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Synthesis of (*R*)-2-diphenylphosphino-2′-diphenylphosphinomethyl-1,1′-binaphthyl and its use for asymmetric hydrogenation of α-alkylstyrenes

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Abstract

A new chiral bisphosphine ligand ((*R*)-2-diphenylphosphino-2′-diphenylphosphinomethyl-1,1′-binaphthyl) was synthesized from enantiomerically pure (*R*)-1,1′-binaphthalene-2,2′-diol. Rhodium(I) complexes of this bisphosphine ligand have been used as catalysts for asymmetric hydrogenation of α-alkylstyrenes to give the corresponding aromatic hydrocarbons in up to 77% *ee*.

Keywords: Rhodium; Asymmetric hydrogenation; Bisphosphine ligand; α-Alkylstyrene

1. Introduction

Recently, asymmetric synthesis using transition metal catalysts containing chiral ligands has been the subject of considerable interest (for recent reviews see Ref. [1]). One of the most important subjects in this field is to develop new chiral ligands which achieve high enantioselectivity. Many chiral bisphosphine ligands have so far been synthesized and used for a variety of asymmetric transformations. In contrast, axially chiral binaphthyl compounds are widely used to construct an effective chiral environment for asymmetric reactions and chiral molecular recognitions (for recent reviews of binaphthyl compounds see Ref. [2]). For example, the chiral bisphosphine ligand BINAP [3] has been employed for transition-metal-catalyzed asymmetric transformations such as hydrogenation. The chiral monophosphine ligands, MOP derivatives, were applied for asymmetric hydrosilylation of olefins [4] and asymmetric reduction of allylic esters [5]. Binaphthol was used as a chiral element for aluminum hydride reagent for asymmetric reduction of ketones [6], for chiral Lewis acid catalysts containing titanium and aluminum (for a recent review see Ref. [7]), and for asymmetric catalysts including rare earth metal for Michael reactions and aldol reactions [8]. In all of these cases, chiral environments created by 1,1′-binaphthyls have been demonstrated to exhibit high enantioselectivities. However, many of these chiral binaphthyl compounds are C_2-symmetric; in particular, there has been no unsymmetric bisphosphine ligand bearing binaphthyl skeleton.

We report here the preparation of a new unsymmetric bisphosphine ligand bearing binaphthyl skeleton, (*R*)-2-diphenylphosphino-2′-diphenylphosphinomethyl-1,1′-binaphthyl (**1**), and its use as a chiral ligand in Rh(I)-catalyzed asymmetric hydrogenation of α-alkylstyrenes without heterofunctionality. There were a few successful studies of asymmetric hydrogenation of these relatively simple olefins catalyzed by chiral early transition metal or chiral lanthanide complexes (asymmetric hydrogenation of unfunctionalized olefins using early transition metal and lanthanide catalysts was reported, see Ref. [9]), but these unfunctionalized olefins were hydrogenated in only moderate enantioselectivity by using conventional late transition metal catalysts containing chiral phosphine ligands (for asymmetric hydrogenation of 2-phenyl-1-butene using late transition metal complexes see Ref. [10,11]). This seems to be because these olefins have no heteroatoms which can interact with the

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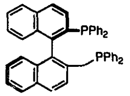
metal center of the catalyst in a bidentative mode. Therefore, we thought that higher steric control was necessary to accomplish highly enantioselective hydrogenation of the simple olefins, and expected steric bulkiness of this novel chiral bisphosphine ligand to control the enantioselection.



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2. Experimental details

2.1. General

^{1}H NMR spectra were taken on Jeol JNM-EX-270 spectrometer (270 MHz) using tetramethylsilane as an internal standard. ^{31}P{^{1}H} NMR spectra were measured on a Jeol JNM-EX-270 (109 MHz) and chemical shifts were reported in parts per million relative to 85% phosphoric acid as an external standard. Optical rotations were measured on a Jasco DIP-360 instrument using a glass cell (50 mm or 1.0 mm). Gas chromatographic (GLC) analyses were conducted on a Shimadzu GC-15A equipped with a flame ionization detector. High resolution mass spectra (HRMS) were taken on a Hitachi M-80B spectrometer. All melting points were measured by a Yanaco NT-500D micro melting point apparatus and were not corrected.

2.2. Chemicals

All manipulations of oxygen- and moisture-sensitive materials were conducted under a purified argon atmosphere (BASF-Catalyst R3-11) by use of standard Schlenk techniques. Acetonitrile, toluene, benzene, xylene, and dichloromethane were distilled from P_2O_5. Triethylamine, hexane, and dimethylsulfoxide were dried over CaH_2. Methanol and ethanol were distilled from the corresponding magnesium alkoxides. Tetrahydrofuran and ether were dried over sodium benzophenone ketyl. $Ph_2P(O)H$ [12], $[RhCl(cod)]_2$ [13], and $[Rh(cod)_2]BF_4$ [14] were prepared according to reported procedures. All of olefinic substrates for asymmetric hydrogenation were synthesized via Wittig reactions of the corresponding ketones with Ph_3PCH_2 in ether [15].

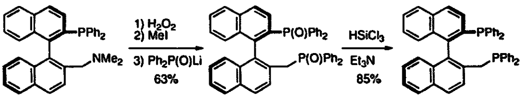
2.3. Preparation of (*R*)-(−)-2-diphenylphosphinyl-2′-diphenylphosphinylmethyl-1,1′-binaphthyl (3)

To a solution of (*R*)-2-dimethylaminomethyl-2′-diphenylphosphino-1,1′-binaphthyl (**2**) [16] (1.09 g, 2.19 mmol) in $CHCl_3$ (13 ml) was added 6.0% aqueous H_2O_2 (13 ml) at room temperature.

The mixture was stirred for 12 h. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic phases were dried over $MgSO_4$ and concentrated to a solid residue. The crude material was dissolved in acetone (18 ml) and treated with CH_3I (1.40 ml, 22.5 mmol) at room temperature overnight. The reaction mixture was concentrated under reduced pressure to give the crude corresponding ammonium salt. ^{1}H NMR ($CDCl_3$): δ 3.07 (s, 9H), 4.50 (d, 1H, $J = 13.9$ Hz), 4.73 (d, 1H, $J = 13.9$ Hz) 6.64–6.71 (m, 2H), 6.81 (d, 1H, $J = 8.3$ Hz), 6.87 (dd, 1H, $J = 7.4$, 1.5 Hz), 6.95 (dd, 1H, $J = 12.2$, 1.3 Hz), 6.97 (d, 1H, $J = 12.2$ Hz), 7.07 (ddd, 1H, $J = 8.4$, 7.0, 1.4 Hz), 7.16 (d, 1H, $J = 8.6$ Hz), 7.32–7.37 (m, 2H), 7.47–7.64 (m, 6H), 7.69–7.84 (m, 4H), 8.00 (d, 1H, $J = 8.2$ Hz), 8.05 (dd, 1H, $J = 8.6$, 2.0 Hz); ^{31}P{^{1}H} NMR($CDCl_3$): δ 26.75(s). The crude product was taken on to the next step without further purification. A solution of the crude ammonium salt obtained above in MeCN (25 ml) was transferred to $Ph_2P(O)Li$ at room temperature; this was prepared by the reaction of 1.0 ml of BuLi (2.8 M in hexane) and diphenylphosphine oxide (488 mg, 2.41 mmol) at 0 °C for 30 min and then at room temperature for 1 h in ether (40 ml). The reaction mixture was heated at reflux for 13 h. After being cooled to room temperature, the mixture was quenched with 1 N HCl (30 ml) and extracted with AcOEt. The organic layer was washed with saturated $NaHCO_3$ aq. and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane–acetone = 1:1 to 1:5) to give **3** (925 mg, 63% yield): m.p. 64.0–66.0 °C; $[\alpha]_D^{24}$ −44.15 (*c* 0.53, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 3.50 (dd, 1H, $J = 16.2$, 8.9 Hz), 4.29 (dd, 1H, $J = 16.2$, 16.2 Hz), 6.62–6.72 (m, 3H), 6.79 (d, 1H, $J = 8.6$ Hz), 6.85–6.99 (m, 5H), 7.08–7.20 (m, 6H), 7.35–7.59 (m, 9H), 7.65–7.97 (m, 8H); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 26.68 (s), 29.93 (s). HRMS (EI) calc. for $C_{45}H_{34}O_2P_2$ 668.2032 (M+), found 668.1996.

2.4. Preparation of (*R*)-(−)-2-diphenylphosphino-2′-diphenylphosphinomethyl-1,1′-binaphthyl (1)

In a 100 ml two-necked flask equipped with a reflux condenser which was connected to an argon inlet tube and a bubbler through a three-way stopcock, was placed **3** (782 mg, 1.11 mmol). The flask was flushed with



2 3 1

Scheme 1.

argon and to this was added toluene (23 ml), triethylamine (4.50 ml, 34.8 mmol), and trichlorosilane (1.80 ml, 17.8 mmol) at 0 °C. The reaction mixture was refluxed for 17 h. After being cooled to 0 °C, the resulting mixture was quenched with degassed 30% NaOH aq. (25 ml). The resulting suspension was separated and extracted with deoxygenated ether. The combined organic layer was filtered through a Celite pad and then dried over $MgSO_4$ under argon atmosphere. The organic material was concentrated under reduced pressure to give the crude product The crude material was dissolved into CH_2Cl_2 (3.0 ml) and then cooled to 0 °C. To an EtOH (10 ml) portion was added dropwise the cooled solution at 0 °C. The resulting suspension was stirred for 1 h at 0 °C. Then the precipitates were washed with three 5.0 ml portions of EtOH and dried in vacuo at 80 °C for 5 h to give pure **1** (633 mg, 85% yield): m.p. 81.5–83.5 °C $[\alpha]_D^{21}$ -13.29 (c 0.54, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 3.02 (br s, 2H), 6.73 (d, 1H, $J = 8.3$ Hz), 6.83–6.89 (m, 2H), 6.95–7.35 (m, 23H), 7.41–7.49 (m, 2H), 7.76–7.88 (m, 4H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -15.29 (d, $J = 4.6$ Hz), -14.34 (d, $J = 4.6$ Hz). HRMS (EI) calc. for $C_{45}H_{34}P_2$ 636.2135 (M +), found 636.2087.

2.5. General procedure for asymmetric hydrogenation of α-alkylstyrenes catalyzed by Rh(I)–1 complex

A solution of 2-phenyl-1-butene (**4a**) (155 mg, 1.17 mmol) in MeOH (5.0 ml) and benzene (5.0 ml) was degassed by three freeze–thaw cycles. This solution was transferred to a mixture of $[RhCl(cod)]_2$ (2.9 mg, 0.0060 mmol) and **1** (9.0 mg, 0.014 mmol). After the resulting yellow solution was degassed by three freeze–thaw cycles, it was transferred into an 50 ml autoclave and then stirred at 30 °C under hydrogen pressure (25 atm) for 24 h. The conversion was determined by ^1H NMR analysis of crude product. After evaporation of the solvent, bulb-to-bulb distillation afforded pure 2-phenylbutane (**5a**).

Enantiomeric excesses of **5c**, **5e**, **5f**, and **5g** were determined by GLC analysis using a chiral capillary column (Chrompack Cyclodex β-236M).

Optical purities of **5a**, **5b**, and **5d** were determined based on the following optical rotation values: (S)–**5a**: $[\alpha]_D$ +28.4 (c 1.00, 95% EtOH) [11]; (S)–**5b**: $[\alpha]_D^{26}$ +10.7 (neat) [17]; (R)–**5d**: $[\alpha]_D^{23.5}$ -20.4 (c 1.27, MeOH) [18].

3. Results and discussion

First, we tried to synthesize (R)-2-diphenylphosphinomethyl-2′-diphenylphosphino-1,1′-binaphthyl (**1**) starting from (R)-2-diphenylphosphinyl-2′-hydroxymethyl-1,1′-binaphthyl [16]. [3] The latter compound was converted to the corresponding mesylate, and then this was treated with $LiPPh_2$. The desired compound, (R)-2-diphenylphosphinomethyl-2′-diphenylphosphinyl-1,1′-binaphthyl was obtained in only low yield (10–20% yield). Accordingly, bisphosphine **1** was synthesized from 2-dimethylaminomethyl-2′-diphenylphosphino-1,1′-binaphthyl (**2**), whose preparation had been reported by Hayashi and co-workers [16]. The dimethylamino group of **2**, which was derived from enantiomerically pure 1,1′-binaphthalene-2,2′-diol via several steps, was converted to the quaternary salt with iodomethane after the diphenylphosphino group was oxidized to phosphine oxide. The ammonium salt was treated with lithium diphenylphosphinylide in acetonitrile at reflux temperature to give bisphosphine oxide **3** in 63% yield. Reduction of **3** with a large excess of trichlorosilane and triethylamine in toluene at reflux temperature gave **1** in good yield (Scheme 1). The optical purity of this bisphosphine **1** was not measured because of its air sensitivity. This compound was synthesized from optically pure (R)-2-dimethylaminomethyl-2′diphenylphosphino-1,1′-binaphthyl, and it is known that even 2-diphenylphosphino-1,1′-binaphthyl can be prepared in optically pure form by similar reduction of its phosphine oxide, see Ref. [16]. In the preparation of 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphthyl, its bisphosphine oxide was synthesized from the Arbuzov reaction of optically active 2,2′-bis(bromomethyl)-1,1′-binaphthyl and methyl diphenylphosphinite without racemization, see

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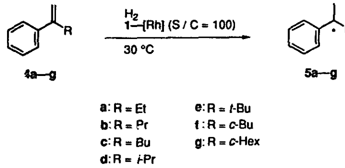
[3] Optically active bisphosphine ligand, 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphthyl was synthesized and applied for asymmetric reactions. This bisphosphine ligand was prepared from optically active 2,2′-bis(bromomethyl)-1,1′-binaphthyl; see Ref. [19].



Scheme 2.

Ref. [19]. Therefore, we think that no racemization happened in the preparation of **1**.

In order to investigate the utility of this ligand for catalytic enantioselective reactions, we carried out asymmetric hydrogenation of relatively simple olefins having no heterofunctionality catalyzed by Rh(I) complexes. Hydrogenation of 2-phenyl-1-butene (**4a**) was carried out at 30°C in the presence of 1.0 mol% Rh(I) catalyst prepared by simply mixing the chiral ligand and Rh(I) precursor in the specified solvent (Scheme 2). The results are summarized in Table 1.

The rates of hydrogenation were slightly dependent on hydrogen pressures (entries 6–8) and the nature of solvents (entries 1–6). Relatively low rates were obtained under lower pressure of hydrogen and with less polar solvent. The nature of the solvent did not seem to have considerable influence on enantioselectivity. In addition, a cationic Rh(I) complex showed very low enantioselectivity (entry 9). A similar tendency was observed in the case of the hydrogenation of unfunctionalized olefin catalyzed by cationic Rh(I)-(*R*)-BINAP complex. (Hydrogenation of 1-methylenetetralin catalyzed by the $[Rh(cod)_2]BF_4$-(*R*)-BINAP system gave the hydrogenated product with the opposite absolute configuration to those obtained with a neutral Rh(I) catalyst derived from $[RhX(cod)]_2$ (X = Cl, Br, I, OAc, OPh) and (*R*)-BINAP, see Ref. [15].) The highest optical yield obtained for **5a** was 65%. To our knowledge this is the highest value ever reported for the hydrogenation of 2-phenyl-1-butene catalyzed by chiral diphosphine complexes of late transition metals [10,11].

Hydrogenation of various other substrates also proceeded smoothly. α-Alkylstyrenes having linear alkyl chain (entries 1, 10, and 11, **4a**–**4c**) were hydrogenated smoothly in relatively high enantioselectivities. In particular, hydrogenation of 2-phenyl-1-pentene (**4b**) proceeded with the highest enantiomeric excess so far reported (entry 10, 77% *ee*). In contrast, α-alkylstyrenes bearing a secondary or tertiary alkyl group were hydrogenated in very low enantiomeric excesses (entries 12–15). Lower enantioselectivities for the substrates with bulky substituents suggest that only steric bulkiness of alkyl substituents exerts an important influence on enantioselectivity. The present catalytic system appears to give higher enantioselectivities for the substrates having linear alkyl chains. Furthermore, hydrogenation of **4a** catalyzed by (*R*)-BINAP-Rh(I) complex proceeded with very low enantioselectivity to give the product with opposite absolute configuration ((*S*)-(+), 29% *ee*) [15]. This result seemed to show that, in the catalytic system of Rh(I) complex containing bisphosphine ligand **1**, the steric control of diphenylphosphinomethyl group of **1** functioned effectively for enantioselectivities. The $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum of a mixture of $[RhCl(cod)]_2$ and **1** in a ratio of 1:2 showed the existence of a major complex and several undefined species at room temperature. The major complex:

Table 1
Asymmetric hydrogenation of α-alkylstyrenes catalyzed by Rh(I)–**1** complexes [a]

Entry	Substrate	Catalyst [b,c]	Solvent	H_2 (atm)	Time (h)	Conversion [d] (%)	*ee* [e] (%)	Configuration [f]
1	**4a**	A	Benzene–MeOH (1:1)	25	24	100	65	(*R*)-(−)
2	**4a**	A	THF	25	24	100	61	(*R*)-(−)
3	**4a**	A	EtOH	25	40	100	65	(*R*)-(−)
4	**4a**	A	THF–MeOH (1:5)	25	24	100	43	(*R*)-(−)
5	**4a**	A	Benzene	25	37	93	63	(*R*)-(−)
6	**4a**	A	CH_2Cl_2	25	24	92	50	(*R*)-(−)
7	**4a**	A	CH_2Cl_2	10	66	78	53	(*R*)-(−)
8	**4a**	A	CH_2Cl_2	1	92	75	47	(*R*)-(−)
9	**4a**	B	EtOH	25	24	100	3	(*R*)-(−)
10	**4b**	A	Benzene–MeOH (1:1)	25	58	100	77	(*R*)-(−)
11	**4c**	A	Benzene–MeOH (1:1)	25	24	100	55	(*R*)-(−)
12	**4d**	A	Benzene–MeOH (1:1)	25	24	100	17	(*R*)-(−)
13	**4e**	A	Benzene–MeOH (1:1)	25	27	75	31	(*R*)-(−)
14	**4f**	A	Benzene–MeOH (1:1)	25	24	100	16	(−)
15	**4g**	A	Benzene–MeOH (1:1)	25	64	100	2	(*R*)-(−)

[a] All reactions were carried out in a 50 ml autoclave under H_2 atmosphere. [b] Prepared by simply mixing Rh precursor and **1** in each solvent. Substrate/[Rh] = 100 mol/mol, **1**/[Rh] = 1.2. [c] A: $[RhCl(cod)]_2$–**1**; B: $[Rh(cod)_2]BF_4$–**1**. [d] As given by ^1H NMR analysis. [e] Determined by optical rotation value or GLC analysis with a Chrompack Cyclodex β-236M capillary column. [f] The absolute configuration was determined by the sign of optical rotation.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 46.31 (dd, $J_{Rh-P} = 198.4$ Hz, $J_{P-P} = 45.8$ Hz), 61.82 (dd, $J_{Rh-P} = 204.5$ Hz, $J_{P-P} = 45.8$ Hz).

Acknowledgements

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