[5+2] Cycloaddition

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Rhodium(I)-Catalyzed Intramolecular [5+2] Cycloaddition Reactions of Alkynes and Allenylcyclopropanes: Construction of Bicyclo[5.4.0]undecatrienes and Bicyclo[5.5.0]dodecatrienes**

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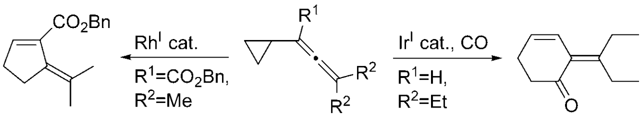
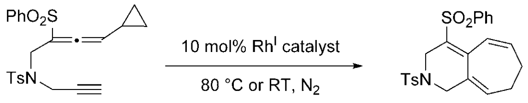
Highly strained cyclopropane derivatives have served as useful and powerful C_3 building blocks[1] for the construction of various ring systems, and the metal-catalyzed cleavage of the activated carbon-carbon σ bond of the cyclopropane ring[2,3] must be one of the most attractive methods from a synthetic point of view. Of particular interest is the Rh^{I}-catalyzed [5+2] cycloaddition of vinylcyclopropanes[3–5] with carbon–carbon π-components for the efficient formation of seven-membered compounds. In 1995, Wender et al. reported the first example[3a] of the Rh^{I}-catalyzed [5+2] cycloaddition reaction of vinylcyclopropanes with alkynes to provide bicyclo[5.3.0]decadienes.[3c,g,j] This method[3,4] was successfully applied to the [5+2] cycloaddition reactions of allenes[3e,f,h] as well as alkenes[3b,d,g,j,4a] as an alternative carbon–carbon π-counterpart. In sharp contrast to the extensive investigation of vinylcyclopropanes,[2b,c,e,3–5] very few examples[6] of the ring-closing reaction of allenylcyclopropane, which is regarded as an alkylidene homologue of vinylcyclopropane, have been reported. Two representative examples are shown in Scheme 1; one involves the Rh^{I}-catalyzed cycloisomerization[6b] of allenylcyclopropanes into α-alkylidenecyclopentenes, and the other is the formation of the α-alkylidene-3-cyclohexen-1-one frameworks by the Ir^{I}-catalyzed carbonylative [5+1] ring-closing reaction[6c] of allenylcyclopropanes.



Scheme 1. Metal-catalyzed ring-closing reaction of allenylcyclopropanes.

Our continuing interest in the field of the $[\{RhCl(CO)_2\}_2]$- and $[\{RhCl(CO)dppp\}_2]$-catalyzed cycloaddition reactions of phenylsulfonylallenes[7] prompted us to investigate the intramolecular cycloaddition reaction between phenylsulfonylallenes that contain a cyclopropyl group at the allene terminus and alkynes. Herein, we describe the preliminary results of the Rh^{I}-catalyzed ring-closing reaction of alkyne-allenylcyclopropane derivatives for the facile preparation of the bicyclo[5.4.0]undecatrienes and bicyclo[5.5.0]dodecatrienes. Our initial evaluation of the Rh^{I}-catalyzed [5+2] cycloaddition of an alkyne-allenylcyclopropane derivative focused on the preparation of the bicyclo[5.4.0]undecatriene framework. Treatment of *N*-Ts derivative **1**, which possesses a terminal alkyne group, with 10 mol % of $[\{RhCl(CO)_2\}_2]$ in toluene at 80 °C under a nitrogen atmosphere for 2 h produced the desired bicyclo[5.4.0]undecatriene derivative **2** in 66 % yield (Table 1, entry 1).[8] This ring-closing reaction even occurred at room temperature to give **2** in 57 % yield, although a more prolonged reaction time (24 h) was required (Table 1, entry 2). It is noteworthy that these results are in sharp contrast to those obtained for the $[\{RhCl(CO)_2\}_2]$-catalyzed [5+2] cycloaddition of alkyne-vinylcyclopropanes,[3c] in which an internal alkyne consistently and efficiently afforded the corresponding ring-closed products, whereas no [5+2] cyclo-

Table 1: Rhodium(I)-catalyzed [5+2] cycloaddition reaction of **1**.[a]



1 **2**

Entry	Rh^{I} catalyst	Solvent	T [°C]	t [h]	Yield [%][b]
1	$[\{RhCl(CO)_2\}_2]$	toluene	80	2	66
2	$[\{RhCl(CO)_2\}_2]$	toluene	RT	24	57
3	$[\{RhCl(CO)dppp\}_2]$	toluene	80	0.2	90
4	$[\{RhCl(CO)dppp\}_2]$	toluene	RT	1	88
5	$[\{RhCl(CO)_2\}_2]$	dioxane	80	0.3	64
6	$[\{RhCl(CO)_2\}_2]$	dioxane	RT	1.5	55
7	$[\{RhCl(CO)_2\}_2]$	DCE	80	1	80
8	$[\{RhCl(CO)_2\}_2]$	DCE	RT	30	66
9	$[\{RhCl(CO)dppp\}_2]$	dioxane	80	1	72
10	$[\{RhCl(CO)dppp\}_2]$	dioxane	RT	11	n.r.[c]
11	$[\{RhCl(CO)dppp\}_2]$	DCE	80	0.5	69
12	$[\{RhCl(CO)dppp\}_2]$	DCE	RT	3	79

[a] Reaction conditions: 0.1 M solution of alkyne-allenylcyclopropane **1** was treated with the Rh^{I} catalyst (10 mol %) under a nitrogen atmosphere. [b] Yield of isolated product. [c] n.r. = no reaction. DCE = dichloroethane, dppp = 1,3-bis(diphenylphosphino)propane, Ts = 4-toluenesulfonyl.

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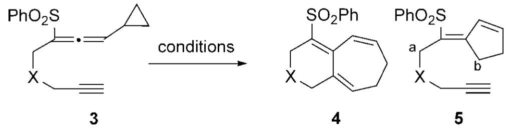
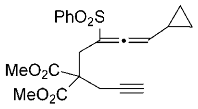
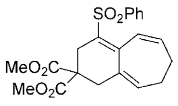
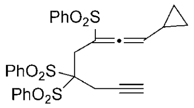
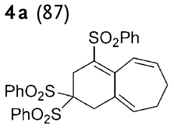
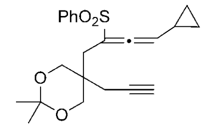
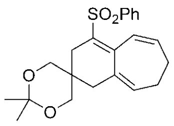
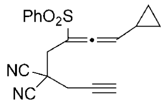
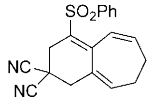
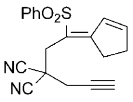
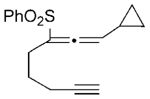
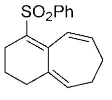
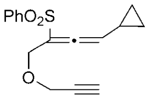
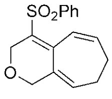
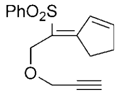
addition product was formed when a terminal alkyne was employed.[9] Other catalysts were tested, such as $[RhCl(PPh_3)_3]$, $[RhCl(CO)(PPh_3)_2]$, $[\{RhCl(cod)\}_2]$, $[\{RhCl(CO)dppp\}_2]$, $[Rh(C_{10}H_8)cod]^+BF_4^-$, and $[Rh(CO)(dppp)_2]^+Cl^-$, with or without a silver salt; however, much lower yields or no reaction at all was observed in all cases, apart from $[\{RhCl(CO)dppp\}_2]$. Indeed, the addition of compound **1** to 10 mol% $[\{RhCl(CO)dppp\}_2]$ in toluene at 80 °C for 10 min afforded **2** in a higher yield (90%; Table 1, entry 3). Similarly, a satisfactory yield was obtained when the reaction was performed at room temperature for 1 h (Table 1, entry 4). Therefore, $[\{RhCl(CO)_2\}_2]$ and $[\{RhCl(CO)dppp\}_2]$ were found to be suitable catalysts for our purpose. Next, we examined two solvents, dioxane and dichloroethane, both of which are frequently employed in rhodium-catalyzed reactions.[3] Dichloroethane furnished higher yields in the $[\{RhCl(CO)_2\}_2]$-catalyzed reaction (Table 1, entries 7 and 8), although $[\{RhCl(CO)dppp\}_2]$/toluene (Table 1, entries 3 and 4) was superior to both dioxane and dichloroethane (Table 1, entries 9–12).

The [5+2] cycloaddition of several substrates that contain a terminal triple bond was examined using the complementary and interchangeable use of two sets of conditions: $[\{RhCl(CO)_2\}_2]$/dichloroethane and $[\{RhCl(CO)dppp\}_2]$/toluene (Table 2). Treatment of **3a** with $[\{RhCl(CO)_2\}_2]$ afforded the corresponding ring-closed product **4a** in satisfactory yields at both 80 °C and at room temperature (Table 2, entry 1). Bis(phenylsulfonyl) derivative **3b** and dimethyl acetal derivative **3c** showed similar behavior to **3a** under the $[\{RhCl(CO)_2\}_2]$ conditions to furnish **4b** and **4c** in high yields (Table 2, entries 2 and 3). In the case of malononitrile derivative **3d**, the [5+2] product **4d** was formed in moderate yield (53%) with the formation of a cyclopentene derivative by-product **5d** [10] when exposed to $[\{RhCl(CO)dppp\}_2]$ (Table 2, entry 4). Compound **3e**, which contained a simple methylene tether between two reaction centers, provided the corresponding [5+2] product **4e** in 65% or 51% yields for the two reaction conditions (Table 2, entry 5). A slightly lower yield of **4e** (compared with those of **4a**–**c**) might be largely due to a loss of the bis(substituent) effect.[11] Oxygen analogue **4f** was obtained in moderate yields with $[\{RhCl(CO)dppp\}_2]$ (Table 2, entry 6). Therefore, the results in Tables 1 and 2 may be summarized as follows: 1) judicial choice of two catalysts consistently and complementarily afforded the corresponding [5+2] products **4** (and **2**) in moderate to high yields; and

Table 2: Rhodium(I)-catalyzed [5+2] cycloaddition reaction of **3**.[a]



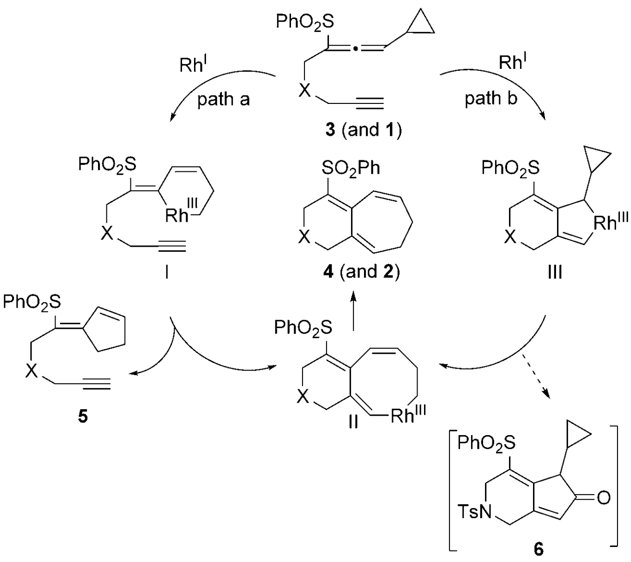
Rh^I catalyst A: $[\{RhCl(CO)_2\}_2]$
B: $[\{RhCl(CO)dppp\}_2]$

Entry	Substrate	Rh^I cat.	T [°C], t [h]	Product (yield [%])[b]	
1	 **3a**	A	80, 0.5	 **4a** (86)	
		A	RT, 3	**4a** (87)	
2	 **3b**	A	80, 0.2	 **4b** (80)	
		A	RT, 6	**4b** (76)	
3	 **3c**	A	80, 0.2	 **4c** (83)	
		A	RT, 1	**4c** (64)	
4	 **3d**	B	80, 1	 **4d** (53)	 **5d** (12)
		B	RT, 24	**4d** (10)[c]	**5d** (28)
5[d]	 **3e**	A	80, 0.2	 **4e** (65)	
		A	RT, 1	**4e** (51)	
6	 **3f**	B	80, 1	 **4f** (52)	 **5f** (trace)
		B	RT, 24[e]	**4f** (60)	**5f** (19)

[a] Reaction conditions: 0.1 M solution of alkyne-allenylcyclopropane **3** was treated with 10 mol% of $[\{RhCl(CO)_2\}_2]$ in dichloroethane or with 10 mol% of $[\{RhCl(CO)dppp\}_2]$ in toluene under a nitrogen atmosphere. [b] Yield of isolated product. [c] Compound **3d** was recovered in 35% yield. [d] Reaction was performed in 0.05 M solution of toluene in the presence of 20 mol% of $[\{RhCl(CO)_2\}_2]$. [e] Reaction was carried out in 0.05 M solution.

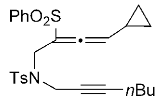
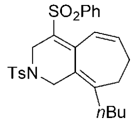
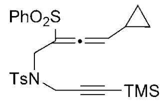
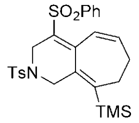
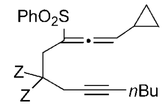
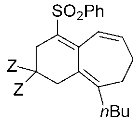
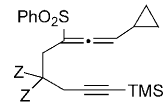
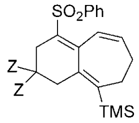
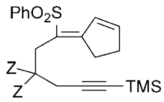
2) $[\{RhCl(CO)_2\}_2]$ usually produced better results than those with $[\{RhCl(CO)dppp\}_2]$, although this depends on the substrate.

There are two plausible mechanisms for the production of the [5+2] product **4**, based on the previously proposed mechanism for the metal-catalyzed [5+2] cycloaddition of vinylcyclopropanes containing π-π multiple bonds (Scheme 2).[3,4] Path a involves the initial production of a rhodacyclohexene intermediate I from the Rh^I-catalyzed cycloisomerization reaction between a cyclopropane ring and the distal double bond of an allenyl moiety.[6b,c] The insertion reaction of the C_{sp^2}–Rh^{III} bond into the triple bond of I would lead to rhodabicyclo[6.4.0]dodecatriene intermediate II. Reductive elimination of Rh^{III} from intermediate II should then provide **4**. Isolation of cyclopentene derivative **5**[6b] would strongly rationalize the intermediacy of I (path a). Reductive elimination, instead of the insertion reaction of I, would result in the formation of **5**. The other possible reaction pathway is indicated by path b. The oxidative addition reaction of the Rh^I catalyst to an alkyne group and the distal double bond of the allenyl moiety would initially form the rhodabicyclo[4.3.0]nonadiene intermediate III, which might be susceptible to a ring expansion assisted by the release of the ring strain in the cyclopropane ring to generate the eight-membered intermediate II. Path b, via intermediate III, might be indirectly supported by the fact that a carbonylative [2+2+1] product **6** was obtained as a by-product together with **2**, when **1** was reacted under a carbon monoxide atmosphere instead of nitrogen.[12] Thus, it seems that both reaction pathways are feasible for this [5+2] ring-closing reaction, depending on the reaction conditions.



Scheme 2. A plausible mechanism for the formation of **4**, **5**, and **6** from **3**.

Table 3: Rhodium(I)-catalyzed [5+2] cycloaddition reaction of **7**.[a]

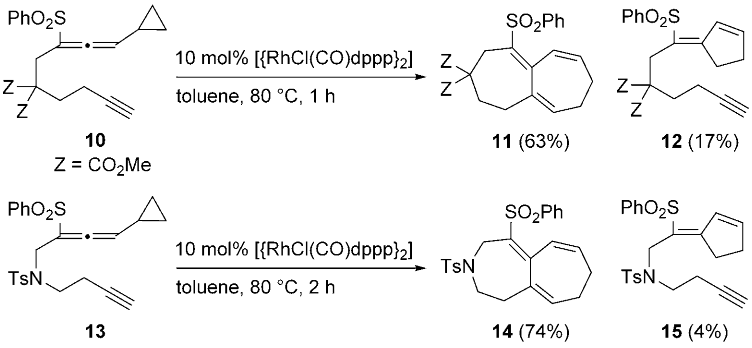
Entry	Substrate	T [°C], t [h]	Product (yield [%])[b]	
1	 **7a**	80, 0.2 RT, 1	 **8a** (76) **8a** (75)	
2	 **7b**	80, 0.2 RT, 1	 **8b** (59) **8b** (67)	
3	 **7c** (Z = CO_2Me)	80, 0.2 RT, 1	 **8c** (89) **8c** (81)	
4	 **7d** (Z = CO_2Me)	80, 0.5 RT, 24	 **8d** (58) **8d** (50)	 **9d** (25) **9d** (9)

[a] Reaction conditions: 0.1 M solution of alkyne-allenylcyclopropane **7** was treated with 10 mol% of $[\{RhCl(CO)_2\}_2]$ in dichloroethane under a nitrogen atmosphere. [b] Yield of isolated product. TMS = trimethylsilyl.

Next, we examined the Rh^I-catalyzed [5+2] cycloaddition reaction between an allenylcyclopropane and internal alkyne groups (Table 3). Treatment of *N*-Ts derivative **7a** and malonate derivative **7c**, both of which contain a 2-heptynyl residue, with a catalytic amount of $[\{RhCl(CO)_2\}_2]$ provided bicyclo[5.4.0] derivatives **8a** and **8c** in satisfactory yields (Table 3, entries 1 and 3). The terminal TMS compounds **7b** and **7d** furnished their corresponding [5+2] cycloaddition products **8b** and **8d**, respectively, in lower yields compared to those of **8a** and **8c** (Table 3, entries 2 and 4). In the case of **7d**, the formation of cyclopentene derivative **9d**, which is structurally similar to **5d** and **5f** (Table 2), was observed (Table 3, entry 4). The alternative $[\{RhCl(CO)dppp\}_2]$ catalyst was not as effective in the transformation of **7** into **8**.

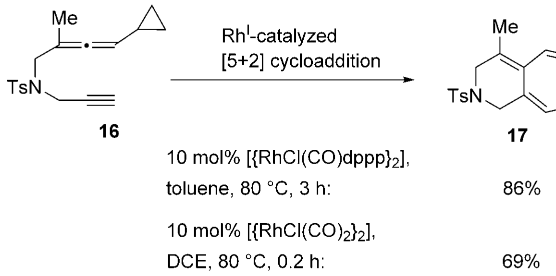
Our next objective was the application of the alkyne-allenylcyclopropane ring-closing reaction to the construction of the larger-sized bicyclo[5.5.0]dodecatriene to preliminarily confirm the scope of this procedure (Scheme 3). Exposure of one-carbon homologated substrate **10** to a catalytic amount of $[\{RhCl(CO)_2\}_2]$ under the standard condition provided the desired bicyclo[5.5.0]derivative **11** in low yields (22–32%). Changing the catalyst from $[\{RhCl(CO)_2\}_2]$ to $[\{RhCl(CO)dppp\}_2]$ produced a significant improvement to furnish **11** in 63% yield along with the formation of **12** (17%). $[\{RhCl(CO)dppp\}_2]$ was also effective for nitrogen-atom-containing substrate **13**. Indeed, **14** was obtained in 74% yield together with **15** (4%) when heated in toluene for two hours.

Finally, it was shown that having a phenylsulfonyl substituent on the allenyl moiety was not essential for the efficient [5+2] ring-closing reactions of the alkyne-allenylcyclopropane derivatives. Furthermore, treatment of **16** with



Scheme 3. Construction of a bicyclo[5.5.0]dodecatriene skeleton.

10 mol% of [{RhCl(CO)dppp}$_2$] effected the cycloisomerization to produce the corresponding methyl derivative **17** exclusively in 86% yield. Faster consumption of **16** was observed in the presence of 10 mol% of [{RhCl(CO)$_2$}$_2$] at 80°C to furnish **17** in 69% yield (Scheme 4).[13]



Scheme 4. Ring-closing reaction of methyl-substituted allene **16**.

In summary, we have developed a Rh^I-catalyzed intramolecular [5+2] cycloisomerization reaction between alkyne and allenylcyclopropane functionalities under mild conditions, which leads to the facile formation of the bicyclo[5.4.0]undecatriene frameworks. Judicious choice of the Rh^I catalyst, [{RhCl(CO)$_2$}$_2$] or [{RhCl(CO)dppp}$_2$], consistently afforded the desired products in satisfactory yields. This method was successfully applied to the construction of larger bicyclo[5.5.0]dodecatriene skeletons. Further investigation into the scope and limitations of this method, as well as its applications in the synthesis of natural products, are now underway.

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

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[8] The reaction of **1** with 5 mol% of [{RhCl(CO)$_2$}$_2$] produced **2** in 37% yield. Thus, we used 10 mol% of Rh^I catalyst for the next investigation.

[9] A successful example of [{RhCl(CO)$_2$}$_2$]-catalyzed [5+2] cycloaddition between the terminal alkyne and (*E*)-2-(1-ethoxycyclopropyl)vinyl moieties was reported; see Ref. [3g].

[10] The *Z* configuration of **5** was determined by NOE experiments in which enhancement between H$_a$ and H$_b$ was observed.

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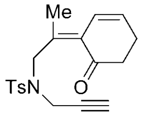
[12] Compound **6** (13%) was formed along with **2** (48%) when a solution of **1** was heated in toluene at 100°C in the presence of 10 mol% of [{RhCl(CO)$_2$}$_2$] under 10 atm of CO for 1 h.

[13] A small amount of a by-product was obtained, the structure of which may be assigned as **18** from its ^{1}H NMR and IR spectra. The formation of **18** could be rationalized in terms of participation of carbon monoxide derived from the [{RhCl(CO)$_2$}$_2$] catalyst.



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