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Preparation and Reactions of a Novel Five-Coordinate Ruthenium Complex $[RuH(BINAP)_2]PF_6$ and Formation of the First Chiral Molecular Hydrogen Complex $[RuH(\eta^2-H_2)(BINAP)_2]PF_6$ (BINAP = (*R*)-Bis(diphenylphosphino)-1,1'-binaphthyl)

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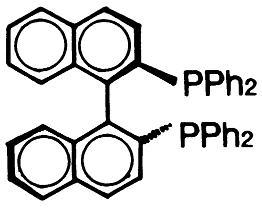
A five-coordinate ruthenium complex with the chiral bisphosphine, (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), $[RuH(BINAP)_2]PF_6$ (**1**) was prepared. The complex **1** was found to be a mixture of two isomers in solution. The exposure of **1** to hydrogen gas gave a chiral molecular hydrogen complex, *trans*-$[RuH(\eta^2-H_2)(BINAP)_2]PF_6$ (**2**). $[RuD(\eta^2-HD)(BINAP)_2]^+$ ion formed by introducing D_2 gas into a THF-d_8 solution of **1** has a H-D coupling constant *J*(H,D) = 30 Hz (1:1:1), diagnostic of η^2-HD complex.

Asymmetric hydrogenation of functionalized olefins and carbonyl compounds catalyzed by ruthenium-BINAP complexes[1,2] (BINAP = (*R*) or (*S*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl), such as $Ru_2Cl_4(BINAP)_2(NEt_3)$[3a] and *trans*-$RuHCl(BINAP)_2$[3a,b] has been intensively studied in recent years. Although the detailed mechanisms of the hydrogenation have not been elucidated, it is highly probable that coordinatively unsaturated ruthenium complexes, derived in situ from the isolable complexes, function as catalytically active species. This prompted us to prepare a five-coordinate ruthenium complex containing the BINAP ligand. Here we report the preparation and reactions of a novel five-coordinate ruthenium complex $[RuH(BINAP)_2]PF_6$ (**1**), and further the first isolation of a molecular hydrogen complex with the chiral diphosphine, *trans*-$[RuH(\eta^2-H_2)(BINAP)_2]PF_6$ (**2**), obtained by the contact of **1** with H_2 gas.



(*R*)-BINAP

The preparation of five-coordinate hydridobis(diphosphine)ruthenium complexes has been described in a preliminary report.[4] A similar reaction of $[RuH(COD)(NH_2NMe_2)_3]PF_6$[5] (COD = 1,5-cyclooctadiene) with two equivalents of BINAP in refluxing ethanol for 1.5 h under argon or nitrogen atmosphere gave rise to a dark-red solution. After the evaporation of solvent, the residue was crystallized from THF-diethyl ether to afford dark red crystals of complex (**1**) in 66% yield (Found: C, 69.4; H, 4.5%. Calcd for $C_{88}H_{65}F_6P_5Ru$: C, 70.9; H, 4.4%). The electric conduc-

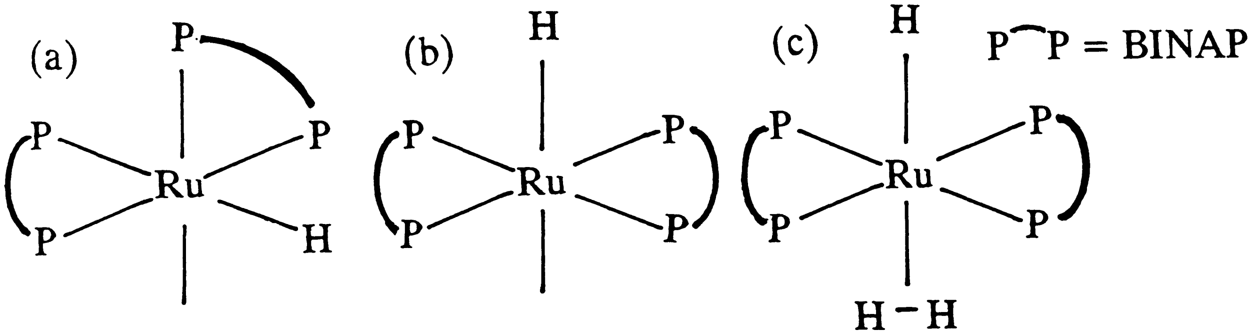


Fig. 1. Structures of "cis" and "trans" isomers of $[RuH(BINAP)_2]^+$ ion, (a) and (b), and trans-$[RuH(\eta^2\text{-}H_2)(BINAP)_2]^+$ ion, (c).

tivity measurement indicated that **1** is a uni-univalent electrolyte (Λ_M = 6.8×10^{-3} $S\cdot m^2\cdot mol^{-1}$; 4.7×10^{-4} $mol\cdot dm^{-3}$ in CH_3NO_2). The ^1H-NMR spectrum (400 MHz) of **1** in $CDCl_3$ revealed two hydride signals at -22.23 (broad singlet) and -6.25 ppm (doublet of quartets, J(H,P:trans) = 69 Hz, J(H,P:cis) = 27, 21 Hz). The intensity ratio of these signals at room temperature was 2:1. These spectral features, along with ^{31}P-NMR (162 MHz) data,[6] indicate the coexistence of two isomers, which are stereochemically rigid within the time scale of NMR. The structures of two isomers can be described as follows, assuming the complex ions to have the five-coordinate square pyramidal geometry. Thus, the minor isomer, which shows the hydride resonance at -6.25 ppm and four distinct ^{31}P resonances, is ascribed to the "cis" isomer, where the hydride and the vacant site are adjacent to each other and four phosphorus atoms are non-equivalent to one another (Fig. 1(a)). The dominant isomer with the hydride at -22.23 ppm and a broad single ^{31}P resonance is assigned to the "trans" isomer; i.e. four phosphorus atoms occupy the basal plane and the hydrido ligand at the apex is located at the anti position of the vacant site (Fig. 1(b)).

One of the significant problems to be investigated is whether any complex that is five-coordinate in the solid state remains five-coordinated in solution or not.[7] For a five-coordinate complex a solvent molecule possibly interacts with the central metal ion at the sixth "vacant" coordination site to generate a six-coordinate complex in solution. We observed in fact that complex **1** gradually changed into $[RuHCl(BINAP)_2]$ in chloroform solution at room temperature; a strong piece of evidence for the interaction between chloroform and $[RuH(BINAP)_2]^+$ ion. It is supposed, therefore, that the isomers of complex ion $[RuH(BINAP)_2]^+$, which were considered to be five-coordinated in the foregoing discussion, are, at least in part, coordinated weakly with a solvent molecule (chloroform), giving rise to the six-coordinate $[RuH(S)(BINAP)_2]^+$ ion (S = solvent).

Interestingly, complex **1** was found to catalyze the hydrogenation of itaconic acid under very mild conditions.[8] Further, the color of THF solution of **1** turned immediately from red to pale yellow upon contact with H_2 gas in the hydrogenation procedure. Similar color change was detected in the formation of the molecular hydrogen complex $[RuH(H_2)(dppe)_2]BF_4$ from $[RuH(dppe)_2]BF_4$ (dppe = 1,2-bis(diphenylphosphino)ethane.[9] The exposure of complex **1** in THF to H_2 gas at room temperature resulted in the formation of hydrido(η^2-dihydrogen) complex trans-[RuH(η^2-H_2)-(BINAP)$_2$]PF_6 (**2**) in 67% yield as white crystals (Found: C, 78.1; H, 5.0%. Calcd for $C_{88}H_{67}F_6P_5Ru$: C, 78.4; H, 4.9%.). Under reduced pressure or inert gas atmosphere such as argon and nitrogen, the color of crystals **2** immediately changed from white to red, but its original color, white, was instantly restored upon contacted again with H_2 gas.

The ^{1}H- and ^{31}P-NMR$^{10)}$ spectra of complex **2** in $CDCl_3$ are consistent with a pseudo-octahedral structure in which the η^2-dihydrogen ligand occupies the coordination site trans to the terminal classical hydride (Fig. 1(c)). The terminal hydride resonance appeared at -5.87 ppm as a triplet of triplets, *J*(H,P) = 14 and 23 Hz. This pattern resembles closely to the hydride signal of trans-RuHCl(BINAP)$_2$, the molecular structure of which has been established by an X-ray study.$^{3b)}$ The η^2-dihydrogen resonance of **2** was monitored at -1.13 ppm as a broad singlet (Fig. 2), the pattern of which was basically similar to those previously reported for molecular hydrogen complexes.$^{11)}$

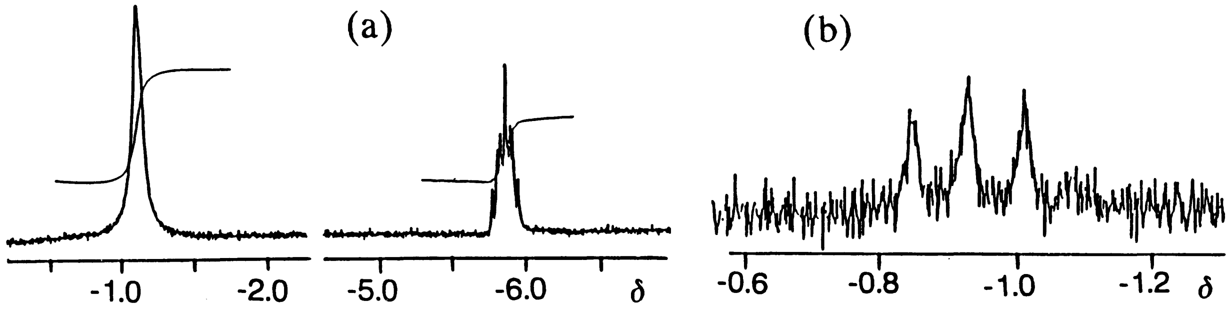


Fig. 2. High field ^{1}H-NMR spectra (400 MHz); (a) trans-[RuH(η^2-H_2)(BINAP)$_2$]PF_6 (**1**) in $CDCl_3$, (b) trans-[RuD(η^2-HD)(BINAP)$_2$]PF_6 (**3**) in THF-d_8.

The ^{1}H-NMR measurement clarified further that the introduction of H_2 gas into a THF-d_8 solution of complex **1** caused the immediate disappearance of the two hydride resonances of **1** and the alternative emergence of the signals of complex **2**. This shows that the isomers of [RuH(BINAP)$_2$]$^+$ converge on trans-[RuH(η^2-H_2)-(BINAP)$_2$]. The exposure of complex **1** to D_2 gas at room temperature in THF-d_8 immediately gave a mixture of isotopomers including [RuD(η^2-HD)(BINAP)$_2$]PF_6 (**3**). Its H-D coupling constant *J*(H,D) was 30 Hz (1:1:1) (Fig. 2), which was indicative of η^2-HD complex. The H-D coupling constant values *J*(H,D) reported so far for molecular hydrogen complexes range from 21.9 to 34 Hz.$^{11)}$ Although the detailed molecular structure of **2** has not been determined yet due to the difficulty in obtaining single crystals, the results described above strongly support the structure assignment to complex **2**.

Besides H_2 gas, complex **1** reacted readily with Cl^-, Br^-, and CO at the vacant coordination site to afford saturated complexes trans-RuHX(BINAP)$_2$ (X = Cl^-,$^{3)}$ Br^- $^{12,13)}$ and trans-[RuH(CO)(BINAP)$_2$]$PF_6$$^{13,14)}$ in good to high yields. The addition of CH_3ONa (ca. 1.5 equiv. in methanol) to a solution of complex **1** in THF at room temperature resulted in the formation of dihydrido complex

$Ru(H)_2(BINAP)_2$,[13,15] which was produced by the β-elimination of coordinating methoxide. It is clarified, therefore, that the five-coordinate complex **1** is an excellent precursor for a variety of novel Ru-BINAP complexes due to its active vacant site. In addition, some of the newly obtained Ru-BINAP complexes revealed notable catalytic activity for hydrogenation and hydrogen transfer reactions.8) We will report the details of the asymmetric hydrogenation of olefins using **1** and **2** in a subsequent paper.

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12) Found: C, 73.5; H, 4.6%. Calcd for $C_{88}H_{65}BrP_4Ru$: C, 74.1; H, 4.6%.

13) Satisfactory ^1H- and ^{31}P-NMR spectral data were obtained.

14) Found: C, 69.9; H, 5.2%. Calcd for $C_{89}H_{65}F_6OP_5Ru$: C, 70.3; H, 4.3%.

15) Found: C, 78.1; H, 5.0%. Calcd for $C_{88}H_{66}P_4Ru$: C, 78.4; H, 4.9%.

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