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Enantioselective ruthenium-mediated hydrogenation: developments and applications

Virginie Ratovelomanana-Vidal, Jean-Pierre Genêt *

Laboratoire de Synthèse Sélective Organique et Produits Naturels associé au CNRS (UMR 7573), 11 rue P. et M Curie, 75231 Paris Cedex 5, France

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Abstract

A general preparation of chiral ruthenium(II) catalysts and the homogeneous enantioselective hydrogenation of prochiral olefins and keto groups are presented. Some applications to the synthesis of biologically active compounds are reported.

Keywords: Ruthenium; Catalysts; Hydrogenation; Dynamic kinetic resolution

1. Introduction

Asymmetric catalysis [1–12] is now an important part in drug design and development. A great number of optically active compounds are synthesized using asymmetric catalytic routes and among them asymmetric hydrogenation provides a practical access to chiral building blocks of biological interest. One concern of the synthetic organic chemist is to develop new asymmetric catalytic methodologies using transition metal complexes. For a few years, we have been interested in homogeneous enantioselective hydrogenation using chiral Ru(II) catalysts. We have developed a general synthesis of chiral Ru(II) catalysts compatible with a wide variety of chiral ligands. We report herein an overview of the utility of this method for highly enantioselective hydrogenation of olefins and functionalized keto groups as well as some applications to the synthesis of pharmaceutical intermediates and biologically active compound.

* Corresponding author. Fax: +33 44071062; e-mail: genet@ext.jussieu.fr

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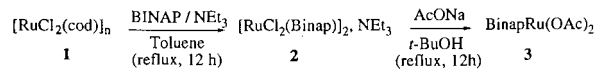
2. Transition metal catalysts

2.1. Chiral ligands

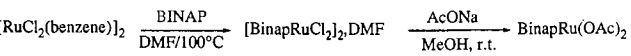
In the 1970's, Kagan, Knowles and others discovered efficient ligands for Rh-mediated hydrogenation of dehydroaminoacids. Since this time, a great number of diphosphines have been prepared and used as chiral ligands [13,14] for homogeneous catalysis. The most typical ligands are chiral bidentate diphosphines such as 1,2 and 1,4 diphosphines which can be classified related to their structures: those bearing chirality on the carbon skeleton (CHIRAPHOS, CBD, PROPHOS, DIOP, Me or Et-DuPHOS, *i-Pr* BPE …) including atropoisomeric type (BINAP, MeO-BIPHEP, BIPHEMP, BICHEP …) and on the phosphorus center (DIPAMP, BIPNOR [15]). Chiral bidentate ligands such as bisaminophosphinites (BPPM, CAP) and ferrocenyl phosphines (BPPFA, BPPFOH …) have also been developed. Among these chiral diphosphines, only few useful 1,3-substituted diphosphines have been prepared (SKEWPHOS). Some diphosphines used in asymmetric catalysis are shown in Fig. 1.

2.2. Chiral ruthenium(II) catalysts

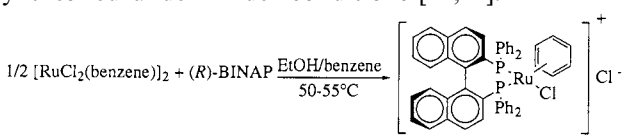
The first chiral ruthenium catalyst $Ru_2Diop_3Cl_4$ prepared from $RuCl_2(PPh_3)_3$ and excess of DIOP was discovered in 1975 by James [16]. Later, Ikariya reported the synthesis of a dinuclear catalyst $Ru_2Cl_4Binap_2$, NEt_3 **2** [17] obtained from $[RuCl_2(cod)]_n$ with (*R*) or (*S*)-BINAP and triethylamine in toluene at 110°C. This complex was used to prepare the first mononuclear catalyst $BinapRu(OAc)_2$ **3** [18,19] synthesized by Noyori in 1986.



This synthesis was recently improved and the BINAPRu(II) dicarboxylate complex was obtained more conveniently by sequential treatment of $[RuCl_2(benzene)_2]_2$ with BINAP in DMF at 100°C followed by reaction of sodium acetate at room temperature [20].

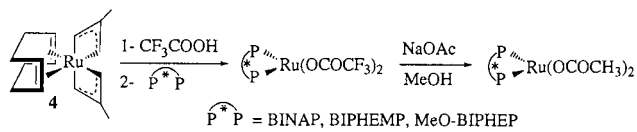


Some other BinapRu(II) catalysts have also been synthesized under milder conditions [21,22].



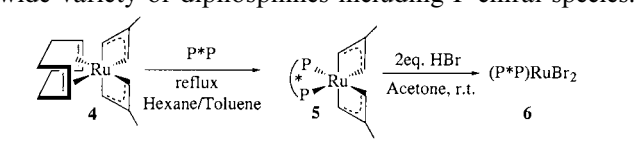
The BINAPRu(II) complexes were highly efficient catalysts for the asymmetric hydrogenation of a large variety of prochiral substrates [23] including olefins, carbonyl groups and imines.

Heiser and coworkers [24] described the synthesis of atropoisomeric diphosphine ruthenium dicarboxylato complexes $P^*PRu(OCOR)_2$ ($R = CF_3$ and CH_3) using the $(COD)Ru(\eta^3\text{-}(CH_2)_2CCH_3)_2$ as starting material.



Some other syntheses of chiral Ru(II) catalysts containing atropoisomeric diphosphines have also been described [25].

We have focused our efforts on the development of a new general and practical route to ruthenium complexes of any kind of diphosphines [26–28]. Our investigations afforded the first general synthesis of chiral Ru(II) catalysts, **5** and **6**, prepared from the commercially available $(COD)Ru(\eta^3\text{-}(CH_2)_2CCH_3)_2$ **4** and a wide variety of diphosphines including P-chiral species.



P*P=BINAP, BIPHEMP, CHIRAPHOS, DIOP, PROPHOS, DIPAMP, SKEWPHOS ...

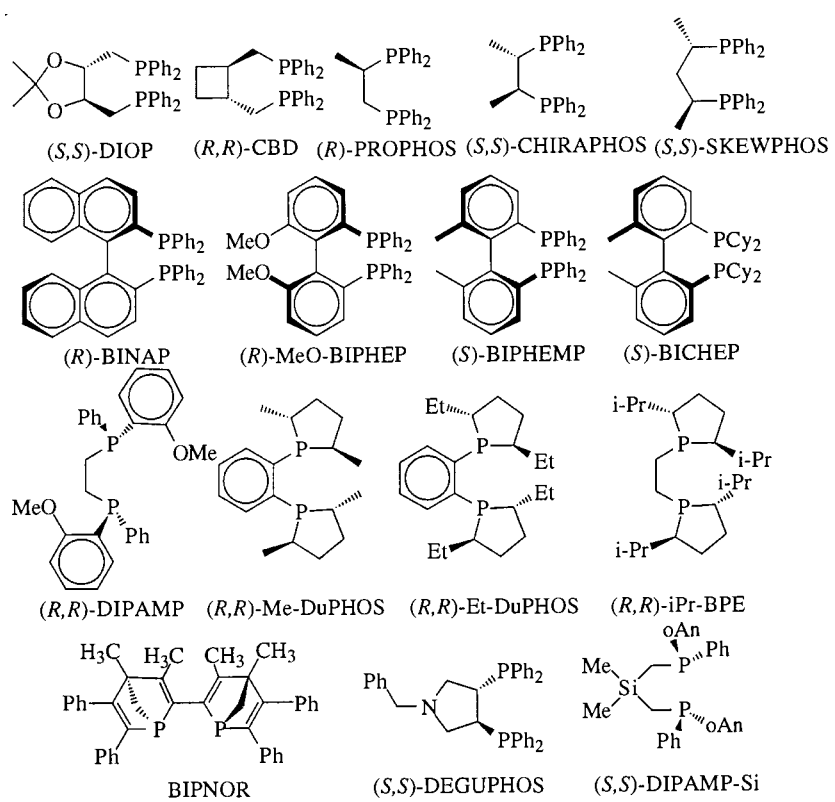
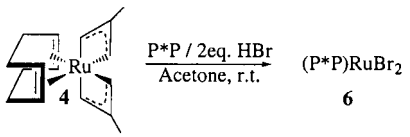


Fig. 1. Some representative diphosphines.

This general method was recently improved and the Ru-catalysts **6** were synthesized in situ [29] under milder conditions in a one step reaction from (COD)Ru(η^3-$(CH_2)_2CCH_3)_2$ **4**.



P*P= BINAP, MeO-BIPHEP, Me-DuPHOS, SKEWPHOS ...

A large variety of chiral Ru(II) catalysts have been prepared using this methodology, including the $DuPHOSRuBr_2$ [29] and $SkewphosRuBr_2$ complexes [30]

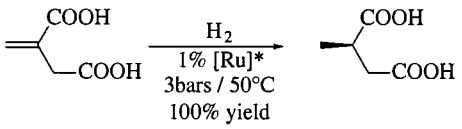
3. Homogeneous asymmetric hydrogenation

3.1. Asymmetric hydrogenation of olefins [29]

The Ru-catalyzed hydrogenation of a number of α,β-unsaturated acids was considered. The hydrogenation of tiglic acid is discussed hereafter as a representative example. The reaction was best carried out in methanol under 3–4 bars of hydrogen pressure. The different chiral Ru-catalysts performed enantioselective hydrogenation with degrees of selectivities which depended on the ligands. The best results were obtained with atropoisomeric ligands i.e. BINAP and MeO–BIPHEP. The C_2 symmetric bisphospholanobenzene Me–DuPHOS and CBD gave good selectivities (80 and 70% e.e.) while DIOP and DIPAMP were less efficient (51 and 25% e.e., respectively) (Table 1).

3.1.1. Asymmetric hydrogenation of itaconic acid

Hydrogenation of itaconic acid was carried out at 50°C under 3 bars of hydrogen pressure. The in situ (*R*)-$BinapRuBr_2$ and (*R*)-MeO–$BiphepRuBr_2$ afforded (*R*)-methyl succinic acid with very high enantioselectivity.

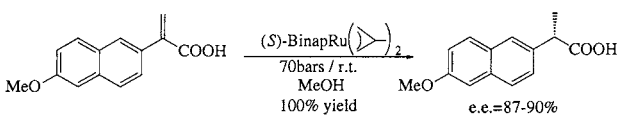


in situ (*R*)-$BinapRuBr_2$ 3 bars/50°C e.e.=98%

in situ (*R*)-MeO-$BiphepRuBr_2$ 3 bars/50°C e.e.=95%

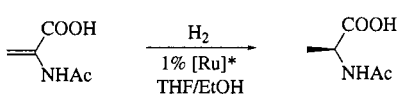
3.1.2. Asymmetric hydrogenation of Naproxen precursor

An application of this methodology to the synthesis of the antiinflammatory drug Naproxen was achieved with good selectivity (87–90%).



3.1.3. Asymmetric hydrogenation of N-acetyl dehydroaminoacids

In a similar manner, α-aminoacids derivatives were easily obtained from the corresponding amido substituted olefins in good yields and enantiomeric excesses.



(*S*)-$BinapRuBr_2$ 20bars / 25°C Yield=70% / e.e.=75%

(*S*)-$BiphempRuBr_2$ 20bars / 25°C Yield=80% / e.e.=77%

3.1.4. Asymmetric hydrogenation of allylic alcohol

The hydrogenation of an allylic alcohol, possessing a chiral azetidinone unit was achieved diastereoselectively and in good yield by using the in situ (*R*)-MeO–$BiphepRuBr_2$, leading to the corresponding 1β-methylcarbapenem intermediate.

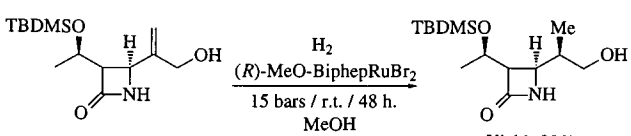
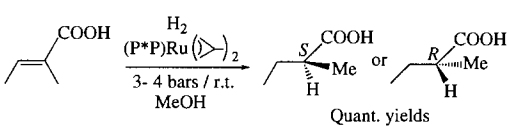


Table 1
Asymmetric hydrogenation of tiglic acid

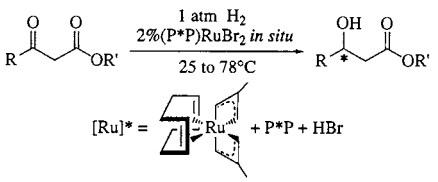


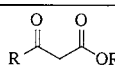
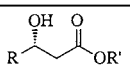
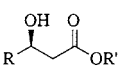
P*P	Products	e.e.
(*R,R*)-DIOP		51
(*R*)-BINAP		90
(*R,R*)-Me-DupHOS		80
(*R,R*)-CBD		70
(*S*)-BIPHEMP		90
(*R,R*)-DIPAMP		25

3.2. Asymmetric hydrogenation of ketones

Halogen-containing Ru(II) complexes prepared in situ were very efficient catalysts for the enantioselective hydrogenation of various functionalized ketones

Table 2
Asymmetric hydrogenation of β-ketoesters



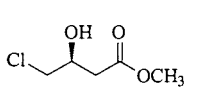
	P*P	T °C	Time h	Products	yield	e.e.
						
R=Me, R'=Me	(*S*)-BINAP	r.t.	48		80	97
R=*i*-Pr, R'=Et	(*S*)-BINAP	50	48		100	97
R=C_5H_{11}, R'=Me	(*S*)-MeO-BIPHEP	50	5		100	97
R=$C_{15}H_{31}$, R'=Me	(*S*)-BINAP	78	48		100	96
R=  R'=Me	(*S*)-BINAP	50	3		100	87
R=Et, R'=Me	(*R*)-MeO-BIPHEP	50	48		100	99
R=Ph, R'=Et	(*R*)-MeO-BIPHEP	50	44		82	96

3.2.1. Asymmetric hydrogenation of β-ketoesters

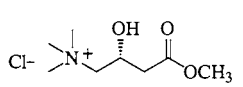
3.2.1.1. Saturated β-ketoesters. The asymmetric hydrogenation of β-ketoesters to β-hydroxyesters under atmospheric pressure with 2% of chiral Ru(II) catalysts found a wide generality and was applicable to alkyl or aryl substituted β-ketoesters [31]. At room temperature, conversion was not complete. At higher temperature (50–78°C), excellent conversion and high chiral induction were reached with the in situ halogen containing Ru(II) catalysts (e.e. = 87–99%) (Table 2).

In addition to these examples, a screening of ligands [29] was performed with the standard substrate methylacetoacetate: the catalysts (*R*,*R*)-DiopRuBr$_2$, (*S*,*S*)-CbdRuBr$_2$ prepared in situ provided the β-hydroxybutyrate under 10 bars of hydrogen pressure and 80°C with very poor e.e. (5–22% e.e.). A higher enantiofacial discrimination was observed using (*R*)-PROPHOS or (*S*,*S*)-CHIRAPHOS as ligands at 20 bars and 50°C leading to the β-hydroxyester with selectivity approaching 60%. Interestingly, the bisphospholanobenzene ligand Me–DuPHOS afforded β-hydroxybutyrate with e.e. up to 87%.

This reaction has been extended to other β-ketoesters bearing additional functional groups. High optical purities have been obtained. Some examples are given below.



in situ (*R*)-MeO-BiphepRuBr$_2$
10bars / 98°C e.e. = 90%



(*S*)-BiphempRuBr$_2$
80 bars / r.t. e.e. = 90%

3.2.1.2. Unsaturated β-ketoesters. Furthermore, β-ketoesters having an unsaturated alkyl chain were chemoselectively hydrogenated to optically pure unsaturated β-hydroxyesters under controlled reaction conditions (4–6 bars, 40–80°C) and very short reaction times (Table 3).

3.2.2. Asymmetric hydrogenation of β-ketophosphonates [32]

The in situ prepared (P*P)RuBr$_2$ catalyzed the enantioselective hydrogenation of various β-ketophosphonates in alcoholic media to give the corresponding β-hydroxyphosphonic esters with excellent enantiofacial discrimination either at atmospheric pressure or 100 bars of hydrogen with temperature varying from r.t. to 50°C (Table 4).

3.2.3. Asymmetric hydrogenation of β-ketothiophosphonates [32]

The asymmetric hydrogenation of β-ketothiophosphonates was performed in methanol under 10–100 bars of hydrogen pressure at room temperature to afford β-hydroxythiophosphonates with very good selectivities (e.e. 90–94%) (Table 5).

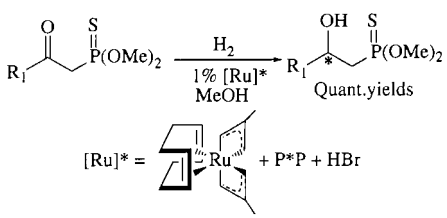
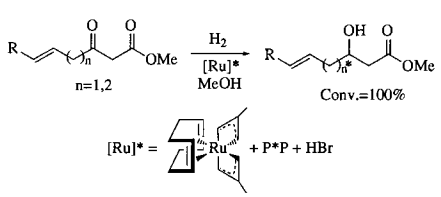


Table 3
Asymmetric hydrogenation of unsaturated β-ketoesters



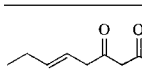
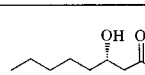
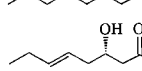
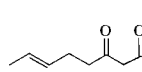
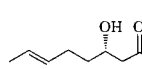
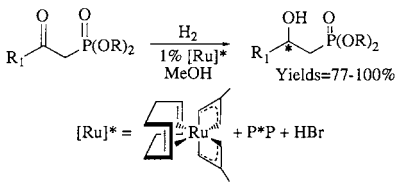
	P*P	P bars	T °C	Time h		e.e.
	(*S*)-BIPHEMP (0.3%)	20	40	65		99
	(*S*)-BIPHEMP (0.3%)	6	80	0.5		99
	(*S*)-BINAP (0.2%)	4	80	0.25	 + 5% Saturated	99

Table 4
Asymmetric hydrogenation of β-ketophosphonates



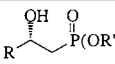
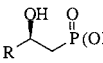
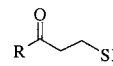
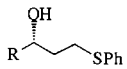
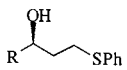
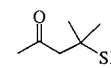
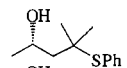
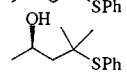
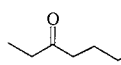
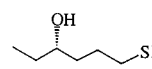
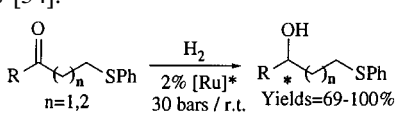
Substrate	P*P	P (bars)	Temp. (°C)	Time (h)	Products	e.e.
						
R=Me, R'=Et	(*S*)-BINAP	1	50	48		99
R=*n*-C_5H_{11}, R'=Et	(*S*)-BINAP	100	r.t.	88		98
R=  R'=Et	(*S*)-BINAP	75	50	48		94
R=  R'=Et	(*S*)-MeO-BIPHEP	10	r.t.	70		97
R=  R'=Et	(*S*)-MeO-BIPHEP	10	r.t.	70		96
R=  R'=Et	(*R*)-MeO-BIPHEP	75	50	48		93

Table 6
Asymmetric hydrogenation of phenylthiosulfides

Substrate	P*P	Products	e.e.
			
R=Me	(*S*)-BINAP		96
R=Me	(*S*)-MeO-BIPHEP		98
R=Et	(*S*)-BINAP		81
R=Et	(*S*)-MeO-BIPHEP		88
R=Me	(*R*)-BINAP		96
R=Me	(*R*)-MeO-BIPHEP		98
R=Et	(*R*)-BINAP		81
R=Et	(*R*)-MeO-BIPHEP		88
	(*S*)-BINAP		80
	(*R*)-MeO-BIPHEP		90
	(*S*)-BINAP		70

3.2.4. Asymmetric hydrogenation of phenylthiosulfides [33]

Because organosulfur compounds are widely used in organic syntheses, the asymmetric hydrogenation of β and γ phenylthio ketones was investigated. All reactions were carried out with 2% of chiral dibromide rutheniu-m(II) complexes prepared in situ. The presently reported hydrogenation procedure showed to be compatible with a divalent sulfur. The chiral alcohols were obtained in good yields with e.e. ranging from 70 to 97% (Table 6). These enriched phenylthio alcohols were interesting building blocks for natural product synthesis [34].



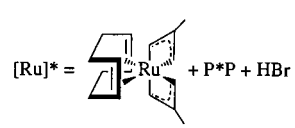
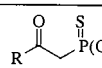
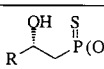
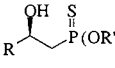


Table 5
Asymmetric hydrogenation of β-ketothiophosphonates

Substrate	P*P	P (bars)	Temp. (°C)	Time (h)	Products	e.e.
						
R=*i*-Pr, R'=Et	(*S*)-MeO-BIPHEP	10	r.t.	70		93
R=*n*-C_5H_{11}, R'=Et	(*S*)-BINAP	100	r.t.	88		90
R=*n*-C_5H_{11}, R'=Et	(*S*)-MeO-BIPHEP	100	r.t.	88		94
R=*i*-Pr, R'=Et	(*R*)-MeO-BIPHEP	10	r.t.	70		92

In addition to these experiments with atropoisomeric chiral ligands, we pointed out that the SkewphosRuBr$_2$ catalyst prepared in situ was also very efficient for asymmetric hydrogenation of various prochiral ketones [30](Table 7).

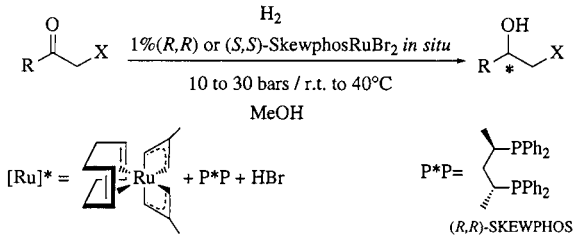
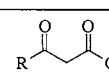
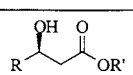
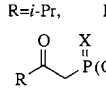
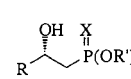
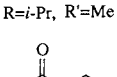
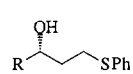
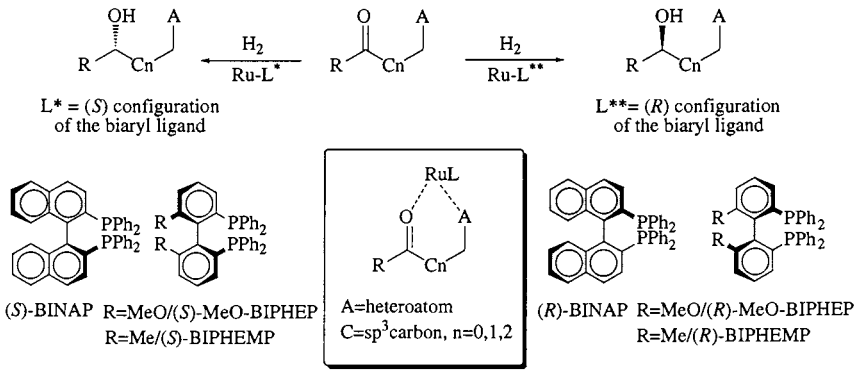


Table 7
Asymmetric hydrogenation with (*R*,*R*) or (*S*,*S*)-SkewphosRuBr$_2$

Substrate	P*P	P (bars)	Temp. (°C)	Time (h)	Products	e.e.
						
R=Me, R'=Me	(*R*,*R*)-SKEWPHOS	10	30	24		89
R=*i*-Pr, R'=Et	(*R*,*R*)-SKEWPHOS	10	40	24		91
						
R=Me, R'=Et X=O	(*S*,*S*)-SKEWPHOS	30	r.t.	24		94
R=*i*-Pr, R'=Me X=S	(*S*,*S*)-SKEWPHOS	30	r.t.	24		80
						
R=Me,	(*S*,*S*)-SKEWPHOS	30	r.t.	30		94
R=Et	(*S*,*S*)-SKEWPHOS	30	r.t.	30		95

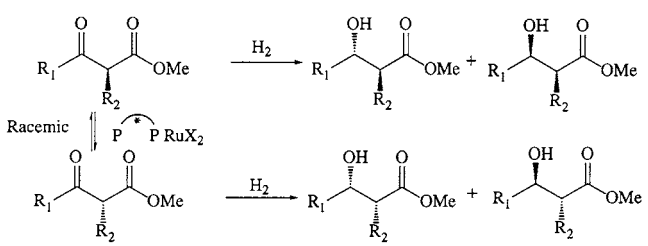
A general sense of the enantioselectivity has been proposed by Noyori and coworkers for the BINAP assisted hydrogenation of substituted ketones [19]b bearing an heteroatom at the α, β or γ position. The absolute configuration of the hydroxy-bearing position can be predicted by the absolute configuration of the atropoisomeric ligand as shown below.



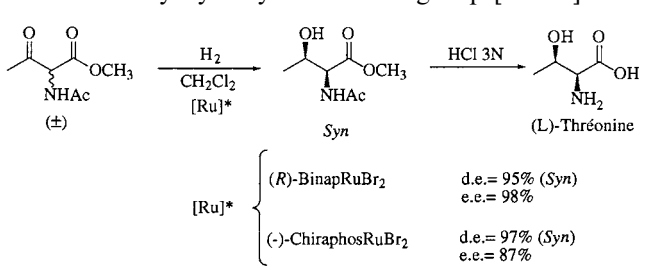
This observation is applicable to any atropoisomeric ligands such as MeO–BIPHEP or BIPHEMP etc.

4. Dynamic kinetic resolution

Racemic substrates possessing an epimerisable center such as α-substituted β-ketoesters can be converted to one single α-substituted β-hydroxyester under controlled hydrogenation conditions. This reaction where the chiral ruthenium(II) catalyst can select one of the diastereoisomeric transition states and which resulted in a single product is the so-called dynamic kinetic resolution.



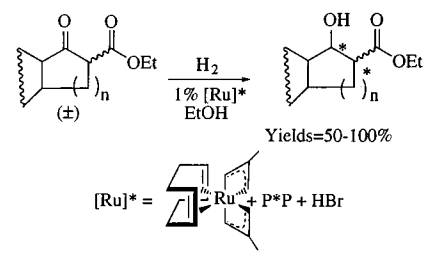
The first example of dynamic kinetic resolution of α-acetamido β-ketoesters was pointed out in 1989 simultaneously by Noyori and our group [35–37].



4.1. Cyclic β-ketoesters [38]

The kinetic dynamic resolution applied to racemic cyclic β-ketoesters such as 2-substituted-3-oxo car boxylic esters revealed that the stereochemical course of the reaction was influenced by the structures of the substrates: in the case of five membered ring (Table 8, entry 1), the hydrogenation carried out with the in situ (*R*)-BinapRuBr$_2$ proceeded with high diastereo and enantioselectivity (e.e. = 85%) to give the corresponding (*2R,3R*) *trans* products. In contrast, the diastereoselectivity was decreased to some extent (d.e. = 47%) by increasing the ring size of the racemic cyclic β-ketoester from five to six membered ring by using the

Table 8
Dynamic kinetic resolution of cyclic β-ketoesters



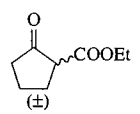
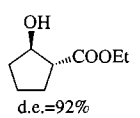
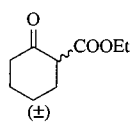
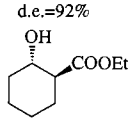
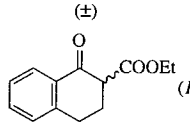
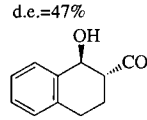
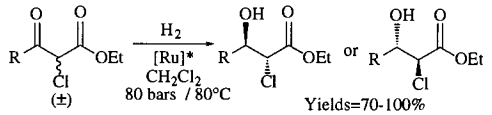
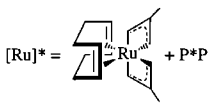
entry		P*P	P bars	T °C	Time h	d.e.(*trans*)	e.e.
1		(*R*)-BINAP	100	80	48	 d.e.=92%	85
2		(*S*)-BINAP	20	80	3	 d.e.=47%	91
3		(*R*)-MeO-BIPHEP	10	80	85	 d.e.=97%	95

Table 9
Dynamic kinetic resolution of α-chloro β-ketoesters





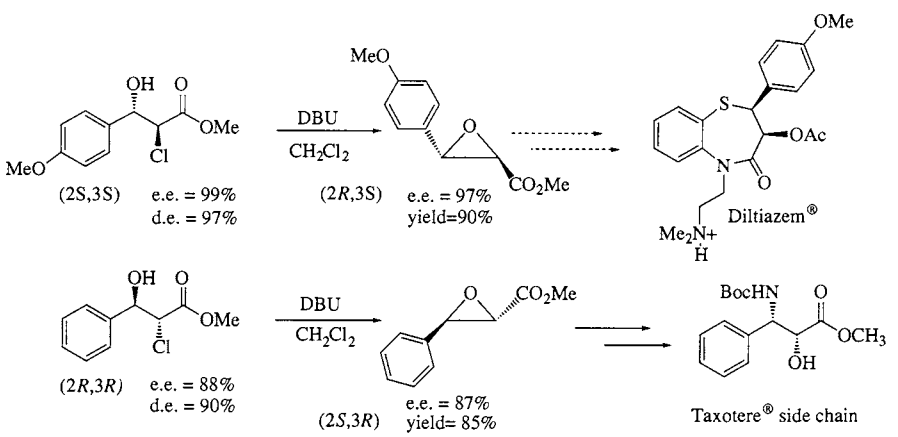
entry	P*P	d.e.(*anti*)	e.e.
1	(*R*)-MeO-BIPHEP	d.e.=99%	98
2	(*S*)-BINAP	d.e.=93%	88
3	(*R*)-BINAP	d.e.=70%	90

temperature (80 bars and 80°C) exclusively in dichloromethane with a new type of in situ chiral Ru(II) catalysts easily prepared by mixing the chiral ligand (BINAP and MeO–BIPHEP) and (COD)Ru(η^3-$(CH_2)_2CCH_3)_2$. The *anti* α-chloro β-hydroxyesters were synthesized with very high diastereoselection when the β-ketoesters were substituted with a linear alkyl side chain (Table 9, entries 1 and 2, d.e. = 99% and 93%) although the diastereoselection was decreased (Table 9, entry 3, d.e. = 70%) with a ramified side chain. In all cases, enantiomeric excesses were satisfactory (e.e. up to 98%).

The reaction was then applied to α-chloro β-ketoesters bearing an aromatic side chain under the same reaction conditions (Table 10), i.e. high pressure and temperature (80 bars, 80°C) in dichloromethane to afford the corresponding *anti* chlorhydrins (d.e. = 88–97%) with excellent enantio and diastereofacial discrimination (e.e. up to 99%).

5. Synthetic applications

These enantiomerically enriched α-chloro β-hydroxy esters were precursors for the synthesis of optically active glycidates [39] which were key intermediates in the synthesis of the potent channel blockers diltiazem® and of Taxotere® side chain.



same catalyst (Table 8, entry 2), while enantiomeric excess of the major (*2S,3S*) product was very high (e.e. = 91%). Finally, an ideal dynamic kinetic resolution was achieved in the case of cyclic β-ketoesters containing the tetralone structure (Table 8, entry 3) under 10 bars and 80°C with the in situ (*R*)-MeO–BiphepRuBr$_2$ which was an extremely effective catalyst: the racemic tetralone was hydrogenated with an excellent level of enantio and diastereoselectivity (d.e. = 97%, e.e. = 95%) to afford the *trans* cyclic β-hydroxyester.

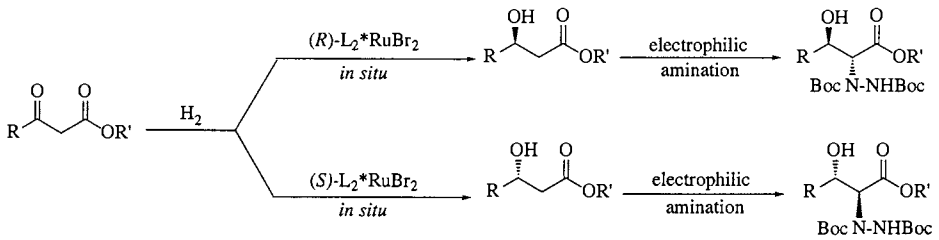
4.2. α-Chloro β-ketoesters [39]

Behavior of the open-chain α-substituted β-ketoesters was somewhat different from that of the cyclic substrates. Concerning the α-chloro β-ketoesters, the dynamic kinetic resolution was attempted at high pressure and

Table 10
Dynamic kinetic resolution of α-chloro β-ketoesters

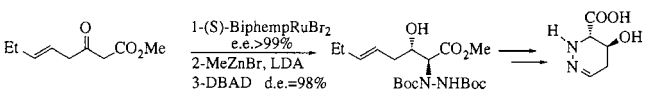
	P*P	d.e.(*anti*)	e.e.
(±)	(*R*)-BINAP	d.e.=88%	91
(±)	(*S*)-BINAP	d.e.=97%	99

The sequential ruthenium catalyzed hydrogenation [29,31] and electrophilic amination [40] was applied to the synthesis of enantiomerically pure *anti* *N*-Boc-α-hydrazino-β-hydroxyesters.

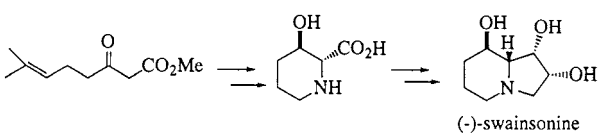


L_2 = BINAP, BIPHEMP, MeO-BIPHEP etc...

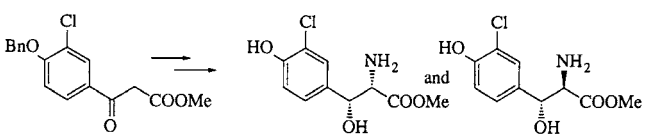
Following this strategy, some heterocycles were synthesized such as (3*S*,4*S*)-4-hydroxy-2,3,4,5-tetrahydropyridazine-3-carboxylic acid [41] which was an unusual aminoacid constituent of luzopeptin A.



A rapid stereocontrolled route to both enantiomers of *trans*-3-hydroxypipecolic [42] acid was achieved from methyl-7-methyl-3-oxooct-6-enoate using (*R*) or (*S*)-BinapRuBr$_2$. This intermediate was used to perform the total synthesis of (−)-swainsonine [43].



(*2S*,*3R*) and (*2R*,*3R*) methyl *p*-chloro-3-hydroxytyrosinates [44] which were components of Vancomycin have been synthesized from 3-chloro-4-hydroxybenzoic acid.



An efficient synthesis of (2*S*,3*R*)-3-hydroxylysine has been achieved from butyric acid via ruthenium catalyzed asymmetric hydrogenation [45]. In conclusion, the results described above demonstrates that the chiral Ru(II) complexes prepared in situ from the commercially available (COD)Ru(η^3-$(CH_2)_2CCH_3)_2$ and chiral diphosphines are efficient catalysts for the homogeneous enantioselective hydrogenation [23] of a number of prochiral substrates. This general method is compatible with a broad variety of diphosphines. Various new ruthenium catalysts have already been prepared using this technology.

Acknowledgements

We would like to thank Dr R. Schmidt (Hoffman La Roche) for a generous gift of (*R*) and (*S*)-MeO–BIPHEP and Dr P. Savignac for samples of β-ketophosphonates and thiophosphonates.

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