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PHOSPHINE COMPLEXES OF RHODIUM AS HOMOGENEOUS CATALYSTS

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Abstract - A general survey is given of the developments leading to enantioselective hydrogenation catalysts based on phosphinerhodium complexes. The rates and optical yields obtained in ketone hydrogenation strongly depend on the structure of the phosphine ligand and on the phosphorous: rhodium ratio. The results can be interpreted by assuming several parallel catalytic mechanisms. The addition of amines often greatly enhances the activity of the catalyst systems which may be used in this form also for hydrodehalogenation and the hydrogenation of nitro compounds. New types of catalysts which are based on rhodium carboxylate complexes have been developed. Using chiral carboxylates asymmetric hydrogenation of olefins has been achieved with nonchiral phosphines as ligands.

INTRODUCTION

Rhodium is one of the most scarce among the elements, probably not only in the earth crust, but also in the whole solar system (Table 1). This should predestinate it to be a laboratory curiousity - nevertheless it has gained industrial importance in recent years even as a homogeneous catalyst which is the more interesting since the problems associated with regeneration argue highly in favour of low-price chemicals in such cases.

TABLE 1. Occurence of platinum metals

	Ru	Rh	Pd	Os	Ir	Pt
Average concentration in the earth crust, ppb	5	1	10	50	1	5
Average concentration in iron meteorites, ppm	13	2	3	7	7	15

Two large scale petrochemical processes based on rhodium complexes as catalyst have been developed in recent years. The first of these was the synthesis of acetic acid from methanol and carbon monoxide (1-3)

$$CH_3OH + CO \xrightarrow[200^{\circ},\ 30\ bar]{[Rh(CO)_2I_2]^-,CH_3I} CH_3COOH \qquad (99\%)$$

which is a technology of Monsanto. The second was the low-pressure hydrofomylation process with a high selectivity for normal butyraldehyde developed by Union Carbide, Dawy Powergas and Johnson Matthey (4-6)

$$CH_3CH{=}CH_2 + CO + H_2 \xrightarrow[100^{\circ},\ 20\ bar]{HRh(CO)(PPh_3)_3} CH_3CH_2CH_2CHO + CH_3\underset{CH_3}{\overset{|}{C}}HCHO$$

10 : 1

Both processes have been realized in large capacity plants and replace earlier technologies based on cobalt complex catalysts requiring more drastic conditions and showing significantly lower selectivity.

The event, which gave the most important impetus to the development of homogeneous catalysts based on rhodium complexes was the discovery of $Rh(PPh_3)_3Cl$ as a catalyst for olefin hydrogenation by Wilkinson and his school (7). During the successive years this compound - often simply referred to only as "Wilkinson's complex" - was recognized to show catalytic activity for an amazing variety of organic reactions like hydrogenations, isomerisations, carbonylations, oligomerizations, etc. It is impossible to give even a brief account of these in this short compilation.

The most probable mechanism of olefin hydrogenation with $Rh(PPh_3)_3Cl$ as catalyst (8) is shown in Figure 1. It is generally accepted, that the catalytic cycle is including species with only two phosphine ligands in the coordination sphere of the rhodium atom and the third phosphine ligand may be replaced also by other (e.g.solvent) molecules. The catalysts developed later are in most cases based on this assumption.

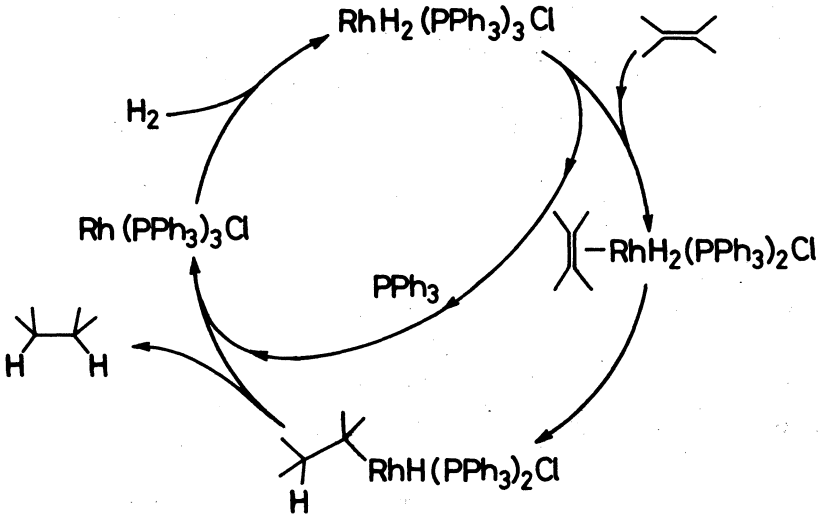


Fig.1. Mechanism of olefin hydrogenation with $Rh(PPh_3)_3Cl$ as catalyst.

The next important step towards those catalyst systems I should like to treat in some more detail was done by Sajus and coworkers (9) who recognized the possibility of preparing a large variety of Rh(I)-phosphine complex catalysts in solution ("in situ") by hydrogenating $[Rh(C_2H_4)_2Cl]_2$ in the presence of phosphines in the reaction mixture:

$$1/2\ [Rh(C_2H_4)_2Cl]_2 + 2PR_3 \xrightarrow[\text{solvent}]{H_2} RhH_2(PR_3)_2(\text{solvent})Cl$$

The coordinated solvent molecule is easily replaced by the olefin and obviously the same catalytic cycle as shown for $Rh(PPh_3)_3Cl$ can evolve in such systems.

In this way a vast number of catalitically active rhodium complexes became accessible. This development was further supported by the work of Schrock and Osborn (10) who found the cationic $[Rh(diene)(PR_3)_2]^+ A^-$ complexes easy to prepare and to be highly active catalysts for hydrogenation. With these results a broad foundation was laid for the successive evolution of a number of selective hydrogenation catalysts based on phosphine complexes of rhodium.

A spectacular achievment using these possibilities was the realization of asymmetric hydrogenation by Horner (11) and Knowles (12) who applied chiral phosphines as ligands. Asymmetric induction is made possible in this case by the fact that both the phosphine and the olefin are coordinated to the same rhodium atom at one stage of the catalytic cycle. If the phosphine is chiral two intermediate complexes of the type $RhH_2(PR^*_3)_2(\text{olefin})X$ may be formed depending

on with which of its two enantiotopic faces the prochiral olefin coordinates to the rhodium atom. These two complexes are diastereomers of each other and therefore the two parallel reaction pathways leading to the two enantiomers (Figure 2) are not equally efficient.

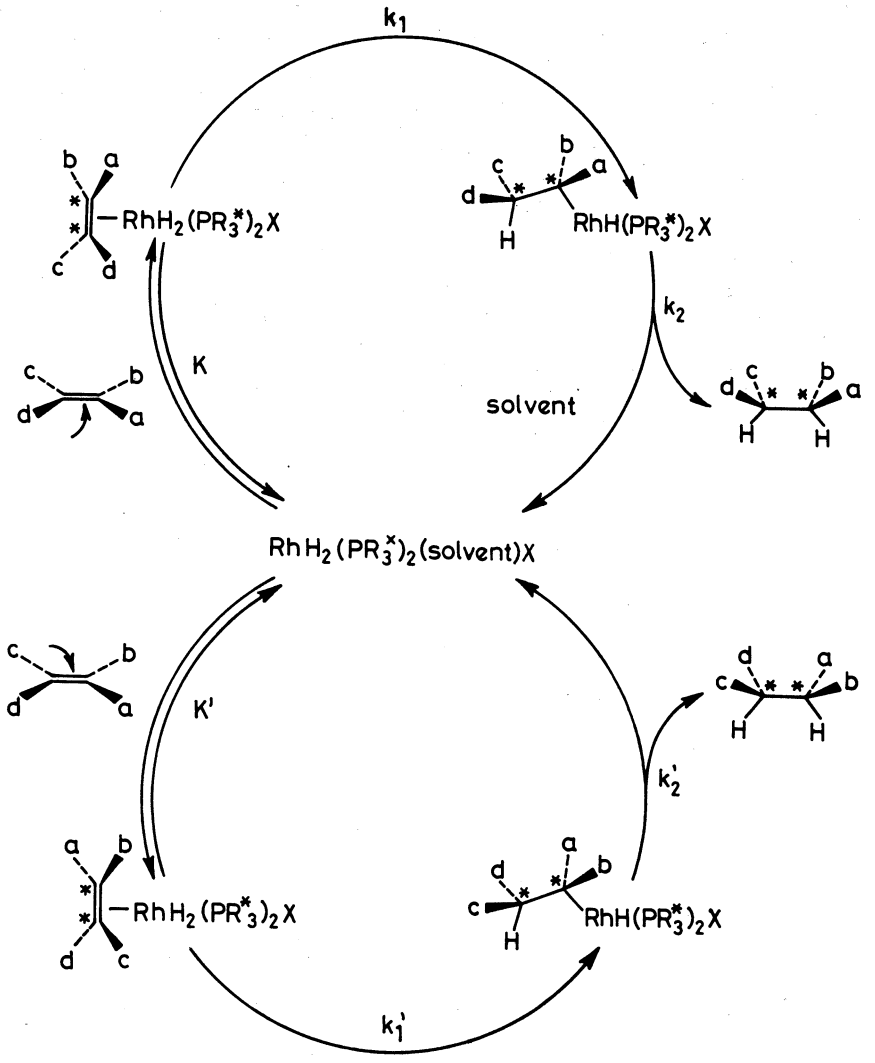
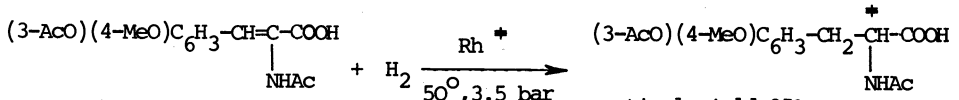


Fig.2. Reaction scheme showing reasons for enantioselectivity of rhodium complex catalyst containing chiral phosphines as ligands in hydrogenating prochiral olefins.

An industrial application of this promising possibility for the catalytic synthesis of chiral organic compounds followed quickly: Monsanto was successful in developing a commercial process for the synthesis of L-DOPA, one step of which is based on this principle (13,14):

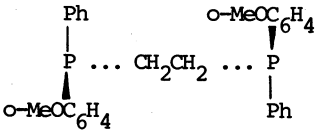


optical yield 95%

[Rh]* = [Rh(COD)(diPAMP)]+(BF4)−

COD = 1,5-cyclooctadiene

diPAMP = (-)-[1,2-bis(o-anisylphenylphosphino)ethane]



Asymmetric hydrogenation using rhodium complex catalysts whith chiral phosphines as ligands has become in recent years one of the most intensively investigated fields of homogeneous catalysis and our own results which I shall treat in the following sections also refer in most cases to this subject.

HYDROGENATION OF KETONES

The hydrogenation of ketones with rhodium phosphine complex catalyst was first achieved by Schrock and Osborn (15) using $[RhH_2(PR_3)_2(solvent)]^+$ complexes containing alkyl phosphines. Later we found that the "in situ" catalyst systems prepared from $[Rh(diene)Cl]_2$ complexes and such phosphines were also active catalysts for ketone hydrogenation (16), but PPh_3 yielded a catalytically inactive system. Apparently being rather sensitive to the structure of the phosphine, ketone hydrogenation promised to be a useful model to investigate relationships between ligand structure and catalytic activity of rhodium phosphine complexes (17).

As a measure for the electronic parameter of the phosphine PR_3 the infrared CO stretching frequencies of $Rh(CO)(PR_3)_2Cl$ complexes were chosen since these complexes are rather similar to the probable intermediates of the catalytic cycle. The catalytic activity of the complexes formed "in situ" from $[Rh(NBD)Cl]_2$ (NBD = norbornadiene) and the same phosphines was determined by hydrogenating acetone, measuring the rate of H_2 consumption at 50° and 1 bar and expressing it as turnover in mole H_2/mole Rh.min. Our results obtained with 23 different catalyst systems are shown in Figure 3.

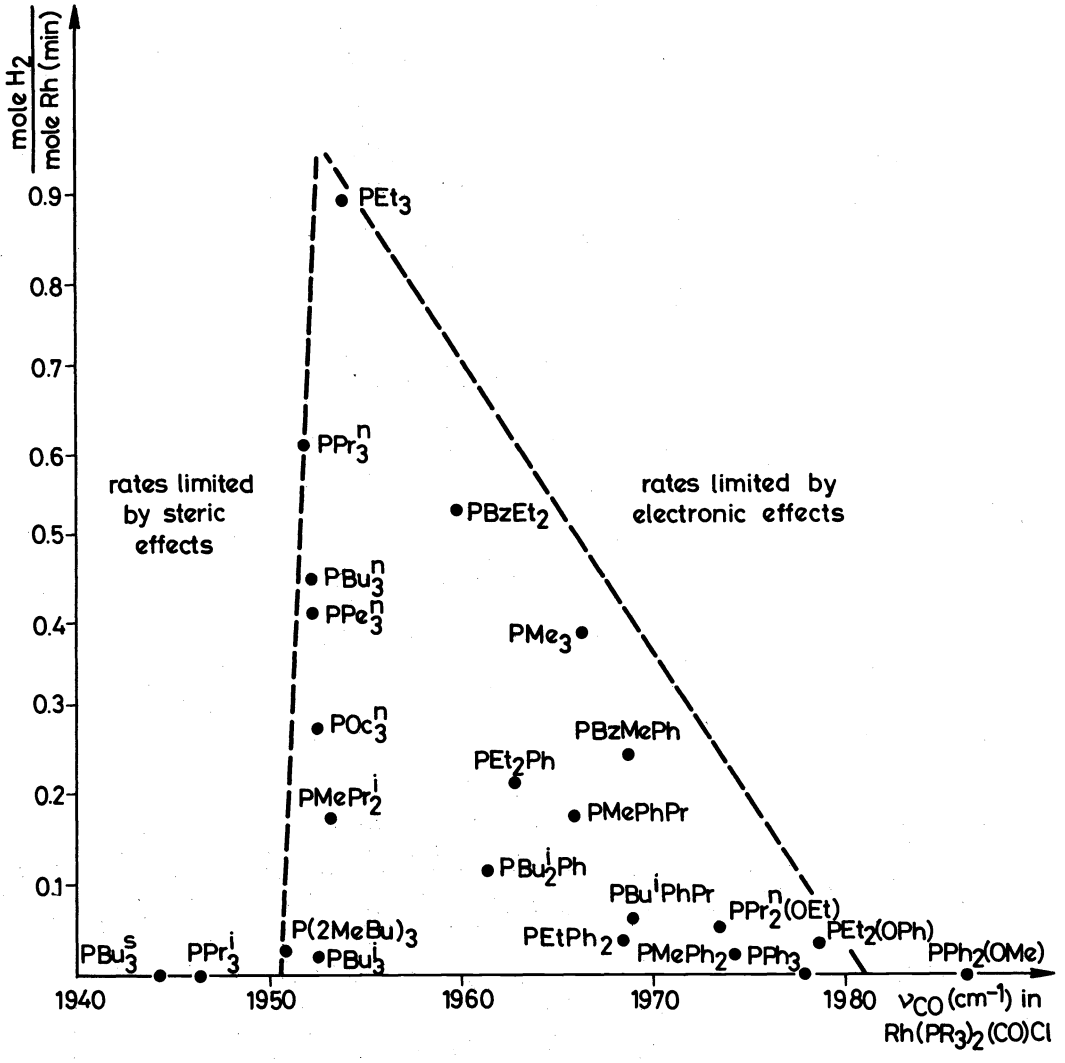


Fig.3. Activity of "in situ" catalysts formed from $[Rh(NBD)Cl]_2$ and different phosphines.

The data in Fig.3. show a clear maximum at PEt_3.P(III)-ligands which are weaker σ-donors (or stronger π-acceptors) than PEt_3 yield lower activity catalysts mainly because of the electronic parameter: the hydrogenation of ketones needs more basic phosphines (15). On the other hand the electron donating power of the ligands can be increased above that of PEt_3 only by attaching larger or branched alkyl groups to phosphorous which, however, strongly increase steric hindrance and ultimately lead to completely inactive catalysts.

The tri-n-alkyl phosphines having approximately the same basicity even show some quantitative correlation, the turnover being inversely proportional to the molecular weight of the ligand:

Ligand	M	Turnover(min^{-1})	(M)x(turnover)
PEt_3	118	0.89	105
PPr^n_3	160	0.63	101
PBu^n_3	202	0.45	91
PPe^n_3	244	0.41	100
POc^n_3	370	0.28	103

This latter result is somewhat surprising, since the ligand cone angles of these phosphines - as defined by Tolman (18) - are also identical and accordingly also their steric requirements are usually regarded as being the same. Obviously this latter approximation is false since due to their thermal movement the longer alkyl chains may cover a larger part of the coordination sphere around the rhodium atom.

All unsymmetrical ketones are prochiral compounds accordingly asymmetric hydrogenation may become a useful method to prepare optically active secondary alcohols. Already our first results did prove that the catalysts prepared "in situ" give better optical yields than the cationic complexes $[Rh(diene)(PR_3)_2]^+ A^-$ used earlier if the same phosphines are applied (16). This observation suggested at least two different mechanisms operating, and investigating the assymetric hydrogenation of acetophenone

$$C_6H_5 - \underset{\underset{O}{\|}}{C} - CH_3 + H_2 \xrightarrow{[Rh]^*} C_6H_5 - \overset{*}{\underset{\underset{OH}{|}}{CH}} - CH_3$$

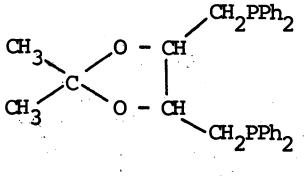
in more detail revealed an even more complex picture (Table 2)(20).

TABLE 2. Hydrogenation of acetophenone with chiral rhodium phosphine catalysts. 50°, 1 bar, solvent methanol

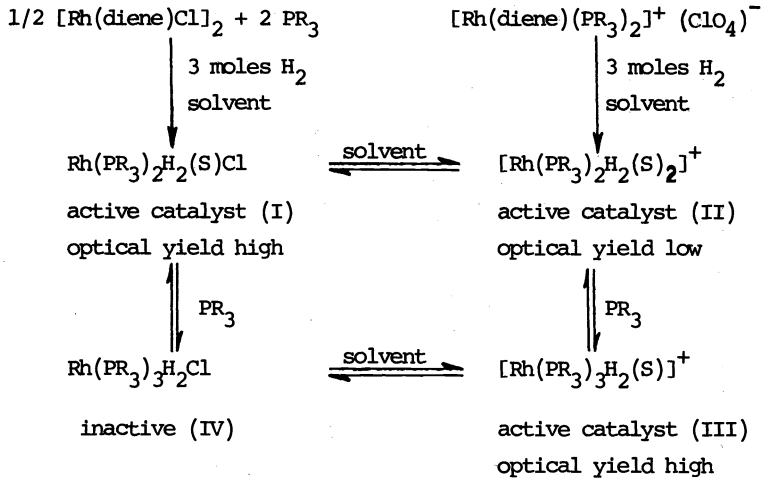
Catalyst	P:Rh ratio	Configuration	Optical yield %
$[Rh(NBD)((S)\text{-BMPP})_2]^+(ClO_4)^-$ a)	2:1	S-(-)	2.5
+ 1 mole (S)-BMPP added	3:1	S-(-)	23
1/2 $[Rh(NBD)Cl]_2$ + 2(S)-BMPP	2:1	S-(-)	28
1/2 $[Rh(NBD)Cl]_2$ + 3(S)-BMPP	3:1	S-(-)	37
$[Rh(NBD)((+)\text{-DIOP})]^+(ClO_4)^-$ b)	2:1	S-(-)	2.8
+ 0.5 mole (+)-DIOP added	3:1	S-(-)	2.3
1/2 $[Rh(NBD)Cl]_2$ + 1 (+)-DIOP	2:1	R-(+)	51
1/2 $[Rh(NBD)Cl]_2$ + 1.5 (+)-DIOP	3:1	R-(+)	54

a) BMPP = benzyl methyl phenyl phosphine

b) DIOP = 2,3-O-isopropylidene-2,3-dihydroxy-1,4 bis(diphenylphosphino)butane (19)



In the case of the monodentate BMPP the optical yield depends not only on the ionic or non-ionic character of the catalytic complex but also on the P:Rh ratio. We assume that there are at least three catalytic cycles operating in the case of a monodentate phosphine, the principal active species of which and their relation to each other and to the starting complexes are shown below:



The active catalysts (I)-(III) all can coordinate a ketone molecule by releasing a solvent ligand but complex (IV) formed in the non-ionic "in situ" system is unable to do so because it is already a 6-coordinate 18-electron species.

At first sight the catalysts obtained from the bidentate DIOP seem to be less variable since if two such phosphine molecules coordinate to rhodium, the catalytically inactive $[Rh(DIOP)_2]^+$ or $Rh(DIOP)_2Cl$ complexes are formed. It was found however, that adding a monodentate phosphine to the "in situ" Rh-DIOP catalyst new combinations may be formed as shown by the dramatic influence of some achiral monophosphines on the optical yields (Table 3).

TABLE 3. Hydrogenation of acetophenone with the "in situ" catalyst formed from $Rh(NBD)Cl_2$ and (+)-DIOP. Effect of added achiral monophosphine PR_3.
Rh:DIOP:PR_3 = 1:1:1, 50°, 1 bar, solvent methanol

PR_3	Configuration	Optical yield, %
-	R-(+)	51
PEt_3	S-(-)	5.6
PPr^n_3	S-(-)	8.4
PBu^n_3	S-(-)	12
PPe^n_3	S-(-)	12
PEt_2Ph	R-(+)	3.9
PPr^i_3	R-(+)	38

To investigate this phenomenon further, two series of experiments were performed with the "in situ" catalyst system with varying PBu^n_3:(+)-DIOP ratios: in one of these the Σ P:Rh ratio was kept at 2:1 and in the other at 3:1. The optical yields achieved are shown in Figure 4.

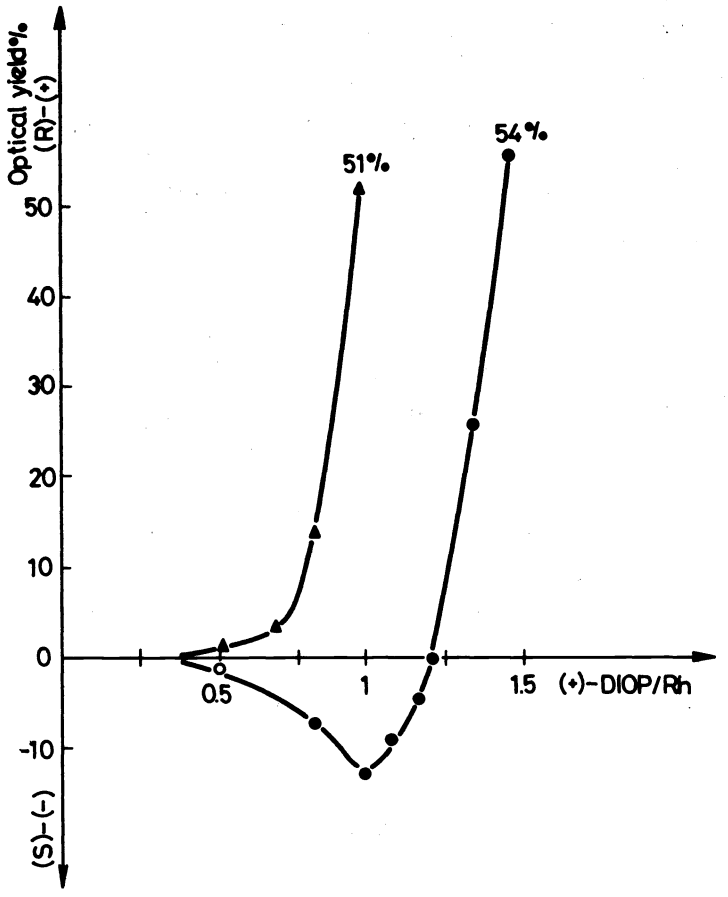


Fig.4. Influence of PBu^n_3 on the enantioselectivity of "in situ" catalysts formed from $[Rh(NBD)Cl]_2$ and (+)-DIOP.
▲ Σ P:Rh = 2:1 ● Σ P:Rh = 3:1

At Σ P:Rh = 2:1 the effect of the gradual replacement of (+)-DIOP by PBu^n_3 could be easily explained by the simultaneous action of two different catalytic cycles involving $[Rh(DIOP)H_2(S)Cl]$ and $[Rh(PBu^n_3)_2H_2(S)Cl]$ as principal active species.

Keeping the Σ P:Rh ratio at 3:1 a completely different picture was observed. Apparently a new catalytic cycle with intermediates containing both phosphine ligands is operating at Rh:DIOP:PBu^n_3 = 1:1:1 and the intermediates of this pose different steric requirements on the coordination of the acetophenone molecule. At other Rh:DIOP:PBu^n_3 ratios the optical yields are obviously determined by the simultaneous action of the only (+)-DIOP or PBu^n_3 containing catalytic cycles and this "mixed-phosphine-cycle" in a similar way as in the case of the experiments with Σ P:Rh = 2:1.

The character of this "mixed-phosphine-cycle" is suggested by H_2-absorption measurements. The catalyst solution obtained with (+)-DIOP alone (Σ P:Rh = 2:1) absorbed about 2 moles of H_2 and that obtained from (+)DIOP and PBu^n_3 (ΣP:Rh = 3:1; DIOP:PBu^n_3:Rh = 1:1:1) about 3 moles of H_2 per mole 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 and H_2 is consumed only for the hydrogenation of the diolefin ligand whereas in the catalyst solution obtained by simultaneously applying (+)-DIOP and PBu^n_3 rhodium is transformed into a dihydride complex. It has recently been shown, that such a difference is characteristic for bidentate and monodentate phosphines, because only the trans bis monophosphine rhodium complexes add molecular hydrogen but the cis isomers which are necessarily formed from bidentate diphosphines do not (21).

Accordingly our results suggest that the cycle involving non-ionic intermediates of type (I) and which is responsible for the catalytic activity of the "in situ" catalyst systems may be differentiated into two variants depending on whether the two phosphorous ligands are trans or cis to each other in the key complexes. The "in situ" catalysts obtained with monophosphines originate a cycle with trans phosphorous ligands and those obtained with bidentate diphosphines a cycle with cis phosphorous ligands. Apparently the combination of 1 mole (+)-DIOP and 1 mole PBu^n_3 per rhodium results in a cycle with trans phosphorous ligands - with (+)-DIOP acting as a monodentate ligand - and the significant structural difference between cis-[Rh(DIOP)H_2(ketone)Cl] and trans-[Rh(DIOP)(PBu^n_3)H_2(ketone)Cl] explains the dramatic change in enantioselectivity observed.

CATALYSTS MODIFIED BY AMINES

The examples above may already give an idea of the variability of rhodium phosphine complex catalysts. Obviously, the number of variants increases considerably if other types of ligands are also added to these systems. One of the possibilities lying near at hand is to use amines besides (or instead) of phosphines.

As already mentioned, triphenyl phosphine containg catalysts are practically inactive for ketone hydrogenation. We found, however, that adding triethyl amine to these solutions, the catalytic activity is increased dramatically. Even the Wilkinson complex, $Rh(PPh_3)_3Cl$ becomes a useful catalyst for the hydrogenation of ketones in the presence of Et_3N. With the DIOP containing catalyst, both activity and enantioselectivity are significantly altered by Et_3N (Table 4). (22)

TABLE 4. Hydrogenation of acetophenone. Effect of triethyl amine 50°, 70 bar, 6 h, solvent methanol

Rhodium complex	Phosphine	Amine	Chemical yield, %	Configuration	Optical yield,%
1/2 $[Rh(NBD)Cl]_2$	1(+)-DIOP	-	10	R-(+)	35
-"-	-"-	$5Et_3N$	98	S-(-)	12
-"-	$3PPh_3$	-	3	-	-
-"-	-"-	$5Et_3N$	95	-	-
$Rh(PPh_3)_3Cl$	-	-	0	-	-
-"-	-	$5Et_3N$	98	-	-

This surprisingly large increase in activity suggested to try these rhodium + + phosphine + amine systems also for such hydrogenation reactions which are usually not easily performed using homogeneous catalysts. As a first trial, aromatic nitro compounds were investigated and reasonable reaction rates could be achieved under mild conditions (23). As can be seen from Table 5, the best catalysts were obtained if besides adding Et_3N an unusually low P:Rh ratio of 1.2:1 was used. This suggests that in these reactions not $[RhH_2(PR_3)_2(S)X]$ or $[RhH_2(PR_3)_2(S)_2]^+$ type complexes are the active species. The rhodium + PPh_3 + + Et_3N catalyst was successfully applied for a number of aromatic nitro compounds (Table 6).

TABLE 5. Hydrogenation of nitrobenzene. Effect of triethyl amine. 50°, 1 bar, solvent benzene/methanol (1/1).

Rhodium complex	Phosphine	Et_3N	ITO, min^{-1} a)
$Rh(PPh_3)_3Cl$	-	-	0.05
-"-	-	3	0.26
1/2 $[Rh(1,5\text{-hexadiene})Cl]_2$	3.2 PPh_3	3	0.24
-"-	2.2 PPh_3	3	0.36
-"-	1.2 PPh_3	3	2.1
-"-	1.2 PBu^n_3	3	0.10
-"-	1.2 $P(OMe)_3$	3	2.6

a) Initial turnover, mole H_2/mole Rh.min

TABLE 6. Hydrogenation of different aromatic nitro compounds with a $[Rh(1.5\text{-hexadiene})Cl]_2 + PPh_3 + Et_3N$ (Rh:P:N=1:1.2:3) catalyst. 50°, 1 bar, solvent benzene/methanol (1/1)

Substrate	Conversion,% a)	Product	Yield,%
$C_6H_5NO_2$	99	$C_6H_5NH_2$	90
α-$C_{10}H_7NO_2$	64	α-$C_{10}H_7NH_2$	52
o-$HOC_6H_4NO_2$	60	o-$HOC_6H_4NH_2$	55
p-$ClC_6H_4NO_2$	73	$C_6H_5NH_2$	48
		p-$ClC_6H_4NH_2$	9
o-$O_2NC_6H_4NO_2$	60	o-$O_2NC_6H_4NH_2$	57
		o-$H_2NC_6H_4NH_2$	1

a) Based on H_2 consumed

The result of the experiment with p-chloro nitrobenzene is of interest the chief product being aniline instead of p-chloro aniline. This suggested that our catalysts may eventually be used for hydrodehalogenating organic halides with molecular hydrogen. This assumption could be verified for both aliphatic and aromatic halogen compounds (Table 7)(24).

TABLE 7. Hydrodehalogenation of organic halides with [Rh(1.5-hexadiene)Cl]$_2$ + PPh_3 + Et_2NH catalyst Rh:P:Substrate = 1:1.1:100

Halide	$t_{0.5}$(min) [a]	Conversion, %
$PhCH_2Cl$	15	88
$PhCH_2Br$	16	63
$PhCH_2I$	110	70
PhCl	400	32
PhBr	210	68
PhI	55	82
n-$C_5H_{11}Cl$	-	-
n-$C_5H_{11}Br$	200	67
n-$C_5H_{11}I$	50	65
$ClCH_2COOEt$	11	84
$Cl_3CCOOEt$	290	-

[a] Time (min) necessary for hydrogenation of 50 moles of substrate per mole Rh (50% conversion).

Even a slow hydrogenation of benzene to cyclohexane takes place with PBu_3 and Et_3N containing catalysts (22). As far as this problem can be unambigously settled, all Et_3N-modified systems were dark brown but homogeneous, clear solutions containing no precipitated metallic rhodium.

It is of course appropriate to ask about the nature of these apparently highly active catalyst systems. Up till now we have one clear-cut information: using at least 4 moles of PPh_3 per mole rhodium the well known complex $RhH(PPh_3)_4$ precipitates from the solutions. This means that one of the functions of Et_3N is to promote hydrogenolysis of the Rh, Cl bond by neutralizing the HCl formed:

$$[Rh(diene)Cl]_2 \xrightarrow[Et_3N]{H_2,\ PPh_3} RhH(PPh_3)_4 + \text{alkene} + Et_3N.HCl$$

We are currently investigating wether the amine is at the same time also functioning as a ligand.

CARBOXYLATO COMPLEXES AS HYDROGENATION CATALYSTS

In some experiments using cinnamic acid as an olefinic substrate we observed the formation of a colorless precipitate which could be identified as cinnamato-bis(triphenylphosphine) rhodium dihydride. Starting from this observation some other complexes of the type $RhH_2(PPh_3)_2(OOCR)$ could be prepared (25):

$$1/2[Rh(diene)Cl]_2 + 2PPh_3 \xrightarrow[H_2]{RCOOH,\ Et_3N} RhH_2(PPh_3)_2(OOCR)$$

R = Ph, $PhCH_2CH_2$, PhCH=CH, nC_5H_{11}.

Based on IR and NMR data we proposed the octahedral structure shown on Figure 5. for these complexes.

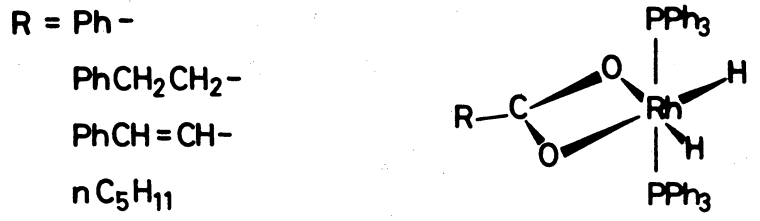


Fig.5. Proposed structure of $RhH_2(PPh_3)_2(OOCR)$ complexes.

Not unexpectedly, these phosphinerhodium complexes proved to be good catalysts for olefin hydrogenation, in some cases their activity even surpassed that of the classical $RhCl(PPh_3)_3$ (Table 8). This called our attention of rhodium carboxylates as potentially useful hydrogenation catalysts and we searched for a method which would make different phosphinerhodium carboxylates easily accessible (26).

TABLE 8. Hydrogenation of olefins with $RhCl(PPh_3)_3$ and $RhH_2(PPh_3)_2$ (OOCCH=CHPh) as catalysts. Rates expressed in initial turnover (ITO), mole H_2/mole Rh.min. 30°, 1 bar, solvent benzene/methanol (1/1).

Olefin	Catalyst	
	$Rh(PPh_3)_3Cl$	$RhH_2(PPh_3)_2(OOCCH=CHPh)$
$PhCH=CH_2$	21	9.2 a)
E-PhCH=CHCOOH	0.14	0.56
Fumaric acid	1.3	9.2
E-MeCH=CHCOOEt	2.7	0.79

a) decreasing rapidly

The most promising route appeared to be to use $[Rh(diene)OOCR]_2$ complexes as starting compounds and prepare the desired complexes "in situ" by reacting with phosphines under hydrogen. In this way many different $RhH_2(PR_3)_2(OOCR)$ type compounds could be formed and their activity and selectivity be studied. Carboxylates prepared from chiral carboxylic acids appeared to be particularly interesing in this respect since they may be useful as catalysts for asymmetric hydrogenations. Many chiral carboxylic acids are cheap and rather common materials and may offer thus a more easy route to enantioselective catalysts than chiral phosphines which are hard to synthetize and accordingly rather expensive.

Analogously to the first synthesis of $[Rh(COD)(OOCMe)]_2$ by Chatt (27), $[Rh(COD)(OOCR)]_2$ complexes may be prepared most easily from $[Rh(COD)Cl]_2$ and some metal salt of the appropriate carboxylic acid. Following the method of Usón (28) we used the Ag salts for this purpose. Dimeric carboxylates were prepared in this manner starting from CH_3COOAg, the Ag salt of L-(+)-mandelic acid and the mono salt of dibenzoyl-(+)-tartaric acid.

The acetato rhodium dimer was found to be an active catalyst for olefin hydrogenation in the presence of different alkyl or aryl phosphines. Highest rates were achieved with a P:Rh ratio of about 2:1 similarily to the "in situ" systems prepared from $[Rh(diene)Cl]_2$ complexes.

The activity of the catalysts obtained from [Rh(COD)(OOCMe)] and PPh_3 or PBu_3 for the hydrogenation of several olefins is shown by the data of Table 9. Comparing Tables 8 and 9 it can be seen that the "in situ" catalysts obtained from the acetate complex are also comparable to the classical Wilkinson catalyst: for some olefins they are less, for others more active that the latter.

TABLE 9. Hydrogenation of olefinic substrates with $[Rh(COD)(OOCMe)]_2$ + PPh_3 or PBu^n_3 "in situ" systems as catalyst (P:Rh = 2.2:1). Rates expressed in initial turnover (ITO), mole H_2/mole.Rh.min. 30°, 1 bar, solvent benzene/methanol (1/1).

Olefin	Catalyst	
	PPh_3	PBu^n_3
$PhCH=CH_2$	5.4	0.87
E-PhCH=CHCOOH	0.40	1.4
Fumaric acid	9.7	38
$E\text{-}CH_3CH=CHCOOEt$	0.60	0.20
Z-PhCH=C(NHAc)COOMe	0.48	25

TABLE 10. Enantioselective hydrogenation of α-acetamido cinnamic acid methyl ester with "in situ" catalysts formed from $[Rh(COD)(OOCR^*)]_2$ 30°, 1 bar, solvent benzene/methanol (1/1).

R^*COO	Phosphine	ITO [a] min^{-1}	Configuration	Optical yield,%	Chiral productivity, min^{-1} [b]
L-(+)-PhCH(OH)COO (=mandelate)	PMe_3	1.2	R-(-)	13.0	0.16
	PEt_3	24	R-(-)	4.2	1.0
	PPr^n_3	28	R-(-)	5.9	1.6
	PBu^n_3	22	R-(-)	4.7	1.0
	PPe^n_3	19	R-(-)	8.1	1.5
	POc^n_3	24	R-(-)	9.5	2.3
	$P(nC_{16}H_{33})_3$	9.4	R-(-)	6.6	0.62
	PPh_3	0.68	S-(+)	0.3	0.002
	PPh_2Et	7.2	R-(-)	1.1	0.08
	$PPhEt_2$	22	-	0	-
(-)-HOOCH(OBz)CH(OBz)COO (=dibenzoyl hydrogen tartarate)	PBu^n_3	10	R-(-)	3.7	0.37
	$P(nC_{16}H_{33})_3$	0.20	R-(-)	5.0	0.01
	PPh_3	1.8	-	0	-

a) Initial turnover, mole H_2/mole Rh.min

b) $\frac{\text{mole enantiomeric excess of product}}{\text{mole chiral component of catalyst.min}}$

The analogies and differences suggest, that the active species formed from $[Rh(diene)Cl]_2$, $Rh(PPh_3)_3Cl$ and $[Rh(diene)(OOCR)]_2$ complexes may be similar but are not the same ones, e.g. $RhH_2(PR_3)_2Cl$ and $RhH_2(PR_3)_2(OOCMe)$.

Rhodium complexes containing chiral carboxylic acids have not been used up till now as catalyst and the only catalyst with a chiral carboxylato ligand applied for asymmetric hydrogenation is the ruthenium complex $RuH(PPh_3)_3$ (mandelate) prepared from R-(-)-mandelic acid. This latter catalyst however, showed only low enantioselectivity: 0.4% optical yield was achieved in the hydrogenation of 2-ethyl-1-hexene (29).

We tested the two chiral rhodium carboxylato complexes prepared from L-(+)--mandelic acid and (-)-dibenzoyl tartaric acid in the presence of different phosphines for the hydrogenation of α-acetamido cinnamic acid methyl ester and obtained the results shown in Table 10. As can be seen the catalysts formed from the rhodium mandelate complex and aliphatic phosphines show the best enantioselectivity allthough the optical yields are generally rather low.

A significant advantage of some of these new catalysts is their rather high activity: turnovers around 20 min^{-1} were often observed. These catalysts therefore show reasonable effectiveness with respect to their "chiral productivity" which we defined as the moles of chiral molecules produced per mole of chiral catalyst component and unit time.

CONCLUSIONS

Rhodium is obviously one of the most versatile metals in homogeneous catalysis and its significance will certainly increase in the years to come. Phosphines had a dominant role in the developments of rhodium chemistry in the last decade because in this way the practically limitless possibilities of organic chemistry could be used in developing new and new homogeneous catalysts. Some of the work shown here demonstrates that also other types of organic molecules like amines or carboxylic acids may be used to shape the catalyst and this significantly broadens the variety of potentially useful complexes. Perheaps only a few spectacular single achievments will characterize future development but a lot of seemingly modest results will surely lead to a "state of the art" which shall resemble that of enzyme chemistry, both with regard to structures and selectivities of catalysts.

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