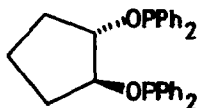


ASYMMETRIC HYDROGENATION BY RHODIUM COMPLEX WITH d-TRANS-1,2-BIS(DIPHENYLPHOSPHINOXY)CYCLOPENTANE AS A CHIRAL LIGAND

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Various chiral ligands have been developed and applied to complex-catalyzed asymmetric hydrogenation.<sup>1)</sup> In the previous communication,<sup>2)</sup> we realized high enantioselectivity in rhodium catalyzed asymmetric hydrogenation using a diphosphinite, d-trans-1,2-bis(diphenylphosphinoxy)cyclohexane (d-trans-BDPCH) as a chiral ligand. However, the phosphinite is conformationally disadvantageous, because it contains a flexible cyclohexane ring. Here we report asymmetric hydrogenation using a new chiral diphosphinite, d-trans-1,2-bis(diphenylphosphinoxy)cyclopentane (d-trans-BDPCP),



whose five-membered ring is conformationally far more rigid than the ring of d-trans-BDPCH.

d-trans-BDPCP, bp 160-175°C (bath temperature)/5-8 × 10<sup>-4</sup> mmHg, [α]<sub>D</sub><sup>19</sup> +45.9° (benzene, c 5.08), was analogously prepared to the method described in our previous communication<sup>2)</sup> (88% yield) from d-trans-1,2-cyclopentanediol (67% e.e.), which was obtained by optical resolution<sup>3)</sup> of stryquinine salt of the bis(hydrogensulfate) of the diol.

The results of hydrogenation are shown in Table. The optical yield in the hydrogenation of α-ethylstyrene using d-trans-BDPCP is much higher than that observed by the use of d-trans-BDPCH or (-)-diop. To our best knowledge, this optical yield, 60%, is the highest one so far attained by the use of homogeneous<sup>4)</sup> complex catalysts for substrates<sup>5)</sup> bearing no polar substituents, such as carboxyl and amido groups. On the other hand, the stereoselectivity was very low in the hydrogenation of unsaturated carboxylic acids, although the corresponding esters and the other substrates showed comparable optical yields to those observed using the other chiral ligands.

These results show that d-trans-BDPCP is a unique ligand suitable for asymmetric hydrogenation of unsaturated substrates bearing no functional group

which causes a secondary interaction between the substrate and the catalyst.

Table. Asymmetric hydrogenation catalyzed by rhodium complexes with chiral ligands.<sup>a)</sup>

Substrate	Reaction temperature (°C)	Optical yield(%) <sup>b)</sup> (absolute configuration)				
		d-trans-BDPCP <sup>c)</sup>		d-trans-BDPCH <sup>c)</sup> (-)-Diop <sup>c)</sup>		
α-Ethylstyrene	50	60	(R)	33	(R)	24.5 (S)
α-Methoxystyrene	50	9.1	(R)	8.8	(R)	—
Atropic acid	50	±0		0.7	(S)	63 (S) <sup>d,e)</sup>
Methyl atropate	50	20	(S)	4.5	(S) <sup>f)</sup>	7 (R) <sup>d,e)</sup>
α-Acetoamidocinnamic acid	0	12	(S)	68.5	(S)	78 (R) <sup>g)</sup>
Methyl α-acetoamidocinnamate	50	43	(S)	—		63 (R) <sup>d,h)</sup>
α-Acetoamidoacrylic acid	-20	±0		78.9	(S)	55 (R) <sup>d,e)</sup>
Acetophenone	80	22	(R) <sup>i)</sup>	—		73 (R) <sup>d,e)</sup>
Propiophenone	80	3.5	(R) <sup>i)</sup>	—		65 (R) <sup>d,h)</sup>
						37.7 (S) <sup>i,j)</sup>

a) The initial pressure of H<sub>2</sub> is 50 atm. The mole ratio of the chiral ligand to [Rh(1,5-hexadiene)Cl]<sub>2</sub> is 2.2. b) Corrected values for the optical purity of the ligands. c) The absolute configuration is 1S,2S. d) A result at room temperature with the initial pressure of 1.1 atm. e) Ref.6. f) A result with ethyl atropate as a substrate. g) A result at 25°C. h) Ref.7, a result using (1R,2R)-1,2-bis(diphenylphosphinomethyl)cyclopentane as a catalyst ligand. i) The initial pressure of H<sub>2</sub> is 200 atm. j) Ref.8.

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