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# ASYMMETRIC HYDROGENATION USING CHIRAL PHOSPHINITE RHODIUM COMPLEXES

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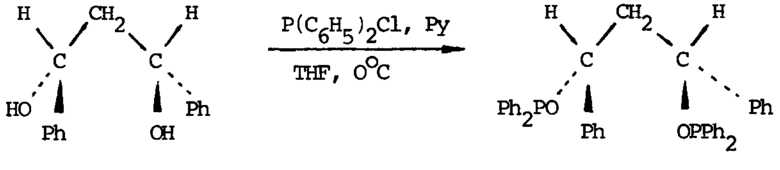
The Cu(I) complex of (1R,3R)-bis(diphenylphosphinoxy)-1,3-diphenylpropane (BDPODP) has been prepared and used for the transfer of the ligand to Rh(I). The Rh(I) complexes of this new phosphinite obtained by this method act as efficient asymmetric homogeneous hydrogenation catalysts for (Z)-α-(acylamino)-cinnamic acids.

Phosphinites used in Rh(I) complexes for the asymmetric reduction of (Z)-α-(acylamino)cinnamic acids are considered to be rather poor ligands[1], although a few exceptions are known[2-4]. We report here the first results of asymmetric hydrogenation of some olefinic substrates catalyzed by Rh(I) complexes containing BDPODP, an efficient phosphinite ligand. The starting material, dibenzoylmethane, is easily available and can be transformed into the chiral diol **1** by asymmetric heterogeneous hydrogenation over Raney-nickel modified with a mixture of tartaric acid and NaBr[5,6]. BDPODP was synthesized from **1** in the usual way according to the scheme:



**1**

(R,R)-BDPODP

(R,R)-BDPODP (a viscous transparent oil) was isolated and purified as its $[Cu(BDPODP)Cl]_n$ complex[6] analogously to the method of Townsend and his coworkers developed for chiral phosphines.[8] A notable feature of this strategy is that the Cu(I) complex of BDPODP could be used not only for the purification but also for the transfer of the ligand to Rh(I). Combination of the Cu(I) complex of BDPODP with $[Rh(NBD)Cl]_2$ or $[Rh(NBD)_2]BF_4$ resulted in active homogeneous hydrogenation catalysts for (Z)-α-(acylamino)acrylic acid derivatives (Table 1.). Experiments with BDPOP, 2,4-bis(diphenylphosphinoxy)pentane[9], proved that the catalysts prepared either from the free phosphinites or from their Cu(I) complexes give similar results.

Table 1.

Asymmetric hydrogenation of (Z)-R'CH=C(NHCOR'')COOR$^{a}$

| Substrate | | | Catalyst<br>$[Rh(NBD)Cl]_2$+$[Cu(R,R)\text{-}(BDPODP)Cl]_n$ | Catalyst<br>$[Rh(NBD)Cl]_2$+$[Cu(R,R)\text{-}(BDPOP)Cl]_n$ | |
|---|---|---|---|---|---|
| R' | R" | R | Optical yield, % | Optical yield, % | |
| Ph | Me | H | 96$^{b}$ | - | (67) |
| Ph | Me | H | 94 | 65 | (68) |
| Ph | Ph | H | 93 | 75 | (78) |
| Ph | Me | Me | 79 | - | (48) |
| H | Me | H | 77 | - | (53) |

a) Reaction conditions: 30°C, 1 bar $H_2$; 2.5 mmol of substrate; substrate/Rh/P = 100/1/2.2 ; 10 ml of solvent, MeOH/PhH = 3/1. Configuration of the products is R. ( ): Results obtained with catalysts formed in situ from $[Rh(NBD)Cl]_2$ and the free ligand.

b) $[Rh(NBD)_2]BF_4$ in methanol.

BDPODP differs from BDPOP in that it has two phenyl groups instead of two methyl groups. The significantly higher optical yields obtained with the diphenyl compounds are somewhat unexpected since the center of chirality is rather far away from the region of hydrogen transfer to the olefin. A possible explanation may be a more rigid conformation of the chelate ring due to phenyl--phenyl interactions.

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