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CATALYTIC ASYMMETRIC HYDROGENATIONS WITH POLYMER SUPPORTED CHIRAL PYRROLIDINEPHOSPHINE-RHODIUM COMPLEXES[1)]

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The syntheses of new polymer supported chiral pyrrolidinephosphine-rhodium catalysts; 4VB-PPM-HEMA-Rh^+ (6a) and 4VB-PPM-HEMA-Rh (6b) and their application to the asymmetric hydrogenation of some olefins were described. Thus, 4VB-PPM-HEMA-Rh^+ in the presence of triethylamine gave (S)-α-methylsuccinic acid and (R)-N-acetylphenylalanine in 82.3 and 70.0% optical yields respectively.

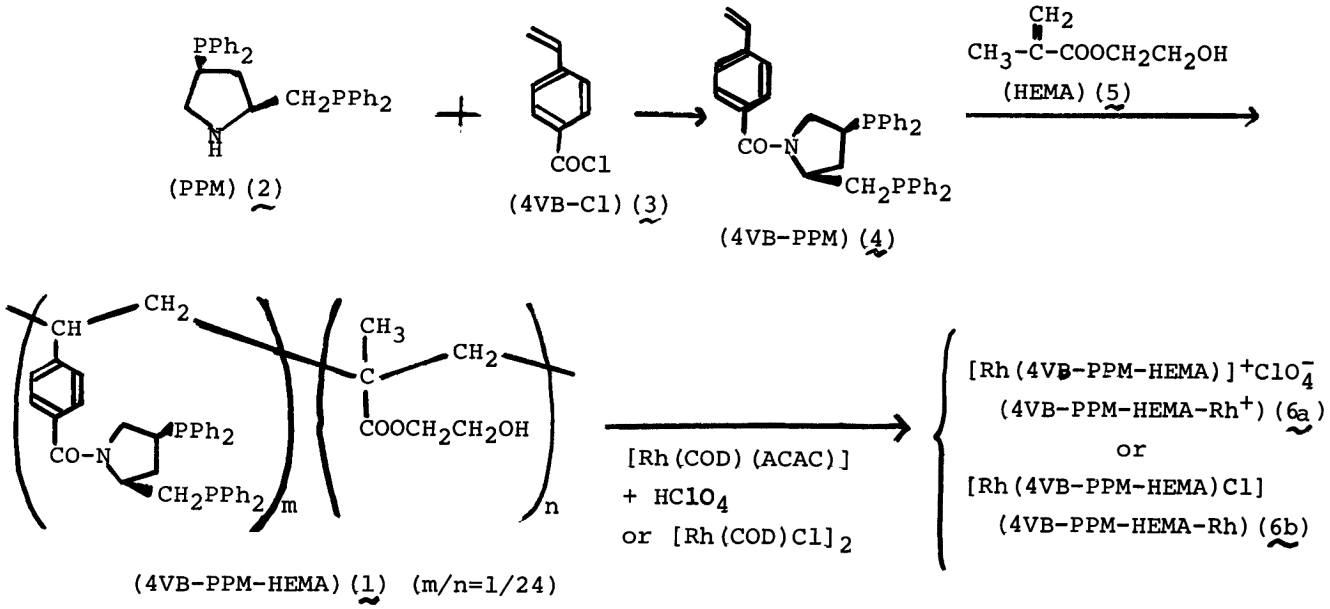
Homogeneous catalytic asymmetric hydrogenations[2)] with chiral phosphine-rhodium catalysts have recently been proven to be practically useful for the preparation of chiral α-amino acids[3)], pantolactone[4)] and α-methylsuccinic acid[5)]. However, in these hydrogenations, chiral ligand-rhodium catalysts could not be reused because of their difficult separation from the reaction mixture. To overcome this point, the polymer supported chiral catalysts have been investigated especially for DIOP ligand[6)].

We wish to describe here the synthesis of new polymer supported pyrrolidine-phosphine-rhodium complexes and their uses in the catalytic asymmetric hydrogenation of itaconic acid and α-acetamidocinnamic acid.

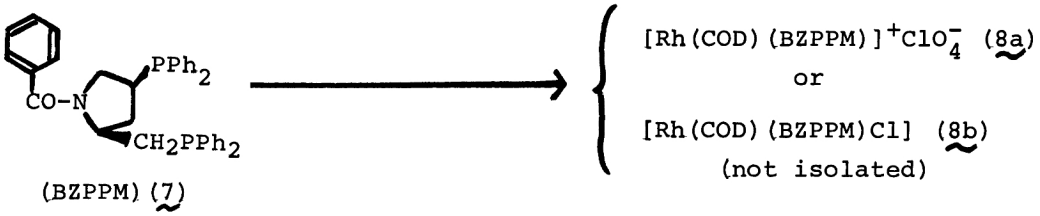
Homogeneous asymmetric hydrogenations with neutral and cationic chiral pyrrolidinephosphine-rhodium catalysts have been already demonstrated to be useful for the syntheses of chiral α-amino acid[3d)], β-amino acids[7)], α-hydroxy esters[8)], pantolactone[4)], isoquinoline alkaloid salsolidine[9)], α-methylsuccinic acid[5)] and β-methylaspartic acid[10)].

As shown in Scheme I, new polymer supported pyrrolidinephosphine(4VB-PPM-HEMA) (1) was synthesized by the reaction of (2S,4S)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine(PPM) (2)[3d)] with 4-vinylbenzoyl chloride(4VB-Cl) (3) in benzene at rt for 5h and successive copolymerization of the product(4VB-PPM) (4)[11,12)] with 2-hydroxyethyl methacrylate(9 eq.)(HEMA) (5) in benzene under reflux in the presence of azobisisobutylonitrile. The composition (4VB-PPM/HEMA=1/24) of the precipitated product(1)[12)](34% yield based on 4VB-PPM) was determined by elemental analysis. Further reaction of 1 with $[Rh(COD)Cl]_2$ (PPM/Rh=1) or [Rh(COD)(ACAC)] and 70% $HClO_4$ (PPM/Rh=1) in THF at rt for 45h afforded new polymer supported insoluble catalysts; 4VB-PPM-HEMA-Rh^+(PPM/Rh=1) (6a)[12)] and 4VB-PPM-HEMA-Rh (PPM/Rh=1) (6b)[12)].

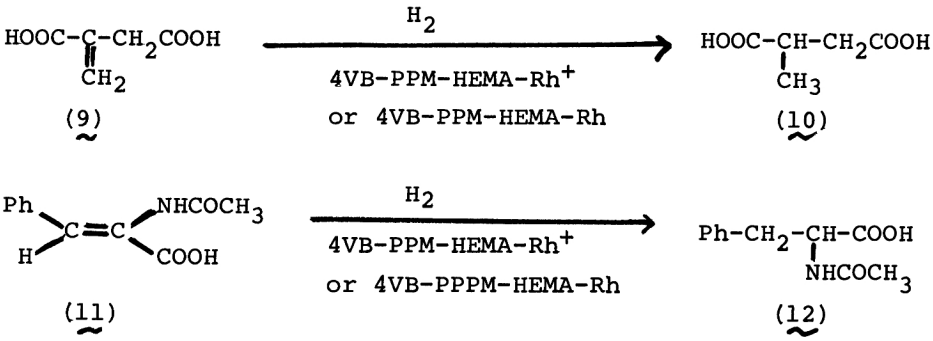
Scheme I



Scheme II



Scheme III



Elemental analysis[13] indicated that both cationic and neutral complex catalysts (6a and 6b) should have the composition of [Rh(4VB-PPM-HEMA)]$^+ClO_4^-$ (PPM/Rh=1) and [Rh(4VB-PPM-HEMA)Cl](PPM/Rh=1) rather than that of [Rh(COD)(4VB-PPM-HEMA)]$^+ClO_4^-$ and [Rh(COD)(4VB-PPM-HEMA)Cl] respectively.

In a typical experiment, the asymmetric hydrogenation of itaconic acid (2 mmole) was run in ethanol under an initial hydrogen pressure of 50 atm at 20°C for 45 h in the presence of 6a (0.02 mmole) and triethylamine (2 mmole). After filtration of the reaction mixture to remove the complex catalyst followed by removal of the solvent and acidification with 10% HCl, the product was extracted with ether. Thus, (S)-methylsuccinic acid, $[\alpha]_D^{20}$-13.9°(c 2.063, ethanol)(82.3% optical yield) was obtained in an almost quantitative yield.

Table I. Asymmetric hydrogenations of α,β-unsaturated acids[a]

Substrate	Chiral reagent	Solvent	$[\alpha]_D^{20}$(EtOH)	Opt.y. (%)	(conf.)[b]
9	BZPPM-Rh$^+$	methanol[c]	-15.0[d]	88.9	(S)
9	BZPPM-Rh$^+$	methanol	-13.9[d]	82.3	(S)
9	BZPPM-Rh	methanol[c]	-13.6[d]	80.6	(S)
9	BZPPM-Rh	methanol	-14.1[d]	83.5	(S)
9	4VB-PPM-HEMA-Rh$^+$	ethanol[c]	-13.9	82.3	(S)
9	4VB-PPM-HEMA-Rh$^+$ e)	ethanol[c]	-13.1	77.6	(S)
9	4VB-PPM-HEMA-Rh$^+$	ethanol	- 4.3	25.5	(S)
9	4VB-PPM-HEMA-Rh	ethanol[c]	- 6.8	40.3	(S)
9	4VB-PPM-HEMA-Rh	ethanol	+ 0.5	3.0	(R)
11	4VB-PPM-HEMA-Rh$^+$	ethanol[c]	-32.2	70.0	(R)
11	4VB-PPM-HEMA-Rh$^+$ e)	ethanol[c]	-31.3	68.0	(R)
11	4VB-PPM-HEMA-Rh	ethanol[c]	-10.4	22.6	(R)

a) All hydrogenations of 9 or 11 (2 mmole) were carried out with 0.02 mmole of the polymer supported catalyst in 4 ml of solvent at 20°C for 45 h under an initial hydrogen pressure of 50 atm, and the products were obtained in almost quantitative yields.
b) Calculated on the basis of the reported values for the optically pure compounds: (R)-10, $[\alpha]_D^{20}$+16.88°(c 2.16, EtOH)(E.Berner and R.Leonardsen, Ann. 583, 1 (1939); (S)-12, $[\alpha]_D^{20}$+46.0°(c 1, EtOH) (ref. 3d).
c) Triethylamine (2 mmole) was added.
d) Data from ref. 5.
e) Recovered catalyst was used.

Table I indicated clearly that the optical yields with polymer supported catalysts depended markedly on the used conditions, especially whether triethylamine was present or not, whereas BZPPM-rhodium complexes, monomer catalysts, gave almost the same optical yields in the same conditions, and also the cationic polymer catalyst was more effective than the neutral complex.

Further investigations on polymer supported pyrrolidinephosphine complex catalysts are actively under way.

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11) 4VB-PPM (4), mp 178-180°C, $[\alpha]_D^{20}$ -100.1° (c 1, $CHCl_3$).
12) Satisfactory spectral and analytical data were obtained for this compound.
13) 6a; Anal. Calcd: for $C_{182}H_{275}NO_{77}P_2ClRh$: C; 55.91, H; 7.09, N; 0.36, P; 1.58, Cl; 0.91. Found: C; 55.59, H; 6.73, N; 0.36, P; 1.50, Cl; 0.89.
6b: Anal. Calcd: for $C_{182}H_{275}NO_{73}P_2ClRh$: C; 56.85, H; 7.20, N; 0.36, P; 1.61, Cl; 0.92. Found: C; 56.44, H; 6.78, N; 0.37, P; 1.59, Cl; 0.89.

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