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BINAP–Ru(II) and BINAP–Rh(I)-catalyzed asymmetric hydrogenation of olefins without heteroatom-functionalities ☆

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Abstract

Asymmetric hydrogenation of 1,1′-disubstituted olefins which have no heteroatom functionalities to allow additional interactions with catalyst centers, have been investigated by use of Ru(II) and Rh(I) complexes of BINAP as catalysts. Enantioselectivities and the sense of asymmetric induction are highly dependent on the structure of substrates and the nature of catalysts. Hydrogenation of 1-methyleneindan (**1a**), a five-membered methylenecycloalkane, gave the highest optical yield (78%) when $Ru(OAc)_2$((*R*)-binap) was used as catalyst, while the use of the catalyst system $[RhI(cod)]_2$/(*R*)-BINAP afforded the highest *ee*s (71–82%) for six-membered analogs, 1-methylenetetralin (**4a**) and its derivatives. In contrast, hydrogenation of seven-membered analog **7** and acyclic olefins **10** resulted in only moderate enantioselectivities by use of these catalysts. The BINAP–Ru(II) catalyzed hydrogenation exhibited a remarkable dependence of enantioselectivities on solvents, while a large anionic ligand effect was observed for the reaction with the BINAP–Rh(I) system. Based on these experimental results, mechanistic aspects of these asymmetric hydrogenation have been discussed.

Keywords: Ruthenium; Rhodium; BINAP; Asymmetric hydrogenation; Simple olefins; Catalysis

1. Introduction

Asymmetric hydrogenation of prochiral olefins is one of the most useful tools for the synthesis of optically active organic compounds. A great success has been obtained in asymmetric hydrogenation of a wide variety of functionalized olefins by use of chiral diphosphine complexes of later transition metals such as Ru and Rh [1]. However, hydrogenation of relatively simple olefins without heteroatom functionalities has rarely been attained in high enantioselectivities with any conventional later transition metal catalysts, although a remarkable success has recently been achieved with chiral cyclopentadienyl complexes of Ti and Sm [2]. By the use of these early transition metal catalysts, enantioselectivity as high as 96% was reported for the hydrogenation of 2-phenyl-1-butene. Recently, highly enantioselective hydrogenation (80–99% *ee*) of trisubstituted unfunctionalized olefins has also been reported by Buchwald and his coworkers by use of chiral titanocene catalysts [3]. However, in the case of hydrogenation catalyzed by later transition metal complexes, the highest enantioselectivity was 60%, reported for the asymmetric hydrogenation of 2-phenyl-1-butene by the use of chiral diphosphine–Rh(I) complexes [4].

We report here asymmetric hydrogenation of unfunctionalized olefins catalyzed by BINAP complexes of later transition metals Ru and Rh. Five- and six-membered 1-methylene-2,3-benzocycloalkanes were hydrogenated in up to 82% *ee*.

2. Experimental details

2.1. General method

All manipulations of oxygen- and moisture-sensitive materials were conducted under purified argon atmosphere (BASF-Catalyst R3-11) by use of standard Schlenk techniques. Column chromatography was conducted on silica gel (Wakogel C-200 from Wako Pure Chemical Industries L.T.D). Analytical thin layer chromatography was performed on E. Merck silica gel 60 F-254 pre-coated plates.

☆ This paper has been dedicated to Professor Dr. Henry Brunner for his 60th birthday.

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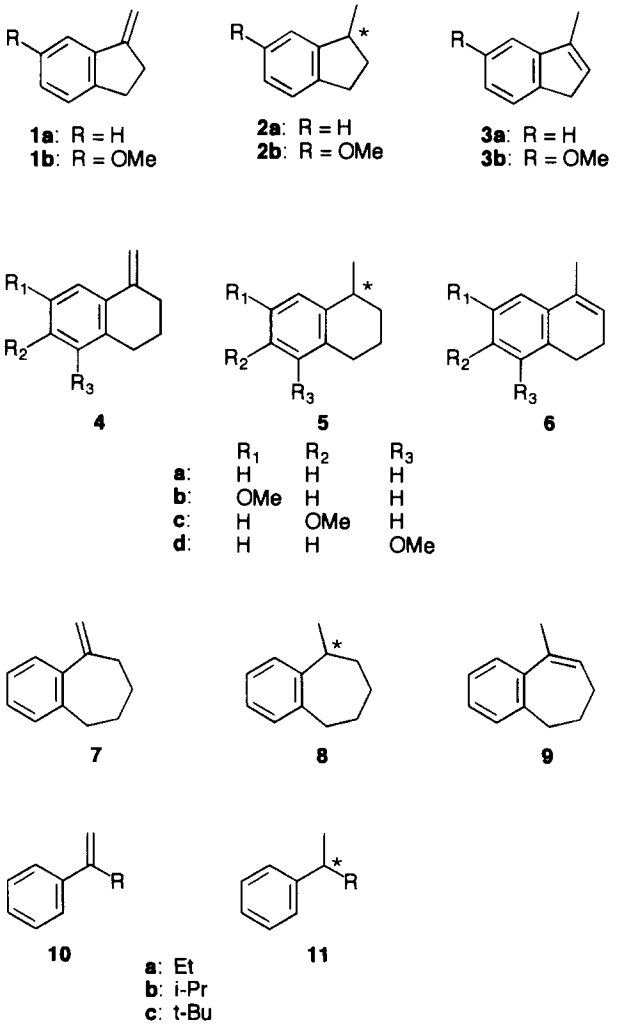
2.2. Apparatus

NMR spectra were taken on JEOL EX-270 (^{1}H 270 MHz) spectrometer using tetramethylsilane (^{1}H) as an internal standard, and coupling constants were given in hertz. Optical rotations were measured on a JASCO DIP-360 spectrometer. Analyses of gas chromatography were performed on Shimadzu GC15A. For high pressure hydrogenation, 50 ml stainless steel autoclave equipped with quartz vessel was used.

2.3. Chemicals

All solvents were dried by standard methods and distilled under argon. (*R*)-BINAP [5], $Ru(OAc)_2$((*R*)-binap) [6], Ru_2Cl_4((*R*)-binap)$_2NEt_3$ [7], [RuI((*R*)-binap)(*p*-cymene)]I [8], $[RhX(cod)]_2$ (X = Cl, Br, I, OAc) [9], and $[Rh(cod)_2]BF_4$ [10] were prepared according to the literature methods.



2.4. General procedure for preparation of olefins 1, 4, 7, 10 by Wittig reaction, depicted for 1-methylenetetralin (4a)

To a solution of 2.20 g (15.1 mmol) of 1-tetralone in anhydrous ether (120 ml) were added under argon methyltriphenylphosphonium bromide (5.35 g, 15.0 mmol) and then 1.68 g (15.0 mmol) of potassium *tert*-butoxide. The mixture was stirred for 20 h at room temperature. The ether was removed under reduced pressure and the residue was extracted with pentane. The pentane extract was filtered through Celite 545 and the solvent was evaporated. The resulting crude product was purified by column chromatography on silica gel with pentane as eluent to give 1.70 g (78% yield) of 1-methylenetetralin (**4a**) after distillation in vacuo. The olefinic substrates **1a**, **1b**, **4b**, **4c**, **4d**, **7**, **10a**, **10b**, **10c** were prepared by the same procedure.

2.5. Preparation of $[Rh(OPh)(cod)]_2$

This compound was prepared by the application of the procedure reported for the synthesis of $[Rh(OAc)(cod)]_2$ and $[Rh(OCH_3)(cod)]_2$ [11]. A mixture of $[RhCl(cod)]_2$ (24.7 mg, 0.050 mmol) and sodium phenoxide (22.5 mg, 0.194 mmol) was stirred in acetone (4 ml) at room temperature in under argon. After one hour, the initial yellow color of the solution became almost colorless. The solvent was evaporated and the residue was dissolved in dichloromethane. The mixture was filtered and the filtrate was concentrated in vacuo to afford $[Rh(OPh)(cod)]_2$ as a pale yellow solid (28.7 mg, 94%); ^{1}H NMR ($CDCl_3$) δ: 7.08 (t, J = 7.7 Hz, 2H), 6.91 (d, J = 7.7 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 3.17 (s, 4H), 2.17–2.33 (m, 4H), 1.34 (broad, 4H).

2.6. General procedure for asymmetric hydrogenation of olefins catalyzed by BINAP–Ru(II) complexes, depicted for 1-methylenetetralin (4a)

A solution of **4a** (154 mg, 1.07 mmol) in dichloromethane (10 ml) was degassed by freeze pump thaw cycles and transferred to an autoclave containing $Ru(OAc)_2$((*R*)-binap) (2.7 mg, 3.2×10^{-3} mmol) under argon atmosphere. The mixture was stirred for 44 h at 30°C under hydrogen atmosphere (100 kg cm^{-2}). After evaporation of the solvent, bulb-to-bulb distillation afforded a mixture of **4a**, **5a**, and **6a** (152 mg, **4a** : **5a** : **6a** = 12 : 81 : 7), which were identified by ^{1}H NMR. The enantiomeric excess of **5a** was determined by GLC analysis using chiral capillary column (Chiraldex B-PH 0.45 mmf × 30 m, He, 80°C; t_1 = 29.2, t_2 = 30.1, 69% *ee*).

2.7. General procedure for asymmetric hydrogenation of olefins catalyzed by BINAP–Rh(I) complexes, depicted for 1-methylenetetralin (4a)

A solution of **4a** (136 mg, 0.944 mmol) in 10 ml of dichloromethane was degassed by freeze pump thaw and then transferred to an autoclave containing $[RhI(cod)]_2$ (5.0 mg, 7.4×10^{-3} mmol) and (*R*)-BINAP (11.1 mg, 1.8×10^{-2} mmol) under argon. The mixture was pressurized with hydrogen (25 kg cm^{-2}) and stirred for 3 h at 30°C. After evaporation of the solvent, bulb-to-bulb distillation afforded a mixture of **4a** and **5a** (116 mg, **4a** : **5a** = 19 : 81), which were identified by ^1H NMR. The enantiomeric excess of **5a** (80% *ee*) was determined by GLC analysis using a chiral capillary column (chiraldex B–PH or Cp cyclodex β-236M). **2b**: B–PH, He 1 kg cm^{-2}, 90°C; $t_1 = 43.3$, $t_2 = 44.6$. **5a**: B–PH, He 1 kg cm^{-2}, 80°C; $t_1 = 29.2$, $t_2 = 30.1$. **5b**: B–PH, He 1 kg cm^{-2}, 120°C; $t_1 = 28.0$, $t_2 = 29.4$. **5c**: B–PH, He 1 kg cm^{-2}, 120°C; $t_1 = 32.9$, $t_2 = 33.3$. **5d**: 5-Hydroxy-1-methyltetralin, obtained by demethylation of **5d**, was analyzed. B–PH, He 1 kg cm^{-2}, 140°C; $t_1 = 39.6$, $t_2 = 40.8$. **8**: B–PH, He 1 kg cm^{-2}, 100°C; $t_1 = 20.6$, $t_2 = 22.1$. **11c**: β-236M, He 1 kg cm^{-2}, 70°C; $t_1 = 35.2$, $t_2 = 36.8$.

Optical purities and absolute configurations of **2a**, **11a**, and **11b** were determined based on the following optical rotation values: (*R*)-**2a**: $[\alpha]_D^{25}$ + 11.6° (neat) [12]; (*S*)-**11a**: $[\alpha]_D$ 28.4° (*c* 1.00, 95% ethanol) [2b]; (*S*)-11b: $[\alpha]_D$ 30.0° (*c* 1.6, CCl_4) [13].

2.8. Demethylation of 5-methoxy-1-methyltetralin (5d)

To 140 mg (0.80 mmol) of **5d** in a dry flask was added 0.5 ml of tetrachloromethane and 0.2 ml (1.4 mmol) of trimethylsilyl iodide under argon. The solution was stirred for 22 h at room temperature and then quenched with 0.5 ml of anhydrous methanol. The volatile components were removed at reduced pressure and the residue was taken up in diethyl ether. The ether layer was washed successively with aqueous sodium bisulfite, aqueous sodium bicarbonate, and brine, and dried. Evaporation of the solvent followed by recrystallization of the residue from hexane gave 5-hydroxy-1-methyltetralin (90 mg, 69%).

3. Results and discussion

3.1. $Ru(OAc)_2$(binap)-Catalyzed asymmetric hydrogenation of unfunctionalized olefins

1-Methylene-2,3-benzocycloalkanes **1**, **4**, **7**, and α-alkylstyrenes **10**, were subjected to hydrogenation by the use of $Ru(OAc)_2$((*R*)-binap) and the results are listed in Table 1. In the course of hydrogenation of **1**, **4**, and **7**, olefin isomerization also occurred. The hydrogenation products, however, did not seem to be formed from these isomerization products **3**, **6**, and **9**, since the latter ones were hydrogenated very slowly compared to the substrates **1**, **4**, and **7**. 1-Methyleneindane (**1a**) was hydrogenated in high optical yield (entry 1), while introduction of methoxy substituent at meta-position resulted in lower enantioselectivity (entry 2). Among the 1-methylenetetralin substrates **4a–d**, six-membered analogs of **1**, **4c** gave the highest enantioselectivity (entries 3–6). Alternatively olefin **7**, a seven-membered ring analog of **1a** and **4a**, was hydrogenated in low enatioselectivity (entry 7). Acyclic olefins **10a–c** were hydrogenated without isomerization, but in poor enantioselectivities (entry 8–10). The benzene rings and C=C bonds are almost in a plane in compounds **1** and **4**, while such planar structures are unlikely for **7** and **10**. These differences in molecular geometry might be re-

Table 1
Asymmetric hydrogenation of olefins catalyzed by $Ru(OAc)_2$((*R*)-binap) [a]

Entry	Substrate	Time (h)	Conv. [b] (%)	Select. [b] (%)	*ee* [c] (%)	Config. [d]
1	**1a**	24	100	98	(78)	*S*-(−)
2	**1b**	20	100	97	45	–
3	**4a**	44	90	96	69	*S*-(+)
4	**4b**	44	100	> 99	65	(+)
5	**4c**	44	100	96	75	–
6	**4d**	44	100	94	61	(+)
7	**7**	44	81	96	23	(−)
8	**10a**	38	100	100	(9)	*R*-(−)
9	**10b**	44	70	100	(16)	*R*-(+)
10	**10c**	44	11	100	30	–

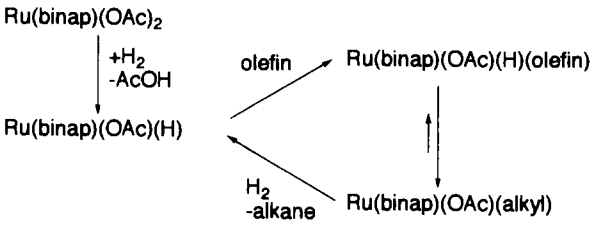
[a] Substrates (1 mmol) and $Ru(OAc)_2$((*R*)-binap) (4.0×10^{-3} mmol) were stirred in CH_2Cl_2 (10 mL) at 30°C under H_2 (100 atm).
[b] Conversions and selectivities were determined by ^1H NMR spectroscopy. The other products were isomerization compounds, **3**, **6**, and **9**.
[c] Enantiomeric excesses were determined by GLC or by the optical rotation values.
[d] Absolute configurations were determined based on the optical rotation values.

flected on the enantioselectivities of the hydrogenation, though the reason for these dependence of enantioselectivities on the structures of substrates is still unclear.

3.2. Asymmetric hydrogenation of 1-methylenetetralin (4a) catalyzed by BINAP–Ru(II) complexes under variable reaction conditions

By use of 1-methylenetetralin (**4a**) as a substrate, effects of anionic ligands OAc, Cl, and I in BINAP–Ru(II) complexes, solvents, and hydrogen pressure on catalytic activities and enantioselectivities were examined. Results are summarized in Table 2. Chemoselectivities were largely dependent on the anionic ligands, while almost no dependence of *ee*s on the nature of anionic ligands were observed. The highest chemoselectivity was obtained in the hydrogenation with the complex bearing acetate ions. Isomerization of **4a** to **5a** was observed in the hydrogenation catalyzed by $Ru(OAc)_2$ ((*R*)-binap) and [RuI((*R*)-binap)(*p*-cymene)]I even in the presence of triethylamine to trap protic species which could arise from the reaction of catalyst precursor with hydrogen. Such isomerization was not observed in the absence of hydrogen. These facts suggest that isomerization of **4a** has been caused by metal hydride species.

The hydrogenation of **4a** catalyzed by $Ru(OAc)_2$ ((*R*)-binap) has been investigated in several solvents such as dichloromethane, THF, toluene, and methanol (entry 5–8). It appears that enantioselectivities largely depend on the solvent. Among the solvent used, dichloromethane gave the highest enantioselectivity and the highest conversion. Coordinating solvents such as THF, toluene, and methanol decreases catalytic activities to a large extent. No remarkable enhancement in enantioselectivity was observed for reactions at lower temperature. Interestingly, opposite enantioface selections were observed between hydrogenations in methanol and in other solvents.



Scheme 1.

Effect of hydrogen pressure was also investigated over the range 5–100 atm (entry 5 and 9). Higher initial hydrogen pressure afforded better chemoselectivity, while enantioselectivities did not depend on hydrogen pressure.

3.3. Consideration on the reaction mechanism and enantioselectivities in BINAP–Ru(II)–catalyzed asymmetric hydrogenation

For BINAP–Ru(II)$(OAc)_2$-catalyzed asymmetric hydrogenation, mono hydride mechanism has been proposed, which involves initial coordination of olefin to Ru hydride species, followed by olefin insertion, and hydrogenolysis of Ru–alkyl bond (scheme 1) [14,15]. In the present catalysis, a similar mechanism can be considered to be operating at least for the hydrogenation catalyzed by $Ru(OAc)_2$((*R*)-binap) (Scheme 1) [16]. Double bond isomerization in substrates during the catalysis suggests that the second step (olefin insertion) is reversible. This reversibility involving olefin insertion into M–H bond and β-hydride elimination in M-alkyl species, has also been supported by the result of the deuteration of styrene in which scramble of hydrogen and deuterium was observed in the reduction product.

Table 2
Asymmetric hydrogenation of **4a** catalyzed by BINAP–Ru(II) complexes [a]

Entry	Cat. [b]	Solvent	H_2 (atm)	Temp. (°C)	Time (h)	Conv. [c] (%)	Select. [c] **5a/6a**	*ee* [d] (%)	Config. [e]
1	A	CH_2Cl_2	100	50	20	100	89/11	66	*S*
2	B	CH_2Cl_2	100	50	63	100	49/51	65	*S*
3	C	CH_2Cl_2	100	50	46	100	0/100	–	–
4	C + NEt_3	CH_2Cl_2	100	50	19	100	7/93	66	*S*
5	A	CH_2Cl_2	100	30	44	90	96/4	69	*S*
6	A	THF	100	30	40	4	79/21	40	*S*
7	A	toluene	100	30	44	3	75/25	24	*S*
8	A	MeOH	100	50	90	41	44/56	22	*R*
9	A	CH_2Cl_2	5	30	24	60	66/34	69	*S*

[a] Conditions: Substrate (1 mmol) and the catalyst were stirred in CH_2Cl_2 (10 mL) at 30°C or 50°C under H_2 (100 atm).
[b] Cat.: A = $Ru(OAc)_2$((*R*)-binap), B = Ru_2Cl_4((*R*)-binap)$_2$(NEt_3). C = [RuI((*R*)-binap)(*p*-cymene)]I.
[c] Conversions and **5a/6a** ratios were determined by ^1H NMR spectroscopy.
[d] Enantiomeric excesses were determined by GLC analysis.
[e] Absolute configurations were determined based on the optical rotation values.

Table 3
Asymmetric hydrogenation of olefins catalyzed by $[RhX(cod)]_2$/(*R*)-BINAP (X = I or Cl) [a]

Entry	Substrate	Cat. (X =)	Time (h)	Conv. [b] (%)	*ee* [c] (%)	Config. [d]
1	**1a**	I	19	100	(66)	*S*-(−)
2	**1a**	Cl	21	100	(18)	*S*-(−)
3	**1b**	I	16	100	43	–
4	**4a**	I	3	81	80	*S*-(+)
5	**4a**	Cl	10	100	35	*S*-(+)
6	**4b**	I	3	85	71	(+)
7	**4c**	I	3	(53)	77	–
8	**4d**	I	21	100	47	(+)
9	**7**	I	19	56	44	(−)
10	**7**	Cl	20	64	34	(−)
11	**10a**	I	45	100	(29)	*S*-(+)
12	**10a**	Cl	70	100	(29)	*S*-(+)
13	**10b**	Cl	68	100	35	*R*-(+)
14	**10c**	I	19	22	7	–
15	**10c**	Cl	44	87	40	–

[a] Conditions: Substrates (1 mmol), $[RhX(cod)]_2$ (7.5×10^{-3} mmol), and (*R*)-BINAP (1.8×10^{-2} mmol) were stirred in CH_2Cl_2 (10 ml) at 30°C under H_2 (25 atm).
[b] Conversions and selectivities were determined by ^1H NMR spectroscopy.
[c] Enantiomeric excesses were determined by GLC or by the optical rotation values.
[d] Absolute configurations were determined based on the optical rotation values.

At higher hydrogen pressure the next hydrogenolysis step would be accelerated, and thus olefin isomerization would be depressed. The reversibility between olefin insersion and deinsertion coupled with little hydrogen pressure effect suggests that the first olefin coordination step might be more probable for the enantioselection step than the others. Solvent effect could be explained in terms that each intermediate is further coordinated or interacted with solvent molecule(s). The reason for the absence of the anionic ligand effect on enantioselectivities is unclear at present.

3.4. *[RhX(cod)]$_2$ / BINAP-catalyzed asymmetric hydrogenation of unfunctionalyzed olefins*

By the use of $[RhX(cod)]_2$/(*R*)-BINAP (X = I, Cl) as catalysts, olefins **1**, **4**, **7**, and **10** were hydrogenated and results are summarized in Table 3. Contorary to the

Table 4
Asymmetric hydrogenation of **4a** catalyzed by BINAP–Rh complexes [a]

Entry	Cat. (X =)	Solvent	H_2 (atm)	Time (h)	Conv. [b] (%)	*ee* [c] (%)	Config. [d,e]
1	I	CH_2Cl_2	25	3	81	78–80 [f]	*S*
2	Br	CH_2Cl_2	25	3	79	53	*S*
3	Cl	CH_2Cl_2	25	3	85	36	*S*
4	OAc	CH_2Cl_2	25	3	11	36	*S*
5	OPh	CH_2Cl_2	25	3	57	35	*S*
6	$[Rh(cod)_2]BF_4$/ (*R*)-BINAP	CH_2Cl_2	25	45	100 [g]	33	*R*
7	I	THF	25	3	44	79–82 [f]	*S*
8	I	CH_2Cl_2	100	3	100	76	*S*
9	I	CH_2Cl_2	3	3	23	73	*S*

[a] Substrate (1 mmol), Rh precursor (1.5×10^{-2} mmol), and (*R*)-BINAP (1.8×10^{-2} mmol) were stirred in CH_2Cl_2 (10 ml) at 30°C under H_2 (25 atm).
[b] Cat.: A = (*R*)-BINAP/$[RhCl(cod)]_2$, B = (*R*)-BINAP/$[RhI(cod)]_2$. C = (*R*)-BINAP/$[RhBr(cod)]_2$. D = (*R*)-BINAP/$[Rh(cod)]BF_4$.
[c] Conversions and selectivities were determined by ^1H NMR.
[d] Enantiomeric excesses were determined by GLC analysis.
[e] Absolute configurations were determined based on the optical rotation values.
[f] The *ee* values varied slightly depending on the source of $[RhI(cod)]_2$.
[g] Isomeriszation was observed in 75-80% yields based on the comsumed **4a**.

results of BINAP–Ru(II)-catalyzed reactions, no isomerization products were observed. Since endo olefins **3**,**6**, and **9** were hydrogenated very slowly compared to the starting olefins and hydrogenation of **6a** catalyzed by $[RhCl(cod)]_2$/(*R*)-BINAP system afforded (*R*)-**5a** in 66% *ee*, opposite absolute configuration to that obtained with **4a**, the hydrogenation products can be considered to be obtained directly from exo olefins. For 1-methylene-2,3-benzocycloalkanes, **1**, **4**, and **7**, hydrogenation with iodide complex $[RhI(cod)]_2$ always gave higher *ee*s than those with chloride complex $[RhCl(cod)]_2$, while for acyclic olefins **10** almost the same level of enantioselectivities were obtained with the iodide and chloride complexes. Among the olefins used, **4a** gave the highest *ee* by the use of iodide (80% *ee*, entry 4). Hydrogenation of seven-membered olefin **7** and acyclic olefins **10** resulted in much lower enantioselectivities compared to five- and six-membered analogs, though *ee*s were always higher than those with BINAP–Ru(II) system. Thus, enantioselectivities were largely dependent on substrates in the hydrogenation catalyzed by BINAP–RhI, while with the BINAP–RhCl complex almost the same level of *ee*s (30–40% *ee*) were obtained for all the substrates used.

3.5. Asymmetric hydrogenation of 1-methylenetetralin (4a) catalyzed by BINAP–Rh(I) complexes under various reaction conditions

Effects of anionic ligands, solvents, and hydrogen pressure on catalytic activity and selectivity were investigated by use of **4a** and BINAP–Rh(I) complexes (Table 4).

Several catalyst systems $[RhX(cod)]_2$/(*R*)-BINAP (X = I, Br, Cl, OAc, OPh) have been tested for the hydrogenation in dichloromethane (entry 1–5). Enantioselectivities depended largely on anionic ligands X in the order of I > Br > Cl, OAc, OPh. To our knowledge, this kind of enantioselectivity dependence on anionic ligands of Rh(I) complexes has not been reported. Hydrogenation promoted by cationic species derived from $[Rh(cod)_2]BF_4$ and (*R*)-BINAP gave the products with opposite absolute configuration to those obtained with neutral Rh(I) species derived from $[RhX(cod)]_2$ and (*R*)-BINAP (entry 6).

When $[RhI(cod)]_2$/(*R*)-BINAP system was used in CH_2Cl_2 or THF, optical yields of the product **5a** were slightly dependent on the source of $[RhI(cod)]_2$ (entries 1 and 7). The addition of a small amount of Et_4NI to the catalytic system sometimes slightly improved the optical yields, which suggests that contamination of $[RhI(cod)]_2$ with a small amount of $[RhCl(cod)]_2$ and/or excess amount of iodide ion exert influence on optical yields.

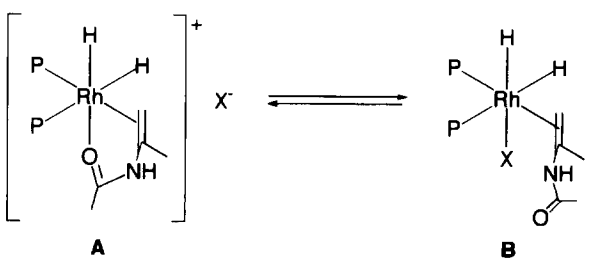
Use of solvents such as dichloromethane and THF did not cause any change in enantioselectivities in the reactions catalyzed by $[RhI(cod)]_2$/(*R*)-BINAP system (entry 1 and 7). Little solvent effect was also observed for $[RhCl(cod)]_2$/(*R*)-BINAP system. On the other hand, enantioselectivities for the hydrogenation in methanol catalyzed by $[RhI(cod)]_2$/(*R*)-BINAP system varied to a large extent, and even products with opposite absolute configuration were often obtained. This suggests that in methanol certain cationic species are acting as catalysts.

Considerable enhancement in reaction rates were observed at higher hydrogen pressure, but little hydrogen pressure effect on enantioselectivities were observed in the $[RhI(cod)]_2$/(*R*)-BINAP and $[RhCl(cod)]_2$/(*R*)-BINAP-catalyzed reactions (entries 8 and 9).

3.6. Consideration on the reaction mechanism and enantioselectivities in BINAP–Rh(I)–catalyzed asymmetric hydrogenation

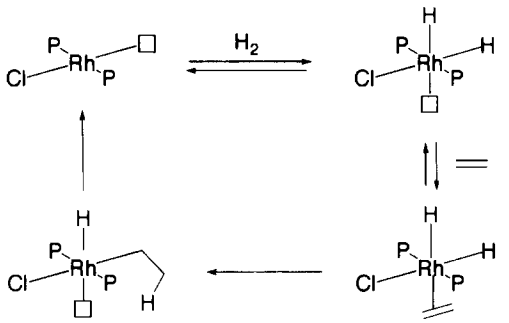
In most of the Rh(I)-catalyzed asymmetric hydrogenations, cationic complexes have been used [1], and only a few examples with neutral Rh(I) complexes have been reported. Kagan investigated asymmetric hydrogenation of enamides catalyzed by neutral DIOP–Rh(I) complexes in ethanol [17], and suggested that the key intermediate is the cationic species A based on the fact that the same enantioselectivity and the same absolute configuration were obtained even when cationic precursor was used (Scheme 2). When neutral precursor was used as catalyst in benzene, however, the key intermediate was regarded as B, because opposite sense of asymmetric induction was observed between the reactions with the neutral and the cationic precursors. In the present case, the neutral and cationic precursors gave products with opposite absolute configuration in dichloromethane, which suggests that the key intermediate in $[RhX(cod)]_2$/BINAP-catalyzed reactions is a neutral Rh(I) species.

Mechanism of asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate catalyzed by diphosphine–Rh(I) complexes have been extensively studied. According to the mechanism established by Halpern [18], the oxidative addition of hydrogen to olefin–Rh(I) complexes is the rate determining and enantioselection step. As for the mechanisms of the hydrogenation catalyzed

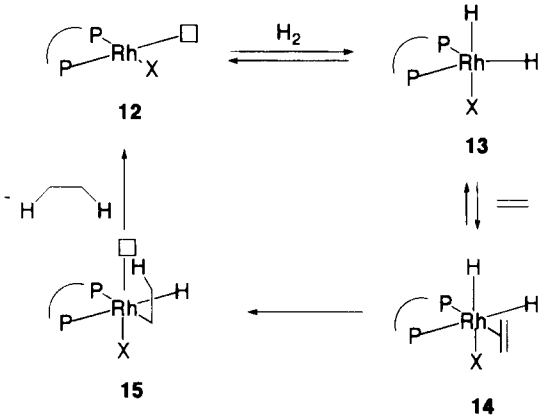


A B

Scheme 2.



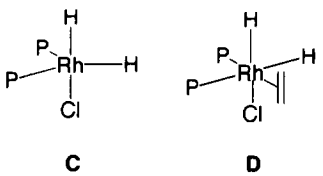
Scheme 3.



Scheme 4.

by neutral Rh(I) complexes, those with Wilkinson's catalyst ($RhCl(PPh_3)_3$) have been well studied. Halpern concluded that olefin insertion is rate determining step (Scheme 3) [19]. Intermediates involved in the catalytic cycle, though they were not detected by spectroscopic methods, had been considered to have the structures in which two phosphine ligands coordinate to the rhodium center in trans manner. Recently, however, Brown and his coworkers proposed a mechanism in which two phosphines are located in cis position in the intermediate rhodium dihydride complex C and olefin–rhodium dihydride complex D [20]. Though mechanistic aspects of the hydrogenation catalyzed by neutral rhodium(I) complexes of cis chelating diphosphines has not been well studied, Brown's mechanism can be considered to be applicable to our present hydrogenation catalyzed by neutral BINAP–Rh(I) complexes.

From the analogy of the mechanism of hydrogenation with Wilkinson's catalyst, it is conceivable that the catalytic cycle of hydrogenation catalyzed by $[RhX(cod)]_2$/BINAP system proceeds successively along oxidative addition of hydrogen, olefin coordination, insertion of olefin, and reductive elimination (Scheme 4). In the present catalysis, it might also be reasonable to assume that the olefin insertion to Rh–H bond (**14** to **15**) is rate determining step as has been already established for Wilkinson's catalysis. The above consideration is consistent with the fact that no remarkable solvent and/or hydrogen pressure effect on enantioselectivities were observed. The key intermediate **14** in the catalytic cycle (Scheme 4) has six ligands on the metal center and it is coordinatively saturated. The absence of the solvent participation in the enantiodetermining step is the reason for the absence of the *ee* dependence on solvents. The present mechanism suggests that the rate of oxidative addition of hydrogen is only related to the overall reaction rates, but not to enantioselection. The almost no olefin isomerization in substrates in the $[RhX(cod)]_2$/BINAP system can be explained in terms that the last reductive elimination step is sufficiently fast compared to the olefin insertion step.



C **D**

The profound effect of anionic ligands X in Rh(I) catalytic species on enantioselectivity might also be explained based on the above hypothesis: the rate determining step is the insertion step **14** to **15** and the enantioselection occurs at this step. This means that the enantioselectivity is determined by the activation free energy defference (the one calculated on the basis of common energy ground) of a diasteromeric pair of the transition state from **14** to **15**. It might be probable to assume that the free energy difference between the diastereomeric pair of olefin complex **14** is larger compared to that of alkyl complex **15**, since the structural difference between the corresponding diastereomers of **15** should be much smaller than that of **14**. Thus, if the transition state structure resembles **14** rather than **15**, activation free energy difference in the diastereomeric pair of the transition state would increase. Hence, the transition states resembles more to **14**, the higher enantioselectivities are to be obtained. Usually trans influence of ligands decreases in the order of I > Br > Cl. The large trans effect of iodide makes the transition state in which hydride occupies the site trans to iodide more unstable. Thus the relative stability of **14** to **15** would decrease when the iodide complex (X = I) is used compared to the chloride complex (X = Cl). Such decrease in relative thermodynamic stability of **14** would lead to the path **14** to **15** more downhill, which means that the transition state of the iodide complex resembles more to complex **14** (X = I) than the cases of the other complexes (X = Cl, OAc, OPh). Thus the highest enantioselectivity was obtained for the reactions catalyzed by the iodide complexes.

4. Conclusion

1,1-Disubstituted unfunctionalized olefins were subjected to hydrogenation using BINAP–Ru(II) and Rh(I) complexes. 1-Methyleneindan (**1a**) and 1-methylenetetralins (**4**) were hydrogenated in good enantioselectivities by the use of $Ru(OAc)_2$((R)-binap) and/or $[RhX(cod)]_2$/BINAP. In the former catalyst system, a large solvent effect was observed, while in the latter system, remarkable anionic ligand effect was observed. Based on the hypothesis that olefin insertion step is the enantioselection step and the anionic ligands on the metal center show major influence on the transition state energies, we have explained the experimental results of BINAP–Rh(I)-catalyzed asymmetric hydrogenations.

Acknowledgments

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