

Cycloadditions

Rhodium(I)-Catalyzed Cyclization of Allenynes with a Carbonyl Group through Unusual Insertion of a C=O Bond into a Rhodacycle Intermediate**

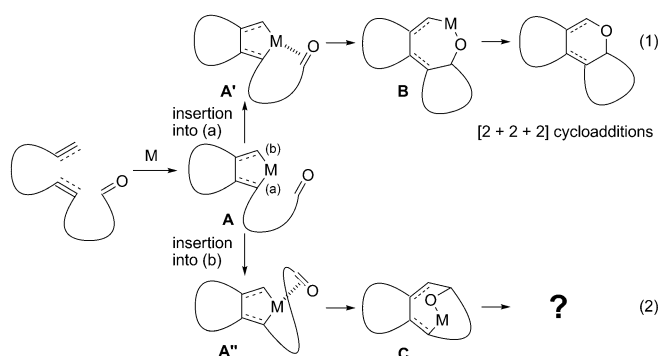
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Abstract: Rhodium(I)-catalyzed cyclization of allenynes with a tethered carbonyl group was investigated. An unusual insertion of a C=O bond into the C(sp²)-rhodium bond of a rhodacycle intermediate occurs via a highly strained transition state. Direct reductive elimination from the obtained rhodacycle intermediate proceeds to give a tricyclic product containing an 8-oxabicyclo[3.2.1]octane skeleton, while β -hydride elimination from the same intermediate gives products that contain fused five- and seven-membered rings in high yields.

Transition-metal-catalyzed [2+2+2] cycloadditions of two C–C multiple bonds with C=O bonds, as in aldehydes and ketones, are useful methodologies for the construction of oxygen-containing polycyclic compounds.^[1–4] Intramolecular variants are particularly attractive reactions that enable us to easily access polycyclic compounds from acyclic substrates in one pot [Scheme 1, Eq. (1)].^[2a,g,h,3]

These cycloadditions begin with the formation of the metalacycle intermediate **A** through oxidative cycloaddition of two multiple C–C bonds to a low-valent transition-metal complex, and cyclized products are produced through insertion of a C=O bond into the M–C bond (a) of the intermediate **A** followed by reductive elimination from the intermediate **B**. In these reaction processes, if insertion of a C=O bond into the M–C bond (b) of **A** occurs, the intermediate **C** would be produced [Scheme 1, Eq. (2)]. However, most transition-metal-catalyzed cycloadditions proceed through intermediate **B**,^[2a,g,h,3] and there has been no report on cyclization through the intermediate **C**, probably owing to the highly strained transition state **A''**.

Recently, we have reported a Rh^I-catalyzed [6+2] cycloaddition of 4-allenals with alkynes or alkenes^[5] in a tether [Scheme 2, Eq. (1)].^[5a] During ongoing investigation of this cycloaddition, it was found that reaction of **1a** with [Rh(dppe)]ClO₄ (10 mol %) instead of [Rh(IMes)(cod)]ClO₄ did not produce the expected product **2a**, which contains fused five- and eight-membered rings, but produced the bicyclic alcohol **3a**, which contains fused six- and seven-membered rings, in 27% yield.^[6–8] The formation of **3a** could not be explained by the mechanism of the reported [6+2] cycloaddition, but it might be formed via the above-mentioned unknown intermediate **C'** followed by β -hydride elimination [Scheme 2, Eq. (2)]. This unexpected result prompted us to investigate Rh^I-catalyzed cycloaddition of allenynes with tethered aldehydes giving the product **3a**.



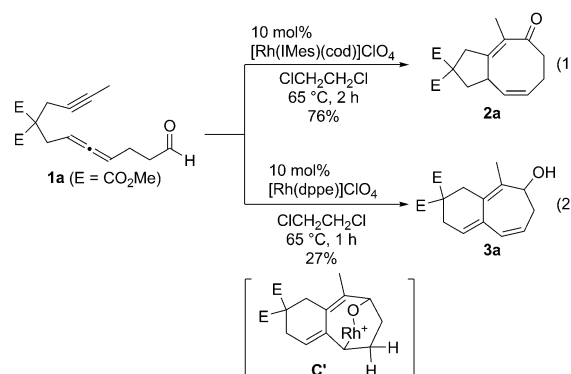
Scheme 1. Intramolecular cycloadditions of C–C multiple bonds with C=O bonds.

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[**] This work was supported in part by Grants-in-Aid for Scientific Research (B) (No. 23390001) from the Japan Society for the Promotion of Science (JSPS) and by a Grant-in-Aid for Scientific Research on Innovative Areas “Molecular Activation Directed toward Straightforward Synthesis (No. 25105701)” from MEXT (Japan). A.H. thanks JSPS for providing a Research Fellowship for Young Scientists.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201308824>.



Scheme 2. Rh^I-catalyzed cycloadditions of **1a** with [Rh(IMes)(cod)]ClO₄ or [Rh(dppe)]ClO₄. IMes = 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene, cod = cyclooctadiene, dppe = bis(diphenylphosphanyl)ethane.

To improve the yield of **3a**, cycloaddition of **1a** under various conditions was reinvestigated. However, the yield of **3a** was only improved to 39% when using [Rh(dppe)]ClO₄ (10 mol %) in ClCH₂CH₂Cl at room temperature. Thus, the substrate was changed from **1a** to **4a**, which had two carbon units between allene and alkyne (Table 1). The cyclization of **4a** with [Rh(dppe)]ClO₄ (10 mol %) in ClCH₂CH₂Cl at 50 °C for 1 h gave the desired bicyclic compound **5a** in 80% yield (Table 1, entry 1).^[9] Screening of Rh^I complexes in the

Table 1: Rh^I-catalyzed cycloaddition of **4a**.

Entry	Rh ^I complex	<i>t</i> [h]	Yield [%]
1 ^[a]	[Rh(dppe)]ClO ₄	1	80
2	[RhCl(PPh ₃) ₃]	18	5 ^[d,e]
3 ^[a]	[Rh(dppb)]ClO ₄	24	— ^[e]
4 ^[a]	[Rh(DPEphos)]ClO ₄	26	— ^[e]
5 ^[a]	[Rh(dppbz)]ClO ₄	1	91
6 ^[b]	[Rh(dppbz)]ClO ₄	2	80
7 ^[c]	[Rh(IMes)(cod)]ClO ₄	15	—

[a] Reactions were carried out using 10 mol % [Rh(ligand)]ClO₄ at 50 °C. [Rh(ligand)]ClO₄ was generated in situ from [Rh(ligand)(nbd)]ClO₄ under an atmosphere of hydrogen. [b] The reaction was carried out using 2 mol % [Rh(dppbz)]ClO₄. [Rh(dppbz)]ClO₄ was generated in situ from [Rh(dppbz)(nbd)]ClO₄ under an atmosphere of hydrogen. nbd = norbornadiene, dppb = bis(diphenylphosphanyl)butane, dppbz = 1,2-bis(diphenylphosphanyl)benzene, DPEphos = bis(2-(diphenylphosphanyl)phenyl)ether. [c] The reaction was carried out using 10 mol % [Rh(IMes)(cod)]ClO₄ generated in situ from [Rh(IMes)(cod)]Cl (10 mol %) and AgClO₄ (10 mol %). [d] Yield was determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [e] The starting material was recovered in 66% (entry 2), 75% (entry 3), and 56% (entry 4) yields.

reaction of **4a** was carried out, and it was found that the use of [RhCl(PPh₃)₃], [Rh(dppb)]ClO₄, or [Rh(DPEphos)]ClO₄ was not effective for this cycloaddition (Table 1, entries 2–4). Surprisingly, the reaction using [Rh(dppbz)]ClO₄ afforded the cyclic compound **5a** in 91% yield (Table 1, entry 5). Furthermore, the catalyst loading could be reduced to 2 mol % under similar conditions, thereby giving **5a** in 80% yield (Table 1, entry 6). The use of [Rh(IMes)(cod)]ClO₄, which was effective for the above-mentioned [6+2] cycloaddition,^[5a] gave a complex mixture in the cyclization of **4a** (Table 1, entry 7).

Next, the cyclization of various substrates using [Rh(dppbz)]ClO₄ was examined (Table 2). The cyclization of **4b**, having a silyloxy group in the tether, gave the cyclic compound **5b** in 72% yield (Table 2, entry 1). The use of substrate **4c**, which has a TMS group at the alkyne part, afforded **5c** in 91% yield (Table 2, entry 2). In the reaction of **4d** and **4e**, which have an electron-withdrawing group such as a chlorine atom and ester on the alkyne moiety, the corresponding products **5d** and **5e** were obtained in 75% and 88% yields, respectively (Table 2, entries 3 and 4). The cyclization of **4f–4h**, which have various aromatic moieties on

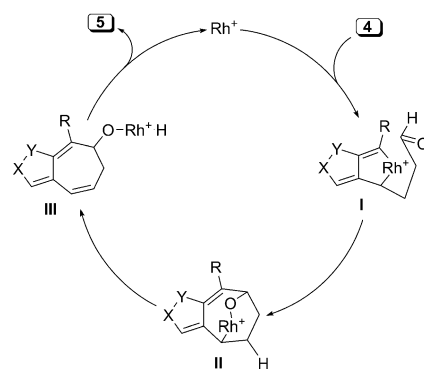
Table 2: Rh^I-catalyzed cyclization of various substrates.^[a,b]

Entry	Substrate	<i>t</i> [h]	Product
1		2	
2 ^[c]		1	
3		1	
4		1	
5		1	
6		2	
7		1	
8		1	

[a] Reactions were carried out using 10 mol % [Rh(dppbz)]ClO₄ at 50 °C. [Rh(dppbz)]ClO₄ was generated in situ from [Rh(dppbz)(nbd)]ClO₄ under an atmosphere of hydrogen. TBS = *tert*-butyldimethylsilyl, TMS = trimethylsilyl. [b] E = CO₂Me. [c] In the presence of MS4A.

the alkyne part, proceeded smoothly, giving the desired products in high yields (Table 2, entries 5–7). When **4i**, the reaction of which was expected to give a heterobicyclic compound, was treated with [Rh(dppbz)]ClO₄ (10 mol %) in ClCH₂CH₂Cl at 50 °C for 1 h, the desired compound **5i** was obtained in 71% yield (Table 2, entry 8).^[10]

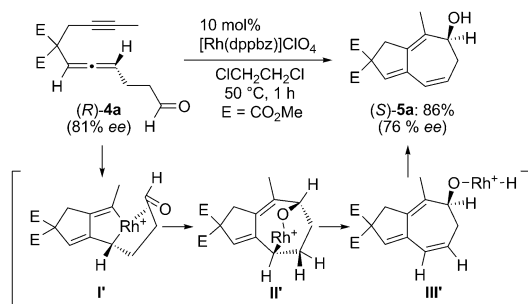
A possible reaction mechanism for the formation of **5** from **4** is depicted in Scheme 3. The rhodacycle **I** would be formed by oxidative cycloaddition of the alkyne part and external C=C bond of the allene moiety of **4** to the Rh^I complex.^[3,11–13] Insertion of an aldehyde moiety of **4** into the C(sp²)–rhodium bond of **I** would occur to give the rhodacycle **II**, from which β-hydride elimination followed by reductive



Scheme 3. Possible reaction mechanism.

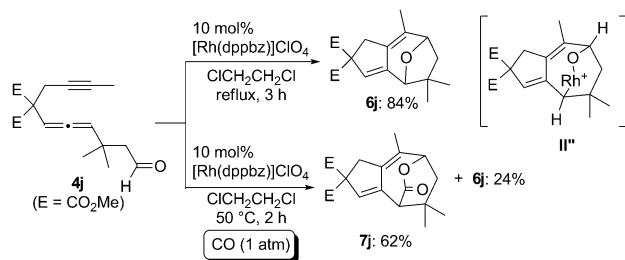
elimination from **III** would occur to give the bicyclic compound **5**.

The most critical step in the mechanism should be the one from **I** to **II** (i.e., from **A** to **C** via **A''** in Scheme 1) since insertion of a C=O bond into the C(sp²)-rhodium bond would yield a highly strained transition state. Thus, to obtain insights into the reaction course, we prepared the substrate **4a** in an enantiomerically enriched form (81 % *ee*) and subjected it to the optimal conditions. As a result, the substrate (*R*)-**4a** was converted to (*S*)-**5a** in 86 % yield, 76 % *ee*, which is explainable according to the mechanism shown in Scheme 3. Thus, the stereospecific formation of a chiral rhodacycle intermediate **I'** from the chiral substrate **4a** occurs, and then the intermediate **II'** is produced by insertion of a C=O into the C(sp²)-rhodium bond of **I'** (Scheme 4).^[14]



Scheme 4. Chiral transfer reaction.

Additionally, we prepared the substrate **4j** having no hydrogen atom at the β -position of the aldehyde moiety to prevent β -hydride elimination from an oxa-rhodacycle intermediate such as **II'** in Scheme 4. When **4j** was treated with [Rh(dppbz)]ClO₄ (10 mol %) at reflux for 3 h, we obtained **6j**, which has an 8-oxabicyclo[3.2.1]octane structure, in 84 % yield.^[15,16] **6j** was surely formed through direct reductive elimination from the oxa-rhodacycle intermediate **II''** (Scheme 5). Furthermore, the cyclization of **4j** under a CO atmosphere afforded the tricyclic lactone **7j** in 62 % yield along with the cyclic compound **6j** in 24 % yield, the structure of which was unambiguously determined by X-ray analysis.^[17] The product **7j** should be produced through the insertion of CO into the oxa-rhodacycle intermediate **II''**, and all of the results in Schemes 4 and 5 strongly support the mechanism in Scheme 3.



Scheme 5. Cyclizations of **4j**.

Table 3: Cyclization through reductive elimination of rhodacycle **II**.^[a,b]

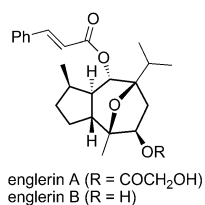
Entry	Substrate	<i>t</i> [h]	Product
1	4k : R = Me	1	6k : 87 %
2	4l : R = Et	24	6l : 90 %
3	4m : R = H	24	6m : 42 %
4	4n : R = OMe	24	6n : — ^[c]
5	4o : R = CO ₂ Me	24	6o : 85 %
6	4p	1	6p : 81 %

[a] Reactions were carried out using 10 mol % [Rh(dppbz)]ClO₄ in the presence of MS4A at reflux. [Rh(dppbz)]ClO₄ was generated in situ from [Rh(dppbz)(nbd)]ClO₄ under an atmosphere of hydrogen.

[b] E = CO₂Me. [c] A complex mixture including the desired compound was obtained.

Next, we turned our attention to investigating the scope of carbonyl groups in the cyclization giving a product having an 8-oxabicyclo[3.2.1] skeleton (Table 3). The cyclization of **4k** and **4l**, which have a dialkyl ketone moiety (R = Me or Et) instead of an aldehyde, proceeded to give 8-oxabicyclo[3.2.1]octane derivatives in 87 % and 90 % yields, respectively, when using MS4A as an additive (Table 3, entries 1 and 2). When aryl ketones **4m–o** were employed in this cyclization, **4o**, having an electron-withdrawing group at the aromatic ring, afforded the corresponding cyclic compound **6o** in high yield, while a complex mixture was obtained in the case of **4n**, bearing an electron-donating group at the aromatic ring (Table 3, entries 3–5). Gratifyingly, this cyclization was applicable for sterically hindered silyl ketone **4p**, and **6p** was obtained in 81 % yield, the structure of which was also unambiguously determined by X-ray analysis (Table 3, entry 6).^[17]

In conclusion, we succeeded in developing novel Rh^I-catalyzed cyclizations of allenynes with a tethered carbonyl group, wherein an unusual insertion of a C=O bond into the C(sp²)-rhodium bond of rhodacycle intermediate **I** occurs nevertheless via a highly strained transition state, and to our knowledge, a metalacycle intermediate such as **II** has been unknown in the literature. Direct reductive elimination from **II** proceeds to give a tricyclic product containing an 8-oxabicyclo[3.2.1]octane skeleton, while β -hydride elimination from **II** gives products that contain fused five- and seven-membered rings via intermediate **III** in high yields. It is



known that polycyclic compounds containing an 8-oxabicyclo[3.2.1] skeleton such as englerins^[18] have an interesting biological activity, and the present cyclization is a unique methodology for construction of such a skeleton.

Further studies along this line including applications to the synthesis of natural products are in progress.

Received: October 10, 2013

Revised: October 29, 2013

Published online: December 4, 2013

Keywords: alkynes · allenes · carbonyl compounds · cycloadditions · rhodium

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