Asymmetric hydrogenation of acrylic acid derivatives by novel chiral rhodium–phosphinediamine complex catalysts by selective ligation between two amino units of the ligand and electrostatic interaction

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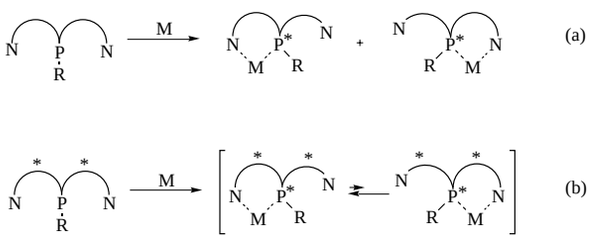
The novel chiral phosphinediamine ligand (PN_2) having two amino units has been readily prepared from (*S*)-1-phenylethylamine derivatives and dichlorophosphine. In the hydrogenation of acrylic acids by a rhodium–PN_2 catalyst, high enantioselectivities were achieved by the effective chiral field formed through selective P-N chelation and electrostatic interaction between the amino unit of the ligand and the carboxy unit of the substrate.

Introduction

Asymmetric reactions have been carried out by using transition metal complex catalysts with a variety of chiral diphosphine ligands.[1] Of the chiral phosphine ligands available, optically active ligands having stereogenic phosphorus atom(s) are very effective for asymmetric reactions; for example, a rhodium–diPAMP catalyst achieved high enantioselectivities in the asymmetric hydrogenation of didehydro amino acids.[2] However, most of these ligands have problems of synthesis associated with them.[3] We were interested therefore in designing novel chiral ligands which are readily prepared and have a latent chiral phosphorus atom in the molecule.

When a phosphinediamine ligand having two identical amino units on the phosphorus atom chelates as a bidentate ligand to a metal through its phosphorus and nitrogen atoms, the former atom becomes a chiral centre [Scheme 1(a)]. However, the chiral



Scheme 1

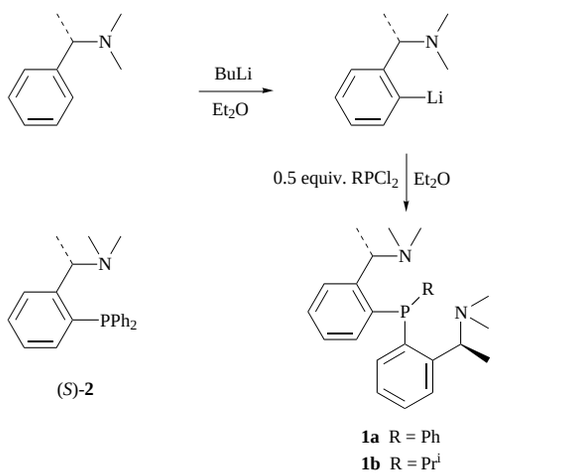
complexes are obtained as a racemic mixture. When chirality is introduced into the two side arms on the phosphorus atom, two stereoisomers become diastereoisomeric, and the ratio of the two diastereoisomeric complexes may be unequally biased [(Scheme 1(b)]. By introducing either an appropriate chiral carbon centre or molecular asymmetry, selective ligation between the two amino groups becomes possible and the phosphorus atom will become stereogenic to afford an effective chiral field. In addition, the uncoordinated amino group in the ligand may interact electrostatically with the reactants having a carboxy group, *e.g.* acrylic acids.[4] Therefore, effective chiral discrimination may be expected from a chiral phosphorus atom together with electrostatic interaction. To the best of our knowledge, no attempt has been made to create the chiral field described above.[5]

In this paper, we report the coordination properties of the novel bidentate ligands, (*S*,*S*)-alkylbis[2-(1-*N*,*N*-dimethylaminoethyl)phenyl]phosphines (PN_2), which have been readily prepared, together with their application as rhodium–PN_2 complexes to the asymmetric hydrogenation of acrylic acids.

Results and discussion

Synthesis of PN_2 ligands

The novel (*S*,*S*)-PN_2 ligands, (*S*,*S*)-**1a** and -**1b**,[6] were readily prepared in two steps; *o*-lithiation of (*S*)-*N*,*N*-dimethyl-1-phenylethylamine followed by reaction of the product with dichloroisopropylphosphine or dichlorophenylphosphine (Scheme 2).



Scheme 2 Phosphinediamine ligands **1a**, **1b** and phosphineamine ligand **2**

Structure of the rhodium–PN_2 complexes in solution

The structure of the rhodium–PN_2 complexes was investigated by comparing it with that of the rhodium complex of (*S*)-[2-(1-*N*,*N*-dimethylaminoethyl)phenyl]diphenylphosphine[7] **2**; the latter coordinates to transition metals, such as nickel, platinum, rhodium and palladium, as a P–N bidentate ligand.[8] The rhodium complexes, [Rh{(*S*,*S*)-PN_2}(nbd)]BF_4 and [Rh{(*S*)-**2**}(nbd)]BF_4 (nbd = bicyclo[2.2.1]hepta-2,5-diene) were prepared *in situ* from (*S*,*S*)-PN_2 or (*S*)-**2** and [Rh(nbd)$_2$]BF_4. The configuration of the rhodium–PN_2 complexes in solution was examined by CD and NMR spectroscopy.

The $^{31}P\{^1H\}$ NMR spectrum of [Rh{(*S*)-**2**}(nbd)]BF_4 in methan[$^2H_1$]ol showed a doublet at 23.5 ppm (Table 1, entry 1).[9] For the rhodium–PN_2 complex [Rh{(*S*,*S*)-**1a**}(nbd)]BF_4, two

doublets for the ^{31}P signals were observed at *ca.* 24 ppm (J = 172 Hz) and 29 ppm (J = 169 Hz), and these signals were assigned to two diastereoisomeric complexes from the coupling constants (entry 2). The ratio of the diastereoisomers (93 : 7) indicates that selective ligation of the amino group occurs. For the [Rh{(*S*,*S*)-**1b**}(nbd)]BF_4 complex, similar diastereoisomeric species were observed with different intensities (75 : 25) (entry 3).

Assignment of the proton signals for the major diastereoisomer of the rhodium–PN_2–nbd complexes was achieved by 2D-COSY and NOE measurements. The ^{1}H NMR spectra of the rhodium–PN_2–nbd complex indicated that the PN_2 behaves as a bidentate ligand by P–N chelation: methyl protons for the two amino units appeared with different chemical shifts. The proton signal for the two methyl groups of the lower-field amino unit (*ca.* 2.6 ppm) was split[10] at 0 °C while the methyl proton signal for the upper-field amino unit (*ca.* 2 ppm) remained as a singlet with almost the same chemical shift as that of free PN_2 ligand or ligand **2** (Table 2, entries 1, 4, 5, 7, 8). The chemical shifts for the *N*-CH_3 groups of [Rh{(*S*)-**2**}(nbd)]BF_4 were almost the same as those of coordinated *N*-CH_3 groups of the rhodium–PN_2 complexes (Table 2, entries 2, 5, 8). These results indicate that the rhodium–PN_2 complexes exist as two diastereoisomers in methanol with the PN_2 ligands coordinated in a bidentate fashion to rhodium by the P and N units through the nearly selective ligation of the amino group in the PN_2 ligand.

An X-ray study of a phosphineamine complex was used to investigate the conformation of the rhodium–PN_2 complexes. The rhodium complex of (*S*)-[2-(1-*N*,*N*-dimethylaminoethyl)-phenyl]bis(1,1-dimethylethyl)phosphine, an analogue of (*S*)-**2**, was shown to have a P–N chelate ring in a twisted boat conformation with an absolute configuration of λ and an axial *C*-methyl group.[8] The rhodium–(*S*)-**2** complex in solution would also exist in a twisted boat conformation with an absolute configuration of λ. The CD spectra of the rhodium–PN_2 complexes [rhodium–(*S*,*S*)-**1a** and rhodium–(*S*,*S*)-**1b**] indicated a clear positive Cotton effect at *ca.* 340 and 435 nm similar to that of the rhodium–(*S*)-**2** complex in methanol (Fig. 1). Therefore, the rhodium–(*S*,*S*)-PN_2 complexes are considered to have the twisted boat conformation with an absolute configuration of λ.

The rhodium–(*S*,*S*)-**1** complexes exist as two diastereoisomeric species having a stereogenic phosphorus atom (Fig. 2). The structure of the major isomer was analysed by various NOE techniques. In its NOESY spectra, a correlation between one of the methyl groups of the coordinated amino unit and the methine proton of the uncoordinated phenylethylamine unit was observed (Fig. 3); no correlation was observed between the proton of the coordinated *N*-CH_3 and *C*-CH_3 proton of the free phenylethyl unit. On the basis of these results, the major diastereoisomer is concluded to exist as form **A**, the

Table 1 ^{31}P{^{1}H} NMR spectral data for rhodium complexes

Entry	Ligand	Ratio	δ(ppm)	$J_{Rh,P}$/Hz
1	(*S*)-**2**	—	23.5	174
2	(*S*,*S*)-**1a**	93	24.4	172
		7	29.0	169
3	(*S*,*S*)-**1b**	75	24.5	177
		25	27.1	163

[a] The ratio of integration of diastereotopic ^{31}P signals.

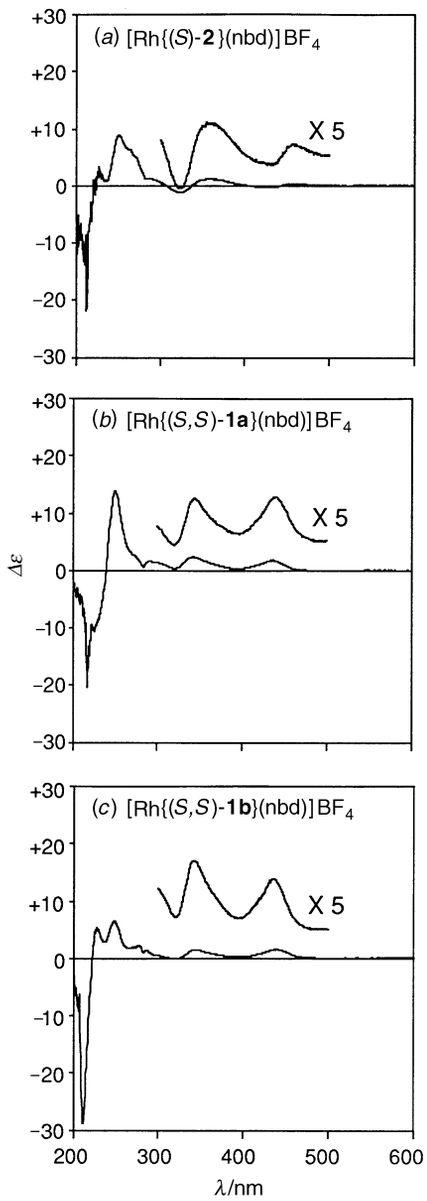


Fig. 1 Circular dichroism spectra of the rhodium complexes

Table 2 ^{1}H NMR spectral data for the ligands and their rhodium complexes[a]

			δ_H (ppm)[c]					
			Coordinated unit			Free unit		
Entry	Ligand	M[b]	*N*-CH_3	CH_3	CH	*N*-CH_3	CH_3	CH
1	**2**	—	—	—	—	2.09	1.15	4.19
2		Rh	2.61, 2.63	1.72	3.68	—	—	—
3[d]		Rh	2.61, 2.63	1.72	3.68	—	—	—
4	**1a**	—	—	—	—	2.19, 2.20	1.08, 1.12	4.07, 4.20
5		Rh	2.59, 2.69	1.38	3.60	2.02	1.97	3.30
6[d]		Rh	2.59, 2.69	1.38	3.60	2.15	2.03	3.50
7	**1b**	—	—	—	—	2.15, 2.24	0.89, 1.35	4.16, 4.26
8		Rh	2.55, 2.65	1.80	3.78	1.96	1.92	2.95

[a] 270 or 400 MHz in CD_3OD. [b] In the presence of [Rh(nbd)$_2$]BF_4. [c] Chemical shifts of two 2-(1-*N*,*N*-dimethylaminoethyl)phenyl units. [d] In the presence of 2-methylcinnamic acid (4 equiv.).

chiral phosphorus atom of which has the absolute configuration *S* (Fig. 2).

Since the uncoordinated amino group of the rhodium–PN_2 complexes could induce an electrostatic interaction with the carboxy group of an acrylic acid derivative when used as a hydrogenation substrate, this possibility was examined for cinnamic acid, the change of chemical shift of the free *N*-methyl group being examined. The proton signals of *N*-CH_3, *C*-CH_3 and CH units of the free 2-(1-*N*,*N*-dimethylaminoethyl)phenyl group of the rhodium–**1a** complex showed downfield shifts in the presence of cinnamic acid (Table 2, entry 6), while the chemical shift of the coordinated amino unit was unchanged for both rhodium–**1a** and rhodium–**2** complexes (Table 2, entries 3, 6). Thus, for the rhodium–PN_2 complexes, the selective ligation leaves one amino group free to serve as an interactive unit with a functional group, such as a carboxy group, in suitable substrates; this induces asymmetric hydrogenation.

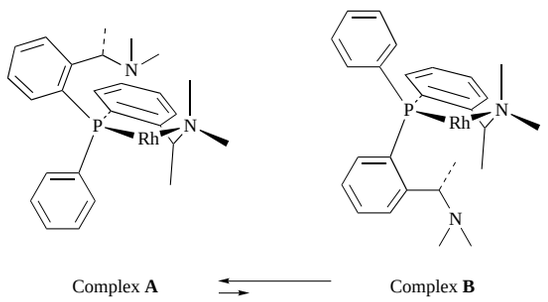


Fig. 2 Two diastereoisomeric rhodium (*S*,*S*)-**1a** complexes with a stereogenic phosphorus atom

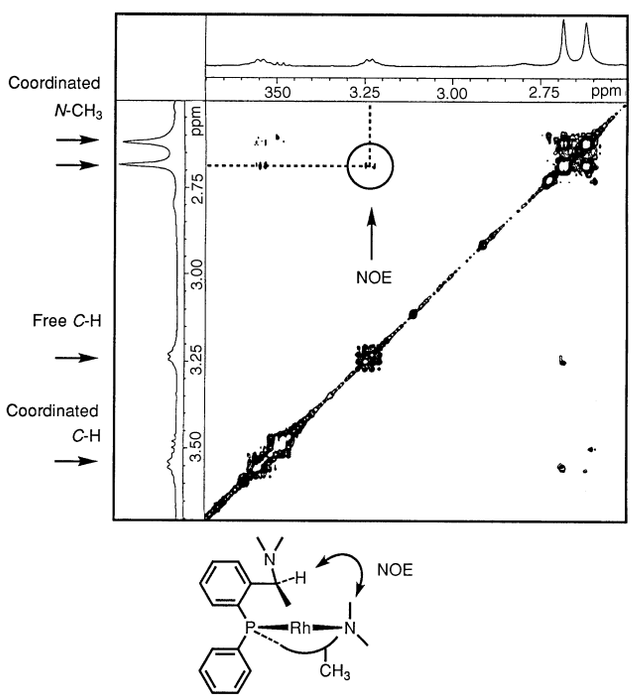


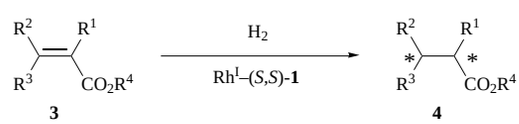
Fig. 3 ^{1}H 2D-NOESY spectrum of the rhodium–**1a** complex showing the NOEs derived from the interaction between one of the protons of the coordinated *N*-CH_3 and free *C*-H (400 MHz, $CDCl_3$)

Asymmetric hydrogenation of acrylic acid derivatives

The asymmetric hydrogenation of acrylic acid derivatives **3** (Fig. 4) was examined using **1a** or **1b** as the ligand, the results for which are summarized in Tables 3–6.

In the asymmetric hydrogenation of **3a** by the 2 mol% rhodium–PN_2 catalyst, the rhodium–**1b** complex effectively catalysed the hydrogenation, while with the rhodium–**1a** complex the substrate was recovered unchanged (Table 3, entries 1 and 2). This suggests that an increase of electron density on the phosphorus atom of the PN_2 ligand accelerates the hydrogenation.[11] The asymmetric hydrogenation of **3a** by the rhodium–**1b** complex gave the highest enantioselectivity at a ligand to rhodium molar ratio of 1.5:1 (Table 3, entries 2–4).

The enantioselectivities obtained here with the ligand **1b** are much higher than those obtained by rhodium–diphosphine catalysis, although with a ruthenium–BINAP catalyst high selectivity (89% ee) was reported.[12] It is to be noted that the enantioselectivity by rhodium–**1b** catalyst indicated a bell-shaped dependency on the hydrogen pressure, and the highest enantioselectivity (92% ee) being obtained at a hydrogen pressure of 40 atm (Table 3, entries 3, 5–7). In the case of tiglic acid **3b**, a similar dependency on the hydrogen pressure was observed (entries 8–10) to give 75% ee at 40 atm.[13] For many chiral rhodium catalysts, an increase in the hydrogen pressure causes a corresponding decrease in the enantioselectivity resulting, finally, in an inversion of the asymmetric induction.[14] The effect of hydrogen pressure observed here for the rhodium–**1b** catalyst is uncommon for rhodium catalysts and worthy of further examination.



3 **4**

Substrate	R^1	R^2	R^3	R^4
3a	Me	Ph	H	H
3b	Me	Me	H	H
3c	Me	2-Thienyl	H	H
3d	Me	3-Thienyl	H	H
3e	Me	1-Naphthyl	H	H
3f	Me	2-Naphthyl	H	H
3g	Et	Ph	H	H
3h	Me	H	Me	H
3i	H	Ph	Me	H
3j	Me	Ph	H	Me

Fig. 4 Asymmetric hydrogenation of acrylic acid derivatives

Table 3 Asymmetric hydrogenation of **3a** and **3b** using a rhodium catalyst*

Entry	Substrate	Ligand	L/Rh[a]	*p*/MPa[b]	*t*/h	Conv.[c] (%)	% ee[d]
1	**3a**	(*S*,*S*)-**1a**	1.1	2	25	~0	—
2		(*S*,*S*)-**1b**	1.1	2	57	75	63 (*R*)
3			1.5	2	120	100	84 (*R*)
4			2.0	2	156	100	77 (*R*)
5			1.5	4	86	100	92 (*R*)
6			1.5	6	35	47	81 (*R*)
7			1.5	8	48	100	77 (*R*)
8	**3b**	(*S*,*S*)-**1b**	1.5	1	240	100	48 (*S*)
9			1.5	2	94	100	75 (*S*)
10			1.5	6	108	100	67 (*S*)

* Reaction conditions; reaction temperature: 25 °C, solvent: methanol, catalyst precursor: $[RhCl(nbd)]_2$. [a] Molar ratio. [b] 101 325 Pa = 1 atm. [c] Conversion was determined by ^{1}H NMR. [d] Enantiomeric excess was determined by ^{1}H or ^{13}C NMR spectroscopy with (*R*)-1-phenylethylamine in $CDCl_3$, and the absolute configuration was determined by the sign of the optical rotation.

Table 4 Asymmetric hydrogenation of acrylic acid derivatives using a rhodium–(*S*,*S*)-**1b** catalyst*

Entry	Substrate	*p*/MPa	*t*/h	Conv. (%)	% ee
1	**3c**	4	96	100	65 (−)
2	**3d**	4	110	100	88 (−)
3	**3e**	4	120	49	65 (*R*)
4	**3f**	4	72	62	66 (*R*)
5	**3g**	4	110	100	77 (−)
6	**3h**	2	132	13	<1
7	**3i**	2	187	17	49 (*R*)
8	**3j**	2	120	6	—
9[a]	**3a**	8	43	100	59 (*R*)
10[a]	**3j**	8	88	17	42 (*R*)

* Reaction conditions: reaction temperature: 25 °C, solvent: methanol, catalyst precursor: $[RhCl(nbd)]_2$. The ratio of ligand : rhodium was 1.5 : 1. [a] Reaction was carried out at 40 °C.

Table 5 Effect of solvent polarity on the enantioselectivities of asymmetric hydrogenation of acrylic acid derivatives using a rhodium–(*S*,*S*)-**1b** catalyst *

Entry	Substrate	Solvent	*t*/h	Conv. (%)	% ee
1	**3a**	Methanol–H_2O[a]	216	100	68 (*R*)
2		Methanol	120	100	84 (*R*)
3		Ethanol	122	18	63 (*R*)
4		Propan-2-ol	164	37	17 (*S*)
5	**3b**	Methanol–H_2O[a]	240	100	44 (*S*)
6		Methanol	94	100	75 (*S*)
7		Ethanol	215	100	40 (*S*)
8		Propan-2-ol	240	100	12 (*R*)

* Reaction conditions: reaction temperature: 25 °C, hydrogen pressure: 2 MPa, catalyst precursor: $[RhCl(nbd)]_2$. The molar ratio of ligand : rhodium was 1.5 : 1. [a] Methanol–H_2O, 4 : 1 (v/v).

Table 6 Effect of addition of triethylamine on enantioselectivities of asymmetric hydrogenation of acrylic acids using a rhodium–(*S*,*S*)-**1b** catalyst *

Entry	Substrate	NEt_3/Rh ratio[a]	*t*/h	Conv. (%)	% ee
1	**3a**	1 : 1	120	100	56 (*R*)
2		2 : 1	120	100	37 (*R*)
3	**3b**	2 : 1	120	100	65 (*R*)

* Reaction conditions: reaction temperature: 25 °C, hydrogen pressure: 2 MPa, solvent: methanol, catalyst precursor: $[RhCl(nbd)]_2$. The molar ratio of ligand : rhodium was 1.5 : 1. [a] The molar ratio.

The asymmetric hydrogenation of other (*E*)-2-methylacrylic acids **3c-g** gave modest to good enantioselectivities (Table 4, entries 1–5). For the acrylic acids with a methyl group *cis* to the carboxy group at the β-position the reaction was slow. In the case of angelic acid **3h**, the reaction was extremely slow and the hydrogenation product was racemic (entry 6).[15] For 3-methylcinnamic acid **3i**, the reaction was extremely slow and the enantioselectivity correspondingly low (49% ee) (entry 7).[16] These results suggest that this rhodium–**1b** catalyst is specific to the structure of the substrate.

Electrostatic interaction

For the ester of **3a**, methyl 2-methylcinnamate **3j**, the reaction was extremely slow and the enantioselectivity was low compared with that of **3a** (Table 4, entries 8–10). This difference strongly suggests the participation of electrostatic interaction between the ligand **1b** and the substrate **3a** for the incorporation of substrate and the asymmetric induction.

The electrostatic interaction in solution would be affected by the solvent polarity, since the ease of ionization of the amino and carboxy groups and the stability of the ion-pair in solution are dependent on the solvent polarity. The bell-shaped dependency of the enantioselectivity on the solvent polarity was observed as expected for the systems of **3a** and **3b** in which the

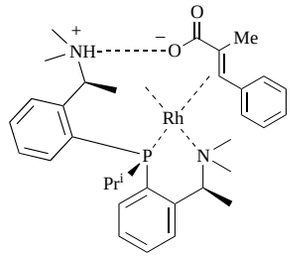


Fig. 5 Proposed structure in catalyst system

electrostatic interaction is possible (maximum enantioselectivity was obtained in methanol; 84 and 75% ee, Table 5).[17] The effect of the added amine also supported the contribution of the electrostatic interaction between the rhodium–**1b** complex and the substrate. The enantioselectivity of the asymmetric hydrogenation of **3a** and **3b** by the rhodium–**1b** catalyst decreased with an increasing amount of triethylamine in methanol (Table 6). The electrostatic interaction between substrate and added amine would compete with the electrostatic interaction in the rhodium–**1b**–substrate complex. It is concluded that the electrostatic interaction enables the multi-site recognition of the substrate by the rhodium–PN_2 complex to afford high stereoselectivity (Fig. 5).

Conclusion

The asymmetric hydrogenation of acrylic acid derivatives using the rhodium–**1b** catalyst gave high or good selectivities (up to 92% ee). The high selectivity by the rhodium–**1b** catalyst may be attributed to the effective chiral field formed by the selective ligation between two amino units of the ligand, and to the multi-site recognition of the substrate by the electrostatic interaction between the free amino unit of the ligand and substrate.

Experimental

General procedure

^1H and ^{31}P NMR spectra were recorded on a JEOL EX-270 or JEOL LA-400 spectrometers, with tetramethylsilane (Me_4Si) as an internal standard and 85% H_3PO_4 as an external standard, respectively. *J* Values are given in Hz. Mass spectra were obtained with a JEOL LX-1000 instrument with a fast atom bombardment ionization method. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyser. Column chromatography was carried out on silica gel (Merck, 230–400 mesh) using ethyl acetate–hexane as eluent. $[\alpha]_D$ Values are recorded as 10^{-1} deg cm^2 g^{-1}.

Preparation of (*S*,*S*)-alkylbis[2-(1-*N*,*N*-dimethylaminoethyl)-phenyl]phosphines 1a and 1b

(*S*)-*N*,*N*-Dimethyl-1-phenylethylamine (8.3 g, 55.6 mmol) was dissolved in dry, freshly distilled diethyl ether (60 ml), and BuLi in hexane (1.6 M; 34 ml) was added to the solution. The mixture was stirred for 24 h at 25 °C and then cooled to 0 °C when $RPCl_2$ (R = Ph or Pr^i) (27.8 mmol) was added to it slowly. The mixture was stirred for 24 h after which it was diluted with water (20 ml) and cooled. The organic layer was separated and the aqueous phase was extracted with diethyl ether (3 × 50 ml). The combined organic phase and extracts were dried ($MgSO_4$) and evaporated and the residue was dissolved in diethyl ether and the solution filtered. The ligand was purified by column chromatography. Evaporation under reduced pressure gave the phosphinediamine ligand (**1a** 35%, **1b** 32%).

(*S*,*S*)-Bis[2-(1-*N*,*N*-dimethylaminoethyl)phenyl]phenylphosphine 1a

A highly viscous oil (Found: C, 77.25; H, 8.09; N, 6.90. Calc. for $C_{26}H_{33}N_2P$: C, 77.20; H, 8.22; N, 6.92%); δ_H(270 MHz, $CDCl_3$) 1.04 (3 H, d, CH*Me*), 1.16 (3 H, d, CH*Me*), 2.14 (12 H, s,

NMe), 3.98 (1 H, m, CH), 4.11 (1 H, m, CH) and 6.80–7.62 (13 H, m, ArH); $\delta_P\{^1H\}$(109 MHz, $CDCl_3$) −28.9; *m/z* (FAB) 405 [$(M + 1)^+$]; $[\alpha]_D^{21}$ −41 (*c* 0.20 in EtOH).

(*S*,*S*)-Isopropylbis[2-(1-*N*,*N*-dimethylaminoethyl)phenyl]-phosphine 1b

A highly viscous oil (Found: C, 74.61; H, 9.51; N, 7.22. Calc. for $C_{23}H_{35}N_2P$: C, 74.56; H, 9.52; N, 7.56%); δ_H(270 MHz, $CDCl_3$) 0.89 (3 H, d, CH*Me*), 1.00 (3 H, dd, CH*Me*), 1.13 (3 H, dd, CH*Me*), 1.35 (3 H, d, CH*Me*), 2.15 (6 H, s, NMe), 2.24 (6 H, s, NMe), 2.40 (1 H, m, CH), 4.16 (1 H, m, CH), 4.26 (1 H, m, CH) and 7.06–7.60 (8 H, m, ArH); $\delta_P\{^1H\}$(109 MHz, $CDCl_3$) −29.0; *m/z* (FAB) 371 [$(M + 1)^+$]; $[\alpha]_D^{21}$ −101 (*c* 0.23 in EtOH).

Asymmetric hydrogenation of acrylic acids

The catalyst solution, prepared from $[RhCl(nbd)]_2$ and the ligand **1** or **2** in absolute alcohol, was transferred with a fine stainless steel tube to a hydrogenation vessel containing acrylic acids. The substrate–catalyst solution was stirred under nitrogen for 1 h, after which hydrogen gas was introduced. After the reaction, the rhodium catalyst was removed with DOWEX 50 cation-exchange resin. The enantiomeric excess was determined by ^1H or ^{13}C NMR spectral measurement made in the presence of (*R*)-1-phenylethylamine, the signals of the diastereotopic methyl protons or the methyl or methylene carbon of the salt of the hydrogenated products, being integrated. The absolute configurations of the chiral acids were determined from the sign of optical rotation.[18]

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11 Using a phosphinediamine ligand in which a *p*-methyl substituent was introduced into the phenyl units of the ligand **1b**, the reaction was faster and the selectivity was higher than with **1b**. For 2-methylcinnamic acid under the conditions of 60 atm and 25 °C, the enantioselectivity was 90% ee while **1b** gave 81% ee.

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