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Rhodium-catalyzed highly diastereoselective intramolecular [4 + 2] cycloaddition of 1,3-disubstituted allene-1,3-dienes[†]

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RhCl(PPh₃)₃-catalyzed [4 + 2] intramolecular cycloaddition of allene-1,3-dienes afforded *cis*-fused [3.4.0]-bicyclic products with three chiral centers in good yields with excellent chemo- and diastereo-selectivity. The configuration of the C=C bonds in the 1,3-diene unit controls the relative configurations of the non-bridging tertiary carbon atom in the six-membered ring. Based on the experimental results, a mechanism involving cyclometalation has been proposed.

Cycloaddition reactions are a practical and efficient method to construct cyclic products from simple acyclic starting materials by generating at least two bonds and one ring in only one step.¹ For example, [4 + 2] cycloaddition between 1,3-dienes and alkenes or alkynes is one of the most powerful synthetic tools to assemble six-membered cyclic structures.²⁻⁴ In 1995, Wender and coworkers reported the intramolecular [4 + 2]cycloaddition reaction of disubstituted terminal allenes with 1,3-dienes to afford cis-6,6-fused rings or cis-6,5-fused rings with a nickel or rhodium complex as catalyst (Scheme 1, a).⁵ The chemoselectivity mainly depends on the length of the tether between the diene and terminal allene. In 2009, the groups of Toste and Mascareñas independently demonstrated the gold-catalyzed intramolecular [4 + 2] cycloaddition reaction of symmetric tetrasubstituted allene with 1,3-diene to give trans-6,5-fused rings (Scheme 1, b).⁶ So far, there have been very limited reports on applying the 1,3-disubstituted allene unit as the dienophile.⁷ The challenge is the Z/E selectivity of the remaining C=C bond as well as the diastereoselectivity of the three chiral centers generated during the reaction (Scheme 1, c).8 Recently, there have been many advances in the development of new synthetic approaches to prepare 1,3-disubstituted allenes.^{9,10} Herein, we present the $RhCl(PPh_3)_3$ -catalyzed intramolecular [4 + 2] cycloaddition of

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Scheme 1 Metal-catalyzed intramolecular [4 + 2] cycloaddition of allene-1,3-dienes.

1,3-disubstituted allene–dienes, during which the internal C=C bond of the allene moiety reacted with the 1,3-diene unit to produce *cis*-6,5-fused bicyclic products with an excellent Z/E selectivity for the remaining C=C bond and an excellent diastereoselectivity referring to the three chiral centers (Scheme 1, c).

We started our study on the reaction with 1,3-disubstituted allene-1,3-diene **1a** as the model substrate. The desired product was not formed under the catalysis of $Ni(COD)_2$ or $[Rh(COD)_2Cl]_2$ (entries 1 and 2, Table 1). The cationic rhodium catalyst $[Rh(COD)_2]BF_4$ also couldn't catalyze the reaction



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Table 1Optimization of rhodium-catalyzed intramolecular [4 + 2]cycloaddition of racemic allene-1,3-diene $1a^a$

TsN	Cat. (2 toluene	mol%) , T, t	TsN H ⁿ Bu Z-	H CH ₃ 2a	+ TsN H H E-2	H CH ₃ ⁿ Bu
Entry	[Rh]	Т (°С)	<i>t</i> (h)	Yield of $2a^{b}$	Z/E	Recovery of 1a ^b
1	$Ni(COD)_2$	80	12	N.D.	_	68
2	[Rh(COD)Cl] ₂	80	12	N.D.	_	90
3	Rh(COD) ₂]BF ₄	80	12	N.D.	_	77
4	$[RhCl(CO)_2]_2$	80	12	81	50:50	N.D.
5 ^c	$[(C_{10}H_8)Rh(COD)]^+$ SbF ₆ ⁻	rt	12	59	100:0	12
6	$RhCl(CO)(PPh_3)_2$	80	12	90	100:0	N.D.
7	RhCl(PPh ₃) ₃	80	12	93	100:0	N.D.
8	$RhCl(PPh_3)_3$	60	5	92	100:0	N.D.
9	$RhCl(PPh_3)_3$	40	3	91	100:0	N.D.
10^d	RhCl(PPh ₃) ₃	40	3	95	100:0	N.D.
11^e	$RhCl(PPh_3)_3$	40	10	85	100:0	N.D.

^{*a*} The reaction was conducted with **1a** (0.2 mmol) and catalyst (2 mol%) in 2 mL of toluene. ^{*b*} Determined using ¹H NMR analysis with mesitylene as the internal standard and N.D. = not detected. ^{*c*} The reaction was conducted with **1a** (0.1 mmol) and catalyst (3 mol%) in 2 mL of 1,2-dichloroethane. ^{*d*} 1 mL of toluene was used. ^{*e*} 1 mol% RhCl (PPh₃)₃ and 1 mL of toluene were used.

either (entry 3, Table 1). Interestingly, when $[RhCl(CO)_2]_2$ was used, the reaction processed smoothly to afford the expected bicyclic product **1a** in 81% yield with a *Z/E* ratio of 50:50 (entry 4, Table 1). The structure and relative configurations of *Z*-**2a** and *E*-**2a** were established *via* analogy with the X-ray single crystal diffraction study of **2c** (Fig. 1)¹¹ and the NOESY spectra (see the ESI†). The catalyst $[(C_{10}H_8)Rh(COD)]^*SbF_6^$ used in Trost's report^{7*a*} can facilitate the reaction to afford the cycloaddition product *Z*-**2a** with an incomplete conversion (entry 5, Table 1). To our delight, the yield was improved to 90% when RhCl(CO)(PPh₃)₂ was used with the exclusive formation of *Z*-**2a** (entry 6, Table 1). With RhCl(PPh₃)₃ as the catalyst, the yield was improved to 93% (entry 7, Table 1). The desired product could also be obtained in 92% and 91% yield



Fig. 1 The ORTEP representations of (3aR*,5S*,7aR*,Z)-2c.

at a lower temperature of 40 °C (entries 8 and 9, Table 1). The yield was 95% when running the reaction at a concentration of 0.2 M (entry 10, Table 1). The yield dropped to 85% with 1 mol% RhCl(PPh₃)₃ (entry 11, Table 1). Thus, the reaction conducted with **1a** and RhCl(PPh₃)₃ (2 mol%) in toluene at 40 °C was chosen as the standard conditions for further study.

With the optimized conditions in hand, the scope of substrates was investigated. The substrates with NTs as the linker were investigated firstly. The reaction afforded the corresponding products Z-2a-2c in decent yields when R^1 was methyl, n-butyl, and cyclohexyl, respectively (entries 1-3, Table 2). The relative configurations in 2c were established by the X-ray single crystal diffraction study¹¹ (Fig. 1) – all three H atoms are *cis* oriented with a Z-C=C bond. R² may be H, methyl, or n-propyl (entries 1-4, and 10, Table 2). The substrates with R² being aryl groups in the terminal of the diene moiety could afford the target products under the standard conditions with lower yields. The yields were improved by conducting the reactions at 80 °C (entries 5-7, Table 2). With a substituent such as o-Br, the reactions only afforded 2h in 15% yield with 36% recovery of 1h even at 80 °C for 36 h (entry 8, Table 2). To our delight, 66% yield of 2h was obtained when the reaction was conducted with the extra addition of AgSbF₆ (3 mol%) (entry 9, Table 2). R³ may be H or alkyl. It is worth mentioning that the reactions produced products 2a-2h as the only diastereoisomers while in entry 10 of Table 2 a minor amount of other diastereoisomers was formed. Malonate could also be used as the tether of the substrates. However, the reaction of 1j became sluggish as compared to the substrates with NTs as the tether and the corresponding product 2j was afforded with the help of $AgSbF_6$ (entry 11, Table 2).

When the phenyl-substituted 1,3-diene-incorporated substrate (2E,4E)-**1j** was reacted with RhCl(PPh₃)₃ and AgSbF₆ at 80 °C for 20 h, in addition to 40% yield of $(3aR^*,5R^*,7aR^*,E)$ -**2j**, 29% yield of $(3aR^*,7aS^*,E)$ -**3j** was obtained (eqn (1)). The relative configuration of $(3aR^*,7aS^*,E)$ -**3j** was also established using X-ray single crystal diffraction¹² (Fig. 2) – the C=C bond in the six-membered ring was conjugated with the exocyclic double bond.



In addition, when we applied the C=C bond stereoisomer (2E,4Z)-**1b** and **1k**, the reaction at 80 °C afforded the diastereoisomers $(3aR^*,5R^*,7aR^*,Z)$ -**2b** and $(3aR^*,5R^*,7aR^*,Z)$ -**2k** (Scheme 2). The relative configuration of $(3aR^*,5R^*,7aR^*,Z)$ -**2b** was also established by the X-ray single crystal diffraction studies (Fig. 3)¹³ – the H atom of C5 in the six-membered ring is *trans* to the two H atoms of the bridged carbon atoms C3a and C7a. Thus, the configuration of the C5 was controlled by the *E*/*Z* configuration of the distal C=C bond in the diene moiety of the substrates (eqn (2), (3) *vs.* entry 2, Table 2).

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	R ³ R ² R ¹ toluene, T	$(2 \text{ mol}\%) \xrightarrow{X^2 \to 0^{-R^3}} X^2 \xrightarrow{R^3}_{A^2 \to R^3} \xrightarrow{R^3}_{R^2} R^3$ R^1 2	N H CH ₃ CY 3i	
				2
Entry	$X/R^{1}/R^{2}/R^{3}$ (1)	T (°C)	<i>t</i> (h)	Isolated yield (%)
1	$NTs/^{n}Bu/CH_{3}/H((2E,4E)-1a)$	40	3	81 ((3a <i>R</i> *,5 <i>S</i> *,7a <i>R</i> *, <i>Z</i>)-2a)
2	NTs/CH ₃ /CH ₃ /H $((2E, 4E)-\mathbf{1b})$	40	8	82 ((3a <i>R</i> *,5 <i>S</i> *,7a <i>R</i> *, <i>Z</i>)-2 b)
3	$NTs/Cy/CH_3/H((2E,4E)-1c)$	40	3	73 $((3aR^*, 5S^*, 7aR^*, Z) - 2c)$
4	$NTs/^{n}Bu/n-C_{3}H_{7}/H((2E, 4E)-1d)$	40	4	78 ((3a <i>R</i> *,5 <i>S</i> *,7a <i>R</i> *, <i>Z</i>)-2d)
5^{b}	NTs/CH ₃ /Ph/H ((2 <i>E</i> ,4 <i>E</i>)-1e)	80	24	$39((3aR^*,5R^*,7aR^*,Z)-2e)$
6^b	$NTs/CH_3/p-FC_6H_4/H((2E,4E)-1f)$	80	21.5	71 ((3a $R^*, 5R^*, 7aR^*, Z)$ -2f)
7 ^b	$NTs/CH_3/p-ClC_6H_4/H((2E,4E)-1g)$	80	15	63 ((3aR*,5R*,7aR*,Z)-2g)
8^b	$NTs/^{n}Bu/o-BrC_{6}H_{4}/H$ ((2 <i>E</i> ,4 <i>E</i>)-1 h)	80	36	15^{c} ((3aR*,5S*,7aR*,Z)-2h)
9^d	$NTs/^{n}Bu/o-BrC_{6}H_{4}/H((2E,4E)-1h)$	80	8	66 ((3a <i>R</i> *,5 <i>S</i> *,7a <i>R</i> *, <i>Z</i>)- 2h)
10	$NTs/Cy/H/CH_3$ ((E)-1i)	40	4	87 ^e ((3aR*,7aR*,Z)-2i)
11^d	$C(CO_2Me)_2/^nBu/Ph/H((2E,4E)-1j)$	40	24	81 ((3a <i>R</i> *,5 <i>R</i> *,7a <i>R</i> *, <i>É</i>)-2 j)

^{*a*} Conditions A: The reaction was conducted with 1 (1.0 mmol) and RhCl(PPh₃)₃ (2 mol%) in 5 mL of toluene. ^{*b*} The reaction was conducted on a 0.5 mmol scale. ^{*c*} 36% yield of **1h** was recovered and the yield of **2h** was determined with the NMR spectrum of the crude reaction mixture. ^{*d*} Conditions B: The reaction was conducted with 1 (0.5 mmol), RhCl(PPh₃)₃ (2 mol%), and AgSbF₆ (3 mol%) in 2.5 mL of toluene. ^{*e*} The ratios of **2i/3i** in the isolated product and the crude product were 27:1 and 15:1, which were determined with the ¹H NMR analysis of the isolated product and the crude product.



Fig. 2 The ORTEP representations of (3aR*,7aS*,E)-3j.



Scheme 2 Rhodium-catalyzed intramolecular [4 + 2] cycloaddition of (2E,4Z)-1b and (2E,4Z)-1k.

Based on the X-ray diffraction study of $(3aR^*,5S^*,7aR^*,Z)$ -**2c**, $(3aR^*,5R^*,7aR^*,Z)$ -**2b** and the observed diastereoselectivity, a mechanism is proposed (Scheme 3). Firstly, RhCl(PPh₃)₃ reacts with AgSbF₆ to generate the cationic catalyst [Rh(PPh₃)₃]⁺SbF₆⁻. The reaction of the *R*-isomer (*R*_a,2*E*,4*E*)-**1**



Fig. 3 The ORTEP representation of (3aR*,5R*,7aR*,Z)-2b.

with the Rh catalyst would generate intermediate A, in which the "inner" C=C bonds in allene and the s-cis-1,3-diene coordinated with the rhodium atom in such a way that the two H atoms in intermediate A are cis oriented in order to make the R^1 group pointing away from the 1,3-diene unit. Subsequent cyclometalation leads to the formation of intermediate B. The allylic rearrangement leads to the formation of rhodiabicycloheptene C, in which the three tertiary hydrogen atoms are cis orientated. Subsequent reductive elimination and ligand exchange with $(R_a, 2E, 4E)$ -1 provide the product (3aR, 5S, 7aR, Z)-2 and regenerate the catalytically active species A to finish the catalytic cycle. For the S-enantiomer $(S_a, 2E, 4E)$ -1, intermediate A' other than intermediate A" (which has the same coordination mode as intermediate A) would be formed in order to keep the R¹ group far away from the catalyst. Subsequent cyclometalation, $\eta^3 - \eta^1$ rearrangement, reductive elimination, and ligand exchange with $(S_a, 2E, 4E)$ -1 would afford the enantiomer (3aS, 5R, 7aS, Z)-2.





Scheme 3 A proposed mechanism for the rhodium-catalyzed intramolecular [4 + 2] cycloaddition of allene-dienes (2*E*,4*E*)-1 ($\mathbb{R}^3 \neq aryl$).

When the optically active allene-1,3-diene (R_a ,2E,4E)-1a was reacted under the standard conditions, only one diastereomer (3aR,5S,7aR,Z)-2a was obtained in 76% yield; unfortunately, the efficiency of chirality transformation was low and the ee of (3aR,5S,7aR,Z)-2a was only 75% (eqn (4)). We are still working on this issue.



In conclusion, we have developed the RhCl(PPh₃)₃-catalyzed intramolecular [4 + 2] cycloaddition of 1,3-disubstituted allene-1,3-dienes, giving cis-6,5-fused bicyclic products with a very high diastereoselectivity. In addition, the relative configurations in the C3a, C5, and C7a of the products are controlled by the configuration of the C=C bonds in the 1,3-diene unit in the starting materials. The three H atoms of the tertiary carbon in the product are cis to each other when (2E,4E)-1,3-disubstituted allene-dienes were used; the two cis-H atoms of the bridged carbon and the H atom of the other tertiary carbon in the six-membered ring are trans to each other if the (2E, 4Z)-1,3-disubstituted allene-dienes were applied. A concerted cyclometalation, allylic rearrangement, and reductive elimination has been proposed to account for the observed diastereoselectivity. Further studies of the chirality transfer of optically active allene-1,3-dienes are being conducted in our laboratory.

Conflicts of interest

There are no conflict of interest to declare.

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