$(dpm)_2$, 80846-11-3; $Rh_2(CO_2)(CO)_2(dpm)_2$, 80865-88-9; $[Rh_2(H)(CO)_2(dpm)_2]PF_6$, 80846-12-4; $[Rh_2(H)(CO)_2(dpm)_2]$-p-$CH_3C_6H_4SO_3$, 74507-91-8; $[Rh_2(\mu\text{-}O_2CH)(CO)_2(dpm)_2]PF_6$, 80846-14-6; $[Rh_2(\mu\text{-}O_2CCH_3)(CO)_2(dpm)_2]BF_4$, 80846-15-7; $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]PF_6$, 80876-88-6; $[Rh_2(\mu\text{-}Cl)(CO)_2(dpm)_2]PF_6$, 80448-77-7; $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$, 67202-36-2; $Rh_2Cl_2(CO)_2(dpm)_2$, 22427-58-3; $RhH(CO)(PPh_3)_3$, 17185-29-4.

Supplementary Material Available: Listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Asymmetric Hydrogenation: Chiral Bis(phosphine)rhodium Catalysts with Phenyl Group Derivatives

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Some attempts to achieve optically active products were carried out by new catalysts of the type $[Rh(COD)(P^*)_2]^+$, where the chiral phosphorus ligands are α-naphthylphenyl(o- or p-tolyl)phosphine (NPTP), bis[phenyl(o- or p-tolyl)phosphino]ethane (BPTE), bis(α-naphthylphenylphosphino)ethane (BNPE), and 1-phenyl-1,2-bis(diphenylphosphino)ethane (R-PDPE). Optical yields of 50–75% ee (ee = enantiomeric excess) were obtained in the hydrogenation of acetamidoacrylic acid. The ortho isomer of the tolyl group gave a higher optical yield than the para one. Isoalcohols were effective solvents. It was found that these catalysts can be recovered and reused for asymmetric hydrogenation.

Introduction

Many studies (for example, ref 1–4) of selective asymmetric hydrogenation with metal catalysts have been made. Ligands which have optical activity on an atom of phosphorus, nitrogen, or carbon can give optically active products. It has been said that ligands containing optically active phosphorus atoms are more effective than others, but in recent years it has been shown that ligands having optical activity on carbon[5] and nitrogen[6] may be very effective for asymmetric hydrogenation. Many asymmetric hydrogenation catalysts are sensitive to air and moisture, so they require special handling.

We have prepared catalysts which are stable in air and effective for asymmetric hydrogenation. The ligands described have optical activity residing on a phosphorus atom (P* or $\overline{P^*P^*}$) and contain phenyl, tolyl, and naphthyl groups. Those compounds were expected to give complexes having large optical activity because of their bulky structures. Also 1-phenyl-1,2-bis(diphenylphosphino)ethane[7] (R-PDPE or R-phenphos) was used as a typical aromatic ligand having optical activity on one carbon atom.

Results and Discussion

Ligand I, NPTP, is monodentate, so it presents the possibility that either one or two groups may coordinate to give $[Rh(COD)(P^*)X]$ or $[Rh(COD)(P^*)_2]X$. The first was tested by using the monophosphine complex for hydrogenation of α-acetamidoacrylic acid. However, so the completely hydrogenated product could be obtained, it was found that the hydrogenation had to be carried out with a relatively large concentration of catalyst (S/Rh = 5). The reaction was slow. On the other hand, the rhodium compound containing two monophosphine molecules was effective under moderate conditions. Therefore, in all later studies on asymmetric hydrogenation, we used bidentate phosphine rhodium compounds.

The ligands described in this paper are shown in Figure 1. Ligands I and II each exist in two isomeric forms (ortho and para), both optically active. The other ligands exist as meso-, levo-, and dextrorotatory isomers. Optical resolutions were carried out by fractional precipitation of the D-α-bromocamphor-π-sulfonate (BCS)–rhodium compounds. In each case, the fractional precipitation was repeated until the limiting optical activity was obtained. The resulting optically active compounds were converted to the desired salts as described in the Experimental Section.

Figure 2 shows the relationship between hydrogenation yield and time of reaction. All of the catalysts have the ability to completely hydrogenate α-acetamidoacrylic acid in 4 h. Therefore, the following asymmetric hydrogenations (except with the monophosphine catalyst and others especially noted) were carried out under the following conditions: 1 atm pressure, room temperature, substrate/Rh = 50–100, solvent 95% EtOH. Yields at less than 4 h show that all of these catalysts can hydrogenate at about the same rate (Figure 2).

Table I gives the optical yields of products hydrogenated asymmetrically by these catalysts. In general, the optical yield seems to depend upon the magnitude of the optical activity of the catalyst. The optical yield with $[Rh(COD)(NPTP)(H_2O)]^+$ as the catalyst is very much lower than with the diphosphine catalysts. On the other hand, catalysts with diphosphine ligands give good optical yields, especially $[Rh(COD)(BNPE)]^+$. The results suggest that tolyl and phenyl groups on the phosphorus atoms in NPTP exist in the same conformation as in BPTE. If the naphthyl groups in NPTP have the same spatial relationship as do those in BNPE, the yield might be close to the value given by $[Rh(COD)(BNPE)]^+$.

Effects of Catalyst Anions. As noted by Knowles,[8] there is little difference in optical yield when the catalysts contain different anions.

Effects of Position Isomers. The position of the methyl group on the tolyl ring is very important in achieving high

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Table I. Optical Yields[a]

catalysts	comformation	counter-anion	isomer[b]	*P*, atm	time, h	$[\alpha]_D$[f]	optical yield, % ee[c,d]
$[Rh(COD)(NPTP)(H_2O)]^+$[e]	(+)	Cl	*o*	2	6	+10.0	15.0
			p			+5.5	8.3
	(−)	Cl	*o*	2	6	−9.8	14.7
			p			−5.6	8.4
	(+)	PF_6	*o*	2	6	+11.2	16.8
			p			+5.4	8.1
	(−)	PF_6	*o*	2	6	−10.6	15.9
			p			−5.3	8.0
	(+)	ClO_4	*o*	2	6	+10.7	16.1
			p			+5.3	8.0
	(−)	ClO_4	*o*	2	6	−10.6	15.9
			p			−5.4	8.1
$[Rh(COD)(NPTP)_2]^+$	(+)	Cl	*o*	1	4	+35.8	53.8
			p			+15.2	22.9
	(−)	Cl	*o*	1	4	−35.9	54.0
			p			−15.3	23.0
	(+)	ClO_4	*o*	1	4	+35.9	54.0
			p			+15.0	23.0
	(−)	ClO_4	*o*	1	4	−35.9	54.0
			p			−15.3	23.0
$[Rh(COD)(BPTE)]^+$	(+)	Cl	*o*	1	4	+32.8	49.3
			p			+12.6	18.9
	(−)	Cl	*o*	1	4	−32.5	48.9
			p			−12.6	18.9
	(+)	ClO_4	*o*	1	4	+32.3	48.6
			p			+12.7	19.1
	(−)	ClO_4	*o*	1	4	−32.5	48.9
			p			−12.6	18.9
$[Rh(COD)(BNPE)]^+$	(+)	Cl		1	4	+50.7	76.2
	(−)	Cl		1	4	−50.6	76.1
	(+)	ClO_4		1	4	+50.6	76.1
	(−)	ClO_4		1	4	−50.5	75.9
$[Rh(COD(R\text{-}PDPE)]^+$	(−)	Cl		1	4	−46.9	70.5
	(−)	ClO_4		1	4	−47.1	70.8

[a] Conditions: solvent = 95% EtOH; [C] of substrate = 5×10^{-1} mM; substrate/Rh = 50–100; *T*, 25 °C; chemical yield, 95–100%. [b] *o* and *p* show the position isomer, ortho and para, of the tolyl group in ligand. [c] Enantiomeric excess. [d] All rotations were measured by comparing with a blank, with pure *N*-acetyl-(*R*)-alanine [$[\alpha]_D$ 66.5° (C 2.0, H_2O)] taken as a standard: S. M. Birbaum et al., *J. Biol. Chem.*, 194, 455 (1952). [e] 5–10 for $[Rh(COD)(NPTP)(H_2O)]^+$; substrate/Rh = 5–10. [f] Rotation of products.

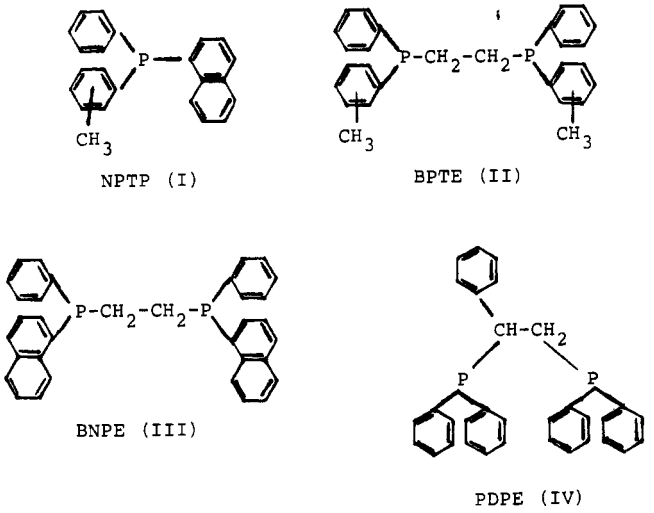

Figure 1. Chiral phosphine ligands.

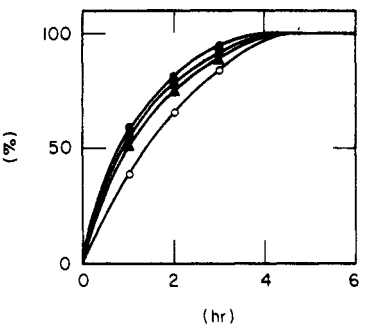

Figure 2. Relationship between chemical yield and time of reaction, with $[Rh(COD)(P^*)]^+$, where the ligands are (●) BPTE, (▲) BNPE, (■) $(NPTP)_2$, and (○) R-PDPE.

Table II. Optical Yields with $[Rh(COD)(P^*)]ClO_4$ in Various Alcohols

alcohol	% ee $(NPTP)_2$[a,b]	BPTE[a]	BNPE	PDPE
MeOH	44.1	43.9	69.3	67.5
EtOH (95%)	54.0	48.6	76.1	70.8
n-propyl	56.1	52.3	76.2	71.8
isopropyl	65.3	58.0	80.3	75.5
n-butyl	59.8	53.8	77.1	72.0
isobutyl	67.1	63.2	82.6	76.1

[a] These ligands contain *o*-tolyl groups. [b] See corresponding footnotes in Table I.

optical yields. In fact, the optical yield when the ligand contains the *o*-tolyl group is more than twice the yield when the *p*-tolyl group is present.

Effect of Solvents. In these studies, 95% ethanol was used as the solvent because both the catalysts and α-acetamidoacrylic acid dissolve relatively easily in it. However, it is interesting to note that other alcohols give different effects in asymmetric hydrogenation. Table II shows the optical yields in various alcohols. In general, increasing the number of carbon atoms in the solvent increases the optical yield. Particularly, alcohols with branched chains give higher yields than straight-chain alcohols of the same number of carbon atoms; this is especially marked for catalysts which give relatively low

Table III. Optical Yields[a] with Recovered Catalysts

catalysts	1st time, h	1st % ee[b]	P, atm	2nd[c] time, h	2nd % ee	2nd/1st
(−)-[Rh(COD)(NPTP)(H_2O)]Cl	6	14.7	2	6	2.0	13.6
(−)-[Rh(COD)(NPTP)$_2$]Cl	4	54.2	1	4	45.9	84.7
(−)-[Rh(COD)(BPTE)]Cl	4	49.6	1	4	44.8	90.3
(−)-[Rh(COD)(BNPE)]Cl	4	76.4	1	4	68.0	89.0
(−)-[Rh(COD)(PDPE)]Cl	4	70.6	1	4	64.1	90.8
(−)-[Rh(COD)(PDPE)]ClO_4	8	70.8	1			
(−)-[Rh(COD)(PDPE)]ClO_4	4	70.8	1	4	65.9[d]	93.1
(−)-[Rh(COD)(BNPE)]ClO_4	4	76.4	1	4	70.0[d]	91.6

[a] Conditions: solvent, 95% EtOH; [C] of substrate, 3 mM; substrate/Rh = 100; T, 25 °C; chemical yield, 95–100%. [b] See corresponding footnotes in Table I. [c] The recovered catalysts which were taken out after first hydrogenation were used for the 2nd asymmetric hydrogenation. [d] After the substrate (1.5 mM) and catalyst (0.03 mM) were hydrogenated for 4 h, additional substrate (1.5 mM) was added to the mixture and hydrogenation was continued for 4 h.

optical yield such as $[Rh(COD)(NPTP)_2]^+$ and $[Rh(COD)(BPTE)]^+$. These results suggest that the structure of the solvent coordinated to the catalyst plays an important role in the interaction between the alcohol and the unsaturated double bond of the substrate. It would be interesting to hydrogenate in *sec*- and *tert*-butyl alcohol and higher alcohols instead of *n*-butyl alcohol. However, it was difficult to dissolve α-acetamidoacrylic acid, acetoalanine, and the catalysts in these solvents.

Recycle of Catalysts. It is important that the catalyst can be employed repeatedly in the hydrogenation. Although catalysts are used in much smaller amounts than the substrate, in industrial work the amount of catalyst cannot be neglected. In the present studies, at first, the recycled catalysts (as the chlorides) were used and found to give as high yields as in the first hydrogenation. However, the recycled catalysts were shown by elemental analysis and NMR to have been converted to $[Rh(\overline{P^*P^*})Cl]_2$ by the elimination of cyclooctadiene. $[Rh(\overline{P^*P^*})Cl]_2$ can be made by passing hydrogen gas through solutions of the catalysts. The $[Rh(\overline{P^*P^*})Cl]_2$ catalyst showed the same chemical and optical yield as $[Rh(COD)(\overline{P^*P^*})]^+$.

The perchlorate and hexafluorophosphate recycled catalysts were not effective for asymmetric hydrogenation. Furthermore, $[Rh(COD)(\overline{P^*P^*})]ClO_4$ did not lose cyclooctadiene when hydrogen gas was passed through the solution containing only the catalyst.[9] By passing hydrogen gas through the solution of any of the catalysts for a long time, part of the catalyst was reduced to rhodium metal.

In one experiment, when hydrogenation was complete, additional substrate (0.5 mM) was added to the solution of catalyst (0.01 mM) and substrate (0.5 mM), and hydrogenation was carried out for an additional 4 h. The optical yield of the product was 65.9% (93.1% of that obtained in the first run). On the other hand, when the mixture of substrate (1 mM) and catalyst (0.01 mM) was hydrogenated for 8 h, the optical yield was 70.8%; that is, the second net optical yield is 86.2% of the first. This value is close to the value obtained for the recycled chloride catalyst. This suggests that catalysts with the perchlorate anion, too, can be recycled if the solvent is not evaporated. It may be that the recycled catalysts which were not effective for asymmetric hydrogenation underwent some changes when the catalyst was taken out of the mixture after the hydrogenation.

The recycled catalysts with diphosphines gave optical yields of 85–90%, while the catalyst with only one monophosphine gave only 13.6%. In the case of $[Rh(COD)(P^*)(H_2O)]^+$, the monophosphine ligand has a large degree of freedom.

Experimental Section

A. Instrumentation. Routine ^1H NMR spectra were recorded with a Varian EM-390, 90-MHz spectrometer with Me_4Si as the internal reference. Optical rotations were obtained with a Rudolph Research Automatic Polarimeter Model III.

B. Chemicals. All of the solvents used were distilled in the presence of grains of sodium metal and kept in a nitrogen atmosphere. α-Acetamidoacrylic acid was purchased from Aldrich Chemical Co. The silica gel plate was "pre-coated TLC plate SIL G-200 UV 254" made by Machery-Nagel in Germany.

C. Workup. Hydrogenation was carried out by passing hydrogen gas through the solution at a pressure of a little more than 1 atm. The solution was in a 50-mL flask equipped with two needles (No. 14) for input and output. α-Acetamidoacrylic acid (0.5 mM) was added in 95% ethanol or other solvent (30 mL) and prehydrogenated for 10 min, and catalysts which were prehydrogenated in another vessel were injected by a syringe. Then hydrogen was passed through the solution for the desired time at room temperature. When the hydrogenation was finished, the solution was evaporated under vacuum. To the powder which remained was added water (15 mL), and the filtrate was evaporated to dryness in a vacuum. Hydrogenation yields were determined by NMR spectra in Me_2SO-d_6, and optical yield was determined by the ratio of the optical rotation of the product and that of the optically pure amino acid derivative.

D. Preparation of the Ligand and Catalysts. Phenyl-*p*-tolylchlorophosphine. This compound was prepared by a modification of the known method.[10] Aluminum chloride (58 g, 0.435 M), toluene (230 mL, 2.16 M), and phenyldichlorophosphine (56 mL, 0.413 M) were placed in a 500-mL round-bottomed flask equipped with a condenser, a dropping funnel, and a magnetic stirrer. A nitrogen atmosphere was maintained. The solution was refluxed for 20 h under vigorous stirring. The mixture was stirred at 60 °C for 1 h, and pyridine (110 mL, 1.36 M) was added dropwise with stirring. After an additional 1 h of stirring, the mixture separated into two layers. The pale yellow-orange filtrate was twice distilled; bp 120–130 °C (0.5 torr), d 1.15. Anal. Calcd for $C_{13}H_{12}ClP$: C, 66.5; H, 5.2; Cl, 15.1; P, 13.2. Found: C, 66.1; H, 5.1; Cl, 15.4; P, 12.9. Yield = 82.4 g, 85%.

Phenyl-*o*-tolylchlorophosphine. *o*-Bromotoluene (12.3 mL, 0.1 M) was dissolved in 40 mL of ether at 0 °C and was kept in an ice-salt bath for 1 h. To the cold solution was added a *n*-butyllithium solution (95 mL of 2.1 M solution, 0.2 M) over a period of 1 h, and stirring was continued for 2 h under the same conditions while an ether solution (40 mL) of (diethylamino)chlorophenylphosphine[11] (21.6 g, 0.1 M) was added. The mixture was stirred for 2 h and filtered. Ether (50 mL), saturated with hydrogen chloride, was added to the filtrate, and hydrogen chloride was bubbled through the solution for 10 min. The mixture was filtered, and the solvent was removed by vacuum distillation; then the product was distilled under high vacuum to give a pale yellow liquid; bp 110–120 °C (0.05 torr). Yield = 17.6 g, 75%.

Naphthylphenyltolylphosphine (NPTP). *n*-Butyllithium (21 mL, >0.04 M) in ether solution (40 mL) was gradually added dropwise with stirring to α-bromonaphthalene (2.8 mL, 0.02 M) cooled by ice water. After completion of addition, stirring was continued for 5 h at room temperature. The solution was cooled to 0 °C, and phenyltolylchlorophosphine (3.8 mL, 0.02 M) was added during 20 min. The mixture was stirred at room temperature for 20 h after which the solution was filtered. The excess lithium compounds were eliminated by adding air-free water (10 mL) to the filtrate, after which the ethereal layer was separated and the ether was removed by distillation. The byproducts in the resulting yellowish brown semisolid were removed by distillation (0.1 mmHg) at a temperature below 160 °C. The pale yellowish orange remainder was recrystallized from dioxane and then absolute ethanol: mp 106–108 °C, yield 3.5 g (54%) for naphthylphenyl-*p*-tolylphosphine; mp 101–103 °C, yield 3.1 g (48%) for naphthylphenyl-*o*-tolylphosphine. Anal. Calcd for $C_{23}H_{19}P$:

(9) J. M. Brown and B. A. Murrer, *Tetrahedron Lett.*, **50**, 4859 (1979).

(10) G. Nagy and D. Balde, French Patent 1 450 681, Aug 26, 1966 (Applied for on July 6, 1965); *Chem. Abstr.*, **67**, P3142*s* (1967).

(11) W. Seidel and K. Issleib, *Z. Anorg. Allg. Chem.*, **325**, 113 (1963).

C, 84.6; H, 5.9; P, 9.5. Found for *p*-tolyl product: C, 84.3; H, 6.1; P, 9.6. Found for *o*-tolyl product: C, 84.4; H, 6.1; P, 9.3.

[Rh(COD)(NPTP)Cl], (1,5-Cyclooctadiene)chloro(naphthylphenyltolylphosphine)rhodium(I). A THF solution (5 mL) containing naphthylphenyltolylphosphine (575 mg, 1.76 mM) was added in THF solution to $[Rh(COD)Cl]_2$[12] (435 mg, 0.88 mM). The color of the solution changed from pale yellow to red-orange after stirring overnight. The solution was evaporated to dryness and washed with ether to remove the unreacted ligand. By successive recrystallizations from THF and ether, yellow-orange crystals were obtained. Anal. Calcd for $C_{31}H_{31}ClPRh$: C, 65.0; H, 5.5; Cl, 6.2; P, 5.4. Found: C, 64.9; H, 5.8; Cl, 6.2; P, 6.0. Yield = 419 mg, 83%.

[Rh(COD)(NPTP)(H_2O)]BCS, (1,5-Cyclooctadiene)aqua(naphthylphenyltolylphosphine)rhodium(I) α-Bromocamphor-π-sulfonate. Silver bromocamphorsulfonate[13] ($Ag(BCS)\cdot H_2O$, 227 mg, 0.52 mM) was added in the dark to 40 mL of 95% ethanol containing [Rh(COD)(NPTP)Cl] (281 mg, 0.49 mM). Stirring was continued for 3 h, and the filtrate was evaporated to dryness. The resulting orange powder was dissolved in benzene (10 mL), water (5 mL) was added, and the benzene layer was taken out. This process was repeated, and the benzene layer was collected and dried over sodium sulfate. The filtrate was then evaporated to dryness. The resultant yellow powder was recrystallized from benzene and then ether. Anal. Calcd for $C_{41}H_{47}BrO_5PRhS$: C, 56.9; H, 5.5; P, 3.6; S, 3.7. Found: C, 57.2; H, 5.4; P, 4.0; S, 4.1. Yield = 378 mg, 89%.

Fractional Precipitation of [Rh(COD)(NPTP)(H_2O)]BCS. The ether solution (500 mL) containing [Rh(COD)(NPTP)(H_2O)]BCS (1.03 g) was stirred at room temperature for 10 h and filtered. By gradually concentrating the filtrate in a vacuum, fractional precipitates having different optical activity were obtained: racemic (yield 42%) and levo- (28%) and dextrorotatory (28%) compounds in turn. This fractional precipitation was repeated until the limiting optical activity was obtained.

Conversion to Chloride, Hexafluorophosphate, and Perchlorate. To the cold ethanol solution (10 mL) containing [Rh(COD)(NPTP)(H_2O)]BCS (100 mg, 0.116 mM) were added a cold 1 M hydrochloric acid solution containing ammonium chloride (50 mg, 0.935 mM), ammonium hexafluorophosphate (150 mg, 0.920 mM), or a saturated solution of sodium perchlorate (80 mg, 0.653 mM), and the mixture was stirred for 1 h. The resulting precipitate was dried over silica gel.

Anal. Calcd for the chloride $C_{31}H_{33}ClOPRh$: C, 63.0; H, 5.6; Cl, 6.0; P, 5.2. Found for the *p*-tolyl product: C, 62.9; H, 5.4; Cl, 5.7; P, 5.0; $[\alpha]_D$ −3.8°, +3.9°. Found for the *o*-tolyl product: C, 62.9; H, 5.7; Cl, 5.7; P, 5.1; $[\alpha]_D$ −8.8°, +9.2°. Calcd for the hexafluorophosphate $C_{31}H_{33}F_6OP_2Rh$: C, 53.2; H, 4.7; P, 8.8. Found for the *p*-tolyl product: C, 53.1; H, 5.5; P, 9.0; $[\alpha]_D$ −3.3°, +3.5°. Found for the *o*-tolyl product: C, 53.2; H, 4.9; P, 8.5; $[\alpha]_D$ −8.9°, +9.0°. Calcd for the perchlorate $C_{31}H_{33}ClO_5PRh$: C, 56.9; H, 5.1; P, 4.7. Found for the *p*-tolyl product: C, 57.0; H, 5.3; P, 4.7; $[\alpha]_D$ −3.0°, +3.0°. Found for the *o*-tolyl product: C, 57.2; H, 5.5; P, 4.5; $[\alpha]_D$ −8.2°, +8.6°.

[Rh(COD)(NPTP)$_2$]BCS, (1,5-Cyclooctadiene)bis(naphthylphenyltolylphosphine)rhodium(I) Bromocamphorsulfonate. To a THF solution (5 mL) containing freshly prepared $[Rh(COD)Cl]_2$ (309 mg, 0.626 mM) was added a THF solution (25 mL) of NPTP (899 mg, 2.75 mM). The mixture was stirred for 10 h at 0 °C. In the dark, $Ag(BCS)\cdot H_2O$ (540 mg, 1.24 mM) was added to the mixture, and stirring was continued for 3 h. The filtrate was concentrated gradually to 1 mL, whereupon a yellow-orange powder was obtained. This was filtered and dried over silica gel under vacuum. Recrystallization was carried out from THF and then ether. Anal. Calcd for $C_{64}H_{64}BrO_4P_2RhS$: C, 65.5; H, 5.5; P, 5.3; S, 2.7. Found: C, 65.7; H, 5.2; P, 5.3; S, 2.8. Yield = 1.50 g (93%).

After [Rh(COD)(NPTP)$_2$]BCS (1 g) was added to ether (400 mL) and stirred at room temperature for 20 h, the filtrate was concentrated gradually for fractional precipitation. Fractionation was repeated until constant values for the optical activity were obtained: racemic (yield 62%) and levo- (19%) and dextrorotatory (19%), in that order.

Conversion to Chloride and Perchlorate. When concentrated hydrochloric acid or saturated aqueous $NaClO_4$ solution was added dropwise to a cold THF solution of each of these precipitates, a yellow-orange powder was obtained. Recrystallization was carried out by adding ether to the THF solution of the crude compounds.

Anal. Calcd for the chloride $C_{54}H_{50}ClP_2Rh$: C, 72.1; H, 5.6; P, 6.9. Found for the *p*-tolyl product: C, 72.1; H, 5.8; P, 6.9; $[\alpha]_D$ −12.3°, +12.3°. Found for the *o*-tolyl product: C, 72.3; H, 5.8; P, 6.8; $[\alpha]_D$ −32.4°, +32.2°. Calcd for the perchlorate $C_{54}H_{50}ClO_4P_2Rh$: C, 67.3; H, 5.2; P, 6.4. Found for the *p*-tolyl product: C, 67.1; H, 5.5; P, 6.3; $[\alpha]_D$ −11.8°, +11.6°. Found for the *o*-tolyl product: C, 67.5; H, 5.4; P, 6.4; $[\alpha]_D$ −31.7°, +31.9°.

Bis(phenyltolylphosphino)ethane, BPTE. Sodium metal (1.9 g, 83 mM) and dioxane (75 mL) were placed in a 250-mL three-necked flask equipped with a condenser, dropping funnel, and mechanical stirrer. After 10 min of refluxing, phenyltolylchlorophosphine (4 mL, 20 mM) was added dropwise over a period of 30 min. The mixture was refluxed 6 h and then cooled in ice water for 30 min. When THF (50 mL) was added to the mixture, the color changed from brown to yellow-orange. The solution was filtered through glass wool and cooled in ice water. A THF solution (40 mL) with ditosylethane[14] (2.7 g, 7 mM) was added to the filtrate over a 30-min period with constant stirring. The pale yellow mixture was stirred overnight at room temperature and filtered. After distillation of the filtrate under vacuum, an orange oily substance remained. Absolute ethanol (15 mL) was added to it, and the mixture was kept in the refrigerator. The resulting white precipitate was filtered and washed twice with absolute ethanol (0.5 mL). The THF solution (1 mL) of this compound (400 mg) was placed on TLC (2 mm silica gel) and developed by benzene. The desired belt (R_f 0.58) was cut out and extracted by THF (100 mL), and the solution was filtered. The filtrate was evaporated under vacuum, diluted with absolute ethanol (10 mL), and kept in the refrigerator. The resulting white precipitate was recrystallized from THF and absolute ethanol, mp 104–108 °C. Yield = 1.79 g, 42%. The compound is extremely soluble in THF, soluble in acetone and benzene, and slightly soluble in ethanol. Anal. Calcd for $C_{28}H_{28}P_2$: C, 78.9; H, 6.6; P, 14.5. Found: C, 78.7; H, 6.9; P, 14.4.

[Rh(COD)(BPTE)]BCS, (1,5-Cyclooctadiene)(bis(phenyltolylphosphino)ethane)rhodium(I) Bromocamphorsulfonate. A THF solution (5 mL) containing BPTE (448 mg, 1.05 mM), a THF solution (3 mL) containing 36% hydrochloric acid (101 mg, 1 mM), and a THF solution (10 mL) containing [Rh(COD)(acac)][15] (311 mg, 1 mM) were mixed. The resulting solution changed from yellow to yellow-orange. After 2 h of stirring, $Ag(BCS)\cdot H_2O$ (437 mg, 1 mM) was added in the dark, and the mixture was stirred for 3 h and filtered. When the filtrate was evaporated under vacuum, a yellow-orange powder was obtained. Recrystallization was carried out by adding ether to a THF solution of the crude compound. Anal. Calcd for $C_{46}H_{54}BrO_4P_2RhS$: C, 58.3; H, 5.7; P, 6.5; S, 3.4. Found: C, 58.0; H, 5.7; P, 6.3; S, 3.3. Yield = 834 mg, 88%.

Fractional Precipitation and Introduction of Other Counteranions. These treatments were carried out as described for $[Rh(COD)(NPTP)_2]^+$. This yielded the meso isomer (52%), the levo isomer (24%), and the dextro isomer (24%) in that order. Anal. Calcd for the chloride $C_{36}H_{40}ClP_2Rh$: C, 64.2; H, 6.0; P, 9.2. Found: C, 64.2; H, 6.1; P, 8.9; $[\alpha]_D$ −11.5, +11.5. Found for the *o*-tolyl product: C, 64.5; H, 6.2; P, 9.3; $[\alpha]_D$ −37.7, +37.5. Calcd for the perchlorate $C_{36}H_{40}ClO_4P_2Rh$: C, 58.7; H, 5.5; P, 8.4. Found for the *p*-tolyl product: C, 58.6; H, 5.6; P, 8.3; $[\alpha]_D$ −10.3, +10.1. Found for the *o*-tolyl product: C, 58.9; H, 5.5; P, 8.6; $[\alpha]_D$ −36.8, +36.8.

Bis(naphthylphenylphosphino)ethane, BNPE. Sodium metal (0.63 g, 27 mM) was placed in dioxane (25 mL) in a 250-mL round-bottomed flask equipped with a condenser, dropping funnel, and mechanical stirrer under nitrogen. When the mixture was refluxed for 10 min, the sodium metal because fine grains. To the mixture was added a dioxane solution (10 mL) containing naphthylphenylchlorophosphine[16] (1.94 g, 7.2 mM) over a period of 30 min, and reflux was continued for 6 h. The mixture was cooled in ice water, and THF (30 mL) was added. The red-brown filtrate was passed through glass wool. When a THF solution (20 mL) containing ditosylethane (1 g, 3 mM) was added dropwise, the mixture changed to a pale yellow. This was stirred for 10 h at room temperature, filtered, and evaporated under vacuum to remove the solvent. When absolute alcohol (10 mL)

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was added and the solution cooled to −5 °C for 10 h and filtered, a yellow powder was obtained. A THF solution (1 mL) of the crude powder was placed on a separating TLC and eluted by means of benzene, and the desired belt (R_f 0.53) was cut out. This belt was stirred with THF (80 mL) for 1 h, the solution was filtered, the solvent was removed under vacuum, absolute ethanol was added (10 mL), and the mixture was placed in the freezer. A pale yellowish white powder was obtained by recrystallizing from absolute ethanol. Yield = 1.79 g (28%). The compound is extremely soluble in THF and $CHCl_3$, soluble in acetone, and insoluble in ethanol.

Anal. Calcd for $C_{34}H_{28}P_2$: C, 81.9; H, 5.7; P, 12.4. Found: C, 82.1; H, 5.9; P, 12.3.

[Rh(COD)(BNPE)]BCS, (1,5-Cyclooctadiene)(bis(naphthylphenylphosphino)ethane)rhodium(I) Bromocamphorsulfonate. A THF solution (35 mL) containing [Rh(COD)(acac)] (218 mg, 0.7 mM) was cooled in ice water and added to a cooled THF solution (35 mL) of 36% hydrochloric acid (78 mg, 0.77 mM) and stirred for 10 min. To this mixture was added dropwise a cooled THF solution (35 mL) containing BNPE (384 mg, 0.77 mM), and the solution was stirred for 2 h in an ice bath. Ag(BCS)·H_2O (336 mg, 0.77 mM) was added, and stirring was continued for 3 h in a cold, dark environment. The solvent was removed under vacuum. The resulting yellow precipitate was dissolved in THF (14 mL) and recrystallized by dropwise addition of ether.

Anal. Calcd for $C_{52}H_{54}BrO_4P_2RhS$: C, 61.2; H, 5.3; P, 6.1. Found: C, 60.9; H, 5.4; P, 6.1. Yield = 557 mg (78%).

Fractional Precipitation and Conversion to Other Counteranions. These treatments were carried out in a similar manner to that used for $[Rh(COD)(NPTP)_2]^+$ and gave meso (66%), levo (17%), and dextro (17%) isomers in that order. Anal. Calcd for the chloride $C_{42}H_{40}ClP_2Rh$: C, 67.7; H, 5.4; P, 8.3. Found: C, 67.5; H, 5.4; P, 8.2; $[\alpha]_D$ −37.4°, +37.2°. Calcd for the perchlorate $C_{42}H_{40}ClO_4P_2Rh$: C, 62.3; H, 5.0; P, 7.7. Found: C, 62.3; H, 5.0; P, 7.6; $[\alpha]_D$ −36.8°, +36.8°.

[Rh(COD)(R-PDPE)](Cl, ClO_4), (1,5-Cyclooctadiene)(1-phenyl-1,2-bis(diphenylphosphino)ethane)rhodium(I) Chloride and Perchlorate. To a THF solution (2 mL) containing [Rh(COD)(acac)] (107 mg, 0.343 mM) was added 36% hydrochloric acid (35 mg, 0.35 mM) or 70% perchloric acid (50 mg, 0.347 mM) diluted by THF (1 mL), and then a THF solution (2 mL) of R-PDPE[7] (166 mg, 0.35 mM) was added. The mixture was stirred for 2 h, and when evaporated under vacuum, a yellow-orange powder was obtained. Recrystallization was carried out by concentrating an etheral solution.

Anal. Calcd for the chloride $C_{40}H_{40}ClP_2Rh$: C, 66.6; H, 5.6; P, 8.6. Found: C, 66.7; H, 5.6; P, 8.7; $[\alpha]_D$ −32.0. Yield = 228 mg (92%). Calcd for the perchlorate $C_{40}H_{40}ClO_4P_2Rh$: C, 61.2; H, 5.1; P, 7.9. Found: C, 60.9; H, 5.1; P, 7.8; $[\alpha]_D$ −31.3°. Yield = 256 mg (95%).

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Registry No. Rh(COD)(*o*-NPTP)Cl, 81157-96-2; Rh(COD)(*p*-NPTP)Cl, 81177-86-8; (±)-[Rh(COD)(*o*-NPTP)(H_2O)]BCS, 81202-89-3; (±)-[Rh(COD)(*p*-NPTP)(H_2O)]BCS, 81202-90-6; (−)-[Rh(COD)(*o*-NPTP)(H_2O)]BCS, 81202-92-8; (−)-[Rh(COD)(*p*-NPTP)(H_2O)]BCS, 81202-94-0; (+)-[Rh(COD)(*o*-NPTP)(H_2O)]BCS, 81202-96-2; (+)-[Rh(COD)(*p*-NPTP)(H_2O)]BCS, 81202-98-4; (−)-[Rh(COD)(*o*-NPTP)(H_2O)]Cl, 81244-28-2; (−)-[Rh(COD)(*p*-NPTP)(H_2O)]Cl, 81244-29-3; (+)-[Rh(COD)(*o*-NPTP)(H_2O)]Cl, 81244-30-6; (+)-[Rh(COD)(*p*-NPTP)(H_2O)]Cl, 81244-31-7; (−)-[Rh(COD)(*o*-NPTP)(H_2O)]PF_6, 81244-32-8; (−)-[Rh(COD)(*p*-NPTP)(H_2O)]PF_6, 81244-33-9; (+)-[Rh(COD)(*o*-NPTP)(H_2O)]PF_6, 81244-34-0; (+)-[Rh(COD)(*p*-NPTP)(H_2O)]PF_6, 81244-35-1; (−)-[Rh(COD)(*o*-NPTP)(H_2O)]ClO_4, 81244-36-2; (−)-[Rh(COD)(*p*-NPTP)(H_2O)]ClO_4, 81244-37-3; (+)-[Rh(COD)(*o*-NPTP)(H_2O)]ClO_4, 81244-38-4; (+)-[Rh(COD)(*p*-NPTP)(H_2O)]ClO_4, 81244-39-5; (±)-[Rh(COD)(*o*-NPTP)$_2$]BCS, 81202-99-5; (±)-[Rh(COD)(*p*-NPTP)$_2$]BCS, 81203-00-1; (−)-[Rh(COD)(*o*-NPTP)$_2$]BCS, 81203-02-3; (−)-[Rh(COD)(*p*-NPTP)$_2$]BCS, 81203-04-5; (+)-[Rh(COD)(*o*-NPTP)$_2$]BCS, 81204-38-8; (−)-[Rh(COD)(*o*-NPTP)$_2$]Cl, 81203-06-7; (−)-[Rh(COD)(*o*-NPTP)$_2$]Cl, 81244-40-8; (−)-[Rh(COD)(*p*-NPTP)$_2$]Cl, 81244-41-9; (+)-[Rh(COD)(*o*-NPTP)$_2$]Cl, 81244-42-0; (+)-[Rh(COD)(*p*-NPTP)$_2$]Cl, 81244-43-1; (−)-[Rh(COD)(*o*-NPTP)$_2$]ClO_4, 81244-44-2; (−)-[Rh(COD)(*p*-NPTP)$_2$]ClO_4, 81244-45-3; (+)-[Rh(COD)(*o*-NPTP)$_2$]ClO_4, 81244-46-4; (+)-[Rh(COD)(*p*-NPTP)$_2$]ClO_4, 81244-47-5; *meso*-[Rh(COD)(*o*-BPTE)]BCS, 81203-07-8; *meso*-[Rh(COD)(*p*-BPTE)]BCS, 81203-08-9; (−)-[Rh(COD)(*o*-BPTE)]BCS, 81203-10-3; (−)-[Rh(COD)(*p*-BPTE)]BCS, 81203-12-5; (+)-[Rh(COD)(*o*-BPTE)]BCS, 81203-14-7; (+)-[Rh(COD)(*p*-BPTE)]BCS, 81203-16-9; (−)-[Rh(COD)(*o*-BPTE)]Cl, 81244-48-6; (−)-[Rh(COD)(*p*-BPTE)]Cl, 81244-49-7; (+)-[Rh(COD)(*o*-BPTE)]Cl, 81244-50-0; (+)-[Rh(COD)(*p*-BPTE)]Cl, 81244-51-1; (−)-[Rh(COD)(*o*-BPTE)]ClO_4, 81244-52-2; (−)-[Rh(COD)(*p*-BPTE)]ClO_4, 81244-53-3; (+)-[Rh(COD)(*o*-BPTE)]ClO_4, 81244-54-4; (+)-[Rh(COD)(*p*-BPTE)]ClO_4, 81244-55-5; *meso*-[Rh(COD)(BNPE)]BCS, 81203-17-0; (−)-[Rh(COD)(BNPE)]BCS, 81204-40-2; (+)-[Rh(COD)(BNPE)]BCS, 81203-19-2; (−)-[Rh(COD)(BNPE)]Cl, 81244-56-6; (+)-[Rh(COD)(BNPE)]Cl, 81244-57-7; (−)-[Rh(COD)(BNPE)]ClO_4, 81244-58-8; (+)-[Rh(COD)(BNPE)]ClO_4, 81244-59-9; (−)-[Rh(COD)(*R*-PDPE)]Cl, 81158-04-5; (−)-[Rh(COD)(*R*-PDPE)]ClO_4, 81203-21-6; *o*-NPTP, 81157-81-5; *p*-NPTP, 81157-82-6; *o*-BPTE, 81157-83-7; *p*-BPTE, 81157-84-8; BNPE, 81157-85-9; [Rh(COD)Cl]$_2$, 12092-47-6; Rh(COD)(acac), 12245-39-5; phenyl-*p*-tolylchlorophosphine, 1016-80-4; phenyl-*o*-tolylchlorophosphine, 41924-67-8; phenyldichlorophosphine, 644-97-3; toluene, 108-88-3; *o*-bromotoluene, 95-46-5; (diethylamino)chlorophenylphosphine, 4073-31-8; α-bromonaphthalene, 90-11-9; ditosylethane, 6315-52-2; (+)-*o*-NPTP, 34069-15-3; (+)-*p*-NPTP, 81157-86-0; (−)-*o*-NPTP, 34069-16-4; (−)-*p*-NPTP, 81157-87-1; (+)-*o*-BPTE, 81157-88-2; (+)-*p*-BPTE, 81157-89-3; (−)-*o*-BPTE, 81157-90-6; (−)-*p*-BPTE, 81157-91-7; (+)-BNPE, 81157-92-8; (−)-BNPE, 81157-93-9; (−)-(*R*-PDPE), 69381-91-5.