A new class of polymeric monodentate phosphoramidite ligands for asymmetric hydrogenation of α-dehydroamino acid derivatives

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Abstract

A new class of rigid and sterically regular polymeric monodentate phosphoramidite ligands derived from (*R*)-BINOL were prepared and applied in the Rhodium-catalyzed asymmetric hydrogenation of α-dehydroamino acid derivatives. High catalytic activities and enantioselectivities (up to 99% ee) were achieved, which are comparable to those obtained with MonoPhos. The optimal mol ratio of Rh/ligand was proved to be 1:1.

Keywords: Asymmetric hydrogenation, monophosphine ligands, polymer, binol

Introduction

Transition-metal-catalyzed asymmetric hydrogenation of prochiral olefins is an important method for achieving highly enantiopure molecules, which were widely used in pharmacy and fine chemicals industries.[1,2] Chiral phosphine ligands, especially bisphosphorus derivatives, have been widely used for asymmetric hydrogenation.[3] More recently, due to the readily accessibility, high stability and excellent performance in the catalytic reactions,[4] many chiral monophosphine ligands such as phosphonites, phosphites and phosphoramidites have been emploied in asymmetric hydrogenation of functionalized olefins showing high enantioselectivities.[5] However, for most homogeneous catalysis systems, the separation of the catalyst was a problem. Some polymer-supported chiral monophosphine catalysts have been developed for asymmetric hydrogenation to overcome the difficulties.[6] In the classical approaches, these polymer-supported ligands were usually obtained by tethering phosphine ligands with a flexible and linear polymer backbone such as polyethylene glycol or polystyrene. The mutual winding or self-twisting caused by the flexibility of polymer backbone might lead to the change of the microenvironment of the active centers. Compared to the corresponding homogeneous ligands, polymer-supported catalysts often displayed reduced enantioselectivity and less efficiency in the catalysis.[7, 8] As an improvement, dendrimer supported phosphoramidite ligands have been developed and successfully applied in asymmetric hydrogenations.[9]

Pu [10-13] has developed a novel main-chain chiral conjugated polymers derived from (R)-BINOL and studied their applications in asymmetric catalysis reactions. This new type of polymers possessed a high degree of structural rigidity, therefore the steric and electronic environments of BINOL were difficult to be altered. In this paper, we report the synthesis of a new class of polymeric monodentate phosphoramidites ligands derived from (R)-BINOL and their applications in the rhodium-catalyzed asymmetric hydrogenation of α-dehydroamino acid derivatives.

Results and Discussion

Preparation of ligands

The preparation of polymeric monodentate phosphoramidites (R)-**2** and (R)-**3** derived from (R)-BINOL is illustrated in Scheme 1. Treatment of the corresponding secondary amine with PCl$_3$/NEt$_3$ and subsequent reaction with (R)-**1**[10] in the presence of NEt$_3$ could provide the desired product as a white solid. The structures of (R)-**2** and (R)-**3** were confirmed by ^{1}H NMR, ^{31}P NMR spectra.
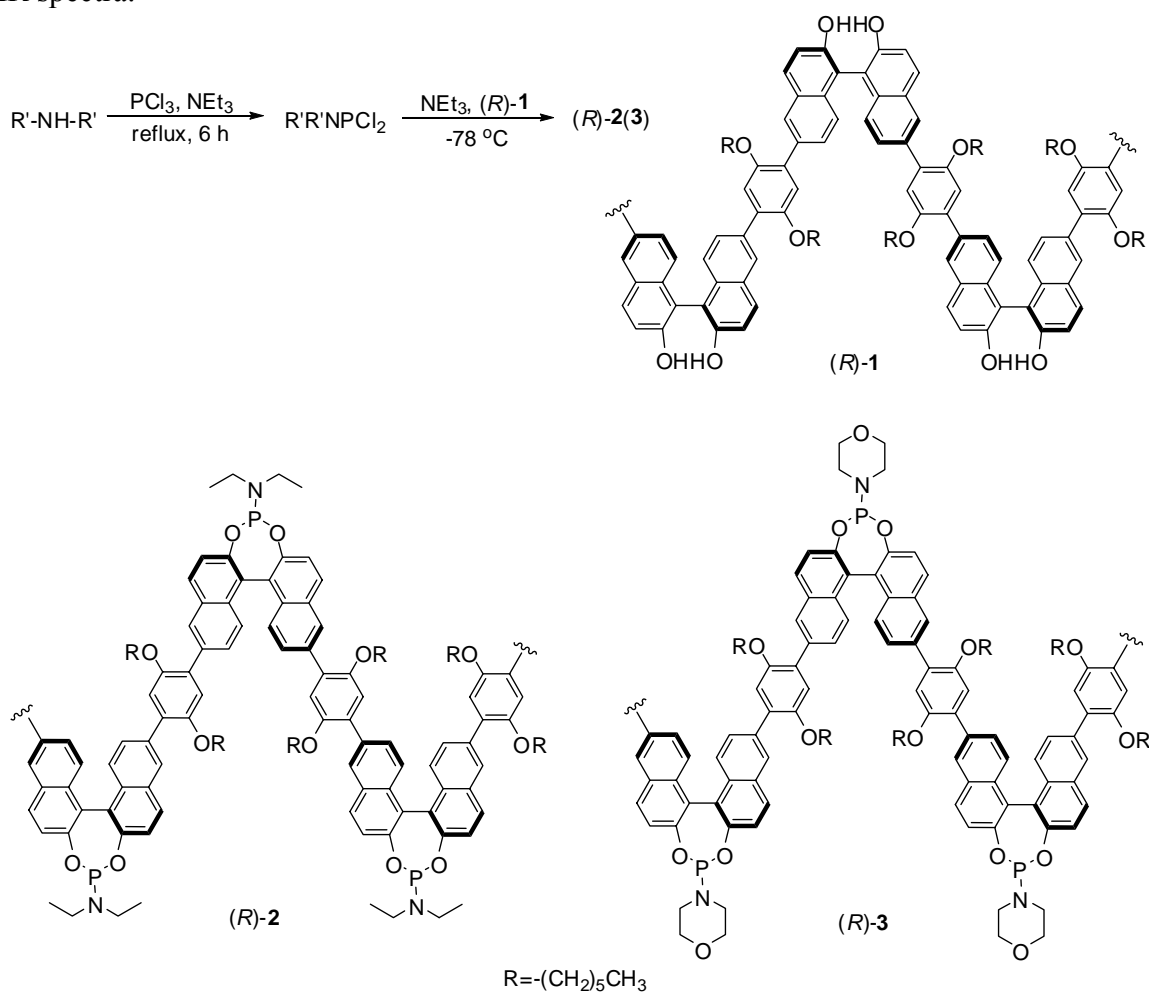

Scheme 1. Preparation of polymeric monodentate phosphoramidites ligands (R)-**2** and (R)-**3**.

Asymmetric hydrogenation of α-dehydroamino acid derivatives

The conditions of asymmetric hydrogenation reaction catalyzed by Rh/(R)-**2** complex were optimized, and the results are listed in Table 1. We found that the reaction carried out in THF gives higher yield and ee than that in dichloromethane. When the reaction was cooled to 5ºC, higher ee value was obtained (entries 3 and 5). Interestingly, the mole ratio of Rh/ligand played an important role in the catalytic hydrogenation. Unlike other reported asymmetric hydrogenation catalyzed by Rh- monodentate phosphine ligands, only moderate conversion and ee was obtained for the reaction with the mole ratio 1:2 of Rh/(R)-**2** (entry 2). Meanwhile, an insoluable yellow solid was deposited. The mole ratio 1:1.1 of Rh/(R)-**2** afforded best catalytic results (entry 3). In order to investigate the effect of the Rh/L ratio, we performed stoichiometric reactions with Rh/L ratio from 2:1 to 1:4 at 5ºC (entry 6–10). In agreement with earlier reports,[5f,9b,14] The poorer catalytic activity was displayed when the reaction was catalyzed by a 1:3 or 1:4 Rh/L ratio. The yellow precipitate was observed in both cases. The reaction with 2:1 Rh/L mole ratio gave exactly the same ee value than that of 1:1 Rh/L mole ratio, but a black precipitate (rhodium black) was observed in the former reaction. In addition, the use of Rh(COD)$_2$SbF$_6$ instead of Rh(COD)$_2$BF$_4$ (entries 5 and 9) or higher H$_2$ pressure (entries 5 and 11) seemed to have little effects on the reaction.

Table 1. Asymmetric Hydrogenation of Methyl (Z)-2-Acetamidocinnamate[a]
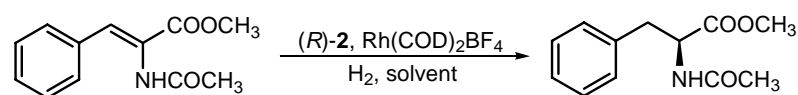
Entry	Solvents	[Rh] : L	H$_2$ (atm)	T (°C)	t (h)	Yield (%)[b]	ee (%)[c]
1	CH$_2$Cl$_2$	1 : 2	1.2	30	8	10	nd
2	THF	1 : 2	1.2	30	8	86	84.3(S)
3	THF	1 : 1.1	1.2	30	8	100	92.5(S)
4	THF	1 : 0.9	1.2	30	8	100	92.1(S)
5	THF	1 : 1.1	1.2	5	8	100	95.6(S)
6[d]	THF	1 : 4	1.2	5	8	0	nd
7[d]	THF	1 : 3	1.2	5	8	34.7	86.2(S)
8[d]	THF	1 : 2	1.2	5	8	82.5	86.4(S)
9[d]	THF	1 : 1.1	1.2	5	8	100	96.2(S)
10[d]	THF	2 : 1	1.2	5	8	100	96.8(S)
11	THF	1 : 1.1	4.0	5	8	100	95.2(S)

[a] Reactions were performed with 0.1 M solutions of substrates with S/C=100 : 1.
[b] Yields were determined by GC-MS. [c] EE's were determined by HPLC on a Chiralcel OD-H column[15]. The configurations of all the predominant products were in S- form.
[d] Rh(COD)$_2$SbF$_6$ was used instead of Rh(COD)$_2$BF$_4$.

The mechanism of rhodium-catalyzed asymmetric hydrogenation of functionalized olefins using monodentate phosphoramidite ligands has not been well addressed. The prevailing viewpoint was that two ligand molecules would bond to rhodium in the active catalytic species[16]. However, Zhou[5f] and Fan[9b] found that in the asymmetric hydrogenation of (Z)-2-(acetamido)cinnamate catalyzed by Rh-monodentate phosphine, the reaction with 1:1 Rh/L ratio was faster than that with 1:2 Rh/L ratio, and the Rh/L ratio had little influence on the conversion and enantioselectivity. Van den Berg[14] proved that a number of different complexes are formed during hydrogenation.

Due to its unique structure, the polymeric ligands (R)-**2** and (R)-**3** with their rigid polymeric chains can prevent the coordination between Rh and two phosphoramidite units in one macromolecule. Thus, when reaction was processed with the Rh/L ratio of 1:2, two phosphoramidite units from different polymer chains might bind to one Rh to form RhL$_2$ species (Figure 1). It would result in a cross-linking reaction among the rigid polymer chains, and the catalyst would therefore deposit and lose its activity. When Rh/ligand ratio is 1:1, enough Rh atoms may prevent the cross-linking reaction among the linear rigid polymer chains, so the catalyst exhibits excellent reactivity and enantioselectivity in the catalytic applications.
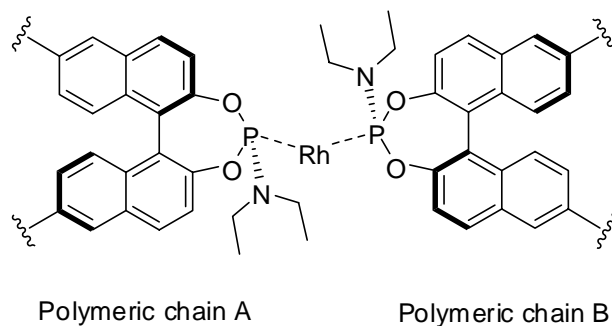

Polymeric chain A   Polymeric chain B

Figure 1. Fragment of the product of supposed cross-linking reaction among the polymeric chains of (R)-2 with 1 : 2 Rh/L ratio.

The asymmetric hydrogenation of other α-dehydroamino acid derivatives catalyzed by Rh/(R)-**2** was also investigated under the optimized conditions. The results are listed in Table 2. All of the tested substrates could be completely converted to the desired products with excellent enantioselectivities (92-99% ee), which were comparable to those obtaining with the corresponding monomeric ligand (97% ee).[5j] The morpholine-containing ligand (R)-**3** exhibited relatively lower enantioselectivity (88-91% ee) in comparison with its homogeneous counterpart (98% ee).[5j] After the completion of the reaction, these polymeric Rh complexes could be easily precipitated through the addition of methanol. Unfortunately, due to the change in the structure of the Rh complex, the solid that separated from the reaction system could not be reused for another catalytic round.

Table 2. Asymmetric hydrogenation of α-dehydroamino acid derivatives[a]
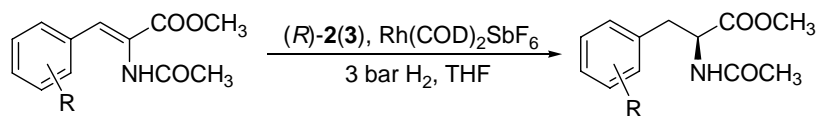
Entry	L	R	t (h)	Yield (%)[b]	Ee (%)[c]
1	(R)-2	H	8	100	96.2
2	(R)-2	2-CH$_3$	8	100	99.5
3	(R)-2	4-CH$_3$	8	100	97.8
4	(R)-2	4-OCH$_3$	8	100	92.1
5	(R)-2	4-F	8	100	99.0
6	(R)-2	4-Cl	8	100	99.2
7	(R)-2	4-Br	8	100	97.1
8	(R)-3	H	8	100	88.5
9	(R)-3	2-CH$_3$	8	100	91.3
10	(R)-3	4-CH$_3$	8	100	90.5
11	(R)-3	4-OCH$_3$	8	100	86.6
12	(R)-3	4-F	8	100	90.1
13	(R)-3	4-Cl	8	100	90.3
14	(R)-3	4-Br	8	100	89.9

[a] The reaction was performed with 0.1 M solutions of substrates with S/C = 100 : 1 at 5°C in 5 mL of THF, [Rh]/L = 1:1.1. [b] Yields were determined by GC-MS.
[c] Ee's and conversions were determined by HPLC on a Chiralcel OD-H column[15]. The configurations of all the predominant products were in *S*- form.

Conclusions

In summary, we developed a new class of polymeric monodentate phosphoramidite ligands with rigid and sterically regular polybinaphthyl structure as a backbone. Their rhodium complexes were successfully applied in the asymmetric hydrogenation of α-dehydroamino acid derivatives. Comparable enantioselectivities were achieved as compared to that obtained from MonoPhos. The best Rh/L ratio for asymmetric hydrogenation was 1:1 instead of 1:2. Increase of the amount of ligand led to the formation of precipitate and the conversion as well as the enantioselectivity decrease.

Experimental Section

General Procedures. The ^{1}H NMR spectra were measured on a Varian INOVA-400 spectrometer and the chemical shifts were referenced to tetramethylsilane (^{1}H) as internal standard or H_3PO_4 (^{31}P) as external standard. GC-MS spectra data were recorded on a Agilent 6890-5973N spectrometer with a HP-5 (30 m × 0.25 mm) column. All reactions were performed under argon atmosphere, using standard Schlenk techniques. Solvents were dried and distilled before use following standard procedures. Chemicals and reagents were purchased from commercial suppliers and used as received.

Copolymer (R)-1

This material was prepared following literature procedures.[10] Pale yellow solid in 80% yield. GPC analysis showed the molecular weight as M_w = 16,981 and M_n = 11,305 (PDI = 1.50). $[\alpha]_D$ =-397.2° (c = 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.16 (m, 2H), 8.01 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 7.11 (s, 2H), 3.94 (m, 6H), 1.62-1.72(m, 4H), 1.35 (m, 4H), 1.24-1.36 (m, 8H), 0.80 (s, 6H).

Polymeric monodentate phosphoramidite (R)-2

Under argon atmosphere, a solution of diethylamine (0.05 mL, 0.48 mmol) and triethylamine (0.074 mL, 0.52 mmol) in THF (2 mL) was added dropwise to the solution of phosphorus trichloride (0.042 mL, 0.48 mmol) in THF (2 mL). The mixture was stirred at 70°C for 6 h and allowed to cool to room temperature. Triethylamine (0.074 mL, 0.52 mmol) was then added dropwise, and the solution was cooled to -78°C. A solution of (R)-1 (0.27 g, 0.48 mmol based on the repeated unit) in THF (4 mL) was added dropwise. The resulted mixture was allowed to warm up slowly to room temperature and was stirred for additional 12 h. The mixture was filtered and the filtrate was concentrated to 3 mL under reduced pressure. MeOH (3 mL) was added to the residue to precipitate the product polymer as a white solid. Yield: 0.21 g (65%). $[\alpha]_D$ = -434.9° (c = 1.00, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 8.17 (s, 2H), 7.92-8.01 (m, 2H), 7.40-7.60 (m, 4H), 7.27 (m, 2H), 7.10 (m, 2H), 3.96 (m, 4H), 3.0-3.08 (m, 4H), 1.35-1.68 (m, 8H), 1.18 (m, 8H), 1.07-1.09 (m, 6H), 0.74 (s, 6H). ^{31}P-NMR: δ = 149.79. Anal. Calcd. for $C_{42}H_{48}NO_4P$: C, 76.22; H, 7.31; N, 2.12; found: C, 75.46; H, 6.60; N, 2.42.

Polymeric monodentate phosphoramidite (R)-3

The title compound was prepared from morpholine following the preparation of (R)-2 as a pale yellow solid. Yield: 66%. $[\alpha]_D$ =-337.2° (c = 1.00, $CHCl_3$). H-NMR ($CDCl_3$, 400 MHz): δ = 8.22-8.00 (m, 4H), 7.66-7.28 (m, 6H), 7.13-7.18 (m, 2H), 3.97 (4H), 3.40-3.65 (m, 4H), 3.04-3.16 (m, 4H), 1.71(m, 4H), 1.38 (m, 4H), 1.24-1.30 (m, 8H), 0.79 (s, 6H). ^{31}P-NMR: δ = 144.86. Anal.Calcd. for $C_{42}H_{46}NO_5P$: C, 74.65; H, 6.86; N, 2.07; found: C, 74.17; H, 7.24; N, 1.70.

General procedure for the Rh(I)-catalyzed asymmetric hydrogenation

The catalyst was formed *in situ* by mixing [Rh(COD)$_2$]BF$_4$ or [Rh(COD)$_2$]SbF$_6$ (0.005mmol) and the polymeric monodentate phosphoramidite ligands (0.0055mmol) in THF (5 mL) for 10 min. The clear catalyst solution was transferred into a 100 mL stainless steel autoclave, which contained α-dehydroamino acid derivatives (0.5 mmol) and a magnetic stirring bar, through a glass liner. After purging with hydrogen for 6 times, the system was pressurized with hydrogen (5 bar) and the reaction mixture was stirred for 8 h. Then the reaction mixture was filtered over a short pad of gel and analyzed by HPLC.[15] All of the catalytic experiments were independently repeated 2 times to confirm the results.

Enantiomeric excess determinations

The racemic mixtures of all products were prepared by hydrogenation of the substrates using Pd/C or Wilkinson's catalyst.

(*S*)-**Methyl 2-acetamido-3-phenylpropionate.** 95.8% ee, (HPLC, Daicel Chiralcel OD-H, 0.5 mL/min, 10% isopropanol/hexane, (R) t_1 = 22.485 min; (S) t_2 = 28.882min).

(*S*)-**Methyl 2-acetamido-3-(2-methylphenyl)propionate.** 99% ee, (HPLC, Daicel Chiralcel OD-H, 0.5 mL/min, 10% isopropanol/hexane, (R) t_1 =21.4 min; (S) t_2 = 27.5 min).

(*S*)-**Methyl 2-acetamido-3-(4-methylphenyl)propionate.** 98% ee, (HPLC, Daicel Chiralcel OD-H, 0.5 mL/min, 10% isopropanol/hexane, (R) t_1 = 19.6 min; (S) t_2 = 25.4 min).

(*S*)-**Methyl 2-acetamido-3-(4-methoxyphenyl)propionate.** 92% ee, (HPLC, Daicel Chiralcel OD-H, 0.5 mL/min, 10% isopropanol/hexane, (R) t_1 = 29.0 min; (S) t_2 = 36.1 min).

(*S*)-**Methyl 2-acetamido-3-(4-Fluorophenyl)propionate.** 99% ee, (HPLC, Daicel Chiralcel OD-H, 0.5 mL/min, 10% isopropanol/hexane, (R) t_1 = 23.3 min; (S) t_2 = 29.0 min).

(*S*)-**Methyl 2-acetamido-3-(4-chlorophenyl)propionate.** 99% ee, (HPLC, Daicel Chiralcel OD-H, 0.5 mL/min, 10% isopropanol/hexane, (R) t_1 = 26.4 min; (S) t_2 = 32.1 min).

(*S*)-**Methyl 2-acetamido-3-(4-bromophenyl)propionate.** 97.2% ee, (HPLC, Daicel Chiralcel OD-H, 0.5 mL/min, 10% isopropanol/hexane, (R) t_1 = 28.8 min; (S) t_2 = 35.6 min).

Acknowledgements

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