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H_8-MonoPhos and its application in catalytic enantioselective hydrogenation of α-dehydroamino acids

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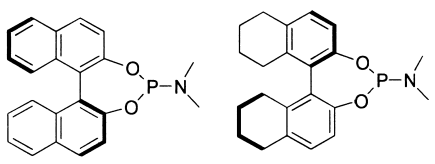
Abstract—H_8-MonoPhos, a new stable and readily soluble monodentate phosphoramidite ligand, has been facilely prepared from H_8-BINOL. The ligand achieved up to 99.9% ee and 96.7% ee in hydrogenation of dehydroalanine and dehydrohomophenylalanine in a S/C ratio of 500:1, respectively, which are among the best results to date. For dehydrophenylalanine derivatives, it gave good to excellent enantioselectivity. Some factors controlling the enantioselectivity and conversion were examined and are discussed. The interesting effects of ligand/rhodium ratio on the enantioselectivity and conversion were observed, which a mechanism was proposed to explain.

1. Introduction

In the catalytic enantioselective hydrogenation of functionalized prochiral olefins, bidentate phosphorus-containing ligands are superior to monodentate analogues in asymmetric induction, for example, DIPAMP and PAMP,[1] and all of the best ligands are bidentate in the past nearly 30 years;[2] but recently Pringle[3] and Feringa[4] found that monodentate ligands could be superior to bidentate analogues, and Feringa's MonoPhos **1** (Scheme 1) was even comparable to the best bidentate ligands in hydrogenation in some solvents. In our preliminary research, we found the crystalline MonoPhos was not readily soluble in some solvents, which decreased the rate of hydrogenation as noted in Feringa's paper, and will limit its application to some substrates, which only dissolve in the solvents in which selectivity is poor for the MonoPhos. We thought that if the BINOL backbone was partially hydrogenated into H_8-BINOL, the resulting compound would have better solubility.



(*S*)-MonoPhos **1** (*R*)-H_8-MonoPhos **2**

Scheme 1. (*S*)-MonoPhos **1** and (*R*)-H_8-MonoPhos **2**.

Furthermore, the H_8-BINOL skeleton is more electron-rich and larger dihedral angle than BINOL one as Takaya's report.[5] Takaya's H_8-BINAP shows higher asymmetric induction in the hydrogenation of olefins than BINAP.[5] In our Laboratory, H_8-BINAM based aminophosphite ligands were better ligands than their analogues in hydrogenation;[6] H_8-BINOL was used as a ligand in the asymmetric alkylation of aldehydes[7] and the hetero-Diels–Alder reaction[8] and gave better enantioselectivity than BINOL. Prompted by these results and the facile preparation of H_8-BINOL from BINOL,[9] we synthesized *N*,*N*-dimethyl 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthyl phosphoramidite **2** (labeled as H_8-MonoPhos, Scheme 1) and investigated its application in the enantioselective hydrogenation of α-dehydroamino acids in detail.[10]

2. Results and discussion

2.1. Synthesis of chiral H_8-MonoPhos

(*R*)-H_8-MonoPhos **2** was readily obtained by refluxing the benzene solution of (*R*)-H_8-BINOL and hexamethylphosphorous triamide. Unlike MonoPhos, H_8-MonoPhos is a white solid and is soluble in various common organic solvents, which provide a wide scope of solvents for

Keywords: catalytic enantioselective hydrogenation; dehydrohomophenylalanine; monodentate phosphoramidite ligand.

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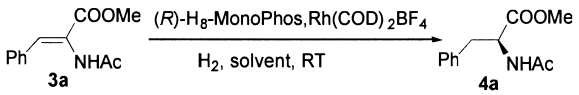
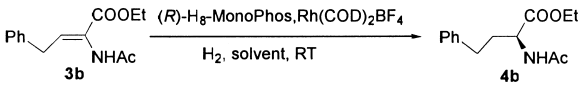


Scheme 2.



Scheme 3.

optimizing the reaction conditions for various substrates. H_8-MonoPhos **2** is stable to purification by flash column chromatography and storage for 1 year under a nitrogen atmosphere. The stability is especially beneficial to its potential use in large-scale processes.

2.2. Enantioselective hydrogenation of methyl (*Z*)-acetoamidocinnaminate by Rh–H_8-MonoPhos catalyst

With (*R*)-H_8-MonoPhos in hand, we first investigated various conditions in the enantioselective hydrogenation of methyl (*Z*)-acetoamidocinnaminate (Scheme 2). The catalyst was prepared in situ by mixing $Rh(COD)_2BF_4$ and (*R*)-H_8-MonoPhos in acetone solution. All of the ee values in the tested solvents were higher than or comparable to those of MonoPhos (entries 1–8). Importantly, the substrate could not be completely hydrogenated in toluene with MonoPhos,[4a] but it could with H_8-MonoPhos, which shows the advantage of the soluble H_8-MonoPhos (entry 1). The effects of solvents on the chiral induction were small except for MeOH (entry 7). The conversion was low and the ee value decreased a little, probably because the nucleophilicity and low steric hindrance of MeOH resulted in the decomposition of H_8-MonoPhos by MeOH in the reaction conditions, which has been observed for monodentate phosphites.[11] Hydrogen pressure accelerated the reaction but played a minor role in enantioselectivity (entries 8–11). Like MonoPhos, the ee value increased a little when the temperature decreased to 0°C (entry 12). Interestingly, when the substrate to catalyst ratio increased from 100 to 500, the reaction gave a consistent ee value (entries 8 and 13). As a comparison, the substrate could not be completely hydrogenated in 0.5 h in the optimized solvents with (*R*)-MonoPhos (entries 14 and 15), which implied that H_8-MonoPhos was more efficient (Table 1).

Table 1. Rhodium-catalyzed enantioselective hydrogenation of methyl (*Z*)-acetoamidocinnaminate **3a**

Entry	*P* (bar)	*t* (h)	Solvent	%ee[a]	%conv.[a]
1	20	2	Toluene	94.9	99.1
2	20	0.5	$ClCH_2CH_2Cl$	95.0	99.7
3	20	0.5	CH_2Cl_2	94.4	99.3
4	20	0.5	AcOEt	95.7	96.9
5	20	0.5	THF	94.2	90.2
6	20	1	Acetone	95.4	99.2
7	20	0.5	MeOH	90.8	47.4
8	20	0.5	*i*-PrOH	95.5	98.0
9	1	6	*i*-PrOH	94.8	99.7
10	10	1	*i*-PrOH	95.6	96.8
11	40	0.5	*i*-PrOH	95.6	99.6
12[b]	20	12.5	*i*-PrOH	97.0	99.3
13[c]	20	8	Acetone	96.4	99.9
14[d]	20	0.5	CH_2Cl_2	92.3	25.6
15[d]	20	0.5	AcOEt	93.0	56.8

Reactions were performed with 0.1 M solutions of substrates at S/C=100:1 at rt and 20 bar initial hydrogen pressure unless otherwise noted.
[a] Ee and conversion were determined by GC on a CP-Chirasil-L-Val column. The configurations of all the predominant products were in *S* form.
[b] 0°C.
[c] The substrate to catalyst mole ratio is 500.
[d] Ligand is (*R*)-MonoPhos.

2.3. Enantioselective hydrogenation of ethyl (*Z*)-2-acetoamido-4-phenylcrotonate by Rh–H_8-MonoPhos catalyst

As a key intermediate of most commercially important angiotensin converting enzyme (ACE) inhibitors, asymmetric synthesis of L-homophenylalanine has received increasing attention,[12] but only a few excellent results were achieved by asymmetric catalytic method.[13] So we tested this catalyst system in the hydrogenation of ethyl (*Z*)-2-acetamido-4-phenylcrotonate to prepare homophenylalanine (Scheme 3). Excellent enantioselectivities and conversions were achieved in various solvents except MeOH (Table 2, entries 1–5). Under ambient hydrogen pressure the reaction was completed within 2 h (entry 6), which was the most efficient for the substrate among all of the reported ligands. Even in the presence of only 0.2 mol% Rh-complex of H_8-MonoPhos, the substrate was hydrogenated into homophenylalanine with up to 96.7% ee (entry 11). Compared with the known chiral ligands for the catalytic synthesis of homophenylalanine such as SpirOP (96.2% ee, 1 mol% catalyst)[13b] and DPAMPP (95.7% ee, 1 mol% catalyst),[13d] H_8-MonoPhos **2** showed the most efficient asymmetric catalytic property for the synthesis of optical pure homophenylalanine. The facile preparation, stability and high efficiency demonstrate the promising prospect of H_8-MonoPhos **2** in large scale production of homophenylalanine.

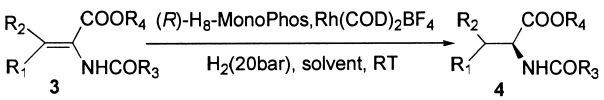
2.4. Enantioselective hydrogenation of other dehydroamino acids catalyzed by Rh–H_8-MonoPhos complex

The hydrogenation of other dehydroamino acids were also investigated (Scheme 4, Table 3). Interestingly, the simple dehydroalanine, for which it is hard to achieve a high ee value with a number of bidentate phosphine ligands, was

Table 2. Enantioselective hydrogenation of ethyl (*Z*)-2-acetomido-4-phenylcrotonate **3b** by H_8-MonoPhos–Rh complex

Entry	*t* (h)	Solvent	%ee[a]	%conv.[a]
1	0.5	*i*-PrOH	95.9	99.0
2	0.5	Acetone	95.0	99.9
3	0.5	CH_2Cl_2	92.9	99.9
4	0.5	THF	96.6	99.9
5	0.5	MeOH	96.2	42.0
6[b]	2	*i*-PrOH	95.9	99.6
7[c]	8	Acetone	96.7	99.9

Reactions were performed with 0.1 M solutions of substrates at S/C=100:1 at rt and 20 bar initial hydrogen pressure unless otherwise noted.
[a] Ee and conversion were determined by GC on a CP-Chirasil-L-Val column. The configurations of all the predominant products were in *S* form.
[b] The hydrogen pressure is ambient pressure.
[c] The substrate to catalyst mole ratio is 500.



Scheme 4.

effectively hydrogenated with Rh–H_8-MonoPhos catalyst system (entries 16–18).

2.5. Effect of the ligand/Rh ratio on enantioselective hydrogenation

Different from the finding by Reetz[14] and Feringa,[4a] we found that, with 3 equiv. or more of ligand **2**, the hydrogenation of dehydro-*N*-acetylphenylalanine methyl ester became much slower; while with 1 equiv. of the ligand, the conversion dropped obviously. A 2:1 mole ratio of ligand/Rh is preferential (Scheme 2, Table 4). We suppose, the RhL_2S_2 (S=solvent or COD) is the precursor to coordination with the dehydroamino acid substrate. RhL_4 and RhL_3S should be dissociated into RhL_2, and two $RhLS_3$ will turn into a RhL_2S_2 and RhS_4, but RhS_4 has much lower activity than RhL_2S_2 and can easily be reduced into rhodium black in catalytic hydrogenation (Scheme 5). So the ratio of ligand/Rh does not effect enantioselectivity but conversion (entries 1–4). The mechanism can well explain why the ee values are consistent but the conversions differ from each other.

Table 3. Enantioselective hydrogenation of other α-dehydroamino acids **3** by H_8-MonoPhos–Rh complex

Entry	Substrates	R_1	R_3	R_4	*t* (h)	Solvents	%ee[a]	%conv.[a]
1	**3c**	H	Me	Me	0.5	Acetone	99.9	99.9
2[b]	**3c**	H	Me	Me	8	Acetone	99.9	99.9
3	**3d**	Ph	Me	H	0.5	*i*-PrOH	93.3	92.8
4	**3e**	3-Cl–Ph	Me	H	0.5	Acetone	74.0	99.9
5	**3f**	4-Cl–Ph	Me	H	0.5	Acetone	82.6	99.9
6	**3g**	4-Me–Ph	Me	H	0.3	MeOH	82.1	77.8
7	**3h**	Ph	Ph	Me	2	Acetone	84.3	98.2
8[c]	**3i**	H	Ph	Me	2	Acetone	49.3	54.4
9	**3j**	4-F–Ph	Me	Me	0.5	Acetone	82.9	96.6
10	**3k**	2-Cl–Ph	Me	Me	0.5	Acetone	92.5	98.6
11[d]	**3l**	4-Cl–Ph	Me	Me	5	CH_2Cl_2	98.0	99.9
12	**3m**	4-Br–Ph	Me	Me	0.5	Acetone	91.0	77.1
13	**3n**	4-MeO–Ph	Me	Me	0.5	Acetone	94.4	95.9
14[d]	**3o**	4-NO_2–Ph	Me	Me	5	CH_2Cl_2	96.0	99.9
15	**3p**	4-AcO–3-MeO–Ph	Me	H	2	Acetone	95.9	99.9
16	**3q**	Furyl	Me	Me	0.5	Acetone	80.8	62.7
17	**3r**	(E)–PhCH=CH	Me	Me	0.5	Acetone	54.2	12.6
18[e]	**3s**	Me	Ph	Me	10	Acetone	23.3	60.0

Reactions were performed with 0.1 M solutions of substrates at S/C=100:1 at rt and 20 bar initial hydrogen pressure unless otherwise noted; R_2=H unless other mentioned.

[a] Ee and conversion were determined by GC on a CP-Chirasil-L-Val column. The configurations of all the predominant products were in *S* form.

[b] The substrate to catalyst mole ratio is 500.

[c] R_2=Ph

[d] 7 bar of H_2.

[e] 60 bar H_2 pressure; R_2=Me.

hydrogenated in extremely high ee values with H_8-MonoPhos **2**, even with 0.2 mol% catalyst loading (entries 1 and 2). The acid substrates gave lower enantioselectivities (entries 3–6). Replacement of the acetamido group by benzamido decreased the enantioselectivity obviously (entry 7). If the substrate was an *E* isomer, both the ee value and conversion were very low (entries 7 and 8). For most of the substituted dehydrophenylalanine methyl ester derivatives good to excellent ee values were achieved, but there is no clear tendency for the effect on the enantioselectivity and conversion of the substituted group (entries 9–14). The L-Dopa precursor could be obtained in excellent optical purity by hydrogenation in the presence of H_8-MonoPhos–Rh complex (entry 15). Hetero-aromatic or alkenyl or β,β-di-substituted dehydroalanine could not be

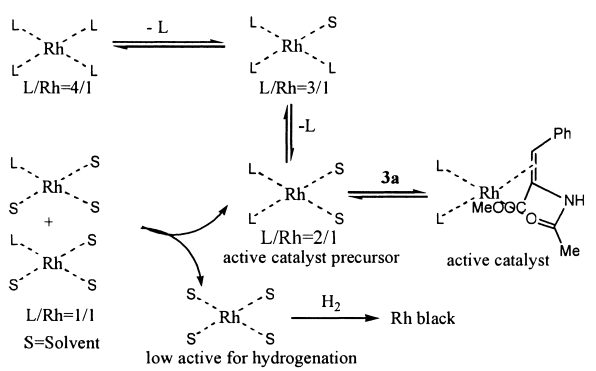
Table 4. The effects of the ligand/Rh ratios on enantioselective hydrogenation of methyl (*Z*)-acetoamidocinnaminate **3a**

Entry	L/Rh	%ee[a]	%conv.[a]
1	4.4	–[b]	1.2
2	3.3	95.9	78.9
3	2.2	95.5	98.0
4	1.1	94.8	53.8

Reactions were performed with 0.1 M solutions of substrates at S/C=100:1 at rt and 20 bar initial hydrogen pressure unless otherwise noted.

[a] Ee and conversion were determined by GC on a CP-Chirasil-L-Val column. The configurations of all the predominant products were in *S* form.

[b] Only one enantiomer peak detected on GC but too low to be measured accurately.



Scheme 5.

3. Conclusion

In summary, H_8-MonoPhos, a new stable and easily prepared monodentate phosphoramidite ligand, holds much better solubility and gives higher ee values and reaction rate than MonoPhos in most of solvents in the hydrogenation of dehydrophenylalanine. With the H_8-MonoPhos–rhodium complex, the highest enantioselectivity (96.7% ee at a S/C ratio of 500:1) and reaction rate were achieved in the hydrogenation of ethyl (*Z*)-2-acetoamido-4-phenylcrotonate; 99.9% ee was achieved for dehydroalanine, which is comparable to the result obtained by the best bidentate ligands. But the catalyst system was not suitable for some other substrates. The interesting effects of ligand/Rh mole ratio in hydrogenation with H_8-MonoPhos were observed. A reasonable mechanism was proposed to explain this.

4. Experimental

4.1. General aspects

All melting points were determined on a digital melting point apparatus and were uncorrected. ^{1}H NMR and ^{31}P NMR spectra were recorded on Brucker AC-E 300 and Brucker AC-400 spectrometers. Infrared spectra were recorded on a Nicolet MX-1 spectrometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. All reactions involving air- and moisture-sensitive compounds were carried out under a dry argon atmosphere using standard Schlenk line techniques. THF, benzene and pyridine were distilled from sodium benzophenone ketyl; solvents used in hydrogenation were degassed by three freeze–thaw cycles prior to use.

4.2. Materials

(*R*)-H_8-BINOL was prepared according to the literature procedure.[8b] $Rh(COD)_2BF_4$ was purchased from Aldrich Chemical Co. Hexamethylphosphorous triamide and 2-acetoamidoacrylic acid were purchased from Acros Chemical Co. All 2-acylamidoacrylic acids were synthesized in accordance with the process developed by Blatt.[15] Their corresponding methyl esters were prepared by the reaction of free acids with MeI in the presence of $KHCO_3$ in DMF. The preparation of ethyl (*Z*)-2-acetamido-4-phenylcrotonate was achieved using the literature procedure with slight modification.[13a]

4.2.1. *N*,*N*-Dimethyl (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthyl phosphoramidite (H_8-MonoPhos). Under N_2 atmosphere, (*R*)-(+)-H_8-BINOL (147 mg, 0.5 mmol), hexamethylphosphorous triamide (109 mg, 0.74 mmol), 4 mg NH_4Cl and 4 ml dry benzene were added into a flask equipped with a stirrer and heated to reflux for 3 h. The mixture was directly purified by flash column chromatography on silica gel eluted with petroleum ether/ethyl acetate (5:1) to gave a white solid compound. Yield 121 mg (66.2%); mp: 56–57°C; $[\alpha]_D^{32}=-310$ (*c* 0.610, THF); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52–1.62 (m, 2H), 1.74–1.81 (m, 6H), 2.18–2.36 (m, 2H), 2.49 (d, 6H, *J*=8.8 Hz), 2.56–2.71 (m, 2H), 2.74–2.87 (m, 4H), 6.84 (d, H, *J*=6.0 Hz), 6.99 (d, H, *J*=3.9 Hz), 7.01 (d, H, *J*=3.9 Hz), 7.07 (d, H, *J*=6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.5, 22.7, 22.8, 27.6, 27.7, 22.7, 29.0, 29.1, 35.6, 35.9, 118.5, 118.6, 128.2, 128.3, 129.2, 132.9, 137.4, 137.8, 137.9, 148.2, 148.3, 148.6; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 143.6; MS (EI, 70 eV, *m*/*z*): 367 (M^+, 100%), 324 (76%); IR (KBr): 3010, 1585, 1469, 1248, 1233, 1222, 982, 937 cm^{-1}. Anal. calcd for $C_{22}H_{26}NO_2P$: C, 71.92; H, 7.13; N, 3.81; P, 8.43; found: C, 71.32; H, 7.10; N, 3.89; P, 8.34.

4.3. A general procedure for enantioselective hydrogenation catalyzed by Rh–H_8-MonoPhos complex

In a dry box, 40 μl 0.025 M $Rh(COD)_2BF_4$ acetone solution, 80 μl 0.0275 M (*R*)-H_8-MonoPhos acetone solution, 0.1 mmol substrate and 1 ml solvent were added into a glass tube equipped with a stirrer in a 50 ml autoclave under Ar atmosphere. The autoclave was pressurized with H_2 and the hydrogenation was carried out under the chosen conditions. After the hydrogen was released, the mixture was filtered through a short silica gel column to remove the catalyst. The methyl or ethyl ester was directly analyzed via chiral capillary GC with a 25 m Chrowpak capillary column (CP-Chirasil-L-Val). The acid was converted to the corresponding methyl ester with methyl iodide/$KHCO_3$/DMF before GC analysis.

Acknowledgements

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