A New Optically Active Monodentate Phosphine Ligand, (*R*)-(+)-3-Diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen): Preparation and Use for Palladium-Catalyzed Asymmetric Reduction of Allylic Esters with Formic Acid

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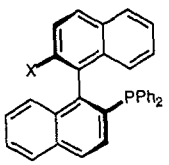
Received 20 January 1994

(*R*)-(+)-3-Diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen, **8**) was prepared starting with (−)-3,3'-dihydroxy-4,4'-biphenanthryl. The absolute configuration of (+)-**8** was determined to be *R* by X-ray crystal structure analysis of its π-allylpalladium complex. The monodentate optically active phosphine **8** was found to be a more enantioselective ligand than (*R*)-(+)-2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (MOP, **1a**) for palladium-catalyzed asymmetric reduction of allylic esters with formic acid giving optically active olefins of up to 85% ee.

We have previously reported that (*R*)-(+)-2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (MOP, **1a**) and its derivatives,[1,2] which are optically active monodentate phosphines bearing a 1,1'-binaphthyl axial chirality, are efficient chiral ligands for several types of palladium-catalyzed asymmetric reactions including asymmetric hydrosilylation of olefins,[3] asymmetric 1,4-hydroboration of 1,3-enynes forming allenylboranes,[4] and asymmetric reduction of allylic esters with formic acid.[5] In these reactions the use of the monodentate chiral phosphine ligand is essential for realization of the high catalytic activity and/or high regioselectivity as well as high enantioselectivity.[6] X-ray crystal structure analysis of palladium complexes $PdCl(\pi^3\text{-}1,1\text{-dimethylallyl})$ (MOP) **(2)**[5] and *trans*-$PdCl_2(MOP)_2$[7] (Figure 1) revealed that the A ring of the naphthyl group on MOP which is substituted with a methoxy group is located close to the central metal on coordination, and the high enantioselectivity observed in the catalytic asymmetric reactions is expected to be due mainly to steric interactions between the A ring and the reacting substrate coordinated to the metal. In order to enhance the enantioselectivity of the chiral monodentate phosphine ligands, we modified the A ring by replacing the naphthyl group by a more bulky phenanthryl group. We report here the preparation of the biphenanthrylmonophosphine and its use for the palladium-catalyzed asymmetric reduction of allylic esters with formic acid which demonstrates its higher enantioselectivity than its binaphthyl analog.



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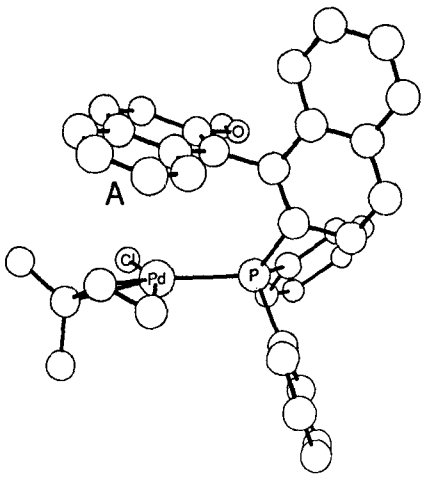
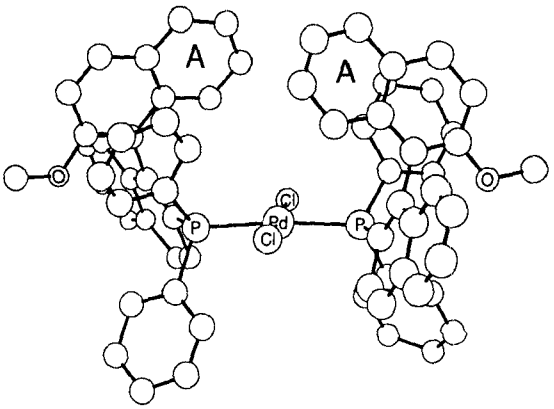
X = OMe: (*R*)-MOP (**1a**)

In our previous report[1] we described the preparation of optically active 2-diphenylphosphino-1,1'-binaphthyls **1** which are substituted with alkoxy or alkyl groups at the 2'-position, by way of 2-diphenylphosphinyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl as a key intermediate, whose preparation had been reported by Morgans, Jr. and co-workers.[8] The optically active monophosphine containing the biphenanthryl skeleton was prepared by a sequence of reactions which are essentially the same as those for the binaphthyl analog **1a** (Scheme 1). The starting (−)-3,3'-dihydroxy-4,4'-biphenanthryl **(3)** {$[\alpha]_D^{20}$ −67 (c = 0.13, chloroform)} was obtained by the HPLC resolution of its racemate with a chiral stationary-phase column (Sumichiral OA-2000). The absolute configuration of diol **3** has previously been assigned by Yamamoto[9] to be (−)-(*S*), but the measurement of the CD spectrum of (−)-**3** in cyclohexane showed a positive Cotton effect at 248 nm and negative Cotton effect at 265 nm, suggesting that (−)-**3** has an *R* configuration.[10] We unambiguously assigned (−)-**3** to have an *R* configuration by X-ray crystal structure analysis of a palladium complex of (+)-MOP-phen **(2)** derived from (−)-**3** (vide infra).

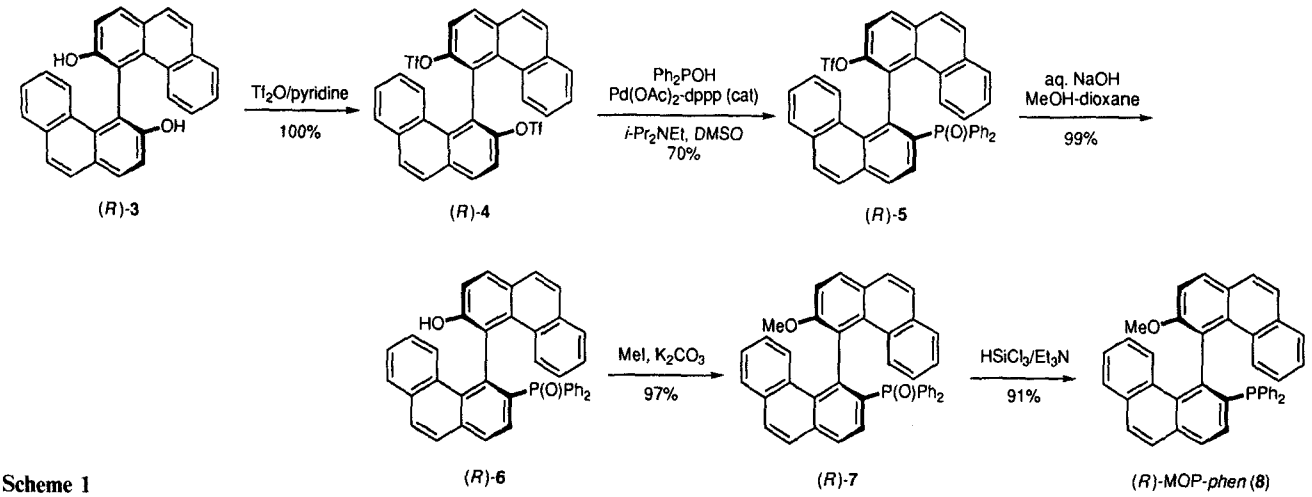


$PdCl(\eta^3\text{-}1,1\text{-dimethylallyl})((R)\text{-MOP})$ (**2**)



trans-$PdCl_2((R)\text{-MOP})_2$

Figure 1. Molecular structure of palladium-MOP (**1a**) complexes.



Scheme 1

The ditriflate (*R*)-**4**, which was obtained from (*R*)-(−)-**3** in a quantitative yield, was subjected to the monophosphinylation with an excess of diphenylphosphine oxide and diisopropylethylamine in the presence of a catalytic amount of palladium diacetate and 1,3-bis(diphenylphosphino)propane (dppp) in dimethyl sulfoxide at 150 °C for 10 h, which gave 70% yield of monophosphine oxide (*R*)-**5**. The phosphinylation was slower than that for the binaphthyl analog and it required a higher reaction temperature and a larger amount of the palladium catalyst. Hydrolysis of the remaining triflate with aqueous sodium hydroxide in 1,4-dioxane and methanol (2:1) gave (*R*)-**6** in 99% yield. The phenolic hydroxy group of (*R*)-**6** was easily methylated by treatment with methyl iodide in the presence of potassium carbonate in acetone to give the methyl ether (*R*)-**7** in 97% yield. Reduction of phosphine oxide in (*R*)-**7** was achieved with trichlorosilane and triethylamine[11] in refluxing toluene to give (*R*)-(−)-MOP-phen **(8)** $\{[\alpha]_D^{20} + 271.6$ ($c = 1.3$, chloroform)$\}$ in 91% yield.

The coordination of MOP-phen **(8)** to a transition metal was studied by X-ray crystal structure analysis of the palladium complex PdCl(η^3-1,1-dimethylallyl) [(*R*)-MOP-phen)] · Et_2O **(9)** (Figures 2 and 3), which was obtained by crystallization of a mixture of (*R*)-MOP-phen and $[PdCl(\eta^3\text{-}1,1\text{-dimethylallyl})]_2$[12] in Et_2O/THF. The π-allylpalladium complex **9** is an important complex as a model for the key intermediate in the palladium-catalyzed asymmetric reduction which will be described below. The absolute configuration of the biphenanthryl axial chirality of MOP-phen was determined to be *R* by the Bijvoet method. The basic structure around palladium atom in **9** is similar to that in its binaphthyl analog **2** (see also Figure 1). Thus, it adopts a square planar geometry with phosphorus and chlorine atoms and two π-allyl carbons where MOP-phen ligand **8** coordinates to palladium with the phosphorus atom as a monodentate ligand. The η^3-1,1-dimethylallyl group coordinates to palladium with the absolute configuration of *R* at the C-2 position, and the C-1 carbon on the π-allyl, which is substituted with two methyl groups, is trans to the phosphorus. The conformation of the biphenanthryl is also similar to that of the MOP analog **2**. The aromatic rings on one of the phenanthryls, which is substituted with methoxy, spreads over the π-allyl moiety on palladium, with the methoxy group being far away from the palladium. The more bulky aromatic groups in close proximity to the π-allyl makes the biphenanthrylphosphine MOP-phen **(8)** a more enantioselective ligand for the palladium-catalyzed asymmetric reduction than the binaphthylphosphine **1**.

The chiral biphenanthrylphosphine ligand, MOP-phen **(8)**, was used for the palladium-catalyzed asymmetric reduction of 3,3-disubstituted methyl 2-propenyl carbonates **10** with formic acid to produce optically active terminal olefins **11** with over 99% regioselectivity (Scheme 2).[5] This catalytic reduction is a transition metal catalyzed reaction which requires a monodentate phosphine ligand for high catalytic activity and regioselectivity.[13]

Biographical Sketch

Tamio Hayashi (born in Gifu, Japan, in 1948) received his Ph. D. degree from Kyoto University in 1975 where he studied with Professor M. Kumada. In the same year he was appointed as Assistant Professor of Kyoto University. In 1989 he was promoted to a Professor in Hokkaido University. He spent the year 1976–1977 as a postdoctral fellow at Colorado State University with Professor L.S. Hegedus.

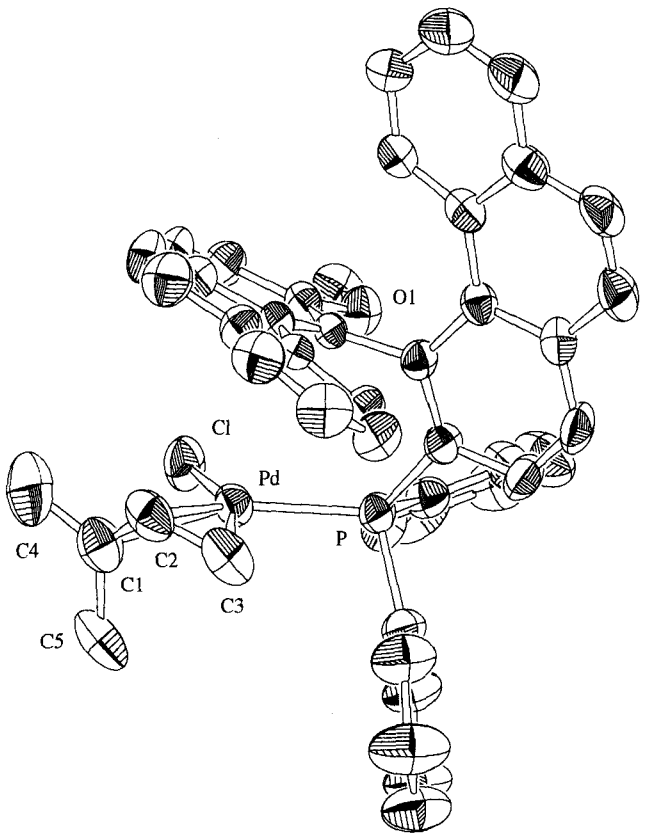


Figure 2. ORTEP drawing of PdCl(η^3-1,1-dimethylallyl)((*R*)-MOP-phen)·Et_2O (**9**). Thermal ellipsoids are drawn with 50% probability boundaries. The ether molecule is omitted for simplicity. Selected bond distances (Å) and angles (deg): Pd-C1, 2.292(6); Pd-C2, 2.149(5); Pd-C3, 2.096(5); Pd-Cl, 2.389(1); Pd-P, 2.303(1); C1-C2-C3, 120.8(6); C1-Pd-C2, 36.7(2); C2-Pd-C3, 38.9(2); C1-Pd-C3, 67.7(2); C1-Pd-Cl, 89.7(1); Cl-Pd-P, 106.17(5); C3-Pd-P, 95.3(2).

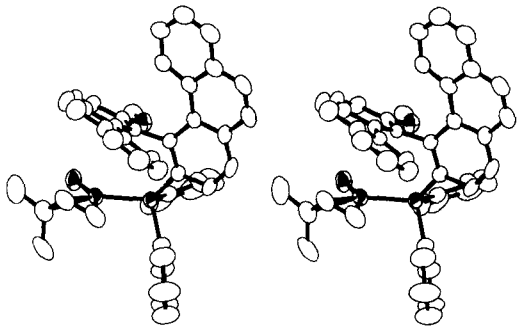


Figure 3. Stereoview of PdCl(η^3-1,1-dimethylallyl)((*R*)-MOP-phen)·Et_2O (**9**).

The results obtained are summarized in Table 1, which also includes those obtained with MOP (**1a**) for comparison. Reaction of geranyl methyl carbonate [(*E*)-**10a**] with formic acid (2.2 equiv) and 1,8-bis(dimethylamino)naphthalene (proton sponge) (1.2 equiv) in the presence of 1 mol% of a palladium catalyst generated in situ from $Pd_2(dba)_3 \cdot CHCl_3$ and (*R*)-MOP-phen (**8**) (P/Pd = 2:1) in dioxane at 20 °C for 17 h proceeded regioselectively to give a quantitative yield of (*S*)-3,7-dimethyl-1,6-octadiene (**11a**) {$[\alpha]_D^{20}$ +8.1 (*c* = 1.6, chloroform); lit.[14] for (*R*)-**11a**, $[\alpha]_D$ −9.82 (*c* = 6.18, chloroform)} (entry 2). The enantiomeric purity was determined to be 85% ee by a HPLC analysis of the dianilide of 2-methylpentanedioic acid (**12a**). The asymmetric reduction of *Z* carbonate, methyl neryl carbonate [(*Z*)-**10a**], under the same reaction conditions gave the olefin (*R*)-**11a** of 82% ee (entry 5). These enantioselectivities obtained with MOP-phen (**8**) are higher by 7–9% than those observed with MOP (**1a**) ligand (entries 1 and 4). The enantioselectivity in the reduction of (*E*)-3-cyclohexyl-2-propenyl carbonate (**10b**) and (*E*)-3-phenyl-2-propenyl carbonate (**10c**) was also improved by use of MOP-phen (**8**) (entries 6, 7, 9, and 10).

Table 1. Asymmetric Reduction of Allylic Carbonates **10** with Formic Acid Catalyzed by Palladium-MOP or Palladium-MOP-phen[a]

Entry	Allylic carbonate	Ligand	Reaction time (h)	Product	Yield[b] (%)	Abs. config.[c]	% ee[d]
1	(*E*)-**10a**	(*R*)-MOP (**1a**)	14	**11a**	95	*S*	76
2	(*E*)-**10a**	(*R*)-MOP-phen (**8**)	17	**11a**	>99	*S*	85
3[e]	(*E*)-**10a**	(*R*)-MOP-phen (**8**)	15	**13a**	93	*S*	84
4	(*Z*)-**10a**	(*R*)-MOP (**1a**)	14	**11a**	99	*R*	75
5	(*Z*)-**10a**	(*R*)-MOP-phen (**8**)	15	**11a**	>99	*R*	82
6	(*E*)-**10b**	(*R*)-MOP (**1a**)	19	**11b**	>99	*R*	71
7	(*E*)-**10b**	(*R*)-MOP-phen (**8**)	22	**11b**	96	*R*	85
8[e]	(*E*)-**10b**	(*R*)-MOP-phen (**8**)	20	**13b**	94	*R*	85
9	(*E*)-**10c**	(*R*)-MOP (**1a**)	15	**11c**	88	*R*	60
10	(*E*)-**10c**	(*R*)-MOP-phen (**8**)	19	**11c**	91	*R*	64

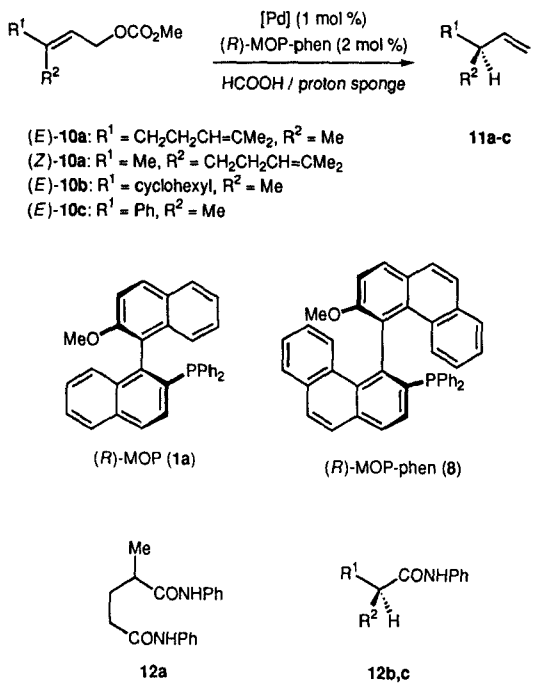
[a] The reduction was carried out at 20 °C with 2.2 equiv of formic acid in dioxane in the presence of 1.2 equiv of 1,8-bis(dimethylamino)-naphthalene and 1.0 mol% of catalyst prepared in situ by mixing $Pd_2(dba)_3 \cdot CHCl_3$ and a chiral ligand (2 equiv to Pd).

[b] Isolated yield by silica gel column chromatography.

[c] Determined by the optical rotation of **11** and **13**. For **11a** in entry 2, $[\alpha]_D^{20}$ +8.1 (*c* = 1.6, $CHCl_3$) (ref 14). For **11b** in entry 7, $[\alpha]_D^{24}$ +4.2 (*c* = 1.9, $CHCl_3$) (ref 19). For **10c** in entry 10, $[\alpha]_D^{25}$ −2.2 (*c* = 0.7, $CHCl_3$) (ref 20). For **13a** in entry 3, $[\alpha]_D^{20}$ +10.4 (*c* = 2.0, $CHCl_3$). For **13b** in entry 8, $[\alpha]_D^{24}$ +6.0 (*c* = 1.0, $CHCl_3$).

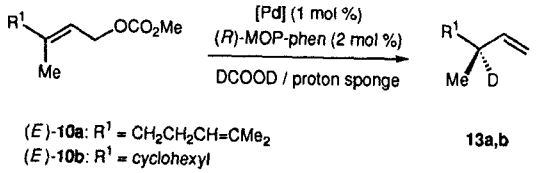
[d] Determined by an HPLC analysis of the dianilide of 2-methylpentanedioic acid (**12a**), *N*-phenyl-2-cyclohexylpropanamide (**12b**), and *N*-phenyl-2-phenylpropanamide (**12c**), obtained through the oxidation ($NaIO_4/KMnO_4$) of the olefins **11**. See experimental section.

[e] Reduction with DCO_2D.



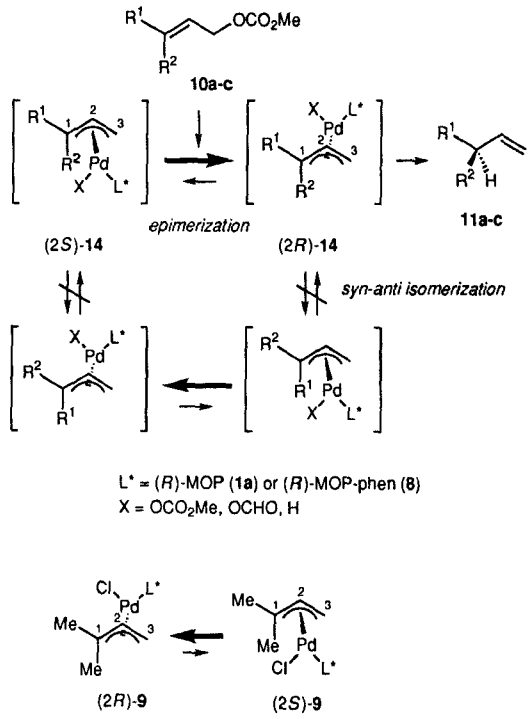
Scheme 2

Asymmetric synthesis of optically active olefins which have a deuterium atom at the stereogenic center in the allylic position was also successful by use of formic acid-d_2 (Scheme 3) (entries 3 and 8 in Table 1). Thus, the reaction of (*E*)-**10a** and (*E*)-**10b** with formic acid-d_2 (DCO_2D) in the presence of 1,8-bis(dimethylamino)-naphthalene and the palladium-MOP-phen catalyst introduced deuterium selectively at the stereogenic center to give the corresponding deuterated olefins (*S*)-**13a** (84% ee) and (*R*)-**13b** (85% ee) with essentially the same enantioselectivity as the reduction with HCO_2H. No deuterium scrambling was observed in the reduction products.



Scheme 3

The reaction pathway in the asymmetric reduction of (*E*)-**10a** and (*Z*)-**10a** which gives the olefin **11a** with opposite absolute configuration has been discussed in the reaction catalyzed by palladium-MOP (**1a**) in our previous paper (Scheme 4).[5] It has been proposed by NMR studies of the model complex PdCl(η^3-1,1-dimethylallyl) [(*R*)-MOP] (**2**) that π-allylpalladium intermediates **14** undergo the epimerization but do not undergo the syn–anti isomerization and the enantiomeric purity of the product is determined mainly by the thermodynamic stability of the epimeric π-allylpalladium intermediates **14**.[5] The asymmetric reduction with the MOP-phen ligand **8** also proceeds by way of the π-allylpalladium intermediates **14**. ^1H and ^{31}P NMR studies of PdCl(η^3-1,1-dimethylallyl)[(*R*)-MOP-phen] (**9**) in $CDCl_3$ revealed that the π-allylpalladium **9** exists as a mixture of isomers which are in an equilibrium state between − 60 and 20 °C, the ratios of the main isomer (2*R*)-**9** to the minor isomer (2*S*)-**9** are 6:1, 10:1, and 13:1 at 20, − 20, and − 60 °C, respectively. The ratios are higher than those observed for the palladium-MOP complex **2** (4.5:1, 5:1, and 6.5:1 at 20, − 20, and − 60 °C, respectively),[5] which is consistent with the higher enantioselectivity of MOP-phen (**8**) over MOP (**1a**) for the present catalytic asymmetric reduction.



Scheme 4

Melting points were measured with a hot-stage microscope (YANACO MP-S3) and are uncorrected. ^1H NMR spectra were measured on a JEOL JNM-EX270 spectrometer (270 MHz) in $CDCl_3$. Chemical shifts of protons are reported in δ ppm referred to tetramethylsilane as an internal standard. ^{31}P NMR spectra were measured on a JEOL JNM-EX270 spectrometer (109 MHz) in $CDCl_3$ using 85% H_3PO_4 as an external standard. Optical rotations were measured on a JASCO DIP-370 polarimeter. EI-mass spectra and high resolution mass spectra were measured on a JEOL JMS-DX 303 spectrometer at an ionization voltage of 70 eV. Silica gel column chromatography was carried out using Merck silica gel 60 (70–325 mesh ASTM). Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. All dry solvents were distilled under N_2. THF and Et_2O were distilled from sodium/benzophenone. Toluene, DMSO, and CH_2Cl_2 were distilled from CaH_2. (−)-3,3′-Dihydroxy-4,4′-biphenanthryl (**3**) was obtained by HPLC resolution of its racemate[9] with Sumichiral OA-2000 (50 mmø × 30 cm, hexane/1,2-dichloroethane/EtOH, 80:15:5). Compounds **4**, **5**, **7–9**, (*E*)-**10b** and (*E*)-**10c** gave C, H ± 0.3%.

(*R*)-(−)-3,3′-Bis(trifluoromethanesulfonyloxy)-4,4′-biphenanthryl (4):

To a solution of (*R*)-(−)-3,3′-dihydroxy-4,4′-biphenanthryl (**3**) {$[\alpha]_D^{20}$ − 67 (*c* = 0.13, chloroform)} (1.91 g, 4.89 mmol) and pyridine (1.97 mL, 24.4 mmol) in CH_2Cl_2 (30 mL) was added trifluoromethanesulfonic anhydride (3.3 mL, 5.5 g, 19.5 mmol) at 0 °C and the mixture was stirred for 1 h. After removal of the solvent, the residue was diluted with 50 mL of EtOAc and then washed with 5% HCl, sat. aq $NaHCO_3$, and brine (once for each). The organic phase was dried (Na_2SO_4), concentrated under reduced pressure, and chro-

matographed on silica gel (elution with CH_2Cl_2) to give **4** as a white powder (3.15 g, 100%): mp 162.5–163 °C; $[\alpha]_D^{20}$ −18.2 (c = 0.4, $CHCl_3$).

^{1}H NMR: δ = 6.97–8.20 (m, aromatics).

(*R*)-(+)-3-Diphenylphosphinyl-3′-trifluoromethanesulfonyloxy-4,4′-biphenanthryl (5):
To a mixture of **4** (3.15 g, 4.84 mmol), diphenylphosphine oxide (2.93 g, 14.5 mmol), palladium diacetate (433 mg, 1.93 mmol), and 1,4-bis(diphenylphosphino)propane (dppp, 796 mg, 1.93 mmol) was added 35 mL of DMSO and diisopropylethylamine (5.2 g, 40.1 mmol), and the mixture was heated with stirring at 150 °C for 10 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure (0.1–0.2 mmHg) to give a dark brown residue. The residue was diluted with EtOAc, and washed with dil. HCl and sat. aq $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed on silica gel (elution with hexane/EtOAc, 1:1) to give **5** as a white solid (2.41 g, 70%): mp 254–255 °C; $[\alpha]_D^{20}$ +15.0 (c = 0.8, $CHCl_3$).

^{1}H NMR: δ = 6.8–8.0 (m, aromatics).

^{31}P NMR: δ = 29.6 (s).

(*R*)-(−)-3-Diphenylphosphinyl-3′-hydroxy-4,4′-biphenanthryl (6):
To a solution of **5** (985 mg, 1.40 mmol) in 2:1 mixture of 1,4-dioxane and MeOH (7.5 mL) was added 3 N aqueous NaOH (5 mL) at r.t. The reaction mixture was stirred for 9 h, acidified (pH ca. 1) by addition of conc. HCl, and then extracted with EtOAc (2 × 30 mL). The organic phase was dried ($MgSO_4$), concentrated under reduced pressure to give pale yellow solid material, which was chromatographed on silica gel (elution with EtOAc) to give **6** as a white solid (794 mg, 99%): mp 178.5–180 °C; $[\alpha]_D^{20}$ −63.4 (c = 0.6, CH_2Cl_2).

^{1}H NMR: δ = 6.26–8.07 (m, 26 H), 8.55 (br s, 1 H).

^{31}P NMR: δ = 32.6 (s).

HRMS: m/z, $C_{40}H_{27}O_2P$, calc.: 570.1771; found: 570.1793.

(*R*)-(+)-3-Diphenylphosphinyl-3′-methoxy-4,4′-biphenanthryl (7):
To a mixture of (*R*)-3-diphenylphosphinyl-3′-hydroxy-4,4′-biphenanthryl (**6**) (792 mg, 1.38 mmol) and K_2CO_3 (1.79 g, 13.0 mmol) in acetone (30 mL) was added MeI (1.85 g, 13.0 mmol), and the reaction mixture was refluxed for 5 h. After cooling to r.t., the mixture was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was concentrated under reduced pressure. The residue was chromatographed on silica gel using hexane/EtOAc (1:3) as eluent to give 781 mg (97%) of **7**: mp 218–219.5 °C; $[\alpha]_D^{20}$ +85.8 (c = 0.5, $CHCl_3$).

^{1}H NMR: δ = 3.43 (s, 3 H), 6.63–7.90 (m, 26 H).

^{31}P NMR: δ = 29.2 (s).

(*R*)-(+)-3-Diphenylphosphino-3′-methoxy-4,4′-biphenanthryl (8):
To a mixture of **7** (185 mg, 0.31 mmol) and Et_3N (1.23 g, 12.1 mmol) in toluene (5 mL) was added Cl_3SiH (617 mg, 4.55 mmol) at 0 °C. The reaction mixture was stirred at 110 °C for 10 h. After cooling to r.t., the mixture was diluted with Et_2O and quenched with small amount of sat. aq $NaHCO_3$. The resulting suspension was filtered through Celite and the solid was washed with Et_2O. The combined organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude phosphine was purified by silica gel column chromatography with hexane/CH_2Cl_2 (1:1) as eluent, giving 161 mg (91%) of **8**: mp 209.5–210 °C (recrystallization from CH_2Cl_2/pentane); $[\alpha]_D^{20}$ +271.6 (c = 1.3, $CHCl_3$).

^{1}H NMR: δ = 3.07 (s, 3 H), 6.58–8.12 (m, 26 H).

^{31}P NMR: δ = −12.3 (s).

PdCl(η^3-Me_2CCHCH_2)[(*R*)-MOP-phen] · Et_2O (9):
A solution of **8** (8.2 mg, 0.014 mmol) and [PdCl(η^3-1,1-dimethylallyl)]$_2$[12] (3.1 mg, 0.007 mmol) in THF (0.5 mL) was placed in a small open bottle (5 mL), and the bottle was placed in a reagent bottle (25 mL) which contained Et_2O (3 mL). After 1d, yellow crystals (7.3 mg, 59%) had formed owing to dispersion of the solvents. The crystals contain one molecule of Et_2O as a crystal solvent.

X-ray Diffraction Study of PdCl(η^3-Me_2CCHCH_2)[(*R*)-MOP-phen] · Et_2O (9):
A single crystal (0.40 × 0.20 × 0.15 mm) of the palladium complex **9** obtained above was sealed in a glass capillary tube. Intensity data were collected on a Rigaku AFC5R diffractometer. Unit cell dimensions were obtained from a least-squares treatment of the setting angles of 25 reflections in the range $25.0 < \theta < 29.3°$. The cell dimensions suggested a monoclinic cell, and systematic absences in the diffractometer data indicated the space group $P2_1$. Diffraction data were collected in the range $5 < 2\theta < 55°$ using the $\omega/2\theta$ scan technique at a scan rate of 8°/min in ω. Three standard reflections, monitored by every 150 reflection measurements, showed no significant variation in the intensities during the data collection. The data were corrected for Lorenz and polarization effects. Of the 5038 unique reflections (R_{int} = 0.090), 3378 reflections were classed as observed [$I > 3\sigma(I)$], and these were used for the solution and refinement of the trial structure. Calculations were performed with the TEXSAN Crystal Structure Analysis Package provided by Rigaku Corp. The scattering factors were taken from International Tables for X-ray Crystallography.[15] The palladium atom was located from a Patterson map, and other non-hydrogen atoms were found by subsequent difference Fourier syntheses. Hydrogen atoms were not located. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized in least squares was $\Sigma w(|F_o| - |F_o|)^2$ ($w = 1/[\sigma^2(F_o)]$). The final R index was 0.045 (R_w = 0.033, S = 1.31). $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$, and $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o is the number of observed data and N_p is the number of parameters varied. The absolute configuration was determined to be (*R*) by Bijvoet utility of Texsan software using 6703 data including Bijvoet reflections. Crystal data and details of data collection and refinement are summarized in Table 2. Positional parameters are listed in Table 3.

Table 2. Crystal Data and Details of the Structure Determination for PdCl(η^3-Me_2CCHCH_2)[(*R*)-MOP-phen] · Et_2O (**9**)

formula	$C_{46}H_{38}Cl_2OPClPd \cdot C_4H_{10}O$
formula weight	853.75
crystal size (mm)	0.40 × 0.20 × 0.15
crystal system	monoclinic
space group	$P2_1$ (# 4)
a (Å)	9.630 (2)
b (Å)	23.752 (3)
c (Å)	9.837 (2)
β (deg)	108.45 (2)
V (Å^3)	2134.5 (7)
Z	2
d_{calc} (g cm^{-3})	1.33
μ (Mo-Kα) (cm^{-1})	5.73
F (000)	884
radiation	Mo-Kα (λ = 0.71069 Å)
monochromator	graphite
data collected	$\pm h, +k, +l$; $\pm h, -k, -l$
maximum 2θ, deg	55.0
scan type	ω-2θ
scan width (deg)	$1.04 + 0.35 \tan\theta$
scan rate (deg min^{-1})	8.0 (in ω)
temperature (K)	298
no. of reflections measured	10942
no. of unique reflections	5038 (R_{int} = 0.090)
no. of observed reflections	3378 with $I > 3\sigma$ (I)
no. of parameters refined	495
R	0.045
R_W	0.033
S	1.31
max shift/error in final cycle	0.07
max and min peak (e/Å^3)	0.86, −0.50

Table 3. Positional and Equivalent Isotropic Thermal Parameters for PdCl(η^3-Me_2CCHCH_2)[(*R*)-MOP-phen] · Et_2O (**9**)

Atom	*x*	*y*	*z*	B_{eq}[a] (Å^2)
Pd	−0.25299(6)	−0.0029	−0.23214(5)	3.32(1)
Cl	−0.1873(2)	−0.0326(1)	0.0122(2)	4.52(5)
P	−0.4669(2)	−0.0493(1)	−0.3508(2)	3.09(5)
O(1)	−0.5855(5)	0.0140(2)	−0.1320(4)	3.8(1)
O(2)	−0.0410(8)	0.2851(4)	0.015(1)	8.6(2)
C(1)	−0.024(1)	0.0344(4)	−0.192(1)	5.1(2)
C(2)	−0.131(1)	0.0607(3)	−0.298(1)	4.8(2)
C(3)	−0.2245(8)	0.0315(4)	−0.4169(8)	5.0(2)
C(4)	0.050(1)	0.0635(5)	−0.055(1)	7.7(3)
C(5)	0.0536(9)	−0.0178(4)	−0.220(1)	6.3(3)
C(6)	−0.6633(7)	0.0439(3)	−0.4059(7)	2.9(2)
C(7)	−0.6322(6)	−0.0092(4)	−0.4494(6)	3.1(2)
C(8)	−0.7330(8)	−0.0359(3)	−0.5679(8)	4.5(2)
C(9)	−0.8593(7)	−0.0100(5)	−0.6395(7)	4.4(2)
C(10)	−0.9003(7)	0.0416(3)	−0.5958(7)	3.4(2)
C(11)	−1.0366(8)	0.0667(4)	−0.6768(8)	4.7(2)
C(12)	−1.0770(8)	0.1159(4)	−0.6381(8)	4.8(2)
C(13)	−0.9915(9)	0.1448(4)	−0.5136(9)	4.3(2)
C(14)	−1.043(1)	0.1950(4)	−0.471(1)	6.0(3)
C(15)	−0.970(1)	0.2215(4)	−0.348(1)	7.7(3)
C(16)	−0.845(1)	0.1974(4)	−0.258(1)	5.6(3)
C(17)	−0.791(1)	0.1501(4)	−0.296(1)	4.2(2)
C(18)	−0.8569(7)	0.1208(3)	−0.4263(8)	3.5(2)
C(19)	−0.8046(7)	0.0685(3)	−0.4720(7)	3.2(2)
C(20)	−0.5461(7)	0.0760(3)	−0.2985(7)	2.6(2)
C(21)	−0.5137(7)	0.0606(3)	−0.1534(7)	3.1(2)
C(22)	−0.4197(8)	0.0927(4)	−0.0437(7)	4.3(2)
C(23)	−0.3640(8)	0.1413(4)	−0.078(1)	4.4(2)
C(24)	−0.3933(8)	0.1597(4)	−0.2190(8)	4.0(2)
C(25)	−0.3374(9)	0.2122(4)	−0.247(1)	5.0(2)
C(26)	−0.366(1)	0.2310(4)	−0.381(1)	5.5(3)
C(27)	−0.4451(8)	0.1993(3)	−0.5004(8)	3.7(2)
C(28)	−0.462(1)	0.2186(4)	−0.639(1)	5.2(2)
C(29)	−0.525(1)	0.1871(4)	−0.756(1)	5.4(3)
C(30)	−0.5774(9)	0.1343(4)	−0.7395(8)	4.4(2)
C(31)	−0.5656(8)	0.1138(3)	−0.6063(8)	3.7(2)
C(32)	−0.4999(7)	0.1459(3)	−0.4793(8)	3.3(2)
C(33)	−0.4814(7)	0.1255(3)	−0.3333(7)	3.2(2)
C(34)	−0.5569(7)	−0.0071(5)	0.0093(7)	4.5(2)
C(35)	−0.4232(8)	−0.0926(3)	−0.4870(7)	3.7(2)
C(36)	−0.377(1)	−0.1472(3)	−0.4574(8)	4.8(2)
C(37)	−0.320(1)	−0.1777(4)	−0.548(1)	6.7(3)
C(38)	−0.308(1)	−0.1528(5)	−0.668(1)	6.7(3)
C(39)	−0.352(1)	−0.0994(5)	−0.701(1)	7.7(3)
C(40)	−0.411(1)	−0.0690(4)	−0.6125(8)	5.9(3)
C(41)	−0.540(1)	−0.1014(3)	−0.2549(8)	3.4(2)
C(42)	−0.686(1)	−0.1161(4)	−0.290(1)	5.5(3)
C(43)	−0.733(1)	−0.1561(5)	−0.217(2)	7.2(4)
C(44)	−0.637(2)	−0.1852(5)	−0.107(1)	7.3(4)
C(45)	−0.488(1)	−0.1720(4)	−0.0683(9)	6.1(3)
C(46)	−0.443(1)	−0.1312(4)	−0.1423(9)	4.5(2)
C(47)	0.064(2)	0.221(1)	0.186(2)	20(1)
C(48)	0.077(2)	0.257(1)	0.113(2)	13.4(7)
C(49)	−0.010(2)	0.3352(7)	−0.028(2)	10.8(5)
C(50)	−0.133(2)	0.3591(6)	−0.136(1)	11.4(5)

[a] $B_{eq} = (4/3)\,\Sigma_i \Sigma_j \beta_{ij}\,\mathbf{a}_i \cdot \mathbf{a}_j$.

NMR Study of PdCl(η^3-Me_2CCHCH_2)[(*R*)-MOP-phen] (9):
(*R*)-MOP-phen (**8**) (2.0 mg, 0.0035 mmol) and [PdCl(η^3-1,1-dimethylallyl)]$_2$[12] (0.74 mg, 0.0017 mmol) were placed in an NMR sample tube. The tube was filled with nitrogen, and $CDCl_3$ (0.5 mL) was added. ^{1}H NMR and ^{31}P{^{1}H}NMR spectra were measured at 20, −20, and −60 °C. The spectra at −20 °C are shown below. The ratios of major isomer (2*R*)-**9** to minor isomer (2*S*)-**9** are shown in the text.

Major isomer (2*R*)-**9**:
^{1}H NMR: δ = 0.77 (d, J_{H-P} = 5.0 Hz, 3 H, *anti*-Me on C-1), 1.18 (d, J_{H-P} = 9.9 Hz, 1 H, *anti*-H on C-3), 1.26 (d, J = 8.6 Hz, 3 H, *syn*-Me on C-1), 1.91 (d, J = 6.6 Hz, 1 H, *syn*-H on C-3), 2.48 (dd, J = 6.6, 9.9 Hz, 1 H, H on C-2), 3.22 (s, 3 H, OMe), 6.42–8.08 (m, 26 H, aromatics).
^{31}P{^{1}H} NMR: δ = 22.2 (s).
Minor isomer (2*S*)-**9**: ^{31}P{^{1}H} NMR: δ = 32.8 (s).

Catalytic Asymmetric Reduction of Allylic Carbonates; Preparation of Allylic Carbonates (10):
(*E*)-3-cyclohexyl-2-butenol,[16] (*E*)-3-phenyl-2-butenol,[17] (*E*)-**10a**,[18] and (*Z*)-**10a**[18] were prepared according to the reported procedures. Carbonates (*E*)-**10b** and (*E*)-**10c** were obtained by treatment of the corresponding alcohols with methyl chloroformate and pyridine.[18]

(*E*)-**10b**:
^{1}H NMR: δ = 1.15–1.92 (m, 11 H), 1.70 (s, 3 H), 3.79 (s, 3 H), 4.66 (d, J = 7.0 Hz, 2 H), 5.36 (t, J = 7.0 Hz, 1 H).

(*E*)-**10c**:
^{1}H NMR: δ = 2.13 (s, 3 H), 3.80 (s, 3 H), 4.85 (d, J = 6.9 Hz, 2 H), 5.91 (t, J = 6.9 Hz, 1 H), 7.24–7.42 (m, 5 H).

Catalytic Asymmetric Reduction of Allylic Carbonates; Typical Procedure:
Under nitrogen, a solution of (*R*)-MOP-phen (**8**) (6.24 mg, 0.011 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (2.6 mg, 0.0025 mmol) in dioxane (1.0 mL) was stirred at r. t. In about 30 min, the dark-red solution turned orange. The solution was cooled to 0 °C, and 1,8-bis(dimethylamino)naphthalene (128.8 mg, 0.60 mmol), formic acid (52.5 mg, 1.14 mmol), and geranyl methyl carbonate (*E*)-**10a** (104.5 mg, 0.49 mmol) were added. The mixture was stirred at 20 °C for 17 h. The completion of the reduction was confirmed by GLC. Pentane and water were added to the reaction mixture, the organic phase was separated, and passed through short silica gel column to give (*S*)-3,7-dimethyl-1,6-octadiene (**11a**) (68.0 mg, >99% yield). {$[\alpha]_D^{20}$ + 8.1 (*c* = 1.6, $CHCl_3$), lit[14] for (*R*)-**11a**: $[\alpha]_D$ −9.82 (*c* = 6.18, $CHCl_3$)}. The results including optical rotation data obtained for other carbonates are summarized in Table 1. The reported specific rotations for (*R*)-**11b** (89% ee)[19] and (*R*)-**11c**[20] are $[\alpha]_D^{24}$ + 4.1 (*c* = 0.7, $CHCl_3$) and $[\alpha]_D^{22}$ − 5.91 (neat), respectively. The ^{1}H NMR spectra for the reduction products are shown below.

11a: ^{1}H NMR: δ = 0.98 (d, J = 7.0 Hz, 3 H), 1.27–1.36 (m, 2 H), 1.60 (s, 3 H), 1.67 (s, 3 H), 1.96 (q, J = 7.0 Hz, 2 H), 2.12 (heptet, J = 7.0 Hz, 1 H), 4.90 (d, J = 10.1 Hz, 1 H), 4.92 (d, J = 17.1 Hz, 1 H), 5.05–5.15 (m, 1 H), 5.70 (ddd, J = 17.1, 10.1, 7.0 Hz, 1 H).

11b: ^{1}H NMR: δ = 0.98 (d, J = 6.9 Hz, 3 H), 0.92–1.78 (m, 11 H), 1.91–2.04 (m, 1 H), 4.88–4.94 (m, 2 H), 5.68 (m, 1 H).

11c: ^{1}H NMR: δ = 1.39 (d, J = 6.8 Hz, 3 H), 3.48 (quintet, J = 6.8 Hz, 1 H), 5.02 (d, J = 10.5 Hz, 1 H), 5.05 (d, J = 16.0 Hz, 1 H), 6.02 (ddd, J = 6.8, 10.5, 16.0 Hz, 1 H), 7.19–7.34 (m, 5 H).

13a: ^{1}H NMR: δ = 0.98 (s, 3 H), 1.30 (t, J = 6.8 Hz, 2 H), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.96 (q, J = 6.8 Hz, 2 H), 4.89 (d, J = 9.9 Hz, 1 H), 4.91 (d, J = 17.1 Hz, 1 H), 5.05–5.15 (m, 1 H), 5.70 (dd, J = 17.1, 9.9 Hz, 1 H).

13b: ^{1}H NMR: δ = 0.95 (s, 3 H), 0.88–1.78 (m, 11 H), 1.91–2.04 (m, 1 H), 4.88–4.94 (m, 2 H), 5.65–5.76 (m, 1 H).

Catalytic Asymmetric Reduction of Allylic Carbonates; Determination of Enantiomeric Purities:
Olefins **11a, b, c** were converted into the dianilide of 2-methylpentanedioic acid (**12a**),[21] *N*-phenyl-2-cyclohexylpropanamide (**12b**),[22] and *N*-phenyl-2-phenylpropanamide (**12c**),[23] respectively, by oxidation with $NaIO_4/KMnO_4$ followed by treatment of the resulting carboxylic acids with aniline and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC). The conditions for the determination of the enantiomeric purities of **12** with chiral stationary phase columns were as follows. **12a**: Sumichiral OA-4100; hexane/1,2-dichloroethane/EtOH, 50:15:1; *R* isomer eluted faster than *S* isomer. **12b**

and **12c**: Sumichiral OA-2000; hexane/1,2-dichloroethane/EtOH, 250:20:1; *S* isomers eluted faster than *R* isomers.

A typical procedure for the conversion: To a solution of (*S*)-**11a** (61 mg, 0.44 mmol) in *t*-BuOH (10 mL) and water (20 mL), were added $KMnO_4$ (185 mg, 1.17 mmol), $NaIO_4$ (1.46 g, 6.86 mmol), and K_2CO_3 (366 mg, 2.64 mmol), and the mixture was adjusted to pH 8 with 3 N aq NaOH. After stirring at r.t. for 2 h, the mixture was acidified with conc. hydrochloric acid to pH 1 and sodium hydrogen sulfite was added to reduce MnO_2. The mixture was extracted with Et_2O, and the ether layer was extracted with 3 N aq NaOH. The aqueous solution was acidified with conc. hydrochloric acid and extracted with Et_2O. The ether extracts were dried ($MgSO_4$) and evaporation of the solvent gave 2-methylpentanedioic acid (38 mg). To a solution of the carboxylic acid (10 mg) obtained above in THF (0.5 mL), were added aniline (15 mg, 0.16 mmol) and WSC (30 µL), and the mixture was stirred at 40 °C for 1 h. Conc. hydrochloric acid was added and the mixture was extracted with EtOAc. Evaporation of the solvent followed by silica gel column chromatography (hexane/EtOAc, 1:1) gave **12a** (11 mg).

We thank the Ministry of Education, Japan for Grant-in-Aid for Scientific Research and Asahi Glass Foundation for partial financial support of this work.

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