Cyclization

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Rhodium(I)-Catalyzed Cycloisomerization of Benzylallene-Alkynes through C–H Activation**

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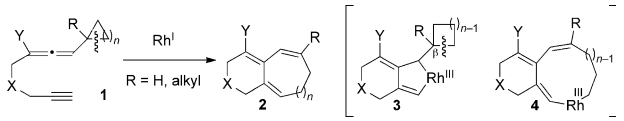
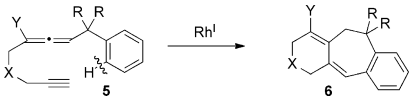
Abstract: *The efficient Rh^I-catalyzed cycloisomerization of benzylallene-alkynes produced the tricyclo[9.4.0.0^{3,8}]pentadecapentaene skeleton through a C_{sp^2}–H bond activation in good yields. A plausible reaction mechanism proceeds via oxidative addition of the acetylenic C–H bond to Rh^I, an ene-type cyclization to the vinylidenecarbene–Rh^I intermediate, and an electrophilic aromatic substitution with the vinylidenecarbene species. It was proposed based on deuteration and competition experiments.*

In the last decade, transition-metal-catalyzed C–H[1] and C–C[2] bond-activation reactions have been extensively studied as powerful step- and atom-economical methods for the synthesis of complex organic molecules. These activation reactions often require directing groups in the substrates, which direct transition metals to the right position close to the reactive sites. The relief of strain would be an alternative driving force to facilitate the cleavage of C–C bonds on cycloalkanes. We recently disclosed that the Rh^I-catalyzed cycloaddition of allenylcyclopropane-alkynes **1** ($n=1$) afforded the bicyclo[5.4.0]undecatrienes **2** ($n=1$)[3a,4] in the [5+2] ring-closing manner (Scheme 1). The reaction was assumed to proceed through cleavage of the cyclopropane ring driven by the release of the high strain energy (27.5 kcal mol^{-1}).[5] A similar ring construction could be realized using allenylcyclobutane-alkynes **1** ($n=2$) producing the eight-membered bicyclic compounds **2** ($n=2$)[3b] in high yields ([6+2] cycloaddition). The simple cyclobutane ring without any activating functional group could generally not be opened, let alone be used as a C_4 building block.[2e–g,6] The production of **2** ($n=2$) could tentatively be rationalized by the initial formation of the rhodabicyclo[4.3.0] intermediate **3** ($n=2$),[3,7] followed by β-C elimination,[2e–g,6] which would release the cyclobutane ring strain (26.3 kcal mol^{-1}),[8] giving rise to the nine-membered rhodabicycle **4**. Reductive elimination of **4** would then provide the final products. The successful application of this methodology to the cyclopentane derivative **1** ($n=3$) afforded the nine-membered bicyclic compounds **2** ($n=3$).[3c] This novel [7+2] cycloaddition involves the unprecedented cleavage of the "normal-sized" cyclopentane ring by releasing its small strain energy of 6.3 kcal mol^{-1}[8] presumably via the intermediate **3** ($n=3$).[3] Thus, it might be assumed that the allene-alkyne unit works as a highly reactive π component toward the Rh^I catalyst[9] resulting in the formation of the rhodabicyclic intermediate, which would subsequently activate the C–C and/or C–H bond near the Rh species. Here we describe another type of C–H activation of benzylallene-alkynes which formally involves cleavage of a C_{sp^2}–H bond on the benzene ring to furnish the tricyclo[9.4.0.0^{3,8}]pentadecapentaene derivatives in high yields (Scheme 2).



Scheme 1. Previous study: Rh^I-catalyzed cycloaddition of allenylcycloalkane-alkynes ($n=1$–3).[3]



Scheme 2. This study: Rh^I-catalyzed cycloisomerization of benzylallene-alkynes.

In our initial experiments we used the benzylallene-alkyne **5a** possessing a phenylsulfonyl group on the allenyl moiety. Treatment of **5a** with 10 mol% of [RhCl(PPh$_3$)$_3$], which was effective for the ring-opening of the allenylcyclopentane-alkyne **1**,[3c] in refluxing toluene for 9 h surprisingly produced the tricyclo[9.4.0.0^{3,8}]pentadecapentaene derivative **6a** in 61% yield (Table 1, entry 1). The reaction with [RhCl(CO)(PPh$_3$)$_2$] was less efficient and the yield was lower (entry 2). Neither [RhCl(dppp)$_2$], which is a suitable catalyst for the ring-opening of the allenylcyclobutane,[3b] or its CO analogue, [{RhCl(CO)(dppp)}$_2$], provided good results (entries 3 and 4). Several other catalysts, such as [{RhCl(CO)$_2$}$_2$], [{RhCl(cod)}$_2$], [Rh(cod)$_2$]BF$_4$/PPh$_3$, and [Rh(cod)$_2$]OTf/PPh$_3$, were examined, but all of them except for [{RhCl(CO)$_2$}$_2$] furnished poor results. Indeed, the reaction with [{RhCl(CO)$_2$}$_2$] at 80 °C was complete within 2 h to afford **6a** in 93% yield (entry 5).

Two sets of complementary and interchangeable conditions (10 mol% [{RhCl(CO)$_2$}$_2$] or [RhCl(PPh$_3$)$_3$] in toluene

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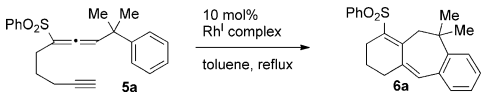
Table 1: Optimization of reaction conditions for Rh^{I}-catalyzed cycloisomerization of benzylallene-alkyne **5a**.



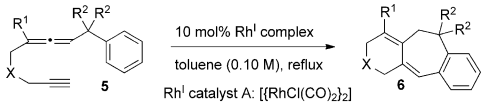
Entry	Rh^{I} complex	*t* [h]	Yield [%][a]
1	$[RhCl(PPh_3)_3]$	9	61
2	$[RhCl(CO)(PPh_3)_2]$	24	40
3	$[RhCl(dppp)_2]$	6	complex mixture
4	$[\{RhCl(CO)dppp\}_2]$	3	complex mixture
5[b]	$[\{RhCl(CO)_2\}_2]$	2	93

[a] Yield of the isolated product. [b] Reaction was performed at 80 °C.

heated at reflux) were applied to several benzylallene-alkynes (Table 2). The malonate derivative **5b** with the *gem*-disubstituent effect[10] was treated with $[\{RhCl(CO)_2\}_2]$ to give the product **6b** in 94% yield (entry 1).[11] The nitrogen and oxygen congeners **5c**,**d** produced the corresponding aza compound **6c** (71% yield) and oxa compound **6d** (62% yield), respectively (entries 2 and 3). It was shown that the phenylsulfonyl substituent on the allenyl moiety was not essential for this transformation. Thus, the cycloisomerization of the phosphonate derivative **5e** easily occurred to give **6e** in 84% yield (entry 4). Furthermore, upon exposure to the standard conditions with $[RhCl(PPh_3)_3]$, the benzylallenes having methyl (**5f**), butyl (**5g**), and phenyl groups (**5i**) on the allenyl moiety underwent cycloisomerization to furnish the tricyclic products **6f** (95% yield), **6g** (86% yield), and **6i** (78% yield), respectively (entries 5, 6, and 8). The reaction of the bulky *tert*-butyl derivative **5h** in the presence of $[\{RhCl(CO)_2\}_2]$ proceeded without any trouble to provide the desired product **6h** in 67% yield (entry 7). The substrates **5j** and **5k** with dibutyl or cyclohexyl groups instead of a dimethyl group could be converted into the tricyclic adducts **6j** (80%) and **6k** (72%) (entries 9 and 10). The phenyl congener **5l** required rather drastic conditions (heating at 150 °C in a microwave reactor for 15 h, with $[RhCl(PPh_3)_3]$) and gave a low yield (entry 11). As mentioned in Scheme 1, the allenylcyclobutane derivatives **1** ($n=2$, R = alkyl) produced the ring-expanded products **2** presumably via **3**. We thought it would be interesting to investigate the reaction of allenylcyclobutane derivative **5m**, which has a phenyl group instead of the alkyl substituent, in the presence of the Rh catalyst. Thus, the standard conditions ($[\{RhCl(CO)_2\}_2]$ in toluene at reflux) were applied to compound **5m**. The starting material **5m** was completely consumed within 0.2 h, but an intractable mixture was obtained (entry 12).

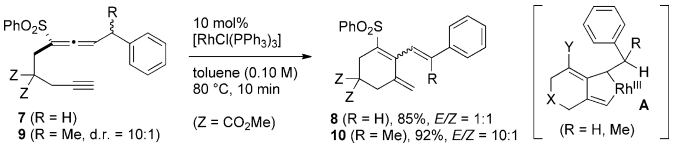
Two control experiments were performed. Upon exposure of **7** to the standard conditions, the desired product was not produced at all, but the triene compound **8** was obtained in 85% yield as a 1:1 mixture of (*E*) and (*Z*) isomers (Scheme 3).

Table 2: Rh^{I}-catalyzed cycloisomerization of benzylallene-alkyne **5**.



Entry	**5**	R^1	R^2	X	Rh^{I} cat.	*t* [h]	**6:** Yield [%][a]
1	**5b**	SO_2Ph	Me	$C(CO_2Me)_2$	A	0.2	**6b**: 94
2[b]	**5c**	SO_2Ph	Me	NTs	A	0.2	**6c**: 71
3[b]	**5d**	SO_2Ph	Me	O	A	0.2	**6d**: 62
4	**5e**	$P(O)(OEt)_2$	Me	$C(CO_2Me)_2$	A	0.5	**6e**: 84
5	**5f**	Me	Me	$C(CO_2Me)_2$	B	0.2	**6f**: 95
6	**5g**	*n*Bu	Me	$C(CO_2Me)_2$	B	0.2	**6g**: 86
7	**5h**	*t*Bu	Me	$C(CO_2Me)_2$	A	1	**6h**: 67
8	**5i**	Ph	Me	$C(CO_2Me)_2$	B	0.2	**6i**: 78
9	**5j**	SO_2Ph	*n*Bu	$C(CO_2Me)_2$	A	0.2	**6j**: 80
10	**5k**	SO_2Ph	$-(CH_2)_5-$	$C(CO_2Me)_2$	B	1	**6k**: 72
11[c]	**5l**	SO_2Ph	Ph	$C(CO_2Me)_2$	B	15	**6l**: 31
12	**5m**	SO_2Ph	$-(CH_2)_3-$	$C(CO_2Me)_2$	A	0.2	—[d]

[a] Yield of the isolated product. [b] An 0.025 M solution was used. [c] Reaction was performed in a microwave reactor at 150 °C. [d] An intractable mixture was obtained.

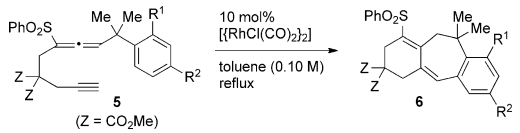


Scheme 3. Rh^{I}-catalyzed cycloisomerization of **7** and **9**.

A similar treatment of the monomethyl derivative **9** afforded **10** ($E/Z = 10:1$) in 92% yield. The formation of **8** and **10** could be well rationalized in terms of the intermediacy of the rhodabicyclic species **A**, which undergoes β-hydride elimination.[9a,12] These two experiments strongly indicated that the geminal disubstituent moiety at the benzyl position of **5** is essential for the efficient transformation to the desired tricyclic compound **6**.

The effect of the substituent on the benzene ring was examined next (Table 3). Substrates **5n**,**o** with a methyl group at the *p*- or *o*-position gave the cyclized products **6n** and **6o** in a quantitative and 78% yield, respectively (entries 1 and 2). In the case of **5p**, which has an electron-donating methoxy

Table 3: Examination of the effect of the substituent on the benzene ring of **5**.



Entry	**5**	R^1	R^2	*t* [h]	**6:** Yield [%][a]
1	**5n**	H	Me	0.2	**6n**: 99
2	**5o**	Me	H	0.2	**6o**: 78
3	**5p**	H	OMe	0.2	**6p**: 71
4	**5q**	H	Cl	0.5	**6q**: 71
5	**5r**	H	NO_2	2	**6r**: 82

[a] Yield of the isolated product.

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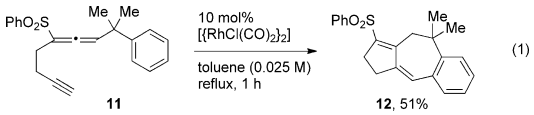
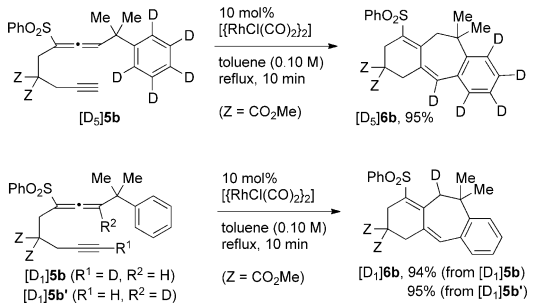
group, the reaction was complete within 0.2 h, but the yield of **6p** (71%) slightly decreased because of the formation of unidentified by-products. On the other hand, compounds **5q** and **5r** with electron-withdrawing chloro and nitro groups needed a prolonged reaction time (0.5 h and 2 h; **6q**: 71% and **6r**: 82% yield; entries 4 and 5). Thus, it was concluded that the ring-closing reaction consistently occurred irrespective of the electronic properties of the substituent on the benzene ring of **5**, although electron-withdrawing groups tend to slow down the reaction.

Treatment of the one-carbon-shortened substrate **11** with the Rh^I catalyst effected the construction of the tricyclic framework to produce **12** in 51% yield [Eq. (1)].



(1)

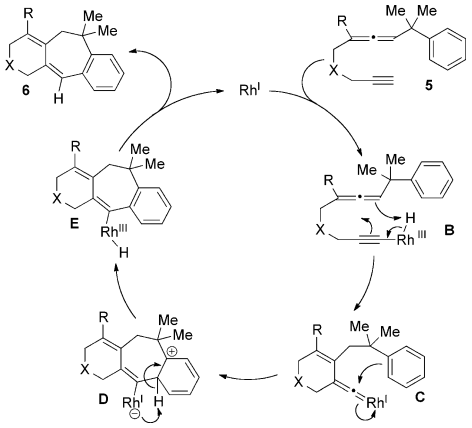
To obtain information on the mechanism of the novel transformation of **5** into **6**, we performed three experiments with the deuterated substrates, [D_5]**5b**, [D_1]**5b**, and [D_1]**5b′** (Scheme 4). Treatment of the pentadeuterated substrate



Scheme 4. Rh^I-catalyzed cycloisomerization of [D_5]**5b**, [D_1]**5b**, and [D_1]**5b′**.

[D_5]**5b** with [{RhCl(CO)$_2$}$_2$] under the standard conditions produced the deuterated product [D_5]**6b** in 95% yield. It became apparent that one deuterium atom was exclusively incorporated at the olefinic position on the seven-membered ring and the other four deuterium atoms remained on the benzene ring. In the case of the monodeuterated substrate [D_1]**5b**, the deuterium atom at the triple bond terminus was incorporated completely at the allylic position of the seven-membered ring of [D_1]**6b**. Another monodeuterated substrate [D_1]**5b′** afforded the same product [D_1]**6b**.

These deuteration experiments provided an informative insight into the mechanism of the cycloisomerization of **5** (Scheme 5). On the basis of these experiments in combination with the fact that substrates **5q** and **5r** with electron-withdrawing groups required longer reaction times (Table 3), the following plausible reaction mechanism is proposed. The oxidative addition of the acetylenic C–H bond to Rh^I initially occurs to form the Rh^{III} intermediate **B**.

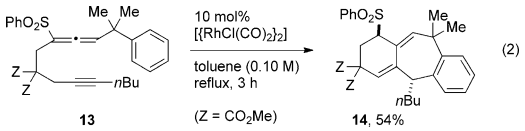


Scheme 5. Proposed reaction mechanism.

An ene-type cyclization of intermediate **B** then forms the vinylidenecarbene–Rh^I intermediate **C**.[13,14] Activation of a C_{sp^2}–H bond on the benzene ring could happen at this stage by nucleophilic addition of the pendant benzene ring to the α-carbon of the vinylidenecarbene species **C** to give **D**. A subsequent proton transfer from the benzene ring to the Rh center would then produce the intermediate **E**,[15] which undergoes reductive elimination to form the product **6**.

A competition experiment using an equimolar amount of **5b** and [D_5]**5b** revealed a kinetic isotope effect (KIE) value of 1.0,[16] indicating that the cleavage of the C–H bond of the benzene ring is not the rate-determining step. Furthermore, the similarly low KIE value (1.2) observed in the experiment using **5b** and [D_1]**5b**[16] suggested that oxidative addition of the acetylenic C–H bond to Rh^I is also not the rate-determining step. These results indirectly support the proposed reaction mechanism, which involves the conversion of the intermediate **C** to **E** through a stepwise Friedel–Crafts-type substitution reaction on the benzene ring.

Finally, the reaction of the substrate **13**, which has an internal alkyne, was examined not only to compare it with the reactions of the terminal alkyne derivatives, but also to obtain additional information about the mechanism of this cycloisomerization. Upon exposure to the standard conditions, the internal alkyne derivative **13** was converted into the tricyclic compound **14**, which was produced as a single diastereomer in rather lower yield (54%) [Eq. (2)]. The structure of **14** is



(2)

similar to that of **6**,[17] but differs in the position of the double bonds.[18] This result indicates that the reaction pathway from **13** to **14** is different from that for the formation of **6**.

In summary, we have developed the novel and efficient Rh^I-catalyzed cycloisomerization of benzylallene-alkyne derivatives leading to the formation of tricyclo[9.4.0.0^{3,8}]-pentadecapentaene derivatives. Preliminary investigations

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using deuterated substrates provided the basis for the proposed reaction mechanism which involves the following steps: 1) oxidative addition of acetylenic C–H bond to Rh^I, 2) ene-type cyclization to form the vinylidenecarbene-Rh^I intermediate, and 3) electrophilic aromatic substitution followed by proton transfer to the rhodium center (C_{sp^2}–H bond activation). The results presented here provide new insight into the chemistry of the C–H bond activation and transition-metal–vinylidene intermediates in catalysis. We are currently examining the scope and limitations of this method and conducting further mechanistic studies.

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[7] In the case of the allenylcyclopropane derivatives **1** (R = H, *n* = 1), we assumed the initial formation of the six-membered rhodacycle intermediate because cyclopropane has a fairly high ring strain energy.[3a] A similar rhodacycle intermediate could be considered for the reaction of the allenylcyclopropane-alkenes, see K. Sugikubo, F. Omachi, Y. Miyanaga, F. Inagaki, C. Matsumoto, C. Mukai, *Angew. Chem.* **2013**, *125*, 11579 – 11582; *Angew. Chem. Int. Ed.* **2013**, *52*, 11369 – 11372.

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[18] The isomerization of the double bonds of both **14** and **6** could not be observed. We do not have a suitable explanation of the mechanism for the formation of **14** from **13**.

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