Asymmetric Hydrogenation of Prochiral Olefins Catalyzed by Rhodium Complexes with Chiral Pyrrolidinodiphosphines. Crucial Factors for the Effective Asymmetric Induction

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Remarkable effects of hydrogen pressure on the stereoselectivity were observed in the asymmetric hydrogenations of itaconic acid, α-(acylamino)acrylic acid, and their derivatives catalyzed by rhodium complexes of chiral pyrrolidinodiphosphines. Effects of added triethylamine on the pressure dependency of stereoselectivity were also studied. Marked differences in the direction of asymmetric induction were found in the asymmetric hydrogenations of the methylsuccinic acid precursors itaconic acid, citraconic acid, and mesaconic acid. This result clearly indicates that the chiral recognition by the rhodium catalyst is extremely sensitive to the stereochemistry of the prochiral olefins. Possible mechanisms are discussed on the basis of these results. $^{31}P\{^1H\}$ NMR studies on the key intermediates in asymmetric hydrogenations have revealed that the mode of the bidentate complexation of the prochiral substrates is extremely regioselective. The "induced-fit" phenomena of the chiral rhodium complex were observed. A possible mechanism for the chiral recognition of enantiofaces in the chiral coordination sphere is proposed.

Asymmetric hydrogenation of olefins and carbonyl compounds catalyzed by rhodium(I) complexes with chiral phosphine ligands has been attracting much interest, and in the case of (Z)-α-(acylamino)cinnamic acid and its derivatives excellent stereoselectivities have been achieved. Several efforts have been made to analyze the mechanism of asymmetric induction together with mechanistic studies of the simple hydrogenation of olefins catalyzed by Wilkinson-type complexes with mono- or bidentate ligands based on kinetics and coordination chemistry. Nevertheless, a detailed understanding of the mechanism of asymmetric induction must await further investigation. Accordingly, it is a significant approach to clarify the crucial factors for the effective asymmetric induction in each catalyst system. The requisites for understanding how a chiral rhodium catalyst makes chiral recognition toward a prochiral substrate would be summarized as follows: (i) the determination of the key step for asymmetric induction, which is involved in asymmetric hydrogenation and (ii) the stereochemical approach for stereoselection in the coordination sphere of the chiral complex on the basis of X-ray analysis, structure models, NMR studies etc. We describe here such crucial factors in the effective asymmetric hydrogenation of prochiral olefinic substrates catalyzed by rhodium complexes with (2S,4S)-N-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM) or (2S,4S)-N-pivaloyl-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (PPPM).

BPPM, R = *t*-BuO
PPPM, R = *t*-Bu
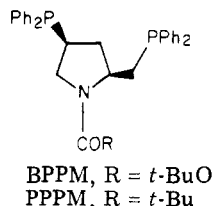
Effects of Hydrogen Pressure on the Stereoselectivity. Although homogeneous asymmetric hydrogenation of dehydroamino acids has been extensively studied,[1] little attention has been focused on the pressure dependency of stereoselectivity in these reactions.[2a] Accordingly, we

carried out the asymmetric hydrogenation of (Z)-α-benzamidocinnamic acid (1), (Z)-α-(acetamido)cinnamic acid (2), methyl (Z)-α-(acetamido)cinnamate (3), α-(acetamido)acrylic acid (4), and itaconic acid (5) under a variety of hydrogen pressures using rhodium complexes with BPPM as a chiral ligand.[2b] We have found that the hydrogen pressure exerts a significant influence on the stereoselectivity, and the pressure dependency is sensitive to the structure of the substrate. During the course of the hydrogenation, the reaction mixture was exactly homogeneous regardless of the hydrogen pressure; viz., precipitation of rhodium metal was not observed at all in every case examined. Thus, a possibility that the rhodium complexes with chiral diphosphines decompose under high pressures of hydrogen can be completely excluded. Results are summarized in Table I. For example, (R)-N-benzoylphenylalanine is a predominant product of the asymmetric hydrogenation of 1 at 25 °C and 1 atm of hydrogen whereas the production of the S isomer is preferred under high pressures such as 50 and 100 atm of hydrogen on using either (BPPM)Rh(COD)Cl (I) prepared in situ or [(BPPM)Rh(COD)]+ClO4- (II), where COD stands for cycloocta-1,5-diene, as shown in Table I (see also Figures 1 and 2). As Table I shows, the pressure dependency of stereoselectivity is extremely strong in 4, fairly strong in 3, and rather weak in 2 and 5; i.e., the inversion of the configuration of the product is also found in the reaction of 4, while the optical yield decreases only a little even at 20 atm of hydrogen in the cases of 2 and 5.

In regard to the argument for an attractive interaction between chiral ligands and substrates, the asymmetric hydrogenation of 3 catalyzed by I is worth mentioning. As Table I shows, the reaction gave (R)-N-acetylphenylalanine methyl ester with 95.0% ee under an atmospheric pressure of hydrogen. The result clearly demonstrates that a carboxylic acid moiety is not a requisite for achieving a high optical yield even when BPPM is employed, like the case of diPAMP[27] or chiraphos,[22,28] although Achiwa discussed[8d] a characteristic feature of BPPM on the basis of the fact that only a low optical yield was obtained in the reaction of 3 catalyzed by I under a high pressure of hydrogen.

(1) D. Valentine, Jr., and J. W. Scott, *Synthesis*, 329 (1978), and references therein.

(2) (a) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Adv. Chem. Ser.*, No. 132, 274 (1974). (b) For preliminary results, see I. Ojima, T. Kogure, and Y. Yoda, *Chem. Lett.*, 495 (1979).

Table I. Dependency of Stereoselectivity on Hydrogen Pressure [% ee (Configuration)]ᵃ

substr	catal	solvent	pressure of H_2, atm			
			1	20	50	100
1 (Ph–C=C, NHCOPh, COOH)	II	EtOH	83.8 (R)	21.2 (R)	4.7 (S)	8.4 (S)
	II (Et₃N)ᵇ	EtOH	93.3 (R)	78.7 (R)	66.2 (R)	64.2 (R)
	I	EtOH	84.0 (R)	12.9 (R)	8.6 (S)	14.4 (S)
	I (Et₃N)ᵇ	EtOH	91.8 (R)	75.5 (R)	66.6 (R)	63.2 (R)
2 (Ph–C=C, NHCOMe, COOH)	II	EtOH	87.1 (R)	82.3 (R)		
	II (Et₃N)ᵇ	EtOH	93.5 (R)	93.1 (R)		
	I	EtOH	91.6 (R)	83.6 (R)		
	I (Et₃N)ᵇ	EtOH	93.1 (R)	90.9 (R)		
3 (Ph–C=C, NHCOMe, COOMe)	II	EtOH	95.0 (R)	89.7 (R)		
	II (Et₃N)ᵇ	EtOH	95.9 (R)	89.1 (R)		
	I	EtOH	95.2 (R)	59.6 (R)		
	I (Et₃N)ᵇ	EtOH	96.8 (R)	59.3 (R)		
4 (H–C=C, NHCOMe, COOH)	II	MeOH	95.2 (R)	21.8 (S)		
	II (Et₃N)ᵇ	MeOH	98.5 (R)	7.3 (S)		
	I	MeOH	86.3 (R)	5.8 (S)		
	I (Et₃N)ᵇ	MeOH	88.7 (R)	5.7 (S)		
5 (H–C=C, CH₂COOH, COOH)	II	MeOH	91.3 (S)	85.3 (S)		
	II (Et₃N)ᶜ	MeOH	94.8 (S)	93.1 (S)		
	I	MeOH–PhH	92.3 (S)	79.7 (S)		
	I (Et₃N)ᶜ	MeOH–PhH	94.5 (S)	91.3 (S)		

ᵃ Optical purities were determined on the basis of the reported maximum rotations: N-benzoyl-(S)-phenylalanine, [α]^{27}D −40.3° (c 1.0, MeOH);²² N-acetyl-(S)-phenylalanine, [α]^{26}D +46.0° (c 1.0, EtOH);²² N-acetyl-(S)-phenylalanine methyl ester, [α]^{25}D +15.9° (c 2.0, MeOH);²⁴ N-acetyl-(R)-alanine, [α]^{26}D +66.3° (c 2.0, H₂O);²² (R)-methylsuccinic acid, [α]^{20}D +16.88° (c 2.16, EtOH).²⁵ ᵇ Et₃N/Rh ratio of 2. ᶜ Et₃N/Rh ratio of 100; Et₃N/5 ratio of 1.
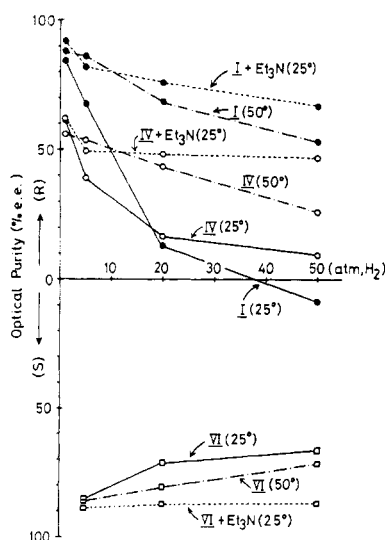

Figure 1. Pressure dependency of stereoselectivity in the asymmetric hydrogenation of (Z)-α-benzamidocinnamic acid (1) catalyzed by neutral rhodium complexes. All hydrogenations were run with 1.0 × 10⁻³ mol of 1 and 1.0 × 10⁻⁵ mol of the catalyst in 12 mL of absolute EtOH at 25 or 50 °C for 3–15 h: I, (BPPM)Rh(COD)Cl; IV, ((−)-DIOP)Rh(COD)Cl; VI, (diPAMP)Rh(COD)Cl.

On the other hand, it is found that the addition of a small amount of triethylamine to the reaction system not only increases the optical yield under a given hydrogen pressure but also markedly attenuates the pressure dependency of stereoselectivity. It also turns out that the marked effects of added triethylamine are observed only for the free acid substrates, and virtually no effects are observed for the ester 3.

In order to check the generality of these phenomena, we carried out the asymmetric hydrogenation of 1 using (−)-DIOP²⁶ and diPAMP as chiral ligands. As Figures 1 and 2 show, there is a clear pressure dependency of stereoselectivity in general, and the pressure effect on the DIOP complex catalyzed reaction is closely similar to that on the BPPM complex catalyzed one, while the pressure effect is considerably smaller for the diPAMP complex catalyzed
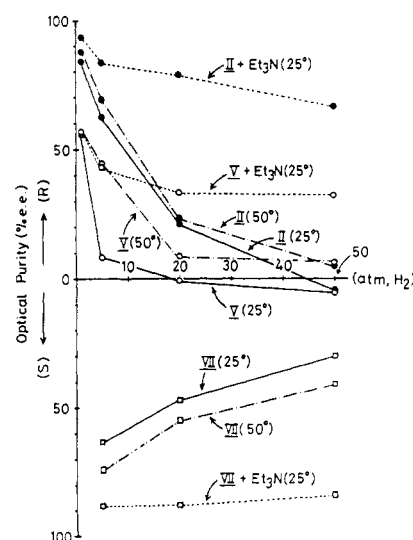

Figure 2. Pressure dependency of stereoselectivity in the asymmetric hydrogenation of 1 catalyzed by cationic rhodium complexes. For the scale and the reaction conditions, see the caption of Figure 1: II, [(BPPM)Rh(COD)]⁺ClO₄⁻; V, [((−)-DIOP)Rh(COD)]⁺ClO₄⁻; VII, [(diPAMP)Rh(COD)]⁺ClO₄⁻.

one. This may be due to the fact that the former two complexes have rather fluxional seven-membered-ring chelate structures whereas the latter forms a rigid five-membered-ring chelate with a C_2 axis. We also looked at the effects of temperature on the pressure dependency of stereoselectivity. To our surprise, a higher temperature (50 °C) brings about a higher stereoselectivity than a lower temperature (25 °C) does in almost all cases examined (the only exception is the case of IV at 1 atm of hydrogen), and as a result, the higher temperature considerably releases the pressure dependency of stereoselectivity as shown in Figures 1 and 2. The temperature effect is remarkable for the neutral complex catalyzed reactions (Figure 1), but it is relatively mild for the cationic complex catalyzed ones (Figure 2). The observed temperature effects on stereoselectivity are rather unusual since it has been generally accepted in these reactions that the higher the tempera-

Scheme I. Change of Rate-Determining Step
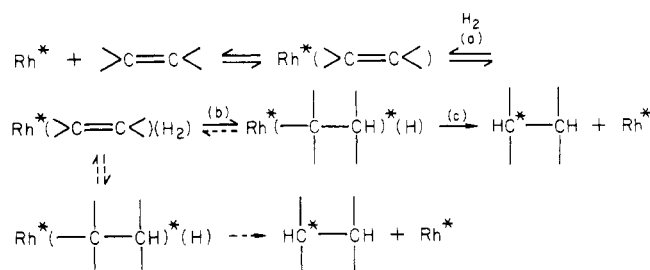
Scheme II
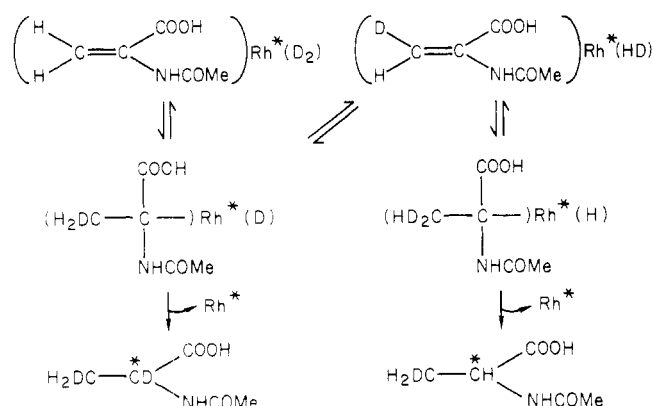
ture, the lower is the stereoselectivity at a given hydrogen pressure.[2a]

These phenomena could be caused by either (i) a change in the rate-determining step or (ii) an exchange of one mechanism for another, provided that the reaction proceeds via two competitive mechanisms. According to the mechanism of the hydrogenation catalyzed by a rhodium complex with a cis chelating diphosphine ligand proposed by Halpern et al.,[3a] the rate-determining step is suggested to be the oxidative addition of molecular hydrogen to the preformed rhodium–substrate complex, i.e., step a in Scheme I. Thus, if the former were the case, a high hydrogen pressure makes the oxidative addition of hydrogen (step a) easy, and the rate-determining step may change to the second hydride migration (step c) since no change in stereoselectivity would be expected even if the first hydride migration (step b) is the rate-determining step; i.e., an isomerization of the coordinating olefinic substrate may occur to facilitate the formation of the other enantiomer. The reaction paths involved in this mechanism are shown in Scheme I.

However, a mechanistic study[3b,c] on the hydrogenation of olefins catalyzed by (Ph₃P)₃RhCl revealed that step c is a fast process while step b is a slow one, and, moreover, recent work on the dideuteration of (E)-(acylamino)-cinnamic acid by Kagan's[4] and Knowles' groups[5] reinforced the conclusion that there is no equilibrium in step b. We also carried out the dideuteration of 4 in methanol at 20 atm of dideuterium at which pressure the production of the S isomer was preferred. If there were such an equilibrium in step b, at least 3,3-dideuterio-*N*-acetylalanine

(3) (a) J. Halpern, D. P. Riley, A. S. C. Chan, and J. Pluth, *J. Am. Chem. Soc.*, 99, 8055 (1977); (b) J. Halpern in "Organotransition-Metal Chemistry", Y. Ishii and M. Tsutsui, Eds., Plenum Press, New York, 1975, pp 109–117; (c) J. Halpern, T. Okamoto, and A. Zakhariev, *J. Mol. Catal.*, 2, 65 (1976).

(4) C. Detellier, G. Gerbard, and H. B. Kagan, *J. Am. Chem. Soc.*, 100, 7566 (1978).

(5) K. E. Koenig and W. S. Knowles, *J. Am. Chem. Soc.*, 100, 7561 (1978).

Table II. Asymmetric Hydrogenation of Methylsuccinic Acid Precursors[a] Catalyzed by II

substr	amine	amine/ substr ratio	catal, mol %	optical purity,[b] % ee (config)
5	Et₃N		0.5	85.3 (S)
	Et₃N	0.10	0.5	91.2 (S)
	Et₃N	1.00	0.5	93.1 (S)
	Et₃N	2.00	0.5	93.1 (S)
	C₅H₁₁N	1.00	0.5	93.0 (S)
	PhNH₂	1.00	0.5	90.9 (S)
6	Et₃N		1.0	22.0 (S)
	Et₃N	0.10	1.0	33.4 (S)
	Et₃N	1.00	1.0	34.5 (S)
	Et₃N	2.00	1.0	12.6 (S)
7	Et₃N		2.0	50.9 (R)
	Et₃N	0.10	2.0	65.0 (R)
	Et₃N	1.00	2.0	54.0 (R)
	Et₃N	2.00	2.0	10.6 (R)

[a] All reactions were run with 5 mmol of the substrate in 10 mL of benzene-methanol (1:3) at 20 °C for 20 h under an initial hydrogen pressure of 20 atm. [b] Optical purity was determined on the basis of the reported maximum rotation of (R)-methylsuccinic acid, $[\alpha]^{20}_D$ +16.88° (c 2.16, EtOH).[25]

should be produced as shown in Scheme II and further deuterated products are also possible. We found that there was no scrambling of deuterium at all; viz., 2,3-dideuterio-*N*-acetylalanine was obtained exclusively (eq 1). Consequently, the first assumption is unlikely in the present reaction.
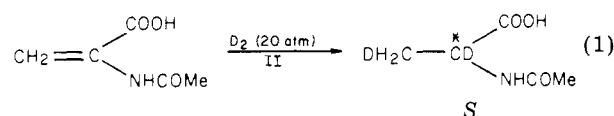
The observed results are well accommodated by taking into account the competitive mechanisms, A and B, shown in Scheme III. Mechanism A follows the one proposed by Halpern et al.,[3a] in which the rate-determining step is the oxidative addition of molecular hydrogen to the intermediate complex 1. Mechanism B follows the one which has been widely accepted for the hydrogenation of olefins catalyzed by (Ph₃P)₃RhCl.[3b,c] Mechanism A is exclusively operative at 1 atm of hydrogen whereas mechanism B becomes predominant at higher pressures. Namely, it is reasonable to assume that the dihydride complex 4 is stable and is easily formed at high pressures of hydrogen even though the formation of 4 is unfavorable for a complex with chelating diphosphines.[3a] As for the stereoselectivity of these mechanisms, mechanism A should extremely favor the production of the R isomer (S isomer for diPAMP) while mechanism B should prefer the other isomer in order to accommodate the results. Inspection of a CPK model based on the X-ray structure[6] of [(PPPM)Rh(COD)]⁺ClO₄⁻ (III) supports the proposed stereochemical requirements in the coordination sphere of the intermediate complexes 2 and 5; viz., (i) in the formation of 1, the olefinic substrate occupies the coordination site in such a way to minimize the steric repulsion and gain the attractive interaction, and then molecular hydrogen undergoes oxidative addition, keeping the orientation of the substrate to give 2, and (ii) in the formation of 4, hydrogens occupy the most favorable site first, and then the olefinic substrate comes into the coordination sphere to give 5 in which the preferable

(6) Y. Ohga, Y. Iitaka, K. Achiwa, T. Kogure, and I. Ojima, 25th Symposium on Organometallic Chemistry, Japan, 1978, Abstract No. 3A15.

orientation for the substrate may well be opposite to that of 2.[7] Although it seems to be generally considered that
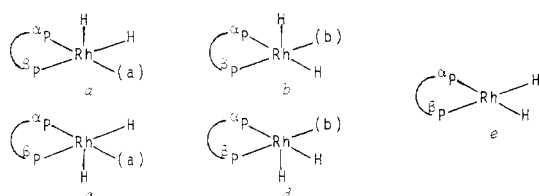
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(7) In the case of the complexes which do not have a C_2 axis with regard to the diphosphine–rhodium metal moiety, there are conceptually four possible modes (A–D) of complexation for the intermediate 1. If the
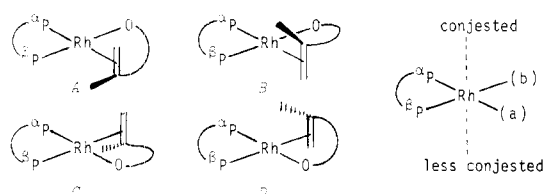
coordination site a is by far more favorable for the complexation of the olefinic substrate as well as hydrogen than site b and the upper apical position is more conjested than the lower apical one, it is quite reasonable to assume that the intermediate 1A is the most favorable. Since the
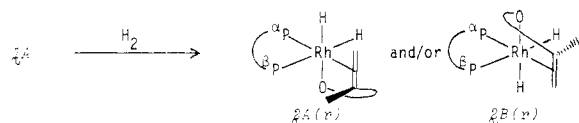
enantioface selection is already done at this stage, the oxidative addition of molecular hydrogen will give the key intermediate 2 in the mode A(r) or the B(r) both of which will further give a hydrogenated product having the same configuration. Under the presumed stereoregulations, 2A(r) should be by far more favorable than 2B(r). Accordingly, an extremely high stereoselectivity can be expected in this process (mechanism A). The highly regioselective and stereoselective complexation of the prochiral substrate is confirmed by ^{31}P NMR spectroscopy (vide infra). On the other hand, there are conceptually five possible modes for the intermediate 4 (a–e). Under the presumed stereoregulations, 4b or 4d is fa-

vorable. The contribution of 4e may be negligible because of its inherent instability due to the trans effects of phosphorus.[3a] The complexation of the olefinic substrate will then give the key intermediate 5 in the mode C(s), C(r), D(s), or D(r). Among them, 5C(s) may be the most favorable
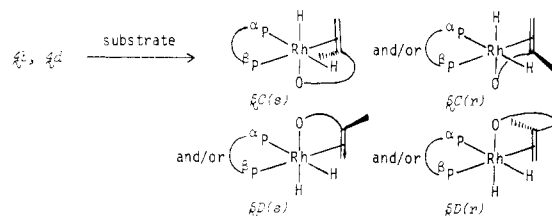
on the basis of the presumed stereoregulations, which will give the hydrogenated product having the configuration opposite to that of the product from 5A(r). This is actually the case when BPPM or DIOP is employed as chiral ligand, in which the inversion of the preferred configuration of the product is observed only by changing hydrogen pressure. As the stereoregulations for hydrogens in 4 may not be so severe as those for the olefinic substrate in 2 and the olefinic substrate is forced to coordinate with the unfavorable site (b) in 5, the stereoselectivity would be considerably lower in mechanism B which involves 5. The observed results exactly support this prediction. Similar discussions about the complex which has a C_2 axis with regard to the diphosphine–rhodium metal moiety (e.g., diPAMP–rhodium complex) are simpler than those for the complexes with BPPM or DIOP since there are only two possible modes for 1, i.e., the mode A (=D) and the mode B (=C), and also two possible modes for 4, i.e., the mode a (=d) and the mode b (=c). If 1A is the more favorable of the two, the oxidative addition of molecular hydrogen will lead to 2A(r), and extremely high stereoselectivity is expected because of the severe stereoregulation in 1. On the other hand, 4a will give 5A(r) or 5A(s), while 4b will lead to the formation of 5B(r) or 5B(s). If 5A(r) is more favorable than 5A(s) for stereoelectronic reasons, 5B(s) should be more preferable than 5B(r). Thus, 5A(r) is produced from 4a, and 5B(s) is formed from 4b, preferentially. Compound 5A(r) gives the product which has a configuration opposite to that arising from 5B(s). As the stereochemical difference between 4a and 4b is very small, comparable amounts of 5A(r) and 5B(s) may be formed. Thus, the stereoselectivity in this process is anticipated to be low.

mechanism A is always operative for cis chelating diphosphine ligands, our results strongly indicate that mechanism B makes a significant contribution at higher hydrogen pressures even when cis chelating diphosphines are employed.

The observed effects of added triethylamine and temperature on the pressure dependency of stereoselectivity are also well explained on the basis of the competitive mechanisms mentioned above. It has been shown[8] that the addition of a small amount of amine or other bases to the reaction system increases the stereoselectivity, dramatically in some cases, in the asymmetric hydrogenation of olefinic acid, e.g., α-acetamidocinnamic acid. However, reasons for this enhancement have not been clarified yet. We have obtained interesting information about this enhancement. As described above, the addition of a small amount of triethylamine to the reaction system involving free acid substrate not only increases the optical yield at a given hydrogen pressure but also markedly attenuates the pressure dependency of stereoselectivity, and as a result, the production of the R isomer (S isomer for di-PAMP) is favored; i.e., mechanism B is considerably suppressed by the addition of triethylamine even at a high pressure. The results may imply that the amine generates the carboxylate anion of the free acid substrate, which has a much larger binding (equilibrium) constant with the rhodium catalyst to give 1 than does nonionized substrate, i.e., $K_1 \gg K_{4'}$, and as a result, the formation of 4 is suppressed. Consequently, the results strongly suggest that the most significant effect of the added amine is to make mechanism A predominate over mechanism B although the possibility that the addition of triethylamine improves the stereochemical requirements in the coordination sphere could not completely be excluded. The temperature effects on the pressure dependency of stereoselectivity are also well accommodated by taking into account the proposed two competitive mechanisms. Namely, it is reasonable to assume that the formation of the dihydride complex 4 is unfavorable at higher temperatures because of its inherent instability as far as cis chelating ligands are concerned. This means that a higher temperature favors mechanism A.

Our results show that one should be very careful about the pressure dependency of optical yield when discussing precisely the stereochemistry of a given chiral catalyst in asymmetric hydrogenations.

Asymmetric Hydrogenations of Itaconic Acid, Citraconic Acid and Mesaconic Acid. In connection with the determination of the chiral recognition step, we carried out the asymmetric hydrogenation of itaconic acid (5), citraconic acid (6), and mesaconic acid (7), which leads to the formation of methylsuccinic acid in every case. If asymmetric induction occurs after the formation of an alkylrhodium complex (3 or 6 in Scheme III), the optical yield and the direction of asymmetric induction are independent of the olefin stereochemistry, while if the chiral recognition takes place in the step of olefin complexation, the asymmetric induction is seriously dependent upon the olefin stereochemistry. As Table II shows, 5 and 6 gave (S)-methylsuccinic acid whereas 7 gave the R isomer. Thus, it is clearly indicated that the chiral recognition takes place in the olefin complexation step. Although the same conclusion was already reported by using an E–Z pair of N-(acylamino)cinnamic acids, our results provide an-

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(8) (a) T. P. Dang and H. B. Kagan, *Chem. Commun.*, 481 (1971); (b) A. P. Stoll and R. Süess, *Helv. Chim. Acta*, **57**, 2487 (1974); (c) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **97**, 2576 (1975); (d) K. Achiwa, *ibid.*, **98**, 8265 (1976).

Scheme III.[a] Competitive Mechanism

Mechanism A (favorable under low hydrogen pressure)

Mechanism B (favorable under high hydrogen pressure)
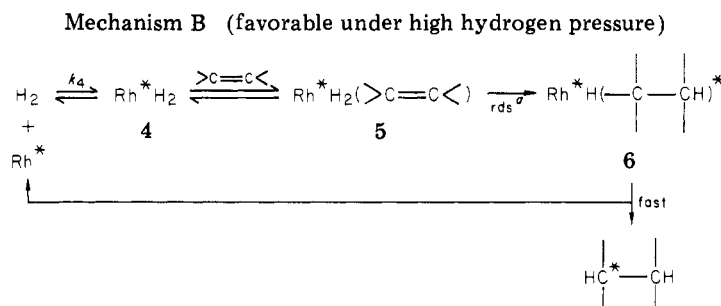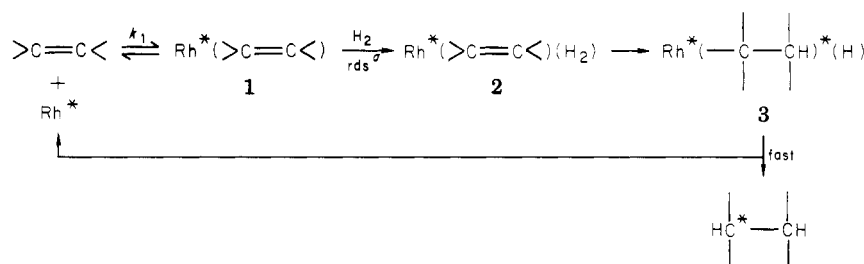
[a] rds = rate determining step; K = binding (equilibrium) constant.

Scheme IV. Asymmetric Hydrogenation of
Methylsuccinic Acid Precursors
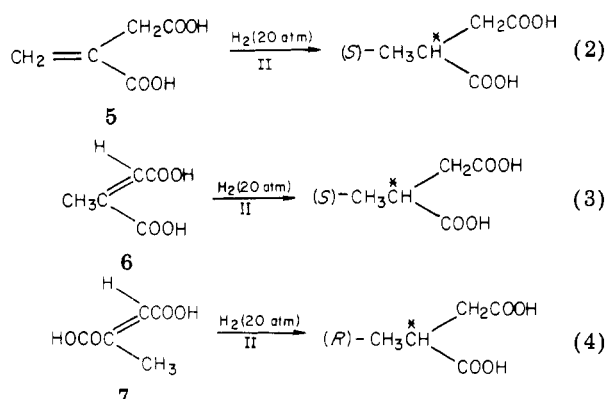
other strongly supporting example.

We also looked at the effects of added amine on the stereoselectivity of the reaction of these olefinic diacids catalyzed by II (Scheme IV) and observed a clear difference between 5 and 6 (or 7). Namely, when triethylamine was added to the reaction system of 5, the optical yield was increased up to 93.1% ee but was not increased by the addition of more than 1 equiv of triethylamine.[32]

Piperidine and aniline behaved almost the same as triethylamine. In sharp contrast with this, a steep decrease in optical yield was observed on adding 2 equiv of triethylamine to 6 or 7 although small amounts of added triethylamine ($\leq$1 equiv) increased the optical yield.

The observed clear difference is interpreted as follows. (i) Addition of 2 equiv of triethylamine to 6 or 7 generates a dianion, one carboxylate of which competes with the other to occupy the same coordination site of the chiral rhodium complex, and this competition seriously decreases the stereoselectivity. (ii) A certain carboxylate anion of 5 interacts highly selectively with the rhodium center even when the dianion of 5 is generated.

The result discloses another aspect of the effect of triethylamine, which is different from that observed in the attenuation of the pressure dependency of stereoselectivity.

As to the marked selectivity in the coordination of the carbonyl group (or carboxylate anion) of 5 with the rho-
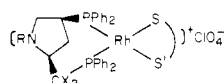
dium center, one should consider the stereochemistry of the chelation of the olefinic acid. Namely, the chelation of the vinylacetic acid moiety is much more preferable than that of the methacrylic acid moiety because the former coordination forms a quasi-five-membered-ring chelate whereas the latter forms a less favorable quasi-four-membered-ring chelate. Thus, the methacrylate anion moiety cannot compete with the vinylacetate anion moiety for the occupation of a certain coordination site of the rhodium complex even when the dianion of 5 is generated (vide infra).
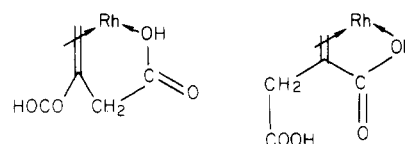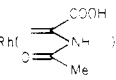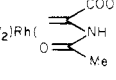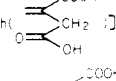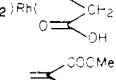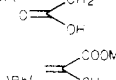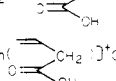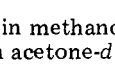

In connection with these results, Christopfel and Vineyard proposed a mechanism for the anomalous behavior of itaconic acid in its asymmetric hydrogenations, which could be attributed to the existence of intermolecular hydrogen bonding.[33]

^{31}P NMR Studies on the Structure and the Behavior of the Substrate–Chiral Rhodium Complexes. As mentioned above, the most significant step for the chiral recognition of a prochiral face of olefinic substrate is the complexation of an olefin molecule to the chiral rhodium catalyst when the reaction proceeds via mechanism A in Scheme I. It is extremely important to directly look at the behavior of the substrate–chiral rhodium complex in solution. In 1977, Slack and Baird demonstrated the possibility of the direct observation of the intermediate complexes in solution by means of ^{31}P NMR study, expecting the direct observation of the chiral rhodium complexes coordinated with substrate molecule.[9] While our study was in progress, Brown and Chaloner succeeded in observing such diastereomeric intermediate complexes with (Z)-α-benzamidocinnamic acid or its ester with DIOP[10a] and diPAMP[10b] as chiral ligands by ^{31}P NMR.

(9) D. A. Slack and M. C. Baird, *J. Organomet. Chem.*, 142, C69 (1977).

Table III. ^{31}P NMR Data for the Complexes[a]

$$(RN\!\!\diagdown\!\!\overset{PPh_2}{\diagdown}\!\!\overset{}{\underset{CX_2}{\diagup}}\!\!\overset{PPh_2}{\diagup}Rh\!\!\overset{S}{\underset{S'}{\diagup}})]^+ClO_4^-$$

PPM, R = H; X = H
PPPM, R = CO-t-Bu; X = H
BPPM, R = COO-t-Bu; X = H
PPM-d_2, R = H; X = D
PPPM-d_2, R = CO-t-Bu; X = D
BPPM-d_2, R = COO-t-Bu; X = D

complex	temp, K	$^{\alpha}$P	$^{\beta}$P	$J_{Rh-^{\alpha}P}$	$J_{Rh-^{\beta}P}$	$J_{^{\alpha}P-^{\beta}P}$
[(PPM)Rh(COD)]$^+$ClO$_4^-$	303	29.52	38.87	109	114	36
[(PPM-d_2)Rh(COD)]$^+$ClO$_4^-$	303	29.49	39.46	109	114	36
[(PPPM)Rh(COD)]$^+$ClO$_4^-$	303	43.12	12.12	146	139	37
[(PPPM-d_2)Rh(COD)]$^+$ClO$_4^-$	303	43.37	11.78	146	140	37
[(BPPM)Rh(COD)]$^+$ClO$_4^-$	333	41.61	12.56	145	140	37
	303	41.57	a 12.72 / b 12.32		a 140 / b 140	a 37 / b 36
	233	a 41.51 / b 40.64	a 12.51 / b 11.62	a 145 / b 146	a 140 / b 139	a 36 / b 36
[(BPPM-d_2)Rh(COD)]$^+$ClO$_4^-$	303	41.52	a 12.40 / b 12.01	145	a 140 / b 140	a 36 / b 36
[(PPPM)Rh(CD$_3$OD)$_n$]$^+$ClO$_4^-$	303	69.64	42.54	201	197	65
[(PPPM-d_2)Rh(CD$_3$OD)$_n$]$^+$ClO$_4^-$	303	69.59	42.12	201	197	65
[(BPPM)Rh(CD$_3$OD)$_n$]$^+$ClO$_4^-$	303	a 67.96 / b 67.56	a 42.22 / b 43.16	a 200 / b 200	a 197 / b 197	a 66 / b 66
[(BPPM-d_2)Rh(CD$_3$OD)$_n$]$^+$ClO$_4^-$	303	a 68.11 / b 67.73	a 42.85 / b 41.96	a 201 / b 200	a 197 / b 197	a 66 / b 66
[(PPPM)Rh(D$_3$CC(O)CD$_3$)]$^+$ClO$_4^-$ [b]	303	66.64	42.54	201	197	65
[(BPPM)Rh(D$_3$CC(O)CD$_3$)]$^+$ClO$_4^-$ [b]	303	a 65.05 / b 64.77	a 38.81 / b 38.32	a 195 / b 195	a 192 / b 192	a 64 / b 64
[(BPPM)Rh(structure: COOH, NH, O=, Me)]$^+$ClO$_4^-$ [c]	303	30.57	32.45	140	137	34
[(BPPM-d_2)Rh(structure: COOH, NH, O=, Me)]$^+$ClO$_4^-$ [c]	303	30.50	32.06	140	137	34
[(BPPM)Rh(structure: COOH, CH$_2$, O=, OH)]$^+$ClO$_4^-$ [d]	303	36.27	34.57	151	137	37
[(BPPM-d_2)Rh(structure: COOH, CH$_2$, O=, OH)]$^+$ClO$_4^-$ [d]	303	36.28	34.38	150	136	36
[(PPPM)Rh(structure: COOMe, CH$_2$, O=, OH)]$^+$ClO$_4^-$ [d]	303	40.59	30.69	128	143	43
[(PPPM-d_2)Rh(structure: COOMe, CH$_2$, O=, OH)]$^+$ClO$_4^-$ [d]	303	40.66	30.36	129	142	43
[(PPPM)Rh(structure: CH$_2$, O=, OH)]$^+$ClO$_4^-$ [d]	233	38.15	30.74	130	145	45

[a] Measured in methanol-d_4 unless otherwise noted. The chemical shifts are given in δ units and the J values in hertz. [b] Measured in acetone-d_6. [c] Threefold excess of the substrate was used. [d] Twentyfold excess of the substrate was used.

Although a chiral rhodium complex having a potential C_2 axis, e.g., [(DIOP)Rh(CH$_3$OH)$_n$]$^+$BF$_4^-$ (VIII) and [(diPAMP)Rh(CH$_3$OH)$_n$]$^+$BF$_4^-$ (IX), shows only one averaged signal as doublet in its ^{31}P NMR spectrum, the rhodium complexes with pyrrolidinodiphosphines show a set of two distinct signals which arise from nonequivalent phosphorus nuclei. This feature has a great advantage for looking at the mode of olefin coordination since it is well-known that there is a strong trans effect of the coordinated ligand on the chemical shift of phosphorus nuclei of rhodium complexes.[9] Thus, in principle, one can determine how the olefinic substrate occupies the possible

coordination sites on the basis of the ^{31}P NMR spectra of the substrate–rhodium complex.

Actually, the chemical shifts of the phosphorus nuclei were found to change dramatically, depending on the sort of coordinated molecule in the trans position,[11a] as shown in Table III. For instance, the methanol complex of PPPM or BPPM showed ca. a 25-ppm downfield shift from the corresponding COD complex, and a similar downfield shift was observed for the acetone complexes.

At first, we tentatively made an assignment[11b] of $^{\alpha}$P and $^{\beta}$P, taking into account the fact that, in general, there is a clear difference in phosphorus chemical shift between primary alkyldiphenylphosphines and secondary and

(10) (a) J. M. Brown and P. A. Chaloner, *J. Chem. Soc., Chem. Commun.*, 321 (1978); (b) J. M. Brown and P. A. Chaloner, *Tetrahedron Lett.*, 1877 (1978).

(11) (a) I. Ojima and T. Kogure, *Chem. Lett.*, 1145 (1978); (b) *ibid.*, 641 (1979).

Table IV. ^{31}P NMR Data (δ) for Ligands[a]

ligand	αp	βp	temp, K
PPM	-6.2	-22.7	273
PPM-d_2	-6.2	-23.1	273
PPPM	-12.3	-25.7	273
PPPM-d_2	-12.1	-26.0	273
BPPM	-9.2	-23.6	303
	a -10.0	a -23.9	273
	b -10.5	b -24.2	
	a -13.7	a -26.4	195
	b -13.9	b -26.2	
BPPM-d_2	-9.2	-24.0	303
DIOP[b]	-24.0		303
chiraphos[c]	-16.7		303

[a] Measured in methanol-d_4. [b] The signal of [(DIOP)Rh-(COD)]$^+$ClO$_4^-$ appears as doublet (J_{Rh-P} = 199 Hz) at 41.6 ppm in methanol-d_4 at 303 K (cf. Table III). [c] The signal of [(chiraphos)Rh(COD)]$^+$ClO$_4^-$ appears as doublet (J_{Rh-P} = 145 Hz) at 55.5 ppm in methanol-d_4 at 303 K (cf. Table III).
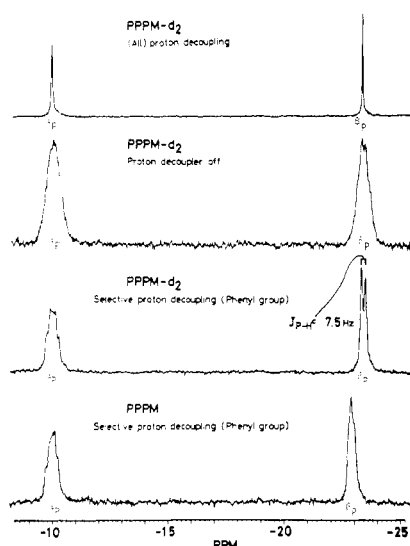

Figure 3. ^{31}P NMR spectra of PPPM and PPPM-d_2 measured in chloroform-d at 30 °C.

tertiary alkyl- or cycloalkyldiphenylphosphines; i.e., the former phosphorus signal appears at considerably lower field than the latter does.[12] However, the phosphorus chemical shifts of DIOP, chiraphos and their COD complexes do not follow this general trend, as shown in Table IV. Consequently, we prepared BPPM-d_2, PPPM-d_2,[13]
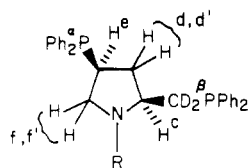
BPPM-d_2, R = COO-t-Bu[a]
PPPM-d_2, R = CO-t-Bu[a]
PPM-d_2, R = H[a]

and their rhodium complexes, in which the methylene protons of the 2-(diphenylphosphino)methyl group were deuterated and made the unambiguous assignment of $^\alpha$P and $^\beta$P on the basis of the facts that (i) by use of a *selective proton decoupling* of the phenyl protons, the coupling
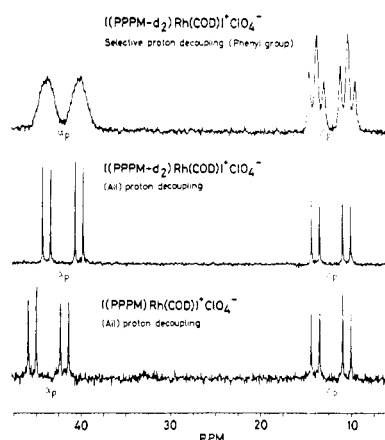
(12) G. M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds", Vol. 1, Wiley-Interscience, New York, 1972, pp 124–206, and references therein.
(13) PPM stands for (2S,4S)-4-(diphenylphosphino)-2-[(diphenyl-phosphino)methyl]pyrrolidine. See ref 8d.

Figure 4. ^{31}P NMR spectra of [(PPPM)Rh(COD)]$^+$ClO$_4^-$ and [(PPPM-d_2)Rh(COD)]$^+$ClO$_4^-$ measured in chloroform-d at 30 °C.
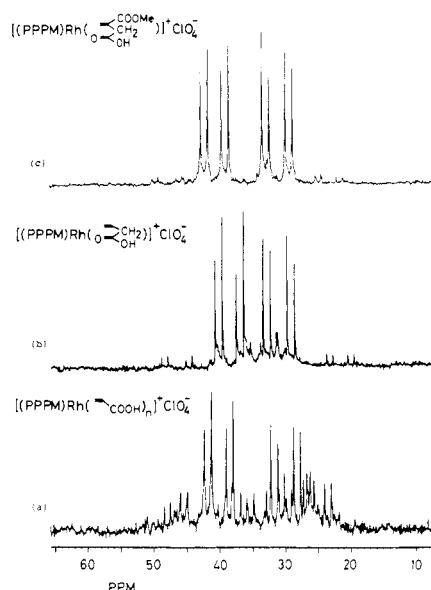

Figure 5. ^{31}P{^{1}H} spectra of the rhodium–substrate complexes with PPPM as chiral ligand measured in methanol-d_4 at 30 °C.

between $^\beta$P and H^c (e.g., 7.5 Hz for PPPM-d_2 in CDCl$_3$ and 33 Hz for [(PPPM-d_2)Rh(COD)]$^+$ClO$_4^-$ in CDCl$_3$) was observed, while $^\alpha$P appeared as an unresolved signal because of the coupling with the pyrrolidine ring protons (see Figures 3 and 4), and (ii) the intensity of $^\beta$P signal was considerably smaller than that of $^\alpha$P signal (see Figure 4). This phenomenon is reasonably ascribed to the increase in the relaxation time (T_1) of the $^\beta$P nucleus, which is caused by the deuteration of the geminal methylene protons.[14] NMR spectral data for the rhodium complexes are

(14) There is a precedent for such a phenomenon in ^{13}C NMR spectroscopy: C. C. Levy in "Topics in Carbon-13 NMR spectroscopy", Vol. 1, Wiley, New York, 1974, pp 112–113. During the course of our ^{31}P NMR study with the deurated ligands, Achiwa et al. reported the assignment of $^\alpha$P and $^\beta$P on the basis of the *broadening* of the phosphorus signal arising from phosphorus–deuterium coupling [K. Achiwa, Y. Ohga, and Y. Iitaka, *Chem. Lett.*, 865 (1979)]. However, our study clearly shows that the proposed phosphorus–deuterium coupling is negligible in every case, and thus, the basis proposed by Achiwa et al. for the assignment of phosphorus signals is found to be erroneous. We observed that the intensity of either the $^\alpha$P signal or the $^\beta$P signal was decreased by the deuteration of the methylene protons of the 2-(diphenylphosphino)methyl group, and the intensity of the $^\beta$P signal was considerably smaller than that of the $^\alpha$P signal. We also found that the relative decrease of the intensity of the $^\beta$P signal was released when a sufficiently longer delay time was employed for the measurement. Thus, the observed relative decrease of the phosphorus signals is reasonably ascribed to the increase of the T_1 of the phosphorus nuclei, especially of $^\beta$P which is exposed to the stronger dipole–dipole interaction with the geminal deuterium.
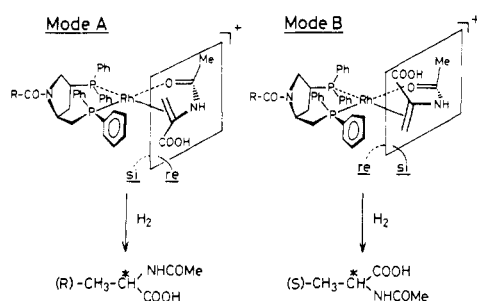
Figure 6. Modes of the chiral recognition of enantiofaces by the chiral rhodium catalyst.

summarized in Table III and those for the ligands are listed in Table IV.

As Table III and Figure 7 show, the α-acetamidoacrylic acid complex of BPPM displays a set of two signals at 32.45 ($^{\alpha}$P) and 30.57 ppm ($^{\beta}$P) as doublet of doublets for each phosphorus. By taking into account the remarkable change in the chemical shift of each phosphorus signal caused by the trans ligand listed in Table III, we concluded that the olefin moiety occupies the trans position of $^{\alpha}$P and that the carbonyl oxygen occupies the trans position of $^{\beta}$P as depicted in Figure 6. If the olefin moiety and the carbonyl oxygen coordinate in an opposite manner, a considerably separated set of two signals should appear in the regions, e.g., 10–20 and 50–60 ppm.

Since the quasi-four-membered-ring chelate with the acrylic acid moiety is disadvantageous for steric reasons, the chelation is reasonably ascribed to that of the enamide moiety. Similarly, itaconic acid may form a quasi-five-membered-ring chelate by using its vinylacetic acid moiety (vide supra). To confirm the quasi-five-membered-ring chelate formation, we employed vinylacetic acid and acrylic acid as substrate. As Figure 5 shows, the former substrate–PPPM–rhodium complex displays a spectrum very similar to that of the methyl itaconate complex as expected whereas the latter displays a complicated one which indicates the multimode complexation of the substrate with the rhodium complex. As is immediately seen from Figure 7d, there is no trace of the other regioisomer complex in which α-acetamidoacrylic acid coordinates in an opposite manner. The result with itaconic acid brings us the same conclusion (Figure 7c).

It should be noted that evidence for the extremely regioselective complexation of prochiral substrates to chiral rhodium catalysts was obtained for the first time by using ^{31}P NMR spectroscopy.[29]

The results provide a crucial basis for the stereochemical inspection of the mechanism of asymmetric induction in the chiral coordination sphere. As the coordination of the prochiral substrate becomes extremely regioselective, there remain only two possible modes of complexation, mode A and mode B, as depicted in Figure 6. For instance, the asymmetric hydrogenation of α-acetamidoacrylic acid catalyzed by II at 1 atm of hydrogen has been found to give (*R*)-*N*-acetylalanine with 98.5% ee (see Table I), and thus, the mode of the complexation of the substrate to the rhodium catalyst is determined to be mode A.[30] Similarly, the rhodium catalyst chooses the *re* face of itaconic acid (mode A) to give (*S*)-methylsuccinic acid with 94.8% ee.

As for the behavior of BPPM–rhodium complexes in solution, very interesting phenomena were observed. Namely, from the ^{31}P NMR spectra of [(BPPM)Rh-(COD)]$^+$ClO$_4^-$ (II) and [(BPPM)Rh(CD$_3$OD)$_n$]$^+$ClO$_4^-$ (X), it turns out that (i) there are two species in nearly equal amounts in methanol-d_4 at ambient temperature since there appear two sets of doublets of doublets in either the
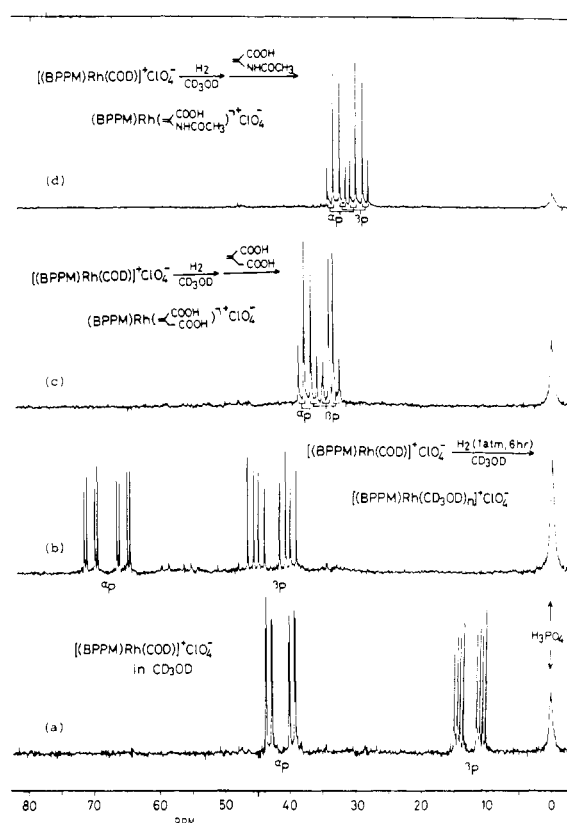

Figure 7. "Induced-fit" phenomena observed in the rhodium complexes with BPPM. ^{31}P{^{1}H} NMR spectra were measured in methanol-d_4 at 30 °C.

$^{\alpha}$P or $^{\beta}$P region as shown in Figure 7, (ii) the ratio of the two species is changed by changing the solvent or the temperature, and (iii) the coalescence of the two sets of signals is observed when the solution of the complex is warmed up in the case of II. The coalescence temperature for II is found to be 318 K.[31] The results clearly show that there are two conformational isomers in solution. However, when α-acetamidoacrylic acid, for example, was added to VI, the features of the spectrum changed dramatically, and the predominant formation of a diastereomeric complex was observed (Figure 7). Namely, the rhodium complex takes a preferred conformation when α-acetamidoacrylic acid comes into the coordination sphere. The result is best interpreted as the "induced-fit" action of the chiral rhodium complex by the complexation of the substrate.

As Figure 8 shows, the observed two conformers could be ascribed to either the quasi-chair or the quasi-boat conformers[11a] with regard to the seven-membered ring or the rotational isomers arising from the slow rotation of the *tert*-butoxycarbonyl group around the N–C(O) bond, which is characteristic of an amide or a carbamate structure.

In order to clarify this point, we measured the spectra of the free ligands PPM, PPPM, and BPPM and their COD complexes at various temperatures in methanol-d_4.

The spectrum of PPM or PPPM does not change in the temperature range 223–333 K except for the chemical shifts, while BPPM shows two sets of singlets below the coalescence temperature, 291 K. Similarly, the spectra of the COD complexes of PPM and PPPM do not change in the temperature range 223–333 K whereas the COD complex of BPPM shows two sets of doublet of doublets below the coalescence temperature, 318 K.

The results are best explained by taking into account the slow rotation of the *tert*-butoxycarbonyl group around the N–C(O) bond in BPPM. The rotation of the pivaloyl group around the N–C(O) bond seems to be completely
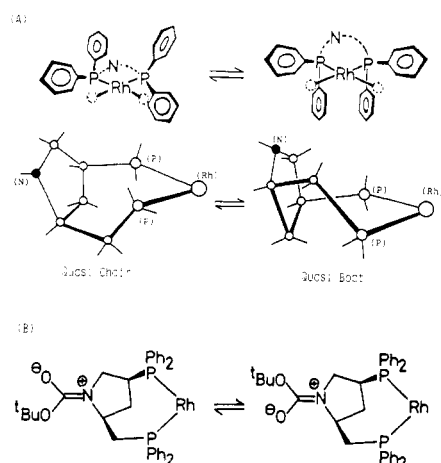
Figure 8. Possible roots for the observed conformational isomerism: (A) interconversion between the quasi-chair and the quasi-boat conformer, (B) slow (hindered) rotation around the N–C(O) bond.

Figure 9. Perspective views of [(PPPM)Rh(COD)]$^+$ClO$_4^-$ (III). Cycloocta-1,5-diene is omitted for simplicity in a.

fixed because of its bulky *tert*-butyl moiety. Accordingly, the quasi-chair–quasi-boat interconversion of the seven-membered ring would be easy, as in the case of the corresponding DIOP complex.[15,16] Nevertheless, inspection of CPK models clearly shows that the interconversion between the quasi-chair and the quasi-boat conformers is impossible once the chelating substrate comes into the coordination sphere to form the substrate–rhodium complex. Only the quasi-chair conformer is accessible for the complexation of the chelating substrate, which happens to correspond exactly to the X-ray structure of [(PPPM)Rh(COD)]$^+$ClO$_4^-$ (III) as shown in Figure 9.[6,17]

Is should be noted that even the rotation of the distal *tert*-butoxycarbonyl group around the N–C(O) bond in BPPM is found to be fixed by the complexation of the prochiral substrate, and this fixation is observed as the "induced-fit" action of the chiral rhodium complex.

Experimental Section

Measurements. Melting points and boiling points were uncorrected. Infrared spectra were recorded on a Hitachi 223 spectrophotometer using samples as neat liquid or KBr disks. ^{1}H NMR spectra were measured with a Varian XL-100, T-60, or HR-200 spectrometer using Me$_4$Si as the internal standard. ^{31}P NMR spectra were recorded on a Varian XL-100 using H$_3$PO$_4$ as the external standard. Optical rotations were measured with a Union PM 201 automatic digital polarimeter.

Materials. Itaconic acid, citraconic acid, mesaconic acid, and α-acetamidoacrylic acid were obtained from commercial sources and purified by recrystallization before use. (Z)-α-Acetamidocinnamic acid and (Z)-α-benzamidocinnamic acid were prepared by a reported method.[18] Methyl (Z)-α-acetamidocinnamate was prepared by the methylation of (Z)-α-acetamidocinnamic acid with diazomethane. 1-Methyl itaconate was prepared by a se-
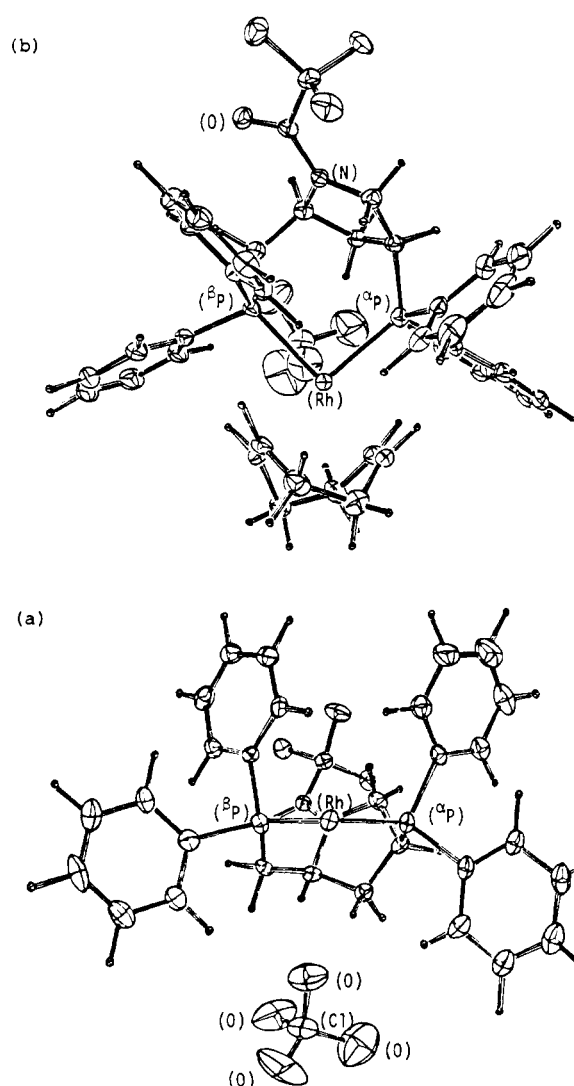
lective hydrolysis of dimethyl itaconate. 4-Hydroxy-L-proline, chlorodiphenylphosphine and p-toluenesulfonyl chloride were used as purchased. [Rh(COD)Cl]$_2$[19] and Rh(COD)(acac)[20] (acac = acetylacetonato) were prepared by the literature methods. All solvents and amines were dried, degassed, and stored under argon.

Preparation of (2S,4S)-N-(tert-Butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM). 4-Hydroxy-L-proline Ethyl Ester (6). 4-Hydroxy-L-proline (26.2 g, 0.20 mol) was suspended in ethanol (600 mL) and dry hydrogen chloride gas was bubbled at ambient temperature. Then, an exothermic reaction took place. After all the crystals of 4-hydroxy-L-proline were dissolved, the reaction mixture was cooled to 0–5 °C, dry hydrogen chloride gas was bubbled in for another 30 min, and the solution was stirred for 8 h. Evaporation of the solvent left crystalline 4-hydroxy-L-proline ethyl ester hydrochloride, which was washed with dry ether to give colorless needles (39.0 g, 99.7%).

Gaseous ammonia was bubbled into the solution of the ethyl ester hydrochloride (39.0 g, 0.199 mol) in 800 mL of chloroform at 0–5 °C for 30 min with stirring. The resulting precipitates of ammonium chloride were filtered off with a G4 glass filter, and the filtrate was concentrated in vacuo to give 4-hydroxy-L-proline ethyl ester (6; 31.7 g, 100%).

N-(tert-Butoxycarbonyl)-4-hydroxy-L-proline Ethyl Ester (7). A mixture of 6 (31.7 g, 0.199 mol) and tert-butyl (S)-4,6-dimethylpyrimidine-2-thiocarbonate (52.9 g, 0.220 mol) in aqueous

(15) We measured the ^{31}P NMR spectra of [((–)-DIOP)Rh(COD)]$^+$-ClO$_4^-$ at various temperatures in methanol-d_4 and found that the feature of the spectrum (appeared as doublet) did not change even at 183 K. The result strongly suggests the rapid interconversion between two conformers: see ref 16.

(16) J. M. Brown and P. A. Chaloner, *J. Am. Chem. Soc.*, **100**, 4307 (1978).

(17) Although Achiwa demonstrated[8d] that BPPM was expected to have a characteristic stereoregulation by attractive interaction between the nitrogen atom of the pyrrolidine ring and the functional group(s) of the substrates, the result of X-ray analysis clearly shows that the nitrogen atom cannot participate in the proposed attractive interaction at all, and the N-acylpyrrolidine moiety simply plays a role in determining the arrangement of the four phenyl groups; i.e., BPPM does not behave as a "functionalized ligand" in the original sense.

(18) R. M. Herbst and D. S. Shemin, "Organic Syntheses", Collect. Vol. 2, Wiley, New York, 1943, pp 1, 490.

(19) J. Chatt and L. M. Venanzi, *J. Chem. Soc. A*, 4735 (1957).

(20) D. Sinou and H. B. Kagan, *J. Organomet. Chem.*, **114**, 325 (1976); R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

N,N-dimethylformamide (120 and 80 mL of DMF and H_2O, respectively) was stirred overnight and heated at 50 °C for another 2 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in 400 mL of water and extracted by ethyl acetate (3 × 400 mL). Compound 7 was obtained as orange oil after drying of the extract over anhydrous magnesium sulfate and evaporation of the solvent: 51.6 g (100%); IR (neat) 3440 (ν_{OH}), 1745 and 1685 ($\nu_{C=O}$) cm^{-1}; NMR (CDCl$_3$) δ 1.23 (t, $J = 7$ Hz, 3 H, H^b), 1.38 (s, 9 H, H^a), 2.20 (m, 2 H, H^e), 2.35 (s, 1 H, H^h), 3.52 (m, $J_{fg} = 4$ Hz, $J_{fg} = 0$. $J_{gg'} = 11$ Hz, 2 H, H^g), 4.12 (q, $J = 7$ Hz, 2 H, H^c), 4.40 (m, 2 H, H^d, H^f).


7
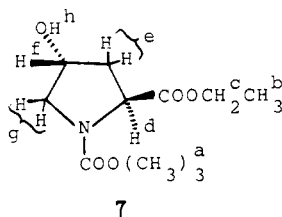
(2S,4S)-N-(tert-Butoxycarbonyl)-4-hydroxy-2-(hydroxymethyl)pyrrolidine (8). In 400 mL of dry tetrahydrofuran was dispersed 8.35 g (0.220 mol) of lithium aluminum hydride, and the mixture was cooled with an ice bath. Compound 7 (51.6 g, 0.199 mol) in 150 mL of dry tetrahydrofuran was added dropwise to this dispersion, and the mixture was stirred overnight. Then, the reaction mixture was heated under reflux for another 3 h. After being cooled with an ice bath, the reaction mixture was hydrolyzed by adding 200 mL of cold water. To this solution was added 400 mL of ethyl acetate with stirring. After the organic layer was separated, the water layer was further extracted with 200 mL of ethyl acetate two times. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated to yield 8 (41.1 g) as a yellow oil, which was used without any purification for the preparation of the ditosylate 9. Pure 8 was obtained by column chromatography on silica gel using ethyl acetate as eluent. The obtained colorless oil solidified upon being allowed to stand in a refrigerator for several days: mp 55–58 °C; [α]$^{20}_D$ -58.87° (c 1.009, EtOH); IR (KBr disk) 3400, 3340 (s, ν_{OH}), 1675 ($\nu_{C=O}$) cm^{-1}; NMR (CDCl$_3$) δ 1.44 (s, 9 H, H^a), 2.05 (m, 2 H, H^d), 3.40 (m, $J_{ef} = 4$ Hz, $J_{ef'} = 0$ Hz, $J_{ff'} = 11$ Hz, 2 H, H^f), 3.59 (m, 2 H, H^b), 3.59 (br s, 1 H, H^g or H^h), 4.02 (m, 1 H, H^c), 4.30 (m, 1 H, H^e), 5.20 (br s, 1 H, H^h or H^g).


8
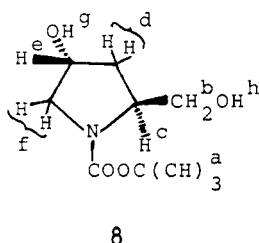
(2S,4S)-(tert-Butoxycarbonyl)-4-(p-toluenesulfonyloxy)-2-[(p-toluenesulfonyloxy)methyl]pyrrolidine (9). To a solution of 8 (41.1 g, 0.189 mol) in 300 mL of dry pyridine was added p-toluenesulfonyl chloride (109 g, 0.57 mol) with cooling in an ice–salt bath. Pyridine hydrochloride began to precipitate within 30 min. The mixture was stirred for 24 h at 0–5 °C. Then, ice–water (500 mL) was added with stirring, and the ditosylate 9 precipitated. The resulting precipitates were collected over a G3 glass filter (94.5 g, 95%; mp 101.5–103 °C) and were further recrystallized from ethanol to give colorless prisms of 9: 82.6 g (83%); mp 106.5–107.5 °C; [α]$^{20}_D$ -26.43° (c 0.401, benzene); IR (KBr disk) 1695 ($\nu_{C=O}$), 1360 and 1170 (ν_{SO_2}) cm^{-1}; NMR (CDCl$_3$) δ 1.33 (s, 9 H, H^a), 2.12 (m, 2 H, H^d), 2.38 (s, 3 H, H^g or H$^{g'}$), 2.40 (s, 3 H, H$^{g'}$ or H^g), 3.42 (m, 2 H, H^f), 3.95 (m, 2 H, H^b), 4.30 (m, 1 H, H^c), 4.92 (m, 1 H, H^e), 7.20–7.80 (m, 8 H, H^h, H$^{h'}$).

(2S,4S)-N-(tert-Butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM). A mixture of sodium (11.0 g, 0.48 mol) and chlorodiphenylphosphine (25 g, 0.113 mol) in 100 mL of dioxane was heated under reflux for 15 h under argon. To the resulting greenish yellow suspension was added a solution of 9 (20.0 g, 0.038
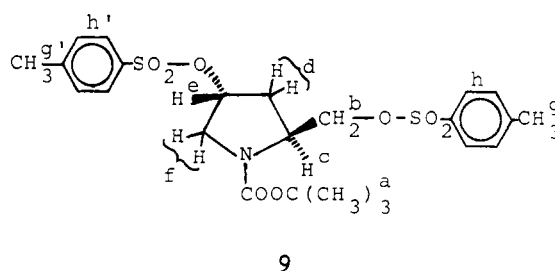

9

mol) in 120 mL of tetrahydrofuran, and the mixture was stirred overnight at ambient temperature. The precipitates formed were filtered off with a G4 glass filter under argon and were washed with 500 mL of benzene. The filtrate was concentrated and submitted to column chromatography on degassed silica gel under argon with benzene as eluent. The obtained BPPM was recrystallized from *n*-hexane to give colorless crystalline BPPM: 13.0 g (61.8%); mp 102–103 °C (lit.[8d] mp 104–105 °C); [α]$^{20}_D$ -40.44° (c 0.602, benzene) [lit.[8d] [α]$^{20}_D$ -36° (c 0.6, benzene)]; IR (KBr disk) 1685 ($\nu_{C=O}$) cm^{-1}; NMR (CDCl$_3$) δ 1.37 (s, 9 H, H^a), 1.70–2.43 (m, 3 H, H$^{b'}$, H^d, H$^{d'}$), 2.43–3.45 (m, 2 H, H^b, H^e), 3.15 (dt, $J_{ff'} = J_{PCCH^f} = 11$ Hz, $J_{ef} = 8$ Hz, 1 H, H^f), 3.78 (m, 2 H, H^c, H$^{f'}$), 7.10–7.60 (m, 20 H, H^g, H$^{g'}$).
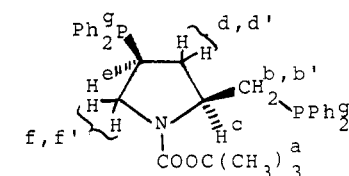
BPPM

Preparation of (2S,4S)-N-Pivaloyl-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (PPPM). Preparation of (2S,4S)-4-(Diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (PPM). BPPM (2.02 g, 3.75 × 10^{-3} mol) was dissolved in 10 mL of freshly distilled trifluoroacetic acid at 0 °C under argon, and the solution was stirred for 1 h. Then, trifluoroacetic acid was evaporated under reduced pressure to give an oily PPM-trifluoroacetic acid salt. To the salt in 10 mL of chloroform was added 8 mL of 10% ammonia–water. After the mixture was shaken for 5 min, the organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent left 1.59 g (3.51 × 10^{-3} mol, 94%) of PPM [mp 100–102 °C; [α]$^{20}_D$ -15.60° (c 1.006, benzene)], which was sufficiently pure for preparative purposes. A pure sample of PPM was obtained by recrystallization from *n*-hexane: mp 103–104 °C (lit.[21] mp 103–104 °C); [α]$^{20}_D$ -15.75° (c 1.003, benzene) [lit.[21] [α]$^{20}_D$ -7° (c 1.84, benzene)]; IR (KBr disk) 3280 (ν_{NH}) cm^{-1}; NMR (CDCl$_3$) δ 1.34 (m, 1 H, H$^{d'}$), 1.80 (s, 1 H, H^a), 1.85–2.50 (m, 3 H, H^b, H$^{b'}$, H^d), 2.50–3.30 (m, 4 H, H^c, H^e, H^f, H$^{f'}$), 7.10–7.70 (m, 20 H, H^g, H$^{g'}$).
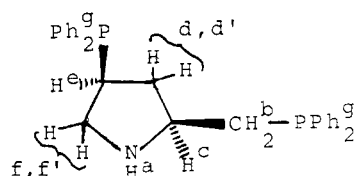
PPM

Preparation of (2S,4S)-N-Pivaloyl-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (PPPM). To a solution of PPM (1.00 g, 2.21 × 10^{-3} mol) and triethylamine (1.10 g, 1.10 × 10^{-2} mol) in 10 mL of chloroform was added pivaloyl chloride (281 mg, 2.33 × 10^{-3} mol), and the mixture was stirred at ambient temperature for 30 min. The solution was washed with water and dried over anhydrous mag-

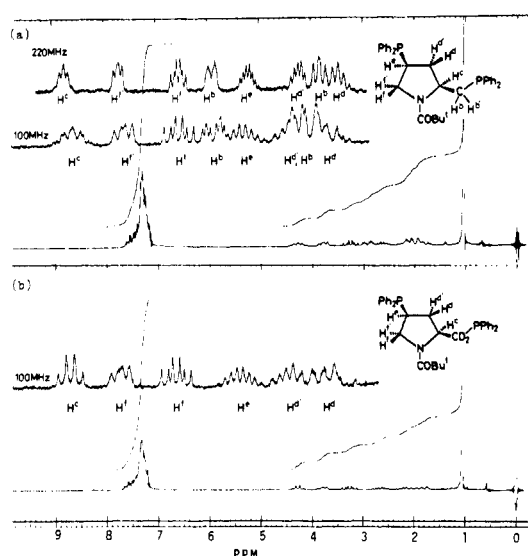(21) K. Achiwa, *Chem. Lett.*, 777 (1977).

Figure 10. ^{1}H NMR spectra of PPPM (a) and PPPM-d_2 (b).

nesium sulfate. Evaporation of the solvent gave 1.12 g (94%) of PPPM: mp 152–153 °C (lit.[21] mp 155–156 °C); $[\alpha]^{20}{}_D$ −4.36° (c 1.007, benzene) [lit.[21] $[\alpha]^{20}{}_D$ −2° (c 1.02, benzene)]; IR (KBr disk) 1615 ($\nu_{C=O}$) cm^{-1}; NMR (CDCl$_3$) δ 1.04 (s, 9 H, H^a), 1.60–2.38 (m, 3 H, H$^{b'}$, H^d, H$^{d'}$), 2.61 (m, $J_{de} = J_{d'e} = J_{ef} = J_{ef'} = 7$ Hz, J_{PCH^e} = 17 Hz, 1 H, H^e), 2.93 (m, $J_{bb'} = 14$ Hz, $J_{b'c} = J_{PCH^{b'}}$ = 3.5 Hz, 1 H, H^b), 3.26 (dt, $J_{ff} = 11$ Hz, $J_{ef} = 7$ Hz, $J_{PCCH^f} = 11$ Hz, 1 H, H^f), 3.78 (dd, $J_{ff'} = 11$ Hz, $J_{ef'} = 7$ Hz, $J_{PCCH^{f'}} = 0$ Hz, 1 H, H$^{f'}$), 4.26 (m, $J_{bc} = 3.5$ Hz, $J_{b'c} = J_{cd} = J_{cd'} = J_{PCCH^c} = 8$ Hz, 1 H, H^c), 7.10–7.70 (m, 20 H, H^g, H$^{g'}$) (see Figure 10).
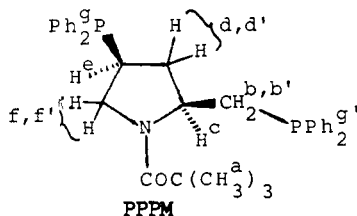
PPPM

Preparation of BPPM-d_2, PPM-d_2 and PPPM-d_2. BPPM-d_2 was prepared in a similar manner to the preparation of BPPM by using lithium aluminum deuteride instead of lithium aluminum hydride for the reduction of 7: mp 97–99 °C; $[\alpha]^{20}{}_D$ −40.29° (c 0.603, benzene); IR (KBr disk) 1685 ($\nu_{C=O}$) cm^{-1}; NMR (CDCl$_3$) δ 1.37 (s, 9 H, H^a), 1.65–2.40 (m, 2 H, H^d, H$^{d'}$), 2.60 (m, 1 H, H^e), 3.16 (dt, $J_{ff} = J_{PCCH^f} = 11$ Hz, $J_{ef} = 8$ Hz, 1 H, H^f), 3.78 (m, 1 H, H$^{f'}$), 3.87 (q, $J_{cd} = J_{cd'} = J_{PCCH^c} = 7.5$ Hz, 1 H, H^c), 7.10–7.65 (m, 20 H, Ph).

PPM-d_2 was prepared from BPPM-d_2 by following the procedure for the preparation of PPM mentioned above: mp 79–80 °C; $[\alpha]^{20}{}_D$ −17.14° (c 1.003, benzene); IR (KBr disk) 3150 (ν_{NH}) cm^{-1}; NMR (CDCl$_3$) δ 1.40 (m, 1 H, H$^{d'}$), 2.10 (m, 1 H, H^d), 2.55–3.35 (m, 4 H, H^c, H^e, H^f, H$^{f'}$), 2.70 (s, 1 H, H^a), 7.10–7.60 (m, 20 H, Ph).

PPPM-d_2 (see Figure 10) was prepared from PPM-d_2 in accordance with the procedure for the preparation of PPPM mentioned above: mp 154–155 °C; $[\alpha]^{20}{}_D$ −4.33 (c 1.015, benzene); IR (KBr disk) 1615 ($\nu_{C=O}$) cm^{-1}; NMR (CDCl$_3$) δ 1.06 (s, 9 H, H^a), 1.60–2.38 (m, 2 H, H^d, H$^{d'}$), 2.66 (m, $J_{de} = J_{d'e} = J_{ef} = J_{ef'} = 7$ Hz, $J_{PCH^e} = 17$ Hz, 1 H, H^e), 3.27 (dt, $J_{ff'} = J_{PCCH^f} = 11$ Hz, $J_{ef} = 7$ Hz, 1 H, H^f), 3.81 (dd, $J_{ff'} = 11$ Hz, $J_{ef'} = 7$ Hz, 1 H, H$^{f'}$), 4.29 (q, $J_{cd} = J_{cd'} = J_{PCCH^c} = 7.5$ Hz, 1 H, H^c), 7.15–7.70 (m, 20 H, Ph).

Preparation of Neutral Diphosphine–Rhodium Catalyst Solution. The neutral catalysts were prepared in situ by the reaction of [Rh(COD)Cl]$_2$ with chiral diphosphine in degassed solvent. Typically, 6.1 mg (1.25 × 10^{-5} mol) of [Rh(COD)Cl]$_2$ and 15.2 mg (2.75 × 10^{-5} mol) of BPPM were dissolved in 5 mL of benzene under argon, and the solution was stirred for 15 min. The complexes of DIOP and diPAMP were prepared in a similar manner.

Preparation of [(BPPM)Rh(COD)]$^+$ClO$_4^-$·Et$_2$O (II). To the solution of Rh(COD)(acac) (233 mg, 7.50 × 10^{-4} mol) in 1.0

mL of tetrahydrofuran under argon was added 70% perchloric acid (107 mg, 7.45 × 10^{-4} mol), and the mixture was stirred for 30 min at ambient temperature. Then, BPPM (402 mg, 7.26 × 10^{-4} mol) in 1.0 mL of tetrahydrofuran was added to the mixture. After the mixture was stirred for 1.5 h at room temperature, 10 mL of diethyl ether was added, and the resulting orange solid was collected by filtration, washed with diethyl ether, and dried under vacuum. II was obtained in 98% yield (665 mg).

Preparation of [(PPPM)(COD)]$^+$ClO$_4^-$ (III). III was prepared in a similar manner as described above from Rh(COD)(acac) (100 mg, 3.22 × 10^{-4} mol), 70% perchloric acid (46 mg, 3.20 × 10^{-4} mol), and PPPM (170 mg, 3.16 × 10^{-4} mol) in 5 mL of tetrahydrofuran. In contrast with the case of II, the orange crystals of III precipitated immediately in tetrahydrofuran on addition of PPPM. III was obtained in 91% yield (244 mg).

Hydrogenation Procedure. (*Z*)-α-**Benzamidocinnamic Acid (1), α-Acetamidocinnamic Acid (2), and Methyl (*Z*)-α-Acetamidocinnamte (3).** Typically, 1 (200 mg, 7.49 × 10^{-4} mol) was hydrogenated in the presence of II (7.0 mg, 7.5 × 10^{-6} mol) in 9 mL of ethanol under an atmospheric pressure of hydrogen at 25 °C for 2 h. Then, Bosnich's workup[22] was employed to remove the catalyst, and the solution was further treated with a small amount of activated charcoal. *N*-Benzoylphenylalanine was obtained in 98% yield (198 mg); $[\alpha]^{27}{}_D$ +37.58° (c 1.02, absolute MeOH).

α-**Acetamidoacrylic Acid (4).** In a typical run, 4 (200.3 mg, 1.55 × 10^{-3} mol) was hydrogenated in the presence of II (14.4 mg, 1.53 × 10^{-5} mol) and triethylamine (3.2 mg, 3.1 × 10^{-5} mol) in 25 mL of methanol under an atmospheric pressure of hydrogen at 20 °C for 2 h. Then, Kagan's workup[23] was employed in order

(22) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977).
(23) H. B. Kagan and T.-P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972).
(24) R. Glaser and B. Vainas, *J. Organomet. Chem.*, **121**, 249 (1976).
(25) E. Berner and R. Leonardsen, *Justus Liebigs Ann. Chem.*, **538**, 1 (1939).
(26) DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. See ref 23.
(27) diPAMP stands for (1*R*,2*R*)-1,2-ethanediylbis[(*o*-anisylphenyl)phosphine]. See, B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachmann, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **99**, 5946 (1977).
(28) Chiraphos stands for (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane. See ref 22.
(29) In order to certify that the observed substrate–rhodium complex is the "active intermediate" of the reaction, we carried out the hydrogenation of the sample solution of the substrate–rhodium complex, which was actually used for the measurement of ^{31}P NMR spectra. Namely, we wanted to observe the change of the ^{31}P NMR spectrum with the catalytic cycle of the rhodium complex. All the measurements were carried out at 30 °C. First, [(BPPM) Rh(COD)]$^+$ClO$_4^-$ (II) was dissolved in benzene-d_6/methanol-d_4 (1/1), and the ^{31}P NMR spectrum was measured: δ (a) 41.69, (b) 41.31 ($^\alpha$P), δ (a) 13.00, (b) 12.41 ($^\beta$P), $J_{\alpha P-Rh}$ = (a) 145, (b) 146 Hz, $J_{\beta P-Rh}$ = (a) 140, (b) 140 Hz, and $J_{\alpha P,\beta P}$ = (a) 37, (b) 36 Hz. Then, the solution was exposed to hydrogen (1 atm) to remove the COD and generate the benzene-d_6 complex, [(BPPM)Rh(C$_6$D$_6$)$_n$]$^+$ClO$_4^-$: ^{31}P NMR δ (a) 57.09, (b) 56.99 ($^\alpha$P), δ (a) 22.81, (b) 24.04 ($^\beta$P), $J_{\alpha P-Rh}$ = (a) 200, (b) 201 Hz, $J_{\beta P-Rh}$ = (a) 198, (b) 198 Hz, and $J_{\alpha P,\beta P}$ = (a) 50, (b) 50 Hz. To this solution was added 20 equiv of itaconic acid under argon to form the itaconic acid–rhodium complex, [(BPPM)Rh(CH$_2$ = C(COOH)-CH$_2$COOH)]$^+$ClO$_4^-$: ^{31}P NMR δ 35.86 ($^\alpha$P), 34.17 ($^\beta$P) ($J_{\alpha P-Rh}$ = 151 Hz, $N_{\beta P-Rh}$ = 136 Hz, and $J_{\alpha P,\beta P}$ = 36 Hz). The solution of this substrate–rhodium complex was submitted to hydrogenation by using a usual hydrogenation apparatus. Apparently almost all the required amount of hydrogen was absorbed within 1 h. However, the ^{31}P NMR spectrum of the solution did not show any change. Thus, the solution was exposed to 10 atm of hydrogen for 24 h in an autoclave. Then, the ^{31}P NMR spectrum of this solution displayed the exclusive regeneration of the benzene-d_6 complex as expected (^{31}P NMR): δ (a) 57.22, (b) 57.04 ($^\alpha$P), δ (a) 22.91, (b) 23.99 ($^\beta$P), $J_{\alpha P-Rh}$ = (a) 200, (b) 201 Hz, $J_{\beta P-Rh}$ = (a) 198, (b) 198 Hz, and $J_{\alpha P,\beta P}$ = (a) 50, (b) 50 Hz. The results clearly indicate that *another molecule of the olefinic substrate, itaconic acid in this case, effectively promotes the reductive elimination of the hydrogenated product, and thus, at the end of the hydrogenation some forcing conditions are necessary to remove the last molecule of the olefinic substrate from the rhodium complex catalyst.* At any rate, the observed substrate–rhodium complex is unambiguously ascribed to the "active intermediate" of the reaction. In addition, when methanol-d_4 was used as solvent instead of benzene-d_6/methanol-d_4, the last molecule of itaconic acid could not completely be removed even under rather forcing conditions (10 atm of H$_2$, 20 °C, 24 h). The results are well accommodated by Halpern's demonstration[3a] that benzene is a rather strongly coordinating solvent for cationic rhodium complexes with cis chelating ligands while methanol is a weakly coordinating solvent.

to remove the catalyst. The optical rotation of the *N*-acetylalanine thus obtained was directly measured; $[\alpha]^{26}_D$ +65.30° (*c* 2.00, H$_2$O). As a trace amount of triethylamine might be included in the product, we checked the effect of added triethylamine on the optical rotation of *N*-acetylalanine and found that the addition of a small amount of triethylamine caused only a slight decrease of the optical rotation of *N*-acetylalanine in water.

Dideuteration of α-Acetamidoacrylic Acid (4). In a glass ampule was placed a mixture of **4** (200 mg, 1.55 × 10^{-3} mol) and II (14 mg, 1.50 × 10^{-5} mol) in 25 mL of methanol under argon. This ampule was put into an autoclave, and the mixture was purged by filling and releasing with argon and finally with D$_2$. The dideuteration was carried out at 25 °C for 1 h with stirring under an initial pressure of 20 atm. The catalyst was removed by following Kagan's[23] workup procedure. The NMR spectrum of the product was measured in D$_2$O by using sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$ as internal standard: δ 1.39 (br s, 2 H, H^a), 2.02 (s, 3 H, H^b). If **8b** were formed, there should

CH$_2$DCDCOOD (8a)   CD$_2$H—CH—COOD (8b)
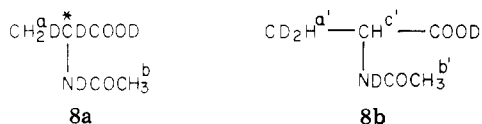
appear a doublet for the methine proton (H$^{c'}$) around δ 4.2. However, such a signal was not detected at all in the spectrum. Thus, it is concluded that the dideuteration of **4** gives **8a** exclusively, and the scrambling of deuterium does not take place at all.

Itaconic Acid (5), Citraconic Acid (6), and Mesaconic Acid (7). In a typical experiment, **5** (650 mg, 5.00 × 10^{-3} mol), II (22 mg, 2.34 × 10^{-5} mol), triethylamine (506 mg, 5.00 × 10^{-3} mol), and 6 mL of methanol were placed in a glass ampule equipped with a magnetic stirring bar. This ampule was put into an autoclave, and the mixture was purged by filling (30 atm) and releasing with

hydrogen four times. The mixture was stirred for 3 h at 20 °C under an initial hydrogen pressure of 20 atm. Evaporation of the solvent gave an oily residue, to which was added 2 N hydrochloric acid, and the mixture was extracted with ether (5 × 20 mL). After the extract was dried over anhydrous magnesium sulfate, the solvent was evaporated to give methylsuccinic acid in a 94% yield (624 mg); $[\alpha]^{20}_D$ −15.72° (*c* 2.03, absolute EtOH).

^{31}P NMR Measurement. The samples for ^{31}P NMR measurement were prepared as follows. A cationic rhodium complex [II or III; 50–100 mg, (5.5–12.0) × 10^{-4} mol] was dissolved in 2.2 mL of degassed deuterated solvent and the mixture stirred for 50 min under an atmospheric pressure of hydrogen to give the rhodium–solvent complex of the type [(L*-L)Rh(solvent)$_n$]$^+$-ClO$_4^-$(L*-L = BPPM or PPPM). The rhodium–substrate complex of the type [(L*-L)Rh(substrate)]$^+$ClO$_4^-$ was prepared by mixing the rhodium–solvent complex with 5–20 equiv of the substrate under argon.

Registry No. 1, 26348-47-0; **2**, 55065-02-6; **3**, 60676-51-9; **4**, 5429-56-1; **5**, 97-65-4; **6**, 498-23-7; **7**, 498-24-8; **8**, 61478-26-0; **8a** (isomer 1), 74929-89-8; **8a** (isomer 2), 74929-90-1; **9**, 61478-27-1; I, 74983-80-5; II, 67322-49-0; III, 67322-51-4; IV, 70832-59-6; V, 70832-57-4; VI, 70953-83-2; VII, 70896-64-9; BPPM, 61478-28-2; PPPM, 64145-67-1; PPM, 61478-29-3; PPM-trifluoroacetic acid salt, 74929-91-2; BPPM-*d*$_2$, 74929-92-3; PPM-*d*$_2$, 74929-93-4; PPPM-*d*$_2$, 74929-94-5; (−)-DIOP, 32305-98-9; chiraphos, 64896-28-2; *N*-benzoyl-(*R*)-phenylalanine, 37002-52-1; *N*-benzoyl-(*S*)-phenylalanine, 2566-22-5; *N*-acetyl-(*R*)-phenylalanine, 10172-89-1; *N*-acetyl-(*R*)-phenylalanine methyl ester, 21156-62-7; *N*-acetyl-(*S*)-alanine, 97-69-8; *N*-acetyl-(*R*)-alanine, 19436-52-3; (*S*)-methylsuccinic acid, 2174-58-5; (*R*)-methylsuccinic acid, 3641-51-8; 4-hydroxy-L-proline ethyl ester, 61478-25-9; 4-hydroxy-L-proline, 51-35-4; 4-hydroxy-L-proline ethyl ester HCl, 33996-30-4; *N*-(*tert*-butoxycarbonyl)-4-hydroxy-L-proline ethyl ester, 37813-30-2; *tert*-butyl (*S*)-4,6-dimethylpyrimidin-2-ylthiocarbonate, 41840-28-2; chlorodiphenylphosphine, 1079-66-9; pivaloyl chloride, 3282-30-2; [Rh(COD)Cl]$_2$, 12092-47-6; Rh(COD)(acac), 12245-39-5; [(PPM)Rh(COD)]$^+$ClO$_4^-$, 74929-68-3; [(PPM-*d*$_2$)Rh(COD)]$^+$ClO$_4^-$, 74929-70-7; [(PPPM-*d*$_2$)-Rh(COD)]$^+$ClO$_4^-$, 74929-72-9; [(BPPM-*d*$_2$)Rh(COD)]$^+$ClO$_4^-$, 74929-74-1; [(BPPM)Rh(α-(acetylamino)propenoic acid)]$^+$ClO$_4^-$, 74929-76-3; [(BPPM-*d*$_2$)Rh(α-(acetylamino)propenoic acid)]$^+$ClO$_4^-$, 74929-78-5; [(BPPM)Rh(methylenebutanedioic acid)]$^+$ClO$_4^-$, 68913-92-8; [(BPPM-*d*$_2$)Rh(methylenebutanedioic acid)]$^+$ClO$_4^-$, 74929-80-9; [(PPPM)Rh(methyl methylenebutanedioate)]$^+$ClO$_4^-$, 74929-82-1; [(PPPM-*d*$_2$)Rh(methyl methylenebutanedioate)]$^+$ClO$_4^-$, 74929-84-3; [(PPPM)Rh(3-butenoic acid)]$^+$ClO$_4^-$, 74929-86-5; [(chiraphos)Rh-(COD)]$^+$ClO$_4^-$, 61886-02-0; diPAMP, 55739-58-7.

(30) Although one cannot directly determine whether the observed substrate–rhodium complex is the mode A complex or the mode B complex by means of ^{31}P NMR spectroscopy, it is most probable that the extremely high enantioface selection in the substrate–rhodium complex is well kept throughout the reaction. Thus, it is quite reasonable to assume that the enantioselectivity exhibited in the asymmetric hydrogenation reflects the mode of the substrate–rhodium complex.

(31) The coalescence of the signals of X could not be observed in the temperature range 213–333 K. The considerably large coupling constants, $J_{\alpha P\text{-}Rh}$, $J_{\beta P\text{-}Rh}$, and $J_{\alpha P\text{-}\beta P}$ of X compared with those of II may suggest some difference in the conformational rigidity between X and II.

(32) For a preliminary communication on the effects of triethylamine on the stereoselectivity in the asymmetric hydrogenation of itaconic acid catalyzed by BPPM–Rh complexes, see I. Ojima, T. Kogure, and K. Achiwa, *Chem. Lett.*, 567 (1978).

(33) W. C. Christopfel and B. D. Vineyard, *J. Am. Chem. Soc.*, **101**, 4406 (1979).