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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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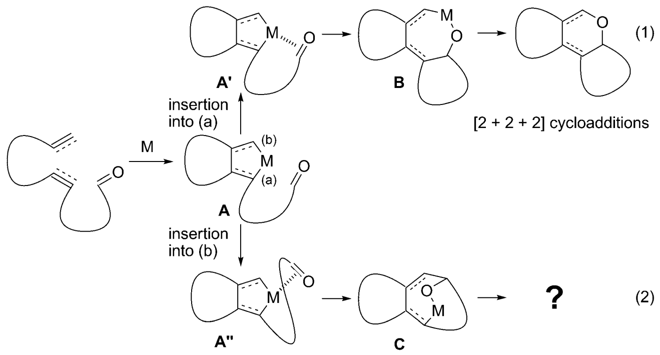
Abstract: *Rhodium(I)-catalyzed cyclization of allenynes with a tethered carbonyl group was investigated. An unusual insertion of a C=O bond into the C(sp^2)–rhodium bond of a rhodacycle intermediate occurs via a highly strained transition state. Direct reductive elimination from the obtained rhodacyle 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.*

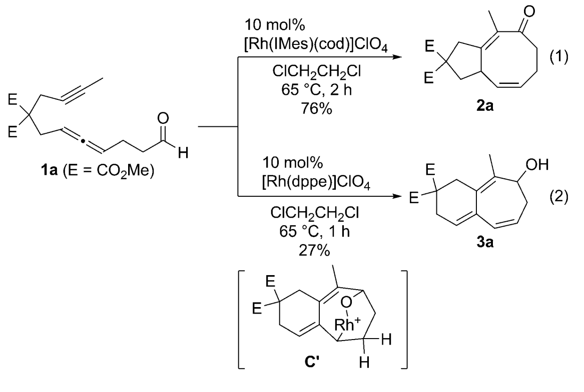
Transition-metal-catalyzed [2+2+2] cycloadditions of two C–C multiple bonds with C=O bonds, as in aldehydes and ketones, are useful methodologies for the construction of oxygen-containing polycyclic compounds.[1–4] Intramolecular variants are particularly attractive reactions that enable us to easily 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)]ClO_4 (10 mol%) instead of [Rh(IMes)(cod)]ClO_4 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.



Scheme 2. Rh^I-catalyzed cycloadditions of **1a** with [Rh(IMes)(cod)]ClO_4 or [Rh(dppe)]ClO_4. IMes = 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene, cod = cyclooctadiene, dppe = bis(diphenylphosphanyl)ethane.

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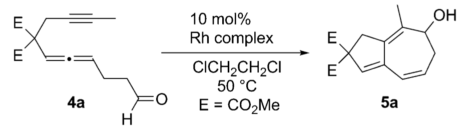
To improve the yield of **3a**, cycloaddition of **1a** under various conditions was reinvestigated. However, the yield of **3a** was only improved to 39% when using [Rh(dppe)]ClO$_4$ (10 mol%) in ClCH$_2$CH$_2$Cl at room temperature. Thus, the substrate was changed from **1a** to **4a**, which had two carbon units between allene and alkyne (Table 1). The cyclization of **4a** with [Rh(dppe)]ClO$_4$ (10 mol%) in ClCH$_2$CH$_2$Cl 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 reaction of **4a** was carried out, and it was found that the use of [RhCl(PPh$_3$)$_3$], [Rh(dppb)]ClO$_4$, or [Rh(DPEphos)]ClO$_4$ was not effective for this cycloaddition (Table 1, entries 2–4). Surprisingly, the reaction using [Rh(dppbz)]ClO$_4$ 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)]ClO$_4$, which was effective for the above-mentioned [6+2] cycloaddition,[5a] gave a complex mixture in the cyclization of **4a** (Table 1, entry 7).

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

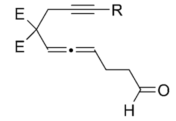
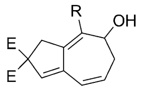
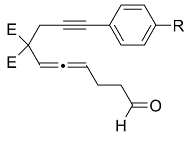
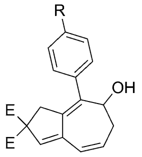
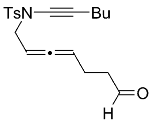
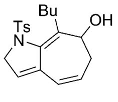


Entry	Rh^I complex	*t* [h]	Yield [%]
1[a]	[Rh(dppe)]ClO$_4$	1	80
2	[RhCl(PPh$_3$)$_3$]	18	5[d,e]
3[a]	[Rh(dppb)]ClO$_4$	24	–[e]
4[a]	[Rh(DPEphos)]ClO$_4$	26	–[e]
5[a]	[Rh(dppbz)]ClO$_4$	1	91
6[b]	[Rh(dppbz)]ClO$_4$	2	80
7[c]	[Rh(IMes)(cod)]ClO$_4$	15	–

[a] Reactions were carried out using 10 mol% [Rh(ligand)]ClO$_4$ at 50°C. [Rh(ligand)]ClO$_4$ was generated in situ from [Rh(ligand)(nbd)]ClO$_4$ under an atmosphere of hydrogen. [b] The reaction was carried out using 2 mol% [Rh(dppbz)]ClO$_4$. [Rh(dppbz)]ClO$_4$ was generated in situ from [Rh(dppbz)(nbd)]ClO$_4$ 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)]ClO$_4$ generated in situ from [Rh(IMes)(cod)]Cl (10 mol%) and AgClO$_4$ (10 mol%). [d] Yield was determined by ^{1}H 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.

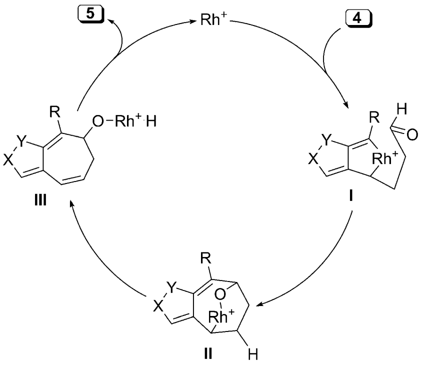
Next, the cyclization of various substrates using [Rh(dppbz)]ClO$_4$ was examined (Table 2). The cyclization of **4b**, having a silyloxy group in the tether, gave the cyclic compound **5b** in 72% yield (Table 2, entry 1). The use of substrate **4c**, which has a TMS group at the alkyne part, afforded **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 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)]ClO$_4$ (10 mol%) in ClCH$_2$CH$_2$Cl at 50°C for 1 h, the desired compound **5i** was obtained in 71% yield (Table 2, entry 8).[10]

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

Entry	Substrate	*t* [h]	Product
			
1	**4b**: R = CH$_2$OTBS	2	**5b**: 72%
2[c]	**4c**: R = TMS	1	**5c**: 91%
3	**4d**: R = Cl	1	**5d**: 75%
4	**4e**: R = CO$_2$Me	1	**5e**: 88%
			
5	**4f**: R = H	1	**5f**: 83%
6	**4g**: R = OMe	2	**5g**: 82%
7	**4h**: R = CO$_2$Me	1	**5h**: 76%
			
8	**4i**	1	**5i**: 71%

[a] Reactions were carried out using 10 mol% [Rh(dppbz)]ClO$_4$ at 50°C. [Rh(dppbz)]ClO$_4$ was generated in situ from [Rh(dppbz)(nbd)]ClO$_4$ under an atmosphere of hydrogen. TBS = *tert*-butyldimethylsilyl, TMS = trimethylsilyl. [b] E = CO$_2$Me. [c] In the presence of MS4A.

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(sp^2)–rhodium bond of **I** would occur to give the rhodacycle **II**, from which β-hydride elimination followed by reductive



Scheme 3. Possible reaction mechanism.

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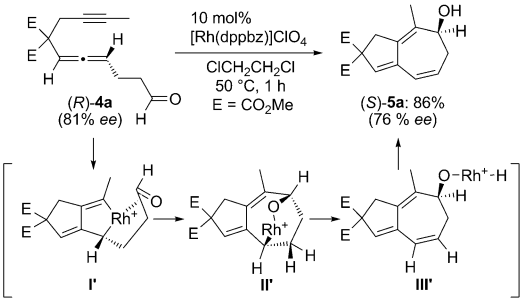
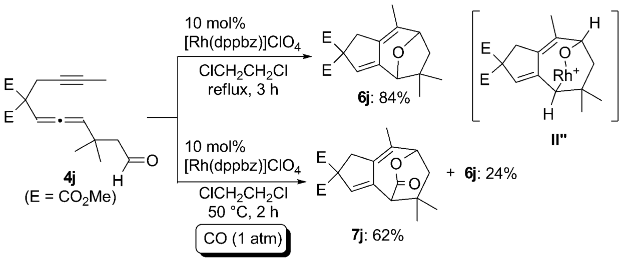
elimination from **III** would occur to give the bicyclic compound **5**.

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(sp^2)–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(sp^2)–rhodium bond of **I′** (Scheme 4).[14]



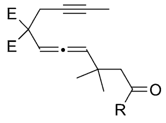
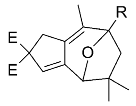
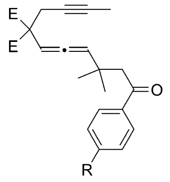
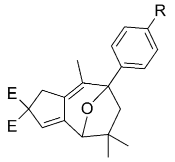
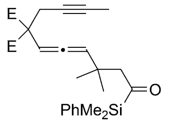
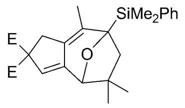
Scheme 4. Chiral transfer reaction.

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)]ClO_4 (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**.

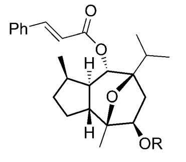
Table 3: Cyclization through reductive elimination of rhodacycle **II**.[a,b]

Entry	Substrate	*t* [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_2Me	24	**6o**: 85 %
			
6	**4p**	1	**6p**: 81 %

[a] Reactions were carried out using 10 mol % [Rh(dppbz)]ClO_4 in the presence of MS4A at reflux. [Rh(dppbz)]ClO_4 was generated in situ from [Rh(dppbz)(nbd)]ClO_4 under an atmosphere of hydrogen.
[b] E = CO_2Me. [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 MS4 A 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(sp^2)–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



englerin A (R = $COCH_2OH$)
englerin B (R = H)

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.

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[6] A similar tendency, that is, the formation of a rhodacycle through oxidative cycloaddition of C−C multiple bonds occurs in preference to oxidative addition of a C−H bond of an aldehyde to a Rh^I complex when using dppe as a ligand, has been also observed for a Rh^I-catalyzed cycloisomerization reported by us, although the reason is unclear at this stage, see: a) Y. Sato, Y. Oonishi, M. Mori, *Organometallics* **2003**, *22*, 30; b) Y. Oonishi, A. Saito, M. Mori, Y. Sato, *Synthesis* **2009**, 969.

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[9] The structure of **5a** was determined by 2D NMR spectroscopy (see the Supporting Information).

[10] The reaction of substrate **4** having a terminal alkyne under similar conditions did not proceed, but unreacted starting material was recovered in 26% yield.

[11] Recent reviews on transition metal-catalyzed cycloaddition of allenes and unsaturated bonds: a) F. López, J. L. Mascareñas, *Chem. Eur. J.* **2011**, *17*, 418; b) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria, A. Simonneau, *Chem. Rev.* **2011**, *111*, 1954; c) F. Inagaki, S. Kitagaki, C. Mukai, *Synlett* **2011**, 594.

[12] Selected examples of Rh^I-catalyzed cycloisomerizations of allenynes: a) K. M. Brummond, H. Chen, P. Sill, L. You, *J. Am. Chem. Soc.* **2002**, *124*, 15186; b) T. Shibata, Y. Takesue, S. Kadowaki, K. Takagi, *Synlett* **2003**, 268; c) C. Mukai, F. Inagaki, T. Yoshida, S. Kitagaki, *Tetrahedron Lett.* **2004**, *45*, 4117; selected examples of Rh^I-catalyzed Pauson–Khand reaction (PKR) of allenynes: d) T. Kobayashi, Y. Koga, K. Narasaka, *J. Organomet. Chem.* **2001**, *624*, 73; e) C. Mukai, I. Nomura, K. Yamanishi, M. Hanaoka, *Org. Lett.* **2002**, *4*, 1755; f) K. M. Brummond, H. Chen, K. D. Fisher, A. D. Kerekes, B. Rickards, P. C. Sill, S. J. Geib, *Org. Lett.* **2002**, *4*, 1931; g) T. Shibata, S. Kadowaki, M. Hirase, K. Takagi, *Synlett* **2003**, 573; h) C. Mukai, I. Nomura, S. Kitagaki, *J. Org. Chem.* **2003**, *68*, 1376; examples of Rh^I-catalyzed cycliza-

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tion of allenyne through C(sp^3)–C(sp^3) bond activation: i) F. Inagaki, K. Sugikubo, Y. Oura, C. Mukai, *Chem. Eur. J.* **2011**, *17*, 9062; j) C. Mukai, Y. Ohta, Y. Oura, Y. Kawaguchi, F. Inagaki, *J. Am. Chem. Soc.* **2012**, *134*, 19580, and also see Ref. [8c]. An example of Rh^I-catalyzed [2+2+2] cycloaddition of allenynes with alkynes: k) X. Jiang, S. Ma, *J. Am. Chem. Soc.* **2007**, *129*, 11600.

[13] Our recent study of Rh^I-catalyzed cyclization of allenyne through C–H bond activation: Y. Oonishi, Y. Kitano, Y. Sato, *Angew. Chem.* **2012**, *124*, 7158; *Angew. Chem. Int. Ed.* **2012**, *51*, 7052, and also see Ref. [12j].

[14] The absolute configuration of (*S*)-**5a** was determined by a modified Mosher's method after reaction with MTPACl (see the Supporting Information).

[15] The structure of **6j** was determined by INADEQUATE and HMBC (see the Supporting Information).

[16] Wender (Ref. [8a,b]), Mukai (Ref. [8c]), and Tang (Ref. [8d,e]) have also reported on the access to the similar bicyclic compounds including 7-membered rings through Rh^I-catalyzed cycloaddition. According to these previous methods, however, 8-oxabicyclo[3.2.1]octane skeleton having an oxygen-bridged structure cannot be constructed. Also, see: K. E. O. Ylijoki, J. M. Stryker, *Chem. Rev.* **2013**, *113*, 2244.

[17] CCDC 963500 (**7j**) and 963499 (**6p**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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