ELSEVIER

Journal of Molecular Catalysis A: Chemical 159 (2000) 37–43

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

A highly effective water-soluble polymer-supported catalyst for the two-phase asymmetric hydrogenation: preparation and use of a PEG-bound BINAP ligand

Qing-Hua Fan [a], Guo-Jun Deng [a], Xiao-Min Chen [a], Wen-Chun Xie [a], Da-Zhi Jiang [a], Dong-Sheng Liu [b], Albert S.C. Chan [b,*]

[a] *Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[b] *Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, People's Republic of China*

Abstract

A new type of amphiphilic PEG-bound BINAP ligand was synthesized through polycondensation of 5,5′-diamino BINAP (**1**), polyethylene glycol and terephthalyol chloride in the presence of pyridine. It was proven that ruthenium complex based on the new polymeric ligand was an effective catalyst for the asymmetric hydrogenation of prochiral α,β-unsaturated carboxylic acids in both ethyl acetate/water two-phase and in methanolic solvent systems. The activity and/or enantioselectivity in two-phase systems were observed to be higher than that in ethyl acetate or methanol–water homogeneous systems. The replacement of water with ethylene glycol increased the activity and enantioselectivity. The activity of the new catalyst was shown to be about 30 times higher in the two-phase hydrogenation of 2-(6′-methoxy-2′-naphthyl)-acrylic acid than the Ru(BINAP-4SO_3Na) catalyst without the long hydrophilic polymer chain, which illustrated the importance of the amphiphilic structure of the polymeric ligand.

Keywords: Water-soluble catalyst; Polymer-supported catalyst; Phosphine; Asymmetric hydrogenation; Amphiphile

1. Introduction

Homogeneous asymmetric catalysis is one of the most important developments in modern chemistry over the past three decades. Many chiral catalysts are known to exhibit high activities and enantioselectivities [1]. However, a major problem associated with the most homogeneous catalyst systems is the separation and recycling of the expensive chiral catalyst. One way to solve this problem is to use water-soluble ligands. Since the rhodium-TPPTS [TPPTS = $P(C_6H_4$-*m*-$SO_3Na)_3$] system was first applied in industry at Hoechst in Oberhausen, Germany, the idea of two-phase catalysis, which simplified the separation of catalysts from products by decantation, has become a very active

E-mail address: fanqh@infoc3.icas.ac.cn (Q.-H. Fan).
* Corresponding author. Tel.: +86-10-6255-4472; fax: +86-10-6255-9373.

1381-1169/00/$ - see front matter
PII: S1381-1169(00)00168-0

field of research [2–4]. Over the past several decades, many water-soluble ligands have been synthesized. New methods have been developed for asymmetric hydroformylation [5], asymmetric hydrogenation [6], amination [7] and even bioorganic applications [8]. The activities and selectivities were highly obtained in the hydroformylation of olefins catalyzed by rhodium complexes containing sulfonated phosphine ligands such as BISBIS-Na [9], BINAS-Na [10], BINAS6-Na [11] and others. In striking contrast to the broad success in hydroformylation of olefins in two-phase catalysis, only limited success has been achieved on the asymmetric hydrogenation of prochiral substrates. The well-known water-soluble chiral sulfonated phosphine ligands such as BDPP [12,13], Chiraphos [12,13] and BINAP [14,15] were used as ligands in the asymmetric hydrogenation of amino acid precursors and α,β-unsaturated carboxylic acids in two-phase systems. However, in most cases, the activity and/or enantioselectivity of the water-soluble catalysts are normally lower than those of the organo-soluble parent catalysts. The lower activity was attributed to the limited solubility of the organic substrates in the aqueous solution of the catalyst and the poor enantioselectivity partially due to the solvation of water. The reaction rates and enantioselectivities can be increased by the addition of cosolvents such as alcoholic solvent, surfactants as well as inorganic salts, which enhance mutual solubility or mobility of the components across the phase boundary or increase the concentration of the catalyst to the interface [4,16–18]. The remarkable enhancement of activity and enantioselectivity with the addition of surfactants in some cases was explained by the assumption of the formation of micelles [4,16,17]. These micelles may act as ''microreactors'' [19], and thus adjust the catalyst–substrate orientation or distinguished conformations of the chirality-inducing catalyst similar to that featured in organic solvent. The micelle-forming concept of the surfactant thus encouraged us to develop amphiphilic polymer-supported catalyst, which provides a lipophilic metal center and a hydrophilic long chain. In contrast to the broad use of sulfonated phosphine ligands, water-soluble polymeric ligands were used to a lesser extent [20–25].

We reported herein the synthesis of a new amphiphilic polymer-supported BINAP ligand and its use in ruthenium-catalyzed hydrogenation of α,β-unsaturated carboxylic acids in two-phase system. In choosing a model ligand for this study, we noticed that from among all the known chiral phosphine ligands, which had been studied for asymmetric catalysis, BINAP was probably the most versatile and effective [26]. Both rhodium and ruthenium BINAP complexes have been extensively studied and several commercial processes based on these catalysts have been developed [27].

2. Experimental

All experiments were carried out under nitrogen atmosphere by using standard Schlenk-type techniques, or performing in a glovebox.

2.1. Materials and equipment

All solvents were dried using standard, published methods and were distilled under nitrogen atmosphere before use. Except as specified, commercial reagents were used as received without further purification. 5,5′-Diamino-2,2′-bis(diphenylphosphino)-1,1′-binaphthyls (5,5′-diamino BINAP (**1**)) was synthesized according to published method [28].

The nuclear magnetic resonance (NMR) spectra were taken on a BRUKER Model AVDANCE DPX 400 spectrometer (400 MHz ^{1}H and 162 Hz ^{31}P) using tetramethylsilane for ^{1}H as an internal standard, 85% of H_3PO_4 in D_2O for ^{31}P as an external standard. All signals are reported in parts per million. For high pressure hydrogenation, 50 ml stainless autoclave equipped with a glass liner was used.

2.2. Synthesis of amphiphilic PEG-bound BINAP ligand

In a three-necked flask, which was equipped with a stirring bar, a solid chemical transferring funnel, and a reflux condenser, was added 2.00 g (0.5 mmol) polyethylene glycol (Mw = 4000), 2.0 ml pyridine and 5 ml dichloromethane. To this mixture was added portionwise 130 mg (0.64 mmol) of terephthaloyl chloride in a period of 10 min. A solution of 100 mg (0.153 mmol) of (*R*)-5,5′-diamino-BINAP in 2 ml dichloromethane was further added dropwise. The reaction mixture was stirred at 40–50°C for 2 h and at room temperature overnight under nitrogen, and then was poured into a flask containing 100 ml of cool ethyl ether. The precipitated polymer was collected by filtration and washed with cool ethyl ether, methanol and ethyl ether. The polymer was then collected and dried in vacuo to give 2.14 g PEG-bound BINAP ligand (98.0% theoretical yield). The amount of BINAP moieties in the polymer was 3.2 wt.%, which was determined by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2): 3.27–3.80 (polyethylene glycol peaks), 6.79 (t, $J = 7.80$ Hz, 2 H), 7.02–7.20 (m, 20 H), 7.45 (t, 2 H) 7.60 (s, 2 H), 8.09–8.16 (m); ^{31}P NMR (CD_2Cl_2): −16.82.

2.3. Preparation of in situ PEG-bound Ru(BINAP) catalyst

A mixture of 500 mg (0.026 mmol BINAP) of PEG-bound BINAP ligand and 7.5 mg (0.012 mmol) of $[Ru(cymene)Cl_2]_2$ in 5 ml toluene/MeOH (1/1, v/v) was magnetically stirred under N_2 atmosphere at about 50–60°C for 60 min. The reaction mixture was dried under vacuum to give pale yellow powder. The in situ prepared catalyst was directly used without further purification. ^{31}P NMR ($CDCl_3$): 38.6 (d, $J = 63.0$Hz), 24.2 (d, $J = 60.6$ Hz).

2.4. Standard asymmetric hydrogenation

In a typical experiment, the 50-ml glass-lined stainless autoclave with a magnetic stirring bar was charged with 0.1 mmol of substrate, 0.001 mmol ruthenium of PEG-bound Ru(BINAP) catalyst, 0.2 mmol of NEt_3 and 3 ml of the corresponding solvent. The autoclave was closed and was pressurized with H_2 to 4–60 atm. The mixture was stirred with a magnetic stirrer under the H_2 pressure at 24–30°C. After the reaction time, the H_2 was vented. The final mixture was extracted with ethyl acetate (3×5 ml). The combined organic phase was washed twice with saturated sodium chloride aqueous solution and dried over magnesium sulfate and analyzed by gas chromatography (GC). Enantioselectivity excesses were measured by GC or HPLC using a chiral column after the acids had been transformed into the corresponding methyl esters.

3. Results and discussion

3.1. Preparation of amphiphilic PEG-bound BINAP ligand and in situ ruthenium catalyst

Since BINAP itself cannot be easily attached to a polymer, (**1**) was used for this study. PEG-bound BINAP ligand (**2**) was easily synthesized through polycondensation of *R*-**1**, polyethylene glycol and terephthaloyl chloride in the presence of pyridine in dichloromethane (Fig. 1). The PEG-bound ligand (**2**) was precipitated upon the addition of ethyl ether, which had more than 98% yield. This type of catalyst [Ru(BINAP)(cymene)Cl_2] was prepared in situ by the reaction of the precipitated ligand (**2**) with $[Ru(cymene)Cl_2]_2$ in methanol–toluene (1:1, v/v) at 50–60°C for 60 min. Organic solvent was evaporated and the catalyst was directly used in the hydrogenation reaction without further purification. The obtained catalyst was well soluble in water. The ^{31}P NMR of this new PEG-bound BINAP ligand and its ruthenium complex was in close agreement to those of the parent ones.

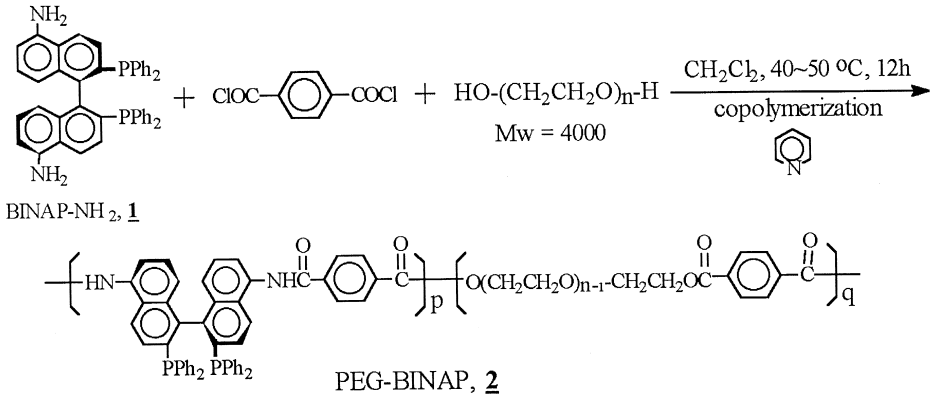
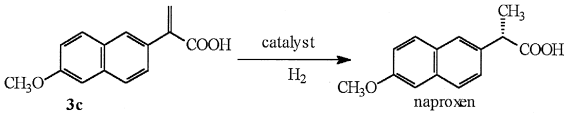


Fig. 1. Synthesis of PEG-bound BINAP ligand via polycondensation.

3.2. Asymmetric hydrogenation

In order to assess the efficiency of the new catalyst in asymmetric catalysis, the α, β-unsaturated acids, 2-[*p*-(2-methylpropyl) phenyl]acrylic acid (**3a**), trans-2,3-dimethyl-acrylic acid (**3b**) and 2-(6′-methoxy-2′-naphthyl)acrylic acid (**3c**) were chosen as standard reactions for comparing their performances. The choice was based on the fact that Ru(BINAP)-type catalysts were effective in the asymmetric hydrogenation of 2-arylacrylic acids and the reduced products represented an important class of anti-inflammatory drugs.



catalyst = PEG-BINAP ligand + $[Ru(cymene)Cl_2]_2$

3.2.1. Homogeneous catalytic studies

According to the previous studies on Ru(BINAP)-type complexes catalyzed hydrogenation of 2-arylacrylic acids, the solvent and some additives such as organic base are known to affect the activity and enantioselectivity of the reaction. In order to choose the preferred conditions for two-phase systems and for the purpose of comparison, we focused our effort on the homogeneous hydrogenation of substrate **2a** by using different solvent systems in our initial study. The catalytic results were summarized in Table 1. In contrast to the most sulfonated phosphine systems, the PEG-bound Ru(BINAP) catalyst was quite soluble in neat methanol and performed the highest activity and enantioselectivity in the hydrogenation of **2a** in the presence of triethylamine (entries 1 and 2). The triethylamine improved the activity and enantioselectivity significantly (entries 1, 2 and 3, 4 and 5). Similar effects were observed in the parent $[Ru(BINAP)(cymene)Cl_2]$ catalyzed hydrogenation of α,β-unsaturated carboxylic acids with the addition of triethylamine [15]. It was indicated that the presence of water tended to lower the activity and enantioselectivity (entries 4 and 5). This was probably attributed to the compositional change of the ruthenium catalyst and the solvation of the catalytic intermediates in the presence of water [13–15]. Moderate activity and enantioselectivity were observed when ethylene glycol was used as solvent (entry 6). Hydrogenation conducted in aprotic solvent such as ethyl acetate gave poor enantioselectivity and low activity compared to those in methanol (entry 7). A slight increase of enantioselectivity was obtained when water-saturated ethyl acetate was used as solvent, albeit with slow activity (entries 8).

3.2.2. Two-phase catalytic studies

In our initial study on two-phase catalysis, we chose ethyl acetate as the organic solvent.

Table 1
Homogeneous hydrogenation of **3a** catalyzed by PEG-bound Ru(BINAP)[a]

Entry	S/C[b]	Solvent	NEt_3/Substrate	Time/h	TOF/h^{-1}[c]	e.e./%[d]
1	100	MeOH	4:1	1	92.2	86.4
2	125	MeOH	2:1	1	58.1	82.4
3	125	MeOH	0	2	< 5.0	–
4	125	MeOH/H_2O	2:1	2	45.0	74.3
5	125	MeOH/H_2O	0	2	3.2	34.1
6	125	EG[e]	2:1	2	45.0	67.0
7	125	EA[f]	2:1	2	37.4	32.4
8	125	EA (saturated H_2O)	2:1	2	17.5	49.8

[a]Hydrogenation was carried out in 0.016 M **3a** solution under the following conditions: reaction temperature = 24–30°C; reaction pressure: 60 atm H_2.
[b]Substrate to ruthenium ratio.
[c]All TOFs mentioned are average TOFs calculated over the given reaction time.
[d]Based on GLC analysis with a Chrompack Chirasil-dex (25 m × 0.25).
[e]EG = ethylene glycol.
[f]EA = ethyl acetate.

The PEG-bound Ru(BINAP) catalyst was effective in the ethyl acetate/water two-phase hydrogenation of substrate **3a**. When substrate **3a** was charged into the hydrogenation reactor along with an aqueous solution of the ruthenium catalyst (3 ml of 1:1 ethyl acetate/water and S/C = 125), 81.2% conversion and 63.9% e.e. were observed in 2 h with an initial turnover frequency of 50.8 h^{-1} (entry 1 in Table 2). In contrast to methanol, water and ethyl acetate were poor solvents for the hydrogenation (entries 4, 7 and 8 in Table 1). Therefore, it was reasonable that the activity and enantioselectivity were lower in the ethyl acetate/water two-phase hydrogenation than in the homogeneous system in methanol (entry 2 in Table 1 and entry 1 in Table 2). However, it was clearly observed that the two-phase reaction rate was higher than the homogeneous systems in ethyl acetate or methanol–water (1:1) (entries 4, 7, 8 in Table 1 and entry 1 in Table 2). Turnover frequencies of 50.8 and 17.5 h^{-1}, and e.e. of 63.9% and 49.8 % were observed in ethyl acetate/water two-phase and water-saturated ethyl acetate homogeneous hydrogenation, respectively (entry 1 in Table 2 and entry 8 in Table

Table 2
Two-phase hydrogenation of **3a** catalyzed by PEG-bound Ru(BINAP) catalyst[a]

Entry	S/C	Solvent	Time/h	Conversion/%	TOF/h^{-1}[b]	e.e./%[c]
1	125	EA/H_2O	2	81.2	50.8	63.9
2	100	EA/H_2O + SDS[d]	1	40.1	40.1	61.6
3	100	EA/H_2O + SDS[e]	1	55.0	55.0	66.0
4	100	EA/EG	1	66.5	66.5	70.0
5	125	EA/EG + SDS[e]	1	61.6	77.0	82.2
6	125	Toluene/H_2O	2	16.7	8.3	47.4
7	125	Toluene/EG	2	48.2	24.1	78.4

[a]Hydrogenation was carried out in 0.016 M **3a** solution under the following conditions: reaction pressure: 60 atm H_2. Subtrate/NEt_3 = 2:1 (mol/mol) except for entry 6 (4:1); reaction temperature = 24–30°C.
[b]All TOFs mentioned are average TOFs calculated over the given reaction time.
[c]Based on GLC analysis with a Chrompack Chirasil-dex (25 m × 0.25).
[d]Substrate/SDS = 10:1 (mol/mol).
[e]Substrate/SDS = 1:1 (mol/mol).

1). It was shown that the hydrogenation reaction did not take place in ethyl acetate phase and phase boundary. The striking improvement of activity and enantioselectivity was probably due to the formation of micelles by the amphiphilic catalyst itself, which provided a microenvironment different from ethyl acetate and water systems for hydrogenation reactions. These results are consistent with the rationale of designing amphiphilic polymeric chiral catalysts.

The observation of a further improvement of activity after the addition of nonfunctional amphiphiles like SDS to the two-phase system due to the formation of mixed micelles was expected. In fact, there was no observation in the presence of small concentrations of SDS (entry 2). Slight enhancement of activity and enantioselectivity was obtained in the presence of high concentration of SDS (entry 3). The replacement of water by ethylene glycol as polar phase increased the activity and enantioselectivity (entry 4). This was partially due to the elimination of the negative effect of water. The highest activity (77.0 h^{-1} TOF) and enantioselectivity (82.2% e.e.) were observed in ethyl acetate/ethylene glycol two-phase hydrogenation in the presence of SDS (entry 5). It was interesting to note that the activity and enantioselectivity of the two-phase hydrogenation were higher than those of ethylene glycol homogeneous hydrogenation (entry 6 in Table 1 and entry 4 in Table 2). Also, it was probably due to the formation of micelles by the amphiphilic catalyst itself which preferred the hydrogenation reaction over the homogeneous system. In comparison with ethyl acetate/water system, toluene/water two-phase hydrogenation showed low activity and enantioselectivity (entry 6). High enantioselectivity with low activity was observed in toluene/ethylene glycol system (entry 7).

The asymmetric hydrogenation of substrates **3b** and **3c** in two-phase and homogeneous systems had been studied and the results were summarized in Table 3. The results of **3b** and **3c** were similar to the observation in the asymmetric hydrogenation of **3a**. It showed that the amphiphilic PEG-bound Ru(BINAP) catalyst was effective in the two-phase systems. Turnover frequencies of 3.92 and 0.25 h^{-1}, and e.e. of 83.0% and 17.8% were observed in ethyl acetate/water two-phase and ethyl acetate homogeneous hydrogenation of **3b**, respectively (entries 1 and 6). The replacement of water with ethylene glycol gave higher activity (entries 2, 8 to 1, 7). The activity of hydrogenation of **3c** in ethyl acetate/water two-phase system decreased sharply compared to that in methanol among the

Table 3
Two-phase and homogeneous hydrogenation of **3b** and **3c** catalyzed by PEG-bound Ru(BINAP) catalyst[a]

Entry	Substrate	H_2/atom	Solvent	Time/h	Conversion/%	TOF/h^{-1}[b]	e.e./%[c]
1	**3b**	4	EA/H_2O	24	90.1	3.92	83.0
2	**3b**	4	EA/EG	24	100	–	77.1
3	**3b**	4	MeOH	15	80.0	5.33	89.2
4	**3b**	4	MeOH/H_2O	68	86.4	1.27	85.3
5	**3b**	4	EG	24	67.0	4.46	74.5
6	**3b**	4	EA	24	5.94	0.25	17.8
7	**3c**	60	EA/H_2O	8	80.4	10.1	76.8
8	**3c**	60	EA/EG	8	100	–	86.4
9	**3c**	60	MeOH	1	74.0	74.0	87.2
10	**3c**	93	MeOH	–	–	131.0	88.2[d]
11	**3c**	95	EA/H_2O	84	53.6	0.34	78.4[d]

[a] Hydrogenation was carried out in 0.01–0.04 M solution under the following conditions: subtrate/catalyst = 100 (mol/mol) except for entry 11 (substrate/catalyst = 50). Subtrate/NEt_3 = 2:1 (mol/mol) except for entries 7–9 (4:1); reaction temperature = 24–30°C.

[b] All TOFs mentioned are average TOFs calculated over the given reaction time.

[c] Based on GLC analysis with a Chrompack Chirasil-dex (25m × 0.25).

[d] [Ru(BINAP-4SO_3Na)Cl_2] was used as catalyst (Ref. [15]).

three cases (entries 7 and 9, 1 and 3, and entry 1 in Table 2 and entry 2 in Table 1). This was probably due to the lower solubility of **3c** than those of **3a** and **3b** in water. The activity of the amphiphilic PEG-bound Ru(BINAP) catalyst was about 30 times higher than the Ru(BINAP-4SO_3Na) catalyst by comparing the experimental results of entries 7 and 11.

4. Conclusion

We have developed a new, easily prepared and highly effective amphiphilic polymeric catalyst for the asymmetric hydrogenation in two-phase systems. The activity and/or enantioselectivity in ethyl acetate/water two-phase system were observed to be higher than those in ethyl acetate or methanol–water (1:1) homogeneous systems in the asymmetric hydrogenation of α,β-unsaturated carboxylic acids, **3a**, **3b** and **3c**. The replacement of water with ethylene glycol increased the activity and enantioselectivity. The activity of the amphiphilic PEG-bound Ru(BINAP) catalyst was shown to be 30 times higher than that of Ru(BINAP-4SO_3Na) reported by Van and Davis [15] in the two-phase asymmetric hydrogenation of 2-(6′-methoxy-2′-naphthyl)-acrylic acid.

Tailor-made polymer support of the PEG-bound BINAP ligand and synthesis of amphiphilic dendritic BINAP ligands are now in progress in our laboratory in order to evaluate the positive effect of micelle-forming on this reaction.

Acknowledgements

We would like to thank the Hong Kong Polytechnic University, the Hong Kong Research Grant Council (project no. ERB03), Foundation of the President Chinese Academy of Science and the Foundation of the Director of the Institute of Chemistry, The Chinese Academy Science for financial support. Technical assistance from Mr. Shizhong Tian is appreciated.

References

[1] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, 2nd ed., Wiley, New York, 1992.
[2] E.G. Kuntz, CHEMTECH (1987) 570.
[3] W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem., Int. Ed. Engl. 32 (1993) 1524.
[4] B. Cornils, W.A. Herrmann, Aqueous Phase Organometallic Catalysis-Concept and Applications., Wiley-VCH, Weinherim, 1998.
[5] L. Maat, G. Papadoginakis, R.A. Sheldon, Chem. Commun. (1994) 2659.
[6] K.T. Wan, M.E. Davis, Nature 370 (1994) 449.
[7] T. Prinz, W. Keim, B. Drießen-Hölscher, Angew. Chem., Int. Ed. Engl. 35 (1996) 1708.
[8] I.T. Horvath, F. Joo, in: Aqueous Organometallic Chemistry and Catalysis, NATO Advanced Research Workshop, Debrecen, Hungary, August 29–Setember 1, 1994.
[9] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger, H. Bahrmann, H. Kottmann, J. Mol. Catal. A: Chem. 97 (1995) 65.
[10] H. Bahrmann, H. Bach, C.D. Frohning, H.J. Kleiner, P. Lappe, D. Peters, D. Regnat, W.A. Herrmann, J. Mol. Catal. A: Chem. 116 (1997) 49.
[11] R.W. Eckl, T. Priermeier, W.A. Herrmann, J. Organomet. Chem. 532 (1997) 243.
[12] L. Lecomte, D. Sinou, J. Mol. Catal. 52 (1989) L21.
[13] Y. Amrani, L. Lecomte, D. Sinou, J. Bakos, I. Toth, B. Heil, Organometallics 8 (1989) 542.
[14] K.T. Wan, M.E. Davis, Tetrahedron: Asymmetry 4 (1993) 2461.
[15] K.T. Wan, M.E. Davis, J. Catal. 148 (1994) 1.
[16] G. Oehme, E. Paetzold, R. Selke, J. Mol. Catal. 71 (1992) L1.
[17] A. Kumar, G. Oehme, J.P. Roque, M. Schwarze, R. Selke, Angew. Chem., Int. Ed. Engl. 33 (1994) 2197.
[18] S. Trinkhaus, R. Kadyrov, R. Selke, J. Holz, L. Götze, A. Börner, J. Mol. Catal. A: Chem. 144 (1999) 15.
[19] C.A. Bunton, F. Nome, F.H. Quina, L.S. Romsted, Acc. Chem. Res. 24 (1991) 357.
[20] Y. Amrani, D. Sinou, J. Mol. Catal. 36 (1986) 319.
[21] I. Grassert, U. Schmidt, S. Ziegler, C. Fischer, G. Oehme, Tetrahedron: Asymmetry 9 (1998) 4193.
[22] T. Malmstrom, C. Andersson, Chem. Commun. (1996) 1135.
[23] D.E. Bergbreiter, L. Zhang, V.M. Mariagnanam, J. Am. Chem. Soc. 115 (1993) 9295.
[24] A.N. Ajjou, H. Alper, J. Am. Chem. Soc. 120 (1998) 1466.
[25] Z. Jin, X. Zheng, B. Fell, J. Mol. Catal. A: Chem. 116 (1997) 55.
[26] R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345.
[27] R. Noyori, CHEMTECH (1992) 360.
[28] T. Okano, H. Kumobayashi, S. Akutagawa, J. Kiji, H. Konishi, K. Fukuyama, Y. Shimano, U.S. Patent 4,705,895, 1987.