Research Article

Asymmetric Catalysis with Chiral Bis(oxazolinyl)phenyl Transition-metal Complexes

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Abstract: The chiral ligands, *N*,*N*,*N* and *N*,*C*,*N*-tridentate ligands {bis(oxazolinyl)pyridine [Pybox] and bis(oxazolinyl)phenyl [Phebox]}, have been reviewed to show their high potential for asymmetric catalysis. The methods for preparation of their ligands and the corresponding complexes have been described. In addition, asymmetric catalytic reactions by use of Phebox complexes are introduced concisely to show high enantioselectivities with relatively lower catalyst loading (1 mol% or lower). These tridentate and nitrogen-based ligands and their complexes are useful in modern catalytic organic synthesis.

Keywords: Bis(oxazolinyl)pyridine, Pybox, Bis(oxazolinyl)phenyl, Phebox, Transition-metal complex, Asymmetric catalytic reaction

1. Introduction

Asymmetric catalysis is very important subject to provide optically active compounds, which are often applied to production of pharmaceutical and physically functional materials. Therefore, practical and environmentally benign methods have been desired for efficiently obtaining optically active compounds, especially by using transition-metal catalysts with chiral ligands. We have so far developed the optically active ligands, *N*,*N*,*N* and *N*,*C*,*N*-tridentate ligands [bis(oxazolinyl)-pyridine, abbreviated as Pybox and bis(oxazolinyl)phenyl by Phebox], which consist of two lateral chiral oxazolines and one central nitrogen atom or carbon atom, respectively (Figure 1).[1,2] The oxazoline rings of the Pybox and Phebox ligands make the chiral reaction-site C_2-symmetric to form metal intermediates stereoselectively giving high enantioselectivity. The ligands are modulated by substituents on the oxazoline skeletons and at the remote para-position (Y) in order to control the catalysis sterically and electronically. In this article, preparation of the Phebox and Pybox ligands, preparation of the metal rhodium or ruthenium complexes, and development of asymmetric catalytic reactions are concisely described to show their potential for general use in organic synthesis.

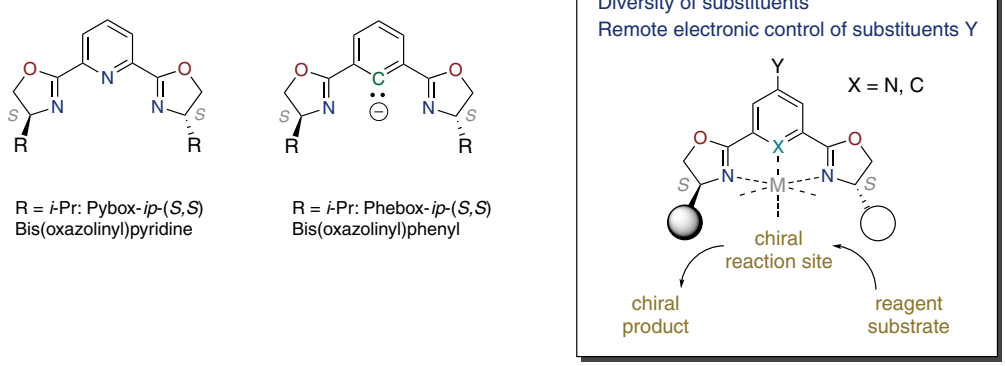


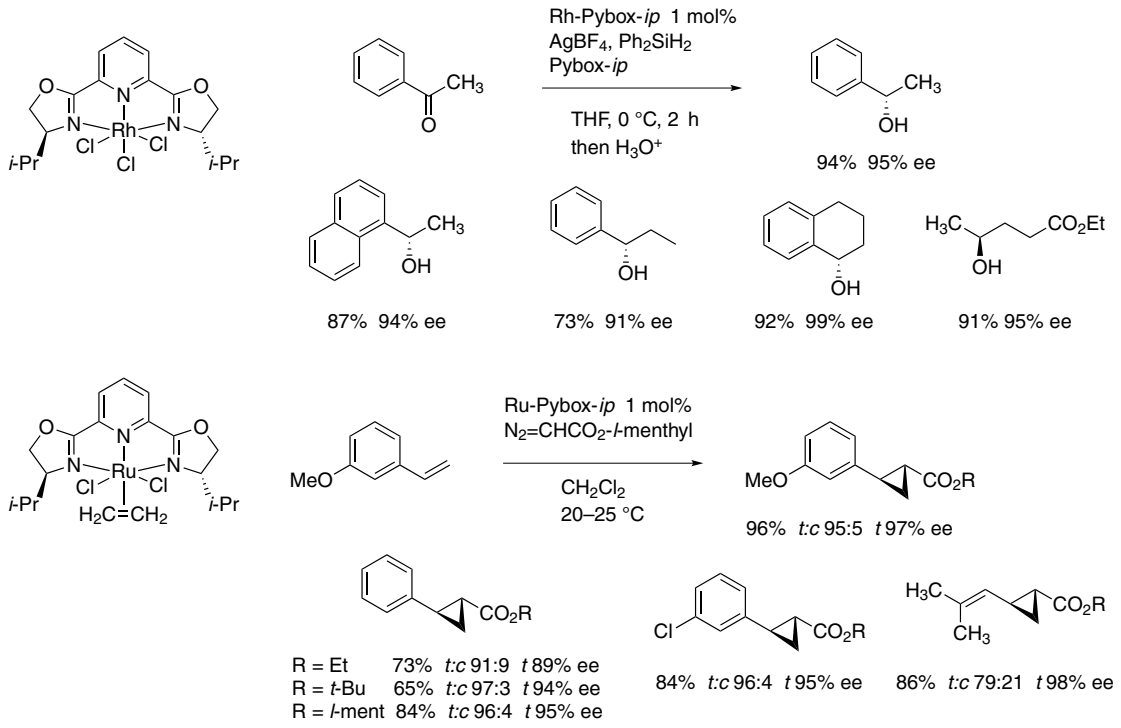
Figure 1. Chiral bis(oxazolinyl)pyridine and bis(oxazolinyl)phenyl ligands: features of the nitrogen-based tridentate coordination and the chiral reaction site

Rh-Pybox complexes catalyzed the hydrosilylation of ketones with diphenylsilane to give optically active secondary alcohols in high enantioselectivity up to 99% (Scheme 1).[3] Although Rh-Pybox trichloride itself did not show the catalytic activity for the hydrosilylation, the complex was treated with silver ion to work efficiently giving the hydrosilylation products. Next, Pybox reacts with a Ru-cymene complex under an ethylene atmosphere (1 atm) to form the corresponding ethylene complex, which exhibits high catalytic activity for asymmetric cyclopropanation of terminal alkenes with diazoacetates.[4] Fortunately, the *trans*-isomer of the cyclopropane product was obtained in a high *trans-cis* ratio up to 97% with high enantioselectivity. The mechanism was clarified by isolation of the intermediate Ru-carbene complex.[4c]

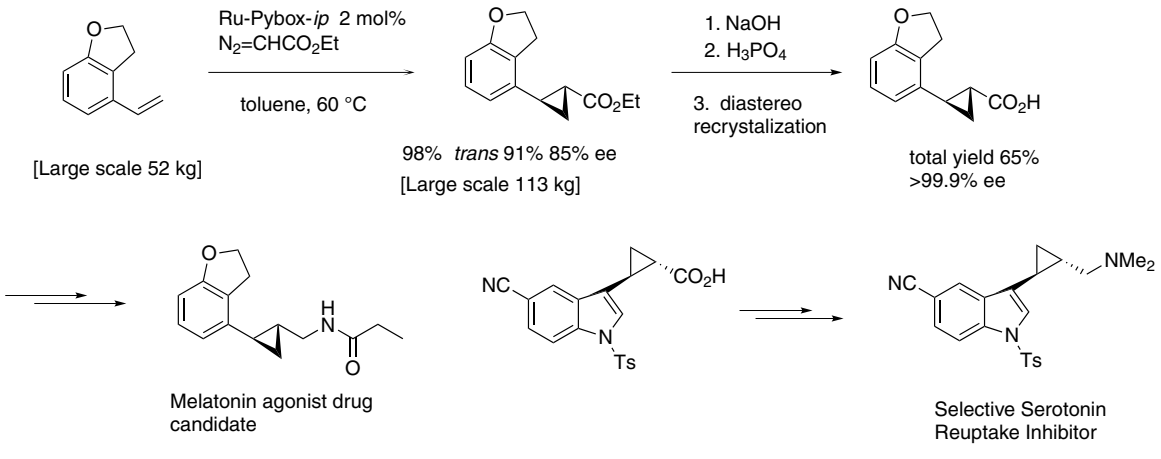
The cyclopropanation with Ru-Pybox catalyst was later applied to the large scale production of pharmaceutical intermediates in industry (Scheme 2).[5]

Ru-Pybox catalysts have been applied to other synthetic reactions, for example, asymmetric transfer hydrogenation of ketones or asymmetric C–H amination.[6,7]

Pybox ligands have been used for a number of asymmetric catalysts with a variety of metals to show high catalytic performance in enantioselective reactions. Pybox-*ip* and *ph* are now commercially available.



Scheme 1. Asymmetric hydrosilylation and cyclopropanation with Pybox catalysts

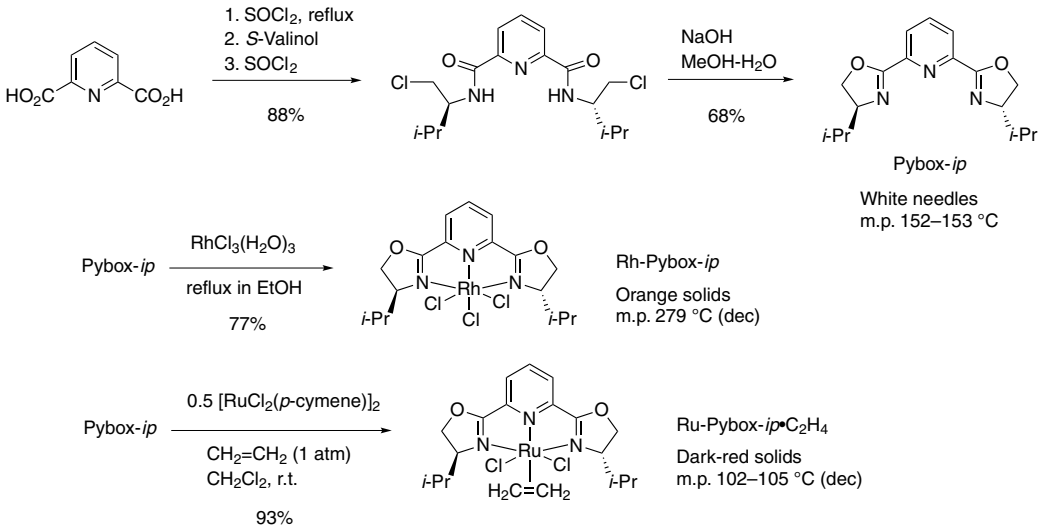


Scheme 2. Large scale production in industry

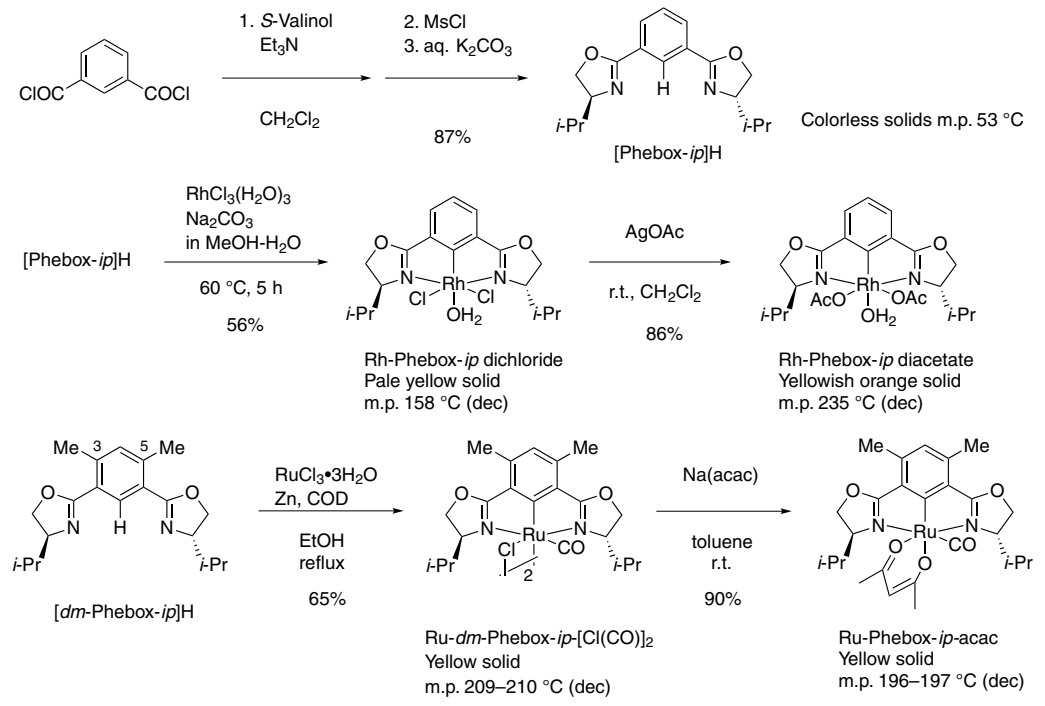
2. Preparation of Pybox and Phebox, and their Rh and Ru complexes

Preparation of Pybox starts from pyridine-2,6-dicarboxylic acid, which is treated with thionyl chloride giving the acid chloride followed by amide formation with valinol (Scheme 3).[3] Then, treatment of the amide-alcohol with thionyl chloride affords the corresponding amide-chloride, which is subsequently cyclized to form oxazoline rings by treatment with alkaline solution. Final product Pybox is purified by recrystallization to give white needles. The corresponding Rh and Ru complexes were prepared by the reaction with rhodium chloride and ruthenium-cymene complex, respectively.[3,4]

Preparation of the Phebox ligand precursor, [Phebox]H, starts from isophtharoyl dichloride, which is treated with valinol followed by the reaction with MsCl forming the sulfonate and subsequently oxazoline formation with base (Scheme 4).[8c] In order to prepare Rh-Phebox-*ip*, a mixture of [Phebox]H and rhodium trichloride at 60 °C gives the corresponding Rh-Phebox dichloro complex, which is readily converted to the Rh-Phebox•H_2O diacetate.[8a] Although the Ru-Phebox complex could not be prepared with [Phebox]H, the 3,5-dimethyl substituted ligand [*dm*-Phebox]H was found to be a good precursor for C–H bond formation.[9,10,11] The mixture of [*dm*-Phebox]H and ruthenium chloride in the presence of Zn and cycloocatadiene was heated at reflux temperature to give the corresponding Ru-Phebox complex, which was proved to be a dimeric complex. Then, the complex was converted to a monomeric form by treatment with acetylacetonate, Ru-*dm*-Phebox-*ip*-acac in good yield.[9,10,11]



Scheme 3. Preparation of Pybox and their Rh and Ru complexes



Scheme 4. Preparation of Phebox and their Rh and Ru complexes

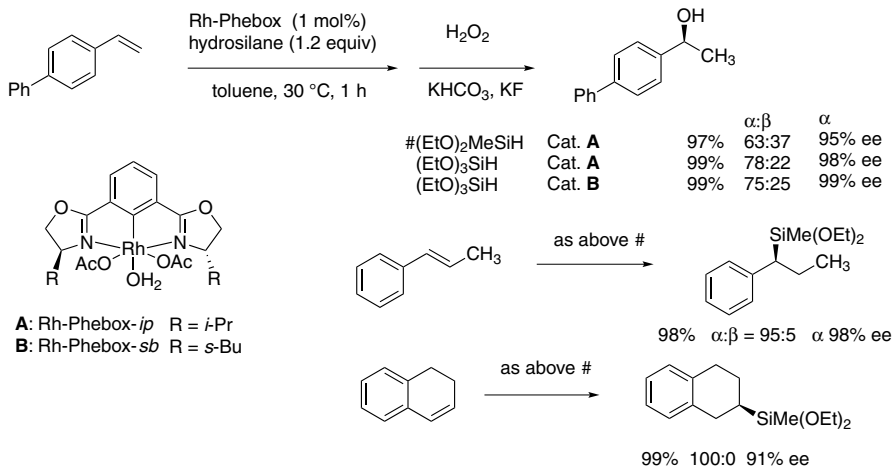
3. Asymmetric Hydrosilylation

3-1. Asymmetric Hydrosilylation of Alkenes

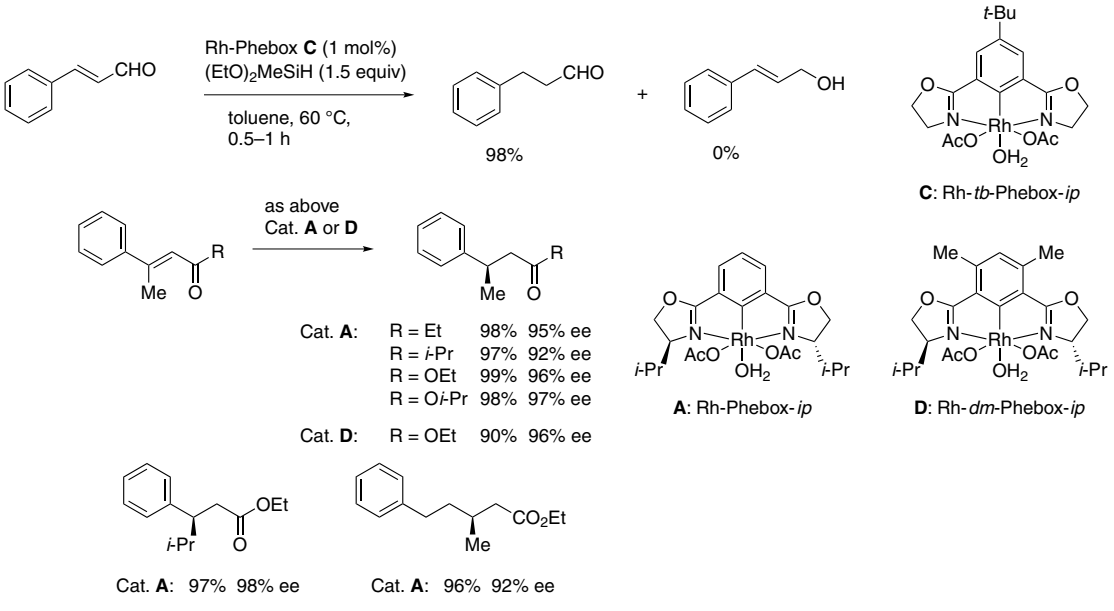
Asymmetric hydrosilylation of alkenes is a preparative method for optically active secondary alcohols via formation of silane-adducts with subsequent oxidation. Rh-Phebox-*R* diacetate complex (**A** and **B**, 1 mol%) works as a catalyst at 30 °C in 1 h efficiently to give the corresponding silane-adducts in high yields and high enantioselectivity up to 99% (Scheme 5). β-Methylstyrene was selectively converted to the α-hydroxy compound.[12)]

3-2. Asymmetric Conjugate Hydrosilylation

Rh-*tb*-Phebox-*ip* diacetate C was examined as an efficient catalyst for conjugate reduction of α,β-unsaturated aldehydes such as cinnamaldehyde to exclusively produce the corresponding conjugate reduction products in high yields (Scheme 6).[13)] When chiral catalyst Rh-Phebox-*ip* **A** was used, the 1,2-reduction product was obtained in ca. 10–30% yield. β,β-Disubstituted α,β-unsaturated ketones and esters were reduced with $(EtO)_2MeSiH$ and the acetate catalysts **A** and Rh-*dm*-Phebox-*ip* diacetate **D** to give the corresponding dihydro compounds in high yields and high enantioselectivities.[8a,14,15)]



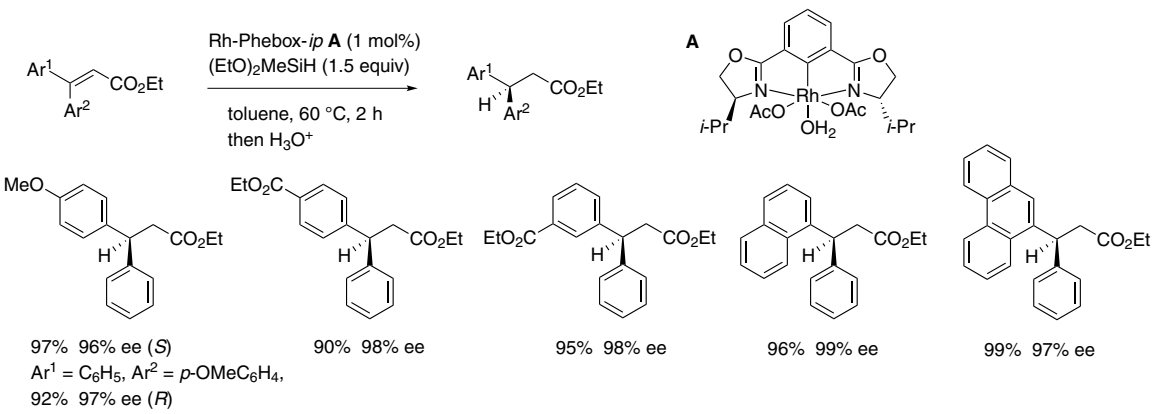
Scheme 5. Asymmetric hydrosilylation of alkenes



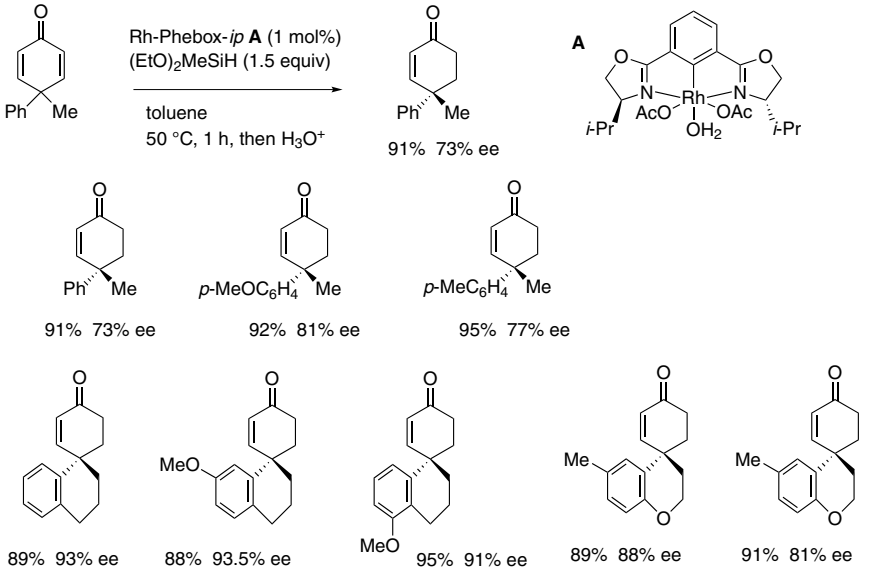
Scheme 6. Asymmetric conjugate reduction of α,β-unsaturated carbonyl compounds

β,β-Diarylacrylates ($Ar^1 \neq Ar^2$) were reduced under the same conditions of the conjugate hydrosilylation to give optically active 3,3-diarylpropanoates, which are useful precursors for various pharmaceutical compounds (Scheme 7).[16] Although it is congested around the β-carbon, the reaction took place smoothly. The reaction on a gram scale was demonstrated. The starting β,β-diarylacrylates can be prepared by a stereospecific copper catalyzed coupling reaction with arylboronic acids and substituted phenylpropiolates according to Yamamoto's procedure.[17]

The conjugate reduction with hydrosilane and the Rh-Phebox catalyst can be applied to reductive desymmetrization of γ,γ-disubstituted cyclohexadienones (Scheme 8).[18] 4-Alkyl-4-aryl-cyclohexadienones were reduced to give the corresponding γ,γ-disubstituted cylcohexenone derivatives in high yields and up to 77% ee. Spiro-carbocyclic skeletons were subjected to the reduction giving higher ees up to 93%. The reaction with Ph_2SiD_2 clarified the direction of hydride attack on the β-carbon atom (Figure 2). A plausible model of the reduction and an optimized structure, which have the hydride in the equatorial position and attacks the *Re* face of the double bond, was described.



Scheme 7. Asymmetric conjugate reduction of β,β-diarylacrylates



Scheme 8. Conjugate reduction of γ,γ-disubstituted cyclohexadienones

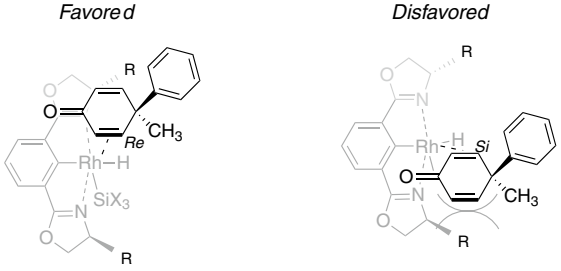


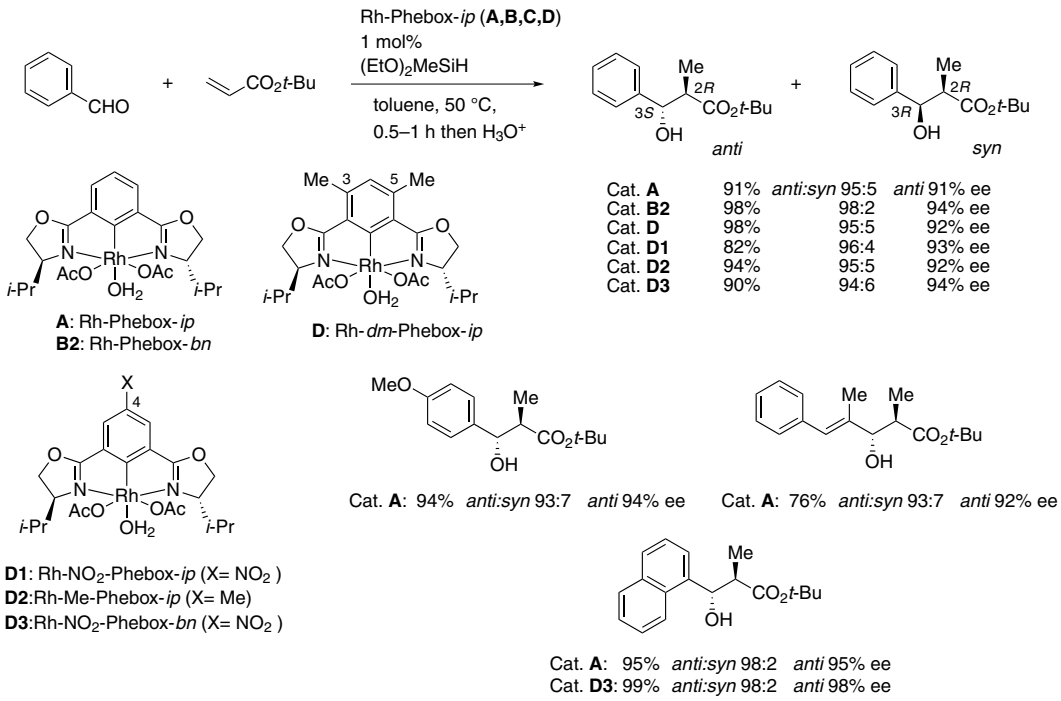
Figure 2. Plausible structure of asymmetric induction and catalytic cycle

3-3. Asymmetric Reductive Aldol Reaction

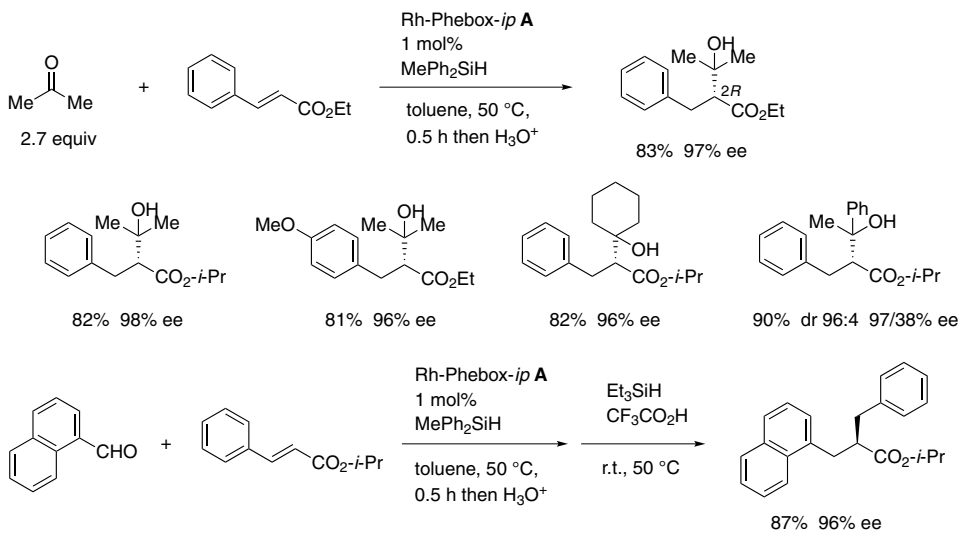
Rh-Phebox diacetate complexes can work as catalysts for the conjugate reduction of α,β-unsaturated carbonyl compounds with hydrosilanes. On the basis of this fact, it was thought that the intermediate rhodium enolate species might be directly trapped with aldehyde to give the aldol coupling product. Into a mixture of benzaldehyde and acrylate, the catalyst Rh-Phebox **B** and hydrosilane were added to start the reaction, which gave the aldol coupling product, propionate derivative, in high yields with high ees for the *anti* isomer and high *anti*-selectivity (Scheme 9).[19] 4-Substituted catalysts and 3,5-dimethyl catalyst **D** work as catalysts giving almost the same yields and up to 98% ee.[15,20]

The conjugate reduction of cinnamates and successive aldol reaction with acetone gives the intermolecular aldol coupling products in high ee up to 98% (Scheme 10).[21] $PhMe_2SiH$ is the best choice of hydrosilane. After the aldol reaction, subsequent dehydroxylation of the β-hydroxy group resulted in formation of α-chiral dihydrocinnamates in high yields and kept the enantioselectivity with 90% ee.[22a] As an extension of the reductive aldol reactions, there is the Felkin-Anh selectivity in the reaction of 2-phenylpropionaldehyde and unsaturated esters.[22b]

Rh-Phebox diacetate complex catalyzed the reductive Mannich-type coupling of acrylates and aldimines to form selectively the *anti*-product, but asymmetric induction could not be observed.[23]



Scheme 9. Asymmetric reductive aldol reaction



Scheme 10. Asymmetric reductive aldol reaction of cinnamates and ketones (upper) and subsequent dehydroxylation (bottom).

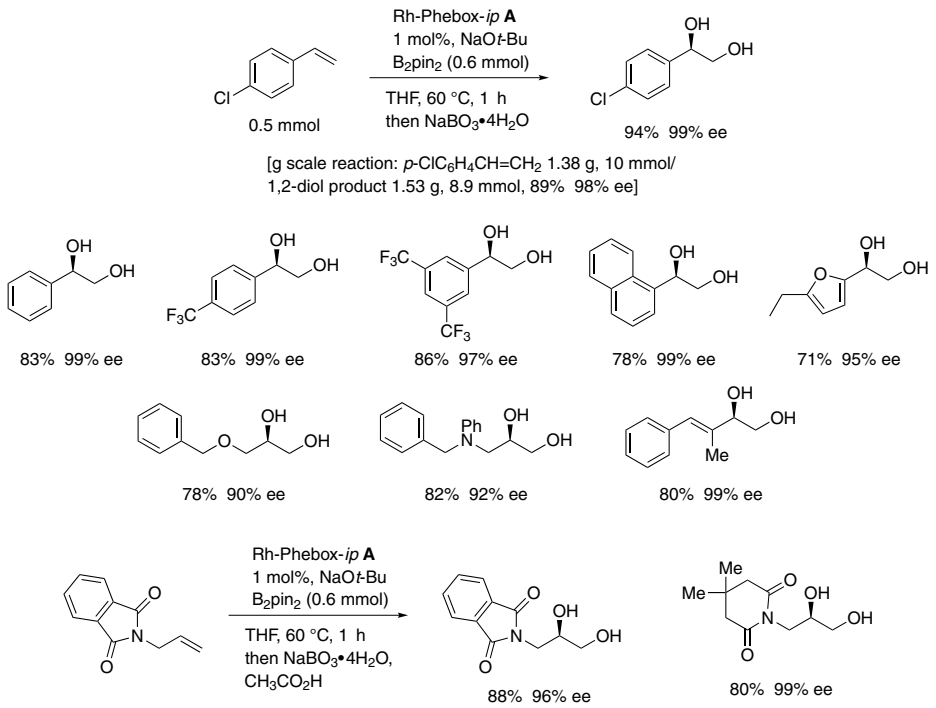
4. Asymmetric Boration

4-1. Asymmetric Diboration of Alkenes

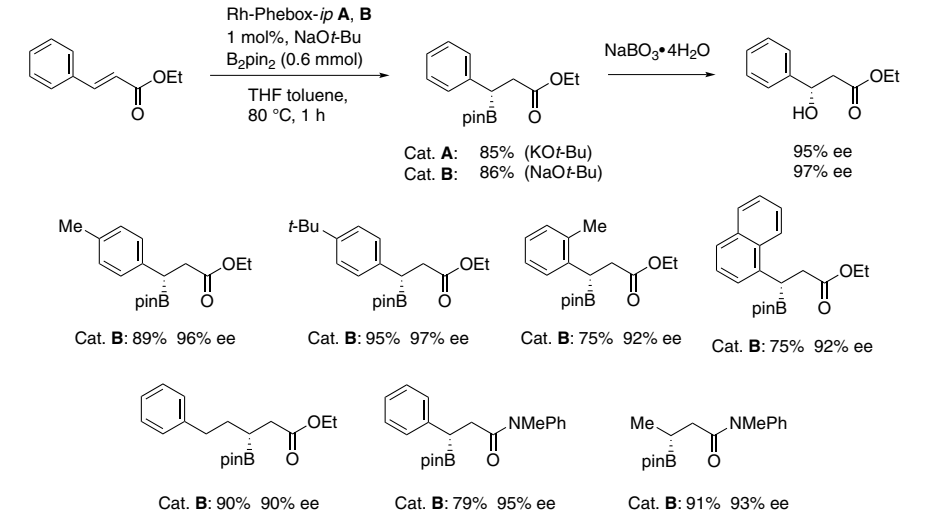
Rh-Phebox diacetate complex **A** is capable of catalyzing the asymmetric diboration of terminal alkenes followed by oxidation to form the corresponding optically active 1,2-diols in high ee (Scheme 11).[24] The diboration reaction was accelerated by addition of a small amount of bases such as NaO*t*-Bu or KO*t*-Bu. The mixture of alkene and bis(pinacolato)-diboron (B_2pin_2) was treated with 1 mol% of the catalyst to give the 1,2-diborated product, which was converted to 1,2-diol by oxidation with aqueous sodium perborate. A variety of terminal alkenes such as ethers, *tert*-amines, dienes can be subjected to the reaction. *N*-Acyl protected allylamines also can be used as substrates to give the diols via the diboration reaction (Scheme 11, bottom).[25] The products are optically active 3-amino-1,2-diols, the skeletons of which are often included in many pharmaceutical compounds or synthetic intermediates.

4-2. Asymmetric Conjugate Boration of α,β-Unsaturated Carbonyl Compounds

Rh-Phebox-*ip* diacetate **A** can catalyze the conjugate boration of α,β-unsaturated carbonyl compounds to produce the β-boryl propanoates in high yields (Scheme 12).[26] Subsequent oxidation of the boryl products resulted in formation of β-hydroxy propanoates and related amides with high ee.



Scheme 11. Asymmetric diboration of alkenes



Scheme 12. Asymmetric conjugate boration of α,β-unsaturated esters and amides

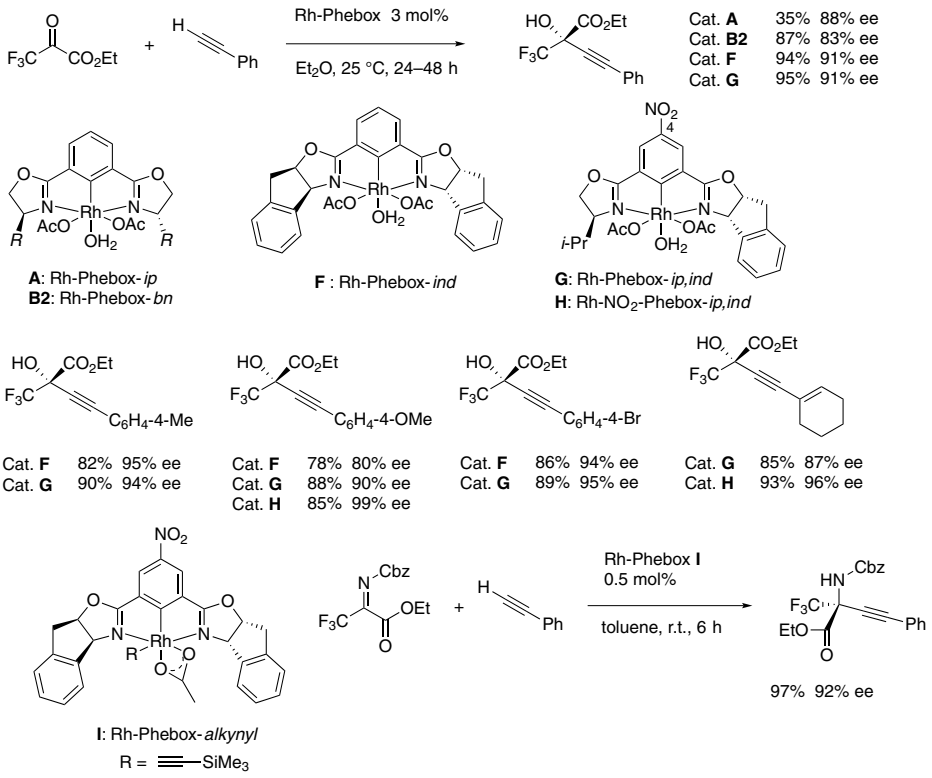
5. Asymmetric Alkynylation

5-1. Asymmetric Alkynylation of α-Ketoesters

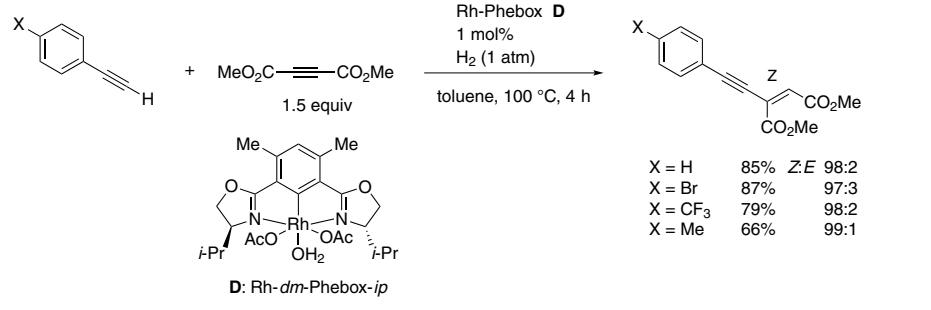
Ohshima and Mashima *et al*. reported that various Rh-Phebox diacetate complexes can be synthesized and catalyze asymmetric alkynylation of α-ketoesters and aryl-substituted or alkyl-substituted terminal alkynes to give functionalized propargylic alcohols in good yields with high ee up to 99% (Scheme 13).[27a] Morimoto and Ohshima extended the reaction using alkynyl complex **I** and found the highly reactive catalyst which was applied to alkynylation of ketiminoesters.[27b]

5-2. Cross-coupling of Alkynes

The cross coupling reaction of terminal alkynes and dimethyl acetylenedicarboxylate proceeded with Rh-Phebox catalyst **D** under hydrogen atmosphere (1 atm) at 100 °C for 4 h to give the corresponding coupling product, the enyne derivatives, in high yield and high *Z* ratio (Scheme 14).[28] The acetylide complex was isolated and analyzed. C–H Bond activation by deprotonation from the terminal alkyne with acetate ligand as a base forms the corresponding acetylide complex followed by insertion of the alkyne and then elimination of the enyne product.



Scheme 13. Asymmetric alkynylation of α-ketoesters



Scheme 14. Cross-coupling of alkynes

6. Other C–C Bond Formation Reactions with Rh-Phebox Catalysts

Rh-Phebox complexes also catalyzed several C–C bond formation reactions as follows: asymmetric direct aldol reaction of benzaldehyde with cylcohexanone and cyclohexenone, respectively,[29,30] asymmetric allylation reaction of benzaldehyde with allyl- or methallyl-tributyltin,[31] asymmetric Michael addition of α-cyanopropionates to acrolein,[32] asymmetric aldol-type condensation of isocyanide group on Rh-Pheobx,[33] asymmetric hetero Diels–Alder reaction of Danishefsky's dienes and glyoxylates.[34] The vacant site of Rh-Phebox intermediate acts as a Lewis acid catalyst for those C–C bond formation reactions.

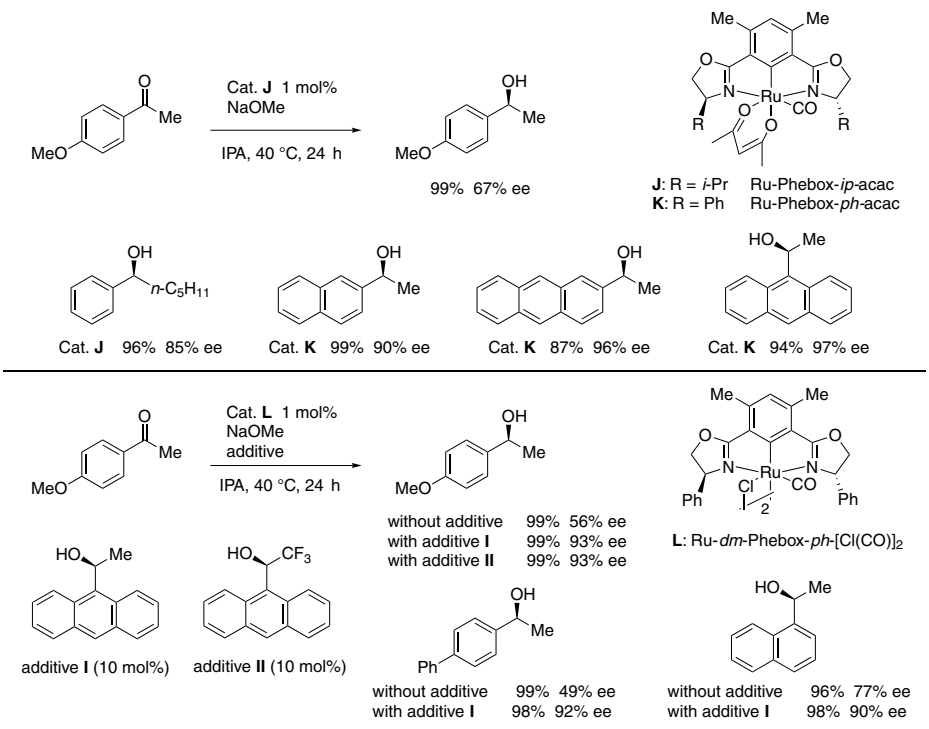
7. Asymmetric Catalysis with Ru-Phebox Complexes

7-1. Asymmetric Hydrogenation of Ketones

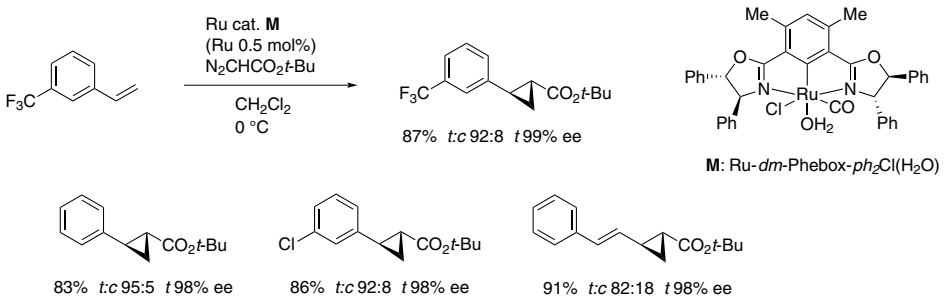
Ru-Phebox complexes **J** and **K** act as catalysts for asymmetric hydrogenation of ketones to give optically active secondary alcohols (Scheme 15).[35] Relatively bulky ketones were reduced with high enantioselectivities of up to 97% ee. Aryl-substituted acetophenones were reduced in the middle range of ee.[36] It was interesting in that using the catalyst **O**, addition of optically active alcohols, such as additives **I** or **II** (10 mol%), enhanced ee over 90%. The bulky anthracenyl alcohol improves the selectivity due to coordination to the Ru atom.

7-2. Asymmetric Cyclopropanation

Mono nuclear Ru-Phebox complex **M** was prepared by C–H bond activation with magnesium as a reducing agent in ethanol (Scheme 16).[10] The complex **M** catalyzed the cyclopropanation of styrene derivatives to form the corresponding *trans*-cyclopropanes in high yields.



Scheme 15. Asymmetric hydrogenation of ketones with Ru-Phebox catalysts (upper): enhancement of ee by alcohol additive (bottom)



Scheme 16. Asymmetric cyclopropanation

7-3. Asymmetric Alkynylation of Aldehydes

Ru-Phebox complexes catalyzed asymmetric alkynylation of aldehydes with terminal alkynes to produce optically active propargylic alcohols with high ee up to 93% (Scheme 17).[11] The acetate complex did not require base additives such as NaOAc to give the alcohols in a similar yield and ee. As an acceptor, α,β-unsaturated carbonyl compounds were used to give Michael addition derivatives in high yields.[37]

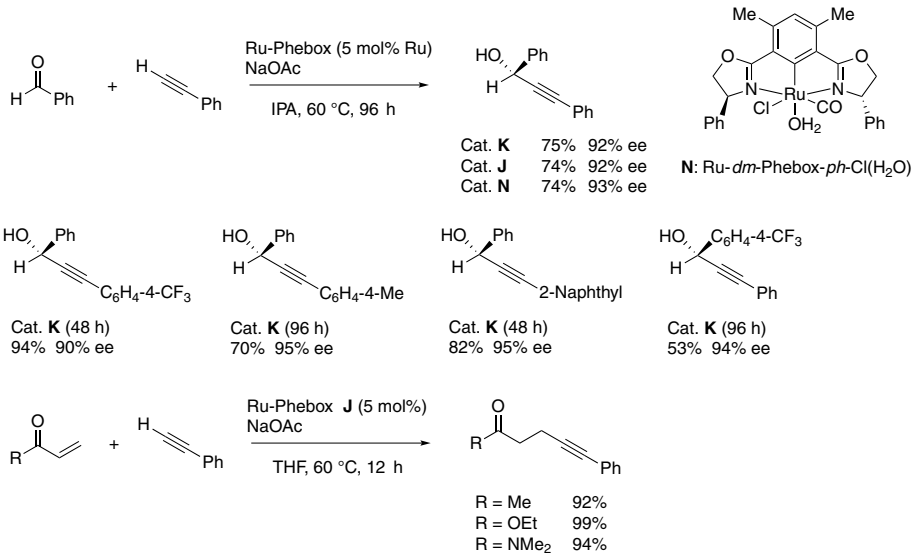
8. Asymmetric Catalysis with Ir-Phebox Complexes

8-1. C–H Activation on Ir-Phebox Complexes

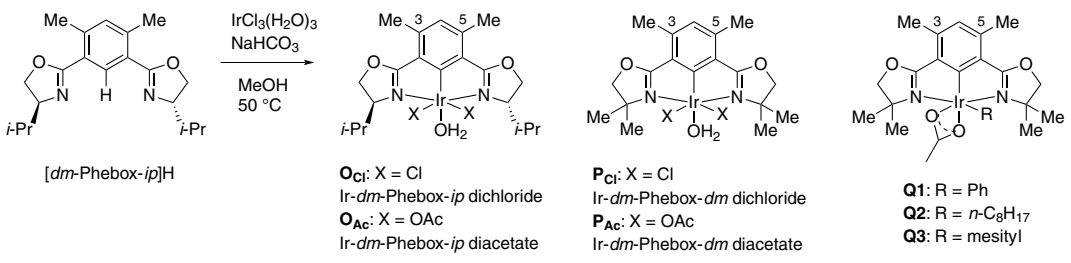
A series of Ir-Phebox dichloro complexes was prepared by the C–H bond activation reaction with [*dm*-Phebox]H or [4-*tb*-Phebox]H and iridium salts, followed by treatment with AgOAc to give the corresponding acetates (Scheme 18).[15,37,38,39,40] The chiral Ir-Phebox **O** catalyzed asymmetric conjugate reduction and asymmetric reductive aldol reaction to attain high enantioselectivity.[15] Our group, the Goldberg group, and the Goldman group reported that the acetate complex $\mathbf{P}_{Ac}$ reacts with benzene, *n*-octane, or mesitylene to form phenyl, octyl or mesityl complexes (R) by C–H activation on the iridium atom, respectively.[37,38,39] Boration of arenes was realized with B_2pin_2 and Ir-Phebox **O**.[15]

8-2. Asymmetric C–H Insertion Reaction

Musaev, Davies, and Blakey group reported Ir-Phebox complexes **R** and **S** catalyzed the asymmetric C–H insertion reaction with cyclohexadienes and phenyldiazoacetate in high ee up to 99% (Scheme 19).[40] The products can be converted to optically active α,α-diarylacetates. They also proposed the reaction pathway and calculated the stereoisomer of the reactive carbene complexes.



Scheme 17. Asymmetric alkynylation of aldehydes and conjugate addition



Scheme 18. Ir-Phebox complexes and the related reactions

9. Phebox Complexes of Other Metals

Phebox complexes of other metals, for examples, iron,[41] cobalt,[42] palladium,[43] and platinum,[44] were prepared by oxidative addition reactions of Phebox-X (X = halogen) (Figure 3). However, asymmetric catalysis with the complexes has not yet been explored extensively. Further applications are strongly expected.

For other metal complexes, for examples, van Koten *et al*. reported synthesis of Phebox-Li and Phebox-Au complexes, which were successively used to prepare the corresponding Ti, V, Cr, Zr, Hf, Nb complexes.[45] Xu and Lu *et al*. reported Phebox-Lu complex, which was applied to the regioselective polymerization of isoprene.[46]

10. Summary

Asymmetric catalysis with bis(oxazolinyl)phenyl ligands and their transition metal complexes, mainly rhodium and ruthenium complexes, has been developed to attain high enantioselectivities with relatively lower catalyst loading (1 mol% or lower). Phebox ligands and their complexes are readily prepared and have high potential for organic reactions including asymmetric reactions and polymerizations. These tridentate and nitrogen-based ligands and the complexes are useful in modern catalytic organic synthesis.

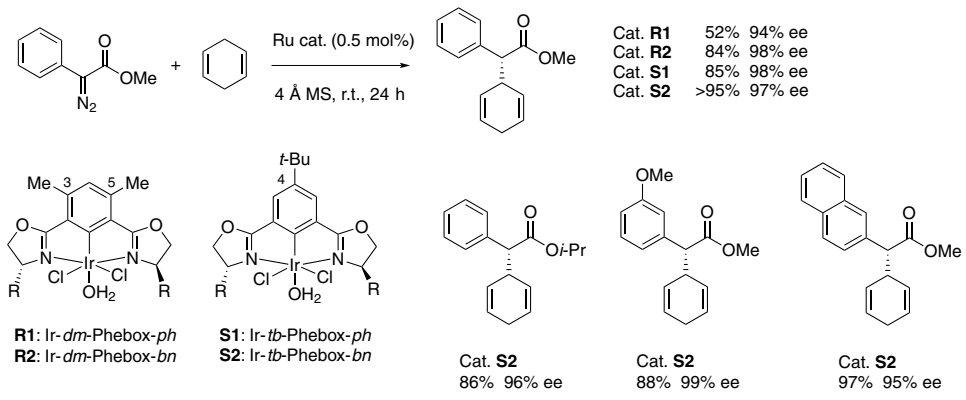
Procedures of Asymmetric Conjugate Reduction and Asymmetric 1,2-Diol Synthesis

Scheme 7. The preparation of (*S*)-ethyl 3-(naphthalen-1-yl)-3-phenylpropanoate[16]

Diethoxymethylsilane (202 mg, 1.5 mmol) was added at 60 °C to a solution of (*E*)-ethyl 3-(naphthalen-1-yl)-3-phenylacrylate (302 mg, 1.0 mmol) and Rh-Phebox-*ip* diacetate **A** (5.4 mg, 0.010 mmol) in toluene (2.0 mL). The mixture was stirred for 2 h. At 0 °C, THF (1 mL) , MeOH (1 mL), and hydrochloric acid (1 mL, 1 *N*) were added, and the mixture was stirred for 1 h. The mixture was then extracted with ethyl acetate, and was washed with aq. sodium bicarbonate and saturated brine. The organic layer was dried over magnesium sulfate, and then concentrated to give a residual oil, which was purified by silica gel column chromatography with ethyl acetate/hexane to give the propanoate (293 mg, 0.961 mmol, 96% yield) as a colorless oil: $[\alpha]_D^{24}$ = +16.8 (c 1.01, $CHCl_3$); Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (97:3, 1 mL/min), 27 °C, retention time = 9.7 min for *R* (minor) and 17.5 min (major) for *S*, 99% ee; HRMS-FAB (m/z, M = $C_{21}H_{20}O_2$): found: 327.1365 $[M+Na]^+$, calcd: 327.1361.

Scheme 11. The preparation of (*R*)-1-(4-chlorophenyl)-ethane-1,2-diol from 4-chlorostyrene[24]

Rh-Phebox-*ip* diacetate **A** (2.7 mg, 0.0050 mmol), bis(pinacolato)diboron (152 mg, 0.60 mmol), and NaO*t*-Bu (2.5 mg, 0.026 mmol), were placed in a flask. 4-Chlorostyrene (69.3 mg, 0.50 mmol) and THF (1.0 mL) were added under an argon atmosphere. The mixture was stirred at 60 °C for 1 h. At room temperature, $NaBO_3$•$4H_2O$ (385 mg, 2.5 mmol), THF (5 mL), and water (2.5 mL) were added to the reaction mixture, which was stirred for 1 h. The mixture was extracted with ethyl acetate (2 mLx5) and concentrated to give a crude product, which was purified by silica gel column chromatography with ethyl acetate/hexane as eluent. The diol was obtained in 94% yield (80.9 mg, 0.469 mmol) as a white solid, m.p. 84–86 °C: $[\alpha]_D^{22}$ –57.4 (c 1.0, $CHCl_3$); Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (98:2, 1.5 mL/min): retention time = 46.0 min (major), 52.8 min (minor), 99.5% ee; Elemental Anal: calcd. (%) for $C_8H_9ClO_2$: C 55.67; H 5.26. Found: C 55.94; H 5.34.



Scheme 19. Ir-Phebox catalyzed asymmetric C–H insertion reaction

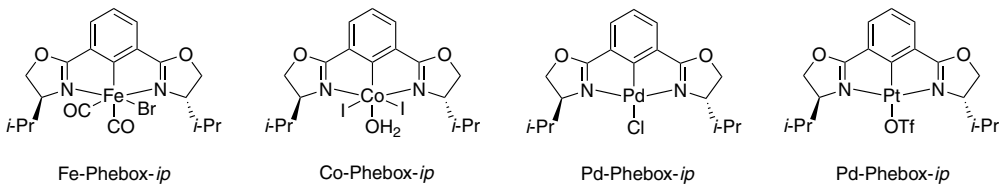


Figure 3. Phebox complexes of other metals

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Hisao Nishiyama was born in 1951 in Mie, Japan. He received his BEng and MSci under the direction of Professor Yoshio Ishii from Nagoya University in 1973–1975, respectively. He received his Dr Sci. from Tokyo Institute of Technology in 1980. He worked at Research Centers of Toray Industries Inc. in 1975–1980. Since 1980, he worked at Toyohashi University of Technology, where he was associate professor from 1985 to 1996 and full professor from 1996 to 2002. In September 2002, he moved to Nagoya University as a professor. His main research interests are homogeneous catalysis, asymmetric catalysis with nitrogen-based ligands and late transition metals, and organometallic chemistry. He received the Progressive Award of Young Chemists from the Chemical Society of Japan in 1984 and the Award of Organic Synthetic Chemistry of Japan in 1996 and 2015.
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TCI Related Products

Ligands for Pybox and Phebox

B2217	(*R*,*R*)-2,6-Bis(4-isopropyl-2-oxazolin-2-yl)pyridine		250mg	1g	5g
B2218	(*S*,*S*)-2,6-Bis(4-isopropyl-2-oxazolin-2-yl)pyridine			500mg	5g
B4196	(*S*,*S*)-4,6-Bis(4-isopropyl-2-oxazolin-2-yl)-*m*-xylene				20mg

Rh-Phebox Complex

B4195	Bis(acetato)aqua[(*S*,*S*)-4,6-bis(4-isopropyl-2-oxazolin-2-yl)-*m*-xylene]rhodium				10mg

Major Reagents for the Synthesis of Ligands and Complexes

P0554	2,6-Pyridinedicarboxylic Acid		25g	100g	500g
I0159	Isophthaloyl Chloride			25g	500g
D4377	4,6-Dimethylisophthalic Acid			200mg	1g
V0058	L-Valinol (*S*-Valinol in the article)			5g	25g
D2751	Dichloro(*p*-cymene)ruthenium(II) Dimer			1g	5g

Aldehydes

C0352	*trans*-Cinnamaldehyde			25mL	500mL
B2379	Benzaldehyde				500g

Alkoxysilanes

D2403	Diethoxymethylsilane				25mL
T1040	Triethoxysilane		25mL	100mL	500mL

Alkynes

A0090	Dimethyl Acetylenedicarboxylate		25mL	100mL	500mL
B3701	1-Bromo-4-ethynylbenzene			1g	5g
E0196	Ethynylbenzene		25mL	100mL	500mL
E0626	1-Ethynyl-4-(trifluoromethyl)benzene			1g	5g
E0655	4-Ethynyltoluene			5g	25g

Boron Compounds

B1964	Bis(pinacolato)diboron (= B_2pin_2)	1g	5g	25g	100g
S0446	Silver Tetrafluoroborate			5g	25g

Esters

A1389	*tert*-Butyl Acrylate (stabilized with MEHQ)			25mL	500mL
A0143	Ethyl Acrylate (stabilized with MEHQ)			25mL	500mL
C0359	Ethyl Cinnamate		25g	100g	500g
T0432	Ethyl Trifluoroacetate		25g	100g	500g

Others

V0054	4-Vinylbiphenyl			1g	5g
C0290	4-Chlorostyrene (stabilized with TBC)			10mL	25mL
C0468	1,4-Cyclohexadiene (stabilized with BHT)			10mL	25mL
D1091	*N*,*N*-Dimethylacrylamide (stabilized with MEHQ)			25g	500g
M0105	4'-Methoxyacetophenone			25g	500g
M0460	Methyl Vinyl Ketone (stabilized with HQ + AcOH)		25mL	100mL	500mL
S0450	Sodium *tert*-Butoxide		25g	100g	500g
S0887	Sodium Perborate Tetrahydrate			25g	500g
T1520	(*R*)-(-)-2,2,2-Trifluoro-1-(9-anthryl)ethanol			100mg	1g
T3354	3-(Trifluoromethyl)styrene (stabilized with HQ)			1g	5g