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PHOSPHINERHODIUM COMPLEXES AS HOMOGENEOUS CATALYSTS

VIII *. ENANTIOSELECTIVE HYDROGENATION OF KETONES: EVIDENCE FOR SEVERAL MECHANISMS WITH CATALYSTS CONTAINING DIOP

SZILÁRD TŐRÖS, BÁLINT HEIL and LÁSZLÓ MARKÓ

Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8200 Veszprém (Hungary)

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Summary

Optical yields obtained in the hydrogenation of acetophenone with cationic and in situ rhodium complex catalysts depend on the P/Rh ratio and on the ionic or non-ionic character of the active species. The enantioselectivity of the in situ catalyst containing (+)-DIOP is reversed by addition of achiral tri-n-alkylphosphines. On the basis of these observations and the amount of H_2 consumed in preforming the catalysts, several different mechanisms are suggested: for example: cycles involving cationic rhodium complexes containing two (or three) phosphorus ligands and cycles involving non-ionic rhodium complexes with two phosphorus ligands in *cis* or *trans* positions. In the in situ catalyst with a Rh/(+)-DIOP/P-n-Bu_3 = 1/1/1 ratio (+)-DIOP functions as a monodentate ligand.

Introduction

Three types of phosphinerhodium catalysts have been used previously for the hydrogenation of ketones: the cationic complexes $[Rh(diene)P_2]^+A^-$ [1—7] (where P = monodentate phosphine or P_2 = bidentate phosphine), the complexes formed in situ from $[Rh(diene)Cl]_2$ and phosphines (P or P_2) using a P/Rh ratio of approximately 2.2/1 [7—9] and catalysts formed from $Rh(C_8H_{12})(PPh_3)Cl$ and NaOH [10]. With chiral phosphines the in situ catalysts gave significantly higher optical yields [8] than the cationic ones [2] prepared with the same ligands.

* For Part VII, see ref. 19.

TABLE 1

HYDROGENATION OF ACETOPHENONE WITH CATALYSTS CONTAINING (S)-(—)-PBzMePh [a]

Reactions conditions: 50°C, 1 bar H_2, in methanol.

Catalyst	P/Rh ratio	ITO [b] (min^{-1})	Reaction time (h)	Chemical yield (%) [c]	Configu-tion	Optical yield (%) [d]
Rh(NBD)[(*S*)-(—)-PBzMePh]$_2^+ClO_4^-$	2/1	0.21	10	72	(*S*)-(—)	2.5 [e]
+ 1 mol (*S*)-(—)-PBzMePh added	3/1	0.012	50	48	(*S*)-(—)	23
1/2 [Rh(NBD)Cl]$_2$ + 2 (*S*)-(—)-PBzMePh	2/1	0.16	20	92	(*S*)-(—)	28
1/2 [Rh(NBD)Cl]$_2$ + 3 (*S*)-(—)-PBzMePh	3/1	0.03	62	76	(*S*)-(—)	37

[a] Enantiomeric purity 74%. [b] Initial turnover, mol H_2/mol Rh (min). [c] α-Phenylethanol. [d] Calculated for 100% optical purity of the phosphine. [e] 8.6% optical yield was obtained earlier [2] with the same catalyst at 30°C in ethanol.

Table 1 shows some of our recent results obtained in the enantioselective hydrogenation of acetophenone with in situ $[Rh(NBD)Cl]_2$ + (*S*)-(—)-PBzMePh combinations * and with $\{Rh(NBD)[(S)\text{-}(-)\text{-}PBzMePh]_2\}^+ClO_4^-$ (with or without added chiral phosphine) as catalysts. These results not only confirm the higher enantioselectivity of the in situ system but also show that the optical yield depends strongly on the P/Rh ratio. Such behaviour strongly suggests the existence of several mechanisms differing both in the ionic or covalent character of the catalysts and the number of phosphine ligands coordinated to rhodium and we began a systematic study of the mechanisms. In this publication we describe our first results, which were obtained with catalysts containing (+)-DIOP [11] as the chiral ligand.

Nomenclature used in this work

To facilitate discussion of the many mechanisms possible for the homogeneous hydrogenation of unsaturated substrates by phosphinerhodium complexes a simple unambiguous notation is used. This is based on the (proved or assumed) ligands present in the 16 or 18 electron key-intermediate of the catalytic cycle. The symbol for the substrate (in this case the ketone) which must obviously be coordinated to the metal is omitted, but the hydride ligands are shown, since the number of them in the key intermediate is not obvious. The following examples serve as illustrations:

Key intermediate	Symbol of possible catalytic cycle
$[Rh(PR_3)_2H_2(substrate)]^+$	$P_2H_2^+$
$Rh(PR_3)_2H_2(substrate)Cl$	cP_2H_2Cl or tP_2H_2Cl for phosphine ligands in *cis* or *trans* positions
$[Rh(PR_3)_3H_2(substrate)]^+$	$P_3H_2^+$

Results and discussion

Use of DIOP alone

With (+)-DIOP as chiral ligand in the hydrogenation of acetophenone the P/Rh ratio has practically no influence on the enantioselectivity of the catalysts (Table 2), because of the bidentate character of this phosphine, apparently no active catalysts can be formed which contain more than two phosphorus atoms coordinated to rhodium. The "excess" phosphine serves therefore only to form catalytically-inactive species, and simply reduces the rate of hydrogenation.

On the other hand, the optical yields were again much higher in the case of the in situ catalyst and the two catalysts even showed opposite enantioselectivities. This can be explained most easily by assuming an ionic, $P_2H_2^+$ and a non-ionic, P_2H_2Cl catalytic cycle, the first producing the (*S*)-(—) enantiomer of α-phenylethanol with low optical yield and the second the (*R*)-(+) enantiomer with a significantly higher enantioselectivity. It should be noted in this connection that

* NBD = norbornadiene, Bz = benzyl.

TABLE 2

HYDROGENATION OF ACETOPHENONE WITH CATALYST CONTAINING (+)-DIOP

Reaction conditions: 50°C, 1 bar, in methanol

Catalyst	P/Rh ratio	ITO [a] (min^{-1})	Reaction time (h)	Chemical yield (%) [b]	Configuration	Optical yield (%)
Rh(NBD)[(+)-DIOP]$^+ClO_4^-$	2/1	0.07	12	40	(*S*)-(—)	2.8 [c]
+ 0.5 mol (+)-DIOP added	3/1	0.04	12	18	(*S*)-(—)	2.3
1/2 $[Rh(NBD)Cl]_2$ + 1 (+)-DIOP	2/1	0.006	100	39	(*R*)-(+)	51
1/2 $[Rh(NBD)Cl]_2$ + 1.5 (+)-DIOP	3/1	0.004	100	27	(*R*)-(+)	54

[a] Initial turnover, mol H_2/mol Rh (min). [b] α-Phenylethanol. [c] 3.2% optical yield was obtained earlier [4] with the same catalyst at 30°.

a similar "duality" of ionic and non-ionic mechanisms was previously suggested by Sinou and Kagan [12] for the hydrogenation of olefins with rhodium complexes containing DIOP. That this dramatic difference in enantioselectivity is mainly due to the presence or absence of the Cl-ligand was proved by adding sodium chloride to the reaction mixture containing the ionic rhodium complex catalyst (Rh^+/Cl^- = 1/1), which resulted in a 42% optical yield of the (*R*)-(+) enantiomer.

Use of DIOP with added achiral phosphine

Additional information about the mechanisms was obtained from experiments performed with the ionic and in situ catalysts in the presence of 1 mol of a non-chiral monodentate phosphine to raise the P/Rh ratio to 3/1. The results are shown in Table 3.

n-Alkylphosphines exert a remarkable influence by reversing the enantioselectivity of the catalysts containing (+)-DIOP (compare the data of Tables 2 and 3). Furthermore, as can be seen from the results obtained with P-n-Bu_3 as added ligand, the effect is much more pronounced with the in situ systems (from 51% of the (*R*)-(+) to 12% of the (*S*)-(—) as favoured isomer) than with the ionic

TABLE 3

EFFECT OF ACHIRAL PHOSPHINES ON THE ENANTIOSELECTIVITY OF Rh(NBD)[(+)-DIOP]$^+$-ClO_4^- (A) AND IN SITU 1/2 $[Rh(NBD)Cl]_2$ + 1(+)-DIOP (B) CATALYSTS

Hydrogenation of acetophenone at 50°C; 1 bar H_2, in methanol.

Catalyst system	Achiral phosphine added [a]	ITO [b] (min^{-1})	Reaction time (h)	Chemical yield (%) [c]	Configuration	Optical yield (%)
A	P-n-Bu_3	0.042	26	41	(*R*)-(+)	0.4
A	P-n-Bu_3	0.045	12	29	(*R*)-(+)	0.1
B	$P(n\text{-}C_5H_{11})_3$	0.016	55	51	(*S*)-(—)	12
B	P-n-Bu_3	0.039	32	44	(*S*)-(—)	12
B	P-n-Pr_3	0.013	54	24	(*S*)-(—)	8.4
B	PEt_3	0.030	48	70	(*S*)-(—)	5.6
B	PEt_2Ph	0.006	74	35	(*R*)-(+)	3.9
B	P-i-Pr_3	0.007	90	27	(*R*)-(+)	38

[a] Rh/(+)-DIOP/PR_3 = 1/1/1. [b] Initial turnover, mol H_2/mol Rh (min). [c] α-Phenylethanol.

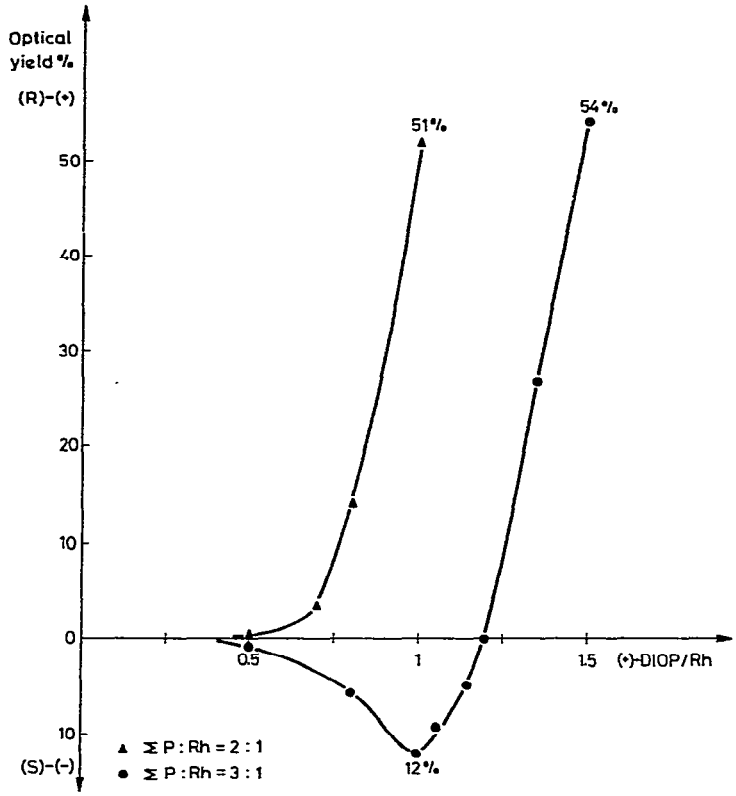

Fig. 1. Hydrogenation of acetophenone with [Rh(norbornadiene)Cl]$_2$ + (+)-DIOP + P-n-Bu$_3$ catalysts.

catalyst (4.0% (*S*)-(—) and 0.4 or 0.1% (*R*)-(+), in two parallel experiments in the second case) and opposite in sign.

To investigate this phenomenon further, two series of experiments were performed with the in situ catalyst system at varying P-n-Bu$_3$/(+)-DIOP ratios: in one of these the P/Rh ratio was kept at 2/1 and in the other at 3/1. The optical yields achieved are shown in Fig. 1.

When the P/Rh ratio was 2/1 the gradual replacement of (+)-DIOP by P-n-Bu$_3$ led only to a rapid and monotonic decrease of enantioselectivity; this can be easily explained in terms of the simultaneous action of two different P_2H_2Cl catalytic cycles involving Rh(DIOP)H$_2$(ketone)Cl and Rh(P-n-Bu$_3$)$_2$H$_2$(ketone)Cl as the key intermediates.When the P/Rh ratio was 3/1 a completely different picture was observed: the gradual replacement of (+)-DIOP by P-n-Bu$_3$ led first to a reversal of the enantioselectivity, which reached its highest value at a Rh/DIOP/P-n-Bu$_3$ = 1/1/1 ratio and then to a monotonic decrease of the optical yield. Apparently a new catalytic cycle with intermediates containing both phosphine ligands is operating at Rh/DIOP/P-n-Bu$_3$ = 1/1/1 and the intermediates of this impose different steric requirements on the coordination of the acetophenone molecule. At other Rh/DIOP/P-n-Bu$_3$ ratios the optical yields are obviously determined by the simultaneous action of the only (+)-DIOP or P-n-Bu$_3$ containing P_2H_2Cl cycles and this "mixed-phosphine-cycle" as already

noted in the experiments with P/Rh = 2/1.

The character of this "mixed-phosphine-cycle" is suggested by H_2-absorption measurements carried out on in situ catalyst solutions obtained with (+)-DIOP alone (P/Rh = 2/1) and with (+)-DIOP and P-n-Bu_3 (ΣP/Rh = 3/1; DIOP/P-n-Bu_3/Rh = 1/1/1). The first catalyst solution absorbed about 2 mol of H_2 and the second about 3 mol of H_2 per mol of rhodium added in the form of [Rh(NBD)-Cl]$_2$. This shows that in the system containing only (+)-DIOP no stable rhodium dihydride is being formed [13] and H_2 is consumed only in the hydrogenation of the diolefin ligand, whereas in the catalyst solution obtained by simultaneously using (+)-DIOP and P-n-Bu_3 rhodium is transformed into a dihydride complex. It has recently been shown [14], that such a difference is characteristic for bidentate and monodentate phosphines, because only the *trans*-bis(monophosphine)rhodium complexes add molecular hydrogen while the *cis* isomers, which are necessarily formed from bidentate diphosphines do not.

Our results suggest that the P_2H_2Cl cycle which is responsible for the catalytic activity of the in situ catalyst systems may be further differentiated into two variants depending on whether the two phosphorus ligands are *trans* or *cis* to each other in the key complexes. The in situ catalysts with monophosphines originate a tP_2H_2Cl cycle with *trans*-phosphorus ligands and those with bidentate diphosphines a cP_2H_2Cl cycle with *cis* phosphorus ligands. Apparently the combination of 1 mol (+)-DIOP and 1 mol P-n-Bu_3 per mol rhodium results in a tP_2H_2Cl cycle with (+)-DIOP acting as a monodentate ligand, and the significant structural difference between *cis*-Rh(DIOP)H_2(ketone)Cl and *trans*-Rh(DIOP)-(P-n-Bu_3)H_2(ketone)Cl explains the dramatic change in enantioselectivity observed. It is noteworthy that results obtained in the hydrogenation of α-acetamidocinnamic acid also suggest such a monodentate behaviour of DIOP [15].

A similar difference between the ionic $P_2H_2^+$ cycles in the case of monodentate and bidentate phosphines has to be considered also (i.e. $tP_2H_2^+$ and $cP_2H_2^+$, respectively) but to obtain similar evidence for these alternatives is more difficult because of the possibility of a $P_3H_2^+$ type catalytic cycle. (The same problem does not exist in the case of the non-ionic cycles since the key intermediate of a hypothetical P_3H_2Cl cycle would be a 20 electron complex, and so rather improbable.) Thus it can not be unambiguously decided whether the small but apparently real reversal of enantioselectivity observed upon addition of P-n-Bu_3 to the {Rh(NBD)[(+)-DIOP]}$^+ClO_4^-$ catalyst is to be attributed to a change from $P_2H_2^+$ to $P_3H_2^+$ or to that from $cP_2H_2^+$ to $tP_2H_2^+$, or, which is most probable, to a combination of the two.

Experimental

(+)-DIOP was purchased from Strem Chemicals Inc., (*S*)-(—)-PBzMePh prepared by the method of Mislow [16] and its optical purity determined according to Horner [17]. Rh(NBD)[(*S*)-(—)-PBzMePh]$_2^+ClO_4^-$ was prepared following the general method used for [Rh(diene)$(PR_3)_2]^+A^-$ complexes [18].

Catalytic experiments

A thermostatted flask connected to a thermostatted gas burette and equipped

with a magnetic stirrer and a silicone rubber cap was used. The rhodium complex (0.1 mmol Rh) and the required amount of phosphine were dissolved in methanol (1.4 ml) at 20°C and stirred under H_2 for 40 min. The temperature was then raised to 50°C, and acetophenone (10 mmol) was added with a syringe. The progress of the reaction was followed by measuring the gas consumption. The product mixture was fractionally distilled and the optical rotation of the α-phenylethanol fraction measured at 589 nm with a polarimeter of Schmidt—Haensch, type LLM.

Prehydrogenation of Rh-DIOP catalysts

46.4 mg $[Rh(NBD)Cl]_2$ (0.2 mmol Rh) and 99.6 mg (+)-DIOP (0.2 mmol) were dissolved in a Schlenk tube in 2.8 ml methanol under Ar. The Ar atmosphere was replaced by H_2 and the gas consumption followed with a gas burette as the solution was stirred magnetically. 9.5 ml (0.39 mmol) H_2 were consumed in about 3 h, corresponding to 1.95 mol H_2/mol Rh. In a parallel experiment with 51.2 μl P-n-Bu_3 (0.2 mmol) added to the catalyst solution, 13.6 ml (0.55 mmol) H_2 were consumed, corresponding to 2.75 mol H_2/mol Rh.

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