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PHOSPHINERHODIUM COMPLEXES AS HOMOGENEOUS CATALYSTS

X *. HOMOGENEOUS HYDROGENATION OF KETONES USING PHOSPHINERHODIUM CATALYSTS MODIFIED WITH TRIETHYLAMINE

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Summary

Triethylamine significantly increases the catalytic activity in ketone hydrogenation of rhodium complexes containing aromatic phosphines. If chiral phosphines are used, optical yields depend on the amount of triethylamine added, suggesting that several catalytically active species are involved.

Introduction

Hydrogenation of ketones is catalyzed by ionic rhodium complexes of the type $[RhH_2(PR_3)_2(solvent)]^+$ [1] and by complexes formed in situ from $[Rh(diene)Cl]_2$ and phosphines [2], but both types of catalysts are rather (or even totally) inactive if arylphosphines are used as ligands [3]. This presents a major problem if such catalysts are to be used in asymmetric hydrogenations, since most chiral phosphines ensuring good enantio-selectivities contain the diphenylphosphino group [e.g. 4—12].

We previously observed that triethylamine has a favourable effect on the activity of in situ phosphinerhodium catalysts used in olefin hydrogenation [13] and we now describe the use of such triethylamine-modified catalysts for hydrogenation of ketones.

Results and discussion

As shown in Table 1, $Rh(PPh_3)_3Cl$ or analogous catalysts formed in situ from $[Rh(nbd)Cl]_2$ ** and PPh_3 are practically inactive for the hydrogenation of aceto-

* For part IX see ref. 16.

** nbd = norbornadiene.

TABLE 1

HYDROGENATION OF KETONES WITH $Rh(PPh_3)_3Cl$ OR RELATED COMPLEXES: EFFECT OF Et_3N [a]

Ketone	Catalyst	Yield of alcohol (%)
Acetophenone	$Rh(PPh_3)_3Cl$	0.5
Acetophenone	$1/2\ [Rh(nbd)Cl]_2 + 3\ PPh_3$	3
Acetophenone	$Rh(PPh_3)_3Cl + 5\ Et_3N$	98
Acetophenone	$1/2\ [Rh(nbd)Cl]_2 + 3\ PPh_3 + 5\ Et_3N$	96
Acetophenone	$1/2\ [Rh(nbd)Cl]_2 + 4\ PPh_3 + 5\ Et_3N$	57
Acetophenone	$HRh(PPh_3)_4$	55
Acetophenone	$HRh(PPh_3)_4 + 5\ Et_3N$	65
Acetophenone	$Rh(PPh_3)_3Cl + 2\ PPh_3 + 5\ Et_3N$	36
Benzophenone	$Rh(PPh_3)_3Cl + 5\ Et_3N$	83
Benzyl-methyl-ketone	$Rh(PPh_3)_3Cl + 5\ Et_3N$	76
Propiophenone	$Rh(PPh_3)_3Cl + 5\ Et_3N$	60
Methyl-α-naphthyl-ketone	$Rh(PPh_3)_3Cl + 5\ Et_3N$	92
Octanone-2	$Rh(PPh_3)_3Cl + 5\ Et_3N$	10

[a] Reaction conditions: 10 mmol ketone and catalyst containing 0.05 mol rhodium in 4 ml methanol/benzene (1/1) at 50°C and 70 bar H_2 for 6 h.

phenone, but addition of triethylamine dramatically increases the rate. The $Rh(PPh_3)_3Cl + Et_3N$ catalyst was also successfully used for several other ketones, including benzophenone which is usually difficult to hydrogenate.

As already shown earlier [13], $HRh(PPh_3)_4$ is formed from $[Rh(diene)Cl]_2$ complexes and excess PPh_3 in the presence of Et_3N and H_2. In keeping with this the phosphinerhodium(I) hydride was also found to be an active catalyst for ketone hydrogenation. Its activity is only slightly increased by Et_3N and does not reach that of the $Rh(PPh_3)_3Cl + Et_3N$ system, presumably because of its higher PPh_3/Rh ratio. This latter explanation is supported by the inhibiting effect of excess PPh_3 in the case of the $Rh(PPh_3)_3Cl + Et_3N$ and $[Rh(nbd)Cl]_2 + PPh_3 + Et_3N$ catalyst systems (cf. Table 1).

As would be expected, the addition of Et_3N has an influence also on the enantio-selectivity of the phosphinerhodium catalysts formed in situ from $[Rh(nbd)Cl]_2$ and chiral phosphines. The data listed in Table 2 show this effect for three different chiral phosphines of the type Ph_2PR. Obviously there is no general trend in the optical yields in the presence of Et_3N, and even a reversal of configuration of the favoured enantiomer may be observed. What seems to be general with these phosphines, however, is the significant increase of reaction rate. Without the use of Et_3N these chiral phosphines would be regarded as almost useless ligands for ketone hydrogenations because of the extremely slow reaction. In the presence of Et_3N good conversions may be achieved within a reasonable time.

Recently we observed that the P/Rh ratio profoundly influences the optical yields achieved in ketone hydrogenation with $[Rh(diene)Cl]_2$ + chiral phosphine catalyst systems [15]. Varying the N/Rh ratio caused a similar effect for the

TABLE 2

EFFECT OF Et_3N ON ENANTIOSELECTIVITY OF CHIRAL PHOSPHINERHODIUM CATALYSTS USED FOR THE HYDROGENATION OF ACETOPHENONE [a]

Phosphine	P/Rh	Et_3N added (N/Rh = 5)	Chemical yield (%)	Optical yield (%)	Configuration
(+)-DIOP	2.2	—	35 [b, c]	35	(*R*)-(+)
(+)-DIOP	2.2	+	99 [c]	10	(*S*)-(—)
MDPP [d]	3	—	6.9	4.5	(*S*)-(—)
MDPP	3	+	47	17	(*S*)-(—)
NMDPP [e]	3	—	~1	—	—
NMDPP	3	+	52	6.0	(*S*)-(—)

[a] Reaction conditions: 10 mmol ketone and 0.025 mmol $[Rh(nbd)Cl]_2$ in 4 ml methanol/benzene (1/1) at 50°C and 70 bar H_2 for 6 h. [b] 100 bar H_2, 24 h. [c] Solvent methanol. [d] MDPP = (—)-menthyl diphenyl phosphine [14]. [e] NMDPP = (+)-neomenthyl diphenyl phosphine [14].

catalyst system modified by Et_3N. Table 3 shows the results obtained with (—)-DIOP as ligand.

As can be seen there is a maximum optical yield around the surprisingly low N/Rh ratios between 0.5 to 1, where the beneficial effect of amine on rate of hydrogenation is still moderate. Increasing the Et_3N concentration above this value results in a progressive decrease of enantioselectivity. In contrast the chemical yield steadily increases with an increasing N/Rh ratio. This suggests the formation of at least two new catalytically active species in presence of Et_3N in addition to that operating in the absence of amines, one with high enantioselectivity and relatively low catalytic activity (operating at low N/Rh ratios) and an other with rather moderate (or perhaps even zero) enantioselectivity but high catalytic activity (predominant at high N/Rh ratios).

TABLE 3

INFLUENCE OF THE N/Rh RATIO ON OPTICAL YIELDS OBTAINED UPON HYDROGENATING ACETOPHENONE WITH A $[Rh(nbd)Cl]_2$ + (—)-DIOP + Et_3N CATALYST SYSTEM [a]

Et_3N/Rh molar ratio	Chemical yield (%)	Optical yield (%)	Configuration
0	6.0	38	*S*-(—)
0.2	11	27	*S*-(—)
0.3	12	19	*S*-(—)
0.4	12	~0	—
0.5	14	53	*R*-(+)
0.6	33	48	*R*-(+)
0.7	40	47	*R*-(+)
1.0	51	43	*R*-(+)
2.0	80	31	*R*-(+)
5.0	99	11	*R*-(+)
100	98	2.3	*R*-(+)

[a] Reaction conditions: 10 mmol acetophenone, 0.025 mmol $[Rh(nbd)Cl]_2$, 1.1 mmol (—)-DIOP and varying amounts of Et_3N in 2.8 ml methanol at 50°C and 70 bar H_2 for 6 h.

Work is in progress to elucidate the mechanism by which the amine exerts its influence on activity and enentioselectivity of the catalyst.

Experimental

(+)- and (—)-DIOP were purchased from Strem Chemicals Inc. (—)-Menthyldiphenylphosphine and (+)-neomenthyldiphenylphosphine were prepared according to Morrison [14].

Hydrogenation experiments

The rhodium complex (0.05 mmol Rh) and the appropriate amount of phosphine were dissolved in methanol or benzene/methanol under Ar and a calculated amount of Et_3N was added. The solution was prehydrogenated for 20 min at room temperature and 10 mmol ketone was then added. This mixture was transferred under H_2 into a 20 ml autoclave already filled with H_2, and hydrogenated at 70 bar and 50°C for 6 h. The product was distilled in vacuum and analysed by GLC. Its optical rotation was determined at 589 nm with a visual polarimeter of the Schmidt Haensch Type LLM (accuracy 0.01°).

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References

1 R.R. Schrook and J.A. Osborn, J. Chem. Soc. Chem. Commun., (1970) 567.
2 B. Heil, S. Törös, S. Vastag and L. Markó. J. Organometal. Chem., 94 (1975) C47.
3 S. Vastag, B. Heil and L. Markó, J. Mol. Catal., in press.
4 J.D. Morrison, R.E. Burnett, A.M. Aguiar, C.J. Morrow and C. Philips, J. Amer. Chem. Soc., 93 (1971) 1301.
5 H.B. Kagan and T.P. Dang, J. Amer. Chem. Soc., 94 (1972) 6429.
6 K. Achiwa, J. Amer. Chem. Soc., 98 (1976) 8265.
7 M.D. Fryzuk and B. Bosnich, J. Amer. Chem. Soc., 99 (1977) 6262.
8 T. Hayashi, T. Mise and M. Kumada, Tetrahedron Lett., (1976) 4351.
9 M. Fiorini, G.M. Giongo, F. Marcati and W. Marconi, J. Mol. Catal., 1 (1975/76) 451.
10 T. Hayashi, M. Tanaka and I. Ogata, Tetrahedron. Lett., (1977) 295.
11 W.R. Cullen and Y. Sugi, Tetrahedron Lett., (1978) 1635.
12 R.B. King, J. Bakos, C.D. Hoff and L. Markó, J. Org. Chem., in press.
13 Z. Nagy-Magos, S. Vastag, B. Heil and L. Markó, Transition Met. Chem., 3 (1978) 123.
14 J.D. Morrison and W.F. Masler, J. Org. Chem., 39 (1974) 270.
15 S. Törös, B. Heil and L. Markó, J. Organometal. Chem., 159 (1978) 401.
16 Z. Nagy-Magos, S. Vastag, B. Heil and L. Markó, J. Organometal. Chem., 171 (1979) 97.