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ASYMMETRIC HYDROGENATION OF α-ACYLAMINOACRYLIC ACIDS BY THE RHODIUM(I) COMPLEX OF (1R,2R)-BIS(N-DIPHENYL-PHOSPHINOMETHYLAMINO)CYCLOHEXANE

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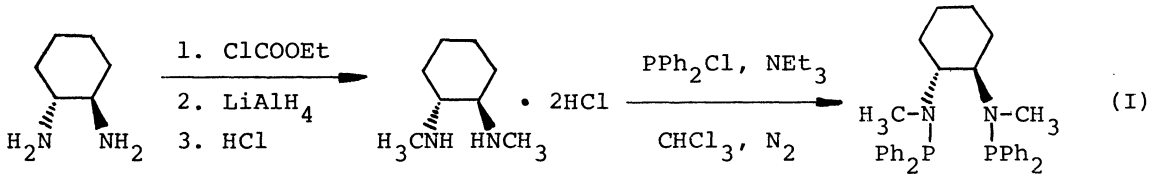
A new rhodium(I)-(1R,2R)-bis(N-diphenylphosphinomethylamino)-cyclohexane complex, the ligand of which is easily prepared from (1R,2R)-bis(methylamino)cyclohexane and chlorodiphenylphosphine, catalyzes asymmetric hydrogenation of some α-acylaminoacrylic acids to yield N-acylated amino acids with high optical purity; N-benzoyl-(S)-leucine, N-benzoyl-(S)-phenylalanine, and N-acetyl-(S)-phenylalanine are obtained in 93, 85, and 73% optical purity, respectively.

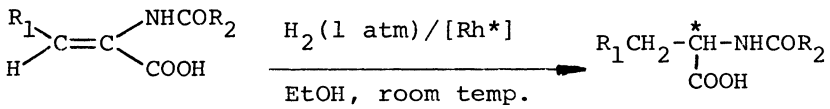
A variety of chiral phosphines have been prepared to investigate asymmetric hydrogenation,[1-3] and some of them are known to be excellently effective. However, tedious procedures are often required for preparing chiral phosphines, in particular those with a chiral phosphorus atom.[1]

We have prepared a new chiral diphosphine from (1R,2R)-diaminocyclohexane ($[\alpha]_D^{22}$= -36°)[4] according to the following scheme:



(I) was easily obtained in a large scale, and identified by elemental analysis and PMR spectroscopy. m.p.= 137-139°C, $[\alpha]_D^{22}$= -7.3°(c 1.1, $CHCl_3$), δ(CH_3)= 2.63ppm(doublet), J(PNCH)= 3.5Hz(in $CDCl_3$, TMS). The aminophosphine (I) forms stable white crystals in air, but is easily oxidized by air in solution, and gives stable complexes with rhodium(I), palladium(II), and platinum(II).

The hydrogenation was carried out under the following conditions:



[Rh*] : 1/2[RhCl(1,5-cyclooctadiene)]$_2$ + 1.0(I)
[Rh*]/Substrate = 1/100 (1 mol%)

The reaction products were carefully isolated so as to avoid the enantiomer enrichment, and identified by optical rotations and PMR spectra. The values given in the Table were reproduced within ±2%.

Table

Substrate	Conversion (%)	Chemical yield(%)	Optical purity(%)	Configuration
$R_1=C_6H_5$, $R_2=CH_3$	97	92	73	S
$R_1=C_6H_5$, $R_2=C_6H_5$	100	99	85	S
$R_1=(CH_3)_2CH$, $R_2=C_6H_5$	100	93	93	S

The specific rotations of the pure enantiomers are taken from ref. 2). The hydrogenation time is 2 to 4 hours depending on the kind and the concentration of the substrate.

The high effectiveness of the present catalyst may be brought about by a conformationally stable, chiral structure of the seven-membered chelate ligand, aminophosphine in the complex. Dreiding molecular models indicate that the two nitrogen atoms are forced to take S configuration to reduce interactions between the two methyl groups and the chiral cyclohexane ring. The models also show that the two phenyl groups on each phosphorus atom adopt different orientations to the square plane of the complex, one axial and the other equatorial, and are hindered or prohibited to rotate around the phosphorus-carbon bonds. Such a rigid and chiral environment around the phosphorus atoms should give rise to the effective asymmetric hydrogenation. The values of the optical purity seem to depend on the bulkiness of the substituents, R_1 and R_2 in the substrates, *i.e.*, the larger the substituents, the higher the optical purity.

Further studies are in progress using chiral phosphines derived from a variety of optically active diamines.

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