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Letter

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Rh-Catalyzed Cycloisomerization of 1,7-Ene-Dienes to Synthesize *trans*-Divinylpiperidines: A Formal Intramolecular Addition Reaction of Allylic C–H Bond into Dienes

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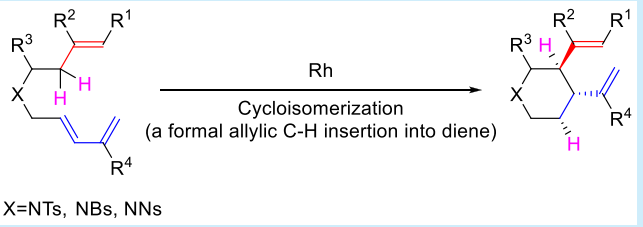
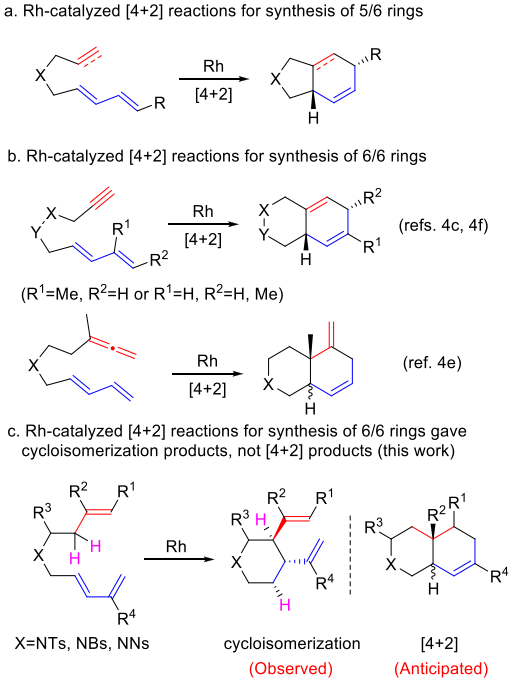
Supporting Information

ABSTRACT: An originally designed Rh-catalyzed [4 + 2] cycloaddition reaction of nitrogen-tethered 1,7-ene-dienes turned out to be a cycloisomerization reaction, which involves allylic C–H activation/alkene insertion into Rh–H bond/reductive elimination processes. Deuterium labeling experiments gave support to the proposed mechanism. This unexpected cycloisomerization reaction provides an efficient way to synthesize *trans*-divinylpiperidines from easily accessed linear 1,7-ene-dienes.



Diels–Alder (D–A) reaction is one of the most effective reactions to synthesize six-membered rings and has been widely applied in synthesis.[1] In most cases, either the dienes or dienophiles in the D–A reactions must be activated by substitution. For example, in the widely used normal electron-demanded D–A reactions, either dienes with electron-donating groups or dienophiles with electron-withdrawing groups must be used. If neither dienes nor dienophiles are substituted by these activating groups, the corresponding D–A reactions, which were called electronically neutral D–A (ENDA) reactions, experience difficulty in proceeding under thermal reaction conditions.[2] Fortunately, the ENDA reactions can be catalyzed by transition metal complexes such as Ni, Rh, Au, etc., so that these reactions can be used for the synthesis of six-membered carbocycles.[3] Both Rh-catalyzed inter- and intramolecular ENDA reactions have been developed to synthesize six-membered carbocycles.[4] DFT study of the mechanism and stereochemistry of the Rh(I)-catalyzed ENDA reactions has been carried out by us.[5] In these [4 + 2] reactions, the dienophiles can be alkenes, alkynes, or allenes. Interestingly, the reported intramolecular ENDA reactions have been mainly used to construct 5/6 bicyclic rings (Scheme 1a).[4a] To the best of our knowledge, the Rh-catalyzed intramolecular ENDA reactions to build 6/6 skeletons were limited to the use of 1,7-yne-dienes or 1,8-allene-dienes (Scheme 1b),[4c,e,f] but not 1,7-ene-dienes (Scheme 1c). We wondered whether under the same reaction conditions, the ENDA reactions of 1,7-ene-dienes could also take place to give 6/6 bicyclic rings (Scheme 1c). In this letter, we report our finding that the designed ENDA reaction of 1,7-ene-dienes did not take place. Instead, a cycloisomerization reaction involving an allylic C–H activation/alkene insertion occurred, giving *trans*-divinylpiperidine. Preliminary mechanistic study of this cycloisomerization is also reported in this paper.

Scheme 1. Rh-Catalyzed [4 + 2] Cycloadditions and Cycloisomerization



We discovered this cycloisomerization reaction by serendipity. We attempted to obtain a [4 + 2] cycloadduct using 1,7-ene-diene **1a**, but cycloisomerization product **2a** was observed instead (Table 1). The proposed mechanism to rationalize this

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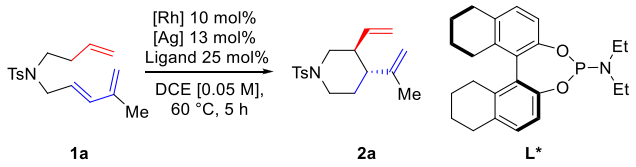
Table 1. Optimization of Reaction Conditions

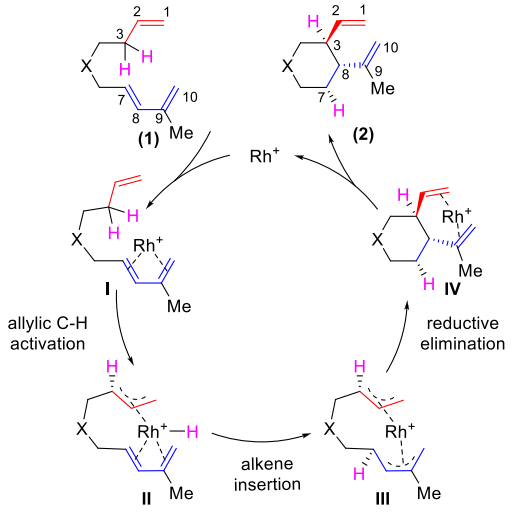


entry	Rh catalyst	Ag salt	ligand	yield of **2a**
1	$Rh(PPh_3)_3Cl$	$AgSbF_6$		62%
2	$Rh(PPh_3)_3Cl$	none		n.r.
3	$Rh(PPh_3)_3Cl$	$AgBF_4$		n.r.
4	$Rh(PPh_3)_3Cl$	AgOTf		n.r.
5	$[Rh(CO)_2Cl]_2$	$AgSbF_6$		decomposed
6	$[Rh(coe)_2Cl]_2$	$AgSbF_6$		decomposed
7	$[Rh(coe)_2Cl]_2$	$AgSbF_6$	$P(4\text{-}MeOC_6H_4)_3$	40%
8	**$[Rh(coe)_2Cl]_2$**	**$AgSbF_6$**	**$P(4\text{-}CF_3C_6H_4)_3$**	**80%**
9[a]	$[Rh(coe)_2Cl]_2$	$AgSbF_6$	$P(4\text{-}CF_3C_6H_4)_3$	70%
10[b]	$[Rh(C_2H_4)_2Cl]_2$	$AgSbF_6$	$P(4\text{-}CF_3C_6H_4)_3$	74%
11	$[Rh(coe)_2Cl]_2$	$AgSbF_6$	dppe[c]	n.r.
12	$[Rh(coe)_2Cl]_2$	$AgSbF_6$	BINAP[c]	n.r.
13	$[Rh(coe)_2Cl]_2$	$AgSbF_6$	L*[d]	64% (67% ee)

[a]Run for 2.5 mol % $[Rh(coe)_2Cl]_2$, 6.5 mol % $AgSbF_6$, 13 mol % $P(4\text{-}CF_3C_6H_4)_3$. [b]Run for 2 h. [c]Ligand for 13 mol %. [d]L* for 15 mol %, n.r. = no reaction.

cycloisomerization process is shown in Scheme 2. The reaction starts with the oxidative addition of an allylic C–H bond by a

Scheme 2. Proposed Mechanism for the Cycloisomerization of 1,7-Ene-dienes



rhodium cation to give Rh–H intermediate **II**, which then undergoes insertion of the internal alkene of diene into the Rh–H bond to give a bis-allylic Rh complex, intermediate **III**. Afterward, intermediate **III** undergoes reductive elimination to give the final cyclization product.[6] This reaction is similar to our previously reported cycloisomerization of ene-2-dienes.[7] The present cycloisomerization of **1a** to **2a** can be regarded as a formal intramolecular addition of allylic C–H bond into the internal alkene's double bond in diene. Considering that piperidine skeleton in **2** is very common and important in various molecules, together with the fact that **2** is a highly functionalized molecule with two vinyl groups ready for further synthetic elaborations, we decided to develop the present method as a general way to synthesize substituted piperidines.

We first devoted our efforts to optimize the reaction conditions (Table 1). We found that, without adding $AgSbF_6$, the neutral catalyst $Rh(PPh_3)_3Cl$ cannot catalyze the reaction (Table 1, entry 2). Cationic Rh complexes with conterions of OTf^- or BF_4^- failed to catalyze the cycloisomerization reaction (Table 1, entries 3 and 4). We also tried other cationic rhodium catalysts such as $[Rh(CO)_2Cl]_2/AgSbF_6$ and $[Rh(coe)_2Cl]_2/AgSbF_6$, finding that both catalysts could not catalyze this reaction and complex mixtures were obtained (Table1, entries 5 and 6). We then investigated how the ligand influenced this reaction. A combination of $[Rh(coe)_2Cl]_2/AgSbF_6$ catalyst with an electron-deficient ligand $P(4\text{-}CF_3C_6H_4)_3$ turned out to be the best for the reaction, giving the target product in 80% isolated reaction yield (Table 1, entry 8). Other combinations or lowering the catalyst loading decreased the reaction yields slightly (Table 1, entries 7–10). Using bidentate phosphines was found to shut down the reaction (Table 1, entries 11 and 12). An asymmetric version of this reaction by using the phosphoramidite ligand was also tested, and an acceptable yield and 67% ee value (the absolute stereochemistry was not determined) were achieved (entry 13). Further screening of the reaction conditions and other chiral ligands did not give improved results (see Supporting Information). Therefore, at this stage, we decided to disclose the racemic version of the present cycloisomerization, using $[Rh(coe)_2Cl]_2/AgSbF_6/P(4\text{-}CF_3C_6H_4)_3$ catalyst in DCE as the best reaction conditions.

The scope of the racemic 1,7-ene-diene cycloisomerization was investigated and summarized in Table 2. When the tether of the substrate was changed to NBs or NNs, the reaction yields were not significantly influenced (Table 2, entries 2 and 3). However, substrates with carbon or oxygen tethers were not suitable for this reaction because, in both cases, complex mixtures were obtained. When the C2 position of the substrate (see atom labeling in Scheme 2) was substituted by a methyl group, the yield of **2f** was also good (71%, Table 2, entry 6). The structure of **2f** was further confirmed by X-ray diffraction study (see the Supporting Information). We tested the reaction of 1,7-ene-diene with the Me substituent at the C4 position, finding that corresponding substrate **1g** gave a diastereomeric mixture of the cycloisomerization products (d.r. = 2:1 determined by ^1H NMR, Table 2, entry 7). Substrate **1h** with two alkyl groups at the homoallylic position of the ene moiety gave a complex mixture (Table 2, entry 8). We were happy to notice that this cycloisomerization reaction can tolerate a phenyl group attached to the terminal carbon of ene moiety in the substrate, because substrate **1i** gave the cycloisomerization product in an isolated yield of 39% (Table 2, entry 9). Substrate **1j** without any substituents underwent the cycloisomerization smoothly to give **2j** in 66% yield (Table 2, entry 10). For substrates **1k**–**1m** with substitutions (Et, *i*-Pr, Bn) at the C9 position, the cycloisomerizations can occur under the standard conditions, even though the formed products underwent further alkene isomerization (Table 2, entries 11–13; the structures of **2l-iso** and **2m-iso** were given in the bottom of Table 2). We were happy to find that the target products **2l** and **2m** can be obtained by using catalyst generated from Wilkinsons catalyst and $AgSbF_6$ (Table 2, entries 12 and 13). Notably, the alkene component in the substrate can be in a six-membered ring because substrate **1n** can give the cycloisomerization product

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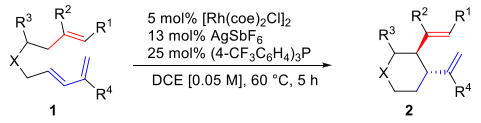
Table 2. Substrate Scope



1 2

entry	substrate	product (isolated yield)[a]
1	1a X=NTs	2a (80%)
2	1b X=NBs	2b (65%)
3	1c X=NNs	2c (73%)
4	1d X=O	complex mixture
5	1e X=C(CO_2Bn)$_2$	complex mixture
6	1f	2f (71%)
7	1g	2g (38%, 2:1[b])
8[c]	1h	complex mixture
9	1i	2i (39%)
10	1j	2j (66%)
11	1k	2k-iso (75%, 2:1[b])
12	1l	2l[d], [e] (74%)
13	1m	2m[d], [f] (75%)
14	1n	2n[d], [g] (81%)
15[h]	1o	complex mixture
16	1p	complex mixture
17	1q	complex mixture

2l-iso (56%) 2m-iso (82%, 3:1[b])

[a]The average yield of two runs. [b]Ratio was determined by ^{1}H NMR. [c]Run for 30 h complete transformation. [d]10 mol % $Rh(PPh_3)_3$ Cl, 13 mol % $AgSbf_6$, 60 °C, 5 h. [e]**2l-iso** was obtained under standard conditions. [f]**2m-iso** was obtained under standard conditions. [g]Complex mixture under standard conditions. [h]Run for 16 h for complete transformation.

in 81% isolated yield by using a catalyst generated from Wilkinson's catalyst and $AgSbF_6$ (under standard conditions, the reaction of **1n** afforded complex mixture). However, for substrate **1o**, which included the replacement of the diene group of the 1,7-ene-diene by an ene group, the cycloisomerization did not occur, which reflected the importance of the diene moiety of the substrate in this reaction (Table 2, entry 15). For substrate **1p** (*cis* configuration for substituted diene) and **1q** (which may form product with a quaternary carbon), unfortunately, they gave a complex mixture under standard conditions (Table 2, entries 16 and 17). In addition, the present reaction can be scaled up, as demonstrated by the reaction of **1a** on 1.0 mmol scale (**2a** was obtained in 76% yield in this case).

In our proposed mechanism, the allylic H atom of the substrate (C3 position in Scheme 2) would transfer to the C8 position of the final product (Scheme 2). To test this, we synthesized D-labeled substrate **1a-d_2** to verify this H transfer mechanism.[8] The synthesis of the substrate **1a-d_2** with more than 90% incorporation of D in the allylic position was given in Scheme 3. To our delight, the cycloisomerization product **2a-d_2**, which was isolated in 66% yield, had the D incorporation in the C8 position of the product. NOESY supported that two D atoms in product are in *cis*-configuration. This result gave further support of the proposed mechanism shown in Scheme 2.

We reasoned that the length of the tether of substrates for the present reaction compared to that of the [4 + 2] reaction in Scheme 1 resulted in different reaction outcomes. Therefore, we tested whether 1, 6-ene-diene **1r**, which has a linker shorter than 1,7-ene-diene substrates, can still give a [4 + 2] cycloadduct under the standard conditions above, not the

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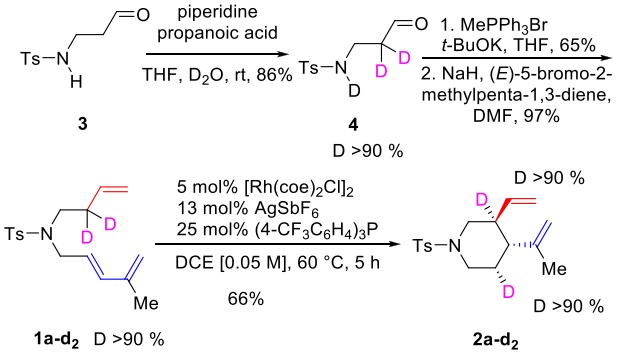
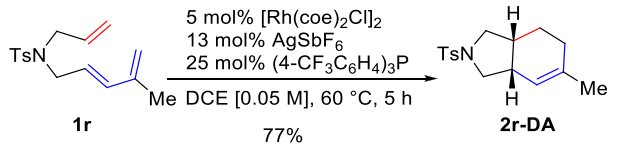
Scheme 3. Deuterium Labeling Experiments for Support of the Cycloisomerization Mechanism



cycloisomerization product (Scheme 4). Our experiments showed that [4 + 2] product **2r-DA** was generated from **1r**,

Scheme 4. 1, 6-Ene-diene for D−A Reaction



indicating that the chain length is crucial for the reaction selectivity between [4 + 2] and cycloisomerization reactions.

In summary, we found unexpectedly a new cycloisomerization method to synthesize substituted piperidines from 1,7-ene-diene substrates. D-labeling experiments have been conducted to support the reaction mechanism involving allylic C−H activation/alkene insertion and reductive elimination (Scheme 2). Further DFT understanding of the mechanism of this cycloisomerization, especially to understand why the competing [4 + 2] reaction of 1,7-ene-dienes did not take place, is under investigation and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02319.

Experimental procedures, deuterium labeling study, enantioselective reaction screening, and NMR spectra (PDF)

Accession Codes

CCDC 1909585 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

†Q.C. and W.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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