **1j–k** with substituents in the VCP moieties underwent the present [3+2] reaction and the desired bicyclic products **2j** and **2k** were obtained in yields of 86% and 81%, respectively (Table 2, entries 10–11).

Finally, we tested substrate **7** with a longer tether, hoping to achieve the 6,5-ring product (Scheme 2a). To our delight, the [3+2] cycloadduct **8** was isolated in 68% yield with a diastereomeric ratio of 4:1 using the standard reaction conditions. The major isomer with a *trans* ring-fusion was further confirmed by X-ray crystallographic analysis (See the Supporting Information). Substrates **9a** and **9b** with shorter tethers were also synthesized and submitted to the optimal reaction conditions (Scheme 2b). These substrates decomposed quickly,



Scheme 2. Cycloaddition reactions of substrates with elongated or shortened tethers.

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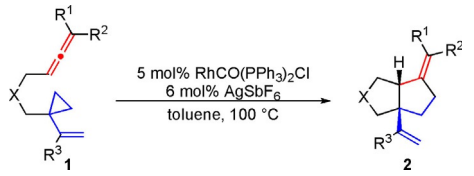
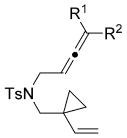
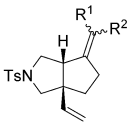
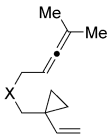
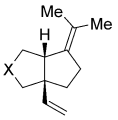
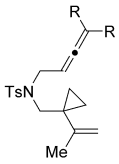
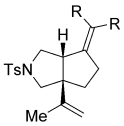
Table 2. Scope of this Rh-catalyzed [3+2] cycloaddition reaction[a]



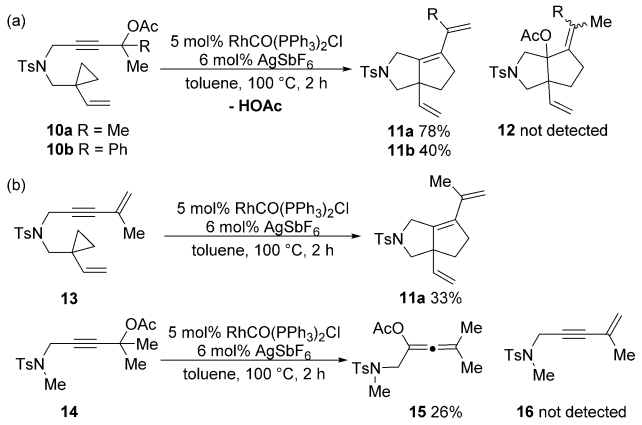
1 2

Entry	Substrate	Product[b,c]
		
1	**1a**, $R^1=R^2=$Me	**2a**, 4 h, 90%
2	**1b**, $R^1=R^2=$Et	**2b**, 4 h, 90%
3	**1c**, $R^1=R^2=$-$CH_2(CH_2)_4CH_2$-	**2c**, 4 h, 88%
4	**1d**, $R^1=R^2=$-$CH_2(CH_2)_3CH_2$-	**2d**, 4 h, 81%
5	**1e**, $R^1=$Me, $R^2=$Et	**2e**, 4 h, 88% (1.2:1)[d]
6	**1f**, $R^1=p$-BrC_6H_4, $R^2=$H	**2f**, 4 h, 76% (3.2:1)[e]
		
7	**1g**, X=NBs	**2g**, 4 h, 89%
8	**1h**, X=$C(CO_2Me)_2$	**2h**, 24 h, NR
9	**1i**, X=O	**2i**, 4 h, mixture
		
10	**1j**, R=Et	**2j**, 4 h, 86%
11	**1k**, R=-$CH_2(CH_2)_4CH_2$-	**2k**, 4 h, 81%

[a] The reaction was performed on a 0.1 mmol scale and 1 mL solution of substrate was added slowly to another 1 mL solution of catalyst using a syringe pump. [b] Isolated yield and the ratio was determined by ^{1}H NMR spectroscopy. The ratio of [3+2] cycloadduct and β-elimination byproduct was above 20:1 if not mentioned. [c] Average yields of two runs. [d] Inseparable isomers. [e] Separated by recrystallization. Bs=*p*-bromobenzenesulfonyl.

probably due to the high reactivity of allenamine and allenone in the substrates.

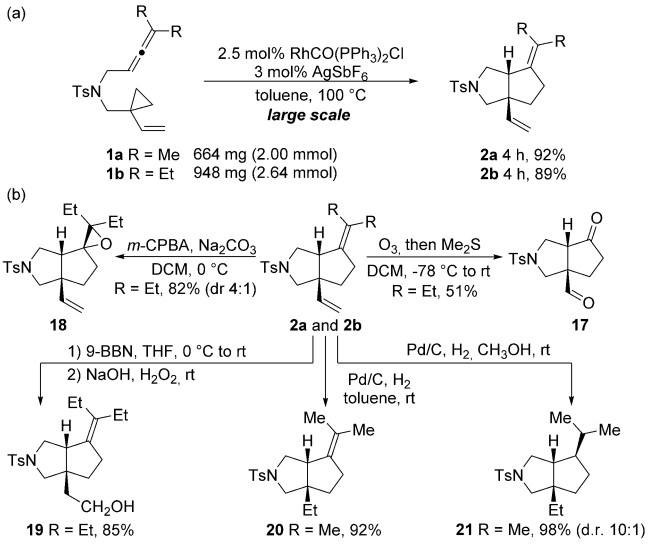
Considering that propargyl esters have been regarded as precursors of allenes (via the 1,3-acyloxy migration process) and used in cycloaddtion reactions by many researchers,[14] we therefore synthesized compounds **10a** and **10b**, hoping to get the cycloadduct **12** by tandem 1,3-acyloxy migration/[3+2] cycloaddition. Surprisingly, the assumed bicyclic compound **12** was not obtained. Instead, the bicyclic triene products **11a–b** were isolated in 78% and 40% yields, respectively (Scheme 3a), which may be generated by the tandem [3+2] cycloaddition/elimination reaction. Another possible pathway of generating **11a–b** is that substrates **10a–b** first underwent elimination of acetic acid to give an enyne intermediate, followed by [3+2] reaction. We can rule out the latter possibility because compound **13** containing the enyne moiety only gave



Scheme 3. Rh^I-catalyzed tandem [3+2] cycloaddition/elimination reactions.

the corresponding [3+2] bicyclic product **11a** in a rather low yield (Scheme 3b). In addition, we found that allene product **15** could be isolated in 26% yield under the standard reaction conditions from propargyl ester **14** by 1,3-acyloxy migration, without the observation of elimination product **16** (Scheme 3b). These experiments excluded the possibility of tandem elimination reaction/[3+2] cycloaddition.

The fused bicyclic skeletons generated from Rh^I-catalyzed [3+2] cycloadditions can be easily prepared in large scales and derivatized to other functionalized molecules (Scheme 4). The bicyclic [3+2] products **2a** and **2b** were isolated in 92% and 89% yields, on 2.00 mmol and 2.64 mmol scales, respectively, and the catalyst loading of rhodium was reduced to 2.5 mol% (Scheme 4a). The product **2b** was further transformed to aldehyde **17** in 51% yield under the ozone oxidation conditions. In addition, the two alkene moieties in **2b** showed different reactivities in *m*-CPBA epoxidation and hydroboration–oxidation conditions. Products **18** and **19** were obtained in 82% and



Scheme 4. Large-scale reactions of **1a–b** and some synthetic applications of the cycloadducts.

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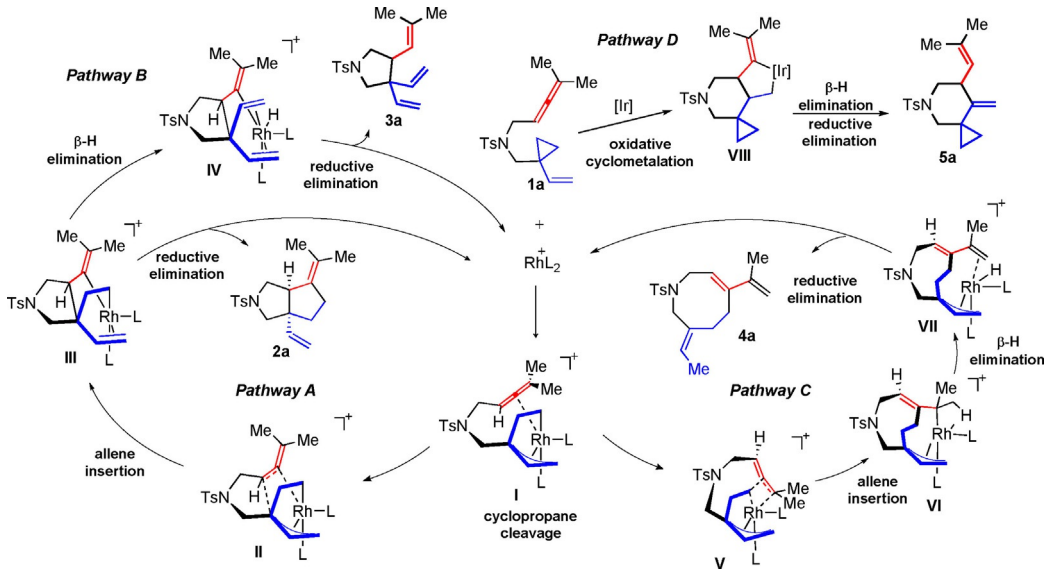

Scheme 5. Proposed mechanisms for the reaction of allene-VCPs.

85% yields, respectively. Finally, hydrogenation was carried out by using Pd/C and hydrogen gas to reduce the double bonds in **2a**. Different reductive products were obtained using different solvents (Scheme 4b).

The proposed mechanisms of this [3+2] cycloaddition and the other pathways involving the formation of byproducts are shown in Scheme 5. The [3+2] catalytic cycle commences with the binding of the catalytic rhodium species to the alkene moiety of the VCP, followed by cleavage of the cyclopropane ring to afford intermediate **I**. Under the standard reaction conditions, the inner double bond of the allene moiety inserts into the Rh–C bond, via transition state **II**, to afford intermediate **III**. Finally, the fused bicyclic product **2a** is formed by reductive elimination and the catalytic rhodium species is regenerated to complete the catalytic cycle (Scheme 5, pathway A). Meanwhile, a small amount of the byproduct **3a** is generated by the β-elimination of intermediate **III**, followed by reductive elimination (Scheme 5, pathway B). However, when the rhodium catalyst with NBD or C_2H_4 ligand is used, the outside double bond of allene prefers to insert into the Rh–C bond, via transition state **V**, to form an eight-membered ring intermediate **VI**. As pathway C shows, the eight-membered ring product **4a** will be delivered by β-elimination/ reductive elimination. In addition, the proposed mechanism about the formation of spiro product **5a** is shown as pathway D. In this pathway, a metallacyclopentane intermediate **VIII** will be generated when $[Ir(COD)Cl]_2$ is used instead of rhodium catalysts.

In summary, we have developed a rhodium catalyzed intramolecular [3+2] cycloaddition of 1-allene-vinylcyclopropanes to construct fused bicyclic **5/5** and **6/5** products with quaternary carbon centers in the bridgehead position. The transformation can give good to excellent yields when using N-tethered substrates. This cycloaddition reactions can also be conducted in large scale with reduced catalyst loading, which builds a useful foundation for further derivatizations and applications of the [3+2] cycloadducts.

Experimental Section

To a mixture of $Rh(CO)(PPh_3)_2Cl$ (3.5 mg, 5 mol%) and $AgSbF_6$ (2.1 mg, 6 mol%) was added toluene (1 mL) and stirred at room temperature under argon for 5 min. Then a solution of substrate (**1a–g**, **1j**, **1k** or **7**, 0.1 mmol) in toluene (1 mL) was added slowly by syringe pump (ca. 1 h) at 100 °C. After the addition of the substrate, the solution was continuously stirred for 3 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA) to afford the corresponding [3+2] cycloadduct **2a–g**, **2j**, **2k** or **8**.[15]

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: allenes · bicyclic compounds · cycloaddition · rhodium · vinylcyclopropanes

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