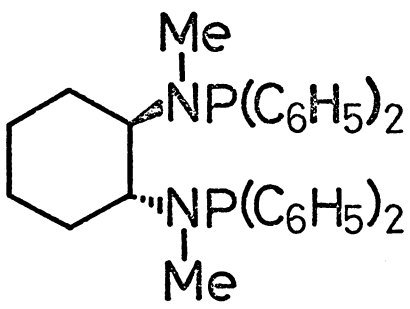
CHEMISTRY LETTERS, pp. 905-908, 1979. Published by the Chemical Society of Japan

ASYMMETRIC HYDROGENATION OF α-ACYLAMINOCINNAMIC ACID DERIVATIVES CATALYZED BY AMINOPHOSPHINE-RHODIUM COMPLEX. INVERSION IN THE STEREOSELECTIVITY OF THE AMINOPHOSPHINE-RHODIUM COMPLEX CATALYST BY N-METHYLATION OF THE LIGAND

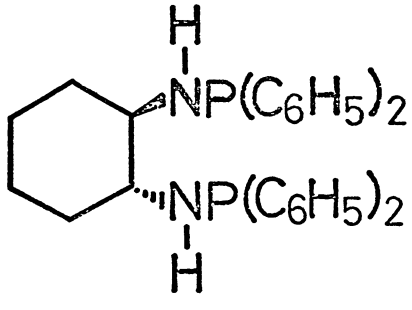
Ken-ichi ONUMA*, Tomiyasu ITO, and Asao NAKAMURA
Central Research Laboratories, Ajinomoto Co., Inc.
1-1 Suzuki-cho, Kawasaki 210

Marked difference in the stereoselectivity of the rhodium complex with (1R,2R)-bis(diphenylphosphinamino)cyclohexane caused by N-methylation of the ligand in the asymmetric hydrogenation of α-acylaminocinnamic acid derivatives is described.

Rencet reports by Hanaki et al.[1a,b] on the asymmetric hydrogenation of α-acylaminocinnamic acids by the chiral aminophosphine rhodium complexes prompt us to publish our own results on the closely related topic. In their reports,[1a,b] Hanaki et al. have shown that N-acyl-(S)-amino acids are selectively obtained by the hydrogenation catalyzed by the rhodium complex with (1R,2R)-bis(N-diphenylphosphino-N-methylamino)cyclohexane, (R,R)-1. It was found that the same reaction but with the rhodium complex with (1R,2R)-bis(diphenylphosphinamino)cyclohexane, (R,R)-2,[2] afforded N-acyl-(R)-amino acids. Since these two chiral rhodium complexes have the same configuration, the origin of the alternative in chirality of the produced N-acylamino acids should further be explored.



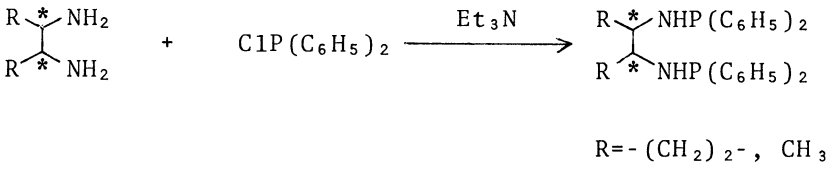
(R,R)-1



(R,R)-2

In this paper, we would like to report several examples of the inversion of the stereochemistry of N-acylamino acids associated with N-methylation of the aminophosphine in chiral rhodium complexes.

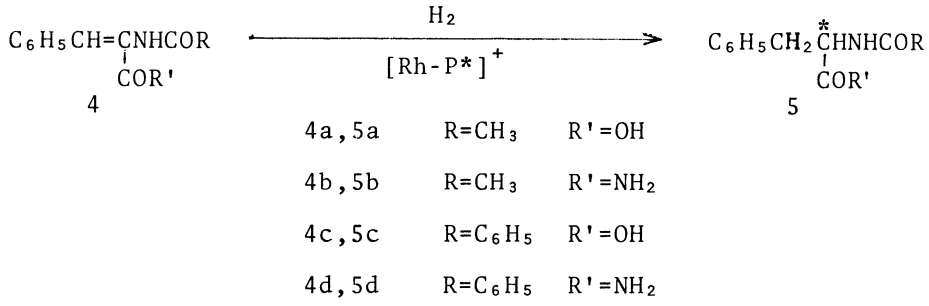
Chiral aminophosphines (R,R)-2, (1S,2S)-bis(diphenylphosphinamino)cyclohexane [(S,S)-2], and (2S,3S)-bis(diphenylphosphinamino)butane [(S,S)-3] were prepared by the reaction of chlorodiphenylphosphine with (1R,2R)-diaminocyclohexane,[3] (1S,2S)-diaminocyclohexane,[3] and (2S,3S)-diaminobutane,[4] respectively (Scheme 1). Each of the aminophosphines was used as a chiral ligand in the cationic complex, $[Rh(COD)(P\text{-}P)]^+ClO_4^-$.[5]



(Scheme 1)

(R,R)-2: mp 130-132°C, $[\alpha]_D^{15}$=-4.51°(c=1.0, C_6H_6); (S,S)-2: mp 130-132°C, $[\alpha]_D^{15}$=+4.48°(c=1.0, C_6H_6); (S,S)-3: mp 83-85°C, $[\alpha]_D^{15}$=+2.98°(c=0.5, C_6H_6).

The hydrogenation reactions always proceeded quantitatively at initial hydrogen pressure of 8Kg/cm^2 and at room temperature (Scheme 2).



(Scheme 2)

The resulting N-acylamino acids were isolated carefully and the optical purities were determined either by measuring optical rotations[6] or by liquid chromatography.[7]

The results are summarized in Table 1. As can be seen in the Table 1, the optical yields vary depending on the substrate structures and solvents. N-Acyl-(R)-amino acids were always obtained in excess by the hydrogenation using the rhodium complex of (R,R)-2. On the other hand, N-acyl-(S)-amino acids were excessively obtained using either (S,S)-2 or (S,S)-3 as a chiral ligand. The most interesting result is that N-acyl-(S)-amino acids were always obtained by using the (R,R)-1 complex instead of the (R,R)-2 complex.

Table 1. Asymmetric hydrogenation with chiral aminophosphine-rhodium complexes

Substrate	Solvent[a)]	Optical yield[b)] (absolute configuration)			
		(R,R)-2	(S,S)-2	(S,S)-3	(R,R)-1[c)]
4a	methanol		30(S)		
"	ethanol	41(R)	41(S)	45(S)	89(S)
"	2-propanol		71(S)	80(S)	
"	methanol/benzene		50(S)		
"	ethanol/benzene	70(R)	72(S)	62(S)	
"	2-propanol/benzene		63(S)	94(S)	
4b	ethanol/benzene	92(R)	92(S)	94(S)	
4c	ethanol	43(R)	43(S)	32(S)	92(S)
"	2-propanol		70(S)	80(S)	
"	ethanol/benzene	62(R)	60(S)	69(S)	
"	2-propanol/benzene		48(S)	93(S)	
4d	ethanol/benzene		70(S)	80(S)	

a) The ratio of the mixed solvent is 1:1 (v/v).

b) N-acetyl-(S)-phenylalanine $[\alpha]_D^{26}=+46.0°$ (c=1.0, C_2H_5OH),[6] N-benzoyl-(S)-phenylalanine $[\alpha]_D^{26}=-40.3°$ (c=1.0, CH_3OH).[6] The optical purities of N-acetylphenylalaninamide and N-benzoylphenylalaninamide were determined by liquid chromatography.[7]

c) Hanaki et al.[1b]

Recently, Hanaki et al.[1b] have reported that the hydrogenation of α-acyl-aminocinnamic acids with a rhodium complex of (R)-1,2-bis(N-diphenylphosphino-N-methylamino)propane results in the N-acyl-(S)-amino acids. Therefore, it can be said that the inversion in the stereoselectivity by N-methylation of the ligand may be an essential feature for these aminophosphine-rhodium complexes.

The origin of this phenomenon may be attributed to the relative spacial arrangement of the two phenyl groups on the phosphorus atom which chould change under the influence of chiral surroundings. A stereochemical consideration using CPK molecular models indicates that the two phenyl planes can exist in a skewed arrangement either with a right-handed helical orientation for the (R,R)-1 complex or with a left-handed helical orientation for the (R,R)-2 complex. The inversion in stereoselectivity of the rhodium complex may therefore be due to the difference of the helical conformation of phenyl groups. A detailed stereochemistry of phenyl groups of the complex is currently studied by X-ray crystallographic analysis, which may hopefully yield further insights to the stereochemical considerations for the origin of induced chirality of the hydrogenation product by rhodium complexes.

References

(1) a) K. Hanaki, K. Kashiwabara, and J. Fujita, Chem. Lett., 1978, 489-490.
b) K. Hanaki, K. Kashiwabara, and J. Fujita, 28th Symposium on Coordination Chemistry, Japan (Matsuyama), 1978, Abstracts 2A07.
(2) K. Onuma, T. Ito, and A. Nakamura, Japanese Patent Pending (Oct. 18, 1977).
(3) R.G. Asperger, and C.F. Liu, Inorg. Chem., 4, 1492 (1965).
(4) F.H. Dickey, W. Fickett, and H.J. Lucas, J. Am. Chem. Soc., 74, 944 (1952).
(5) R.R. Schrock, and J.A. Osborn, J. Am. Chem. Soc., 93, 2397 (1971).
(6) M.D. Fryzuk, and B. Bosnich, J. Am. Chem. Soc., 99, 6262 (1977).
(7) J.M. Manning, and S. Moore, J. Biol. Chem., 243, 5591 (1968).

(Received May 9, 1979)