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^{31}P NMR STUDIES ON THE MECHANISM OF ASYMMETRIC HYDROGENATION CATALYZED BY RHODIUM(I) COMPLEXES WITH CHIRAL PYRROLIDINODIPHOSPHINE LIGAND

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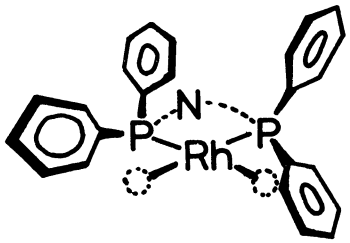
The structures of rhodium(I) complexes with a chiral pyrrolidinodiphosphine, BPPM, are studied by means of ^{31}P NMR spectroscopy. The spectra show that there are two conformational isomers without substrate. However, the complex takes a preferred conformation by the coordination of an olefinic substrate. The results are well accommodated by the "induced fit" model.

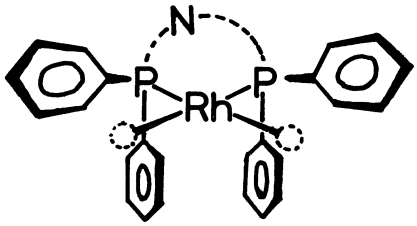
Asymmetric hydrogenation of olefins and carbonyl compounds catalyzed by rhodium (I) complexes with chiral diphosphine ligands has been attracting much interest.[1] As to the mechanism of asymmetric induction, however, there has been little direct evidence. In 1977, Slack and Baird demonstrated the possibility of direct observation of the intermediate complexes in solution by means of ^{31}P NMR spectroscopy.[2] Then, we started our ^{31}P NMR study expecting the direct observation of the chiral rhodium complexes coordinated with substrate molecule. Very recently, Brown and Chaloner succeeded in observing such diastereomeric intermediate complexes with (Z)-α-benzamidocinnamic acid or its ester using DIOP[3a] and DIPAMP[3b] as chiral ligand by ^{31}P NMR. Therefore, their work prompts us to report here our ^{31}P NMR studies on the structure of the rhodium complexes with BPPM[4] as chiral ligand in solution, which are considerably different from those of Brown and Chaloner.[3]

We have employed itaconic acid as substrate since we recently found that the asymmetric hydrogenation of this substrate catalyzed by a rhodium complex with BPPM achieved a very high optical yield (84-92 %e.e.) production of (S)-methylsuccinic acid.[5]

First, we measured the ^{31}P NMR spectra of the neutral and the cationic rhodium (I) complexes with BPPM in CD_3OD. As the figures (a, b) clearly show, (i) two phosphorus atoms in BPPM ligand appear in different region with each other; the lower signals are assigned to the phosphorus of diphenylphosphinomethyl moiety (P_1) and the higher signals are assigned to that of diphenylphosphino group linking to the pyrrolidine ring (P_2), (ii) there are two species with almost equivalent ratio since there appear two sets of quartet in P_1 or P_2 region. On the basis of the stereochemical inspection using CPK models of the rhodium complexes with BPPM or other pyrrolidinodiphosphines, only two conformations are possible. The simplified drawings are as follows:



Conformation A

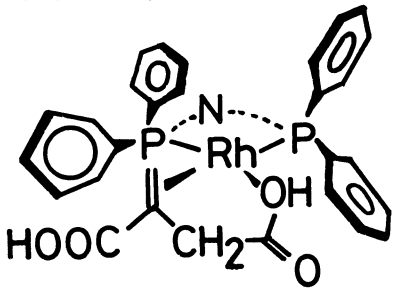


Conformation B

The X-ray analysis of the cationic rhodium complex with PPPM[6] has revealed that the complex takes the conformation A in a crystalline state.[7] We believe that two species observed in solution exactly correspond to the two conformational isomers suggested by the CPK model inspection, and that only the conformation A plays a key role in the asymmetric induction because of the highly symmetrical coordination sphere of the conformation B.

Next, we hydrogenated cyclooctadiene ligand in the cationic complex to get the corresponding methanol-d_4 complex. The ^{31}P NMR spectrum of this methanol complex (figure c) also clearly displays the existence of two conformational isomers, in which the signals of P_1 and P_2 shift to the lower field remarkably.

To this solution, itaconic acid (20 fold excess of the complex) was added. As figure d shows, the addition of itaconic acid changes the spectrum dramatically, and the formation of the predominant diastereomeric complex is observed. Namely, the rhodium complex takes a preferred conformation which we believe to be the conformation A when itaconic acid comes into the coordination sphere.



The results are best interpreted as the "induced fit" phenomena of the chiral rhodium complex by the coordination of the substrate.

At present, the corresponding spectra of the neutral complexes are somewhat complicated because of the presence of chlorine ligand, and considerable broadening is observed even at low temperatures.

Although the observed ratio of the two diastereomers only reflects the preliminary chiral recognition of the enantioface of itaconic acid by the chiral catalyst, and to get the final value of asymmetric induction (% e.e.) the kinetic factors, i.e., the difference in the rate of hydride migration in the two diastereomeric intermediate complexes, should be accounted, we can observe directly what is going on in the coordination sphere of the chiral rhodium catalyst during the course of hydrogenation by ^{31}P NMR spectroscopy. The present approach is of particular signifi-

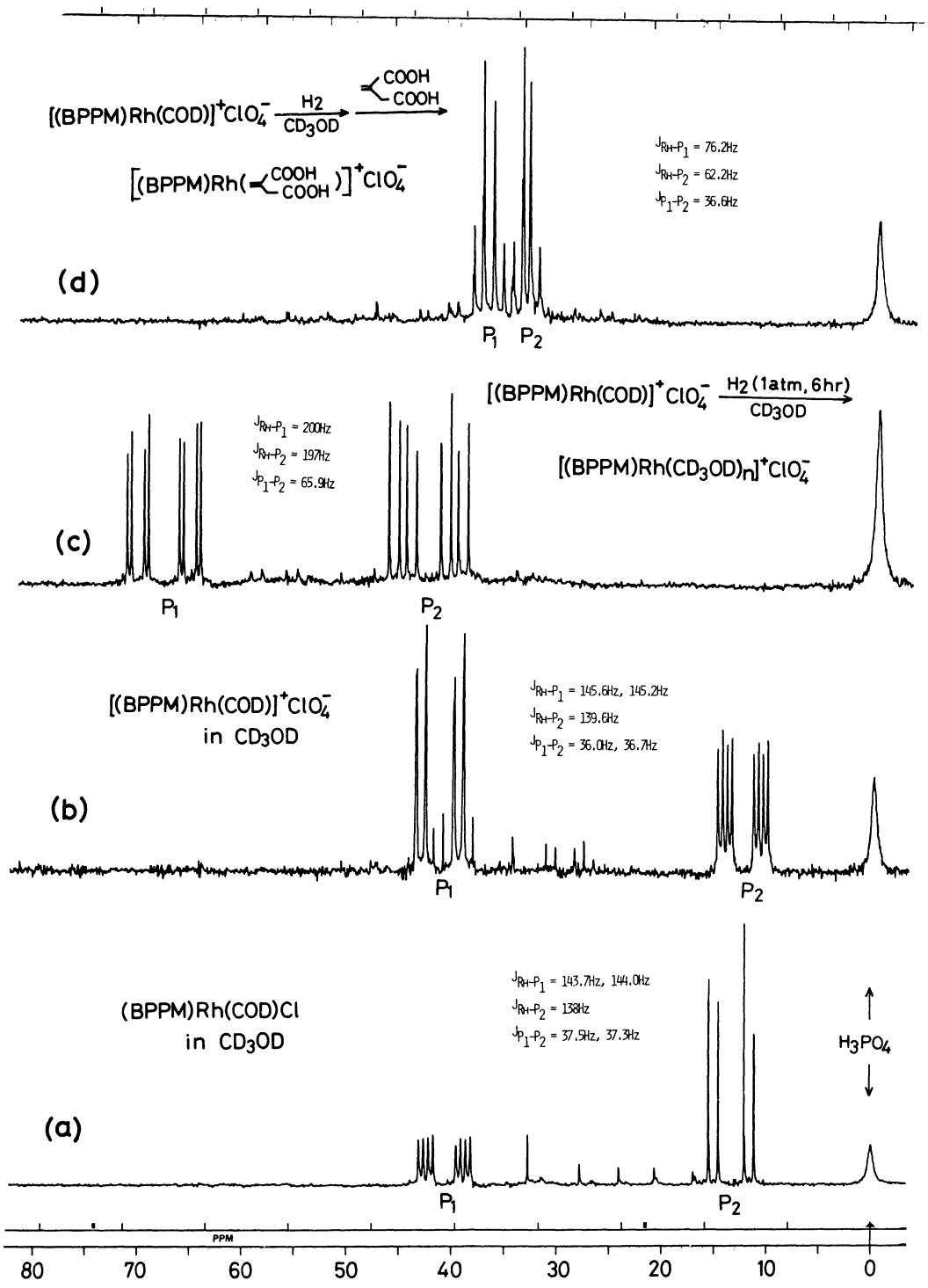


Figure. ^{31}P proton decoupled NMR spectra of BPPM-rhodium complexes

^{31}P Fourier transfer NMR spectra were measured on a Varian XL-100 spectrometer at 302 K with H_3PO_4 as the external standard. Coupling constants, J_{Rh-P_1}, J_{Rh-P_2}, and $J_{P_1-P_2}$, are shown in the figure.

cance with respect to the recently proposed mechanism of the hydrogenation of olefins catalyzed by a rhodium complex with cis-chelate diphosphine ligand, in which it is demonstrated that an oxidative addition of molecular hydrogen takes place after the coordination of olefin.[8]

Mechanistic studies on asymmetric hydrogenation of prochiral olefins and ketones catalyzed by rhodium(I) complexes with chiral diphosphine ligands are actively underway by using ^{31}P NMR spectroscopy.

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