Asymmetric Catalysis

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Chiral Tetrafluorobenzobarrelene Ligands for the Rhodium-Catalyzed Asymmetric Cycloisomerization of Oxygen- and Nitrogen-Bridged 1,6-Enynes**

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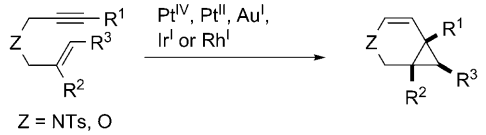
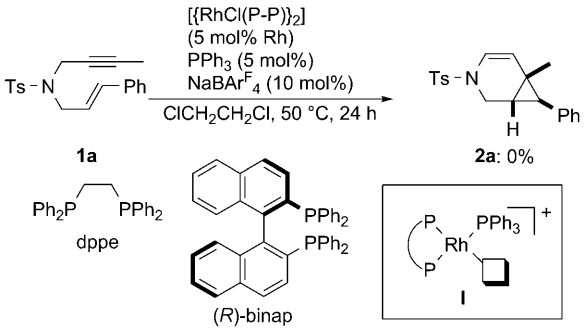
The transition-metal-catalyzed cycloisomerization reaction of 1,*n*-enynes has emerged as an atom-economical process for the preparation of diverse cyclic compounds.[1] Nitrogen- and oxygen-bridged enynes are useful starting materials for the construction of heterocyclic building blocks. Since Blum et al. reported the $PtCl_4$-catalyzed transformation of allyl propargyl ethers into 3-oxabicyclo[4.1.0]heptenes in 1995,[2] this type of 6-*endo-dig* cycloisomerization has been developed by the use of π-acidic metal[3] catalysts such as platinum[4,5] and gold[6] (Scheme 1). The reaction is thought to be promoted by the



Scheme 1. Cycloisomerization of 1,6-enynes.

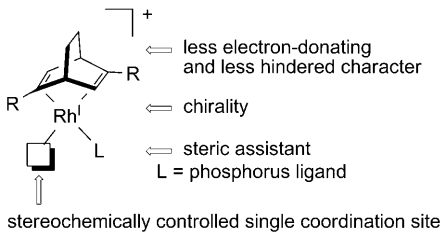
coordination of the alkyne moiety on the enyne to the π-acidic metal center. For less π-acidic metals, such as rhodium[7] and iridium,[8] their high catalytic activities are induced by the use of CO as a ligand and/or by performing the reaction under a CO atmosphere. In spite of its high synthetic utility for the construction of chiral cyclic skeletons as well as chiral cyclopropanes, there have been only a few reports on the asymmetric variant of the 6-*endo-dig* cycloisomerization reaction of 1,6-enynes to afford bicyclo[4.1.0]heptene derivatives.[5,8,9] Shibata and co-workers reported the asymmetric cycloisomerization of nitrogen-bridged 1,6-enynes, catalyzed by an iridium–bis(phosphine) complex under CO.[8] Recently, Marinetti et al. reported high enantioselectivities from the use of a chiral platinum–monophosphine complex.[5c] Herein, we report the asymmetric cycloisomerization of 1,6-enynes to afford 3-aza- and 3-oxabicyclo[4.1.0]heptene derivatives with high enantioselectivity using a rhodium–chiral diene[10] complex that has an achiral monophosphine as the second ligand.

Based on the reported use of active platinum catalysts containing a single vacant coordination site in the cycloisomerization of dienes[11] or enynes,[5] we tested the catalytic activity of a cationic rhodium complex that was coordinated by one bidentate phosphine ligand and one triphenylphosphine ligand for the generation of a cationic rhodium species **I** in the cycloisomerization of a nitrogen-bridged 1,6-enyne **1a** (Scheme 2). However, the use of bis(phosphine) ligands dppe



Scheme 2. Rhodium/phosphine catalysts in the cycloisomerization of 1,6-enyne **1a**. P—P = bis(phosphine) ligand.

and binap did not afford any bicyclo[4.1.0]heptene **2a** product. Next, we focused on the use of chiral diene ligands[10] for the rhodium-catalyzed asymmetric cycloisomerization of 1,6-enynes, based on our catalyst design that involves three characteristic features (Scheme 3): 1) the coordination of one phosphorus ligand to a cationic rhodium center that is also coordinated by a diene ligand provides a single vacant site at the square-planar rhodium(I) complex; this inhibits the simultaneous coordination of an alkyne and an alkene



Scheme 3. Catalyst design for the rhodium-catalyzed asymmetric cycloisomerization of 1,6-enynes.

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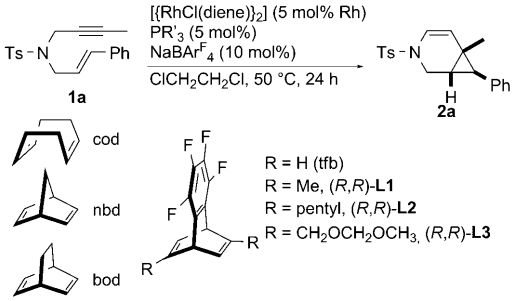
moiety of the 1,6-enyne;[5,11] 2) the less hindered and less electron-donating character of a diene ligand than a bis(phosphine) ligand is expected to stabilize a rhodium complex that is coordinated by a monophosphine ligand; and 3) the C_2-symmetric chiral diene ligand offers a good chiral environment.

To estimate the catalytic activity of our rhodium catalyst, the reaction of 1,6-enyne **1a** was carried out in the presence of [{RhCl(diene)}$_2$] (5 mol% of Rh), PPh_3 (5 mol%), and $NaBAr^F_4$ (10 mol%; Ar^F = 3,5-bis(trifluoromethyl)phenyl) in 1,2-dichloroethane at 50°C for 24 hours (Table 1). The

Table 1: Rhodium-catalyzed cycloisomerization of **1a**.[a]



Entry	Diene	PR′$_3$	Yield [%][b]
1	cod	PPh_3	9
2	nbd	PPh_3	7
3	bod	PPh_3	23
4	tfb	PPh_3	58
5	tfb	-	2[c]
6[d]	tfb	-	0
7	(*R*,*R*)-**L1**	PPh_3	48 (50% *ee*)[e]
8	(*R*,*R*)-**L2**	PPh_3	64 (56% *ee*)[e]
9	(*R*,*R*)-**L3**	PPh_3	94 (80% *ee*)[e]
10	(*R*,*R*)-**L3**	$P(4\text{-}MeC_6H_4)_3$	94 (80% *ee*)[e]
11	(*R*,*R*)-**L3**	$P(4\text{-}CF_3C_6H_4)_3$	19 (57% *ee*)[e]
12	(*R*,*R*)-**L3**	PCy_3	2
13	(*R*,*R*)-**L3**	$P(O\text{-}iPr)_3$	7

[a] Reaction conditions: enyne **1a** (0.10 mmol), [{RhCl(diene)}$_2$] (2.5 μmol, 5 mol% of Rh), PPh_3 (5.0 μmol), $NaBAr^F_4$ (0.010 mmol), 1,2-dichloroethane (0.2 mL) at 50°C for 24 h. [b] Determined by ^{1}H NMR spectroscopy. [c] 82% of **1a** was recovered. [d] Performed without $NaBAr^F_4$. [e] The *ee* was determined by HPLC analysis with a chiral stationary phase column (Chiralpak AD-H). cod:1,5-cyclooctadiene, nbd: norbornadiene, bod: bicyclo[2.2.2]octa-2,5-diene, tfb: tetrafluorobenzobarrelene, Cy: cyclohexyl.

use of rhodium complexes coordinated by cod (1,5-cyclooctadiene), nbd (2,5-norbornadiene), and bod (bicyclo[2.2.2]octa-2,5-diene)[12] gave 9%, 7%, and 23% yield of cycloisomerization product **2a**, respectively (Table 1, entries 1–3); tfb (tetrafluorobenzobarrelene)[13] displayed a higher catalytic activity to give **2a** in 58% yield (Table 1, entry 4). The high catalytic activity of the tfb ligand, which has a similar bicyclo[2.2.2]octadiene skeleton to bod, is probably due to its high π-accepting ability.[14] Reaction in the absence of triphenylphosphine gave a low yield of **2a**, which indicates that a single coordination site at rhodium is essential for the selective formation of the cycloisomerization product (Table 1, entry 5). A neutral complex [{RhCl(tfb)}$_2$] also had no catalytic activity, even though it could provide a single coordination site as a monomeric chlororhodium species (Table 1, entry 6). Next, we examined several C_2-symmetric tfb ligands[15] in the reaction of 1,6-enyne **1a** to find a successful catalyst for the enantioselective cycloisomerization reactions (Table 1, entries 7–9). Chiral tfb ligand (*R*,*R*)-**L1**,[15b] which has methyl group substituents, gave **2a** in 48% yield, and modest enantioselectivity (50% *ee*; Table 1, entry 7). Ligand **L2**, which has longer alkyl chains (pentyl), gave **2a** in 64% yield and 56% *ee* (Table 1, entry 8). (*R*,*R*)-**L3**,[15c] which contains $CH_2OCH_2OCH_3$ substituents, displayed a high catalytic activity and enantioselectivity to afford **2a** in 94% yield and 80% *ee* (Table 1, entry 9). The nature of the phosphorus ligands had a significant influence on both the catalytic activity and enantioselectivity (Table 1, entries 10–13). Tri(*para*-tolyl)phosphine displayed the same catalytic activity and enantioselectivity as PPh_3 (Table 1, entry 10). However, the use of electron-deficient tris(4-trifluoromethylphenyl)phosphine afforded **2a** in low yield (19%) and 57% *ee* (Table 1, entry 11). Both tricyclohexylphosphine (Table 1, entry 12) and triisopropyl phosphite (Table 1, entry 13) gave very low yields of **2a**. The relative and absolute configurations of **2a** that was obtained with (*R*,*R*)-**L3** were determined to be 1*S*,6*R*,7*R* by X-ray crystallographic analysis (Figure 1).[16]

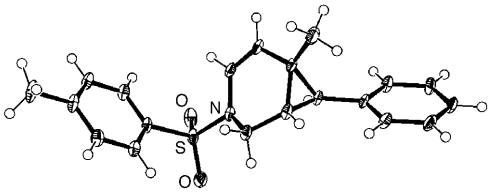
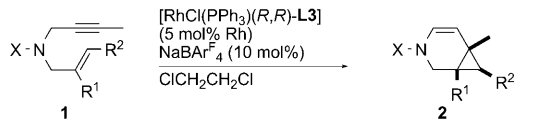


Figure 1. ORTEP illustration of **2a**; thermal ellipsoids are drawn at the 50% probability level.

Table 2 summarizes the results obtained for the cycloisomerization reactions of nitrogen-bridged 1,6-enynes **1**. The reaction was carried out using [RhCl(PPh_3)(*R*,*R*)-**L3**] (5 mol% of Rh) as a precursor to the active catalytic species that possesses one vacant coordination site, which was prepared by the reaction of [{RhCl(*R*,*R*)-**L3**}$_2$] with PPh_3 in dichloromethane. The asymmetric cycloisomerization of 1,6-enynes **1a**–**1e**, which have aryl groups on the alkene moiety, proceeded to give the corresponding bicyclic compounds **2a**–**2e** in good yields,[17] and enantioselectivities in the range 76–95% *ee* (Table 2, entries 1–5). Enynes containing *ortho* substituents on the benzene ring, 2-MeO (**1c**) and 2,6-Me_2 (**1d**), increased the enantioselectivity (90 and 95% *ee*, respectively; Table 2, entries 3 and 4). 1,6-Enyne **1f**, which contains a trifluoromethanesulfonyl substituent on the nitrogen atom, also gave cycloisomerization product **2f** in 73% yield and 73% *ee* (Table 2, entry 6). The reaction of 1,6-enyne **1g**, which has a methallyl group, proceeded smoothly under mild conditions, although the enantioselectivity of the product **2g** was moderate (68% *ee*; Table 2, entry 7).

The same type of cycloisomerization was observed for oxygen-bridged 1,6-enynes [Eqs. (1) and (2)]. Thus, the

Table 2: Rhodium-catalyzed cycloisomerization of 1,6-enyne **1**.[a]



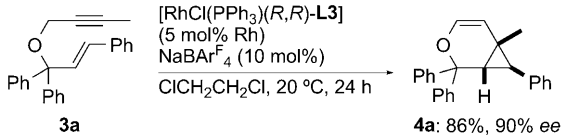
1a: X = Ts, R^1 = H, R^2 = Ph
1b: X = Ts, R^1 = H, R^2 = 4-$MeOC_6H_4$
1c: X = Ts, R^1 = H, R^2 = 2-$MeOC_6H_4$
1d: X = Ts, R^1 = H, R^2 = 2,6-$Me_2C_6H_3$
1e: X = Ts, R^1 = H, R^2 = 4-ClC_6H_4
1f: X = Tf, R^1 = H, R^2 = Ph
1g: X = Ts, R^1 = Me, R^2 = H

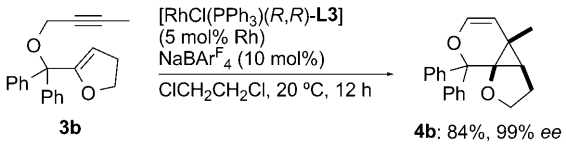
[Ts = $SO_2C_6H_4$-4-Me, Tf = SO_2CF_3]

Entry	Enyne	*T* [°C]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**1a**	50	24	94 (**2a**)	80
2	**1b**	40	24	91 (**2b**)	81
3	**1c**	40	24	87 (**2c**)	90
4	**1d**	60	48	71 (**2d**)	95
5	**1e**	60	24	92 (**2e**)	76
6	**1f**	60	48	73 (**2f**)	73
7	**1g**	40	24	81 (**2g**)	68

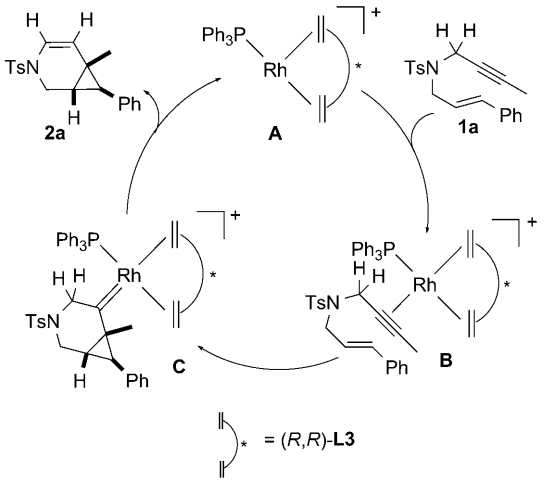
[a] Reaction conditions: enyne **1** (0.20 mmol), [RhCl(PPh_3)(*R*,*R*)-**L3**] (0.010 mmol, 5 mol% of Rh), $NaBAr^F_4$ (0.020 mmol, 10 mol%), 1,2-dichloroethane (0.4 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis with a chiral stationary phase column (Chiralpak AD-H).

reaction of **3a** gave 3-oxabicyclo[4.1.0]heptene **4a** in 86% yield and 90% *ee* [Eq. (1)].[18] Very high enantioselectivity (99% *ee*) was observed for the reaction of 1,6-enyne **3b**, which afforded tricyclic compound **4b** [Eq. (2)].

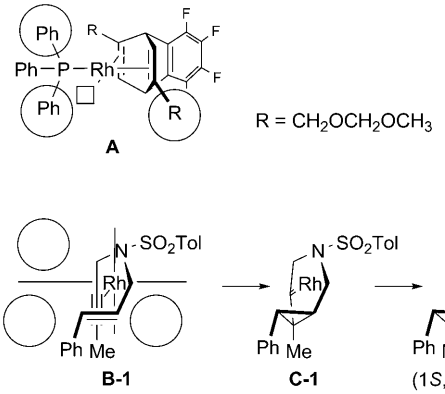




It has been proposed that the mechanism for the Pt^{II}-catalyzed cycloisomerization reaction involves a platinum carbenoid intermediate.[1,4,19] Provided that the mechanism for the π-acidic Rh^I-catalyzed formation of bicyclo-[4.1.0]heptenes is similar to that for the Pt^{II}-catalyzed reaction, we suggest that the catalytic cycle of the cycloisomerization proceeds as shown in Scheme 4. The coordination of the alkyne moiety of 1,6-enyne **1a** to coordinatively unsaturated cationic rhodium(I) species **A**, which was generated from [RhCl(PPh_3)(*R*,*R*)-**L3**] and $NaBAr^F_4$, affords η^2-alkyne–rhodium species **B**. Species **B** undergoes 6-*endo-dig* cyclization with the formation of two carbon–carbon bonds to form rhodium carbenoid **C**. β-Hydrogen shift affords the product (**2a**) whilst also regenerating the cationic rhodium species (**A**). It is most likely that the configuration of the product (**2a**) is determined during the carbon–carbon bond-formation step on η^2-alkyne–rhodium species **B**. The enantioselectivity achieved in this catalytic system can be rationalized using a quadrant diagram (Scheme 5). The ligands on cationic



Scheme 4. Plausible catalytic cycle.



Scheme 5. Proposed stereochemical pathway.

rhodium species **A** effectively shield three quadrants, and the substituents on the tfb ligand shape the less shielded site at the fourth quadrant. The alkene part of the 1,6-enyne approaches the alkyne moiety that has been activated by the π-acidic rhodium center. The 6-*endo-dig* cyclization step is directed by the steric bulk of the tosyl group, the two proximal phenyl groups of the triphenylphosphine, and the $CH_2OCH_2OCH_3$ substituent on the (*R*,*R*)-**L3**. Therefore, cyclization from **B**-**1** (Scheme 5) to give rhodium–carbenoid **C-1** is the most favorable, which leads to (1*S*,6*R*,7*R*)-**2a**.

In summary, we have developed a rhodium-catalyzed asymmetric cycloisomerization reaction of nitrogen- and oxygen-bridged 1,6-enynes that affords 3-aza- and 3-oxabicyclo[4.1.0]heptenes in high yields and high enantioselectivities. The reaction was accomplished using a cationic rhodium complex that was coordinated by PPh_3 and a chiral diene ligand.

Experimental Section

[RhCl(PPh_3)(*R*,*R*)-**L3**] (7.7 mg, 0.010 mmol) and $NaBAr^F_4$ (18.4 mg calculated as dihydrate, 0.020 mmol) were added to a solution of 1,6-enyne **1a** (67.9 mg, 0.20 mmol) in 1,2-dichloroethane (0.4 mL), and the mixture was stirred at 50 °C for 24 hours. The mixture was passed

through a short column of silica gel with hexane/ethyl acetate/Et_3N (20:5:1) as eluent. After evaporation of the solvent, the residue was subjected to flash column chromatography on silica gel (hexane/ethyl acetate/$CHCl_3$/Et_3N = 20:1:1:1) to give **2a** (63.6 mg, 0.19 mmol, 94%).

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[16] CCDC 753308 (**2a**) contains 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.

[17] The reaction of a terminal alkyne analogous to **1a** gave only 4% yield of cycloisomerization product **2**.

[18] The use of an oxygen-bridged 1,6-enyne that has no phenyl groups in the allylic position gave a low yield of the cycloisomerization product (18% yield for 2-butynyl (*E*)-3-phenyl-2-propenyl ether). The reaction of a 1,6-enyne, bridged by carbon atoms, did not give the corresponding bicyclo[4.1.0]heptene derivative.

[19] For examples of theoretical studies of Pt^{II}-catalyzed cycloisomerization, see: a) C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2003**, *9*, 2627; b) E. Soriano, P. Ballesteros, J. Marco-Contelles, *J. Org. Chem.* **2004**, *69*, 8018; c) E. Soriano, P. Ballesteros, J. Marco-Contelles, *Organometallics* **2005**, *24*, 3172; d) E. Soriano, P. Ballesteros, J. Marco-Contelles, *Organometallics* **2005**, *24*, 3182; e) E. Soriano, J. Marco-Contelles, *Acc. Chem. Res.* **2009**, *42*, 1026.

