Table X lists these ϕ values and shows that the overlap between the ligands is fairly closely matched in the cis isomer. Contrariwise, ϕ values are substantially larger in the trans complex, where steric restrictions on PTZ are less stringent. Figures 2 and A[53] illustrate the overlap for the cis isomer, while Figures B[53] and C[53] illustrate the overlap for the trans isomer. Distances between the atoms of PTZ and the associated mean bpy plane average 3.2 (5) Å in the cis isomer and 3.0 (7) Å in the trans isomer. Since these interligand stacking distances are of the same magnitude as those observed (3.37 Å)[54,55] when PTZ associates with aromatic molecules in the solid state, it is possible that they reflect strong π–π attraction between the PTZ and bpy ligands. Such interligand stacking phenomena may be of interest to the design and synthesis of molecular conductors.

In both structures, each independent (PTZ)N–H group is involved in a strong hydrogen bond to either a fluorine atom of hexafluorophosphate or to the solvated water molecule. In the cis complex these values are HN12···O(w) = 2.115 Å, HN5···F9 = 2.327 Å, HN6···F12 = 2.127 Å, and HN11···F6 = 2.366 Å; in the trans complex they are HN6···O1 = 1.882 Å and HN3···F12 = 2.291 Å.

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Supplementary Material Available: Thermal parameters (Table A for cis and Table B for trans), hydrogen positional parameters (Table C for cis and Table D for trans), bond lengths (Table E for cis and Table F for trans), bond angles (Table G for cis and Table H for trans), least-squares planes (Table I for cis and Table J for trans), PLUTO drawings of the cis (Figure A) and trans complexes (Figures B and C), and average bond lengths and angles in the coordinated PTZ ligands (Figure D) (29 pages); observed and calculated structure factors (Table K for cis and Table L for trans) (84 pages). Ordering information is given on any current masthead page.

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BINAP-Ruthenium(II) Dicarboxylate Complexes: New, Highly Efficient Catalysts for Asymmetric Hydrogenations

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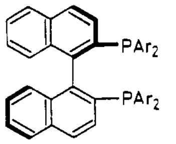
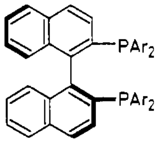
The BINAP–ruthenium(II) complexes $Ru(OCOR)_2$[(*R*)- or (*S*)-2,2′-bis(diarylphosphino)-1,1′-binaphthyl] [aryl = phenyl, *p*-tolyl; R = CH_3, $C(CH_3)_3$] have been prepared. The crystal structure of $Ru[OCOC(CH_3)_3]_2$[(*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl], determined by X-ray crystallography [diffraction data collected at −60 °C, formula $C_{54}H_{50}O_4P_2Ru$, monoclinic, space group $P2_1$, $Z = 2$, $a = 13.272$ (2) Å, $b = 16.224$ (3) Å, $c = 12.701$ (2) Å, $\beta = 124.34$ (1)°, $R = 0.037$, $R_w = 0.043$], indicates that the monomeric ruthenium(II) complex has a distorted octahedron coordination geometry involving two phosphorus atoms of BINAP and four oxygen atoms of pivalate ligands. The complex has a Λ structure, while the BINAP-containing seven-membered chelate ring is fixed in a δ conformation. The molecular structure has been compared with that of Rh[(*R*)-BINAP](norbornadiene)ClO_4. These BINAP–ruthenium complexes serve as highly efficient catalysts for asymmetric hydrogenations of various enamides, α-(acylamino)acrylic acids, α,β- and β,γ-unsaturated carboxylic acids, allylic and homoallylic alcohols, α-amino ketones, etc.

Introduction

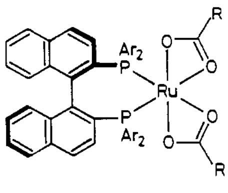
Homogeneous asymmetric hydrogenation with transition metal complexes possessing chiral ditertiary phosphine ligands provides a powerful tool for chemical multiplication of chirality. So far the highly stereoselective reactions have been achieved mainly by the Rh(I)-based complexes. We here report synthesis and structures of new mononuclear Ru(II) complexes (**3**) containing axially dissymmetric (*R*)- or (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*R*)- or (*S*)-BINAP] and its derivatives (**1** and **2**).[2] These complexes exhibit very high catalytic activity and enantioselectivity in hydrogenation of a wide range of substrates such as enamides,[3] α-(acylamino)acrylic acids,[4] alkyl- and aryl-substituted acrylic acids,[5] β,γ-unsaturated carboxylic acids,[5] allylic and homoallylic alcohols,[6] α-amino ketones,[7] etc.[8] The Ru complexes are in many cases superior to the corresponding



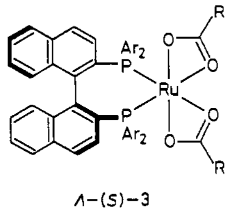
(*R*)-**1**: Ar = C_6H_5
(*R*)-**2**: Ar = *p*-$CH_3C_6H_4$



(*S*)-**1**: Ar = C_6H_5
(*S*)-**2**: Ar = *p*-$CH_3C_6H_4$



Δ-(*R*)-**3**



Λ-(*S*)-**3**

a: R = CH_3, Ar = C_6H_5
b: R = $(CH_3)_3C$, Ar = C_6H_5
c: R = CH_3, Ar = *p*-$CH_3C_6H_4$

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Rh complexes and are now becoming some of the most useful catalysts in this field.

Experimental Section

General Comments. 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, **1**) and 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl (*p*-Tol-BINAP, **2**) were synthesized by the method previously reported.[2c] The complex [RuCl$_2$(cod)]$_n$[9] (cod = cyclooctadiene) and sodium *tert*-butoxide[10] were prepared according to literature methods. Sodium acetate was dried over phosphorus pentoxide under vacuum before use. All solvents and liquid reagents were dried by standard methods and distilled under argon.

Infrared (IR) spectra were recorded on a Hitachi 295 spectrophotometer. Nuclear magnetic resonance [^{1}H (400 MHz), ^{13}C (100 MHz), and ^{31}P (161 MHz) NMR] spectra were measured on a JEOL JNM-GX400 spectrometer. ^{1}H and ^{13}C NMR spectra are reported in ppm relative to an internal tetramethylsilane standard. ^{31}P NMR spectra were measured with 85% phosphoric acid as an external standard. CD spectra were taken on a JASCO J-40C spectrometer for a $(5.2-7.5) \times 10^{-5}$ M solution of **3** in dichloromethane. All melting points were uncorrected. Elemental analyses were performed either at Wako Pure Chemical Industry, Ltd., or at the Elemental Analysis Laboratory, Institute for Molecular Science.

Synthesis of BINAP–Ru(II) Complexes (3). The following procedure for the synthesis of Ru(OCOCH$_3$)$_2$[(*S*)-BINAP] [Λ-(*S*)-**3a**] is illustrative for all BINAP–Ru(II) dicarboxylate complexes. To a mixture of [RuCl$_2$(cod)]$_n$ [0.56 g, 2.0 mmol per RuCl$_2$(cod)] and (*S*)-BINAP (1.37 g, 2.20 mmol) placed in a 250-mL Schlenk tube were added dry toluene (55 mL) and triethylamine (1.2 mL, 8.6 mmol) under argon. This brown suspension was heated at reflux with stirring for 12 h. The resulting clean red-brown solution was cooled to room temperature, and the solvent was removed under vacuum to leave a brown solid. This was dissolved in dichloromethane (40 mL). Insoluble material was removed by filtration through a pad of Celite 545, and the filtrate was concentrated under vacuum. To the residue were added anhydrous sodium acetate (0.88 g, 11 mmol) and *tert*-butyl alcohol (107 mL). The mixture was stirred at reflux temperature for 12 h under argon, and then the solvent was removed under reduced pressure. The resulting solid was extracted with three 20-mL portions of absolute ether, and the combined extracts were evaporated under reduced pressure. The brown residue was extracted repeatedly with absolute ethanol (total volume of 70 mL). Removal of the solvent afforded a yellow brown solid (1.58 g). Recrystallization of the solid from a mixture of toluene (12 mL) and hexane (30 mL) gave 1.23 g (68% yield) of Λ-(*S*)-**3a** as yellow fine needles, mp 185–187 °C dec. This sample is pure enough for use as catalyst for asymmetric hydrogenation. The analytically pure sample (0.90 g, 50% yield) was obtained by further recrystallization of the product from a mixture of toluene (14 mL) and hexane (13 mL); mp 188–190 °C dec. The combined mother liquors were concentrated, and the residue was recrystallized from a mixture of toluene (8 mL) and hexane (10 mL) to afford an additional 0.30 g (17%) of Λ-(*S*)-**3a**, mp 186–188 °C dec. ^{1}H NMR (CDCl$_3$): δ 1.80 (s, 2 OCOCH$_3$), 6.47–7.84 (m, aromatic protons). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 65.13 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 23.50 (OCO*C*H$_3$), 125.2–138.3 (aromatic carbons), 188.1 (O*C*OCH$_3$). IR (CH$_2$Cl$_2$): 1452, 1518 cm^{-1} (acetate). Anal. Calcd for C$_{48}$H$_{38}$O$_4$P$_2$Ru: C, 68.5: H, 4.6. Found: C, 68.8; H, 4.8.

Similarly the complexes Ru[OCOC(CH$_3$)$_3$]$_2$[(*S*)-BINAP] [Λ-(*S*)-**3b**], Ru(OCOCH$_3$)$_2$[(*R*)-*p*-TolBINAP] [Δ-(*R*)-**3c**], and their enantiomers were prepared. Recrystallization of the crude products from ethyl acetate or a mixture of toluene and hexane (1:7) afforded Λ-(*S*)-**3b** and Δ-(*R*)-**3c** in 71% and 87% yield, respectively. The following data were obtained.

Table I. Crystal Data and Data Collection Parameters of Ru[OCOC(CH$_3$)$_3$]$_2$[(*S*)-BINAP] [Λ-(*S*)-**3b**]

formula	C$_{54}$H$_{50}$O$_4$P$_2$Ru
fw	926.0
cryst syst	monoclinic
space group	$P2_1$
a, Å	13.272 (2)
b, Å	16.224 (3)
c, Å	12.701 (2)
β, deg	124.34 (1)
V, Å^3	2258.3 (7)
Z	2
d_{calcd}, g cm^{-3}	1.362
λ, Å	0.71069 (Mo Kα)
cryst size, mm	0.20 × 0.25 × 0.40
μ(Mo Kα), cm^{-1}	4.604
diffractometer	Rigaku AFC-5
monochromator	graphite
temp, °C	−60
scan type	θ–2θ scan
scan range, deg	$1.2 \times 0.5 \tan\theta$
bkgd, s	8
scan speed, deg/min	3
stds	3 every 100 rflns
data collected	$\pm h,k,l$
$2\theta_{max}$, deg	60.0
total rflns measd	6020
indep rflns used	2560 ($\lvert F_o\rvert \geq 3\sigma(F_o)$)
$R_{int}(F)$	0.029 for 100 sym related pairs of rflns
weighting scheme	$w = [\sigma_c^2 + (0.015\lvert F_o\rvert)^2]^{-1}$
no. of variables	679
R	0.037
R_w	0.043
goodness of fit	2.017
$\Delta\rho_{max}$, $\Delta\rho_{min}$ in diff map, e Å^{-3}	0.88, −0.47

Λ-(*S*)-3b. Mp 247–250 °C dec. ^{1}H NMR (CDCl$_3$): δ 0.89 [s, 2 OCOC(CH$_3$)$_3$], 6.35–7.80 (m, aromatic protons). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 65.54 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 26.79 [OCOC(*C*H$_3$)$_3$], 39.39 [OCO*C*(CH$_3$)$_3$], 125.0–138.4 (aromatic carbons), 195.0 [O*C*OC(CH$_3$)$_3$]. IR (CH$_2$Cl$_2$): 1417 cm^{-1} (pivalate). Anal. Calcd for C$_{54}$H$_{50}$O$_4$P$_2$Ru: C, 70.0; H, 5.4. Found: C, 69.5; H, 5.2.

Δ-(*R*)-3c. Mp 183–187 °C dec. ^{1}H NMR (CDCl$_3$): δ 1.70 (s, 2 CH$_3$), 1.76 (s, 2 CH$_3$), 2.31 (s, 2 CH$_3$), 6.20–7.67 (m, aromatic protons). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 63.80 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 20.86, 21.37, 23.33 (three lines due to methyl groups), 124.5–139.5 (aromatic carbons), 187.60 (O*C*OCH$_3$). IR (CH$_2$Cl$_2$): 1449, 1518 cm^{-1} (acetate). Anal. Calcd for C$_{52}$H$_{46}$O$_4$P$_2$Ru: C, 69.6; H, 5.2. Found: C, 70.1; H, 5.4.

X-ray Data Collection for Ru[OCOC(CH$_3$)$_3$]$_2$[(*S*)-BINAP] [Λ-(*S*)-3b]. Dark red air-sensitive plates were grown from a solution of the complex in ethyl acetate. A suitable single crystal was sealed in a thin-walled glass capillary tube under argon saturated with ethyl acetate vapor. Diffraction data were collected on a Rigaku AFC-5 automated four-circle diffractometer at −60 °C with graphite-monochromated Mo Kα radiation. Forty-nine accurately centered reflections in the range $18° < 2\theta < 30°$ were used for the least-squares refinement of the unit cell parameters. The details of data collection and the final cell dimensions are given in Table I. If $\lvert F_o\rvert$ was less than $3\sigma(F_o)$, the reflection was considered to be unobserved. Three standard reflections were monitored every 100 reflections and showed no systematic decrease in intensity, for which no correction was made. The intensities were corrected for Lorentz and polarization factors and used in the structure determination. Corrections for absorption and extinction effects were not made.

Structure Determination and Refinement. The systematic absence ($0k0$) with $k = 2n$ indicated the space group $P2_1$ or $P2_1/m$. The noncentrosymmetric space group $P2_1$ was consistent with the optically active complex. The initial position of the Ru atom was determined by the Patterson maps. A series of Fourier synthesis and block-diagonal least-squares calculation revealed the positions of all the non-hydrogen atoms. The positions of the hydrogen atoms except for those on pivaloyl groups could be located from the subsequent difference Fourier maps. At the final stage, block-diagonal least-squares calculations with anisotropic thermal parameters for non-hydrogen atoms and with isotropic thermal parameters for hydrogen atoms were carried out. The final refinement gave values of $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert = 0.037$ and $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2} = 0.043$. A weighting scheme, $1/w = \sigma_c^2 + (0.015\lvert F_o\rvert)^2$, was employed, where σ_c defined as $\sigma_c = (N)^{1/2}$ is a

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Table II. Selected Bond Distances and Angles with Esd's of $Ru[OCOC(CH_3)_3]_2[(S)\text{-BINAP}]$ [Λ-(*S*)-**3b**]

	Bond Distances (Å)		
Ru–P1	2.241 (3)	Ru–P2	2.239 (3)
Ru–O1	2.216 (8)	Ru–O2	2.116 (7)
Ru–O3	2.137 (6)	Ru–O4	2.185 (7)
P1–C1	1.839 (8)	P1–C21	1.824 (10)
P1–C27	1.840 (12)	P2–C11	1.849 (9)
P2–C33	1.856 (12)	P2–C39	1.839 (11)
O1–C45	1.268 (11)	O2–C45	1.279 (12)
O3–C50	1.268 (13)	O4–C50	1.266 (10)
	Bond Angles (deg)		
P1–Ru–P2	90.6 (1)	P1–Ru–O1	164.5 (2)
P1–Ru–O2	104.1 (2)	P1–Ru–O3	95.4 (2)
P1–Ru–O4	95.3 (2)	P2–Ru–O1	92.6 (2)
P2–Ru–O2	95.3 (2)	P2–Ru–O3	105.8 (2)
P2–Ru–O4	165.1 (2)	O1–Ru–O2	60.6 (2)
O1–Ru–O3	98.4 (3)	O1–Ru–O4	85.5 (3)
O2–Ru–O3	151.1 (2)	O2–Ru–O4	96.6 (3)
O3–Ru–O4	60.0 (3)	Ru–P1–C1	112.1 (4)
Ru–P1–C21	123.3 (3)	Ru–P1–C27	111.8 (3)
C1–P1–C21	100.6 (5)	C1–P1–C27	103.0 (5)
C21–P1–C27	103.7 (6)	Ru–P2–C11	114.8 (4)
Ru–P2–C33	108.6 (3)	Ru–P2–C39	123.1 (4)
C11–P2–C33	104.1 (5)	C11–P2–C39	100.0 (5)
C33–P2–C39	104.1 (5)	Ru–O1–C45	88.4 (6)
Ru–O2–C45	92.6 (5)	Ru–O3–C50	92.5 (5)
Ru–O4–C50	90.4 (6)	O1–C45–O2	118.3 (10)
O3–C50–O4	117.1 (9)		

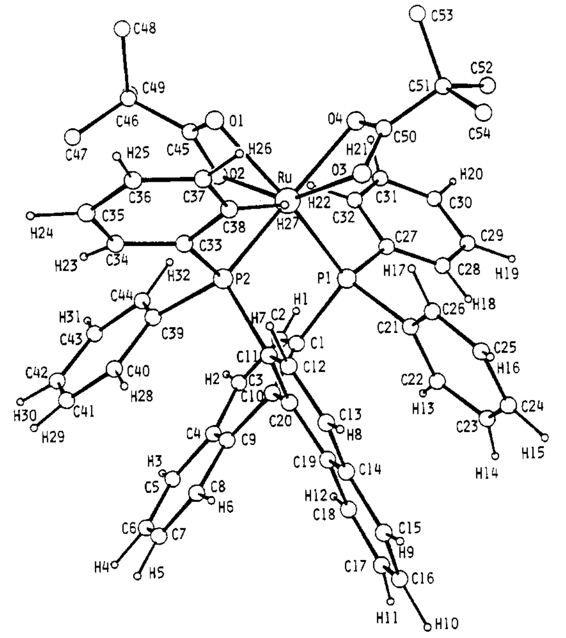

Figure 1. Perspective view of the complex Λ-(*S*)-**3b** with the atom-numbering scheme.

counting statistics error with Gaussian distribution function $P(N) = (\bar{N}/2)^{1/2} \exp[-(N - \bar{N})^2/2\bar{N}]$. The atomic scattering factors and the anomalous-scattering corrections were taken from ref 11. The absolute configuration of the complex was determined to be Λ by being correlated with the known configuration of the (*S*)-BINAP ligand. Selected bond distances and angles and atomic parameters of non-hydrogen atoms are listed in Tables II and III, respectively. The structure of the complex with the numbering scheme and a stereoscopic view are shown in Figures 1 and 2, respectively. Listings of bond distances and angles, atomic parameters of hydrogen atoms, and anisotropic temperature factors and structure factor tables are available as supplementary material. The calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS III.[12]

Table III. Atomic Parameters (×10^4) of $Ru[OCOC(CH_3)_3]_2[(S)\text{-BINAP}]$ [Λ-(*S*)-**3b**][a]

atom	*x*	*y*	*z*	B_{eqv}
Ru	5453 (1)	7249 (1)	3618 (1)	1.6
P1	3524 (2)	7568 (2)	2901 (2)	1.6
P2	5191 (2)	7771 (2)	1848 (2)	1.7
O1	7147 (6)	6596 (4)	4154 (6)	2.5
O2	5358 (5)	6001 (4)	3082 (6)	2.0
O3	6262 (6)	8212 (4)	5007 (6)	2.0
O4	6032 (6)	7009 (4)	5577 (5)	2.3
C1	2452 (7)	7323 (8)	1200 (8)	1.5
C2	1826 (9)	6570 (7)	847 (9)	2.4
C3	1075 (9)	6337 (6)	−411 (10)	2.9
C4	925 (8)	6839 (6)	−1381 (8)	2.2
C5	156 (9)	6628 (7)	−2706 (9)	3.0
C6	46 (9)	7123 (9)	−3625 (8)	3.1
C7	685 (9)	7861 (7)	−3299 (9)	2.8
C8	1443 (9)	8097 (7)	−2081 (9)	2.6
C9	1578 (8)	7601 (6)	−1072 (8)	1.7
C10	2335 (8)	7840 (5)	268 (8)	1.4
C11	4242 (8)	8713 (6)	1233 (8)	1.6
C12	4799 (8)	9514 (6)	1510 (10)	2.4
C13	4114 (9)	10210 (6)	1121 (10)	2.9
C14	2843 (9)	10187 (6)	426 (9)	2.3
C15	2119 (9)	10909 (6)	−16 (10)	2.7
C16	877 (10)	10872 (7)	−726 (11)	3.3
C17	299 (8)	10099 (7)	−985 (9)	2.9
C18	948 (9)	9395 (6)	−546 (9)	2.2
C19	2271 (8)	9405 (6)	165 (9)	1.8
C20	2979 (8)	8665 (6)	568 (8)	1.5
C21	3032 (8)	8609 (6)	2949 (8)	1.8
C22	1789 (9)	8807 (6)	2302 (9)	2.4
C23	1444 (9)	9612 (7)	2358 (10)	2.7
C24	2291 (10)	10217 (7)	2979 (10)	3.0
C25	3510 (10)	10039 (7)	3587 (11)	3.3
C26	3885 (9)	9247 (7)	3601 (9)	2.3
C27	2957 (8)	6937 (6)	3667 (8)	1.9
C28	2152 (9)	7170 (9)	3943 (9)	3.0
C29	1709 (12)	6677 (8)	4466 (12)	4.4
C30	2124 (11)	5858 (8)	4760 (9)	3.4
C31	2953 (10)	5613 (7)	4524 (10)	3.1
C32	3388 (9)	6125 (6)	3993 (10)	2.5
C33	6696 (8)	8107 (6)	2221 (9)	2.0
C34	7156 (9)	7863 (8)	1565 (11)	3.6
C35	8313 (12)	8123 (10)	1910 (12)	5.2
C36	8992 (10)	8621 (8)	2990 (11)	4.2
C37	8559 (9)	8865 (7)	3664 (10)	3.0
C38	7437 (9)	8590 (7)	3320 (9)	2.4
C39	4516 (7)	7182 (9)	358 (7)	2.0
C40	4332 (9)	7540 (7)	−751 (9)	2.8
C41	3729 (8)	7114 (9)	−1888 (8)	3.0
C42	3314 (9)	6326 (7)	−1959 (9)	3.1
C43	3454 (9)	5967 (6)	−912 (10)	2.6
C44	4061 (9)	6385 (6)	265 (9)	2.3
C45	6503 (8)	5967 (6)	3570 (9)	2.0
C46	7073 (9)	5212 (6)	3383 (9)	2.6
C47	7040 (18)	5343 (12)	2227 (15)	9.3
C48	8405 (14)	5097 (10)	4516 (14)	7.7
C49	6372 (17)	4447 (9)	3281 (21)	9.3
C50	6390 (8)	7748 (5)	5877 (8)	1.8
C51	6907 (10)	8036 (7)	7216 (9)	2.6
C52	6085 (12)	7728 (9)	7616 (11)	4.7
C53	8187 (10)	7627 (8)	8093 (10)	4.8
C54	7016 (13)	8993 (8)	7315 (11)	5.6

[a] Thermal parameters are given by the equivalent temperature factors ($Å^2$).

Results and Discussion

Treatment of $[RuCl_2(cod)]_n$ with (*S*)-BINAP [(*S*)-**1**] and triethylamine in toluene at 110 °C and then with sodium acetate in *tert*-butyl alcohol at 80 °C afforded $Ru(OCOCH_3)_2[(S)\text{-BINAP}]$ [(*S*)-**3a**] in good yield after recrystallization from a mixture of toluene and hexane. Similar reactions with BINAP ligands, **1** or **2**, and sodium acetate or pivalate gave the enantiomeric complexes **3b** and **3c**. Thus the present method allows us to obtain complexes of type **3** with high purity and in good yields. Elemental analyses and spectroscopic data[13] supported the stoichiometry of

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(11) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(12) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.

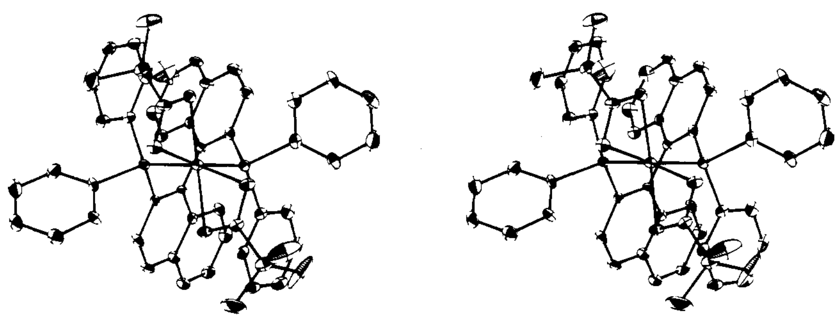

Figure 2. Stereoscopic view of the complex Λ-(*S*)-**3b**.

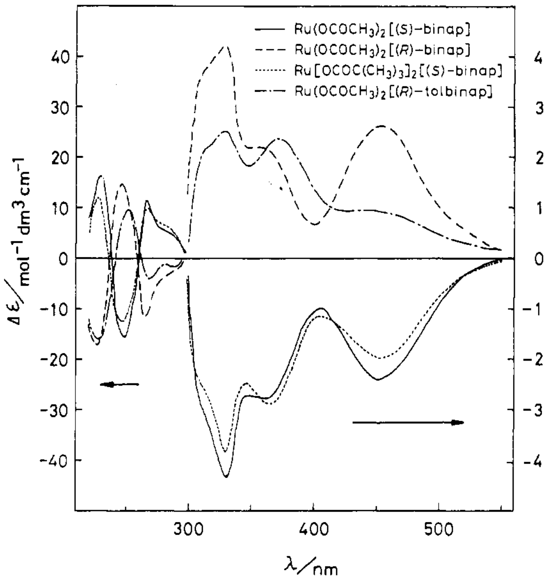

Figure 3. Circular dichroism spectra of Ru(OCOCH$_3$)$_2$[(*S*)-BINAP] [(*S*)-**3a**], Ru(OCOCH$_3$)$_2$[(*R*)-BINAP] [(*R*)-**3a**], Ru[OCOC(CH$_3$)$_3$]$_2$[(*S*)-BINAP] [(*S*)-**3b**], and Ru(OCOCH$_3$)$_2$[(*R*)-*p*-TolBINAP] [(*R*)-**3c**] in dichloromethane [(5.2–7.5) × 10^{-5} M].

each ligand in these complexes. The crystal structure of (*S*)-**3b** has been determined by X-ray crystallography. To our knowledge this provides the first X-ray structural data for cis chelating diphosphine–Ru(II) dicarboxylate complexes.[14-16] The molecular structure and a stereoview of (*S*)-**3b** are shown in Figures 1 and 2, respectively. The central Ru(II) atom has a distorted octahedron coordination geometry involving two phosphorus atoms of BINAP and four oxygen atoms of pivalate ligands. The mean bond distance of Ru to O trans to phosphorus atoms [2.201 (16) Å] is considerably longer than that [2.127 (11) Å] trans to oxygen atoms,[17] perhaps due to the high trans influence of the strongly σ-donating phosphorus atom.[18] The geometry is to be compared with that of Rh[(*R*)-BINAP](nbd)ClO$_4$ (nbd = norbornadiene).[19] In both cases, two of the four phenyl rings are oriented approximately parallel to each naphthalene ring, respectively. The dihedral angle of the two naphthalene rings of (*S*)-**3b** is 65.6°, much smaller than that (74.4°) of the Rh complex. This is correlated with the fact that the Ru–P bond lengths of the octahedral Ru(II) complex **3b** [average distance 2.240 (2) Å] are shorter than those of Rh–P bonds of the square-planar Rh(I)–BINAP complex [average distance 2.313 (8) Å], while the P–Ru–P angle [90.6 (1)°] is only a little smaller than that of P–Rh–P [91.8 (1)°]. These facts demonstrate that the BINAP ligands flexibly change their dihedral angles depending on the nature of the central metal atoms and auxiliary ligands to form stable seven-membered chelate rings. The conformational features of the BINAP ligands in these complexes are reflected in the difference in steric environments around the central metals. For example, the two equatorial phenyl rings of (*S*)-**3b** protrude to the other P–Ru–P in-plane coordination sites to a greater extent compared with those of the Rh complex (vide infra).[20]

The whole structure of Λ-(*S*)-**3b** approximates C_2 chirality. The dissymmetry of the (*S*)-BINAP ligand fixes the δ conformation of the seven-membered diphosphine- and Ru-containing chelate ring. This seven-membered structure is highly skewed, and this configuration in turn determines the chiral dispositions of the four phenyl rings on the phosphorus atoms; two phenyls are oriented in axial directions and the others in equatorial directions. These equatorial phenyls apparently exert steric influence on the ligands situated on the equatorial coordination sites of Ru. As a result, the bidentate ligation of the pivalate moieties to Ru occurs stereoselectively, bringing about exclusive formation of the Λ diastereomer. This diastereomeric differentiation of the two sets of quadrant space sectors is made in such a way to avoid nonbonded interactions between the sterically demanding equatorial phenyl rings and the carboxylate ligands. The absolute configurations of the complexes **3a** and **3c** were substantiated by comparing the CD spectrum of Λ-(*S*)-**3b** with those of (*S*)-**3a**, (*R*)-**3a**, and (*R*)-**3c** (Figure 3).

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Registry No. Λ-(*S*)-**3a**, 104713-03-3; Λ-(*S*)-**3b**, 112019-12-2; Δ-(*R*)-**3c**, 112065-78-8; RuCl$_2$(cod), 50982-12-2.

Supplementary Material Available: Listings of bond distances, bond angles, atomic parameters of hydrogen atoms, anisotropic temperature factors, and least-squares planes and angles between least-squares planes and the table of phenyl C and H distances described in ref 21 (9 pages); a listing of structure factors (13 pages). Ordering information is given on any current masthead page.

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(13) For IR absorptions due to bidentate carboxylate ligands of Ru(II) complexes, see: Rose, D.; Gilbert, J. D.; Richardson, R. P.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 2610.

(14) Ru(OCOCH$_3$)$_2$(PPh$_3$)$_2$ has been prepared, and the cis structure was suggested: Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 1749.

(15) For X-ray analyses of *trans*-RuClH(diop)$_2$ and Ru$_2$Cl$_5$(chiraphos)$_2$, see: Ball, R. G.; James, B. R.; Trotter, J.; Wang, D. K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 460. Thorburn, I. S.; Rettig, S. J.; James, B. R. *Inorg. Chem.* **1986**, *25*, 234.

(16) Recently the X-ray crystal structure of RuClH[(*R*)-BINAP]$_2$ has been reported: Kawano, H.; Ishii, Y.; Kodama, T.; Saburi, M.; Uchida, Y. *Chem. Lett.* **1987**, 1311.

(17) A similar trend is seen in RuH(OCOCH$_3$)[P(C$_6$H$_5$)$_3$]$_3$: Skapski, A. C.; Stephens, F. A. *J. Chem. Soc., Dalton Trans.* **1974**, 390. See also ref 13.

(18) Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. In *Concepts and Models of Inorganic Chemistry*, 2nd ed.; Wiley: New York, 1983; pp 371–375.

(19) Toriumi, K.; Ito, T.; Takaya, H.; Souchi, T.; Noyori, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 807.

(20) The distances of C30 and C36 from the plane that passes through the Ru and is perpendicular to the axis which passes through the Ru and meets at right angles with P(1)–P(2) are 0.10 and 0.32 Å, respectively.[21] On the other hand, the corresponding distances for such carbons in the Rh complex are 0.02 and 0.23 Å, respectively.[19,21]

(21) A table of the distances of carbons and protons in the phenyl rings of Ru[OCOC(CH$_3$)$_3$]$_2$[(*S*)-BINAP] and Rh[(*R*)-BINAP](nbd)ClO$_4$ from the plane defined above is given in the supplementary material.