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THE CRYSTAL STRUCTURE OF CYCLOOCTA-1,5-DIENE-4-DIPHENYLPHOSPHINO-2-DIPHENYLPHOSPHINOMETHYLPYRROLIDINE(PPM)-RHODIUM(I) PERCHLORATE

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The crystal structure of the title compound which has almost no chiral activity in hydrogenation reaction was determined by X-ray diffraction method. The coordination of the rhodium ion was found to be a trigonal bipyramid, the apices being occupied by a diene group and an imino group of the pyrrolidine ring.

In the course of a study on chiral pyrrolidinephosphine-rhodium catalysts, one of the present authors (K.A) synthesized PPM-Rh(I) complex in order to clarify the role of N-substituents in determining the optical yields of the products[1]. It was found that PPM-Rh complex exhibits almost no preference for the absolute configuration of the products in the hydrogenation reaction. Actually, the optical yield for the hydrogenation of itaconic acid was found to be nearly zero[2]. This makes a great difference between PPPM(N-pyvaloyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine)-Rh(I) complex[3] which has a bulky substituted group at the pyrrolidine nitrogen atom. We have therefore undertaken an X-ray crystal structure analysis of the cyclooctadiene PPM-Rh(I) perchlorate complex to elucidate the structure of the complex.

The crystals were grown from a methanol solution as orange plates. A small crystal with approximate dimensions of 0.3 X 0.2 X 0.05 mm was mounted on a Philips PW 1100 four-circle diffractometer. The lattice constants and intensity data were measured using MoKα radiation monochromated by a graphite plate. The crystal data are given in Table 1.

Table 1. Crystal Data

Cyclooctadiene-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine-Rh(I) perchlorate
(COD-PPM-$Rh^{+}ClO_4^{-}$)
$C_{29}H_{29}NP_2Rh \cdot C_8H_{12} \cdot ClO_4$, MW = 764.0.
Triclinic
Space group P1, Z = 2,
Dx = 1.436 gcm^{-3}.
a = 13.489(9), b = 11.998(8), c = 11.205(8)Å
α = 102.27(2)°, β = 89.82(2)°, γ = 94.44(2)°.
μ for MoKα radiation = 6.78 cm^{-1}.

Although the triclinic unit cell contains two molecules, the non-centrosymmetric space group P1 was assigned, because the molecule of PPM is asymmetric. A total of 5409 reflections were measured as above the 2σ(I) level, in the 2θ range 6°∿50°. No absorption correction was applied.

The crystal structure was solved by the heavy atom method

on the basis of Rh and P atoms. The location of perchlorate oxygen atoms was difficult to find due to very large thermal vibrations. Refinement of the atomic parameters was carried out by the least-squares calculations with block-diagonal approximations. Hydrogen atoms were located on the difference electron density map and their positional and isotropic thermal parameters were refined with reduced damping factors. The effect of anomalous dispersion of MoKα radiation for Rh, P, and Cl atoms was also taken into account. The correction terms f' and f" for these atoms were taken from International Tables for X-ray Crystallography[4]. The absolute configuration of the molecule was assumed to be the same as that of COD-PPPM-Rh perchlorate complex determined previously. The refinement was stopped at the stage giving the R value of 0.052.

The two crystallographically independent molecules I and II have very similar structure to each other. In Fig.2 is given the structure of molecule I showing the coordination of two phosphorus atoms, two diene bonds and an imino group around the rhodium ion. Figs.3 are the perspective drawing of the molecules I and II viewed along the line bisecting the P-Rh-P angle. The figures clearly show the similarity of the structures of these two kinds of molecules.

The outstanding feature of the present structure is the trigonal bipyramidal coordination of the rhodium ion[5]. As shown in Fig.1, the bond lengths of the cyclooctadiene molecule especially those of molecule I, indicate that the double bonds are localized to C(34)=C(35) and C(31)=C(38). The former bond lies nearly on the equatorial plane of the coordination while the latter bond is situated nearly at the apical position of the bipyramidal coordination. The other side of the apices is occupied by the pyrrolidine imino group. The distance between the rhodium ion and the nitrogen atom is 2.147(7)Å [2.157(7)Å in molecule II].

Assuming the pyramidal configuration of the nitrogen atom, two possible arrangements of the imino hydrogen atom should be considered. The one is to orient the hydrogen atom close to the rhodium ion and the other is to orient outward from the complex ion. In the former case, the nitrogen atom binds to the rhodium ion through the hydrogen atom, but in the latter case, it coordinates to the rhodium ion by donating the lone pair electrons. The difference electron density map calculated without imino hydrogen atom contributions showed some ghost peaks near the rhodium ions having comparable peak height with hydrogen atoms. It was therefore not possible to locate the imino hydrogen atoms decisively by diffraction methods. The infra-red spectra of the present complex(COD-PPM-$Rh^+ClO_4^-$) and COD-PPPM-$Rh^+ClO_4^-$ showed that no absorption band corresponding to the Rh-H stretching vibrations (∿ 2100 cm^{-1}) was found for both complexes while that of the N-H stretching vibrations was observed only for the PPM complex at 3200 cm^{-1}. All of these facts indicated the latter is actually the case.

It is also to be noted that the perchlorate ion is situated close to the imino nitrogen atom but not to the rhodium ion as has been observed in COD-PPPM-Rh perchlorate complex. The distances between O(3), O(4') and N are 3.036(18)Å and 2.914(25)Å respectively and those between O and H at assumed positions (outward from the complex ion) are 2.60Å and 2.29Å, and the N-H---O angles are 106° and 119° respectively for molecule I and II.

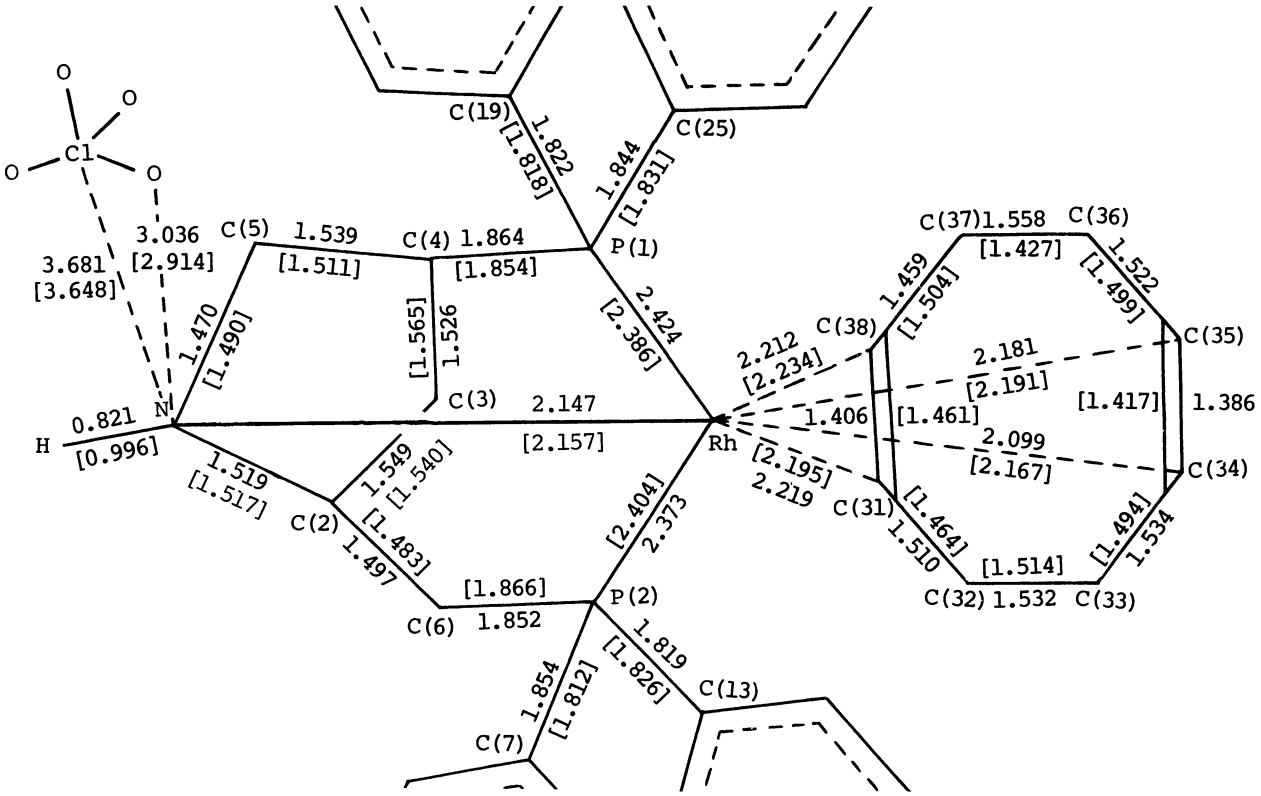

Fig.1 Comparison of the bond lengths found in molecule I and molecule II (in brakets).

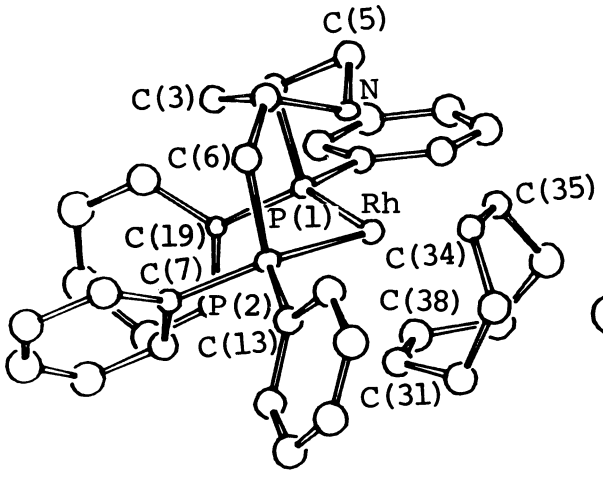

Fig.2 The stereo-structure of the complex formed by molecule I.

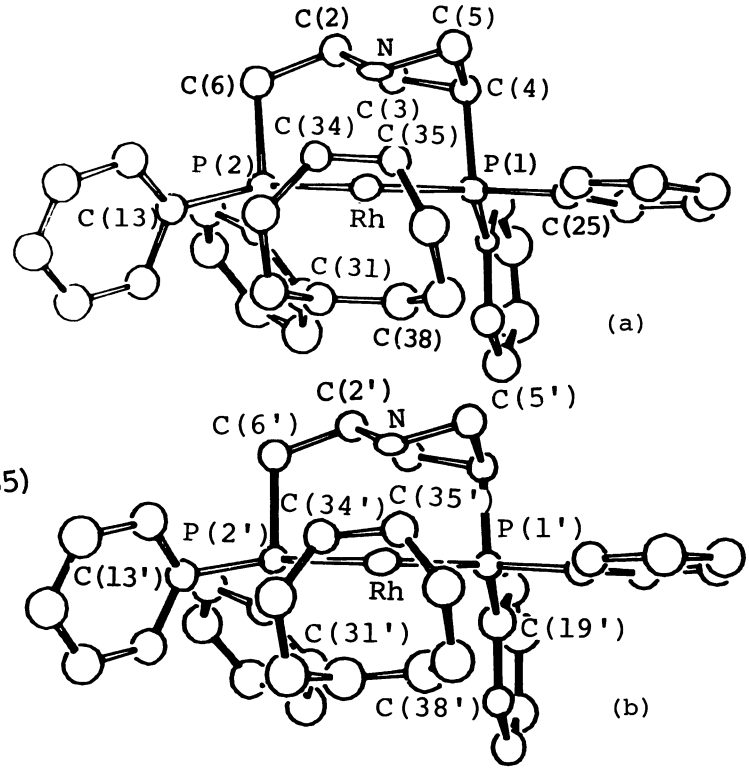

Fig.3 Perspective view of the molecule I (a) and II (b) as seen along the bisector of P-Rh-P.

It is now clearly shown that the unsubstituted pyrrolidine nitrogen atom coordinates directly to the metal ion completing the trigonal bipyramidal five coordination around Rh(I). This may be not surprising since the unsubstituted pyrrolidine nitrogen atom exhibits a rather strong basisity having a strong tendency to coordinate to the metal ion. The poor chiral activity of the present catalyst may be explained by several factors. We should like to point out the following facts.

(1) Symmetrical arrangement of the P- phenyl carbon bonds in the present complex [P(1)-C(19), P(1)-C(25), P(2)-C(7) and P(2)-C(13)] poses a symmetrical field for the substrate. The symmetry may be violated by the preferred asymmetric rotation of the phenyl groups about the above mentioned bonds but if they rotated in a manner of free rotation, the environment at the fourth ligand site would be symmetrical. Furthermore, the skeletal conformation of the phosphinopyrrolidine ligand is fixed by donating the pyrrolidine nitrogen atom to the rhodium ion and there seems to be no possibility of changing the conformation of the skeleton. The fact that the asymmetric orientation of the two phenyl groups near the substrate binding site in the crystals [two phenyl groups involving C(13) and C(25) in Fig.3] does not affect the preference of optical yield, can not be accounted for by the hypothesis proposed by Onuma et al.[6] although the difficulty may be explained by the difference in coordination of Rh(I).

(2) Unusual trigonal bipyramidal coordination of Rh(I) leaves only one ligand binding site for the substrate if the fifth ligand site is occupied by the hydrogen atom. It is therefore probable that the substrate at the ligand site has more freedom of movement or binding than that found in usual six coordinated catalyst in which the substrate is believed to be fixed by coordinating two functional groups to rhodium. Arbitrariness of the binding state of the substrate may result in the lack of stereo-specificity of the catalytic reaction.

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