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Preliminary communication

ASYMMETRIC HYDROCARBOXYLATION OF OLEFINS

IV. INFLUENCE OF PPh_3 IN THE ASYMMETRIC HYDROCARBOXYLATION CATALYZED BY $[(-)\text{-DIOP}]PdCl_2$

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Summary

In the palladium-catalyzed hydrocarboxylation of α-methylstyrene using PPh_3 and (—)-DIOP as ligands, with a constant ratio of phosphorus to palladium atoms of 2, the optical yield depends on the proportions of PPh_3 and (—)-DIOP, showing a maximum for a molar ratio of 2.

Homogeneous asymmetric catalysis by chiral transition metal complexes is a rapidly developing field of research [1]. Several types of asymmetric ligands which give chiral information during the catalytic reaction have been employed Because of their broad applicability, chiral phosphines are the most widely used optically active ligands (the chirality center lies either on the phosphorus atom or on an organic chain attached to the phosphorus) Among phosphino ligands Kagan's DIOP [(—)-2,3-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] [2] (or analogous diphosphino derivatives of tartaric acid [3]) is the most popular because it can be made relatively easily DIOP has been used in many asymmetric reactions [4—7], in some of which high optical yields have been achieved

The efficiency of the DIOP chiral ligand has normally been explained on the basis of its conformational rigidity which arises from its chelating ability [4,8,9], however, some results in palladium-catalyzed asymmetric hydrocarboxylation raise doubts about whether the chelating ability is an essential requisite for this or related optically active ligands, at least in the reaction investigated.

We have observed [10] that in the asymmetric hydrocarboxylation of α-methylstyrene catalyzed by $PdCl_2/(-)$-DIOP the enantiomeric excess observed in the formation of the ester of 3-phenylbutanoic acid increases when the metal to chiral ligand ratio decreases. At a ratio of 0 4 (0 8 phosphorus atoms per metal atom) the optical purity of the recovered ester of (+)(*S*)-3-phenylbutanoic acid was ~60%

Investigation of the reaction for very low (—)-DIOP/$PdCl_2$ ratios was hindered by a considerable decay in selectivity during the hydrocarboxylation reaction, some secondary products being formed in high yield However, by maintaining a constant phosphorus to palladium atom ratio of 2 (through the contemporaneous presence of (—)-DIOP and PPh_3) the selectivity of the reaction can be restored, and it has been possible to investigate the effects of low concentrations of the (—)-DIOP ligand

The results obtained at 100°C using ethanol as the hydrogen donor, α-methylstyrene as the substrate, and a constant pressure of 400 atmospheres of carbon monoxide are shown in Fig 1. The optical purity of the recovered ethyl 3-phenylbutanoate as a function of the (—)-DIOP/$PdCl_2$ ratio shows a maximum which, although rather broad, is clearly centered at a ratio of 0 5. Since DIOP is a potential bidentate ligand, this would correspond to complexation of one phosphorus atom of (—)-DIOP per palladium atom, and suggests that in the catalytic complexes giving predominant formation of (*S*)-ethyl 3-phenylbutanoate, the bidentate (—)-DIOP ligand behaves as a monodentate

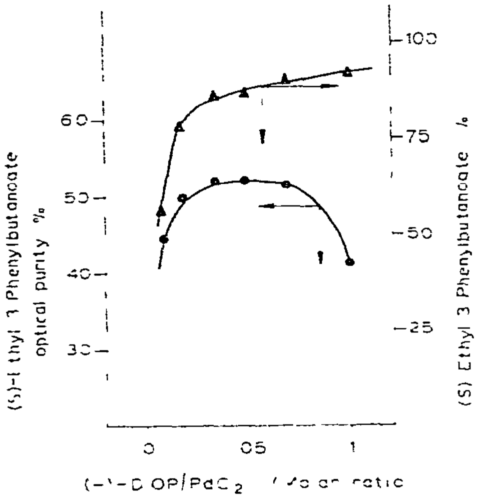

Fig 1

The influence of variation of the phosphino ligand on the isomeric composition of the ester products in the palladium-catalyzed hydrocarboxylation has been reported [11—13]. Monophosphines lead to predominant formation of the branched ester (at least under the carbon monoxide pressure used) apparently independent of their basicity or of their steric requirements, while (—)-DIOP gives mainly the straight chain ester.

The isomeric composition of the ester products (ethyl 3-phenylbutanoate and ethyl 2-methyl-2-phenylpropanoate) in the above experiments has also been determined (Fig 1) The fact that the amount of ethyl 2-methyl-2-phenylpropanoate increases on increasing the quantity of PPh_3 can be reconciled with the above observations (assuming chelation of the ligand is not responsible for regioselectivity with respect to carbonylation in position 1) by assuming that the catalytic species are not mononuclear.

The results also show the importance of ancillary ligands, in addition to the chiral ligand, in determining the extent of the asymmetric induction [14]

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References

1 P. Pino et G Consiglio, in preparation
2 H.B Kagan et T P Dang, J Amer Chem Soc 94 (1972) 6429
3 T P Dang, J C Poulin et H B Kagan, J Organometal Chem 91 (1975) 105
4 H B Kagan, Pure Appl Chem., 43 (1975) 401
5 P. Pino, G Consiglio C Botteghi et C Salomon, Advan Chem Ser 132 (1974) 295
6 C Botteghi, G Consiglio et P. Pino Chimia 27 (1973) 477
7 G Consiglio et C Botteghi, Helv. Chim Acta, 56 (1973) 460.
8 J.D. Morrison, W F Masler et M.K Neuberg, Advan Catal, 26 (1976) 81
9 S Brunie J Mazan, N Langlois et H B Kagan, J Organometal Chem 114 (1976) 225
10 G Consiglio et P Pino Chimia 30 (1976) 193
11 Y. Sugi, K. Bando et S Shin Chem Ind (London), (1975) 397
12 G. Consiglio et M Marchetti, Chimia, 30 (1976) 26
13 Y Sugi et K Bando, Chem Lett (1976) 727
14 See, e g, Y Ohgo, Y Natori, S Takeuchi et Y Yoshimura, Chem Lett, (1974) 1327