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Molecular Structure of a Catalytically Active Chiral Ruthenium(II) Complex. Chlorohydridobis[(R)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium(II)

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Molecular structure of the title complex was determined by the single crystal X-ray diffraction method. The complex has a typical octahedral structure and takes the trans configuration as a whole, where the Cl^- and H^- occupy the apical coordination sites. The configuration of the seven-membered chelate ring of the phosphine ligand is λ-skew(v).

Organic synthesis catalyzed by ruthenium complexes has attracted much attention in recent years because of their versatility, high activity and excellent selectivity, and there have been reported a variety of reactions including C-C bond formation reactions$^{1)}$ as well as functional group transformation reactions.$^{2)}$ However, in contrast to those using rhodium or palladium complexes, the asymmetric catalytic reactions using ruthenium complexes has been severely limited to a few examples dealing with hydrogenation$^{3)}$ and hydrogen transfer reaction.$^{4)}$ Moreover, there have been very few ruthenium catalyzed reactions which achieved practically valuable levels of stereoselectivity (90% e.e.).$^{5)}$ It seems that the major reason for the limitation and unsuccess in the asymmetric reactions by ruthenium complexes is the lack of effective chiral ruthenium catalyst; in fact only a small number of catalytically active chiral ruthenium complexes have been thus far available.$^{6)}$

Recently we have developed a convenient method for preparing ruthenium-BINAP complexes $RuHCl((R)\text{-BINAP})_2$ (1) and $Ru_2Cl_4((R)\text{-BINAP})_2(NEt_3)$ (2) (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl$^{7)}$), and reported that they are highly effective (up to 90% e.e.) for the hydrogenation of olefinic substrates.$^{8)}$ Surprisingly ruthenium-(R)-BINAP complexes shows the stereoselectivity in a completely opposite manner and in similar high levels to that by rhodium-(R)-BINAP complexes.$^{8a)}$ Thus from a viewpoint of elucidating the mechanism of asymmetric induction by a ruthenium-BINAP catalyst, the clarification of molecular structures of catalytically active Ru-BINAP complexes is of much interest. In this communication we wish to describe the molecular structure of one of the most effective ruthenium catalyst precursor, 1.

Orange prismatic crystals were obtained from a methylene chloride-toluene solution of 1, prepared from $[RuCl_2(COD)]_n$ (COD = cyclo-octa-1,5-diene) and (R)-

BINAP by the previously reported method.[8a)] A crystal with dimensions 0.55 x 0.40 x 0.60 mm^3 was sealed in a glass capillary as a precaution against air sensitivity, and was used as a sample for the X-ray diffraction. Intensity data were collected on a Rigaku automatic four circle diffractometer with LiF-monochromatized MoKα 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 $2^\circ \min^{-1}$ (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 corrections were applied. 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.[9)] All non-hydrogen atoms are anisotropic. The space group was $P2_12_12_1$ and the final R value was 0.102. The crystallographic parameters are listed in Table 1.

The crystal contains three molecules of toluene per one molecule of the ruthenium complex as solvent of crystallization, which coincides with the formula derived from the elemental analysis (Found: C, 78.7; H, 5.5%. Calcd for $C_{109}H_{89}ClP_4Ru$: C, 78.9; H, 5.4%). Figure 1 shows a perspective view of the complex with the atom numbering. The absolute configuration of the complex was deduced from the known absolute configuration of the BINAP ligand. Selected bond lengths and angles are listed in Table 2. The ruthenium has a slightly distorted octahedral geometry, in which four P atoms of two BINAP ligands form the P_4 basal plane and the Cl^- and H^- ligands occupy the apical coordination sites. The complex has an approximate two-fold symmetry axis along the Ru-Cl bond.

Although the Ru-P lengths (2.37, 2.39, 2.40, and 2.42 Å) fall within the range of observed values for ruthenium-phosphine complexes (2.20-2.45 Å)[10,11)] and are almost the same as those of structurally closely related complex $RuHCl(DIOP)_2\cdot(PhCH_3)$[11)] (Ru-P = 2.36 and 2.39 Å; DIOP = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane[12)]), they are in the rather longer class among Ru-P bonds. It is presumed that the observed long Ru-P distances are due to the mutual trans-effect of P atoms and steric constraint between two BINAP ligands, and these Ru-P bond weakenings possibly promote the dissociation of the phosphine ligand to afford a catalytically active species.

The (R)-BINAP ligand coordinates to the Ru to form a seven-membered chelate ring fixed in a λ-skew(v) conformation (Fig.2), which is closely similar to that of $[Rh(C_7H_8)((R)\text{-BINAP})]ClO_4$[13)] (3) and in the mirror image relationship to that of $Ru((S)\text{-BINAP})(OCOC(CH_3)_3)_2$.[14)] This 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 value (74.4°) reported for 3.

The Ru-Cl distance of 2.57 Å is among the longest Ru-Cl bonds reported so far,[10,11)] probably due to the strong trans effect of the hydride ligand. This suggests that complex 1 tends to dissociate the chloride to generate a five coordinated cationic complex in solution.[11)] In fact p-tolyl analog of 1, $RuHCl(p\text{-tolyl-BINAP})_2$ (p-tolyl-BINAP = 2,2'-bis(di-p-tolylphosphino)-1,1'-binaph-

Table 1. The crystallographic parameters and experimental conditions

Formula	$C_{109}H_{89}ClP_4Ru$
Mw	1659.32
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Cell dimension	
a /Å	19.368(2)
b /Å	22.806(2)
c /Å	19.038(2)
U /Å^3	8409.2
Z	4
d_{obsd} /Mgm^{-3} (temp./K)	1.31 (293)
d_{calcd} /Mgm^{-3}	1.311
F(000)	3452
μ(MoKα) /cm^{-1}	2.97
No. of unique reflections	7988
R	0.102
Rw	0.142

Table 2. Selected bond lengths (Å) and angles (°)

Ru-Cl	2.574(4)
Ru-P1	2.373(4)
Ru-P2	2.420(4)
Ru-P3	2.402(4)
Ru-P4	2.390(4)
Cl-Ru-P1	87.6(1)
Cl-Ru-P2	101.1(1)
Cl-Ru-P3	85.8(1)
Cl-Ru-P4	97.1(1)
P1-Ru-P2	87.7(1)
P3-Ru-P4	87.7(1)
P1-Ru-P4	93.9(1)
P2-Ru-P3	93.6(1)
P1-Ru-P3	173.4(1)
P2-Ru-P4	161.8(1)

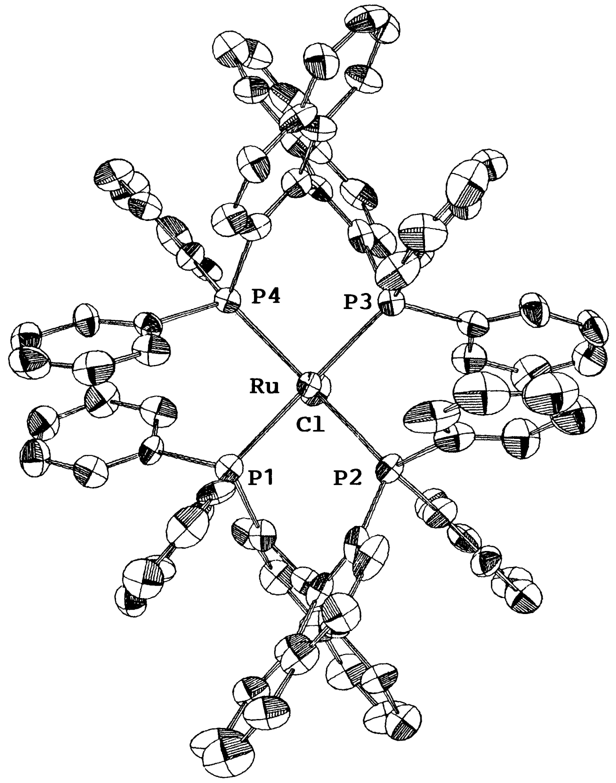

Fig.1. A perspective view of RuHCl((R)-BINAP)$_2$.

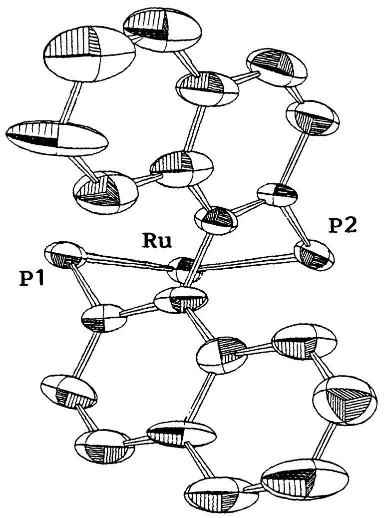

Fig.2. The chelate structure of a (R)-BINAP ligand.

thyl), shows large electric conductivity (Λ_M = 5.9x10^{-2} S m^2/mol; at 4.5x10^{-4} mol/dm^3 in CH_3NO_2). The chloride dissociation could be involved in the catalytic reaction using 1 and studies to elucidate such possibility are in progress.

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