Syntheses and Structures of Novel Ruthenium(II)-Chiral Diphosphine Complexes

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Novel ruthenium complexes coordinated with various chiral diphosphines were synthesized by reactions of polynuclear $[RuCl_2(cycloocta\text{-}1,5\text{-}diene)]_n$ with the respective diphosphines in the presence of triethylamine. The compositions of the complexes thus obtained were varied according to the solvent used (toluene or ethanol). The structures and dynamic properties of the complexes bearing 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap) in solution were elucidated by the ^1H and $^{31}P\{^1H\}$ NMR measurements. The X-ray diffraction analysis of *trans*-$RuHCl((R)\text{-binap})_2$ indicated that the conformation of seven-membered chelate rings and the edge-face manner of phenyl groups were almost the same as those of corresponding rhodium complexes.

Asymmetric synthetic reactions utilizing various transition metal complexes as catalysts have attracted much attention in past two decades. Among efficient catalysts, rhodium(I)-chiral diphosphine complexes successfully achieved very high stereoselection (up to 99% e.e.) in asymmetric hydrogenation of carbon-carbon double bonds.[1] In order to achieve high enantiomeric excesses, several types of chiral diphosphines were designed and prepared, and cationic and/or neutral rhodium complexes containing these phosphines had been employed as the catalysts especially for asymmetric hydrogenation of dehydroamino acids. These rhodium(I)-chiral diphosphine complexes were readily prepared by either of following methods. Cationic rhodium complexes were prepared by ligand exchange reactions of $[Rh(diene)_2]X$ (diene=cycloocta-1,5-diene (cod) or norbornadiene (nbd); $X^-=ClO_4^-$ or BF_4^-) with chiral bidentate phosphines. Neutral rhodium complexes were usually generated in situ by mixing a binuclear complex, $[RhCl(diene)]_2$ and a diphosphine. In these procedures, a diene ligand is considered to be readily replaced with a diphosphine ligand.

By the way, ruthenium complexes bearing some monodentate or polydentate phosphine ligands had been obtained from triphenylphosphine complexes such as $RuCl_2(PPh_3)_3$ [2] by ligand exchange reaction.[3] However, fewer ruthenium(II) complexes with chiral diphosphine ligands had been reported before 1985 compared to the case of rhodium(I) complexes. James[4] reported the syntheses of chiral ruthenium complexes such as $Ru_2Cl_4(diop)_3$, $RuHCl(diop)_2$, and $RuCl_2(diop)_2$ by an ordinary ligand exchange of triphenylphosphine for diop (diop=4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane). Botteghi[5] also reported a few ruthenium carbonyl hydrido clusters containing diop. However these diop complexes were almost only successful examples of the ligand exchange in the preparation of ruthenium(II)-chiral diphosphine complexes. So it was desired to develop a versatile method for preparing a series of ruthenium(II)-chiral diphosphine complexes.

We examined the possibility to employ the polynuclear ruthenium-diene complex, $[RuCl_2(cod)]_n$,[6] readily available from $RuCl_3 \cdot {}_nH_2O$, for the starting complex, taking into account the success in using rhodium-diene complexes as precursors for preparing rhodium-diphosphine complexes. In our preliminary reports since 1985, we have mentioned a synthesis[7] and a catalytic activity[8] of a novel ruthenium(II)-binap complex (binap=2,2′-bis(diphenylphosphino)-1,1-binaphthyl[9]). In this paper, the detailed results on the preparation of ruthenium(II)-diphosphine complexes are described. In addition, the structures of ruthenium(II)-binap complexes, which were applied to the catalysts for asymmetric hydrogenation,[8] are examined based on ^1H and $^{31}P\{^1H\}$ NMR spectra as well as the X-ray crystal structure determination of one of the Ru-binap complexes.[10]

Experimental

Measurements. ^1H NMR spectra were measured with a JEOL JNM-GX400 (400 MHz) spectrometer. $^{31}P\{^1H\}$ NMR spectra were also obtained with a JEOL JNM-GX400 (162 MHz) spectrometer. The chemical shifts were recorded in ppm downfield from internal tetramethylsilane for ^1H NMR and from external 85% H_3PO_4 for $^{31}P\{^1H\}$ NMR. IR spectra were taken on a Hitachi 215 spectrophotometer with KBr disks.

Reagents and Chemicals. Optically active diphosphines used such as (2*S*,3*S*)-bis(diphenylphosphino)butane[11] ((*S*,*S*)-chiraphos), (*R*,*R*)-diop,[12] (2*S*,4*S*)-*N*-(*t*-butoxycarbonyl)-4-(diphenylphosphino)-[(diphenylphosphino)methyl]pyrrolidine[13] ((*S*,*S*)-bppm) and (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine[14] ((*S*)-(*R*)-bppfa) were prepared by the literature methods. (*R*)- and (*S*)-binap were used as received. The starting complex, $[RuCl_2(cod)]_n$ was prepared according to the literature.[6] All the solvents

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and triethylamine were dried, degassed, distilled and stored under nitrogen. All other reagents and chemicals were purchased and used without further purification.

Preparation of $Ru_2Cl_4\{(R)$-(or (S)-)binap$\}_2(N(C_2H_5)_3)$ (1). The binuclear complex **1** was prepared from $[RuCl_2(cod)]_n$ and (R)- (or (S)-)binap according to the following method we had reported before:[7,8c] A mixture of $[RuCl_2(cod)]_n$ (333 mg, 1.19 mmol), (R)-binap (849 mg, 1.36 mmol), and triethylamine (1 cm^3) was reacted for 3 h under toluene (20 cm^3) reflux condition. Then toluene was removed in vacuo and the resulting precipitates were washed with toluene and then with ether three times. The orange-red precipitates were dissolved to dichloromethane (4 cm^3), and after the small amount of insoluble solid was filtered, the complex was crystallized by addition of ether. The orange-red powder was collected by filtration, washed with ether three times, and dried in vacuo. The orange-red complex was obtained. Yield, 796 mg (79%). Found: C, 67.6; H, 4.8; N, 0.79%. Calcd. for $C_{94}H_{79}Cl_4NP_4Ru_2$: C, 66.8; H, 4.7; N, 0.83%.

Preparation of $RuCl_2$(diphosphine)$_n$ (n=1, 3/2 or 2). The following procedure for the synthesis of $RuCl_2((S)$-(R)-bppfa) (**2**) is representative.

A mixture of $[RuCl_2(cod)]_n$ (287 mg, 1.02 mmol), (S)-(R)-bppfa (703 mg, 1.12 mmol), and triethylamine (1 cm^3) in toluene (10 cm^3) was heated under reflux for 3 h. After the toluene was removed under reduced pressure, the resulting

Table 1. Fractional Positional Parameters ($\times 10^4$) and Thermal Parameters ($Å^2$), with Estimated Standard Deviations in Parentheses[a]

Atom	x	y	z	B_{eq}[b]	Atom	x	y	z	B_{eq}[b]
Ru	134.3(0.4)	1475.5(0.4)	41.1(0.4)	2.19	C 224	−1767(18)	926(12)	−2300(15)	0.60
Cl	1460.9(1.4)	1472.3(1.5)	−39.9(1.6)	3.35	C 225	−1978(12)	1122(10)	−1631(15)	7.68
P 1	218.9(1.5)	2421.0(1.3)	554.2(1.5)	2.56	C 226	−1453(11)	1437(9)	−1248(12)	6.72
P 2	−169.4(1.7)	1965.9(1.4)	−1042.8(1.4)	2.68	C 3 1	731(6)	13(5)	29(7)	3.17
P 3	189.8(1.7)	525.0(1.3)	−499.6(1.5)	2.66	C 3 2	498(6)	−276(5)	622(6)	2.54
P 4	45.1(1.3)	985.5(1.2)	1147.2(1.4)	2.16	C 3 3	954(7)	−645(6)	1016(8)	3.52
C 1 1	764(5)	2900(5)	−5(7)	2.86	C 3 4	715(9)	−952(6)	1643(8)	4.27
C 1 2	499(6)	3163(5)	−606(7)	2.79	C 3 5	1130(9)	−1286(8)	2014(9)	4.65
C 1 3	937(6)	3488(5)	−1063(6)	2.77	C 3 6	1856(9)	−1367(7)	1806(10)	4.81
C 1 4	714(7)	3792(6)	−1671(8)	3.71	C 3 7	2101(9)	−1072(7)	1246(11)	5.37
C 1 5	1155(9)	4124(8)	−2086(8)	4.89	C 3 8	1646(7)	−700(6)	815(8)	3.70
C 1 6	1586(9)	4151(8)	−1939(10)	5.52	C 3 9	1886(8)	−419(6)	198(9)	4.33
C 1 7	2118(8)	3877(8)	−1357(9)	4.79	C 310	1447(6)	−39(6)	−177(8)	3.66
C 1 8	1677(6)	3536(6)	−911(8)	3.73	C 4 1	−504(6)	301(6)	1107(6)	2.80
C 1 9	1914(7)	3239(7)	−306(8)	4.00	C 4 2	−243(6)	−211(5)	851(6)	2.79
C 110	1490(6)	2930(6)	134(8)	3.65	C 4 3	−689(7)	−713(6)	810(7)	3.41
C 2 1	−615(5)	2699(6)	−960(6)	2.84	C 4 4	−440(8)	−1287(6)	528(9)	4.05
C 2 2	−258(6)	3183(6)	−753(6)	2.86	C 4 5	−877(9)	−1748(7)	503(8)	4.53
C 2 3	−605(7)	3745(7)	−677(8)	3.78	C 4 6	−1581(9)	−1708(7)	686(9)	4.93
C 2 4	−259(8)	4248(7)	−422(8)	4.31	C 4 7	−1805(9)	−1202(8)	977(9)	4.93
C 2 5	−590(8)	4771(8)	−279(12)	6.00	C 4 8	−1385(7)	−690(6)	1026(7)	3.61
C 2 6	−1310(13)	4811(10)	−398(13)	7.19	C 4 9	−1617(8)	−165(7)	1301(8)	4.10
C 2 7	−1680(9)	4317(8)	−617(10)	5.20	C 410	−1193(8)	345(7)	1363(8)	3.95
C 2 8	−1327(7)	3783(7)	−764(8)	3.91	C 311	559(8)	468(6)	−1407(7)	3.55
C 2 9	−1682(8)	3282(7)	−1116(9)	4.47	C 312	234(11)	182(7)	−1964(8)	5.56
C 210	−1358(7)	2758(9)	−1123(8)	4.65	C 313	542(13)	157(8)	−2632(9)	6.36
C 111	679(6)	2491(5)	1414(5)	2.60	C 314	1193(12)	403(8)	−2738(8)	6.04
C 112	463(7)	2847(6)	1946(8)	3.76	C 315	1508(11)	704(9)	−2216(10)	5.82
C 113	842(10)	2898(8)	2578(8)	5.04	C 316	1229(9)	757(7)	−1509(8)	4.63
C 114	1458(11)	2576(8)	2651(8)	5.37	C 321	−584(7)	50(6)	−606(6)	3.31
C 115	1644(10)	2189(8)	2134(9)	5.31	C 322	−1243(8)	302(8)	−440(9)	4.97
C 116	1285(8)	2134(7)	1494(9)	4.38	C 323	−1822(10)	−53(8)	−552(11)	5.94
C 121	−550(7)	2895(6)	700(6)	3.31	C 324	−1777(10)	−596(19)	−818(9)	6.20
C 122	−1205(7)	2656(6)	590(7)	3.39	C 325	−1123(10)	−856(10)	−981(9)	4.53
C 123	−1791(8)	3011(8)	742(9)	4.81	C 326	−508(8)	−525(7)	−873(8)	4.16
C 124	−1737(9)	3554(8)	1001(9)	5.07	C 411	760(6)	686(5)	1695(6)	2.83
C 125	−1095(10)	3782(7)	1068(8)	4.72	C 412	560(8)	391(6)	2321(8)	3.77
C 126	−488(9)	3464(6)	920(8)	4.08	C 413	1078(10)	187(8)	2776(9)	5.06
C 211	473(7)	2189(6)	−1715(7)	3.56	C 414	1790(11)	241(9)	2597(10)	6.29
C 212	1175(8)	2142(7)	−1623(7)	3.87	C 415	1961(9)	511(8)	1976(10)	5.21
C 213	1665(9)	2339(6)	−2103(8)	4.40	C 416	1438(8)	729(5)	1511(7)	3.68
C 214	1406(11)	2584(8)	−2731(9)	5.87	C 421	−384(7)	1438(5)	1836(6)	3.27
C 215	687(10)	2666(7)	−2851(9)	4.95	C 422	−1029(7)	1654(6)	1699(8)	3.93
C 216	205(11)	2473(7)	−2331(7)	4.90	C 423	−1411(12)	1966(8)	2184(10)	6.05
C 221	−800(9)	1529(7)	−1556(9)	4.62	C 424	−1126(13)	2097(8)	2839(10)	6.27
C 222	−635(12)	1351(9)	−2220(10)	6.12	C 425	−452(10)	1910(7)	2996(8)	4.69
C 223	−1179(14)	1017(10)	−2617(12)	7.81	C 426	−72(9)	1566(6)	2485(7)	3.92

a) Three toluene molecules are eliminated. b) $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$.

solid was dissolved in dichloromethane (3 cm³), and filtered. Orange-red powder was precipitated from the filtrate by the addition of ether. The complex was collected, washed with ether three times, and dried in vacuo. Yield, 476 mg (58%). Found: C, 55.9; H, 4.6; N, 1.8%. Calcd. for $C_{38}H_{37}Cl_2FeNP_2Ru$: C, 57.2; H, 4.7; N, 1.8%.

$RuCl_2$((*S,S*)-bppm) (3): Found: C, 57.9; H, 5.5; N, 1.9%. Calcd. for $C_{34}H_{37}Cl_2NO_2P_2Ru$: C, 56.3; H, 5.5; N, 1.9%.

$RuCl_2$((*S,S*)-chiraphos)$_2$ (4): Found: C, 65.4; H, 5.5; Cl, 7.7%. Calcd. for $C_{56}H_{56}Cl_2P_4Ru$: C, 65.6; H, 5.5; Cl, 6.9%.

Ru_2Cl_4((*R,R*)-diop)$_3$ (5): An IR spectrum of the product was identical with that of the authentic sample.[4]

Preparation of *trans*-RuHCl((*R*)-binap)$_2$ (6). The chlorohydrido complex **6** was prepared from $[RuCl_2(cod)]_n$ or the binuclear complex **1**, and (*R*)-binap. We had already mentioned the former method in the published reports as follows:[7,8c] To the suspension of $[RuCl_2(cod)]_n$ (146 mg, 0.521 mmol) in ethanol (15 cm³) were added (*R*)-binap (650 mg, 1.04 mmol) and triethylamine (1 cm³), and the mixture was refluxed for 3 h under nitrogen atmosphere. The yellow precipitates formed were isolated by filtration, washed with ethanol and ether (three times) successively, and dried up in vacuo. The resulting yellow powder was dissolved in dichloromethane, and the small amounts of insoluble solid were separated by filtration, then ether was added to the solution. The solidified yellow powder was collected, and washed with ether, dried up in vacuo. Yield, 369 mg (51%).

The latter method is as follows: An ethanol solution of a mixture of the complex **1** and the excess amount of (*R*)-binap was refluxed under nitrogen for 3 h in the presence of triethylamine. The yellow precipitate formed was collected by filtration, washed with ethanol and ether (three times) successively, and dried up in vacuo. The resulting yellow powder was dissolved in dichloromethane, and a small amount of insoluble solid was removed by filtration. Ether was added to the filtrate, and the yellow powder thus formed was collected, washed with ether, and dried in vacuo. Found: C, 76.9; H, 4.8; Cl, 3.0%. Calcd. for $C_{88}H_{65}ClP_4Ru$: C, 76.4; H, 4.7; Cl, 2.6%.

Preparation of RuH_2((*S,S*)-bppm)$_2$ (7). To a suspension of $[RuCl_2(cod)]_n$ (125 mg, 0.446 mmol) in ethanol (20 cm³) were added (*S,S*)-bppm (500 mg, 0.903 mmol) and triethylamine (1 cm³), and the mixture was refluxed for 2 h under a nitrogen atmosphere. The yellowish white precipitate formed was separated by filtration, and washed with ethanol (5 cm³). The powder was dissolved in dichloromethane, and a small amount of insoluble solid was filtered off. Ethanol was added to the filtrate. The pale yellow powder precipitated was collected, washed with ether, and dried in vacuo to give RuH_2((*S,S*)-bppm)$_2$. Found: C, 67.5; H, 6.4; N, 2.5%. Calcd. for $C_{68}H_{76}N_2O_4P_4Ru$: C, 67.5; H, 6.3; N, 2.3%.

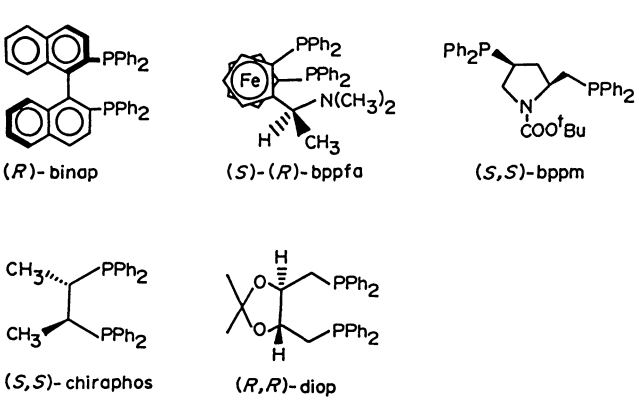
Molecular Structure of *trans*-RuHCl((*R*)-binap)$_2\cdot 3C_6H_5CH_3$. The yellow complex **6** was recrystallized from dichloromethane–toluene to give orange single crystals, *trans*-RuHCl((*R*)-binap)$_2\cdot 3C_6H_5CH_3$, which were suitable for obtaining X-ray diffraction data. *trans*-RuHCl((*R*)-binap)$_2\cdot 3C_6H_5CH_3$: Found: C, 78.7; H, 5.5%. Calcd. for $C_{109}H_{89}ClP_4Ru$: C, 78.9; H, 5.4%.

The orange prismatic crystal with dimensions 0.55×0.40×0.60 mm³ was sealed in a glass capillary as a precaution against air sensitivity, and used as a sample for the X-ray diffraction.

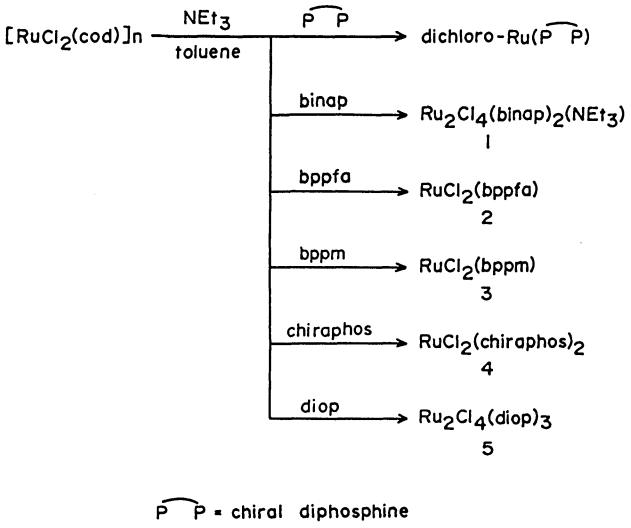
Intensity data were collected on a Rigaku automatic four circle diffractometer with LiF-monochromatized Mo$K\alpha$ radiation (λ=0.71069 Å) by using θ–2θ scan method, where the θ scan width was $(1.0+0.40\tan\theta)^\circ$ with the scan rate of 2° min^{-1} (2θ). A total of 13314 reflections were measured within the range $2.5^\circ<2\theta<60^\circ$, of which 7988 reflections ($|F_o|\geq 3\sigma(|F_o|)$) were used for the structure determination. Lorentz polarization and absorption correction were applied. Crystal data are as follows: $C_{109}H_{89}ClP_4Ru$; F. W.=1659.3; Orthorhombic; space group $P2_12_12_1$; a=19.368(2), b=22.806(2), c=19.038(2) Å; U=8409.2 Å^3; Z=4; D_c=1.31 g cm^{-3}; D_{obsd}=1.31 g cm^{-3}; μ(Mo$K\alpha$)=2.97 cm^{-1}. The structure was solved by the heavy-atom method and refined by the block diagonal least-squares technique. These crystallographic calculations were performed on a Hitac M-280H/M-200H computer using UNICS program system.[15] All non-hydrogen atoms are anisotropic. The final R and R_w values were 0.102 and 0.142, respectively. The selected final positional parameters are listed in Table 1. Tables of the F_o-F_c data, the complete final positional parameters including three toluene molecules and anisotropic thermal parameters are deposited as Document No. 9004 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

Results and Discussion

Syutheses of Ruthenium(II) Chiral Diphosphine Complexes. In the case of (*R*)- (or (*S*)-)binap, no ligand exchange between $RuCl_2(PPh_3)_3$ and the diphosphine occurred, and the starting complex was recovered. However in contrast, it was found that the polynuclear complex $[RuCl_2(cod)]_n$ was the convenient starting material for the synthesis of a wide range of ruthenium chiral diphosphine complexes. Firstly, a reaction of $[RuCl_2(cod)]_n$ with an equimolar amount of (*R*)-binap was examined in the presence of triethylamine under toluene reflux conditions. An orange-red powder was isolated after recrystallization from dichloromethane–diethyl ether mixture in good yield (79%). The elemental analysis showed that the complex had the composition of $RuCl_2$((R)-binap)$(N(C_2H_5)_3)_{1/2}$, which indicated one triethylamine molecule was contained per two ruthenium atoms. The coordination of triethylamine to the ruthenium atom was supported by ^{1}H NMR measurements, in which the methylene proton signals of the amine showed a lower-field shift and the AB pattern coupling (vide infra).

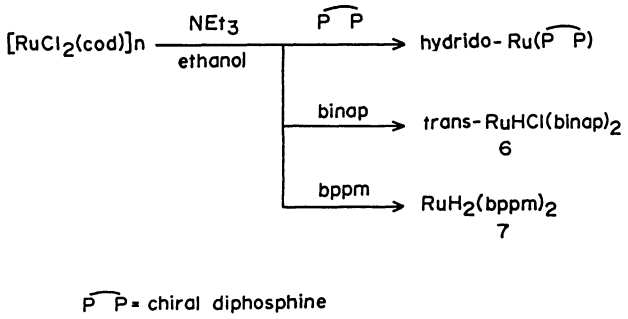


Adopting the same procedure as described above, not only five or seven membered chelate ligands, such as chiraphos, diop and bppm, but a chiral ferrocenyl diphosphine ligand, bppfa, afforded novel chiral ruthenium complexes. Under toluene reflux conditions in the presence of triethylamine, bppfa and bppm gave $RuCl_2$(bppfa) (**2**) and $RuCl_2$(bppm) (**3**), respectively, while chiraphos gave a six-coordinated mononuclear complex, $RuCl_2$(chiraphos)$_2$ (**4**), and diop afforded the well-known binuclear complex, Ru_2Cl_4(diop)$_3$ (**5**).[4] These complexes produced under the above-mentioned conditions are all dichloro complexes formulated generally as $RuCl_2$(diphosphine)$_n$ (n=1, 3/2 or 2). The results revealed that the coordinating diene in the starting complex was readily replaced with various types of chiral diphosphines, although the originally coordinated chloride anions were not replaced during the reaction.



Secondly, with a view to prepare another class of ruthenium(II)–diphosphine complexes, ethanol is employed as the solvent, because it is known that the composition of ruthenium complexes depends considerably on the solvent system. For example, $RuCl_2$-$(PPh_3)_3$ is transformed into the corresponding chlorohydrido complex, $RuHCl(PPh_3)_3$, in alcoholic solvent containing amines.[16]

When $[RuCl_2(cod)]_n$ was treated with two equivalents of (*R*)-binap and excess triethylamine in refluxing ethanol, yellow powder of RuHCl((*R*)-binap)$_2$ (**6**) was obtained in satisfactory yield (51%). This complex **6** was recrystallized from dichloromethane–toluene to give orange single crystals suitable for the X-ray diffraction analysis (vide infra). When bppm were reacted with the cod complex under similar conditions, a dihydrido complex, RuH_2(bppm)$_2$ (**7**) was formed. The absence of chloride was confirmed by the elemental analysis of **7**. Although the precise reasons for varying the composition of the hydrido complex (chlorohydrido or dihydrido) according to the chiral phosphine used are obscure to us, we expect that the size and flexibility of the diphosphine-chelate play a crucial roll for the variation of the hydrido complexes. The formation of the hydrides in ethanol implies that a redox process took place between the ruthenium species and the alcohol, and the hydrogen atom transferred from the alcohol to the ruthenium. Such reaction is supposed as the key reaction in catalytic transfer hydrogenation.[17] Therefore, these chiral hydrido ruthenium complexes **6** and **7** are predicted to be potential catalysts of the asymmetric transfer hydrogenation.



Recently, ruthenium complex catalyzed reactions have attracted considerable attention of chemists, and several successful reports on the preparation of novel ruthenium complexes have published. For example, James reported the preparation of a few types of ruthenium–diphosphine complexes from $RuCl_3(PPh_3)_2$-(dma)·dma (dma=*N*,*N*-dimethyl acetamide),[18] utilizing the ligand exchange with a chiral diphosphine. The complexes they isolated involved two chloro ligands without exception. It is considered to be a limitation of the James' method that a complex with no other anion can be obtained, since it has been clarified that not only the diphosphines but the anionic ligands play a decisive role on the catalytic effectiveness of a ruthenium(II)–diphosphine complex. Takaya, Noyori, and collaborators reported dicarboxylato ruthenium complexes, Ru(OCOR)$_2$(binap), and dihalo complexes, RuX_2(binap) (X=Cl, Br, and I), both of which were prepared from the cod complex in a modified manner of our method.[19] They recognized a significant difference in the catalytic activities between the dicarboxylato and dihalo complexes, demonstrating the effects of anionic ligands. In the present study we easily obtained hydrido ruthenium complexes by means of the diene complex. This presents a remarkable merit in the synthesis of the ruthenium–diphosphine complexes from the diene complex as the starting material because of its availability of Cl^- and H^- as the ligated anions which should affect the catalytic activity of the complexes.

Structures of Ruthenium–binap Complexes. The structures of the ruthenium complexes containing binap, **1** and **6**, in solution were investigated, as the NMR spectra of binap complexes were rather simple

and informative because of the C_2-symmetry and the rigid binaphthyl backbone of the ligand itself. The ^{1}H NMR spectra in $CDCl_3$ of complex **1** having the composition $RuCl_2(binap)(N(C_2H_5)_3)_{1/2}$ showed a triplet at δ=1.43 and two multiplets at δ=3.10 and 3.21 assigned to the methyl and methylene protons of triethylamine, respectively. These multiplets turned into a typical AB quartet when the methyl protons were decoupled. These observations demonstrate that two methylene protons are non-equivalent to each other, and that the triethylamine molecule is coordinated to the ruthenium atom bearing the chiral binap ligand. The coordination of triethylamine was also supported by the fact that the ethyl signals showed detectable broadening in the presence of excess triethylamine due to the exchange among the coordinated amine and the free one. On the other hand, $^{31}P\{^1H\}$ NMR spectra of **1** in CH_2Cl_2 at 30 °C showed only a pair of coupled doublets (δ=51.4 and 55.6, J_{PP}=35 Hz). This observation means all the binap ligands are identical in solution. Although no single crystal of **1** appropriate for the X-ray diffraction measurement has been obtained yet, a reasonable structure of **1** consistent with the NMR spectra (^{1}H and ^{31}P) as well as the elemental analysis data is assumed to be a chloro-bridged binuclear complex; $Ru_2Cl_4(binap)_2(N(C_2H_5)_3)$.

Some of the assumed structures of the complex **1** are shown in Fig. 2, taking the reported structures of various polynuclear ruthenium complexes into consideration.[20] Two dichloro-bridged structures, **1a** and **1b**, and a trichloro-bridged structure **1c** are presented. It is more probable that the solution of the complex **1** at 30 °C is the mixture of interchangeable isomeric structures such as **1a**, **1b**, **1c**, and so on, because of that two binap ligands are considered to be practically equivalent and that the triethylamine is coordinated to the ruthenium atom. The NMR behaviors described above are well explained as follows; in solution, a ligand (a free triethylamine or a solvent molecule) would enter into the vacant coordination site, and it would be replaced with another one considerably faster than the NMR time scale.

Besides, James isolated a closely related complex, $Ru_2Cl_4(chiraphos)_2(acetone)$, which contained another C_2-symmetric ligand, and detected two independent AB quartets with equal intensities in the $^{31}P\{^1H\}$ NMR spectrum at −90 °C. This coincides with the trichloro-bridged structure as **1c**,[18c] which has two inequivalent chiraphos ligands in its molecule. However, the binuclear complex **1** was not frozen to form the structure **1c** since only one AB quartet was still detected in the $^{31}P\{^1H\}$ NMR spectrum of **1** even at −90 °C.

It is noteworthy that one of the ruthenium atoms of **1**, at least, is considered as five-coordinated and to have a vacant site. Very recently, it was reported that a dichloro-bridged diruthenium complex, $Ru_2Cl_4(dppb)_2$

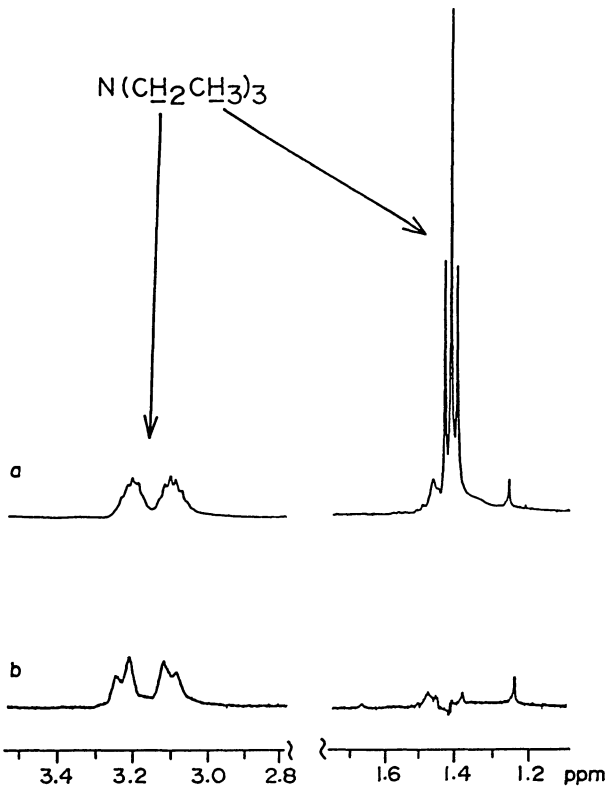


Fig. 1. ^{1}H NMR spectra of **1** in the region of the coordinating triethylamine: a, non-decoupled; b, methyl protons are decoupled.

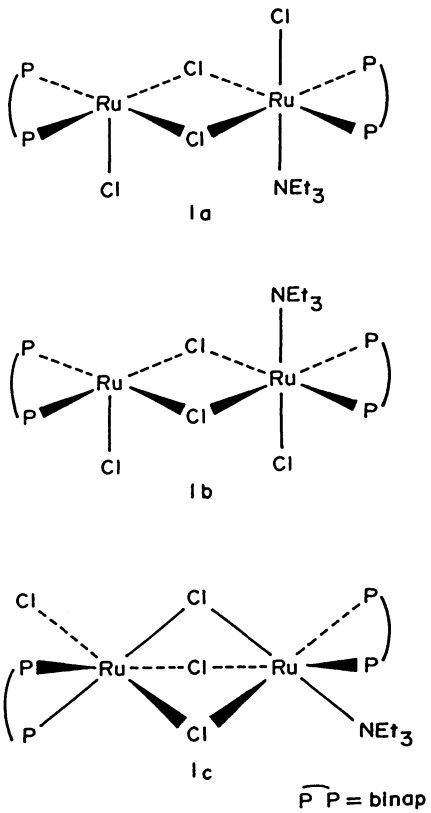


Fig. 2. Possible structures of $Ru_2Cl_4(binap)_2(N(C_2H_5)_3)$ (**1**).

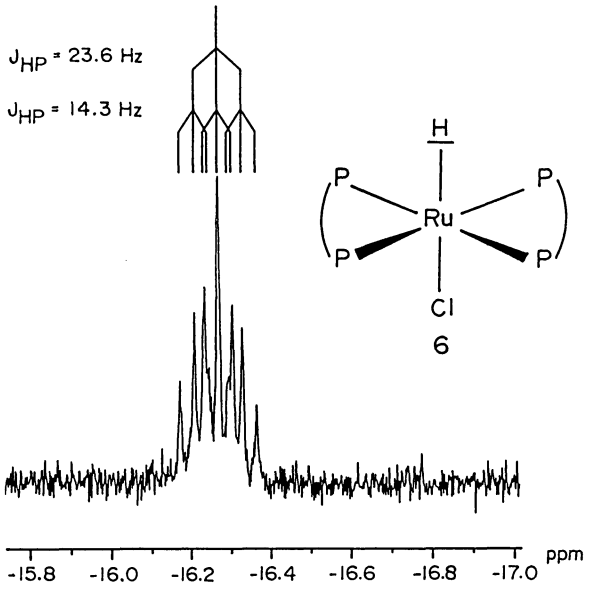


Fig. 3. A ^{1}H NMR spectrum of **6** in the region of the hydride.

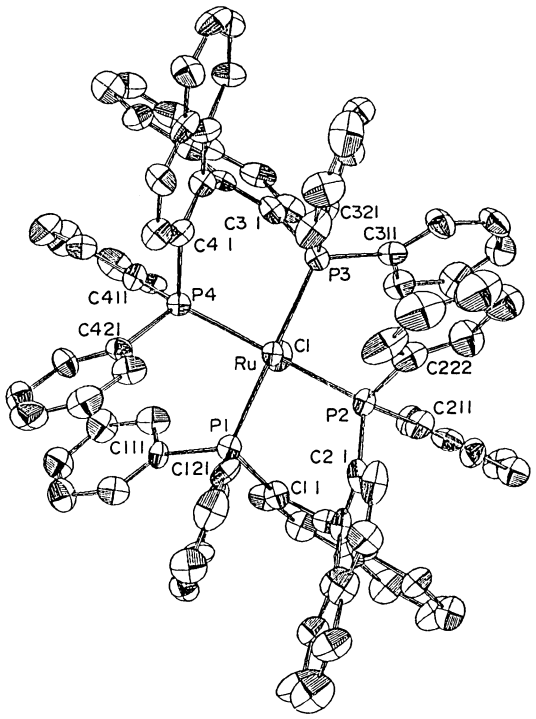


Fig. 4. Perspective view of *trans*-RuHCl((*R*)-binap)$_2$ (**6**). The thermal ellipsoid is 50% probability level. All hydrogen atoms are neglected.

reacted easily with dihydrogen on its vacant site, and was converted into a trichloro-bridged dihydrogen complex.[18d] Such unsaturation of these ruthenium centers is considered to be concerned with the catalytic activity of **1** in the asymmetric hydrogenation.[8]

On the contrary, the related complexes containing other diphosphines such as bppm or bppfa gave rather complicated ^{31}P NMR spectra than that of binap. Both bppm and bppfa are non-symmetrical diphosphines. Therefore, a few number of diastereomers could be formed when such a diphosphine coordinated to a ruthenium atom. Further investigations about these diastereomers has not been achieved.

The structure of the yellow complex **6** is presumed to be a six-coordinated chlorohydrido complex based on the results of the NMR measurements (Fig. 3). An apparent pseudo-septet (triplet of triplets) of the hydride proton detected at $\delta=-16.27$ in CD_2Cl_2 suggests that two pairs of equivalent phosphorus atoms coordinate to the ruthenium and that one of the coupling constant values is nearly twice as large as another (J_{HP}=14.3 and 23.6 Hz). A very similar hydride signal has already reported for the related complex *trans*-RuHCl(diop)$_2$.[4] Hence it is concluded that the complex **6** has the trans configuration with regard to the coordinating hydrido and chloro ligands in the six-coordinate octahedral structure. In addition, the presumption is also supported by the observation of two A_2B_2 pattern coupled triplets in the ^{31}P{^{1}H} NMR spectrum of **6** (δ=21.6 and 37.5, J_{PP}=34 Hz, 30 °C, CH_2Cl_2).

The structure of the complex **6** is confirmed by the X-ray crystal structure analysis. An orange prismatic crystal, which was obtained from a dichloromethane–toluene solution of **6** and was found to contain three toluene molecules per one molecule of the complex as the solvent of crystallization, was employed for the analysis.

Table 2. Selected Bond Lengths (Å) and Angles (degree), with Estimated Standard Deviations in Parentheses

Bond Lengths		Bond Angles	
Ru–Cl	2.574(4)	Cl–Ru–P1	87.6(1)
Ru–P1	2.373(4)	Cl–Ru–P2	101.1(1)
Ru–P2	2.420(4)	Cl–Ru–P3	85.8(1)
Ru–P3	2.402(4)	Cl–Ru–P4	97.1(1)
Ru–P4	2.390(4)	P1–Ru–P2	87.0(1)
P1–C1 1	1.854(17)	P3–Ru–P4	87.7(1)
P1–C111	1.871(16)	P1–Ru–P4	93.9(1)
P1–C121	1.861(14)	P2–Ru–P3	93.6(1)
P2–C2 1	1.889(15)	P1–Ru–P3	173.4(1)
P2–C211	1.856(16)	P2–Ru–P4	161.8(1)
P2–C221	1.854(20)	Ru–P1–C1 1	109.8(5)
P3–C3 1	1.864(18)	Ru–P2–C2 1	116.7(5)
P3–C311	1.874(17)	Ru–P3–C3 1	111.1(6)
P3–C321	1.859(16)	Ru–P4–C4 1	113.0(5)
P4–C4 1	1.891(14)	P1–C1 1–C1 2	121.1(12)
P4–C411	1.863(15)	P2–C2 1–C2 2	120.7(11)
P4–C421	1.865(15)	P3–C3 1–C3 2	123.8(13)
C1 1–C1 2	1.392(22)	P4–C4 1–C4 2	120.8(11)
C1 2–C2 2	1.492(20)	C1 1–C1 2–C2 2	122.0(12)
C2 1–C2 2	1.361(20)	C1 2–C2 2–C2 1	121.9(13)
C3 1–C3 2	1.382(22)	C3 1–C3 2–C4 2	120.0(11)
C3 2–C4 2	1.507(20)	C3 2–C4 2–C4 1	122.8(13)
C4 1–C4 2	1.362(20)		

A perspective view of *trans*-RuHCl((*R*)-binap)$_2$ ((*R*)-**6**) determined by X-ray crystallography is shown in Fig. 4. Table 2 shows the selected bond lengths and bond

angles. The ruthenium has a slightly distorted octahedral geometry, in which four phosphorus atoms of the two binap ligands form the P_4 basal plane and the H^- and Cl^- ligands occupy the apical coordination sites. The complex has an approximate C_2-symmetry axis along the Ru–Cl bond.

Although all the Ru–P lengths fall within the range of observed values for ruthenium phosphine complexes (2.20—2.45 Å) and are almost the same as those of structurally closely related complex *tran*-RuHCl-(diop)$_2 \cdot 2C_6H_5CH_3$[21] (2.36 and 2.39 Å), they are in the rather longer class among Ru–P bonds. It is presumed that the long Ru–P distances are due to the mutual trans effect of P atoms and the steric repulsion between two binap ligands. These Ru–P bond weakenings possibly promote the dissociation of the phosphine ligand from ruthenium to afford a catalytically active species.

The Ru–Cl distance of 2.57 Å is among the longest Ru–Cl bonds reported so far, probably due to the strong trans effect of the hydrido ligand. This suggests that the complex tends to dissociate the chloride anion to generate a five-coordinated cationic complex in solution. In fact, the five-coordinated complex [RuH-(binap)$_2$]$^+$ was isolated as a hexafluorophosphate salt, and was converted easily into the six-coordinated *trans*-RuHCl(binap)$_2$ when it was allowed to react with chloride.[22]

The (*R*)-binap ligands which form seven-membered chelate rings are fixed in a λ-skew(v) conformation, which is closely similar to those of [Rh(nbd)((*R*)-binap)]ClO_4 (**8**)[23] and [Rh((*R*)-binap)$_2$]ClO_4 (**9**)[24] and in the mirror image relationship to that of Ru(OCOC$(CH_3)_3)_2$((*S*)-binap) (**10**).[19a] The framework makes the four phenyl rings on the P atoms of each binap ligand arranged in an alternating edge-face manner. Carbon atoms of each naphthyl group are coplanar within 0.07 Å and the dihedral angles between the planes through the naphthyl groups are 70.9° and 68.4°, which are smaller than the values reported for **8** (77.4°) and **9** (71.0°), respectively, and larger than that of **10** (65.6°).

It is indicated that both the chelate conformation and the edge-face manner in the ruthenium complex **6** are the same as those in the rhodium-binap complexes. However, the reported[7,9] hydrogenation products with complex **6** and also with complex **1** have the opposite configuration to the products of rhodium-binap catalysts. We consider such attracting results reflect the difference between the stereoselection mechanism of the ruthenium catalyst and that of the rhodium catalyst, that will be the subject of our further investigation.

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