

Cycloisomerizations

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Construction of Hexahydrophenanthrenes By Rhodium(I)-Catalyzed Cycloisomerization of Benzylallene-Substituted Internal Alkynes through C–H Activation

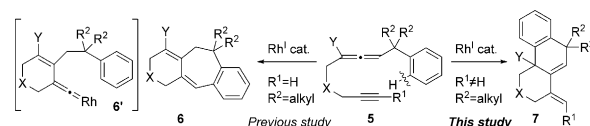
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Abstract: The treatment of benzylallene-substituted internal alkynes with $[\text{RhCl}(\text{CO})_2]_2$ effects a novel cycloisomerization by $\text{C}(\text{sp}^2)\text{--H}$ bond activation to produce hexahydrophenanthrene derivatives. The reaction likely proceeds through consecutive formation of a rhodabicyclo[4.3.0] intermediate, σ -bond metathesis between the $\text{C}(\text{sp}^2)\text{--H}$ bond on the benzene ring and the $\text{C}(\text{sp}^2)\text{--Rh}^{\text{III}}$ bond, and isomerization between three σ -, π -, and σ -allylrhodium(III) species, which was proposed based on experiments with deuterated substrates.

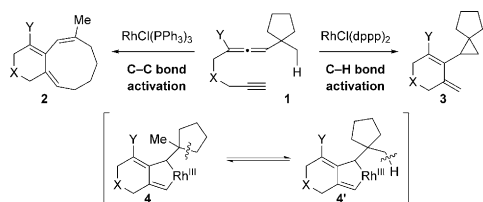
Cyclization reactions that make use of transition-metal-catalyzed $\text{C--H}^{[1]}$ and/or $\text{C--C}^{[2]}$ bond activation are powerful step- and atom-economic methods for the straightforward construction of complex polycyclic skeletons that are inaccessible by other conventional methods. These activation processes often require directing groups in the substrates, which bind the transition-metal catalyst at a position close to the reactive site. Relief of the high strain energy would be an alternative driving force to facilitate the cleavage of C--C bonds in cycloalkanes. We recently disclosed that the $\text{RhCl}(\text{PPh}_3)_3$ catalyzed intramolecular cycloisomerization of alkynes with a pendant allenylcyclopentane moiety **1** efficiently provides bicyclo[7.4.0]tridecatrienes **2** (Scheme 1).^[3,4] We presumed that this reaction occurred by the initial formation of rhodabicyclo[4.3.0] intermediate **4**,^[3,4b,5] followed by β -carbon elimination and reductive elimination. The plausible key intermediate **4** could accelerate the unprecedented cleavage of the unactivated cyclopentane ring by releasing its low strain energy ($6.3 \text{ kcal mol}^{-1}$).^[3,6–8] On the

other hand, changing the Rh^{I} catalyst to $\text{RhCl}(\text{dppp})_2$ effected a unique $\text{C}(\text{sp}^3)\text{--H}$ bond activation to produce the novel spiro[2.4]heptane derivatives **3**.^[3] Some sort of σ -bond metathesis would occur between the $\gamma\text{--C--H}$ bond and the $\text{C--Rh}^{\text{III}}$ bond in intermediate **4'** (a conformational isomer of **4**), which would be followed by reductive elimination to give **3**.^[5] Sato, Oonishi, and co-worker reported a similar cycloisomerization reaction of *tert*-butylallene-substituted alkynes by $\text{C}(\text{sp}^3)\text{--H}$ bond activation.^[9d] Thus these results allow for the assumption that the allene-alkyne unit functions as a highly reactive π component towards the Rh^{I} catalyst^[9] to form a rhodabicyclic intermediate (e.g., **4** or **4'**), which would subsequently activate a C--C and/or C--H bond near the Rh species.

While investigating the Rh^{I} -catalyzed cyclization of allene-alkynes, we observed a novel cycloisomerization for the benzylallene-substituted terminal alkynes **5** ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{alkyl}$) that proceeds through $\text{C}(\text{sp}^2)\text{--H}$ bond activation on the benzene ring to produce **6**.^[10] This reaction was assumed to proceed via the unique vinylidene carbene Rh intermediate **6'**. Herein, we describe another type of C--H activation of benzylallene-alkyne species **5** ($\text{R}^1 \neq \text{H}$, $\text{R}^2 = \text{alkyl}$); the replacement of the terminal alkyne with an internal one dramatically changed the ring-closing mode to furnish the hexahydrophenanthrene skeleton **7** in high yields (Scheme 2).



Scheme 2. Rh^{I} -catalyzed cycloisomerization of benzylallene-alkynes by C--H bond activation.

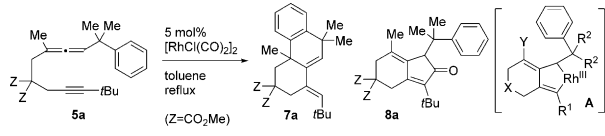


Scheme 1. Our previous study: Rh^{I} -catalyzed intramolecular cyclization of allenylcyclopentane-alkynes by C--C and C--H bond activation.^[3]

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Our initial study employed **5a**, which has a dimethyl group at the benzylic position so that unfavorable β -hydride elimination of the possible rhodacyclic intermediate **A** is avoided (Table 1). A solution of **5a** in toluene was heated to reflux in the presence of 5 mol % $[\text{RhCl}(\text{CO})_2]_2$ (an effective catalyst for the cycloisomerization of **5** when $\text{R}^1 = \text{H}$)^[10] for 0.2 h to produce hexahydrophenanthrene derivative **7a** in 77% yield.^[11] The bicyclo[4.3.0]nonadienone derivative **8a** was isolated in 19% yield as a byproduct (entry 1, method I). Compound **8a** was regarded as the product of a Pauson-Khand-type reaction (PKTR), which is formed by CO insertion into **A** followed by reductive elimination.^[12] Decreasing the amount of $[\text{RhCl}(\text{CO})_2]_2$ to 2.5 mol % diminished the production of **8a** (10%) and **7a** (56%) as well (entry 2). Other catalysts, such as $\text{RhCl}(\text{PPh}_3)_3$, $\text{RhCl}(\text{CO})\text{--}$

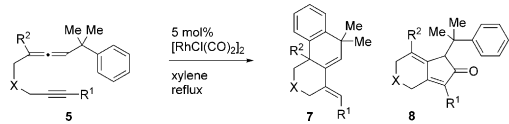
Table 1: Optimization of the reaction conditions for the Rh^I-catalyzed cycloisomerization of benzylallene-alkyne **5a**.^[a]


Entry	Method	Time [h]	Product and yield [%] ^[b]		
1	I	0.2	7a : 77	8a : 19	—
2 ^[c]	I	2	7a : 56	8a : 10	5a : 34
3	II	0.2	7a : 82	8a : 13	—
4 ^[d]	II	0.2	7a : 91	8a : 3	—

[a] Method I: A solution of **5a** in toluene was heated to reflux in the presence of the Rh^I catalyst for 0.2–2 h. Method II: A solution of **5a** in toluene or xylene was added to a toluene or xylene solution of 5 mol % [RhCl(CO)₂]₂ at reflux; the reaction mixture was heated at reflux for an additional 0.2 h. [b] Yield of isolated product. [c] With 2.5 mol % [RhCl(CO)₂]₂. [d] Xylene was used as the solvent.

(PPh₃)₂, RhCl(dppp)₂, and [RhCl(CO)dppp]₂, furnished poor results. To obtain better results, the procedure was slightly modified: A solution of **5a** in toluene was added to a toluene solution of 5 mol % [RhCl(CO)₂]₂ at reflux, and the reaction mixture was heated to reflux for an additional 0.2 h to afford **7a** in 82 % yield together with **8a** in 13 % yield (entry 3, method II).^[13] Finally, the best result (highest yield of **7a** (91 %) and lowest yield of **8a** (3 %)) was obtained when method II was used in combination with a higher reaction temperature (xylene at reflux; entry 4).

The optimized reaction conditions (Table 1, entry 4) were then applied to other substrates **5** (Table 2). Treatment of the ethyl- (**5b**) and *n*-butyl-substituted (**5c**) allene derivatives with [RhCl(CO)₂]₂ in xylene at reflux gave the tricyclic products **7b** and **7c** (96 and 95 %; entries 1 and 2). Substrates

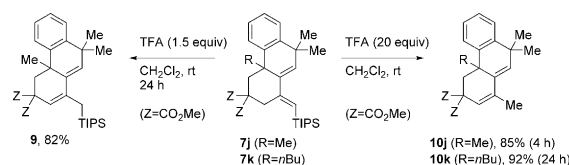
Table 2: [RhCl(CO)₂]₂ catalyzed cycloisomerization of benzylallene-alkynes **5**.^[a]


Entry	5	R ¹	R ²	X	Time [h]	Product and yield [%] ^[b]	
1	5b	<i>t</i> Bu	Et	C(CO ₂ Me) ₂	0.2	7b : 96	8b : 4
2	5c	<i>t</i> Bu	<i>n</i> Bu	C(CO ₂ Me) ₂	0.2	7c : 95	8c : 5
3	5d	<i>n</i> Bu	Me	C(CO ₂ Me) ₂	0.2	7d : 86	8d : 6
4	5e	Et	Me	C(CO ₂ Me) ₂	0.2	7e : 83	8e : 4
5 ^[c]	5f	Me	Me	C(CO ₂ Me) ₂	0.2	7f : 40 ^[d]	— ^[e]
6	5g	<i>t</i> Bu	Me	CH ₂	0.2	7g : 91	—
7	5h	<i>t</i> Bu	Me	NTs	0.2	7h : 89	—
8	5i	<i>t</i> Bu	Me	O	0.2	7i : 85	—
9 ^[f]	5j	TIPS	Me	C(CO ₂ Me) ₂	0.7	7j : 71	8j : 18
10 ^[c]	5k	TIPS	<i>n</i> Bu	C(CO ₂ Me) ₂	1	7k : 70	8k : 18
11 ^[c]	5l	TBS	Me	C(CO ₂ Me) ₂	0.2	7l : 67	8l : 19
12 ^[c]	5m	TBS	<i>n</i> Bu	C(CO ₂ Me) ₂	0.5	7m : 61	8m : 18

[a] The reaction conditions are the same as those in Table 1, entry 3 or 4. [b] Yield of isolated product. [c] Toluene as the solvent. [d] Yield determined by ¹H NMR analysis. [e] Unidentified byproducts were obtained. [f] With 10 mol % [RhCl(CO)₂]₂. TBS = *tert*-butyldimethylsilyl, TIPS = triisopropylsilyl, Ts = *para*-toluenesulfonyl.

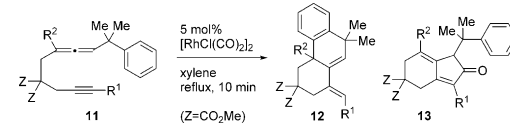
5d and **5e**, with *n*-butyl and ethyl substituents at the alkyne terminus, provided **7d** and **7e** in good yields (86 and 83 %; entries 3 and 4). On the other hand, the less hindered methyl-substituted alkyne derivative **5f** afforded the desired compound **7f** in rather low yield (40 %),^[14] with the formation of considerable amounts of unidentified side products (entry 5). The reaction of **5g**, which does not benefit from geminal disubstitution,^[15] smoothly proceeded to exclusively furnish **7g** in 91 % yield (entry 6). The nitrogen (**5h**) and oxygen (**5i**) congeners also exclusively afforded **7h** and **7i** (89 and 85 %; entries 7 and 8). Overall, a bulky *tert*-butyl group at the alkyne terminus seemed to provide better results than linear alkyl chains. Thus we next examined some silylacetylene derivatives. Treatment of the TIPS derivatives **5j** and **5k** with [RhCl(CO)₂]₂ in xylene or toluene at reflux provided the desired vinylsilane derivatives **7j** (71 %) and **7k** (70 %) along with **8j** (18 %) and **8k** (18 %), respectively (entries 9 and 10). The reactions of the TBS analogues **5l** and **5m** gave similar results to afford **7l** and **7m** (67 and 61 %; entries 11 and 12).

The silane functional group can be easily elaborated in various ways.^[16] We hence attempted transformations of the silane moieties in **7j** and **7k** (Scheme 3). Treatment of **7j** with

**Scheme 3.** Transformations of **7j** and **7k**.

1.5 equiv of trifluoroacetic acid (TFA) effected the isomerization of the vinylsilane group into an allylsilane group to afford **9** in 82 % yield. Exposure of **7j** and **7k** to an excess of TFA led to desilylation, which was accompanied by migration of the *exo* double bond to give **10j** (85 %) and **10k** (92 %).^[17]

We then turned our attention to the Rh^I-catalyzed cycloisomerization of **11**, which has an electron-withdrawing group (EWG) at the alkyne terminus, to determine the effect of the electronic properties of the substituent at the alkyne terminus (Table 3). Treatment of phosphonate derivative **11a** with [RhCl(CO)₂]₂ produced **12a** in 87 % yield alongside a negligible amount of the PKTR adduct **13a** (entry 1). Neither an ester nor a ketone functional group inhibited this cycloisomerization. Indeed, substrates with an ester moiety, **11b** and **11c**, exclusively furnished **12b** and **12c** (80 and 91 %; entries 2 and 3). The acetyl derivative **11d** afforded **12d** (79 %) and **13d** (9 %; entry 4). Chloro-substituted **11e** could be converted into **12e** in acceptable yield (67 %; entry 5). The reaction of **11f**, which features an electron-withdrawing *para*-nitrophenyl group, furnished **12f**^[14] in 79 % yield (entry 6). Although the simple phenyl derivative **11g** also gave **12g**^[14] (entry 7), the yield (62 %) was somewhat lower than for **12f** (entry 7 vs. 6). Phenyl derivative **11h**, with a methyl-substituted allene, gave **12h**^[18] in 96 % yield (entry 8). It thus became clear that various EWGs were tolerated at the alkyne terminus in this cyclization. In combination with the results shown in Tables 2 and 3, we concluded that the ring-closing

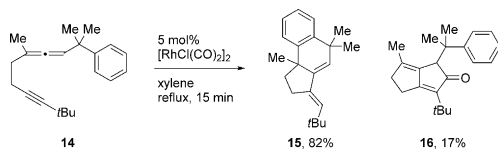
Table 3: $[\text{RhCl}(\text{CO})_2]_2$ catalyzed cycloisomerization of other benzylallene-alkyne substrates **11**.^[a]


Entry	11	R ¹	R ²	Product and yield [%] ^[b]
1	11a	P(O)(OEt) ₂	Me	12a: 87 13a: 3
2 ^[c]	11b	CO ₂ Me	<i>n</i> Bu	12b: 80 —
3 ^[c]	11c	CO ₂ Me	Me	12c: 91 —
4 ^[c]	11d	Ac	Me	12d: 79 13d: 9
5	11e	Cl	Me	12e: 67 —
6	11f	<i>p</i> -NO ₂ C ₆ H ₄	<i>n</i> Bu	12f: 79 ^[d] —
7	11g	Ph	<i>n</i> Bu	12g: 62 ^[d] 13g: 4
8	11h	Ph	Me	12h: 96 13h: 3

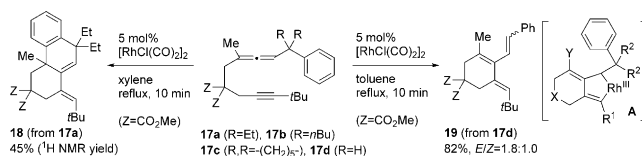
[a] The reaction conditions are the same as those in Table 2. [b] Yield of isolated product. [c] Toluene as the solvent. [d] Yield determined by ¹H NMR analysis.

reaction occurs irrespective of the electronic properties of the substituent at the alkyne terminus while the substituent has to be bulky for successful construction of the hexahydrophenanthrene framework.

Treatment of substrate **14**, with one carbon atom shorter chain, with $[\text{RhCl}(\text{CO})_2]_2$ also led to the construction of a tricyclic framework to afford **15** in 82 % yield along with **16** in 17 % yield [Eq. (1)].^[19]



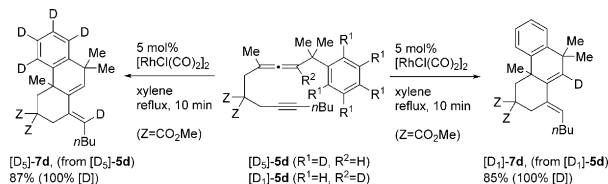
Upon exposure to the standard conditions, substrate **17a**, which features a diethyl group, gave **18** in rather low yield (45 % NMR yield)^[14] along with the formation of considerable amounts of unidentified side products (Scheme 4).

**Scheme 4.** $[\text{RhCl}(\text{CO})_2]_2$ catalyzed cycloisomerization of **17**.

Furthermore, both the butyl (**17b**) and cyclohexyl (**17c**) congeners afforded intractable mixtures. On the other hand, the reaction of the unsubstituted benzyl substrate **17d** produced triene **19** in 82 % yield as a 1.8:1 mixture of the *E* and *Z* isomers. The formation of **19** strongly supports the intermediacy of rhodabicyclic species **A** ($\text{R}^2 = \text{H}$), which then undergoes β -hydride elimination.^[9a,20] These experiments indirectly provide two significant points of information

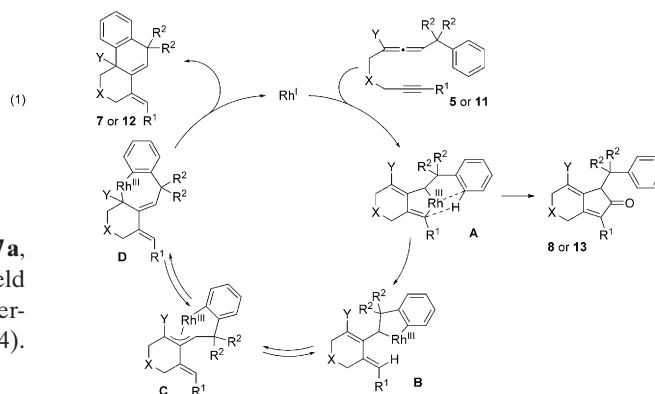
regarding the reaction mechanism (see below), namely that geminal disubstitution of the benzylic position of the starting materials is mandatory and that substituents at the benzylic position that are bulkier than a methyl group retard the cycloisomerization step.

To obtain more information on the mechanism, we performed two experiments with $[\text{D}_5]$ -**5d** and $[\text{D}_1]$ -**5d** (Scheme 5). Treatment of $[\text{D}_5]$ -**5d** with $[\text{RhCl}(\text{CO})_2]_2$ pro-

**Scheme 5.** $[\text{RhCl}(\text{CO})_2]_2$ catalyzed cycloisomerization of $[\text{D}_5]$ -**5d** and $[\text{D}_1]$ -**5d**.

duced $[\text{D}_5]$ -**7d** in 87 % yield. One deuterium atom was exclusively incorporated at the terminal carbon atom of the exocyclic olefin moiety. For monodeuterated substrate $[\text{D}_1]$ -**5d**, the deuterium atom at the allenic position was completely incorporated into the olefinic position of the six-membered ring in $[\text{D}_1]$ -**7d**.

The experimental results in Schemes 4 and 5 provide fairly informative insight into the reaction mechanism (Scheme 6).

**Scheme 6.** Plausible mechanism for the formation of **7** (or **12**) and **8** (or **13**).

Oxidative cyclization of the distal allene double bond and the alkyne in **5** (or **11**) with Rh^{I} would initially occur to form bicyclic rhodacyclopentene intermediate **A** ($\text{R}^2 = \text{Me}$). Then, σ -bond metathesis^[21] between a $\text{C}(\text{sp}^2)\text{-H}$ bond on the benzene ring and the $\text{C}(\text{sp}^2)\text{-Rh}^{\text{III}}$ bond of **A** would lead to σ -allylrhodium intermediate **B**, which would be in equilibrium with another σ -allylrhodium intermediate **D** via π -allylrhodium intermediate **C**. Reductive elimination of Rh^{III} would finally give **7** (or **12**). As mentioned above, **A** can alternatively undergo a carbonylative $[2+2+1]$ cycloaddition to afford **8** (or **13**) by successive insertion of CO and reductive elimination. We succeeded in the suppression of the PKTR process in the

reactions of **11** with an EWG at the alkyne terminus, presumably by avoiding the CO insertion process owing to the electronic effect of the EWG. With alkyl- and silyl-substituted alkyne derivatives **5**, bulky substituents at the alkyne terminus tend to suppress CO insertion into **A** and some other side reactions through steric hindrance. However, substrate **17a**, with a diethyl group at the benzylic position, afforded the desired product **18** in a rather low yield (Scheme 4). This might be due to a significant nonbonding interaction between the diethyl group and the methyl group on the allene moiety during the σ -bond metathesis^[21] leading to **B**. For the dibutyl and cyclohexyl derivatives **17b** and **17c**, the σ -bond metathesis^[21] of **A** can no longer proceed.

In summary, we have developed an efficient method for the construction of the hexahydrophenanthrene skeleton by taking advantage of the Rh^I-catalyzed cycloisomerization of internal alkynes with a pendant benzylallene moiety. Preliminary studies with deuterated substrates and some additional experiments provided some support for the proposed reaction mechanism. Investigations of the scope and limitations of this method as well as further mechanistic studies are currently in progress.

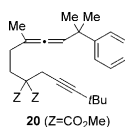
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Keywords: alkynes · allenes · C–H activation · cycloisomerization · rhodium

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