Asymmetric hydrogenation of aromatic ketones with MeO-PEG-supported BIPHEP/DPEN ruthenium catalysts

Li-Ting Chai, Wei-Wei Wang, Quan-Rui Wang [*], Feng-Gang Tao

Department of Chemistry, Fudan University, Shanghai 200433, PR China

Abstract

A soluble polymer (MeO-PEG) supported biphenylbisphosphine (BIPHEP)-Ru/chiral diamine (1,2-diphenylethylenediamine) complex, in which the polymer is attached to the two phenyl rings of BIPHEP ligand, has been prepared, and shown to be highly active with good enantioselectivity for the catalyzed asymmetric hydrogenation of unfunctionalized aromatic ketones. The derived chiral ruthenium complex **5** proved to be stable in air allowing facile catalyst recycling. Especially for 4′-*tert*-butyl-acetophenone and 1-acetonaphthone, excellent ee values up to 96.5% and 95.9% have been obtained which are comparable to or even higher than the enantioselectivity achieved with 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl-Ru-DPEN catalyst under similar conditions.
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1. Introduction

Asymmetric hydrogenation reactions catalyzed by homogeneous chiral transition-metal complexes provide a fundamental tool for the preparation of optically active organic compounds [1]. Polymer supported catalysts have inherent operational and economical advantages: facilitating the separation from reaction mixtures, easy recovery and reuse of the expensive but always toxic chiral compounds. As a consequence, numerous polymer supported (pre)catalysts have been developed during the past decades [2–7]. In recent years, $RuCl_2(phosphine)_2(1,2-diamine)$ complexes, coupled with an alkaline base in 2-propanol, which were introduced by Noyori and coworkers [8–10], have been exploited as effective catalysts for asymmetric hydrogenation of simple ketones. Their high efficiency has prompted Noyori and coworkers' [11] and other groups [12–19] to explore their immobilization on polymers or other solids. Taking the frequently employed 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) and the optically active 1,2-diphenylethylenediamine (DPEN] as examples, the attachment

has been attempted either through the naphthyl rings of the coordinated BINAP ligand or the phenyl rings of DPEN moiety.

Biphenylbisphosphine ligands such as (6,6′-dimethoxy-biphenyl-2,2′-diyl)bis(diphenylphosphine) (MeO-BIPHEP) [20–24] recently aroused great interest. They have demonstrated excellent results in the field of ruthenium-mediated asymmetric hydrogenation, especially for aromatic ketones. However, to the best of our awareness, immobilization of these ligands has not been well addressed [19,25]. Most recently, we have developed a soluble polymer (MeO-PEG) supported chiral BIPHEP-RuBr$_2$ catalyst, which offered high activity in comparison with the parent homogeneous catalyst while retaining high stereoselectivity [26]. This approach combines the advantages of homogeneous and heterogeneous catalysis. In order to establish more generality and versatility of this methodology, we aimed to develop other polymer-supported catalysts with better recovery performance and high enantioselectivity. Herein, we wish to report the preparation of a soluble polymer (MeO-PEG) supported BIPHEP-Ru/chiral diamine (DPEN) complex (MeO-PEG BIPHEP-Ru-DPEN) and its use as a catalyst for the asymmetric hydrogenation of a number of aromatic ketones. It was found that the catalyst furnished high activity, good stereoselectivity and exceptional stability for reuse.

* Corresponding author. Tel.: +86 21 65648139; fax: +86 21 65641740.
E-mail address: qrwang@fudan.edu.cn (Q.-R. Wang).

2. Experimental

2.1. General experimental procedures

The ^{1}H NMR spectra were acquired in CDCl$_3$ as solvent on a JEOL 400 MHz spectrometer. The ^{31}P NMR spectra were acquired in D$_2$O as solvent at 203 MHz on a Bruker spectrometer. The chemical shifts (δ) of ^{1}H NMR resonances are expressed in ppm (parts per million) relative to TMS. The chemical shifts (δ) of ^{31}P NMR resonances are reported in ppm relative to the external standard of 85% H$_3$PO$_4$. Spin–spin coupling constants (J) were measured directly from the spectra and were given in Hz. The reactions were monitored by thin layer chromatography coated with silica gel. Enantiomeric excesses were determined on chiral GC with a Supelco β-Dex 120 (60 m × 0.25 mm) column.

All solvents were purified and dried by standard procedures and kept over a suitable drying agent prior to use. [RuCl$_2$(benzene)]$_2$ was purchased from Aldrich and used as received. The ketone substrates were obtained from Lancaster or previously synthesized and purified by washing with aqueous NaOH solution (0.1 M) and distillation or recrystallization prior to use. The MeO-PEG-immobilized ligand **3** was prepared as previously described [26]. (S,S)-DPEN **4** was prepared according to the literature strategy [27]. The loading amounts of the MeO-BIPHEP on the polymer were revealed to be 0.21 mmol/g by elemental analysis.

2.2. General procedure for preparation of supported diphosphine-Ru-diamine catalysts (S, SS)-5

The polymer supported ligand **3** (4.4 μmol) and [RuCl$_2$(benzene)]$_2$ (2 μmol) were dissolved in anhydrous and degassed DMF (1 mL) under argon. The mixture was heated to 100 °C for 10–20 min. After cooling to room temperature, the chiral diamine **4** (4 μmol) was added and the resultant mixture was heated to 80 °C and stirred for 2 h. The solvent was removed under high vacuum to provide the catalyst (S,SS)-**5**, which was used for hydrogenations without further purification.

2.3. Typical procedure for asymmetric hydrogenation of ketones

Standard procedure at Substrate/Complex = 1000: An autoclave containing a steel liner was charged with the Ru complex (S, SS)-**5** (20 mg, 4 μmol), i-PrOH (20 mL), ketone (4 mmol) and t-BuOK in t-BuOH (1 M, 0.08 mL, 0.08 mmol) in air. The reaction was pressurized to 20 atm with H$_2$. After stirring at room temperature for 12 h, the remaining H$_2$ was carefully released. After removal of the most solvent under vacuum, the mixture was cooled to 0 °C and cold Et$_2$O (20 mL) was added. The mixture was passed through a short silica gel column and the filtrate was concentrated. The residual product was used directly for NMR and chiral GC analysis. The stereochemistry of products was assigned by comparing the GC retention time or optical rotation signs with literature data [Supelco β-Dex 120

(60 m × 0.25 mm) column; carrier gas: nitrogen, 3 atm; injection temperature: 220 °C; detection temperature: 250 °C].

(R)-1-Phenylethanol [18]: column temperature: 100–140 °C, 1 °C/min, hold for 30 min; 35.7 min (R), 36.2 min (S); >99% conversion, 83.6% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.38–7.33 (m, 4H), 7.27 (t, J = 6.8 Hz, 1H), 4.91–4.87 (m, 1H), 1.88 (br, 1H), 1.51 (d, J = 6.4 Hz, 3H).

(R)-1-(2′-Methylphenyl)ethanol [28]: column temperature: 120–160 °C, 1 °C/min, hold for 40 min; 52.6 min (R), 54.9 min (S); >99% conversion, 84.2% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.51 (d, J = 6.4 Hz, 1H), 7.17–7.13 (m, 3H), 5.14–5.10 (m, 1H), 2.34 (s, 3H), 1.86 (br, 1H), 1.46 (d, J = 6.4 Hz, 3H).

(R)-1-(3′-Methylphenyl)ethanol [29]: $[\alpha]_D^{25}$ + 28.6° (neat), (lit. $[\alpha]_D^{24}$ + 39.7° (neat), pure R). Column temperature: 110–160 °C, 1 °C/min, hold for 40 min; 55.5 min (R), 57.0 min (S); >99% conversion, 82.6% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.26–7.08 (m, 4H), 4.88–4.83 (m, 1H), 2.36 (s, 3H), 1.83 (br, 1H), 1.48 (d, J = 6.4 Hz, 3H).

(R)-1-(4′-Methylphenyl)ethanol [18]: column temperature: 110–150 °C, 1 °C/min, hold for 40 min; 64.5 min (R), 65.5 min (S); >99% conversion, 85.7% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.27 (d, J = 7.8 Hz, 2 H), 7.18 (d, J = 7.8 Hz, 2H), 4.89–4.84 (m, 1H), 2.37 (s, 3H), 2.0 (br, 1H), 1.49 (d, J = 6.4 Hz, 3H).

(R)-1-(4′-Methoxyphenyl)ethanol [18]: column temperature: 150–180 °C, 1 °C/min, hold for 40 min; 60.2 min (R), 61.1 min (S); >99% conversion, 83.4% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.28 (d, J = 8.3 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.85–4.80 (m, 1H), 3.80 (s, 3H), 2.2 (br, 1H), 1.46 (d, J = 6.9 Hz, 3H).

(R)-1-(4′-Chlorophenyl)ethanol [18]: column temperature: 150–180 °C, 1 °C/min, hold for 40 min; 47.7 min (R), 48.7 min (S); >99% conversion, 62.4% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.34–7.30 (m, 4H), 4.91–4.86 (m, 1H), 1.82 (br, 1H), 1.47 (d, J = 6.4 Hz, 3H).

(R)-1-(4′-Fluorophenyl)ethanol [28]: column temperature: 150–180 °C, 1 °C/min, hold for 40 min; 28.9 min (R), 29.4 min (S); >99% conversion, 68.1% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.35–7.32 (m, 2H), 7.05–7.00 (m, 2H), 4.91–4.86 (m, 1H), 1.97 (br, 1H), 1.47 (d, J = 6.4 Hz, 3H).

(R)-1-(4′-tert-Butylphenyl)ethanol [18]: column temperature: 130–170 °C, 1 °C/min, hold for 40 min; 68.2 min (R), 69.1 min (S); >99% conversion, 96.5% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.38 (d, J = 8.7, 2H), 7.32 (d, J = 8.7, 2H), 4.91–4.87 (m, 1H), 1.76 (br, 1H), 1.51 (d, J = 6.4 Hz, 3H), 1.33 (s, 9H).

(R)-1-(3-Pyridyl)ethanol: column temperature [30]: $[\alpha]_D^{25}$ + 28.7° (c 0.90, EtOH), (lit. $[\alpha]_D^{24}$ −56.3° (c 1.00, EtOH), 99.6% ee, S). 120–150 °C, 1 °C/min, hold for 60 min; 68.7 min (R), 70.9 min (S); >99% conversion, 54.5% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.51–8.42 (m, 2H), 7.75–7.73 (m, 1H), 7.29–7.27 (m, 1H), 4.95–4.91 (m, 1H), 3.33 (br, 1H), 1.50 (d, J = 6.4 Hz, 3H).

(R)-1-(Thiophen-2-yl)ethanol: column temperature [28]: 130–160 °C, 1 °C/min, hold for 10 min and then 160–180 °C, 2 °C/min; 39.7 min (R), 40.6 min (S); >99% conversion, 72.6% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.27–7.24 (m, 1H), 6.99–6.93 (m, 2H), 5.17–5.12 (m, 1H), 1.90 (br, 1H), 1.61 (d, J = 6.4 Hz, 3H).

(*R*)-1-(1-Naphthyl)ethanol [18]: column temperature: 180–200 °C, 1 °C/min, hold for 40 min and then 200–220 °C, 2 °C/min, hold for 30 min; 75.6 min (*S*), 76.3 min (*R*); >99% conversion, 95.9% ee. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.12 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.56–7.47 (m, 3H), 5.69–5.64 (m, 1H), 2.09 (br, 1H), 1.67 (d, *J* = 6.4 Hz, 3H).

2.4. Catalyst recycle

An autoclave containing a steel liner was charged with the Ru complex (*S, SS*)-**5** (20 mg, 4 μmol), *i*-PrOH (20 mL), 1-acetonaphthone (0.68 g, 4 mmol) and *t*-BuOK in *t*-BuOH (1 M, 0.08 mL, 0.08 mmol) in air. The reaction mixture was degassed with 10 atm H$_2$ five times and finally the autoclave was pressurized to 20 atm with H$_2$. After stirring at room temperature for 12 h, the remaining H$_2$ was carefully released. After removal of the most solvent under vacuum, the mixture was cooled to 0 °C and cold Et$_2$O (20 mL) was added. The precipitated polymeric catalyst was collected by filtration for re-use in the next run. The filtrate was washed with water and brine and dried with anhydrous Na$_2$SO$_4$. After removal of the solvent the residuals were analyzed by NMR and chiral GC to determine the conversion rate and the enantiomeric excesses of the chiral alcohol product.

To start a new run, dry *i*-PrOH (20 mL), acetonaphthone (0.68 g, 4 mmol) and *t*-BuOK in *t*-BuOH (1 M, 0.08 mL, 0.08 mmol) were sequentially added to the catalyst-containing autoclave. The reaction was repeated under 20 atm H$_2$ as above. The third run was performed in the same manner as the second one.

3. Results and discussion

Our strategy commenced with the preparation of enantiomerically pure MeO-BIPHEP (*S*)-**1**, which was achieved using a well-documented procedure [20,21]. Demethylation of **1** with BBr$_3$ gave rise to HO-BIPHEP (*S*)-**2** in high yield [23]. The soluble polymer-supported BIPHEP ligand (*S*)-**3** was synthesized by condensation of HO-BIPHEP (*S*)-**2** with MeO-PEG-OMs

(Mw∼2100) according to our recently reported method [26] (Scheme 1). MeO-PEG was the choice of polymer support due to the following advantages: MeO-PEG is not only commercially available, inexpensive and nontoxic but also it has a broad solubility profile in common organic solvents (soluble in methanol, THF, dichloromethane, toluene, DMF, acetonitrile and water, yet insoluble in diethyl ether, *tert*-butyl methyl ether, cold 2-propanol and cold ethanol) [31]. The supported ligand (*S*)-**3** showed a predominant ^{31}P NMR signal at −14.05 ppm which was very close to the corresponding parent MeO-BIPHEP (−14.00). (*S,S*)-1,2-diphenylethylenediamine [(*S,S*)-DPEN] **4** was chosen as the diamine ligand. The ruthenium catalysts were prepared according to Noyori and Ohkuma's protocol [32]. Thus, for example, the MeO-PEG supported Ru-BIPHEP pre-catalyst was prepared by reacting the MeO-PEG supported BIPHEP ligand (*S*)-**3** with [RuCl$_2$(benzene)]$_2$ at 100 °C in DMF for 10 min, followed by treatment with one equivalent of (*S,S*)-1,2-diphenylethylenediamine **4** [(*S,S*)-DPEN] at 80 °C for additional 2 h. The resulting supported Ru complexes were investigated on the catalytic asymmetric reductions without further treatment.

2-Propanol was chosen as solvent, for the polymer-bound Ru complex **5** was highly soluble in warm 2-propanol, but insoluble in cold 2-propanol.

The reduction was carried out in 20 mL dry 2-propanol at 25 °C for 12 h in a molar ratio of aryl ketone:ligand:Ru:diamine:*t*-C$_4$H$_9$OK = 1000:1.1:1:1:20 with an initial H$_2$ pressure of 20 atm. Under this standard condition, the MeO-PEG supported [RuCl$_2${(*S*)-BIPHEP}{(*S,S*)-DPEN}] catalyst **5** exhibited very good enantioselectivity for the hydrogenation of a range of aryl ketones. The experimental results are summarized in Table 1. For instance, hydrogenation of 1-acetonaphthone and acetophenone catalyzed by MeO-PEG supported catalyst **5** gave 95.9% and 84.3% ee, respectively, which are comparable to the enantioselectivity reported by Noyori et al. under similar conditions using chiral BINAP-Ru-DPEN catalysts [10] (Table 1, entries 1 versus 3; entries 17 versus 19) and higher than that of the heterogeneous poly(BINAP)-Ru catalyst reported by Pu and co-workers
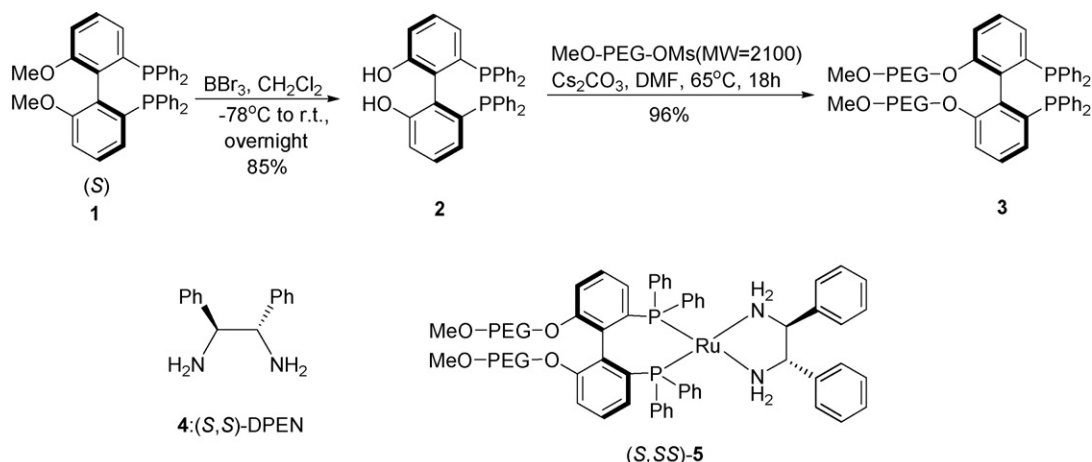
Scheme 1.

Table 1
Asymmetric hydrogenation of aryl ketones using the in situ prepared MeO-PEG supported [RuCl$_2${(S)-BIPHEP}{(S,S)-DPEN}] catalyst **5**

| Entry	Ketones	Ligand	Yield (%)[a]	ee (%)[b]
1		(S)-**3**/(S,S)-**4**	>99	83.6
2		(S)-**1**/(S,S)-**4**	>99	81.2
3		(S)-BINAP/(S,S)-**4**	>99	82.3
4		(S)-**3**/(S,S)-**4**	>99	84.2
5		(S)-**1**/(S,S)-**4**	>99	82.1
6		(S)-BINAP/(S,S)-**4**	>99	95[c]
7		(S)-**3**/(S,S)-**4**	>99	82.6
8		(S)-**3**/(S,S)-**4**	>99	85.7
9		(S)-**3**/(S,S)-**4**	>99	83.4
10		(S)-**3**/(S,S)-**4**	>99	62.4
11		(S)-**3**/(S,S)-**4**	>99	68.1
12		(S)-**3**/(S,S)-**4**	>99	96.5
13		(S)-**1**/(S,S)-**4**	>99	97.2
14		(S)-BINAP/(S,S)-**4**	>99	95.3
15		(S)-**3**/(S,S)-**4**	>99	54.5
16		(S)-**3**/(S,S)-**4**	>99	72.6
17		(S)-**3**/(S,S)-**4**	>99	95.9
18		(S)-**1**/(S,S)-**4**	>99	95.1
19		(S)-BINAP/(S,S)-**4**	>99	97[c]

Unless otherwise stated, the reaction was carried out at 25 °C using 0.4 mmol of aryl ketone in 20 mL of 2-propanol; aryl ketone:ligand:Ru:diamine: *t*-C$_4$H$_9$OK = 1000:1.1:1:1:20 (mol ratio); H$_2$ pressure: 20 atm; reaction time: 12 h.

[a] Determined by GC or ^{1}H NMR.

[b] Determined by chiral GC analysis. The absolute configuration of the product was determined by comparison of GC retention time or optical rotation sign with literature data and all were (R).

[c] See ref. [32].

Table 2

Hydrogenation of 1-acetonaphthone using the in situ prepared MeO-PEG supported BIPHEP-Ru-DPEN catalyst **5**
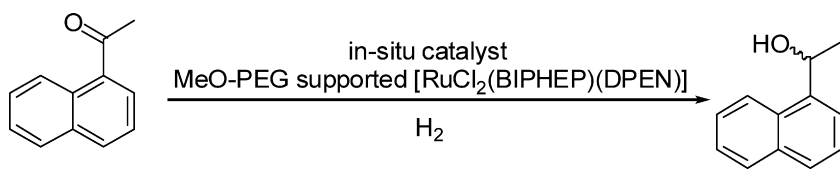
Entry	Ligand	Conversion (%)[a]	ee (%)[b]	Configuration[c]
1	(S)-**1**/(S,S)-**4**	>99	95.1	R
2	(S)-**3**/(S,S)-**4**	>99	95.9	R
3	(R)-**1**/(S,S)-**4**	>99	16.2	S
4	(R)-**3**/(S,S)-**4**	>99	10.3	S
5	(S)-**3**/(±)-**4**	>99	75.9	R

All reactions were carried out at 25 °C using 0.4 mmol of aryl ketone in aryl ketone:ligand:Ru:diamine: t-C_4H_9OK = 1000:1.1:1:1:20 (mol ratio); 20 mL of 2-propanol; H_2 pressure: 20 atm; reaction time: 12 h.

[a] Determined by GC analysis or ^{1}H NMR.
[b] Determined by chiral GC analysis.
[c] The product absolute configuration was determined by comparison of GC retention time or optical rotation sign with literature data.

[13] and also comparable to that of homogeneous dendritic BINAP-Ru-DPEN catalysts reported by Fan and coworkers [14].

Interestingly, hydrogenation of 4′-*tert*-butyl-acetophenone catalyzed by MeO-PEG supported catalyst **5** provided excellent enantioselectivity up to 96.5% ee, which is even higher than that of the homogeneous BINAP-Ru-DPEN catalyst under comparable conditions (Table 1, entries 12 versus 14) and nanoparticles supported BINAP-Ru-DPEN catalysts, which was recently reported by Lin and coworkers [17].

The enantioselective reduction of heteroaryl methyl ketones, such as 3-acetylpyridine and 2-acetylthiophene, was carried out under similar conditions. The reduction was found to proceed with a high conversion (>99%) and good enantioselectivity (Table 1, entries 14 and 15), providing the optically active (R)-1-(heteroaryl)ethanol.

Compared to the parent homogeneous catalyst, the MeO-PEG supported BIPHEP-Ru-DPEN complex offered similar or even higher enantioselectivity (Table 1, entries 1 versus 2, entries 4 versus 5, entries 12 versus 13, entries 17 versus 18). This indicated that the attachment of the active catalyst to the soluble polymer MeO-PEG had no or little influence or even was more profitable to the asymmetric hydrogenation of simple aryl ketones. We also found that the polymer supported ligand **3** was so stable that it could be stored for months while maintaining high activity and enantioselectivity. As such, the work-up of the catalyst could be done in the air conditions, which facilitated the recovery extremely.

We also found that the match of the steric environment of the chiral diamine with that of the MeO-PEG supported chiral BIPHEP ligand plays a pivotal role for achieving high enantioselectivity, which is consistent with Noyori and Ohkuma's observation [10]. Using hydrogenation of 1-acetonaphthone as a standard reaction, we found that matching combination of MeO-PEG supported $RuCl_2$[(S)-BIPHEP] (**3**) and (S,S)-DPEN (**4**) resulted in 95.9% ee, while the mismatching combination of MeO-PEG supported $RuCl_2$[(R)-BIPHEP] (**3**) and (S,S)-DPEN

(**4**) gave only 10.3% ee (Table 2, entries 2 versus 4). It is worth noting that the combination of MeO-PEG supported $RuCl_2$[(S)-BIPHEP] (**3**) with racemic DPEN offered as high as 75.9% ee (Table 2, entry 5). The mismatching polymer supported catalyst gave even lower enantioselectivity than the corresponding mismatching monomeric MeO-BIPHEP-Ru-DPEN catalyst. This may be attributed to the restrictions of the polymer matrix (Table 2, entries 3 versus 4).

An important feature of the design of soluble polymer supported catalyst is the easy and reliable separation and reuse of the expensive chiral catalyst. In this study, the catalyst was facilely separated under the air condition in the light of high stability of the supported catalyst. Upon the completion of the reaction, most solvent and volatiles were removed. Then, cold ether was added to the mixture and the catalyst was quantitatively precipitated and recovered via filtration. The filtrate was colorless and ICP analysis indicated that the content of metal Ru was less than 1 ppm. The recovered catalyst was reused for at least five cycles with essentially similar activity, and the enantioselectivity dropped due to the influence of moisture in the reaction mixture

Table 3

Asymmetric hydrogenation of 1′-acetonaphthone by [$RuCl_2${(S)-**3**}{(S,S)-**4**}]: recycling of the catalyst

Reusing run	Time (h)	Yield (%)[a]	ee (%)[b]
1	12	99	95.9
2	12	99	94.5
3	12	99	94.2
4	12	98	92.1
5	24	95	89.1
6	24	43	73.1

All reactions were carried out at 25 °C using 0.4 mmol of aryl ketone in aryl ketone:ligand:Ru:diamine:t-C_4H_9OK = 1000:1.1:1:1:20 (mol ratio); 20 mL of 2-propanol; H_2 pressure: 20 atm; reaction time: 12 h.

[a] Isolate yield.
[b] Determined by chiral GC analysis. The product configuration was determined by comparison of GC retention time or optical rotation sign with literature data and was (R).

and air condition (as shown in Table 3). At the sixth run, the activity and enantioselectivity dropped sharply, maybe due to the decomposition of the catalyst.

4. Conclusion

In summary, we presented in this paper a MeO-PEG supported BIPHEP-Ru-DPEN catalyst system [(*S*,*SS*)-**5**]. The catalyst is easy to prepare and exceptionally practical to use. The reduction of a series of simple aryl ketones have been successfully performed at a 0.1% mol catalyst dosage with high enantioselectivity up to 96.5% ee. For the asymmetric hydrogenation of 4′-*tert*-butyl-acetophenone, even higher ee than that obtained with the unattached homogeneous BINAP-Ru-DPEN catalyst has been achieved under similar conditions. The catalyst showed high air stability and could be recovered easily and the recycled catalysts were shown to maintain their efficiency in several consecutive runs. The use of these recoverable MeO-PEG supported-BIPHEP ligands in other transformations is in progress.

Acknowledgements

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