

Preliminary communication

ASYMMETRIC HYDROGENATION USING FERROCENYLPHOSPHINE RHODIUM(I) CATIONIC COMPLEXES

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Summary

High optical yields are obtained in the hydrogenation of α -acetamidocinnamic acid using $[(COD)Rh((+)PPFA)]ClO_4$ and related complexes as catalysts. $(+)PPFA$ is (S) - α - $[(R)$ -2-diphenylphosphinoferrocenyl] ethyldimethylamine.

There has been considerable interest in asymmetric homogeneous hydrogenations catalyzed by transition metal derivatives [1]. Chiral ferrocenylphosphines have been used as ligands in rhodium complexes which catalyze the asymmetric hydrogenation of olefins [2] and ketones [3]. Complexes of the same ligands catalyze the asymmetric hydrosilation of ketones [4] and the asymmetric Grignard cross coupling reaction to produce optically active hydrocarbons [5]. Some of these reactions proceed with high optical yield although most employ catalyst solutions prepared *in situ* by mixing the chiral ligands with the appropriate metal complex precursor. The hydrogenations were also carried out at 50 atm

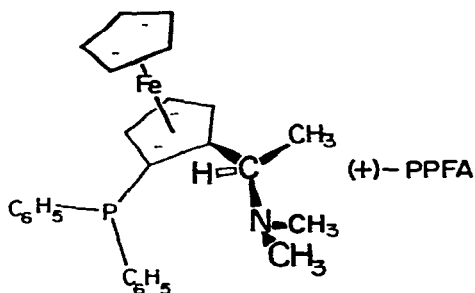
We have also been working with the ferrocenylphosphines for some time and now wish to describe the asymmetric hydrogenation of α -acetamidocinnamic acid under mild conditions, 32°C and 1 atm H_2 , using cationic rhodium complexes of the type $[(diene)Rh((\pm)PPFA)]^+X^-$. (diene = COD or NBD; $X^- = ClO_4^-$, BF_4^- or PF_6^- ; $(+)PPFA = (S)$ - α - $[(R)$ -2-diphenylphosphinoferrocenyl] ethyldimethylamine and $(-)PPFA$ is its optical enantiomer, as shown in the Figure). The ligand is prepared by reacting *N,N*-dimethyl-1-ferrocenylethylamine of known absolute configuration [6,7] with *n*-BuLi

Table 1
Homogeneous Hydrogenation of α -Acetamidocinnamic Acid^a

Catalyst precursor	Solvent	Time (hr)	Conversion (%)	Optical yield (%)	Configuration
[(COD)Rh((-)PPFA)]ClO ₄	methanol	25	91	80	S
[(COD)Rh(+PPFA)]ClO ₄	methanol	25	93	73	R
[(COD)Rh((-)PPFA)]BF ₄	ethanol	40	83	75	S
[(NBD)Rh((-)PPFA)]ClO ₄	methanol	25	93	78	S
[(COD)Rh(+PPFA)]BF ₄	ethanol	48	91	83	R
[(NBD)Rh(+PPFA)]PF ₆	isopropanol	48	>96	80	R
[(NBD)Rh(+PPFA)]PF ₆	ethanol	22	88	84	R

^aReactions were carried out at 1 atm H₂ and 32°C. The concentration of the catalyst was 1.0x10⁻³M and the substrate 1.0x10⁻¹M. Optical yields are based on the rotation of the isolated product in ethanol.

and treating the stereoselective metallated product with chlorodiphenylphosphine. The two enantiomers of the ligand show rotations $[\alpha]_D^{25}$ of $\pm 360^\circ$ (c 0.40 C_2H_5OH). The (+)-isomer has been previously briefly described [4], and has the atomic positions shown in the Figure and the expected absolute configuration [8]. The position of the hydrogen atom at the asymmetric center has not been precisely located yet.



The rhodium(I) complexes were prepared according to the procedure of Schrock and Osborn [9] and are well defined crystalline solids. As an example microanalytical data for $[(NBD)Rh((-)PPFA)]ClO_4$ are as follows: Found C, 53.5; H, 4.84; N, 1.83. Calc. 53.8, H, 4.89, N, 1.90%.

Table 1 shows the results obtained for the catalyzed homogeneous hydrogenation of α -acetamidocinnamic acid under the mild conditions of $32^\circ C$ and 1 atm H_2 . This substrate was chosen because it belongs to a class of compounds which are amino acid precursors. The extent of reaction was monitored using a simple gas uptake apparatus and was checked by determining the NMR spectrum of the final reaction products. High optical yields are obtained in all cases and the results, not unexpectedly [10], seem to be independent of the diene. The anion also has little effect of the optical yield although it does seem to influence the rate of the reaction.

Other workers have reported high optical yields from related substrates using a variety of chiral ligands [1]. In particular Sinou and Kagan [11] using $[(COD)Rh(+Diop)]ClO_4$ obtained an optical yield of

80% from α -acetamidocinnamic acid. They suggest that the reaction intermediate may involve coordination of both the olefin bond and the acyl carbonyl group to the rhodium. Consideration of models of our own system indicates that this is sterically possible and that if it occurs the correct configuration for the hydrogenated product can be predicted.

Acknowledgments

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