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Asymmetric synthesis of planar-chiral paracyclophanes by double C–S bond formation: comparison of catalytic activity and enantioselectivity of Pd and Rh catalysts

Tomoko Hori, Yu Shibata, Ken Tanaka *

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

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Dedicated to Professor Henri Kagan on the occasion of his 80th birthday

ABSTRACT

We have determined that a cationic palladium(II)/(*R*)-BINAP complex is able to catalyze enantioselective double C–S bond-forming reactions between dithiols and dibenzyl dibromides leading to planar-chiral dithiaparacyclophanes. Although the yields and ee values of the palladium(II)-catalyzed syntheses of dithiaparacyclophanes did not exceed our previously reported cationic rhodium(I)/(*S*)-BINAPHANE complex-catalyzed ones, the palladium(II)-catalyzed reactions allowed the use of commercially available and inexpensive (*R*)-BINAP as a ligand. On the other hand, an almost racemic product was obtained by using a cationic rhodium(I)/(*R*)-BINAP complex as a catalyst.

1. Introduction

Planar-chiral paracyclophanes have attracted much attention as useful structures for chiral ligands, catalysts, and functional materials.[1] However, the redundant resolution of racemic compounds has long been employed for their syntheses.[2,3] Recently, crystallization-induced or adsorption-induced dynamic resolution of diastereomeric mixtures of paracyclophanes was reported for the asymmetric synthesis of paracyclophanes possessing thermodynamically flexible ansa chains.[4] However, the straightforward catalytic enantioselective synthesis is more attractive. In 2004 our research group reported that paracyclophanes can be obtained in good yields by catalytic aromatization through the cationic rhodium(I)/H_8-BINAP complex-catalyzed [2+2+2] cycloaddition (Scheme 1).[5,6]

In 2007 we successfully applied this methodology to the first enantioselective synthesis of planar-chiral metacyclophanes (Scheme 2).[7,8] Recently, Shibata et al. applied the rhodium-catalyzed [2+2+2] cycloaddition to the enantioselective synthesis of chiral cage compounds possessing planar-chirality.[9] However, application to the enantioselective synthesis of planar-chiral paracyclophanes has not been reported.

An alternative approach to the synthesis of paracyclophanes is construction of the ansa chain, such as double C–S bond formation leading to dithiaparacyclophanes.[3g,10,11] Our research group reported the $RhCl(PPh_3)_3$-catalyzed C–S bond formation of thiols and polychloroalkanes or alkyl bromides in the presence of Et_3N.[12] We successfully applied this reaction to the first catalytic enantioselective synthesis of planar-chiral paracyclophanes by using dithiols and dibenzyl dibromides as coupling partners and a cationic rhodium(I)/(*S*)-BINAPHANE complex as a catalyst (Scheme 3).[13] Recently, Shibata et al. have reported the enantioselective synthesis of planar-chiral paracyclophanes by palladium-catalyzed Sonogashira coupling.[14] In this paper, we report double C–S bond formation leading to planar-chiral dithiaparacyclophanes catalyzed by a cationic palladium(II)/(*R*)-BINAP complex instead of the cationic rhodium(I)/(*S*)-BINAPHANE complex, and a comparison of the catalytic activity and enantioselectivity of palladium(II) and rhodium(I) catalysts.

2. Results and discussion

In 1988 Page et al. reported the platinum(II)/dppm complex-catalyzed coupling reaction of thiols with diiodomethane in refluxing acetone using sodium carbonate as a base,[15] while the corresponding reaction using palladium(II) catalyst has not been reported. On the other hand, we demonstrated that a rhodium(I) complex showed significantly higher catalytic activity than an iridium(I) complex for the coupling reaction of thiols and dichloromethane.[12a] Therefore we anticipated that a palladium(II) complex would show higher catalytic activity than a platinum(II) complex. Indeed, $Pd(PPh_3)_2Cl_2$ was able to catalyze the coupling reaction of arenethiol **1a** with less reactive dichloromethane at room temperature to yield the corresponding formaldehyde dithioacetal **2a** in 78% yield, which is comparable to that using $RhCl(PPh_3)_3$ as a catalyst (Scheme 4).

The reaction of less nucleophilic alkanethiol **1b** with dichloromethane was effectively catalyzed by $RhCl(PPh_3)_3$, while $Pd(PPh_3)_2Cl_2$ failed to catalyze this reaction. Fortunately, a cationic palladium(II)/*rac*-BINAP complex was able to catalyze this reaction, although the product yield was low (Scheme 5).

* Corresponding author. Tel./fax: +81 42 388 7037.
E-mail address: tanaka-k@cc.tuat.ac.jp (K. Tanaka).

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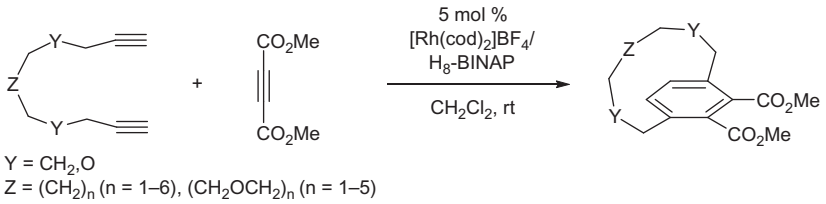
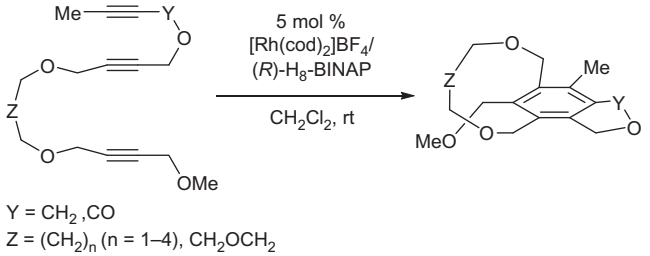
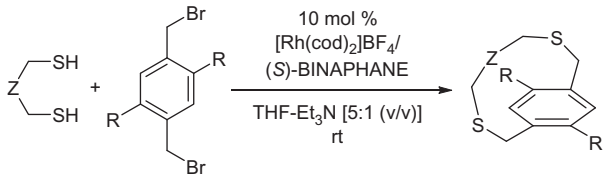


Scheme 1. Synthesis of paracyclophanes by cationic rhodium(I)/H_8-BINAP complex-catalyzed [2+2+2] cycloaddition.

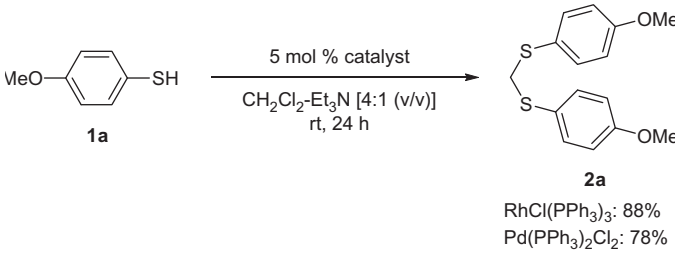


Scheme 2. Enantioselective synthesis of planar-chiral metacyclophanes by cationic rhodium(I)/(*R*)-H_8-BINAP complex-catalyzed [2 + 2 + 2] cycloaddition.

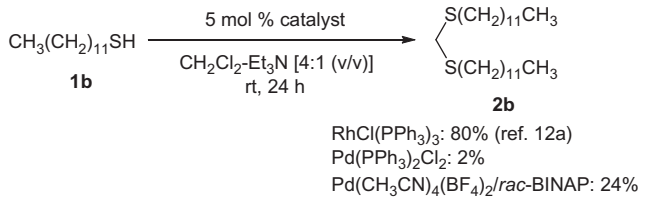


Scheme 3. Enantioselective synthesis of planar-chiral dithiaparacyclophanes by cationic rhodium(I)/(*S*)-BINAPHANE complex-catalyzed double C–S bond formation.

Next, we investigated the asymmetric variant of this reaction by using chiral palladium(II)/axially chiral biaryl bisphosphine (Fig. 1) complexes as catalysts. Table 1 shows a comparison of catalytic activity and enantioselectivity between palladium(II) and rhodium(I) complexes with axially chiral biaryl bisphosphine ligands for the reaction of dithiol **3a** with dibromide **4a** leading to dithia[9]paracyclophane **5aa**. In the rhodium(I) catalysis, the use of bisphosphine ligands possessing sterically demanding substituents on the phosphorus showed significantly higher enantioselectivity than the use of bisphosphine ligands possessing sterically less demanding substituents (phenyl) on the phosphorus (entries 4–6 vs entries 1–3), and the use of (*S*)-BINAPHANE showed the highest enantioselectivity (entry 6). Dihedral angles of the ligands also have a small impact on enantioselectivity (entries 1–3), and the use of H_8-BINAP possessing a large dihedral angle slightly improved the ee value (entry 3). Contrary to rhodium(I) catalysis, the use of (*R*)-BINAP and (*R*)-Segphos possessing small dihedral angles



Scheme 4. Coupling reaction of arenethiol **1a** with dichloromethane by using rhodium(I) and palladium(II) catalysts.



Scheme 5. Coupling reaction of alkanethiol **1b** with dichloromethane using rhodium(I) and palladium(II) catalysts.

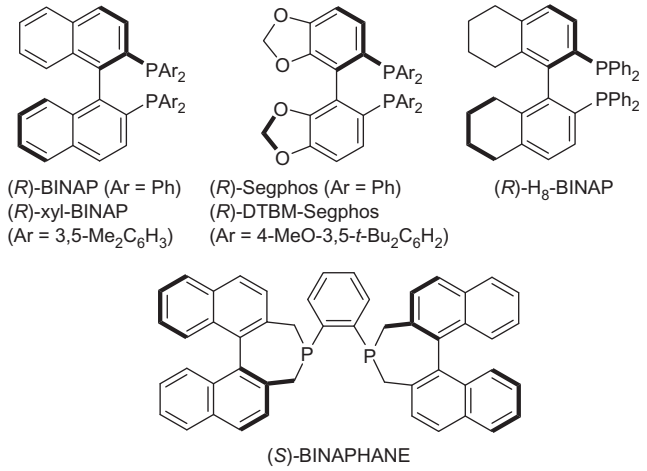
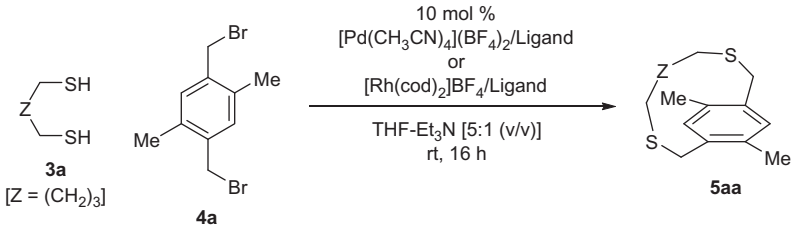


Figure 1. Structures of axially chiral biaryl bisphosphine ligands.

and small substituents (phenyl) on the phosphorus showed high enantioselectivities (entries 1 and 2) in the palladium(II) catalysis. The highest enantioselectivity was obtained by using (*R*)-BINAP as a ligand (entry 1).

The scope of the enantioselective dithiparacyclophane synthesis using the $[Pd(MeCN)_4](BF_4)_2$/(*R*)-BINAP complex or the $[Rh(cod)_2]BF_4$/(*S*)-BINAPHANE complex as a catalyst (10 mol %) is shown in Table 2. In both catalyst systems, the reactions of 1,5-pentanedithiol **3a** with dimethyl-substituted dibenzyl dibromide **4a** leading to dithia[9]paracyclophane **5aa** proceeded in higher enantioselectivities than the reactions of 1,6-hexanedithiol **3b** and 1,8-octanedithiol **3c** with **4a** leading to dithia[10] and [12]paracyclophanes **5ba** and **5ca** (entry 1 vs entries 3 and 4). With respect to dibenzyl dibromides, dibromo-substituted dibenzyl dibromide **4b** could also react with **3a**, while the ee values of the corresponding cyclophane **5ab** (entry 5) were lower than those of cyclophane **5aa** (entry 1). On the contrary, the reactions of dithiol **3d** with dibromo-substituted dibenzyl dibromide **4b** leading to dithia[3.3]paracyclophane **5db** proceeded in higher yields and enantioselectivities than the reactions of dithiol **3d** with dimethyl-substituted dibenzyl dibromide **4a** leading to dithia[3.3]paracyclophane **5da** (entry 6 vs entry 7). Importantly, the catalyst loadings could be reduced to 2 mol % without erosion

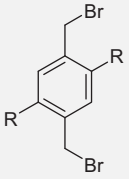
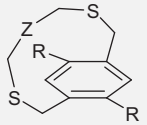
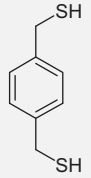
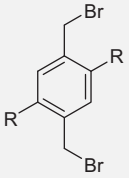
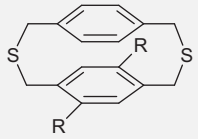
Table 1
Effect of ligands for palladium(II)- and rhodium(I)-catalyzed enantioselective coupling reaction of dithiol **3a** with dibromide **4a**[a]



Entry	Ligand	Pd catalysis yield[b] (%)	ee (%)	Rh catalysis yield[b] (%)	ee (%)
1	**(*R*)-BINAP**	**43**	**43** (−)	38	<2
2	(*R*)-Segphos	47	40 (−)	45	<2
3	(*R*)-H_8-BINAP	48	22 (−)	41	8 (+)
4	(*R*)-xyl-BINAP	42	28 (−)	59	32 (+)
5	(*R*)-DTBM-Segphos	54	33 (+)	53	32 (+)
6	**(*S*)-BINAPHANE**	40	15 (+)	**45**	**49** (−)

[a] $[Pd(CH_3CN)_4](BF_4)_2$ or $[Rh(cod)_2]BF_4$ (0.025 mmol), ligand (0.025 mmol), **3a** (0.25 mmol), **4a** (0.25 mmol), Et_3N (0.8 mL), and THF (4.2 mL) were employed.
[b] Isolated yield.

Table 2
Palladium(II)/(*R*)-BINAP- or rhodium(I)/(*S*)-BINAPHANE-catalyzed enantioselective coupling reactions of dithiols **3a–d** with dibromides **4a**,**b**[a]

Entry	**3** (*Z*)	**4** (*R*)	**5**	Catalyst (mol %)	Pd catalysis yield[b] (%)	ee (%)	Rh catalysis yield[b] (%)	ee (%)
								
1	**3a** [$(CH_2)_3$]	**4a** (Me)	**5aa**	10	43	43 (−)	45[c]	49 (−)[c]
2	**3a** [$(CH_2)_3$]	**4a** (Me)	**5aa**	2	39	40 (−)	51	52 (−)
3	**3b** [$(CH_2)_4$]	**4a** (Me)	**5ba**	10	41	8 (−)	39[c]	<2[c]
4	**3c** [$(CH_2)_6$]	**4a** (Me)	**5ca**	10	33	17 (+)	11[c]	11 (−)[c]
5	**3a** [$(CH_2)_3$]	**4b** (Br)	**5ab**	10	43	6 (+)	43[c]	27 (−)[c]
								
6[d]	**3d**	**4a** (Me)	**5da**	10	6	10 (+)	9[c]	30 (−)[c]
7[d]	**3d**	**4b** (Br)	**5db**	10	21	44 (−)	43[c]	60 (−)[c]

[a] Reactions were conducted using $[Pd(CH_3CN)_4](BF_4)_2$/(*R*)-BINAP or $[Rh(cod)_2]BF_4$/(*S*)-BINAPHANE (0.025 or 0.0050 mmol), **3a–d** (0.25 mmol), **4a**,**b** (0.25 mmol), Et_3N (0.8 mL), and THF (4.2 mL) at rt for 16 h.
[b] Isolated yield.
[c] Data of Ref. 13.
[d] Reactions were conducted using catalyst (0.025 mmol), **3d** (0.25 mmol), **4a**,**b** (0.25 mmol), Et_3N (1.6 mL), and THF (8.4 mL) at rt for 16 h.

of the product yields and ee values in both palladium(II)- and rhodium(I)-catalyzed reactions (entry 2). Although the yields and ee values of the palladium(II)-catalyzed syntheses of dithiaparacyclophanes did not exceed our previously reported cationic rhodium(I)/(*S*)-BINAPHANE complex-catalyzed ones, the use of the commercially available and inexpensive BINAP ligand is advantageous than the use of the expensive BINAPHANE ligand.

3. Conclusion

In conclusion, it was found that a cationic palladium(II)/(*R*)-BINAP complex is able to catalyze enantioselective double C–S bond-forming reactions between dithiols and dibenzyl dibromides leading to planar-chiral dithiaparacyclophanes. Although the yields and ee values of the palladium(II)-catalyzed syntheses of dithiaparacyclophanes did not exceed our previously reported cationic rhodium(I)/(*S*)-BINAPHANE complex-catalyzed ones, the palladium(II)-catalyzed reaction allowed us to use commercially available and inexpensive (*R*)-BINAP as a ligand. On the other hand, an almost racemic product was obtained by using a cationic rhodium(I)/(*R*)-BINAP complex as a catalyst.

4. Experimental

4.1. General

^1H NMR spectra were recorded on 300 MHz (JEOL AL 300). ^{13}C NMR spectra were obtained with complete proton decoupling on 75 MHz (JEOL AL 300). All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. CH_2Cl_2 (No. 27,099-7), THF (No. 18656-2), and Et_3N (No. 471283) were obtained from Aldrich and used as received. Dibromides **4a**[16]

and **4b**[17] were prepared according to the literature. All other reagents were obtained from commercial sources and used as received (without degassing and dehydrating). Dithioacetal **2b** was characterized in a previous report.[12a] Cyclophanes **5aa**, **5ba**, **5ca**, **5ab**, and **5db** were also characterized in a previous report.[13]

4.2. General procedure for rhodium(I)-catalyzed coupling reaction of thiol 1 with dichloromethane (Schemes 4 and 5)

A CH_2Cl_2 (0.5 mL) solution of $RhCl(PPh_3)_3$ (0.025 mmol) was added to a CH_2Cl_2 (1.5 mL) solution of thiol **1** (0.500 mmol) and Et_3N (0.5 mL). The mixture was stirred at rt for 24 h. The resulting solution was concentrated and purified by preparative TLC.

4.3. General procedure for palladium(II)-catalyzed coupling reaction of thiol 1 with dichloromethane (Schemes 4 and 5)

$Pd(PPh_3)_2Cl_2$ catalysis: A CH_2Cl_2 (0.5 mL) solution of $Pd(PPh_3)_2Cl_2$ (0.025 mmol) was added to a CH_2Cl_2 (1.5 mL) solution of thiol **1** (0.500 mmol) and Et_3N (0.5 mL). The mixture was stirred at rt for 24 h. The resulting solution was concentrated and purified by a preparative TLC.

$[Pd(CH_3CN)_4](BF_4)_2$/rac-BINAP catalysis: A CH_2Cl_2 (0.5 mL) solution of *rac*-BINAP (0.025 mmol) was added to a CH_2Cl_2 (0.5 mL) solution of $[Pd(CH_3CN)_4](BF_4)_2$ (0.025 mmol). The mixture was stirred at rt for 1 h. The resulting solution was added to a CH_2Cl_2 (1.0 mL) solution of thiol **1** (0.500 mmol) and Et_3N (0.5 mL). The mixture was stirred at rt for 24 h. The resulting solution was concentrated and purified by a preparative TLC.

4.4. 1-(4-Methoxyphenyl)sulfanylmethylsulfanyl-4-methoxybenzene 2a[18]

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40 (d, J = 8.7 Hz, 4H), 6.85 (d, J = 8.7 Hz, 4H), 4.15 (s, 2H), 3.79 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.5, 134.4, 125.2, 114.5, 55.3, 44.5.

4.5. General procedure for palladium(II)-catalyzed enantioselective coupling reaction of dithiol 3 with dibromide 4 (Table 2)

A THF (1.0 mL) solution of (*S*)-BINAP (0.025 mmol) was added to a THF (1.0 mL) solution of $[Pd(CH_3CN)_4](BF_4)_2$ (0.025 mmol). The mixture was stirred at rt for 1 h. To the mixture was added a THF (2.2 mL) solution of dithiol **3** (0.250 mmol) and dibromide **4** (0.250 mmol). Then, Et_3N (0.8 mL) was added to the mixture. The mixture was stirred at rt for 16 h. The resulting mixture was concentrated and purified by preparative TLC.

4.6. General procedure for rhodium(I)-catalyzed enantioselective coupling reaction of dithiol 3 with dibromide 4 (Table 2)

A THF (1.0 mL) solution of (*S*)-BINAPHANE (0.025 mmol) was added to a THF (1.0 mL) solution of $[Rh(cod)_2]BF_4$ (0.025 mmol). The mixture was stirred at rt for 1 h. To the mixture was added a THF (2.2 mL) solution of dithiol **3** (0.250 mmol) and dibromide **4** (0.250 mmol). Then, Et_3N (0.8 mL) was added to the mixture. The mixture was stirred at rt for 16 h. The resulting mixture was concentrated and purified by a preparative TLC.

4.7. (−)-12,15-Dimethyl-2,9-dithia[10]paracyclophane [(−)-5ba] (Table 2, entry 3)[13]

$[\alpha]_D^{25} = -3.7$ (*c* 1.88, $CHCl_3$) 8% ee; CHIRALCEL OD-H, hexane/2-PrOH = 97:3, 0.7 mL/min, retention times: 19.6 min (major isomer) and 21.9 min (minor isomer).

Acknowledgments

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