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# Enantioselective Rhodium-Catalyzed Cycloisomerization of (*E*)-1,6-Enynes

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***Abstract:*** *An enantioselective rhodium(I)-catalyzed cycloisomerization reaction of challenging (E)-1,6-enynes is reported. This novel process enables (E)-1,6-enynes with a wide range of functionalities, including nitrogen-, oxygen-, and carbon-tethered (E)-1,6-enynes, to undergo cycloisomerization with excellent enantioselectivity, in a high-yielding and operationally simple manner. Moreover, this $Rh^I$-diphosphane catalytic system also exhibited superior reactivity and enantioselectivity for (Z)-1,6-enynes. A rationale for the striking reactivity difference between (E)- and (Z)-1,6-enynes using $Rh^I$-BINAP and $Rh^I$-TangPhos is outlined using DFT studies to provide the necessary insight for the design of new catalyst systems and the application to synthesis.*

The development of new strategies for the efficient and stereoselective construction of highly functionalized polycyclic compounds remains a long-standing challenge for synthetic organic chemistry. To this end, the transition metal-catalyzed cycloisomerization of 1,*n*-enynes, 1,*n*-dienes and 1,*n*-diynes has emerged as powerful tools for the synthesis of various types of cyclic compounds.[1] Hence, the direct transformation of a linear substrate to a cyclic product without additional reactants that results in the rapid increase inmolecular complexity in an atom economic manner provides an attractive strategy. Among these methods, transition metal-catalyzed cycloisomerization of 1,6-enynes, leading to stereodefined cyclic 1,3-dienes and 1,4-dienes, as exemplified by γ-butyrolactones, lactams, tetrahydrofurans, pyrrolidines and cyclopentanes is of particular interest. A number of transition metal complexes, such as palladium,[2] ruthenium,[3] titanium,[4] gold,[5] platinum,[5] cobalt,[6] rhodium[7,8] and iron,[9] have been proven effective for this type of carbon-carbon bond forming cyclization under mild reaction conditions. Previously, Zhang et al. developed a series of cationic rhodium(I)-catalyzed cycloisomerization reations of internal 1,6-enynes to access a variety of functionalized five-membered cycles through a intermediacy of a rhodium(III)-metallacyclopentene.[8a–f,i,j,l] Additional studies resulted in the development of a novel rhodium(I)-catalyzed enyne cycloisomerization with an intramolecular halogen shift, which proceeds through a π-allyl rhodium intermediate.[8g,h,j,m] In related studies, Mikami and Bergens reported a different rhodium-complexes to facilitate a similar process.[8n] More recently, Nicolaou and co-workers also reported a cationic $Rh^I$-BINAP catalyzed asymmetric cycloisomerization of terminal 1,6-enynes with superior results.[8k] Additionally, Krische also reported a related enantioselective hydrogen-mediated reductive cyclization of 1,6-enynes using a cationic $Rh^I$-BINAP system.[10] However, most of these rhodium(I)-based catalytic systems require *(Z)*-configured 1,6-enynes to achieve optimal efficiency and selectivity. In contrast, *(E)*-configured 1,6-enynes are either inert or inefficient in these systems. Since the *(E)*-configured alkene is more readily available and more thermodynamically stable than corresponding *(Z)*-isomer, there are compelling reasons to develop an efficient rhodium(I)-catalyzed cycloisomerization with an *(E)*-1,6-enyne. The inherent challenges with *(E)*-1,6-enyne substrates, which can primarily be ascribed to the increased steric hindrance of *(E)*-1,6-enynes, make it significantly more challenging compared to the corresponding *(Z)*-isomer. Herein, we report the first enantioselective rhodium(I)-catalyzed cycloisomerization of *(E)*-1,6-enynes to access highly functionalized five-membered cycles (Figure 1).

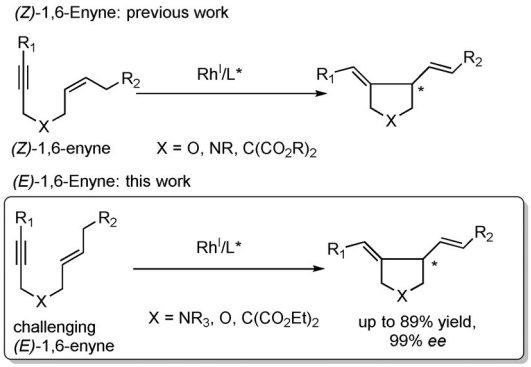


***Figure 1.*** Significance of the present study.

Preliminary studies focused on the identification of the optimal chiral ligand to facilitate the enantioselective rhodium(I)-catalyzed cycloisomerization of challenging *(E)*-1,6-enyne **1a** (see the Supporting Information (SI) for details for the preparation of **1a**). Treatment of **1a** with the chiral complex generated in situ from [{Rh(COD)Cl}$_2$] (5 mol%) with various chiral ligands **L1**–**L5** (12 mol%) and $AgSbF_6$

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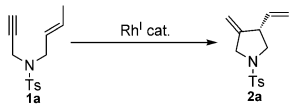
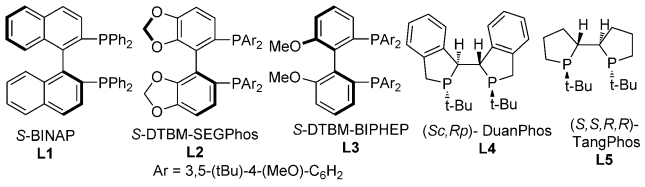
(20 mol%) in degassed 1,2-dicholoroethane (DCE) at room temperature furnished the cycloisomerization product **2a**[11] in good to excellent yields, albeit with significant variation in enantiocontrol (Table 1, entries 1–5). For instance, (*S*)-BINAP (**L1**), which was highly effective for various *(Z)*-1,6-enynes in our previous studies,[8c–f,k] provided poor enantioselective control (entry 1). Interestingly, the related *C*2-symmetric biarylphosphane ligands *(S)*-DTBM-SegPhos (**L2**), *(S)*-DTBM-BIPHEP (**L3**)) also displayed modest enantioselectivities (entries 2 and 3). In contrast, the electron-donating phosphocyclic ligands (*Sc,Rp*)-DuanPhos (**L4**)[12] and *(S,S,R,R)*-TangPhos (**L5**)[13] (entries 4 and 5) furnished **2a** in promising yields and enantiocontrol. Moreover, the neutral metal complex was significantly less effective (entry 7) and $BF_4$ is preferred to $SbF_6$ (entries 5 and 6) as the counter-ion, indicating that the formation of highly coordinatively unsaturated rhodium-species with weakly coordinating counter-ion is important for catalytic turnover. Gratifyingly, changing the catalyst to the preformed cationic catalyst (such as [{Rh(**L4**)(NBD)}$BF_4$], [{Rh(**L5**)(COD)}$BF_4$]),[8k] which avoids the silver salt metathesis,[14] provided **2a** in excellent yields and excellent enantioselectivities (entries 8 and 9). Additional studies to probe the effect of solvent demonstrated that 1,4-dioxane and 1,2-dicholoethane (DCE) were optimal with [{Rh(**L5**)(COD)}$BF_4$] (entries 9 and 13), whereas dichloromethane, tetrahydrofuran and toluene were inferior (entries 10–12). Interestingly, reducing the catalyst loading maintains the overall efficiency, albeit the enantioselectivity is significantly reduced (entry 14).

Table 2 summarizes the application of the optimized conditions (Table 1 entries 8 and 9) to a range of *(E)*-1,6-enynes **1** to demonstrate the scope of the reaction. For nitrogen-tethered *(E)*-1,6-enynes, an examination of different N-protecting groups demonstrated that *N*-benzoyl group gave comparable yield and enantioselectivity to that of *p*-toluenesulfonyl group, whereas *N*-(4-methoxyphenylsulfonyl) group resulted in a slight decrease of the enantioselectivity (entries 1–2). Furthermore, electron-donating protecting group (i.e. *N*-benzyl) was significantly less efficient (not shown), which illustrates the necessity for an electron-withdrawing protecting group. Additional variation at the alkene moiety revealed that increasing the length of alkyl substituent

***Table 1:*** Reaction development and optimization.[a]

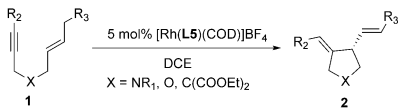


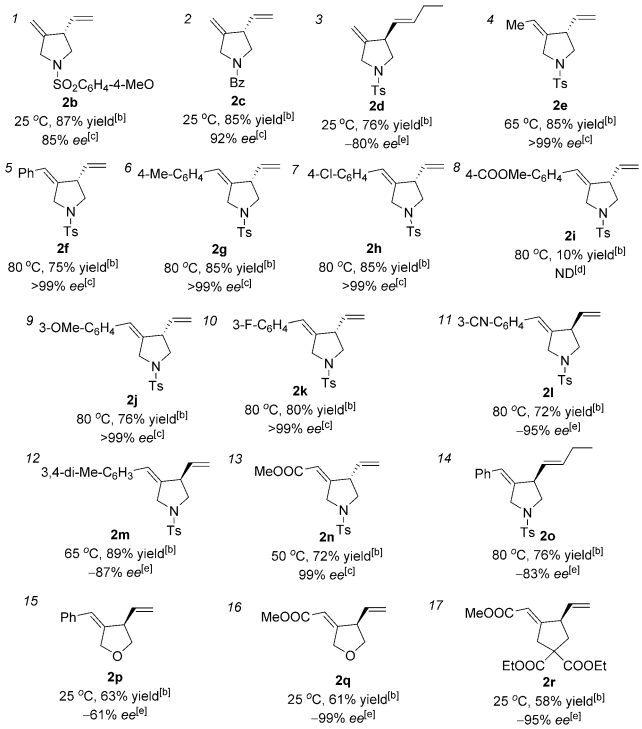

| Entry | $Rh^I$ precatalyst | Ligand | Solvent | Additive | Yield [%][b] | *ee* [%][c] |
|---|---|---|---|---|---|---|
| 1 | [{Rh(COD)Cl}$_2$] | **L1** | DCE | $AgSbF_6$ | 85 | 25 |
| 2 | [{Rh(COD)Cl}$_2$] | **L2** | DCE | $AgSbF_6$ | 70 | 35 |
| 3 | [{Rh(COD)Cl}$_2$] | **L3** | DCE | $AgSbF_6$ | 77 | 35 |
| 4 | [{Rh(COD)Cl}$_2$] | **L4** | DCE | $AgSbF_6$ | 81 | −75 |
| 5 | [{Rh(COD)Cl}$_2$] | **L5** | DCE | $AgSbF_6$ | 65 | 74 |
| 6 | [{Rh(COD)Cl}$_2$] | **L5** | DCE | $AgBF_4$ | 73 | 81 |
| 7 | [{Rh(COD)Cl}$_2$] | **L5** | DCE | none | trace | ND[d] |
| *8* | *[Rh(**L4**)(NBD)]$BF_4$* | – | *DCE* | *none* | *69* | *−91* |
| *9* | *[Rh(**L5**)(COD)]$BF_4$* | – | *DCE* | *none* | *85* | *91* |
| 10 | [Rh(**L5**)(COD)]$BF_4$ | – | DCM | none | 46 | 89 |
| 11 | [Rh(**L5**)(COD)]$BF_4$ | – | THF | none | 11 | ND[d] |
| 12 | [Rh(**L5**)(COD)]$BF_4$ | – | toluene | none | 85 | 64 |
| *13* | *[Rh(**L5**)(COD)]$BF_4$* | – | *dioxane*[e] | *none* | *88* | *92* |
| 14 | [Rh(**L5**)(COD)]$BF_4$[f] | – | dioxane[e] | none | 88 | 67 |




[a] All the reactions were conducted with **1a** (0.1 mmol) in the presence of an in situ generated ligand (12 mol%)-$Rh^I$ (5 mol%) complex in degassed 1,2-dicholoroethane at 25 °C. [b] Isolated yields were reported. [c] Determined by HPLC using a chiral stationary phase, see details in the Supporting Information. [d] Not determined. [e] 1,4-Dioxane. [f] 1 mol% catalyst was used. COD = 1,5-cyclooctadiene, NBD = norbornadiene, DCM = dichloromethane, DCE = 1,2-dicholoroethane, THF = tetrahydrofuran.

***Table 2:*** Scope of asymmetric cycloisomerization reactions.[a]



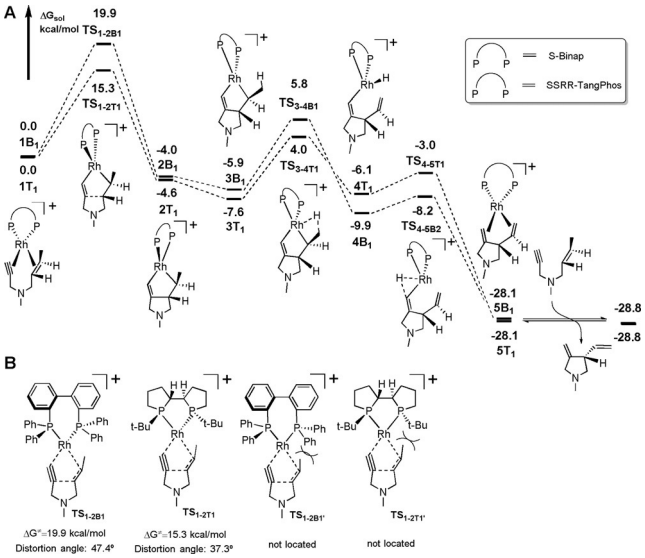

[a Reactions were run with substrates (0.1 mmol) in the presence of 5 mol% [{Rh(**L5**)(COD)}$BF_4$] in degassed 1,2-dicholoroethane at the specific temperature for 0.25–24 h unless otherwise specified. [b] Isolated yields. [c] Determined by HPLC using a chiral stationary phase, see details in the Supporting Information. [d] Not determined. [e] [{Rh(**L4**)(NBD)}$BF_4$] was used as the catalyst. Ph = phenyl, Ts = *p*-toluenesulfonyl, Bz = benzoyl.

leads to a decrease of enantioselectivities (entries 3 and 14). Interestingly, both alkyl (entry 4) and aryl substitution (entries 5–12) on the alkyne afford good yields and excellent enantioselectivities. Moreover, the stereoelectronics of the aryl substitution pattern has an interesting impact on the yield and enantioselectivity. For example, the electron-donating groups at the *para* position of aryl group were favorable for both reactivity and enantioselectivity (entries 6 and 7), whereas electron-withdrawing groups (such as COOMe) are completely unreactive even at high temperature and with prolonged reaction time (entry 8). Nevertheless, electron-withdrawing groups at the *meta* position of aryl group provide high yields and maintain the excellent enantioselectivities (entries 9–11), whereas *ortho* substitution and disubstitution was not tolerated and led to unexpected olefin isomerization product (not shown) and lower enantioselectivity (entry 12), respectively. Interestingly, $Rh^I$-DuanPhos performs better than $Rh^I$-TangPhos for **2d**, **2l**, **2m** and **2o** (entries 3, 11, 12, 14), which suggest that the latter system was sensitive to the stereoelectronic nature of the substrates. In addition, all the carbon, oxygen and nitrogen-tethered functionalized alkyne substrates provided excellent enantiocontrol (entries 13, 16 and 17), which might partially attribute to chelation control through the coordination of rhodium to the carbonyl group.[15] Whereas, the use of oxygen-bridged 1,6-enyne that has a phenyl group in alkyne position leads to significantly lower enantioselectivity (entry 15). Overall, substituted alkynes significantly decrease the reactivity but improve enantioselectivity, which contrasts the impact of substituents on the alkene moiety that exert favorable effect on reactivity but decrease enantioselectivity.

Encouraged by these interesting results among *(E)*-1,6-enyne, we then tried to testify whether *(Z)*-1,6-enynes are also applicable under the optimized reaction condition. Interestingly, both $Rh^I$-TangPhos and $Rh^I$-DuanPhos exhibited comparable reactivity and enantioselectivity to that of $Rh^I$-BINAP[8] for the *(Z)*-1,6-enyne **3** (Table 3, entries A and B). Additionally, $Rh^I$-TangPhos was also proved effective for the mixture of *(E)*-1,6-enyne **1a** and *(Z)*-1,6-enyne **3**, albeit with a slight decreace of enantioselectivity (entry C).

To gain more insights into the essence that why $Rh^I$-TangPhos performs better than $Rh^I$-BINAP for the cycloisomerization reaction of *(E)*-1,6-enynes, DFT calculations were carried out based on the proposed mechanism.[8e] In these theoretical results, the reaction pathway starts with tetra-coordinated square planar $Rh^I$-diphosphine enyne complexes $\mathbf{1B_1}$ and $\mathbf{1T_1}$ (*S*-BINAP in $\mathbf{1B_1}$, *S,S,R,R*-TangPhos in $\mathbf{1T_1}$, Scheme 1). From these square planar $Rh^I$ complexes, the

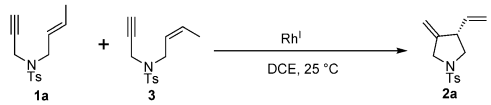



***Scheme 1.*** Reaction pathways for $Rh^I$-catalyzed cycloisomerization.

oxidative cyclization of 1,6-enynes occurs through transition states, $\mathbf{TS_{1\text{-}2B1}}$ and $\mathbf{TS_{1\text{-}2T1}}$ to give the key intermediates, $Rh^{III}$-metallacyclopentene $\mathbf{2B_1}$ and $\mathbf{2T_1}$. During this process, the methyl group on the terminal carbon of olefin gets closer to metal center and the steric effect between this methyl group and the substitutes on phosphine ligand increases accordingly, thus the transition states are distorted to be semi-tetrahedron coordinated. From $\mathbf{2B_1}$ and $\mathbf{2T_1}$, a β-H elimination and reductive elimination occur fast with small reaction barriers. At last, the ligand transfer happens to yield the product and regenerate $\mathbf{1B_1}$ and $\mathbf{1T_1}$. It is obvious that the oxidative cyclization process in the reaction pathways in Scheme 1 is the rate determining step because this step has higher barrier than the other steps from the energy analysis. However $\mathbf{TS_{1\text{-}2T1}}$ is more relatively stable than $\mathbf{TS_{1\text{-}2B1}}$, showing that the cycloisomerization of *(E)*-1,6-enyne can be catalyzed by $Rh^I$-Tangphos rather than $Rh^I$-BINAP. At the same time, this reaction step defines the enantioselectivity of the product because other oxidative cyclization modes which give *R*-isomer have higher barriers than the oxidative cyclization steps in Scheme 1 (Figures S30 and S33 in SI). It is aso revealed that $\mathbf{TS_{1\text{-}2B1}}$ is relatively more unstable than $\mathbf{TS_{1\text{-}2B3}}$ where *(Z)*-1,6-enyne is involved (Figure S31 in SI), while $\mathbf{TS_{1\text{-}2T1}}$ has comparable relative energy to $\mathbf{TS_{1\text{-}2T3}}$ where *cis*-1,6-enyne is involved (Figure S34 in SI). These results are consistent with the experimental observation that $Rh^I$-BINAP can catalyze the cycloisomerization reaction of *(Z)*-1,6-enynes, but not *(E)*-1,6-enynes. However, $Rh^I$-TangPhos works both for *(E)*- and *(Z)*-1,6-enynes.

In order to gain insight into the catalytic ability of these two catalysts towards *(E)*-1,6-enynes, we analyze the struc-

***Table 3:*** $Rh^I$-catalyzed cycloisomerization of (*Z*)-1,6-enynes.[a]




| Entry | Ratio **1a**:**3** | Yield [%][b] | *ee* [%][c] |
|---|---|---|---|
| A | 0:1 | 61 | 99 |
| B[d] | 0:1 | 65 | −98 |
| C | 1:1 | 81 | 86 |

[a] Reactions were run with substrates (0.1 mmol) in the presence of 5 mol% [{Rh(**L5**)(COD)}$BF_4$] in degassed 1,2-dicholoroethane at 25 °C for 0.25–1 h. [b] Isolated yields. [c] Determined by HPLC using a chiral stationary phase. [d] [{Rh(**L4**)(NBD)}$BF_4$] was used as the catalyst.

tural parameters of $\mathbf{TS_{1\text{-}2B1}}$ and $\mathbf{TS_{1\text{-}2T1}}$ and find that the distortion angle of metal center coordination is smaller in $\mathbf{TS_{1\text{-}2T1}}$ than in $\mathbf{TS_{1\text{-}2B1}}$, showing that the steric effect in $\mathbf{TS_{1\text{-}2T1}}$ is smaller than in $\mathbf{TS_{1\text{-}2B1}}$. Here, the square planar transition states $\mathbf{TS_{1\text{-}2B'}}$ and $\mathbf{TS_{1\text{-}2T'}}$ are not located due to very large repulsion between Me and Ph($^t$Bu) as shown in Scheme 1 B. This finding well explains the reactivity difference between Rh$^I$-TangPhos and Rh$^I$-BINAP for cycloisomerization of *(E)*-1,6-enynes.

In conclusion, we have developed the first rhodium(I)-catalyzed asymmetric cycloisomerization of *(E)*-1,6-enyes that afford highly functionalized five-membered cycles. This new process features not only high enantiomeric excess (>99% *ee*), but also broad substrate scope and functionality tolerance, wherein both terminal and internal alkynes with a variety of functional groups are tolerated, which provides a complementary approach for undertaking rhodium(I)-catalyzed cycloisomerization of 1,6-enynes. Moreover, this Rh$^I$-diphosphane catalytic system also exhibited superior reactivity and enantioselectivity for (*Z*)-1,6-enynes. Finally, a DFT study provides the necessary insight to understand the reactivity difference between Rh$^I$-TangPhos and Rh$^I$-BINAP for cycloisomerization of 1,6-enynes. We anticipate that this process will find significant utility in target directed synthesis given the ubiquity of *(E)*-configured olefins.

## Experimental Section

Precedure for the rhodium(I)-catalyzed cycloisomerization of **1a** to form (−)-**2a**: In a flame-dried Schlenk tube, [{Rh(*S,S,R,R*-TangPhos)-(COD)}$BF_4$] (3 mg, 5 mol%) was dissolved in freshly distilled 1,2-dichloroethane (1 mL), then **1a** (26.3 mg, 0.1 mmol) was introduced into the solution at RT under argon. The reaction was completed in 10 min. The reaction mixture was directly subjected to column chromatography, from which (−)-**2a** was obtained. The *ee* value was determined by chiral HPLC with an OJ-H column (*n*-hexane/isopropanol 95:5, 1 mL min$^{-1}$, 254 nm), $[\alpha]_D^{20} = -6.59$ ($c = 0.44$ in $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta = 7.71$ (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 5.51 (ddd, $J = 16.7$, 10.5, 8.1 Hz, 1H), 5.13 (s, 1H), 5.12–5.07 (m, 1H), 5.01–4.92 (m, 1H), 4.91–4.78 (m, 1H), 3.99 (d, $J = 14.1$ Hz, 1H), 3.77–3.67 (m, 1H), 3.67–3.55 (m, 1H), 3.34–3.09 (m, 1H), 2.87 (t, $J = 9.1$ Hz, 1H), 2.44 ppm (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta = 146.6$, 143.7, 135.5, 132.6, 129.7, 127.8, 118.1, 108.3, 53.1, 51.8, 47.7, 21.5 ppm; HR-ESI-MS (*m/z*): calcd for $C_{14}H_{17}NO_2S$ $[M+H]^+$, 264.1053, found 264.1053.

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**Keywords:** (*E*)-1,6-enyne · asymmetric synthesis · cycloisomerization · rhodium catalysis · TangPhos

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