Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 270 (2007) 76–82
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Biphasic asymmetric hydroformylation and hydrogenation by water-soluble rhodium and ruthenium complexes of sulfonated (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl in ionic liquids

Changxi Deng, Guangnan Ou, Jiarong She, Youzhu Yuan *

State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Received 3 October 2006; received in revised form 16 January 2007; accepted 21 January 2007
Available online 24 January 2007

Abstract

A biphasic catalytic system with water-soluble rhodium complexes of sulfonated (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (labeled as (*R*)-BINAPS) in ionic liquid BMI·BF_4 has been developed for the asymmetric hydroformylation of vinyl acetate under mild conditions. The corresponding ruthenium complexes have been investigated for the biphasic asymmetric hydrogenation of dimethyl itaconate. The biphasic asymmetric hydroformylation of vinyl acetate provided 28.2% conversion and 55.2% enantiomeric excess when BMI·BF_4–toluene was used as the reaction medium at 333 K and 1.0 MPa for 24 h. The biphasic asymmetric hydrogenation of dimethyl itaconate in BMI·BF_4–^{i}PrOH at 333 K and 2.0 MPa afforded 65% enantiomeric excess with an activity similar to the homogenous analogs. Both biphasic catalytic systems with (*R*)-BINAPS ligand could be reused several times without significantly decrease in the activity, enantio- and regio-selectivities. The effects of properties of ionic liquid, molar ratio of ligand to rhodium, temperature, pressure and reaction time have been discussed.

Keywords: Ionic liquid; Biphasic catalysis; Water-soluble complexes; Asymmetric hydroformylation; Asymmetric hydrogenation

1. Introduction

Significant enantio-selectivities in asymmetric hydroformylation were induced by a number of chiral phosphorus groups [1–4]. One of the benchmark ligands in asymmetric hydroformylation was achieved by Takaya and his co-workers with the C_2-symmetric phosphine–phosphite ligand BINAPHOS [5,6]. The BINAPHOS–rhodium (Rh) catalysts showed conversions, regio- and enantio-selectivities up to 98% in a broad range of substrates. Very recently, phospholane–Rh catalysts that for the first time offer high turnover rates and high regio- and enantio-selectivities in converting achiral alkenes to chiral aldehydes by hydroformylation were discovered by Aboud and his co-workers [7,8]. The new phospholanes–Rh have shown significant progress toward practical catalytic production of chiral materials in a process that is 100% atom efficient. In 2006, Yan and Zhang developed new hybrid phosphine–phosphoramidite ligands for the Rh-catalyzed aymmetric hydroformylations of styrene and vinyl acetate, where excellent enantio-selectivity as high as 99% has been achieved [9]. Nevertheless, chiral ligands are usually expensive, mainly due to the tedious synthesis pathways. The investigation of asymmetric catalytic reaction associated with the biphasic system is of significant importance from both the fundamental and industrial points of view. In the past several decades, the catalytic reactions with biphasic systems have received considerable attention. However, works in connection to the asymmetric hydroformylation with biphasic catalysis are relatively rare. The technical and ecological advantages of the aqueous biphasic hydroformylation which are used in industrial processes of hydroformylation for lower olefins have not been successfully utilized for the asymmetric hydroformylation. Reports on the asymmetric hydroformylation with biphasic catalytic system are relatively rare [10–14].

* Corresponding author. Tel.: +86 592 2184565; fax: +86 592 2183047.
E-mail address: yzyuan@xmu.edu.cn (Y. Yuan).

1381-1169/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.molcata.2007.01.036

On the other hand, the organic salts which are liquid at ambient temperature, *i.e.*, ionic liquids (ILs), have emerged as alternative solvents because they have essentially no vapor pressure and provide good solubility for a wide range of organic, and organometallic compounds. The ILs have recently been explored as interesting alternatives to organic solvents as reaction media because they are environmentally benign and easy to prepare and modify to impart desirable characteristics. A number of reactions including hydrogenation, oxidation, and C–C bond-forming reactions have already been conducted in ILs [15–21]. Compared to heterogeneous catalysts widely used for the production of commodity chemicals, homogeneous asymmetric catalysts are however often very expensive and difficult to recycle and reuse. Immobilization of homogeneous asymmetric catalysts on solid supports or liquid biphasic systems represents an interesting approach to recycle and reuse of catalysts. The features of ILs particularly make them ideal solvents for the synthesis of high-value chiral organic compounds *via* catalytic processes. In ideal scenarios, not only high enantio-selectivity can be obtained but also both ILs and asymmetric catalysts can be recycled and reused.

Rh complexes formed with sulfonated phosphines showed excellent activities and selectivities particularly in the biphasic hydroformylation of olefins composed of carbon chains less than six. The excellent water-solubility of the phosphines, which is absolutely essential for the aqueous biphasic method, was achieved by the introduction of sodium sulfonate groups. Favre et al. found that the problem of Rh leaching could be minimized by the modification of phosphorus ligands with cationic (guanidinium or pyridinium) or anionic (sulfonate) groups [22]. An easy phase separation has been reported to be viable between the reactants-containing organic phase and the water-soluble phosphine–Rh complexes-containing ionic liquid phase after the hydroformylation [23–28]. We have been working for years on the synthesis and catalytic properties of phosphine ligands for hydroformylation with aqueous biphasic, ionic liquid biphasic and for supported catalysts [27–35]. Herein the chiral bidentate phosphine ligand (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*i.e.*, (*R*)-BINAP), which is conveniently available in the enantio-pure form, was used as chiral model ligand since it was already known to induce enantio-selectivity in several hydroformylation [4,36] and also the ruthenium (Ru) complexes of (*R*)-BINAP are excellent catalysts for asymmetric hydrogenation [37]. We report the catalytic performance and recycling ability of water-soluble Rh and Ru-complexes of sulfonated (*R*)-BINAP (*i.e.*, (*R*)-BINAPS) in ILs for the biphasic asymmetric hydroformylation and hydrogenation of olefins.

2. Experimental

2.1. Ligands and rhodium complexes

2.1.1. General comments

All ligand syntheses were carried out with standard Schlenk techniques under argon atmosphere. Synthesis gas ($CO/H_2 = 1{:}1$, purity 99.98%), hydrogen (99.99%) and argon (99.999%) were purchased from Linde Gas Xiamen Ltd. Vinyl acetate, styrene, dimethyl itaconate and (*R*)-BINAP were purchased from Aldrich and used as-received without further purification.

2.1.2. Spectroscopy

IR spectra were measured on a Nicolet 740 FTIR spectrometer with a resolution of 4 cm^{-1}. NMR spectroscopy was recorded on a Varian FT Unity$^+$ 500 spectrometer. $^{31}P(^1H)$ NMR spectra were recorded at 202 MHz at room temperature in $CDCl_3$ for organic-soluble compounds and in D_2O for water-soluble ones. The chemical shift was referenced to 85% H_3PO_4. ^1H NMR spectra were referenced to $SiMe_4$ for organic-soluble compounds and DSS for water-soluble ones.

2.1.3. Synthesis and characterization

The preparation of the water-soluble chiral ligand (*R*)-BINAPS has been described elsewhere [38]. The spectra data of the product are as follows. $^{31}P\{^1H\}$ NMR (D_2O): −13.8 ppm (the $^{31}P\{^1H\}$ NMR ($CDCl_3$) of (*R*)-BINAP appeared at −15.5 ppm); ^1H NMR (D_2O): 6.69–6.85(m, 4H), 6.98–7.25(m, 18H), 7.54–7.61 (d, 2H), 7.83–7.85 (d, 2H), 8.66–8.68 (d, 2H); Elemental analysis: S/P:Na/P:C/Na ≈ 1.8:1.8:12.2.

[Rh(*acac*)$(CO)_2$] and [Ru(*p*-cymene)$_2Cl_2$] were prepared according to a procedure cited in literature [39,40]. The ILs ($BMI{\cdot}BF_4$ and $BMI{\cdot}PF_6$) were synthesized using the procedures reported in the previous literature [41–46] and were vacuum-treated before each use.

2.2. Hydroformylation and hydrogenation

To exclude air, a 60 mL stainless steel autoclave equipped with a magnetic stirrer was filled using Schlenk techniques with solutions containing the catalyst precursors, ligand, the substrates (for hydroformylations, vinyl acetate and styrene were used as substrates; for hydrogenation, dimethyl itaconate was used as substrate), ionic liquid and organic solvent (if any). After filling in the liquids the autoclave was purged with synthesis gas or with hydrogen three times and heated up to the desired temperature. Synthesis gas or hydrogen was added to adjust the pressure. After the reaction, the reactor was cooled to 273 K and decompressed. Finally, the liquids and the catalysts were separated by decantation. The organic phase, after drying, was taken for GC analysis (FID, hydrogen as carrier gas). A 30 m × 0.25 mm × 0.25 μm capillary with a Supelco β-Dex-225 was used for the separation and quantitative analysis of the sample components including the chiral products [47]. The products were verified using authentic samples. The reaction conversions were calculated by the corrected area normalization method.

3. Results and discussion

3.1. Asymmetric hydroformylation of vinylacetate

We have carried out the sulfonation of (*R*)-BINAP with 50–53 wt% oleum by adopting the reaction conditions in literature in order to eliminate the formation of phosphine oxide

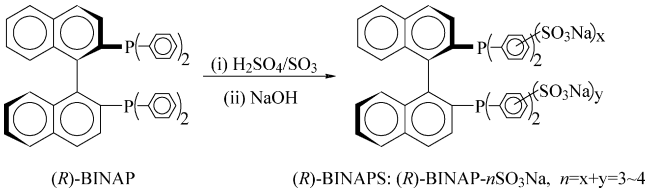
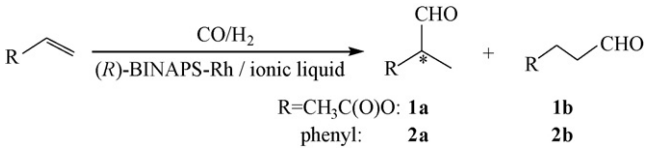


Fig. 1. Synthesis of water-soluble chiral ligand (*R*)-BINAPS.



Scheme 1. Asymmetric hydroformylation of vinyl acetate and styrene.

and to achieve a high yield of a single phosphine species [38]. The water-soluble (*R*)-BINAPS are generally achieved with the purities of 90–95% ($^{31}P\{^1H\}$ NMR) containing 5–10% impurity of oxidized phosphorus (V) species. Our studies on NMR and elemental analysis (see Section 2), along with the results in literature [38], indicated that the formula of (*R*)-BINAPS would be (*R*)-BINAP-$n$$SO_3$Na ($n$ = 3–4) as illustrated in Fig. 1.

The symmetric hydroformylation of vinyl acetate by using [Rh(*acac*)CO]$_2$ as Rh precursor and (*R*)-BINAP or (*R*)-BINAPS as ligand in ILs yielded 2-acetoxypropanal (**1a**) and 3-acetoxypropanal (**1b**), in general, with high chemo- and regioselectivities (Scheme 1). Limited by-products of ethyl acetate and acetic acid were also found. The results are summarized in Table 1. In the case of (*R*)-BINAP–Rh system, the reaction in BMI·BF$_4$ or toluene proceeded homogeneously. Higher conversion but relatively lower enantiomeric excess (ee) were obtained in BMI·BF$_4$ compared to those in toluene (entries 1 and 2). When BMI·BF$_4$–toluene was used as solvent, a biphasic system consisting of lower layer (catalyst layer) of ionic liquid-complexes and upper layer of the reactant was obtained after the reaction, affording conversion similar to that in BMI·BF$_4$ and ee similar to that in toluene (entries 3 and 4), respectively. In this case, it was possible to separate the catalyst layer by decantation although the color of the reactant was light yellowish.

The introduction of water-soluble groups of sodium sulfonates into the phenyl skeletons might disturb slightly the enantio-selection step during the catalytic cycle. As shown in Table 1, the conventional aqueous biphasic system by using (*R*)-BINAPS as ligand provided very low conversion of 1.1% but acceptable 50.3% ee after reaction for 24 h at 2.0 MPa and 333 K (entry 5). When BMI·BF$_4$ was used as solvent, however, the moderate conversion of 22.4% and higher ee of 59.8% associated with biphasic catalytic system were obtained under identical conditions (entry 6), where the biphasic catalytic system was consisted of the lower layer of ionic liquid-complexes and the upper layer of the reactant. By addition of proper amount of toluene to the system, the separation of the two phases was more clearer and easier, without affecting the conversion and ee (entries 7–11) significantly, which would be in favor of catalyst recycling. The conversion increased just by prolonging the reaction time or using milder syngas pressure (entries 10 and 11). However, the result in Table 1 showed that very low ee was obtained by using BMI·PF$_6$ instead of BMI·BF$_4$, probably owing to the hydrophobic property of BMI·PF$_6$ [27,44].

3.2. Effects of molar ratio of ligand to rhodium, pressure and temperature on the asymmetric hydroformylation of vinylacetate

Fig. 2 shows the conversion and ee value in the hydroformylation of vinyl acetate as a function of molar ratio of ligand to Rh with (*R*)-BINAPS–Rh as catalyst and BMI·BF$_4$–toluene as the reaction medium. The ee less than 20% was obtained for the molar ratio of ligand to Rh below 1.0. The conversion and ee value reached almost saturation when the molar ratio of (*R*)-BINAPS to Rh was above 1.5. The results suggested the coordination chemistry and catalytic behavior of water-soluble (*R*)-BINAPS–Rh complexes in ionic liquid biphasic system was

Table 1
The effect of ligand on the asymmetric hydroformylation of vinyl acetate[a]

Entry	Ligand	Solvent system		Conversion (%)	ee (%)	**1a** (%)	Phase
		Toluene (mL)	BMI·BF$_4$ (mL)				
1	BINAP	0	2	41.6	43.3	99.6	One
2	BINAP	5	0	18.9	55.9	93.0	One
3	BINAP	2	2	38.3	54.0	97.8	Two
4	BINAP	1	2	48.2	55.7	99.5	Two
5	BINAPS	2	2 mL H_2O	1.1	50.3	98.8	Two
6	BINAPS	0	2	22.4	59.8	99.8	Two
7	BINAPS	2	1	8.2	53.8	99.6	Two
8	BINAPS	2	2	13.6	53.5	99.7	Two
9	BINAPS	1	2	24.5	55.1	99.8	Two
10	BINAPS[b]	1	2	53.2	53.6	99.8	Two
11	BINAPS[c]	1	2	28.2	55.2	99.8	Two
12	BINAPS	1	2 mL BMI·PF$_6$	32.7	3.3	99.2	Two

[a] Reaction conditions: Rh(*acac*)(CO)$_2$ = 0.02 mmol, olefin/Rh = 300 (molar ratio), ligand/Rh = 3 (molar ratio), CO/H$_2$ = 1 (molar ratio), pressure = 2.0 MPa, temperature = 333 K, reaction time = 24 h, agitation speed = 800 rpm.
[b] Reaction time = 48 h.
[c] Ligand/Rh = 1.5 (molar ratio), P(CO/H$_2$) = 1.0 MPa.

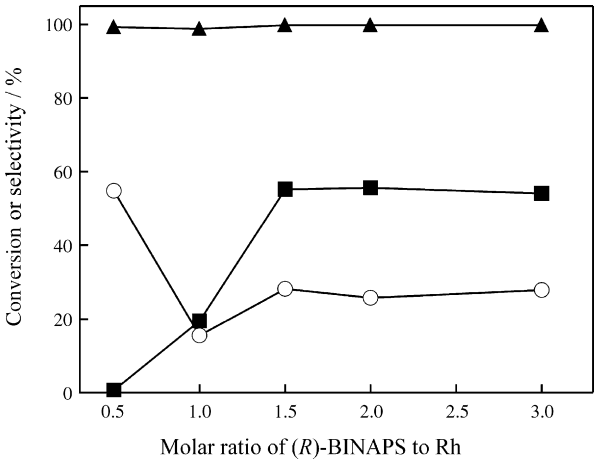


Fig. 2. The effect of molar ratio of ligand to rhodium on the asymmetric hydroformylation of vinyl acetate. Reaction conditions: $P(CO/H_2) = 1.0$ MPa, others are the same as in Table 1. (■) Enantiomeric excess (ee), (▲) selectivity to **1a**, and (●) conversion.

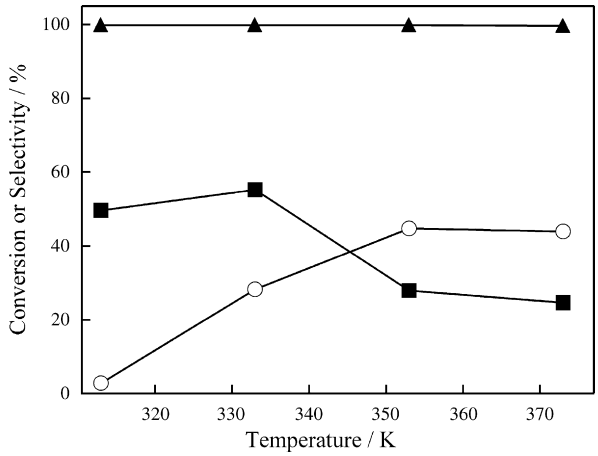


Fig. 4. The effect of temperature on the asymmetric hydroformylation of vinyl acetate. Reaction conditions: ligand/Rh = 1.5 (molar ratio), others are the same as in Table 1. (■) Enantiomeric excess (ee), (▲) selectivity to **1a**, and (●) conversion.

quite similar to those of Rh complexes ligated with phosphorylated BINAP in the organic homogeneous system [11].

With (*R*)-BINAPS–Rh as catalyst and BMI·BF_4–toluene as the reaction medium, the conversion and ee in the hydroformylation of vinyl acetate are plotted against syngas pressure in Fig. 3. The ee value and selectivity to **1a** remained almost unchanged but the conversion dropped continuously when the syngas pressure was increased from 1.0 to 4.0 MPa. The results obtained by employing (*R*)-BINAP–Rh as catalyst for the hydroformylation of vinyl acetate in THF also showed a similar dependence on pressure [36]. A plausible explanation for the phenomena is ascribed to the stable coordination between the bidendate phosphine and Rh species. In the presence of higher CO pressure, several carbonyl species might be formed but without affecting the coordination between the bidendate and Rh species [48,49].

The influence of temperature on conversion and ee by using (*R*)-BINAPS–Rh as catalyst and BMI·BF_4–toluene as reaction medium is illustrated in Fig. 4. The conversion tended to increase considerably and the selectivity to **1a** kept almost unchanged as the temperature increased from 313 to 373 K. The ee, however, increased at first and then passed through a maximum value of 55.2% at 333 K. Above 333 K, the ee dropped. Either changes in the catalyst structure or racemization of the branched aldehydes *via* enolization could explain this effect.

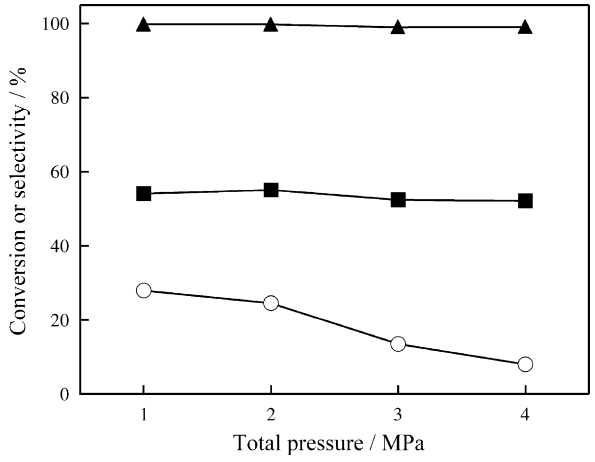


Fig. 3. The effect of pressure on the asymmetric hydroformylation of vinyl acetate. Reaction conditions are the same as in Table 1. (■) Enantiomeric excess (ee), (▲) selectivity to **1a**, and (●) conversion.

3.3. Catalyst recycling ability for the asymmetric hydroformylation of vinylacetate

The recycling ability of the (*R*)-BINAPS–Rh complexes in BMI·BF_4–toluene has been checked by the consecutive runs under the conditions of syngas at 2.0 MPa and temperature at 333 K. For comparison, the counterpart system of (*R*)-BINAP–Rh complexes in BMI·BF_4–toluene was also used for the reaction under identical conditions. The results are shown in Fig. 5. The catalyst based on (*R*)-BINAP lost its original activity gradually from the first to sixth run. The ee and **1a** selectivity showed negligible decreases from the first to fifth runs, but the ee started to decline in the sixth run (Fig. 5a). These results indicated that the organic-soluble (*R*)-BINAP–Rh complexes would be continuously extracted from the layer of ionic liquid by the reactants, but the remaining complexes in the ionic liquid layer was structurally stable and afforded the innate ee and selectivities for **1a**. Attractively, the catalyst generated from the (*R*)-BINAPS could be recovered at least six times without significant losses in the catalytic performance (Fig. 5b).

3.4. Asymmetric hydroformylation of styrene

The results obtained for the hydroformylation of styrene are given in Table 2. The complexes (*R*)-BINAP–Rh in BMI·BF_4–toluene induced 21.6% ee and 2-phenyl-1-propanal (**2a**) selectivity of 96.0%, which were similar to those reported for (*R*)-BINAP–Rh in THF by Claver and his co-workers [50]. Compared to the parent Rh complex of (*R*)-BINAP the catalyst with the (*R*)-BINAPS only afforded 8.1% ee and **2a** selectivity of 94.2% under identical conditions. In addition,

Table 2
The results of asymmetric hydroformylation of styrene[a]

Entry	Ligand	Solvent system (1/2 mL)	Conversion (%)	ee (%)	**2a** (%)
13	(*R*)-BINAPS	Toluene/BMI·PF_6	61.6	8.0	89.5
14	(*R*)-BNIAPS	Toluene/BMI·BF_4	56.3	8.1	94.2
15	(*R*)-BINAP	Toluene/BMI·PF_6	64.1	6.0	94.0
16	(*R*)-BINAP	Toluene/BMI·BF_4	79.0	21.6	96.0

[a] Reaction conditions are the same as in Fig. 4.

Table 3
The effect of ^{i}PrOH/BMI·BF_4 volume ratio on the asymmetric hydrogenation of dimethyl itaconate[a]

Entry	Solvent system		Ligand	Time (min)	Conversion (%)	ee (%)
	^{i}PrOH (mL)	BMI·BF_4 (mL)				
17	0	2	BINAP	240	89.8	63.3
18	0	2 mL BMI·PF_6	BINAP	850	99.7	56.1
19	2	0	BINAP	120	99.9	80.7
20	2	2	BINAP	120	95.4	70.6
21	3	1	BINAP	240	39.8	58.2
22	1	2	BINAP	300	79.6	56.8
23	0	2	BINAPS	1440	72.2	44.9
24	0	2 mL BMI·PF_6	BINAPS	1440	46.6	21.7
25	2	0	BINAPS	1440	99.7	61.6
26	2	2	BINAPS	180	74.7	66.4
27	1	2	BINAPS	360	68.2	50.9
28	3	1	BINAPS	120	92.0	65.0

[a] Reaction conditions: [Ru(*p*-cymene)$_2$Cl$_2$] = 0.01 mmol, olefin/Ru = 300 (molar ratio), ligand/Ru = 1 (molar ratio), pressure (H_2) = 2.0 MPa, temperature = 333 K, agitation speed = 800 rpm.

when BMI·PF_6–toluene was used as reaction medium, the ee and **2a** selectivity were not satisfactory for the catalysts with either (*R*)-BINAP or (*R*)-BINAPS as ligand. Therefore, besides the ligand structure, the properties of ionic liquid could have significant influences on the asymmetric hydroformylation of styrene, but these need further investigations.

3.5. Asymmetric hydrogenation of dimethyl itaconate

As observed in several cases for the asymmetric hydrogenations in water, the ee value was slightly diminished with the aqueous biphasic system [51,52]. The highest ee value for the asymmetric hydrogenation of dimethyl itaconate in the aqueous two-phase system with Ru complexes of phosphorylated BINAP derivatives was reported by Köckritz and co-workers, where a maxium 79.4% ee was achieved. But no catalyst recycling ability were available [11].

We have investigated the potential of the water–soluble ligand (*R*)-BINAPS in the hydrogenation of dimethyl itaconate in the medium of ^{i}PrOH–BMI·BF_4 with biphasic catalysis, where the Ru catalysts were formed *in situ* (Scheme 2). Significant solvent effects on the activity and selectivity were found with the Ru-complex in ionic liquid biphasic as shown in Table 3. It can be seen from Table 3 that the use of BMI·BF_4 as solvent caused decreases in conversion and ee irrespective of whether the catalysts are generated from (*R*)-BINAP or (*R*)-BINAPS (entries 17 and 23). The lowest activity and ee were obtained when BMI·PF_6 was used as solvent. Compared to (*R*)-BINAP, the Ru–complexes with (*R*)-BINAPS showed decreases in the ee and activity. However, such decreases could be improved by the addition of ^{i}PrOH into the system without destroying the biphasis catalysis. As shown in Table 3, at a proper volume ratio of ^{i}PrOH to BMI·BF_4, the Ru–complexes generated from (*R*)-BINAPS could afford 65% ee and a conversion similar to that with the ones generated from (*R*)-BINAP (entry 28).

The catalytic performance of the (*R*)-BINAPS–Ru in the medium of ^{i}PrOH–BMI·BF_4 was influenced by the hydrogen pressure and reaction temperature as shown in Tables 4 and 5. The higher hydrogenation pressure, the higher conversion, but the ee slightly decreased. The results also indicated that higher reaction temperature was beneficial both for the conversion and ee. The 67.6% ee was achieved at 353 K under the reaction conditions shown in Table 5 (entry 37).

The stabilities of the Ru complexes derived from (*R*)-BINAP and (*R*)-BINAPS in ^{i}PrOH–BMI·BF_4 have been checked separately by the consecutive recycling runs. The results are illustrated in Fig. 6. The catalyst based on (*R*)-BINAP lost its original activity in terms of conversion at the forth run, while

Table 4
The effect of pressure on the asymmetric hydrogenation of dimethyl itaconate[a]

Entry	Pressure (MPa)	Conversion (%)	ee (%)
29	1.0	73.9	69.8
31	2.0	92.0	65.0
32	3.0	94.5	66.9
33	4.0	94.0	63.3

[a] Reaction conditions: solvent = ^{i}PrOH (3 mL)/BMI·BF_4 (1 mL), reaction time = 2 h; others are the same as in Table 3.

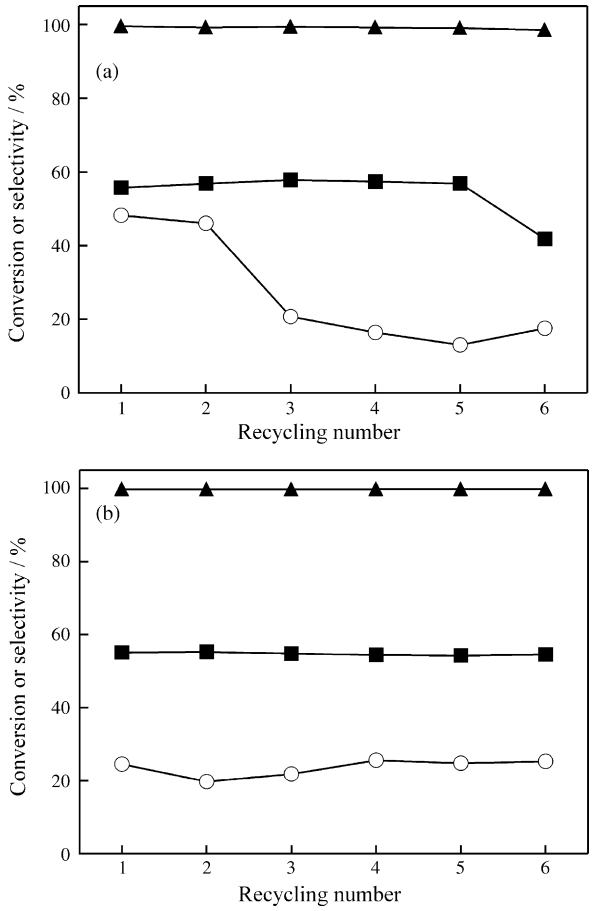
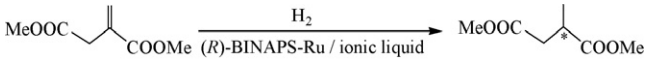


Fig. 5. The recycling of rhodium complexes with (a) (*R*)-BINAP and (b) (*R*)-BINAPS as ligands in BMI·BF_4–toluene for the asymmetric hydroformylation of vinyl acetate. Reaction conditions are the same as in Table 1. (■) Enantiomeric excess (ee), (▲) selectivity to **1a**, and (●) conversion.



Scheme 2. Asymmetric hydrogenation of dimethyl itaconate.

the ee showed negligible decrease from the first to third run but dropped at the forth run. In contrast, the catalyst generated from the (*R*)-BINAPS showed considerable stability in catalytic performance during the recycling runs. The conversion and ee varied from 80 to 87% and of 66 to 69%, respectively, at 333 K and 2.0 MPa from the first to forth run.

Table 5
The effect of temperature on the asymmetric hydrogenation of dimethyl itaconate[a]

Entry	Temperaure (K)	Time (min)	Conversion (%)	ee (%)
34	323	180	47.3	50.4
35	333	120	92.0	65.0
36	343	60	79.4	63.9
37	353	30	96.6	67.6

[a] Reaction conditions: solvent = ^{i}PrOH (3 mL)/BMI·BF_4 (1 mL); others are the same as in Table 3.

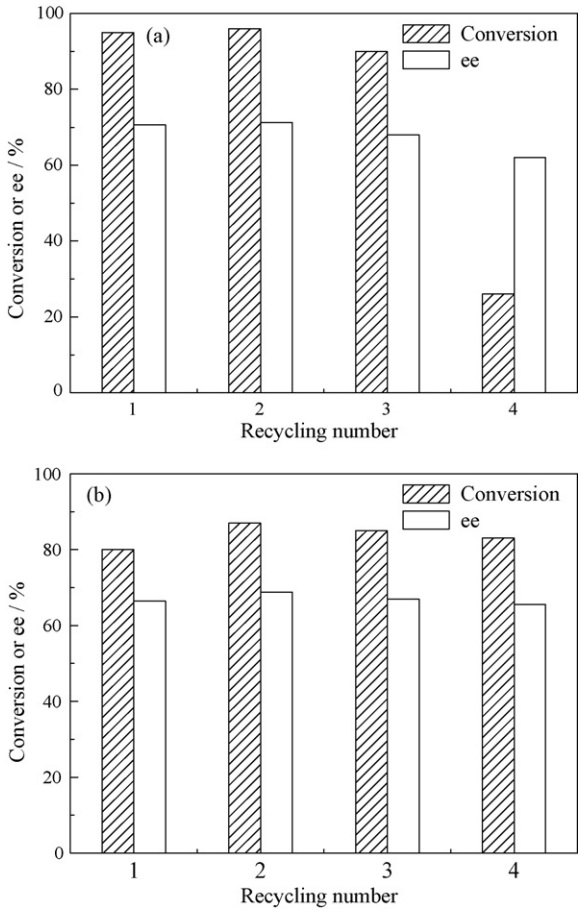


Fig. 6. The recycling of ruthenium complexes with (a) (*R*)-BINAP and (b) (*R*)-BINAPS as ligands in BMI·BF_4–^{i}PrOH (2 mL/ 2 mL) for the asymmetric hydrogenation of dimethyl itaconate. Reaction conditions: olefin/Ru = 300 (molar ratio), ligand/Ru = 1 (molar ratio), T = 333 K, agitation speed = 800 rpm, time = 2 h, $P(H_2)$ = 2.0 MPa.

4. Conclusions

(1) In the biphasic asymmetric hydroformylation of vinyl acetate, a conversion of 28.2% along with 55.2% ee and **1a** selectivity as high as 99.8% was obtained with the catalyst system of (*R*)-BINAPS–Rh in BMI·BF_4–toluene after reaction for 24 h at 333 K and 1.0 MPa. The ee and **1a** selectivity were slightly higher than those obtained by the homogeneous counterpart of (*R*)-BINAP–Rh in toluene. The biphasic catalyst could be reused at least six times without reducing activity, enantio- and regio-selectivities. Analogous biphasic catalytic systems might be formed by using the rhodium complexes of (*R*)-BINAP in the similar conditions. But these biphasic systems showed continuous decreases in activity and enantio-selectivity during the recycling use.

(2) Significant solvent effects on the activity and selectivity were found in the asymmetric hydrogenation of dimethyl itaconate with Ru–complexes in the ionic liquid biphasic system. The 65% ee with a conversion similar to the homogeneous counterpart was achieved by using (*R*)-BINAPS–Ru complexes in BMI·BF_4–^{i}PrOH at 333 K and

2.0 MPa. The conversion and ee varied from 80 to 87% and of 66 to 69%, respectively, at 333 K and 2.0 MPa from the first to forth run, indicating the significant stability during the catalyst recycling use.

(3) The biphasic catalytic systems of (*R*)-BINAPS–Rh and (*R*)-BINAPS–Ru in BMI·BF_6 induced lower enantioselelctivities and conversions in the hydroformylation of vinyl acetate and styrene and also the hydrogenation dimethyl itaconate.

Acknowledgements

The authors gratefully acknowledge the financial supports from the NSFC (Nos. 20021002 20473065 and 20433030), the National Basic Research Programme (973-project) (No. G2000048008), the Key Project of Fujian Province (No. 2005HZ01-3) and the Research Fund for the Doctoral Program of Higher Education (No. 20050384011) and the Key Project of Chinese Ministry of Education (No. 106099).

References

[1] C. Botteghi, G. Consiglio, P. Pino, Chimia 27 (1973) 215.
[2] L. Kollar, J. Bakos, I. Toth, B. Heil, J. Organomet. Chem. 370 (1989) 257.
[3] G. Consiglio, F. Morandini, P. Pino, J. Organomet. Chem. 279 (1985) 193.
[4] L. Kollar, P. Sandor, G. Szalontai, J. Mol. Catal. 67 (1991) 191.
[5] N. Sakai, S. Mano, K. Nozaki, H. Takaya, J. Am. Chem. Soc. 115 (1993) 7033.
[6] K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, J. Am. Chem. Soc. 119 (1997) 4413.
[7] T.P. Clark, C.R. Landis, S.L. Freed, J. Klosin, K.A. Abboud, J. Am. Chem. Soc. 127 (2005) 5040.
[8] A.T. Axtell, C.J. Cobley, J. Klosin, G.T. Whiteker, A. Zanotti-Gerosa, K.A. Abboud, Angew. Chem. Int. Ed. 44 (2005) 5834.
[9] Y. Yan, X. Zhang, J. Am. Chem. Soc. 128 (2006) 7198.
[10] A. Aghmiz, A. Orejón, M. Diéguez, M.D. Miquel-Serrano, C. Claver, A.M. Masdeu-Bultó, D. Sinou, G. Laurenczy, J. Mol. Catal. A: Chem. 195 (2003) 113.
[11] A. Köckritz, S. Bischoff, M. Kant, R. Siefken, J. Mol. Catal. A: Chem. 174 (2001) 119.
[12] R.W. Eckl, T. Priermeier, W.A. Herrmann, J. Organomet. Chem. 532 (1997) 243.
[13] F.A. Rampf, M. Spiegler, W.A. Herrmann, J. Organomet. Chem. 582 (1999) 204.
[14] M.D. Miquel-Serrano, A.M. Masdeu-Bultó, C. Claver, D. Sinou, J. Mol. Catal. A: Chem. 143 (1999) 49.
[15] D.R. MacFarlane, J.M. Pringle, K.M. Johansson, S.A. Forsyth, M. Forsyth, Chem. Commun. (2006) 1905.
[16] S.G. Lee, Chem. Commun. (2006) 1049.
[17] J. Muzart, Adv. Synth. Catal. 348 (2006) 275.
[18] C. Baudequin, D. Brégeon, J. Levillain, F. Guillen, J.C. Plaquevent, A.C. Gaumont, Tetrahedron: Asymm. 16 (2005) 3921.
[19] J.S. Wilkes, J. Mol. Catal. A: Chem. 214 (2004) 11.
[20] C. Baudequin, J. Baudoux, J. Levillain, D. Cahard, A.C. Gaumont, J.C. Plaquevent, Tetrahedron: Asymm. 14 (2003) 3081.
[21] S.T. Handy, Chem. Eur. J. 9 (2003) 2938.
[22] F. Favre, H. Olivier-Bourbigou, D. Commereuc, L. Saussine, Chem. Commun. (2001) 1360.
[23] P. Wasserscheid, H. Waffenschmidt, P. Machnitzki, K.W. Kottsieper, O. Stelzer, Chem. Commun. (2001) 451.
[24] R.P.J. Bronger, S.M. Silva, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (2002) 3044.
[25] P.J.B. Raymond, M.S. Silvana, C.J.K. Paul, P.W.N.M. van Leeuwen, Dalton. Trans. (2004) 1590.
[26] C.C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, Organometallics 19 (2000) 3818.
[27] Q.R. Peng, Y. Wang, C.X. Deng, X.Q. Wang, Y.Z. Yuan, Chin. J. Mol. Catal. 18 (2004) 376.
[28] Q.R. Peng, C.X. Deng, Y. Yang, M.H. Dai, Y.Z. Yuan, React. Kinetics Catal. Lett. 90 (2007) 53.
[29] Q.R. Peng, Y. Yang, C.J. Wang, X.L. Liao, Y.Z. Yuan, Catal. Lett. 88 (2003) 219.
[30] Q.R. Peng, X.L. Liao, Y.Z. Yuan, Catal. Commun. 5 (2004) 447.
[31] Y.Z. Yuan, H.B. Zhang, Y.Q. Yang, Y. Zhang, K.R. Tsai, Catal. Today 74 (2002) 5.
[32] Z.H. Li, Q.R. Peng, Y.Z. Yuan, Appl. Catal. A: Gen. 239 (2003) 79.
[33] Q.R. Peng, Y. Yang, Y.Z. Yuan, J. Mol. Catal. A: Chem. 219 (2004) 175.
[34] Y. Yang, H.Q. Lin, C.X. Deng, J.R. She, Y.Z. Yuan, Chem. Lett. 34 (2005) 220.
[35] Y. Yang, C.X. Deng, Y.Z. Yuan, J. Catal. 232 (2005) 108.
[36] D. Hoegaerts, P.A. Jacobs, Tetrahedron: Asymm. 10 (1999) 3039.
[37] S. Akutagawa, Appl. Catal. A: Gen. 128 (1995) 171.
[38] K.T. Wan, M.E. Davis, J. Chem. Soc. Chem. Commun. (1993) 1262.
[39] Y.S. Varshavskii, T.G. Cherkasova, Russ. J. Inorg. Chem. 12 (1967) 899.
[40] M.A. Bennet, A.K. Smith, J. Chem. Soc. Dalton (1974) 233.
[41] P. Wasserscheid, H. Waffenschmidt, J. Mol. Catal. A: Chem. 164 (2000) 61.
[42] P. Wasserscheid, R. val Hal, A. Bösmann, Green Chem. 4 (2002) 400.
[43] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. de Souza, J. Dupont, Inorg. Chim. Acta 255 (1997) 207.
[44] L.C. Branco, J.N. Rosa, J.J. Moura Ramos, C.A.M. Afonso, Chem. Eur. J. 8 (2002) 3671.
[45] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. de Souza, J. Dupont, Polyhedron 15 (1996) 1217.
[46] K.S. Brendan, G.P. Dennis, Electrochem. Commun. 3 (2001) 712.
[47] C.J. Cobley, J. Klosin, C. Qin, G.T. Whiteker, Org. Lett. 6 (2004) 3277.
[48] S. Gladiali, J.C. Bayon, Tetrahedron: Asymm. 6 (1995) 1453.
[49] F. Agbossou, J.F. Carpentier, A. Mortreux, Chem. Rev. 95 (1995) 2485.
[50] A.M. Masdeu-Bultó, A. Orejón, A. Castellanos, S. Castillón, C. Claver, Tetrahedron Asymm. 7 (1996) 1829.
[51] W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem. 105 (1993) 1588.
[52] P. Kalck, F. Monteil, Adv. Organomet. Chem. (1992) 219.