References and Notes

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(42) These ν(CO) vibrational modes were calculated somewhat low (3–5 cm^{-1}), nevertheless, the approximate CO stretching force field generally provided calculated ν(CO) values (for a total of 30 observed vibrations) within ±1.5 cm^{-1}.
(43) Present studies include a search for possible metal catalysts for chemically converting (on a small scale) ^{13}CO into mixed labeled $^{13}C^{18}O$ and $^{13}C^{17}O$ species via a process involving reversible binding of CO accompanied by a facile oxygen exchange reaction with H_2O. It is important to note here that this procedure is limited to metal carbonyl derivatives where elimination of CO_2 from the hydroxycarbonyl intermediate with concomitant metal hydride formation is slow relative to oxygen exchange.[3] We believe as well that this procedure might form the basis for preparing mixed labeled organic derivatives.
(44) Approximate CO stretching force constants for the reactive CO groups in the species, $[Mn(CO)_6]^+$, $[Mn(CO)_5PMe_2Ph]^+$, and $[Mn(CO)_4(diphos)]^+$ are 18.16, 17.44, and 16.90 mdyn/Å, respectively. It should as well be noted that sterically the carbonyl ligands are more hindered as substitution at the metal center by phosphines occurs. This has been shown to be an important consideration in reaction of $W(CO)_5L$ derivatives with the more bulky reagent $C_6H_5CH_2MgCl$.[17]
(45) These cationic species have been shown to react with a variety of primary and secondary amines, via nucleophilic attack at carbonyl carbon, to give carbamoyl compounds.[20,46-48]
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(50) This hydride species, which has previously been reported in the literature,[51] exhibited ν(CO) bands at 1992 and 1906 cm^{-1} in acetonitrile. Upon extraction of the complex into hexane ν(CO) absorptions at 2002, 1931, and 1922 cm^{-1} were observed in addition to weaker bands attributable to the corresponding oxygen-18 enriched species.
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Asymmetric Hydrogenation. Rhodium Chiral Bisphosphine Catalyst

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Abstract: Enantiomeric excesses of 95-96% are obtained by the asymmetric hydrogenation of α-acylaminoacrylic acids. The olefin configuration, whether *E* or *Z*, has a profound influence on the rate and stereospecificity. Excellent selectivity (~90% ee) was obtained with an α-enol ester, which is the first outstanding result with a nonamide substrate. A catalyst picture is presented and the stereochemical results are discussed.

The efficiency of asymmetric hydrogenation in soluble systems has greatly improved since the original development in 1968.[1,2] Enantiomeric excesses of 95–96% are now possible with α-acylaminoacrylic acids.[3] The optimum selectivity associated with earlier catalysts required rather mild reaction conditions, i.e., ambient temperature and pressure. Discovery of the catalyst precursor [rhodium(1,5-cyclooctadiene)L]$^+$ tetrafluoroborate$^-$ (**6**),[3] L = 1,2-ethanediylbis[(*o*-methoxyphenyl)phenylphosphine], **5**, opened new possibilities. The bisphosphine catalyst was not as sensitive to reaction variables

and excellent results were obtained at higher temperatures and pressures. In this paper, we wish to report the versatility of this new catalyst system.

Catalyst Preparation

The *R,R* bisphosphine **5** was prepared from the known $(R)_P$-menthyl methylphenylphosphinate[4] as outlined in Scheme I. Reaction of the R_P phosphinate **2** with *o*-methoxyphenylmagnesium bromide yielded (*R*)-(*o*-methoxyphenyl)methylphenylphosphine oxide (**3**), which was oxidatively coupled with lithium diisopropylamide and copper salts[5] to give (*R,R*)-1,2-ethanediylbis[(*o*-methoxyphenyl)phenylphosphine oxide] (**4**). The bisphosphine oxide **4** was converted to **5** with inversion at phosphorus centers using a mixture of trichlorosilane and tributylamine in acetonitrile solution. A proper combination of tertiary amine and solvent is required in order to maintain solution; otherwise, reduction is incomplete and significant *meso*-**5** is formed. Finally, **5** was reacted with rhodium(1,5-cyclooctadiene) chloride dimer and sodium tetrafluoroborate to give the catalyst precursor **6**.[6] Since the menthyl ester precursor **2** leading to *R*-**3** is the minor diastereoisomer, it is more convenient on a larger scale to introduce the *o*-methoxyphenyl before the phenyl. The resulting major product, $(S)_P$-menthyl *o*-methoxyphenylmethylphosphinate, is easily separated and reacted with phenylmagnesium chloride to give *R*-**3** using similar procedures.

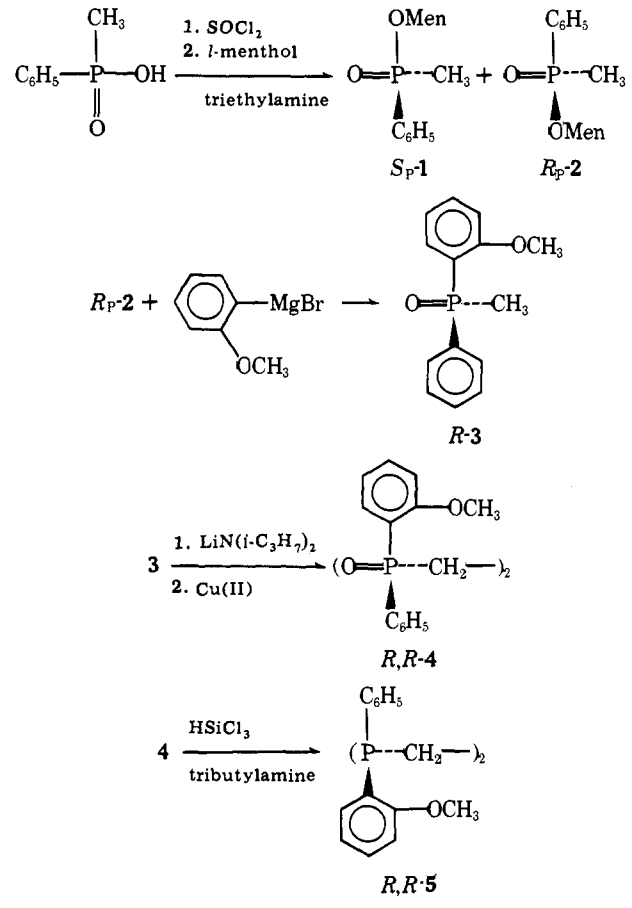
Substrate Studies

In the previous studies,[3,7,8] all the α-acylaminoacrylic acids were prepared by methods which give essentially the *Z* isomer. This was indeed fortuitous, since compounds with the *Z* configuration are reduced with higher stereoselectivities.[8d] Morrison[9] demonstrated with several simple olefins and chiral catalyst systems the wide variation in stereoselectivity that is possible between the *E* and *Z* isomers. Table I shows a comparison of the hydrogenation results from several *E*- and *Z*-α-acylaminocinnamic acid derivatives using the complex **6** as catalyst. The *Z* isomers are hydrogenated with greater enantiomeric excess and the rates are 15–100 times faster, although in all cases, the enantiomer formed in excess has the *S* configuration. It is obvious that complete isomerization of *E* to the *Z* is not occurring;[10] otherwise comparable stereoselectivity would have been observed. Even a symmetrical catalyst derived from 1,2-ethanediylbis[diphenylphosphine] shows a 20-fold *E* vs. *Z* rate difference (Table I, **9**[f]). In the case of the sterically hindered *N*-methylbenzamidocinnamic acid[11] only the *Z* isomer hydrogenated to give 66% *S* (Table I, **9**[g]).

It is believed that the α-acylaminoacrylic acids are excellent substrates because they are tridentate[7d] (olefin and two electronegative polar substituents). Good stereoselectivities are shown with the additional tridentate precursors in Table II. *N*-(β-Cyanostyryl)benzamide (**10**) gave enantiomeric excesses of 89 and 86% at 3 and 27 atm. Ethyl 2-(*N*-ethoxycarbonylamino)-3-phenyl-2-propenoate (**11**) and ethyl 2-(*N*-ethoxythiocarbonylamino]-3-phenyl-2-propenoate (**12**) were hydrogenated with 86 and 60% ee, respectively. These are minimum yields, since they were determined by hydrolysis to L-phenylalanine. The alanine and leucine precursors **13** and **14** are included to show that the excellent stereoselectivity is not confined to the aromatic systems. The enantiomer formed in excess from all these amino acid substrates had the *S* configuration.

The stereospecificity decreases markedly on hydrogenation of bidentate substrates (see Table III). *N*-(β-Methylstyryl)-acetamide (**15**) on reduction using the catalyst precursor **6** gave 50 and <10% enantiomeric excess for the *Z* and *E* isomers, respectively. The *Z* isomer hydrogenated much faster (relative rates 23:3), although the enantiomer formed in excess from

Scheme I

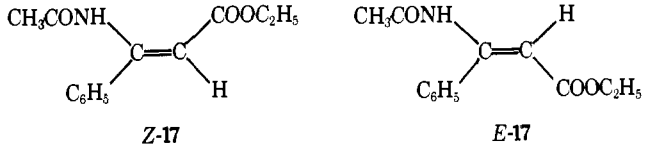


$$5 + {}^1/_2[Rh(1,5\text{-COD})Cl]_2 \xrightarrow{NaBF_4} [Rh(1,5\text{-COD})\text{bisphosphine}]^+BF_4^-$$

6

both isomers had the *R* configuration. Only 1% enantiomeric excess and an extremely slow rate was observed with (*E*)- and (*Z*)-2-methyl-3-phenyl-2-propenoic acid (**16**). To demonstrate that the retarding effect was not catalyst deactivation, addition of *E*-**15** to *Z*-**15** did not change the hydrogenation rate of the *Z* isomer. In addition, *Z*-**7** in the presence of an equal quantity of *E*-**16** hydrogenated at a rate normal for *Z*-**7**.

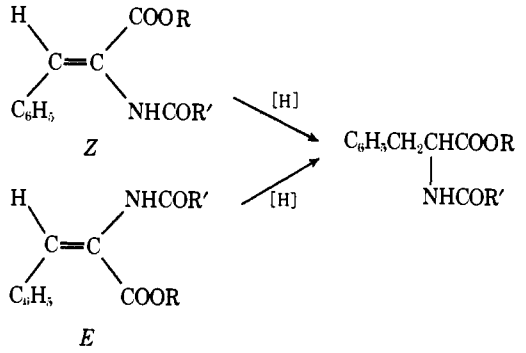
Another system which demonstrated the strong influence of an amide function is *E*- and *Z*-**17**. Product with the *S* con-



figuration is formed in enantiomeric excess of about 30% from (*E*)- and (*Z*)-ethyl 3-acetamido-2-phenyl-2-propenoate. Formation of the *S* product[16] in excess from both isomers furnishes additional evidence that the role of an amide is dominant to that of a carboxyl. If the carboxyl dictates which enantiomer is formed, then the *E* and *Z* isomers should have given the same product with different configuration.

Although the α-acylamino substituted olefins have proven to be excellent precursors, the amide function is not unique. An enantiomeric excess of about 90% was obtained upon hydrogenation of the α-enol ester **18**, (*Z*)-ethyl 2-acetyloxy-3-phenyl-2-propenoate. The product, (*S*)-(−)-ethyl 2-acetyloxy-3-phenylpropanoate,[17] was converted to (*S*)-(−)-3-phenyllactic acid to confirm the results. The β-enol esters **19**, (*E*)- and (*Z*)-ethyl 3-acetyloxy-3-phenyl-2-propenoate, hy-

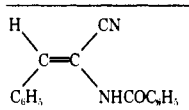
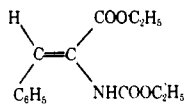
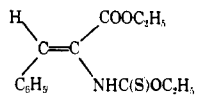
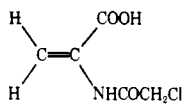
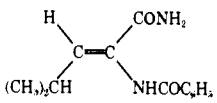
Table I. Hydrogenation of Geometrical Isomers of α-Acylaminocinnamic Acids[a]



	Isomer	Substrate[b] / rhodium	Temp, °C	Pressure, atm	Rel[c] rate	ee, %[d]	Configuration[e]
R = H; R' = CH_3	*Z*-7	1000	50	3	100	94	*S*
	E-7	200	50	3	1	47	*S*
R, R' = CH_3	*Z*-8	900	50	3	78	96	*S*
	E-8	1200	50	3	5	23	*S*
R = H; R' = C_6H_5	*Z*-9	800	50	3	75	93	*S*
	Z-9	800	50	27		78	*S*
	E-9	800	50	27	4	39	*S*
	Z-9[f]	700	50	3	80		
	E-9[f]	700	50	3	4		
	Z-9[g]	200	50	27	1	66	*S*

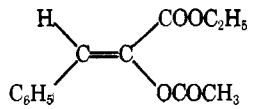
[a] Catalyst precursor **6** used in all runs except 9[f]. [b] Molar equivalence of substrate to rhodium. All runs contained about 0.15 M substrate in MeOH or EtOH. [c] Relative rates are crude numbers to be used for comparative purposes only. Substrate *Z*-7 is the reference material. [d] Enantiomeric excess. [e] All rotations were measured without isolation by diluting to volume and comparing with a blank. The optical rotations of the pure saturated adducts follow: 7, $[\alpha]^{20}_D$ +40.1° (*c* 1.0, MeOH) and +47.4° (*c* 1.0, 95% EtOH); 8, $[\alpha]^{20}_D$ +16.4° (*c* 2.0, MeOH); 9, $[\alpha]^{20}_D$ −39.6° (*c* 1.0, 95% MeOH). [f] The catalyst used was cyclooctadiene-1,5-[1,2-ethanediylbis(diphenylphosphine)] rhodium tetrafluoroborate.[6] [g] The catalyst used was **6**. The substrate was the *N*-methyl derivative of **9**, (*Z*)-α-*N*-methylbenzamidocinnamic acid.[11]

Table II. Hydrogenation of Amino Acid Precursors[a]

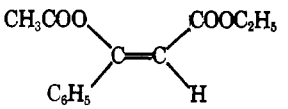
Olefin	Isomer	Substrate[b] / rhodium	Temp, °C	Pressure, atm	Rel[c] rate	ee, %[d]	Configuration[e]
	*Z*-10[f]	200	50	3		89	*S*
		700	50	27	3	86	*S*
	*Z*-11	600	50	3	13	89	*S*
	*Z*-12	100	50	3		62	*S*
		100	50	27	3	56	*S*
	13	1200	50	3	160	95	*S*
	*Z*-14	2300	50	3	230	95	*S*

[a–d] See corresponding footnotes in Table I. [e] All rotations were measured without isolation by diluting to volume and comparing with a blank. The optical rotations of the pure saturated adducts follow: 10, $[\alpha]^{20}_D$ −85.5° (*c* 0.5, MeOH); 11 and 12 reduction products were converted to L-phenylalanine by treatment with anhydrous HBr in acetic acid (75°C), stripping, and treatment with 48% HBr (100°C); 13, $[\alpha]^{20}_D$ −25.1° (*c* 2.0, 95% MeOH); 14, $[\alpha]^{20}_D$ +6.84° (*c* 3.0, MeOH). [f] Addition of 1 equiv of acetic acid per equiv of substrate was required to achieve good rates.

drogenated sluggishly and gave enantiomeric excesses of less than 10%.[18] A relative hydrogenation rate for *Z*-**18** is 4, which compares to 100 for the reference olefin *Z*-7. Success with an α-enol ester offers an efficient route to the corresponding chiral alcohols. Asymmetric reduction of ketones is slow and inefficient.[19]



Z-**18**

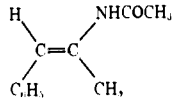
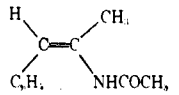
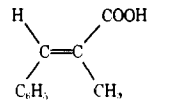
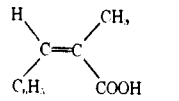


Z-**19**

Catalyst Discussion

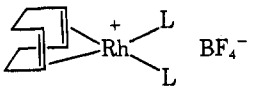
It is well established that the structure of the catalyst precursor is an ionic square planar complex **20**.[6] The counterion

Table III. Hydrogenation of Bidentate Substrates[a]

Olefin	Isomer	Substrate[b]/rhodium	Temp, °C	Pressure, atm	Rel[c] rate	ee, %[d]	Configuration[e]
	*E*-15[f]	250	50	3		9	*R*
		600	50	27	3	<1	*R*
	*Z*-15[f]	1000	50	3		51	*R*
		1200	50	27	23	50	*R*
	*E*-16	300	50	27	0.6	1	*R*
	*Z*-16	300	50	27	0.6	<1	*R*

[a-d] See corresponding footnotes in Table I. [e] All rotations were measured without isolation by diluting to volume and comparing with a blank using the following optical rotations for the corresponding saturated adducts: **15**, $[\alpha]^{25}_D$ +43.5° (*c* 2.0, $CHCl_3$);[12] **16**, $[\alpha]_D$ +27.7° (*c* 2.0, $CHCl_3$).[13] [f] Nuclear Overhauser effect (NOE)[14] comparison of the two isomers indicated that the earlier assignment of configuration was incorrect.[30] See Experimental Section for the details of the NOE data.

is not important. The phosphine ligand L may be monomeric or, as in the present work, a bidentate species. During the



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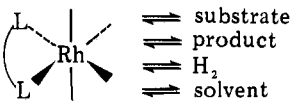
catalyst activation with hydrogen, the 1,5-cyclooctadiene is displaced. The active catalyst **21** can best be described if the



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two phosphine ligands are firmly bound in a cis position; and the remainder of the presumably octahedral structure is in dynamic equilibrium with solvent, substrate, product, hydrogen, and perhaps vicinal methoxyl groups.[7c] The high efficiency and nonvariability observed with the bisphosphine catalyst **6** support such a picture. Any explanation of this catalyst must account for the special role played by the *Z* enamides. Our previous contention that the enhanced rates and efficiency are assisted by hydrogen bonding between the amide hydrogen and one of the methoxyls is not consistent with all the data.[7d]

The very fast rates achievable when methoxyl is absent (Table I), as well as the fairly efficient results obtainable with the (*Z*)-*N*-methyl derivative (Table I), tend to support the contention that the amide is assisting by attaching directly to the metal. It still seems valid that there is a three-point interaction[7b,d] of the olefin, the carboxyl, and the amide with the catalyst, but the amide is the dominant function.

An x-ray structure of the most advanced intermediate **20** indicates, as expected, a square planar complex with the ether oxygens about 3.7 Å from the rhodium. The P_1-Rh-P_2 angle is 83° and the rest of the angles in the five-membered ring are close to tetrahedral. The five-membered ring is nearly flat with the methylene carbons only about 10° above and below the P_1-Rh-P_2 plane. Figure 1 shows a perspective view looking along the plane of the chelate ring, the cyclooctadiene being left out for simplicity. The configuration of the bisphosphine **5** is *R,R*, which gives the *S* isomer with the *Z* enamide **7**. It is noteworthy that the four phenyl groups are arrayed around the metal in an alternating edge-face manner with the rings containing the methoxyls exposing their face. This arrangement would suggest that the role of the ether oxygen is to fix the conformation. Even though the oxygen is not within bonding distance of the rhodium, it is close enough to have some interaction. There may also be some hindrance to rotation caused by the hydrogens on the cyclic methylenes.

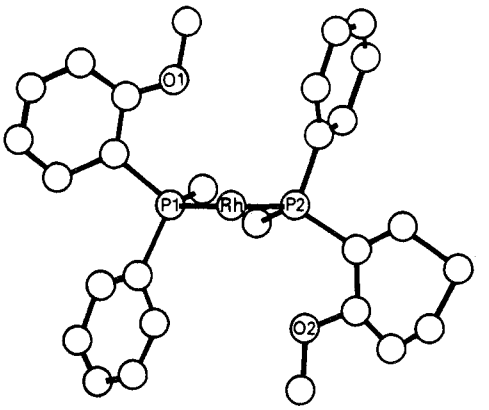


Figure 1. Perspective view of **6** looking along the equatorial plane. The 1,5-cyclooctadiene has been omitted for simplicity.

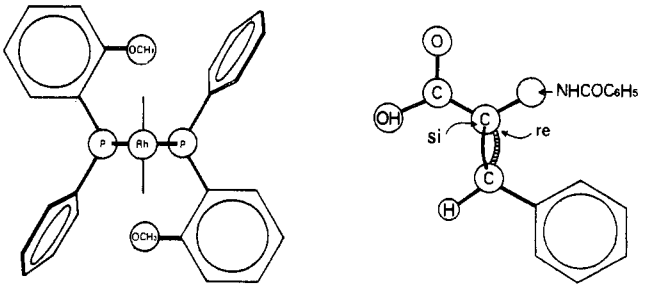
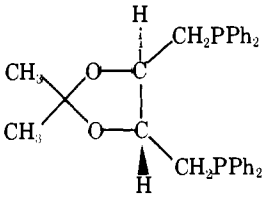


Figure 2. Schematic drawing. (a) Bisphosphine-rhodium complex looking along the plane of the five-membered ring. For simplicity the cyclooctadiene has been omitted. (b) (*Z*)-α-Benzamidocinnamic acid in a linear and flat conformation.

If one looks at a simplified drawing (Figure 2) it seems fairly obvious that a linear and flat substrate could lie along the face-exposed *o*-methoxyphenyl groups more easily than the edge-exposed phenyls. The *Z* enamide also shown in Figure 2 approximates such a substrate if one considers a conforma-

tion where the carboxyl, the olefin, and the phenyl are coplanar with the amide projecting out on one side. If such a substrate approaches the catalyst with the amide oxygen bonding to one of the equivalent axial positions on the rhodium and the olefin coordinating with an equatorial metal bond, then the linear and flat carboxyl–double bond–phenyl system can lie along the face-exposed *o*-methoxyphenyl groups. In this position the double bond will expose its re face toward the metal and become hydrogenated to give the *S* isomer. If we turn the substrate over to expose the si face then the linear part will have to lie along the edge-exposed phenyls where close approach is prevented, resulting in a slow reaction. If one considers the *E* isomer, where the phenyl and the hydrogen are interchanged, then the substrate has lost its flat linear shape. The phenyl will now have to lie along an edge-exposed aryl group, preventing close approach to the metal but still giving a predominance of the *S* isomer in a slow reaction. This agreement is reinforced if one considers that the face-exposed phenyls have π electrons available for interaction with the substrate whereas edge-exposed phenyls do not. Apparently both steric and electronic factors are acting in concert.

A similar explanation can be applied to several efficient catalysts reported by others which also contain four phenyl groups oriented around a rhodium center.[8,20,21,36,37] An x-ray structure of Kagan's DIOP **22**[8] complexed with iridium[22] approximates a conformation of edge–face phenyls on each phosphorus. In this case it is suggested that the configuration is frozen by the severe constraints of the fused ring system behind the metal. An x-ray structure described by Bosnich[21] for [rhodium(*S,S*-bn phos)norbornadiene]$^+$ perchlorate$^-$ where (*S,S*-bn phos) = (*S,S*)-2,3-butanediylbis(diphenylphosphine) (**23**), shows an array of alternating edge–face



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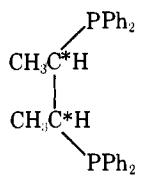

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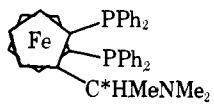

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phenyls. In this system rotation of the aromatic rings is hindered by the vicinal methyl groups in the chelate ring. Although there is no x-ray evidence for Kumada's phosphine **24** it can well be explained by a similar phenyl group array made rigid by the ferrocene backbone. It is interesting that all these catalysts hydrogenate the *Z* enamides efficiently and in the one case reported[8d] the *E* isomer with more difficulty. All are generally inferior when the enamide function is absent. This alternating edge–face array gives a common way of looking at these asymmetric ligands which behave so similarly but are based on entirely different structural concepts.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. UV spectra were recorded on a Cary 118 spectrophotometer. NMR spectra were recorded on Varian A-60 and T-60 spectrometers. The nuclear Overhauser effect (NOE) was determined on a Bruker HX90E spectrometer. GLC analyses were made on a 2 m × ¼ in. glass column packed with 5% W-98 on Chromosorb G. A Varian MAT CH4B mass spectrometer was used for the parent ions and a Perkin-Elmer 141 polarimeter for the optical rotations.

(*R*)$_P$-Menthyl Methylphenylphosphinate (2). The mixture of (*R*)$_P$- and (*S*)$_P$-phosphinate was prepared by the method of Mislow.[4] Separation of the desired (*R*)$_P$ diastereoisomer was documented in an earlier publication,[7d] mp 86–87 °C, $[\alpha]^{20}_D$ −17.2° (*c* 1.0, benzene).

(*R*)-(*o*-Methoxyphenyl)methylphenylphosphine Oxide (3). This material was prepared according to the procedure given previously,[7d] mp 70–75 °C, $[\alpha]^{20}_D$ +25.9° (*c* 1.0, MeOH).

(*R,R*)-1,2-Ethanediylbis[(*o*-methoxyphenyl)phenylphosphine oxide] (4). To a solution of 49.2 g (0.20 mol) of crude (*o*-methoxyphenyl)-methylphenylphosphine oxide (**3**) in 100 mL of tetrahydrofuran at 5 °C was added a solution of lithium diisopropylamide, made by adding 91.6 mL of 2.4 N butyllithium in hexane to 24.5 g (0.24 mol) of diisopropylamine in 100 mL of tetrahydrofuran. After a 0.5-h addition period, the batch was stirred for 0.5 h at 0–5 °C. Then 20.0 g (0.20 equiv) of CuCl was added portionwise at 0–5 °C. After a 0.5-h stir period, 26.9 g (0.2 mol) of $CuCl_2$ was added keeping the temperature at 0–5 °C. The batch was then warmed over 1 h to 20–25 °C and held there for 0.5 h. It was then quenched with 100 mL of concentrated HCl at 15–20 °C. After settling the upper hexane layer was discarded. Then the organics were extracted with chloroform, and the chloroform layer was washed free of copper salts with aqueous ammonia and finally with water. The organic layer was stripped of solvent up to 95 °C and 200 mL of *n*-butyl acetate added. The batch, which was now a slurry of crystals, was heated to 116 °C to remove traces of chloroform and then slowly cooled to 0–5 °C. The product was filtered, washed with 50 mL of cold butyl acetate, and dried at 100 °C under vacuum. The yield was 33.5 g of **4**, mp 203–205 °C, $[\alpha]^{20}_D$ −44.9° (*c* 1.0, MeOH). Pure material melts at 205–207 °C, $[\alpha]^{20}_D$ −46.0°, *m/e* 490 (M^+).

(*R,R*)-1,2-Ethanediylbis[(*o*-methoxyphenyl)phenylphosphine] (5). Reduction of **4** was accomplished by dissolving under N_2 60.0 g (0.122 mol) in 450 mL of dry acetonitrile. Then 150 g of dry tributylamine was added and the slurry heated to 65–70 °C, when all goes into solution. At this point, 97 g of trichlorosilane was added over a 1-h period, keeping the temperature at 70–72 °C.[23] At the end, there was essentially one liquid phase and the batch was held at 70 °C for 2 h. It was then cooled to 30–40 °C and quenched by adding at 25–30 °C to 360 mL of 25% NaOH. At the end of the quench, the temperature was raised to 45–50 °C to facilitate separation.

The organic phase was separated and washed under N_2 with 150 mL more of 25% NaOH. The organic phase, which consisted of two layers, was concentrated at 45–55 °C until only the high-boiling tributylamine remained. Methanol (50 mL) was added to aid crystallization and the batch was cooled to 0–5 °C and filtered. The cake was washed with two 40-mL portions of cold methanol and dried to 60 °C (1 mmHg) giving 50.8 g of **5**, mp 96–101 °C, $[\alpha]^{20}_D$ −79.7° (*c* 1.0 $CHCl_3$). Recrystallization from hot methanol gave a pure product melting at 102–104 °C, $[\alpha]^{20}_D$ −85.0°, *m/e* 458 (M^+). This material can be used directly for an in situ catalyst preparation but is more conveniently converted to an air-stable rhodium complex. Oxidation with H_2O_2 gave **4** of the opposite configuration showing that this reaction went with the expected double inversion.

Cyclooctadiene-1,5[(*R,R*)-1,2-ethanediylbis(*o*-methoxyphenyl)phenylphosphine]rhodium Tetrafluoroborate (6). A slurry of 1.83 g (4.0 mmol) of **5** was added to 12 mL of 90% methanol. Then under nitrogen at 25–30 °C, 0.99 g (2.0 mmol) of bis(cyclooctadiene-1,5)dichlorodirhodium $[Rh(COD)Cl]_2$, was added. The slurry became orange and after stirring for 1 h gave a red-orange solution. The complex was precipitated by adding slowly a solution of 0.66 g (6.0 mmol) of sodium tetrafluoroborate in 5 mL of H_2O over 2 h. After 1 h stirring at 25 °C, the fine crystals were filtered, washed twice with 3-mL portions of water, and dried at 5 mm vacuum and 25 °C. There was obtained 2.8 g (90%) of cyclooctadiene-1,5[(*R,R*)-1,2-ethanediylbis(*o*-methoxyphenyl)phenylphosphine]rhodium tetrafluoroborate (**6**). If necessary, the product may be purified by crystallization from absolute EtOH. Its purity is best measured by its catalytic efficiency.

Crystallographic Study of 6. A suitable crystal was obtained by slow evaporation of an absolute ethanol solution. Crystal data: a = 13.44 (2), b = 16.82 (4), c = 18.33 (3) Å, Z = 4, space group $P2_12_12_1$. The crystals were solvated and the BF_4^- somewhat disordered. The structure was solved using heavy atom techniques. Full matrix least-squares refinement with anisotropic temperature factors converged to R = 0.101.

α-Acetamidocinnamic Acid (*Z*-7). This material was prepared by the procedure given in ref 26, mp 190–192 °C, (MeOH) λ_{max} 277 nm (ϵ 16 534).

α-Acetamidocinnamic Acid (*E*-7). Irradiation at 3100 Å of 30 g of *Z*-7 in a solution of 480 mL of methanol and 120 mL of water for 20 h resulted in about a 50:50 mixture of the *E* and *Z* isomers. The vinyl proton of *Z*-7, ^1H NMR (Me_2SO-d_6) δ 7-7.3 ppm appears under the aromatic protons, while the vinyl proton for *E*-7 appears at

(Me_2SO-d_6) δ 6.7 ppm. The solution was stripped to near dryness then the residue slurried in 1200 mL of H_2O at 25 °C. About 3 g of *E*-**7** was recovered, mp 170-172 °C, (MeOH) λ_{max} 280 nm (ϵ 16 534).

Methyl α-Acetamidocinnamate (*Z*-8). (*Z*)-Methyl-4-benzaloxazolone (30 g, see *Z*-**7** above for preparation) and 0.3 g of sodium acetate in 60 mL of methanol were held at reflux for 3 h. Cooling to 0-5 °C yielded crystals which were collected and washed with 20 mL of toluene, yield 17 g. Crystallization from 30 mL of methanol yielded 11.5 g of *Z*-**8**, mp 122-124 °C.

Methyl α-Acetamidocinnamate (*E*-8). α-Acetamidocinnamic acid (*E*-**7** 0.5 g, 0.0024 mol) was allowed to react with diazomethane in ethyl ether at ambient temperature. The solvent was evaporated at reduced pressure and the residue was recrystallized from methanol. The yield of *E*-**8** was 0.25 g, mp 103-105 °C.

α-Benzamidocinnamic Acid (*Z*-9).[24] This material was prepared according to the method given in ref 26 (notes 2 and 3), mp 235-236 °C dec, (EtOH) λ_{max} 280 nm (ϵ 17 285).

α-Benzamidocinnamic Acid (*E*-9).[25] Ten grams of *Z* azlactone[26] was slurried in 225 mL of glacial acetic acid and the mixture saturated with gaseous HBr for 0.5 h. The thick mass was poured into 300 mL of water. The crystals were filtered and washed giving 9.6 g of *E* azlactone.

This product was hydrolyzed to *E*-**9** by dissolving 8.3 g in 240 mL of methanol and adding 160 mL of 0.5 N NaOH. After 3 h at 30-35 °C the methanol is stripped and any methyl ester extracted with ether. The water solution was acidified giving 7.7 g, mp 189-191 °C dec (ethanol), λ_{max} 294 nm (ϵ 17 800).

The ^{1}H NMR for vinyl proton follows.

	Azlactone	Benzamido acid **9**
E	7.4-7.8 ppm	6.6 ppm
Z	7.2 ppm	7.0-7.5 ppm

The vinyl protons for the *E* azlactone and the *Z* acid were concealed in the aromatic region.

***N*-(β-Cyanostyryl)benzamide (*Z*-10).** This material was prepared from the reaction of benzaldehyde with *N*-benzamidoacetonitrile in an acid media.[27] The resulting 2-phenyl-4-arylidene-5-oxazolinium hydrochloride was converted to *Z*-**10** by treatment with aqueous Na_2CO_3, mp 164-165 °C. Fleury[27] assigned the *Z* configuration to the material.

Ethyl 2-(*N*-Ethoxycarbonylamino)-3-phenyl-2-propenoate (*Z*-11). This compound was prepared according to the procedure of Rosemund et al.[28] The band in the ^{1}H NMR spectrum ($CDCl_3$) at δ 6.48 ppm was assigned to the vinyl proton. Irradiation at 3100 Å in $CHCl_3$ for 48 h produced a 50:50 mixture (GLC analysis) of isomers (vinyl proton resonance of new isomer at δ 7.12 ppm). The lower extinction coefficient of the 50:50 mixture, (MeOH) λ_{max} 280 nm (ϵ 12 882), compared to that of the starting isomer, (MeOH) λ_{max} 280 nm (ϵ 18 069), provided the basis for the tentative assignment of the *Z* configuration (trans phenyl and carbethoxy groups) to the starting isomer.

4-Benzylidene-2-ethoxy-5-thiazolidinone (25). A solution of 10.4 g (0.064 mol) of ethoxythiocarbonylglycine, 7 g (0.066 mol) of benzaldehyde, and 25 mL of acetic anhydride was stirred at 90-95 °C for 30 min. The reaction mass was concentrated at reduced pressure and the solid residue was crystallized from ethanol. The yield of product was 4 g (27%), mp 63-65 °C, *m/e* 233 (M^+).

Ethyl 2-(*N*-Ethoxythiocarbonylamino)-3-phenylpropenoate (*Z*-12). To a stirred 5 °C mixture of 3.72 g (0.016 mol) of **25** in 80 mL of ethanol, there was added dropwise 13.3 mL of a 1.125 N solution of KOH in ethanol. When all of **25** had dissolved, 16 mL of a 1.0 N solution of anhydrous HCl in ethanol was added dropwise. After 15 min, the reaction mass was diluted with ethyl ether and the precipitate of KCl was removed by filtration. The solvents were stripped from the filtrate and the residual solid was crystallized from methylcyclohexane. The yield of **12** was 3.9 g (87.5%): mp 72-74 °C; *m/e* 279 (M^+); (MeOH) λ_{max} 247 nm (ϵ 19 232). The ^{1}H NMR vinyl proton resonance was concealed in the aromatic region. The tentative assignment of the *Z* configuration to this compound was based on the UV spectrum. Irradiation of the above isomer yielded a 60:40 mixture [based on the ^{1}H NMR ($CDCl_3$) methyl multiplet at δ 0.9-1.6 ppm] of the *Z* and *E*, (MeOH) λ_{max} 247 nm (ϵ 16 280).

α-Chloroacetamidoacrylic Acid (13). This compound was prepared according to the procedure of Greenstein et al.,[29a] mp 161-163 °C.

2-Benzamido-4-methyl-2-pentenamide (*Z*-14). 2-Phenyl-4-(2-methylpropylidene)-5-oxazolone was prepared from hippuric acid and isobutyraldehyde by a method similar to that used to form 2-phenyl-4-propylidine-5-oxazolone from propionaldehyde.[29b] The 2-phenyl-4-(2-methylpropylidene)-5-oxazolone, mp 87-89 °C, was reacted with aqueous ammonia to form *Z*-**14**, mp 137-139 °C (crystallized from hexane, 2-propanol).

***N*-(β-Methylstyryl)acetamide (15).** The 2-methyl-3-oxo-1-phenyl-1-butene was prepared from benzaldehyde and 2-butanone.[15] The corresponding oxime, mp 107-109 °C, undergoes the Beckmann rearrangement by the reported procedure.[30] To a solution of 7.7 g (0.044 mol) of the oxime in 100 mL of ethyl ether at 0-5 °C, there was added portionwise about 10.1 g (0.048 mol) of PCl_5. The mixture was stirred for 1 h, then poured into 400 mL of cold water containing 22 g of sodium bicarbonate. The mixture was extracted twice with 100 mL of diethyl ether, which was dried and stripped. NMR of the residue indicated approximately a 50:50 mixture of the *E* and *Z* isomers. The residue was dissolved in 25 mL of hexane-benzene (1:1), which on cooling to 0 °C yielded 1.8 g of material, mp 97-99 °C. Crystallization from hexane-benzene (1:1) raised the melting point to 99-100 °C (lit. 92-93,[30] 98-99 °C[8d]).

The hexane-benzene mother liquor from above was stripped up to 100 °C at 0.2 mm to remove 1.5 g of an unknown impurity. The remaining 2.4 g of residual solid was slurried with 25 mL of hexane-benzene (4:1) and 1.7 g of solid collected. This solid was crystallized from 10 mL of diethyl ether, recovering 0.7 g of material, mp 81-83 °C (lit. 83-84 °C[8d,30]).

The low-melting isomer, ^{1}H NMR ($CDCl_3$) δ 2.10 ppm ($COCH_3$ and CH_3C=), has previously been assigned the *Z* configuration;[30] and the higher melting isomer, ^{1}H NMR ($CDCl_3$) δ 2.00 ($COCH_3$) and 2.30 ppm (CH_3C=), was designated as the *E* isomer. Based on the nuclear Overhauser effect (NOE)[14] data, we believe that the assignments are incorrect. The methyl group was irradiated and the NOE enhancement of the olefinic proton determined. In the low-melting isomer, *E*-**15**, no significant effect was observed, while in the other isomer, *Z*-**15**, an enhancement of 22 ± 7 was observed.

2-Methyl-3-phenyl-2-propenoic Acid (*E*-16). This material was purchased from Eastman Organic Chemicals, mp 79-81 °C.

2-Methyl-3-phenyl-2-propenoic Acid (*Z*-16). This compound was prepared according to the procedure described by Culp et al.,[31] mp 92-93 °C.

Ethyl 3-Acetamido-3-phenyl-2-propenoate (*Z*-17). A solution of 11.5 g (0.06 mol) of ethyl 3-amino-3-phenyl-2-propenoate *Z*[32] and 6.8 g (0.033 mol) of acetic anhydride was refluxed for 2 h. The reaction mixture was distilled, bp 119-122 °C (0.05 mm), to give 9.0 g of *Z*-**17**; (MeOH) λ_{max} 288 nm (ϵ 16 344); ^{1}H vinyl proton resonance ($CDCl_3$) at δ 5.30.

The enantiomeric excess of the hydrogenation product was determined by diluting to volume and comparing with the pure enantiomer, $[\alpha]^{20}_D$ +57° (*c* 2.0, $CHCl_3$).[16]

Ethyl 3-Acetamido-3-phenyl-2-propenoate (*E*-17). A solution of 8 g of the *Z*-**17** isomer and 60 mL of $CHCl_3$ was irradiated with 3100 Å light for 72 h. The solvent was evaporated at reduced pressure and the residue was crystallized from ethanol to give 3.0 g of *E*-**17**: mp 120-122 °C; (MeOH) λ_{max} 268 nm (ϵ 11 073), ^{1}H vinyl proton resonance ($CDCl_3$) at δ 7.02 ppm.

Ethyl 2-Acetyloxy-3-phenyl-2-propenoate (*Z*-18). This compound was prepared according to Gault et al.[33] The melting point of the material was found to be 47-49 °C (lit. mp 33-34 °C). The ^{1}H NMR vinyl proton resonance ($CDCl_3$) was concealed in the aromatic region. Irradiation at 3100 Å for 48 h in $CHCl_3$ yielded (by GLC analysis) a mixture of 45% starting isomer and 55% of a new isomer (vinyl proton resonance at δ 6.8 ppm). The lower extinction coefficient of the 45:55 photolysis mixture [(MeOH) λ_{max} 274 nm (ϵ 13 319)] compared to that of the starting isomer [(MeOH λ_{max} 274 nm (ϵ 24 392)] provided the basis for assignment of the *Z* configuration (trans phenyl and carbethoxy groups) to the starting isomer.

Ethyl 3-Acetyloxy-3-phenyl-2-propenoate (*Z*-19). A solution of 55.6 g (0.29 mol) of ethyl benzoylacetate, 58.0 g (0.58 mol) of isopropenyl acetate, and 0.1 g of *p*-toluenesulfonic acid monohydrate was heated to reflux for 17 h. The cooled reaction mass was poured into 100 mL of 5% $NaHCO_3$ and the mixture was extracted with ethyl ether. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled, giving 12.1 g (18%) of the enol acetate *Z*-**19**: bp 110-115 °C (0.1 mm) [lit.[34] bp 176 °C (13 mm)]; (MeOH) λ_{max}. 272 nm (ϵ 19 843). The band in the ^{1}H NMR spectrum ($CDCl_3$) at δ 6.31 ppm was assigned to the vinyl proton.

Ethyl 3-Acetyloxy-3-phenyl-2-propenoate (*E*-19). A solution of 5.2

g of *Z*-**19** and 60 mL of $CHCl_3$ was irradiated with 3100 Å light for 72 h. The ^1H NMR spectrum ($CDCl_3$) of the solution indicated that 80% of the starting isomer (vinyl proton at δ 6.31 ppm) had been converted to a new isomer (vinyl proton at δ 5.95 ppm). The irradiated solution was concentrated and distilled giving 1.3 g of *E*-**19**; bp 92–98 °C (0.03 mm), 86% pure by GLC.

The lower extinction coefficient of the 80:20 photolysis mixture [(MeOH) λ_{max} 260 nm (ϵ 9524)] compared to that of the starting isomer [(MeOH) λ_{max} 272 nm (ϵ 19 843)] provided the basis for assignment of the *Z* configuration (trans phenyl and carbethoxy groups) to the starting isomer.[35]

On both the α- and β-acetyloxy reduction products the rotations were measured on distilled materials which were assayed by GC and NMR. In the β-acetyloxy reductions, approximately 30% hydrogenolysis of the acetyloxy function occurred. No hydrogenolysis was detected with the α-acetyloxy. The literature value for the optical rotation on the pure β-acetoxy adduct is incorrect (see ref 18). The literature value, $[\alpha]^{23}_D$ −8.7 ° (*c* 6.65, $CHCl_3$),[17] of the pure α-acetyloxy adduct was confirmed by converting it to (*S*)-(−)-3-phenyllactic acid.

Hydrogenation Procedures.[7d] To a 60-mL pressure bottle equipped with a magnetic stirrer were added 25 mL of methanol, 1.00 g of substrate, and between 0.004 and 0.020 g of complex **6**. The solution was purged by filling and evacuating with N_2 and finally with H_2. It was stirred at 50 °C and 3 atm H_2 until gas uptake ceased, then it was held for an additional 1 h. As an example, substrate *Z*-**7** with 0.004 g of **6** was hydrogenated in 40 min, which is assigned a relative rate of 100. The reduction solution was diluted to a known volume and the optical yield checked on a polarimeter by comparison with a standard.

For the high-pressure runs the reactants given above were added to a Hoke bomb. The reactor was purged six to eight times with 20–25 atm of H_2 pressure and hydrogenation completed with a Parr shaker. Relative rates were compared assuming first-order dependence on pressure and catalyst concentration.

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