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2,2′-BIS(DIPHENYLPHOSPHINO)-1,1′-BINAPHTHYL (BINAP)

A NEW ATROPISOMERIC BIS(TRIARYL)PHOSPHINE. SYNTHESIS AND ITS USE IN THE Rh(I)-CATALYZED ASYMMETRIC HYDROGENATION OF α-(ACYLAMINO)ACRYLIC ACIDS

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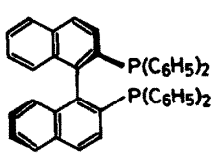
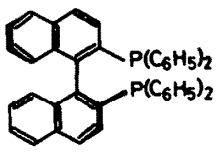
Abstract—Racemic 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl has been synthesized from 2,2′-dihydroxy-1,1′-binaphthyl in two steps and resolved into optically pure (*R*)-(+) and (*S*)-(-) enantiomers by the use of (+)-di-μ-chlorobis[(*S*)-N,N-dimethyl-α-phenylethylamine-2C,N] dipalladium. This new axially dissymmetric bis(triaryl)phosphine serves as an excellent ligand for Rh(I)-catalyzed asymmetric hydrogenations of α-(acylamino) acrylic acids or esters. Factors controlling the enantioselectivity and mechanistic aspects are discussed on the basis of the ^{31}P-NMR measurements.

Much effort has been continued to develop asymmetric reactions with stereoselectivity as high as that of enzymes. An established way to accomplish an asymmetric catalytic reaction is based on a creation of chiral centers under the influence of transition metal complexes bearing chiral organic ligands.[1] The molecular designing and synthesis of new effective chiral ligands are, therefore, the most important requirements for developing useful asymmetric catalysis. Recently, chiral bis-t-phosphine ligands have attracted much attention and a variety of unique diphosphines have so far been prepared.[1] The high efficiency of diphosphines as chiral ligands for asymmetric reactions is attributable, at least in part, to the ability that they form stable metal-containing chelate rings whose dissymmetric structures of the complexes are retained throughout the reactions. Since most catalysts exhibit both reaction and substrate specificity, we have to adopt catalytic systems most suitable for each reaction. Hence it is necessary for us to exert continuous efforts to develop new effective chiral ligands.

We have taken a deep interest in 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (hereafter abbreviated to BINAP).[2] This bis(triaryl) phosphine, contrary to most reported tertiary phosphines whose chirality is centered at an asymmetric P atom or chiral C moieties, has only an axial element of chirality[3,4] and possesses numerous salient structural features. First, BINAP is a fully aryl-substituted diphosphine. Second, the free ligand is conformationally flexible and can accommodate a wide variety of transition metals through proper rotation about binaphthyl C(1)–C(1′) pivot. Third, because this bidentate ligand contains only sp^2-hybridized C atoms, such induced-fit complexation with a metal gives rise to a pliant but structurally unambiguous 7-membered chelate ring. Fourth, the presence of a C_2 axis in the binaphthyl moiety can halve the number of possible diastereomeric intermediates involved in the catalytic process.[5] We report here full details of successful preparation of the new chiral diphosphine **1** and its use in Rh(I)-catalyzed asymmetric hydrogenation of α-(acylamino)acrylic acids.



(*R*)-1



(*S*)-1

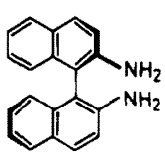
RESULTS AND DISCUSSION

Preparation of BINAP ligands

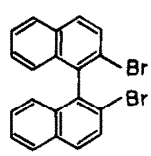
A long-standing problem in synthetic chemistry of biaryl compounds having functionalities at C(2) and C(2′) positions lies in the extreme difficulty in stereospecific conversion of the chiral atropisomeric structures with retention of configuration. This is also the case in the preparation of BINAP. The easily accessible optically pure diamine,[6] (*R*)-(+)-**2** [$[\alpha]_D^{21}$ + 152° (*c* 1.4, pyridine)], seemed to be an attractive starting material for the synthesis of chiral BINAP, but the attempted conversion to the dibromide (*R*)-**3** under the standard Sandmeyer conditions ($NaNO_2$ and CuBr) resulted in considerable racemization. Furthermore, even when we started with optically active **3** [m.p. 145–146°, $[\alpha]_D^{18}$ + 32.5° (*c* 3.4, pyridine)], its dilithiation with t-BuLi at −90° in THF followed by reaction with diphenylphosphinous chloride led to optically inactive or only feebly active diphosphine **1**. In some cases, optically pure (*R*)-**1** can be isolated after repeated recrystallization but in only very low

yield[5–10%, $[\alpha]_D^{19} + 217°$ (*c*2.0, benzene)] and the result was not reproducible.

The failure in the asymmetric preparation of BINAP led us to resolution of the racemate. Racemic BINAP was most conveniently prepared from 2,2′-dihydroxy-1,1′-binaphthyl (**4**). Heating a mixture of **4** and dibromotriphenylphosphorane without solvent at 300–320° afforded **3**.[7] Treatment of **3** with 4 equiv of t-BuLi in THF at −95° followed by exposure of the resulting dilithio derivative to 4 equiv of diphenylphosphinous chloride afforded racemic diphosphine **1** as colorless crystals in 78% yield. Dilithiation of **3** can be conveniently performed by the addition of 2.5 equiv of n-BuLi in THF at −60°. Subsequent addition of 2.5 equiv of diphenylphosphinous chloride afforded (±)-**1** in 70% yield The optically active diphosphines, (*R*)-**1** and (*S*)-**1**, could be obtained by the optical resolution technique using the chiral amine–Pd(II) complex **5** as a resolving agent.[8,9] Addition of a solution of (±)-**1** in benzene to an equimolar amount of **5** in the same solvent afforded a diastereomeric mixture of the complex **6**, which was converted to **7** in quantitative yield by treatment with sodium tetraphenylborate. Fractional recrystallizations from a mixture of dichloromethane, ethyl acetate, and benzene and then from a mixture of dichloromethane and ether afforded the Pd(II) complexes of (*R*)-**1** and that of (*S*)-**1** [(*R*)-**7** and (*S*)-**7**][10] in 39 and 36% yields, respectively, based on (±)-**7**. Finally, reductive decomposition of each diastereomer with lithium aluminum hydride in ether at 0° gave after recrystallization from a 1:1 mixture of benzene and ethanol pure (*R*)-(+)-**1** [m.p. 240–241°, $[\alpha]_D^{25} + 229°$ (*c*0.32, benzene)] and (*S*)-(−)-**1** [m.p. 241–242°, $[\alpha]_D^{25} - 229°$ (*c*0.31, benzene)] in 75–82% yield. Thus this method allows the ready, preparative-scale synthesis of both enantiomers of a new type of diphosphine, BINAP, in an optically pure state.



(*R*)-2



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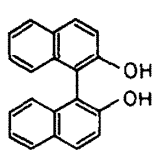

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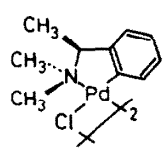

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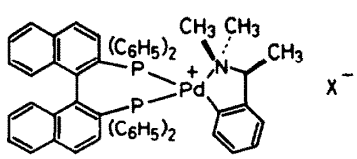


6, X = Cl

7, X = $B(C_6H_5)_4$

Synthesis of Rh-BINAP complexes

Molecular structure of [Rh((R)-*binap*) (*norbornadiene*)]ClO_4 [(R)-8]. Treatment of [Rh(nbd)] ClO_4 (nbd = norbornadiene) with an equimolar amount of (+)-BINAP in dichloromethane at room temperature followed by purification by recrystallization from methanol afforded [Rh((+)-binap) (nbd)]ClO_4 [(*R*)-**8**] in 84% yield. We have carried out the X-ray crystal structure analysis of [(*R*)-**8**].[11] A perspective drawing of the complex is shown in Fig. 1. The absolute configuration of the dextrorotatory phosphine ligand in this complex was determined to be *R*. The Rh(I) atom has nearly square planar structure and is coordinated by two P atoms and two C=C bonds of norbornadiene. The 7-membered chelate ring is fixed to λ-skew(v) conformation. This dissymmetry determines the stereochemistry of the four phenyl rings on the P atoms, which are arrayed in an alternating edge-face manner.[12] The angle between the least-squares planes through the two naphthyl groups is 74.31°.

Catalysts for asymmetric hydrogenations. First, we found that two kinds of Rh complexes form by reaction of hydrogen and a cationic Rh(I)–diene complex containing a chelating BINAP ligand. In methanol, the complex [Rh((*S*)-binap) (nbd)] ClO_4 [(*S*)-**8**] reacted rapidly with exactly 2.0 mol equiv of hydrogen at room temperature to produce norbornane and two Rh complexes, (*S*)-**9a** and **10** in a

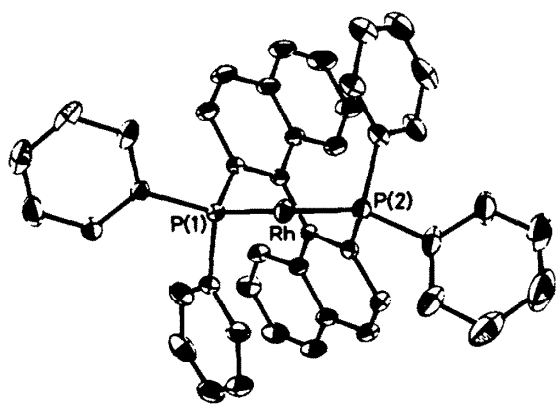
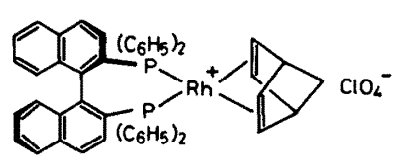
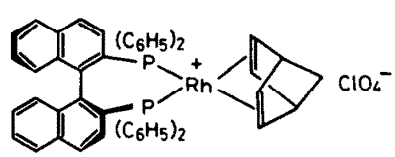


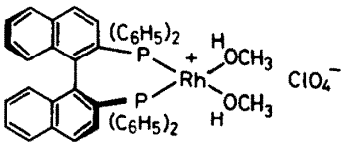
Fig. 1. Molecular structure of [Rh((*R*)-(+)-binap) (norbornadiene)]ClO_4 (**8**). Norbornadiene and perchlorate ion were omitted for simplicity.



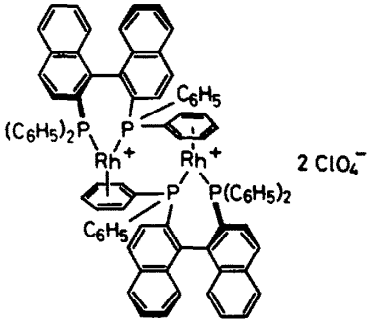
(*R*)-8



(*S*)-8



(S)-9a



10

ratio of 9:1. The major, methanol-soluble complex was isolated as deep red prisms and characterized by ^1H and ^{31}P NMR spectra. This methanol-coordinated complex was stable for a long period at −20° under argon but lost methanol *in vacuo* at room temperature to produce an air-sensitive [Rh((*S*)-binap)]ClO_4 [(*S*)-**9b**], which reverted to (*S*)-**9a** in methanol. The ^1H NMR spectrum of (*S*)-**9b** in CD_2Cl_2 resembles closely that of (*S*)-**9a** but lacks the signals due to methanol. The minor complex **10** was virtually insoluble in methanol and was isolated as brown solid. The ^1H NMR of **10** in CD_2Cl_2 exhibited only signals due to the BINAP ligand, showing a quite different pattern from those of **8**, **9a** and **9b**. Among the four multiplet signal groups observed at δ6.05, 6.55, 6.90 and 7.48, the high-field signal centered at δ6.05 could be assigned to protons of the phenyl group in the BINAP ligand interacted with the second Rh atom through π-arene coordination,[13] which supports the dinuclear structure **10**. NMR analysis revealed that no noticeable amount of rhodium hydride species was formed under these conditions; no further hydrogen uptake was observed either.

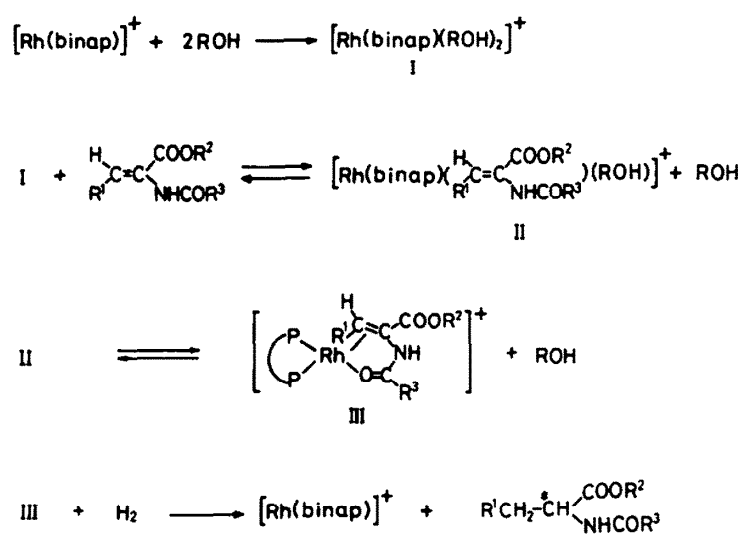
Asymmetric hydrogenations of α-acylaminoacrylic acids catalyzed by Rh(I)*–BINAP complexes*

Results. The methanol-incorporated complex **9a** as well as the methanol-free complex **9b** act as an excellent catalyst for the asymmetric hydrogenation of prochiral α-(acylamino)acrylic acids and esters. The results are given in Table 1. The reaction was generally run with 0.01–0.03 M solution of substrate in ethanol, or THF for configurationally labile *E* substrate,[14] at room temperature under an initial H_2 pressure of 3–4 atm. The olefinic substrate to Rh ratio was 100:150. The optical purity of the products was determined by careful comparison of the rotation values with those of authentic pure samples when they are available.

Following characteristic features have been noted through the asymmetric hydrogenations. (1) The optical yield is sensitive to the substitution pattern of prochiral olefinic substrates. The reaction of α-(acylamino)cinnamic acids (particularly benzamido derivatives), regardless of the double bond configuration, proceeded in a good to excellent optical yield. (2) The optical yield of the reduction of the (*E*)-α-(benzamido) cinnamic acid was among the highest ever reported (entry 4).[14] (3) Free carboxylic acids and the methyl esters gave the comparable results (entry 1, 3, 5 and 6). (4) The sense of asymmetric induction depends on the olefin geometry. The absolute configuration of the major amino acids obtained from *E* olefins and the catalyst (*S*)-**9** was *S*, whereas configuration of the products derived from the *Z* starting materials and (*S*)-**9** was *R*. (5) In usual, a high optical yield was obtained at a low concentration of the substrate.[15] For example, the hydrogenation of 0.013 M solution of (*Z*)-α-(benzamido)cinnamic acid, in the presence of 0.7 mol% of (*R*)-**9b** gave virtually optically pure product (entry 3), while use of the 0.15 M solution of the olefin resulted in only 62% optical yield. (6) The initial hydrogen pressure affected the optical yield to considerable extent (entry 1 and 2).[16,17] (7) The chiral recognition ability of the asymmetric catalyst **9a** or **9b** was drastically reduced upon instantaneous exposure to air. (8) The optical yields of the hydrogenation are highly dependent on the nature of the Rh complexes utilized as catalysts. Unlike **9a** or **9b** displaying a high degree of enantioselection, the diene coordinated starting complex **8** or the dinuclear complex **10** were found to be poor catalysts. Hydrogenation of (*Z*)-α-(benzamido)cinnamic acid with **8** or **10** under the standard conditions afforded the corresponding α-amino acid derivative in 38 and 26% optical yield, respectively.

Mechanism of hydrogenations. The reaction probably starts with initial coordination of an olefinic substrate to Rh atom, since no rhodium hydrides could be detected by NMR under hydrogen atmosphere in the absence of olefinic substrates. Scheme 1 outlines the unsaturate mechanism[13,17–19] for the asymmetric hydrogenations catalyzed by a cationic Rh complex bearing a chiral bis(triaryl)phosphine ligand (P–P = (*R*)- or (*S*)-BINAP). It has been generally observed that, in the asymmetric hydrogenation of (*Z*)-α-(acylamino)acrylic acids, diphosphine–Rh complexes with a λ chelated ring induces predominant production of (*S*)-*N*-acyl-α-amino acids, whereas catalysts with δ chelate structure afford *R* amino acids.[1m,12] This is also the case with the present catalyst systems. The decrease in optical yields observed with high initial H_2 pressure is a quite common phenomenon, and can be explained either by the Halpern's interpretation,[17,18] if one assumes single, unsaturate mechanism (Scheme 1), or by contamination of a dihydride mechanism.[16] In short, all observed chemical phenomena are consistent with the operation of the unsaturate mechanism as major pathway.

^{31}P NMR *Studies on the enantioselection.* The high enantioselectivity observed in the asymmetric hydrogenations prompted us to study ^{31}P NMR behavior of the BINAP–Rh^+ complexes in the presence of olefinic substrates.[20] To a 0.01 M solution of [Rh(*S*)-binap)]ClO_4 [(*S*)-**9b**] in a mixture of dichlo-



Scheme 1.

Table 1. Asymmetric hydrogenations of α-(acylamino)acrylic acids catalyzed by the Rh–BINAP complexes[a]

Entry	Substrate	Confign. of BINAP	Product	Absolute confign.	Yield %	Optical purity[b] % ee
1	(Z)-α-(benzamido)-cinnamic acid	S	N-benzoylphenylalanine	R	96	96
2	(Z)-α-(benzamido)-cinnamic acid	S	N-benzoylphenylalanine	R	98	71[c]
3	(Z)-α-(benzamido)-cinnamic acid	R	N-benzoylphenylalanine	S	97	100
4	(E)-α-(benzamido)-cinnamic acid	S	N-benzoylphenylalanine	S	93	87[d]
5	methyl (Z)-α-(benzamido)cinnamate	S	N-benzoylphenylalanine methyl ester	R	98	93
6	methyl (Z)-α-(benzamido)cinnamate	R	N-benzoylphenylalanine methyl ester	S	97	92
7	(Z)-α-(acetamido)-cinnamic acid	S	N-acetylphenylalanine	R	99	84
8	(Z)-α-(benzamido)-β-(4-hydroxy-3-methoxy)acrylic acid	S	N-benzoyl-3-(4-hydroxy-3-methoxyphenyl)alanine	R	97	79
9	(Z)-α-(benzamido)-β-(4-acetoxy-3-methoxy)acrylic acid	S	N-benzoyl-3-(4-acetoxy-3-methoxyphenyl)alanine	R	92	70
10	α-(benzamido)acrylic acid	S	N-benzoylalanine	R	97	98
11	α-(acetamido)acrylic acid	S	N-acetylalanine	R	97	67

[a] The hydrogenations were carried out with a solution of 0.5—1.0 mmol of olefinic substrate in 20—30 ml ethanol in the presence of 1 mol % of the Rh catalyst at room temperature for 48 h under an initial hydrogen pressure of 3—4 atm.
[b] Optical yields were calculated with respect to the values of the optically pure authentic samples or the reported values (see experimental part). [c] The initial hydrogen pressure was 50 atm. [d] Hydrogenation was carried out in THF.

romethane and methanol was added 6-molar excess of (*Z*)-α-(acetamido)cinnamic acid at −50° and the mixture was gradually warmed up to room temperature. ^{31}P NMR spectrum exhibited two sets of doublet of doublet centered at δ 18.0 and 29.7 due to the chelate complex of type **11** as was shown in Fig. 2. Through coordination of a prochiral olefin to **9b**, the two homotopic BINAP phosphorus nuclei become diastereotopic each other. The observation of a single set of eight-line signal indicates that only one of two possible diastereomers was formed in the reaction system. Similar enantioface differentiation was observed in the NMR measurement when (*Z*)-α-(acetamido)cinnamic acid was replaced by (*Z*)-α-(benzamido)cinnamic acid (see Fig. 3), methyl (*Z*)-α-(acetamido)cinnamate, or methyl (*Z*)-α-(benzamido)cinnamate. Thus, the enantioface differentiation of the present catalysts at the stage of chelate complex formation or prior olefin coordination appeared to be extremely high and led stereospecifically to single chelate complex, though these facts might not be the criterion for getting high optical yields of the asymmetric hydrogenations.[17,21]

It should be noted that the formation of the chelate complex III in Scheme 1 is not instantaneous but rather slow. A freshly prepared mixture of an α-(acylamino)acrylic acid and Rh complex **9** showed interesting NMR behavior, which indicates the presence of a discrete non-chelate olefin–Rh complex prior to the chelate complex formation. When 18-mol excess of (*Z*)-α-(benzamido)cinnamic *acid* was added

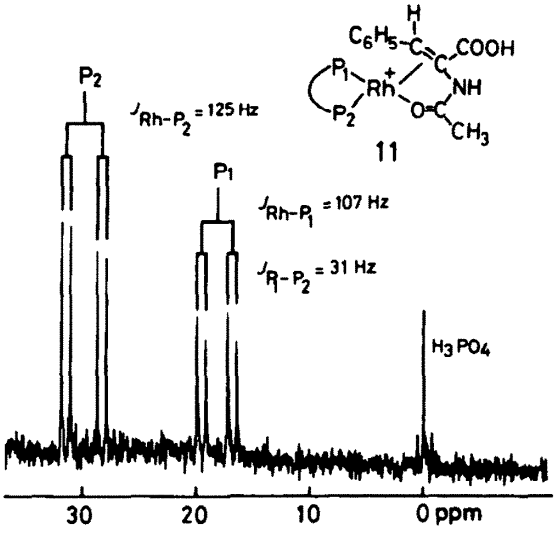


Fig. 2. ^{31}P NMR spectrum of (*S*)-**9a** (0.01 M) in a 2:3 mixture of dichloromethane and methanol in the presence of 6-fold excess of (*Z*)-α-(acetamido)cinnamic acid (20°).

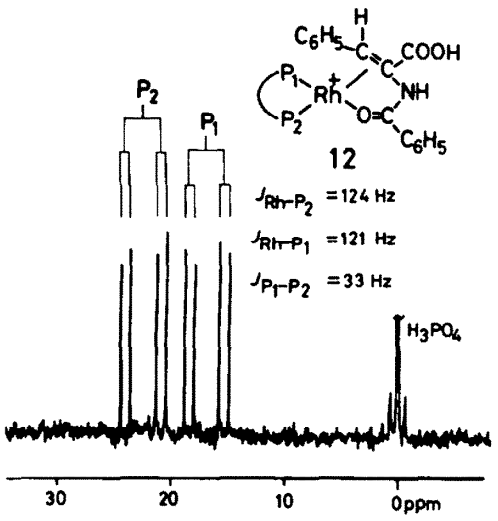
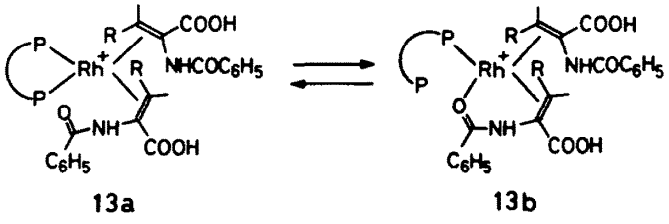


Fig. 3. ^{31}P NMR spectrum of (*R*)-**9a** (0.01 M) in methanol in the presence of 6-fold excess of (*Z*)-α-(benzamido)cinnamic acid (20°).

to 0.006 M solution of (*R*)-**9b** in a 4:1 mixture of methanol and dichloromethane, a broad time-averaged signal was displayed ranging from δ 35 to 60 in addition to a broad doublet due to (*R*)-**9a** and a sharp signal set assigned to **12**. This is interpretable in terms of a rapid equilibrium between (*R*)-**9a** and the Rh complex of type II. (*Z*)-α-(acetamido) cinnamic acid as substrate gave a similar result. By contrast, ^{31}P NMR spectrum of a 0.014 M methanol solution of (*S*)-**9a** with a 15-mol excess of *methyl ester* of (*Z*)-α-(benzamido)cinnamic acid at 20° showed a broad doublet centered at δ 53.4 (J_{Rh-P} = 207 Hz) due to (*S*)-**9a**, and two broad signals around δ 21 and 32. At −50°, the latter two signals sharpened to give two sets of doublet of doublet centered at δ 21.0 (J_{Rh-P} = 162 Hz, J'_{P-P} = 42 Hz) and 32.4 (J_{Rh-P} = 168 Hz) assignable to the structure of type III. Most probably the chelate complex III is in rapid equilibrium with the starting (*S*)-**9a**. A similar spectral behavior was observed for methyl (*Z*)-α-(acetamido)cinnamate. The reason why these olefinic acids and their esters behave differently is unclear at present.

It was also revealed by NMR that there can exist another type of Rh complexes formulated as **13a** ⇌ **13b** at least under some particular conditions and with certain class of olefinic substrates. When to a 0.06 M solution of (*S*)-**9b** in methanol was added 20-fold excess of (*Z*)-α-(benzamido)cinnamic acid at 20°C, the resulting high-concentration mixture gave two new ^{31}P NMR signals, a doublet centered at



δ50.0 (J_{Rh-P} = 165 Hz) and a singlet at δ41.8 with equal intensity, indicating the formation of the rapidly equilibrating 1:2 Rh–cinnamic acid complex **13**. Under such conditions, only small signals due to **12** were observed. The isolated complexes, when dissolved in methanol, liberated the olefinic ligands slowly to give a mixture of (*S*)-**9a** and **13a** ⇌ **13b** accompanied by a small amount of **12**. When a solution of this complex in methanol containing a 2.4-fold excess of (*Z*)-α-(benzamido)cinnamic acid was exposed to an atmospheric pressure of hydrogen, *N*-benzoyl-(*R*)-phenylalanine was formed in only 72% optical yield. This result is consistent with the fact that increase in concentration of the olefinic substrate, lowered enantioselectivity in the present asymmetric hydrogenations.

CONCLUSION

We have synthesized, for the first time, axially dissymmetric bis(triaryl)phosphines, (+)- and (−)-BINAP, and demonstrated that they serve as excellent ligands for the Rh(I)-catalyzed asymmetric hydrogenations of α-(acylamino)acrylic acids and esters. The catalytic hydrogenation system, in general, appeared to contain a variety of catalytically active rhodium complexes, depending on the reaction system, which result in different enantioface differentiation. These facts strongly advise us to carefully control the reaction conditions so that a selected catalyst with high chiral recognition ability is created.

Finally, it should be added that chiral BINAP–Rh(I) complexes of type **8** can catalyze highly enantioselective 1,3-hydrogen migration of certain olefins. For example, an asymmetric isomerization of N,N-diethylnerylamine or -geranylamine producing citronellal (*E*)-N,N-diethylenamine proceeds with more than 95% enantiomeric excess and with virtually complete chemoselectivity.[22]

EXPERIMENTAL

General. M.ps were determined on a Büchi TOTTOLI capillary m.p. apparatus and are uncorrected. Proton and ^{13}C NMR spectra were taken on a JEOL FX-100 (100 MHz) spectrometer and all chemical shifts were recorded as δ values in ppm downfield from internal TMS. Singlet, doublet, triplet, quartet, and multiplet were abbreviated to s, d, t, q and m, respectively. ^{31}P NMR spectra were measured on the same instrument using a soln of 5% H_3PO_4 in CD_3OD in a sealed capillary as an external standard. Mass spectral analyses were recorded on a JEOL JMS-D100 or a JEOL JMS-D300 instrument. IR spectra were taken on Hitachi Model 295 spectrophotometer. Optical rotations were recorded with a 10-cm cell on a JASCO DIP-4 spectrometer calibrated by an aqueous soln of sucrose (E. Merck) before use. The synthetic and authentic samples were alternately subjected to the measurement under the same conditions (solvent source, concentration, temp, etc). Analyses by liquid chromatography were performed on a JASCO TRI ROTAR equipped with a UVIDEC-100-III detector. TLC was carried out on E. Merck Kieselgel 60 PF_{254} and spots were visualized by the irradiation of UV light or a spray of iodine vapor. Elemental analyses were performed at the Microanalytical Center, Kyoto University.

Solvents and chemicals. THF and diethyl ether were dried and degassed at refluxing temp over Na and benzophenone under argon and distilled before use. A 2 M soln of t-BuLi in pentane (Fluka Co.) and a 1.6 M soln of BuLi in hexane (Nakarai Chem. Co.) were titrated with 1 M sec-BuOH in xylene using *o*-phenanthroline as an indicator just before use. Abs. EtOH was obtained by the distillation of the reagent grade EtOH from a mixture of Na and diethyl phthalate under argon. MeOH was distilled over Mg under argon. Other hydrocarbon solvents were heated at reflux for several hr over CaH_2 under a gentle stream of argon and distilled. (*Z*)-α-(Acetamido)cinnamic acid, (*Z*)-α-(benzamido)cinnamic acid, (*Z*)-α-(benzamido)-β-(4-hydroxy-3-methoxyphenyl)acrylic acid, (*Z*)-α-(benzamido)-β-(4-acetoxy-3-methoxyphenyl)acrylic acid, methyl (*Z*)-α-(benzamido)cinnamate and methyl (*Z*)-α-(acetamido) cinnamate were prepared by the hydrolysis or methanolysis of the corresponding (*Z*)-azlactones according to the reported procedures.[23] (*E*)-α-(benzamido)cinnamic acid was obtained by the isomerization of (*Z*)-2-phenyl-4-benzal-5-oxazolone (the azlactone of (*Z*)-α-benzamido)-β-phenylacrylic acid) by HBr in AcOH followed by hydrolysis.[24] α-(Benzamido)acrylic acid and α-(acetamido)acrylic acid were obtained from Aldrich Chem. Co. Purities of the olefinic substrates were confirmed by liquid chromatography using a column (3.3 mm × 250 mm) packed with JASCO SC-01 eluted by a 3:2 mixture of water and MeOH containing 0.03 M AcOH and 0.03 M NaOAc.

Synthesis of 2,2'-dibromo-1,1'-binaphthyl (**3**). In a 1-l. 3-necked flask equipped with a thermometer, a dropping funnel, and a mechanical stirrer was placed commercial triphenylphosphine (240 g, 0.915 mol). Carefully dried acetonitrile (350 ml) was added and the solid was dissolved by warming the flask. The soln was then cooled with an ice–water mixture and to this was added dropwise with stirring bromine (50 ml, 0.969 mol) over a period of 1 hr. The ice–water bath was removed and to the mixture was added a slurry of **4**[25] (120 g, 0.420 mol) in 200 ml dry acetonitrile. The mixture was stirred at 60° for 30 min and the solvent was distilled off. The last trace of acetonitrile was removed under reduced pressure. The remaining mass was heated carefully at 260–270° for 1 hr with stirring. After the exothermic reaction subsided, the stirring was continued for an additional hr at 310–320°. The mixture was cooled to *ca* 200° and to this was added 1000 ml Celite 545 with stirring. The mixture was extracted with a boiling 1:1 mixture of benzene and hexane (500 ml). The solid material separated by filtration was extracted three 200-ml portions of a boiling 1:1 mixture of benzene and hexane. The combined extracts were evaporated to give an orange–yellow viscous oil, which was dried under vacuum. The residue was boiled with added 200 ml of EtOH and the soln was left in a refrigerator to give 90 g of crude **3**. Recrystallization from EtOH afforded pure sample of **3** (78.0 g, 45% yield) as pale yellow fine crystals, m.p. 184–185° (lit.[7] m.p. 180°). R_f 0.50 (1:4 benzene–hexane).

Synthesis of (±)-BINAP [(±)-**1**]. To a soln of **3** (20.6 g, 50.0 mmol) in dry, degassed THF (400 ml) was added dropwise t-BuLi in pentane (1.65 M, 135 ml, 223 mmol) below −80° with mechanical stirring under argon. The resulting yellow-green slurry was stirred at −75° for 1 hr and then at −65° for 30 min. The mixture was again cooled to −78° and to this was added dropwise a soln of diphenylphosphinous chloride (41.2 ml, 50.7 g, 230 mmol) in dry THF (50 ml) over a period of 15 min. After stirring the mixture for 1 hr at −65°, the cooling bath was removed. The mixture was further stirred at room temp overnight. During this period the color of the mixture turned from yellow-green to pale yellow. The solvent was removed under reduced pressure and the yellow residue was extracted four times with 500-ml portions of boiling benzene under argon. The combined extracts were evaporated, and to the residue was added EtOH (150 ml). The mixture was boiled for 5 min under argon. After keeping the mixture at 4° for 24 hr, the solid material was collected on a glass filter, washed with cold EtOH (30 ml), and dried over P_2O_5 *in vacuo* to give 24.31 g (78%) of (±)-BINAP [(±)-**1**]. This product is pure enough for further use for optical resolution. An analytically pure sample was obtained by recrystallization from

a mixture of toluene and EtOH, m.p. 279–280°. IR(KBr): 3030 (m), 1580 (m), 1480 (m), 1430 (s), 1305 (w), 1085 (w), 1020 (w), 815 (s), 743 (s), 735 (s), 700 (m), 515 (m), and 485 cm^{-1} (m). ^1H NMR ($CDCl_3$): δ 6.4–8.0 (m). ^{31}P NMR (4:1 C_6D_6–CD_3OD): δ −12.8 (s). R_f 0.12 (1:4 benzene–hexane). Calc. (Found: C, 84, 62; H, 5.52. Calc. for $C_{44}H_{32}P_2$: C, 84, 87; H, 5.18%.). Low resolution mass spectrum: m/z 622 (M^+), 545 (M^+–C_6H_5), and 437 (M^+–$P(C_6H_5)_2$). High resolution mass spectrum: m/z 622.2002; Calc. for $C_{44}H_{32}P_2$: m/z 622.2025.

Optical resolution of (±)-*BINAP*. The resolving agent (+)-**5** was prepared by the lit. procedure [26]; $[\alpha]_D^{20}$ + 78.5° (*c* 0.56, benzene) [lit.[8] $[\alpha]_D^{20}$ + 72.1° (*c* 0.36, benzene)]; ^1H NMR ($CDCl_3$): δ 1.58 (d, J = 6.5 Hz, $CHCH_3$), 2.66 (bs, NCH_3), 2.93 (bs, NCH_3), 3.87 (q, J = 6.5 Hz, $CHCH_3$), and 6.6–7.3 (m, aromatic protons). Racemic **1** (30.0 g, 48.2 mmol) was dissolved in 1.3 l of boiling benzene under argon and the soln was cooled to room temp. To this was added a soln of **5** (14.0 g, 24.1 mmol) in benzene (250 ml) and the mixture was stirred at room temp. for 12 hr in the dark. After stirring the mixture at 50° for 1 hr, a soln of sodium tetraphenylborate (17.1 g, 50.0 mmol) in EtOAc (240 ml) was added to the mixture at room temp. The mixture was stirred further at room temp. for 30 min and the solvent was removed under reduced pressure. To the residue was added CH_2Cl_2 (300 ml) and the insoluble material was removed by filtration through a pad of Celite 545. The filtrate was concentrated to dryness and to the residue was added CH_2Cl_2 (180 ml). To this was added slowly about 120 ml of a 1:1 mixture of benzene–EtOAc at 40°. When the temp. of the soln dropped to 25°, a small amount of pure crystals of (*R*)-**7** was added. The mixture was further allowed to stand at room temp. for 48 hr and crystals formed were collected on a glass filter under argon to give 25.2 g of white needles. The complex was dissolved in 200 ml CH_2Cl_2 at refluxing temp. under argon and to this was added 155 ml of a 1:1 mixture of EtOAc and benzene. The mixture was allowed to stand in a refrigerator for 24 hr. The white crystalline material was collected on a glass filter to give 19.8 g (34% yield based on (±)-BINAP) of (*R*)-(+)-BINAP–Pd(II) complex [(*R*)-**7**], m.p. 154–155° (dec); $[\alpha]_D^{22}$ + 356° (*c* 0.21, acetonitrile). Another 2.7 g (5%) of the complex was obtained by the recrystallization of the solid recovered from the mother liquor, $[\alpha]_D^{22}$ + 351° (*c* 0.19, acetonitrile). Two recrystallizations from the same solvent system afforded an analytically pure sample, m.p. 157–158° (dec), $[\alpha]_D^{22}$ + 381° (*c*0.16, acetonitrile). ^1H NMR spectrum ($CDCl_3$): δ 1.82 (bs, NCH_3), 1.96 (bs, NCH_3), 2.14 (d, J = 6.5 Hz, $CHCH_3$), 3.34 (m, $CHCH_3$), and 6.1–7.9 (m, aromatic protons). The mother liquor which contained the (*S*)-BINAP–Pd(II) complex was concentrated to dryness and the residue was dissolved in CH_2Cl_2 (130 ml) at reflux temp. To this was added ether (240 ml) at 35° and the mixture was stored in a refrigerator overnight at −20°. The white solid was separated by filtration and recrystallized from a 1:2 mixture of CH_2Cl_2 and ether to give 20.7 g (36% yield based on (±)-BINAP) of (*S*)-**7**, m.p. 159–160° (dec), $[\alpha]_D^{22}$-354° (*c* 0.12, acetonitrile). Optically pure sample of (*S*)-**7** was obtained by two recrystallizations from a mixture of CH_2Cl_2 and ether, m.p. 161–162° (dec), $[\alpha]_D^{21}$-369° (*c* 0.15, acetonitrile). ^1H NMR spectrum ($CDCl_3$): δ 1.20 (d, J = 6.5 Hz, $CHCH_3$), 1.43 (bs, NCH_3), 2.34 (bs, NCH_3), 5.02 (q, J = 6.5 Hz, $CHCH_3$), and 6.0–8.0 (m, aromatic protons).

Reductive decomposition of (*R*)-**7** *or* (*S*)-**7**. In a 300-ml 3-necked flask equipped with a thermometer, an argon inlet tube, and a rubber septum was placed $LiAlH_4$ (440 mg, 11.6 mmol) under argon. Dry, degassed ether was added to it by a syringe and the flask was surrounded by an ice–water mixture. To this was added (*R*)-**7** (2.45 g, 2.05 mmol) all at once. The mixture was stirred for 30 min, and then the cooling bath was removed. After stirring the mixture at room temp. for 2 hr, the flask was again cooled in an ice–water bath. To this was added carefully 1 ml of water and the mixture was stirred at room temp. for 30 min. The mixture was filtered through a pad of Celite 545 under argon and the residue was extracted with three 100-ml portions of hot benzene. Combined filtrate and washings were concentrated *in vacuo* to give 1.23 g of a white solid. Recrystallization from a 1:1 mixture of toluene and EtOH afforded 1.05 g (82% yield) of (*R*)-BINAP [(*R*)-**1**] as colorless prisms, m.p. 240–241°, $[\alpha]_D^{25}$ + 229° (*c* 0.32, benzene). No substantial changes in m.p. and optical rotation value were observed after two recrystallizations from a mixture of toluene and EtOH.

Similarly (*S*)-**7** (2.50 g, 2.09 mmol) was subjected to reductive decomposition with $LiAlH_4$ (450 mg, 11.8 mmol). Work-up as described above gave 980 mg (75% yield) of optically pure (*S*)-BINAP [(*S*)-**1**], m.p. 241–242°, $[\alpha]_D^{25}$ −229° (*c* 0.31, benzene).

Synthesis of [Rh((*S*)-*binap*) (*nbd*)]ClO_4 [(*S*)-**8**]. In a 250-ml Schlenk tube were placed $[Rh(nbd)_2]ClO_4$[27] (251 mg, 0.649 mmol) and (*S*)-**1** (405 mg, 0.650 mmol) under argon and to this was added CH_2Cl_2 (15 ml). The mixture was stirred at room temp. for 1 hr and to the resulting orange-red soln was added slowly THF (15 ml) followed by hexane (15 ml). The mixture was allowed to stand in a refrigerator for 5 hr and orange–red crystals separated were collected on a glass filter under argon to give 557 mg (94%) of crude (*S*)-**8**. Recrystallization from MeOH gave pure (*S*)-**8**, m.p. 248–251° (dec), $[\alpha]_D^{22}$ + 21.1 (*c* 0.15, MeOH). The optical rotation value of the MeOH soln of (*S*)-**8** was variable to some extent because of the deep color of the soln. ^{31}P NMR spectrum of (*S*)-**8** (CD_3OD): δ 25.06 (d, $J_{Rh\text{-}P}$ = 156.3 Hz). (Found: C, 66.25; H, 4.65. Calc. for $C_{51}H_{40}ClO_4P_2Rh$: C, 66.79; H, 4.40%.). Similarly, the complex (*R*)-**8** was prepared in 83% yield, m.p. 242–244°, $[\alpha]_D^{22}$ −19.3° (*c* 0.14, MeOH).

Hydrogenation of (*S*)-**8**. An 80-ml Schlenk tube connected with a gass buret was purged by filling and evacuating with argon and then filled with atmospheric pressure of H_2. To this was added an orange suspension of (*S*)-**8** (1.65 g, 1.80 mmol) in MeOH (40 ml) through a serum cap by a syringe. The mixture was stirred at room temp. until gas uptake ceased (2.5 hr). The amount of H_2 absorbed was 1.99 equiv. to Rh atom. Analysis by gas chromatography (10% diisodecyl phthalate on Celite 545, 2 m, 60°) using EtOAc as an internal standard showed that norbornane was produced in 96% yield accompanied by a trace amount of norbornadiene. Norbornene was not detected. The resulting wine–red soln was separated from the light brown ppts. by a syringe. The soln was concentrated to 20 ml and stored in a refrigerator at −35° to give (*S*)-**9a** as orange–red prisms (1.17 g, 73%), which was recrystallized twice from MeOH. The complex (*S*)-**9a** is air-sensitive and, upon contact with air, the orange–red color turned into yellow. ^1H NMR spectrum of (*S*)-**9a** (CD_2Cl_2): δ 3.42 (s, $2CH_3OH$), 7.50 (m) and 6.82 (m) (BINAP). No signals due to rhodium hydrides were observed in a range from δ 0 to −40. ^{31}P NMR of (*S*)-**9a** (CD_3OD): δ 53.1 (d, $J'_{Rh\text{-}P}$ = 206 Hz). IR (KBr): 1085 cm^{-1} (perchlorate). The coordinated methanol was removed by keeping (*S*)-**9a** at room temp. (1×10^{-5} mmHg) overnight to give (*S*)-**9b**. The proton NMR spectrum of (*S*)-**9b** in CD_2Cl_2 resembles closely to that of (*S*)-**9a** but lacks signal due to MeOH.

The light brown ppts obtained in the hydrogenation of (*S*)-**8** was purified by recrystallization from a 4:1 mixture of CH_2Cl_2 and MeOH to give **10** (130 mg, 9%) as brown fine crystals. The complex **10** is moderately stable in air. The proton NMR spectrum of **10** exhibited four multiplets centered at δ 6.05, 6.55, 6.90, and 7.48 in the intensity ratio of 5:7:12:14.5. ^{31}P NMR (3:2 CD_2Cl_2–CD_3OD): δ 46.41 (d, $J_{Rh\text{-}P}$ = 199.2 Hz).

Asymmetric hydrogenation and work-up procedures. The following experiment is illustrative of the asymmetric hydrogenations of α-(acylamino)acrylic acids and esters catalyzed by BINAP–Rh^+ catalysts. In a 100-ml pressure bottle was placed a magnetic stirrer bar and the air in the reactor was purged by filling and evacuating with argon. To this was

added a solution of (*S*)-**9b** (7.4 mg, 0.009 mmol) and (*Z*)-α-(benzamido)cinnamic acid (216 mg, 0.810 mmol) in 30 ml of EtOH. The pressure bottle was then filled with 3 atm of pure H_2 and the mixture was stirred at room temp. for 48 hr. The mixture was transferred into a 100-ml round-bottomed flask and the solvent was evaporated. The residue was quickly dissolved in 30 ml of 0.5 N NaOH. A small amount of yellow–brown solid was filtered off through Celite pad and the flask and Celite were washed with two 20-ml portions of cold water. The combined filtrate and washings were extracted with two 40-ml portions of ether and the aqueous layer was acidified with 1N HCl. The mixture was extracted three times with each 50 ml of ether and the combined organic layers were dried over Na_2SO_4. Evaporation of the solvent afforded white powder, which was dried at 80° (0.1 mmHg) to give 209 mg (96%) of N-benzoylphenylalanine, $[\alpha]_D^{21} + 40.0°$ (*c* 1.0, MeOH). The proton NMR spectrum of the product was superimposable with that of the authentic sample. For the isolation of the products obtained in entries 5–11, the amino acid derivatives were extracted with 200 ml of hot water instead of the extraction with NaOHaq, and water was removed under reduced pressure. The hydrogenation of (*E*)-α-(benzamido)cinnamic acid was carried out in THF at the H_2 pressure of 5 atm. The following values of the optically pure compounds were used for the calculation of optical yields: N-benzoyl-(*R*)-phenylalanine, $[\alpha]_D^{21} + 41.8°$ (*c* 1.0, methanol) (authentic sample, prepared[27]); N-benzoyl-(*S*)-phenylalanine, $[\alpha]_D^{21} - 41.4°$ (*c* 1.0, MeOH) (authentic sample, prepared[27]); N-benzoyl-(*S*)-phenylalanine methyl ester, $[\alpha]_D^{25} - 45.3°$ (*c* 1.0, EtOH) (reported value[28]); N-acetyl-(*R*)-phenylalanine, $[\alpha]_D^{20} - 42.1°$ (*c* 1.0, MeOH) (authentic sample, prepared[29]); N - benzoyl - 3 - (4 - hydroxy - 3 - methoxyphenyl) - (*S*) - alanine, $[\alpha]_D^{25} - 28.5°$ (*c* 1.0, MeOH) (reported value[30]); N-benzoyl-(*S*)-alanine, $[\alpha]_D^{21} + 26.7°$ (*c* 1.0, 0.1 N NaOH) (authentic sample, prepared[29]).

Isolation and hydrogenation of **13**. To a soln of (±)-**9b** (0.323 g, 0.391 mmol) in MeOH (20 ml) placed in a Schlenk tube was added (*Z*)-α-(benzamido)cinnamic acid (1.06 g, 3.97 mmol) and the mixture was stirred at 40° for 24 hr. The mixture was analyzed at intervals by TLC under argon developed by a 5:95 mixture of MeOH and CH_2Cl_2, R_f 0.12 (**9a**) and 0.58 (**13**). The solvent was removed under reduced pressure and the residue was subjected to column chromatography under argon on silica gel (E. Merck Kieselgel 60, 70–230 mesh) eluted by a 6:94 mixture of MeOH and CH_2Cl_2. The major deep red band was collected and concentrated to a small volume, which was allowed to stand at −20° to give **13** (165 mg, 31% yield based on **9b**) as orange crystals. The ^{31}P NMR spectrum of **13** in MeOH exhibited a doublet centered at δ 50.0 ($J_{Rh-P} = 165$ Hz) and a singlet at δ 41.8 with equal intensity in addition to signals due to **9a** and the complex of type **12**. Addition of free (*Z*)-α-(benzamido)cinnamic acid enhanced the intensity of the signals due to **13**. The complex **13** (625 mg, 0.460 mmol) was hydrogenated in MeOH (20 ml) under an atmospheric pressure of H_2 for 72 hr. During this period 2.10 equiv of H_2 per Rh atom was absorbed. Work-up as described in the asymmetric hydrogenations catalyzed by the complex **9** gave 0.240 g (0.899 mmol, 98% yield based on **13**) of (±)-N-benzoylphenylalanine. Similarly, asymmetric hydrogenation of (*S*)-**13** (59 mg, 0.043 mmol) in MeOH (3 ml) in the presence of (*Z*)-α-(benzamido)cinnamic acid (28 mg, 0.105 mmol) resulted in the formation of N-benzoyl-(*R*)-phenylalanine in 96% yield with 72% optical yield, $[\alpha]_D^{20} + 30.0$ (*c* 1.0, MeOH).

^{31}P NMR measurements. In an NMR sample tube in 10-mm diam. were placed (*S*)- or (*R*)-**9b** (14.9 mg, 0.018 mmol), 10–18 molar excess of an olefinic substrate, and a sealed capillary tube containing 5% H_3PO_4 in CD_3OD under argon and to this was added 3 ml of a specified solvent below −50°. The tube was sealed off and the mixture was warmed up to room temp. over a period of 12 hr with occasional shaking. This sample was placed in an NMR probe kept at the specified temp. and signals were usually accummulated overnight. ^{31}P NMR spectrum of **11** (2:3 CH_2Cl_2–MeOH, 25°): δ 18.0 (dd, $J_{Rh-P} = 107$ Hz, $J_{P-P} = 31$ Hz) and 29.7 (dd, $J_{Rh-P} = 125$ Hz). ^{31}P NMR spectrum of **12** (MeOH): δ 16.6 (dd, $J_{Rh-P} = 121$ Hz, $J_{P-P} = 33$ Hz) and 22.1 (dd, $J_{Rh-P} = 124$ Hz). The ^{31}P NMR spectrum of the 1:1 complex of (*S*)-**9a** and methyl (*Z*)-α-(benzamido)cinnamate in MeOH at −50° exhibited two sets of a doublet of doublet centered at δ 21.0 ($J_{Rh-P} = 162$ Hz, $J_{P-P} = 42$ Hz) and 32.4 ($J_{Rh-P} = 168$ Hz).

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