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NEW ATROPISOMERIC CHIRAL BISPHOSPHINE, (S)-6,6'-DIMETHYL-2,2'-BIS(DIPHENYLPHOSPHINAMINO)BIPHENYL, AND ASYMMETRIC HYDROGENATION USING THE Rh(I) COMPLEX THEREOF

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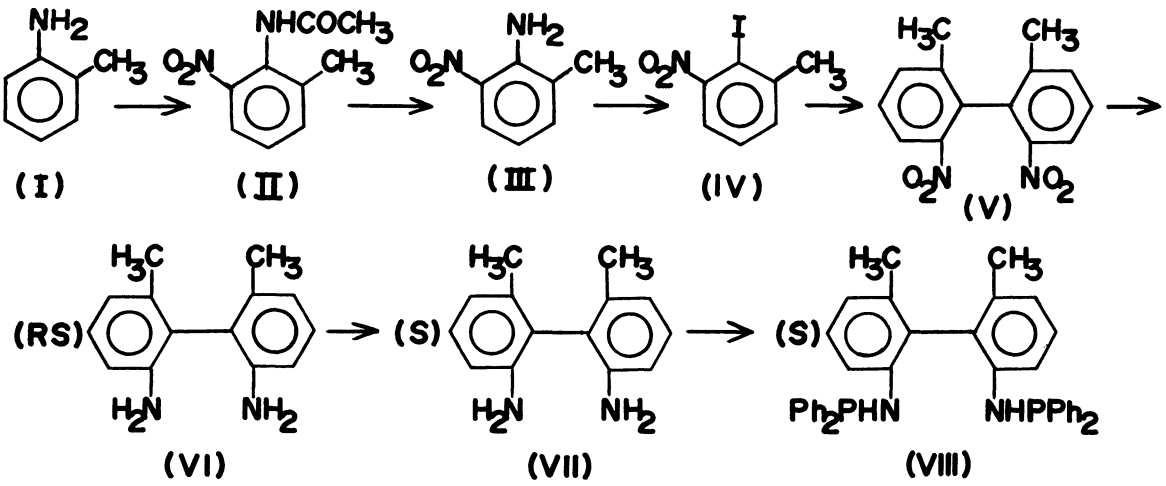
Atropisomeric chiral bisphosphine, (S)-6,6'-dimethyl-2,2'-bis(diphenylphosphinamino)biphenyl (MABP) was newly prepared, and the Rh(I) complex thereof was found to be highly effective for the asymmetric hydrogenation of 2-acetamidoacrylic acid even under 1 atm of hydrogen pressure at a temperature below 0°C.

Asymmetric hydrogenation by the use of the Rh(I) complexes containing chiral phosphines is a matter of current interest because it is a promising method for obtaining preferentially one of a pair of enantiomers from the parent prochiral compounds containing C=C, C=O and C=N groups. In the past decade, many studies have been devoted to developing efficient chiral phosphines. The chiral phosphines reported hitherto can be divided into the following four classes: (1) consists of the chiral P-atom phosphines such as CAMP,[1] DIPAMP[2] and bis(phenyltolylphosphino)ethane (BPTE)[3]; (2), of the chiral C-atom phosphines such as DIOP,[4] BPPM,[5] CHIRAPHOS,[6] (3S)-[N,N'-bis(diphenylphosphino)-3-aminopiperidine (BPPAP)[7] and (R,R)-1,2-bis(diphenylphosphinamino)cyclohexane (BDPMC)[8]; (3), of the chiral ferrocenyl phosphines such as BPPFA, PPFA and BPPFOH[9]; and (4), of the atropisomeric chiral phosphines such as BINAP,[10] NAPHOS,[11] (R)- and (S)-2,2'-bis(diphenylphosphinamino)-1,1'-binaphthyl (BDPAB)[12] and (-)-1,1'-2-naphthylbis(diphenylphosphinite) (NBDP).[13] As for classes (1) to (3), a variety of effective phosphines have extensively been designed, but the phosphines of class (4) have been restricted only to the binaphthyl derivatives. The phosphines whose chirality is due to atropisomerism have the advantage of non-flexibility of conformation and thereby they are certainly useful for clarifying the mechanisms of asymmetric hydrogenation which still remain ambiguous.

Recently, we have succeeded in preparing new atropisomeric chiral phosphine, (S)-6,6'-dimethyl-2,2'-bis(diphenylphosphinamino)biphenyl (MABP). The phosphine is very air-stable and the Rh(I) complex thereof was found to be highly effective for the asymmetric hydrogenation of 2-acetamidoacrylic acid even under 1 atm of hydrogen pressure at a temperature below 0°C.

Preparation of MABP. The preparative route for the ligand is outlined

in Scheme 1. 2-Amino-3-nitrotoluene (III) was prepared from the starting o-toluidine (I) via the formation of 6-nitroacetotoluidine (II) by a slight modification of the procedure of Howard.[14] The 2-amino-3-nitrotoluene (III)



Scheme 1. Preparative Route for MABP.

was then converted into 2-iodo-3-nitrotoluene (IV) according to a procedure similar to that of literature[15] in which nitrosyl sulfate was effectively used in the diazotization step. The derivation of 2,2'-dimethyl-6,6'-dinitrobiphenyl (V) from 2-iodo-3-nitrotoluene (IV) was carried out using pulverized copper through Ullmann's reaction.[16] The reduction of the dinitrobiphenyl (V) by hydrazine in the presence of Raney Ni-W2[17] afforded racemic 6,6'-dimethyl-2,2'-diaminobiphenyl (VI). The resolution of the racemic diaminobiphenyl (VI) by L-(+)-tartaric acid was repeatedly carried out until the observed $[\alpha]_D$ of the diaminobiphenyl (VII) resolved reached that of literature.[18] The optically active (S)-6,6'-dimethyl-2,2'-diaminobiphenyl (VII) thus obtained melts at 156-158°C (lit.: 156-157°C) and gives $[\alpha]_D$= -36° (c 1.6, N HCl)(lit.: -36°).

The desired (S)-6,6'-dimethyl-2,2'-bis(diphenylphosphinamino)biphenyl (VIII) was derived from the (S)-diaminobiphenyl (VII) as follows: under a nitrogen atmosphere, triethylamine (1.52 cm^3, 10.8 mmol) was added to a solution of VII (1.15 g, 5.4 mmol) in dry benzene (30 cm^3), and thereto chlorodiphenylphosphine (2 cm^3, 10.8 mmol) was dropwise added using syringe. The mixture was then continuously stirred for about 4 h at room temperature; after that, it was refluxed for about 3 h and cooled to room temperature. The mixture was then treated with water to remove water-soluble undesired materials. Then, the organic layer was separated and once filtered to remove white unknown materials. The filtrate was roto-evaporated to give yellowish green oily products. TLC revealed that the products contain the desired biphenyl (VIII) together with some impurities. The products were therefore purified by means of silica-gel chromatography using toluene as the eluent. The fractions containing the desired phosphine were combined altogether and roto-evaporated to yield the colorless oily product. The product was dissolved in a small amount of ethanol and thereto a sufficient

amount of water was drop by drop added to induce the precipitation of the phosphine. The resulting mixture was allowed to stand in a refrigerator to complete precipitation. White precipitates thus obtained were collected by filtration and dried over P_2O_5. The precipitates were further purified by redissolving them in ethanol and adding water to the ethanolic solution. Yield: 1.12 g (36 %). mp: 98-100°C. $[\alpha]_D^{25}$: -140° (c 1.1, C_6H_6).

Found: C, 78.47; H, 5.60; N, 4.62%. Calcd for $C_{38}H_{34}N_2P_2$: C, 78.61; H, 5.90; N, 4.82%.

Hydrogenation of 2-acetamidoacrylic acid (AAA) to N-acetyl-(R)-alanine. The hydrogenation was carried out under 1 atm of hydrogen pressure at a temperature of -5-40°C. The Rh(I) catalyst for the hydrogenation was prepared in situ by the reaction of 1/2[RhCl(cod)]$_2$ with MABP (cod: 1,5-cyclooctadiene). The ratio of the catalyst to AAA was 1 : 60. Hydrogenation time was 3 h. The reaction products were worked up by a manner similar to that of literature.[4b] The results are summarized in Table I.

Table I. Results of Hydrogenation

Exp.	Solvent	Temp.(°C)	Optical Yield[a] (%)	Configuration of the Products
1	CH_3OH	-5	81	R
2	CH_3OH	18	70	R
3	CH_3OH	40	68	R
4	$CH_3OH(Et_3N)$[b]	26	74	R
5	CH_3OH[c]	17	70	R

a) Optical yield was calculated based on the value for the optically pure N-acetyl-(R)-alanine, $[\alpha]_D$= 66.5° (c 2, H_2O).[19]

b) Triethylamine (Et_3N) was added to the reaction system. The ratio of Et_3N to the catalyst was 2 : 1.

c) The catalyst recovered after work-up of Exp. 2 was reused in Exp. 5.

Inspection of the table reveals that (1) the optical yield increases as the lowering temperatures (Exp. 1 to 3), (2) the addition of Et_3N increases the optical yield (Exp. 4), and (3) the catalysts can be repeatedly (Exp. 5). The results indicate that the catalyst is very air-stable and highly effective for the asymmetric hydrogenation even at a temperature below room temperature

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