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PHOSPHINERHODIUM COMPLEXES AS HOMOGENEOUS CATALYSTS

XVI *. STEREOSELECTIVE HYDROGENATION OF CYCLIC KETONES **

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Summary

Cyclic ketones have been hydrogenated stereoselectively with various phosphinerhodium complexes as catalysts. Systems containing phosphines of high basicity and consequently forming Rh^{III} dihydrides as active species yielded mainly the thermodynamically more stable alcohol isomers. Catalysts prepared from aryl-type phosphines of low basicity and modified with Et_3N, which contain Rh^{I} monohydrides as active complexes, afforded the less stable alcohol isomers as the major products. The ratio of Rh^{III} and Rh^{I} hydrides, which determines the stereoselectivity of the catalysts prepared in situ could be changed by suitable choice of base.

Introduction

There are only a few examples of the reduction of cyclic ketones with phosphinerhodium complexes as catalysts [1–6]. With 4-t-butylcyclohexanone as the model compound, in most cases predominant formation of the thermodynamically more stable *trans* alcohol was observed in the case of direct hydrogenation [1,2,4] and also in transfer hydrogenation [3,4]. (For an exception see ref. 6.).

We demonstrated previously that in addition to the ketone-hydrogenation catalysts first described by Osborn [1] and which contain $[Rh(PR_3)_2(MeOH)_2]^+$ complexes as active species, two other types of active catalysts may be used for this hydrogenation. One of these is based on $Rh(PR_3)_2(solvent)_2Cl$ type complexes as catalysts and is obtained in situ from $[Rh(diene)Cl]_2$ and phosphines [7]. The other contains $HRh(PR_3)_3$ complexes as active species and can be obtained from $[Rh(diene)Cl]_2$ complexes by addition of Et_3N [8].

* For part XV see ref. 8.

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In the light of this information it seemed of interest to investigate how the nature of the catalyst influences the stereoselectivity of ketone hydrogenation, and thus to obtain more knowledge of the mechanism of this hydrogenation. We describe below the results obtained with various cyclic ketones using two catalysts, the systems formed in situ from $[Rh(NBD)Cl]_2$ * and PR_3 and those formed from $[Rh(NBD)Cl]_2$, PPh_3, and Et_3N. We show that the main factors determining the activity and the stereoselectivity of the catalysts are the basicities of the phosphine ligand and the added base.

Results and discussion

Results obtained with 4-t-butylcyclohexanone are shown in Table 1. It can be seen that with PBu_3-containing rhodium catalysts the *trans* alcohol was always formed irrespective of whether or not Et_3N was added to the reaction mixture. On the other hand the effect of the $[Rh(NBD)Cl]_2 + PPh_3$ catalyst, which itself gave the same thermodynamically more stable isomer (although very slowly), was dramatically changed by the addition of Et_3N, and the *cis* alcohol became the main product. This change in stereoselectivity was not limited to 4-t-butylcyclohexanone, similar phenomena being observed in hydrogenation of other cyclic ketones (Table 2).

The results obtained with N-i-Pr-nortropinone further show that when ketones containing an amine functionality are hydrogenated the substrate itself may play the role of the base, so that use of Et_3N is unnecessary. A similar effect has been noted previously [9].

We have confirmed that under our reaction conditions the alcohol isomers do not undergo interconversion. This means, that the formation of both isomers is a kinetically controlled process. Accordingly, the observed stereoselectivity has to be attributed to a change in the mechanism of hydrogenation. We suggest the following explanation.

TABLE 1

HYDROGENATION OF 4-t-BUTYLCYCLOHEXANONE [a]

Catalyst	Rh/P/N	k_{obs} [b] (min^{-1})	Conversion [c] (%)	Relative amount of alcohol isomers (%)	
				cis	*trans*
$[Rh(NBD)Cl]_2 + PBu_3$	1/2.2	3.7×10^{-2}	98.9	9.9	90.1
$[Rh(NBD)Cl]_2 + PBu_3 + Et_3N$	1/2.2/5	3.5×10^{-2}	97.5	9.6	90.4
$[Rh(NBD)Cl]_2 + PBu_3$	1/3	9.9×10^{-3}	98.0	9.2	90.8
$[Rh(NBD)Cl]_2 + PPh_3$	1/3.2	4.6×10^{-5}	2.1	28.5	71.5
$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	1/3.2/5	5.1×10^{-3}	95.4	72.7	27.3
$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	1/2.2/5	3.2×10^{-3}	83.4	62.4	37.6
$Rh(PPh_3)_3Cl + Et_3N$	1/3/5	4.6×10^{-3}	87.1	76.4	23.6
$HRh(PPh_3)_4$	1/4	7.1×10^{-3} [d]	89.6	80.3	19.7
$HRh(PBu_3)_4$	1/4	4.2×10^{-5}	2.1	62.8	37.2

[a] 50°C, 1 bar H_2; 1 mmol ketone in 5 ml benzene/methanol = 3/7. [b] The reaction is first order in substrate. [c] Reaction time 6 h. [d] Benzene/methanol = 1/1.

* NBD = norbornadiene.

TABLE 2

HYDROGENATION OF VARIOUS CYCLIC KETONES [a]

Ketone	Catalyst	Rh/P/N	k_{obs} [b] (min^{-1})	Conversion [c] (%)	Relative amount of alcohol isomers (%)	
					cis or α	*trans* or β
Menthone	$[Rh(NBD)Cl]_2 + PBu_3$	1/2.2	1.2×10^{-3}	48.4	14.8	85.2
	$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	1/3.2/5	1.3×10^{-3}	40.6	86.0	14.0
Camphor	$[Rh(NBD)Cl]_2 + PBu_3$	1/2.2	7.4×10^{-4}	7.2	38.8	61.2
	$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	1/3.2/5	5.1×10^{-4}	3.1	70.0	30.0
5-α-Androstan-	$[Rh(NBD)Cl]_2 + PBu_3$	1/2.2	6.4×10^{-3}	88.6 [d]	7.6	92.4
-3,17-dione	$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	1/3.2/5	7.6×10^{-4}	12.8 [d]	65.7	34.3
N-i-Pr-nortropinone	$[Rh(NBD)Cl]_2 + PBu_3$	1/2.2	2.8×10^{-3}	58.9	11.9	88.1
	$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	1/3.2/5	6.1×10^{-3}	96.2	97.6	2.4
	$[Rh(NBD)Cl]_2 + PPh_3$	1/3.2	5.8×10^{-3}	83.5	97.5	2.5

[a] For reaction conditions see Table 1, footnote *a*. [b] The reaction is first order in substrate. [c] Reaction time 6 h. [d] Product: 5-α-androstan-3-ol-17-one.

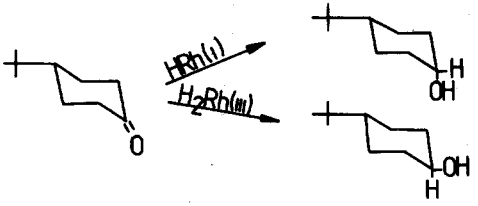
In the presence of a base (B) the Rh^{III} dihydrido complexes formed in situ from $[Rh(NBD)Cl]_2$ and PR_3 may be converted into Rh^{I} monohydrido complexes, according to eq. 1:

$$H_2Rh^{III}(PR_3)_xCl + B \rightleftharpoons HRh^{I}(PR_3)_x + BH^+ + Cl^- \quad (1)$$

Since the position of equilibrium 1 obviously depends on the acidity of the Rh^{III} dihydride and the basicity of the base B, the complexes containing more basic phosphines (such as PBu_3) are less readily deprotonated, and so only small amounts of Rh^{I} monohydrides will be formed in the presence of weak bases. This explains the ineffectiveness of Et_3N in changing the stereoselectivity of the PBu_3-containing catalyst system. On the other hand, if PPh_3 is used as ligand, Et_3N is a strong enough base to shift equilibrium 1 to the right [8] and so the stereoselectivity of the PPh_3-containing catalyst is profoundly changed by Et_3N.

We thus suggest that the thermodynamically more stable (*trans*) alcohol isomer is the favored product if a Rh^{III} dihydride is the catalytically active species, whereas the Rh^{I} monohydride must be responsible for the predominant formation of the *cis* isomer (Scheme 1).

SCHEME 1



Rh^{I} is a soft Lewis-acid and consequently will tend to coordinate the ketone carbonyl group edge-on, like an olefin π-complex. For steric reasons this type of coordination favors attack from the side *trans* to the t-Bu group, and because of the softness of Rh^{I} leads after H-transfer to a σ-complex with a carbon–rhodium bond. On the other hand, Rh^{III} is a hard Lewis-acid, and will coordinate the ketone as an n-donor through its oxygen atom, and this is followed by formation of a σ-complex

TABLE 3

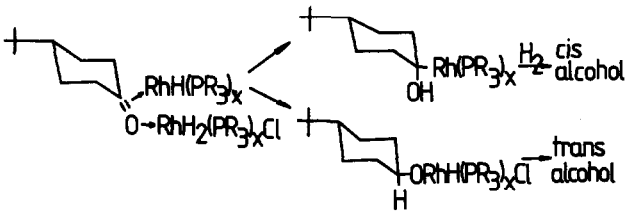
HYDROGENATION OF 4-t-BUTYLCYCLOHEXANONE [a]. Relative amount of *cis* alcohol (%)

Phosphine	Base [b]					
	–	Et_3N	NaOMe	t-BuOK	NaOH	KOH
PPh_3	28.5	72.7	–	–	–	–
PPh_2-i-Pr	10.3	32.9	68.1	–	–	–
PBu_3	9.2	9.5	25.1	50.8	57.2.	65.6

[a] For reaction conditions see Table 1, footnote *a*. [b] Rh/P/base = 1/3/5.

with an oxygen–rhodium bond (Scheme 2). Steric requirements will in both cases force the large $Rh(PR_3)_x$ groups into the equatorial (*trans*) position and result in the predominant formation of the observed alcohol isomers.

SCHEME 2



The explanation presented above is supported by experiments involving stronger bases than Et_3N. As shown in Table 3, even the PBu_3-containing system can be

(Continued on p. 383)

TABLE 4

VALUES OF THE ELECTRONIC PARAMETERS AND LIGAND CONE ANGLES [11]

No.	Phosphine	Electronic parameter, χ	Cone angle, θ
1	P(cyclohexyl)$_3$	0.3	170
2	P(i-Pr)$_3$	3.1	160
3	P(n-Bu)$_3$	4.2	139 [12]
4	PEt$_2$(menthyl)	4.2 [13]	165 [13]
5	PMe(i-Pr)$_2$	4.6 [a]	146 [a]
6	PEt$_3$	5.6	132
7	P(2-Me-Bu)$_2$Ph	5.7 [13]	155 [13]
8	P(i-Bu)$_2$Ph	6.7 [a]	144 [a]
9	PEt$_2$Ph	7.9 [a]	136
10	PMe(i-Pr)Ph	8.0 [a]	141 [a]
11	PMePrPh	8.6 [a]	134 [a]
12	P(t-Bu)Ph$_2$	8.6 [a]	157
13	P(i-Pr)Ph$_2$	9.6 [a]	150
14	P(neo-menthyl)Ph$_2$	10.1 [13]	170 [13]
15	P(CH$_2$Ph)MePh	10.3 [a]	143 [a]
16	P(CH$_2$Ph)$_3$	10.3 [14]	160 [14]
17	PEtPh$_2$	10.6	140
18	P(menthyl)Ph$_2$	10.6 [13]	169 [13]
19	PMePh$_2$	11.2	136
20	P(*o*-tolyl)Ph$_2$	12.1 [a]	161 [a]
21	PPh$_3$	12.9	145

[a] Calculated by the formulas $\chi = \sum_{j=1}^{3} \chi_j$ and $\theta = (2/3) \sum_{i=1}^{3} \theta_i/2$, proposed by Tolman [11].

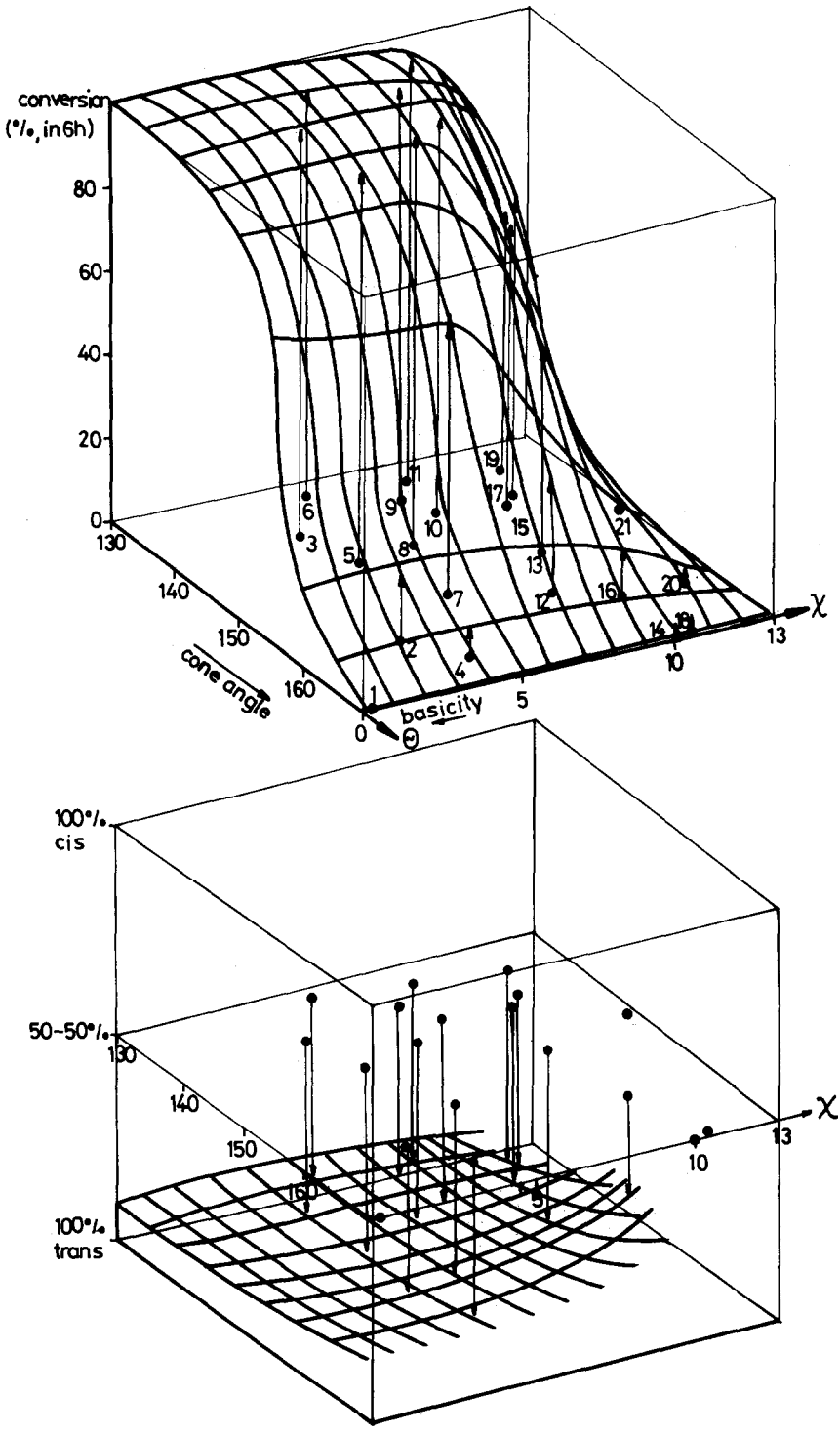


Fig. 1. Hydrogenation of 4-t-butylcyclohexanone with $[Rh(NBD)Cl]_2 + PR_3$ catalytic systems (Rh/P = 1/2.2); Reaction conditions: 50°C, 1 bar H_2; 1 mmol ketone and 0.05 mmol Rh in 5 ml benzene/methanol (3/7).

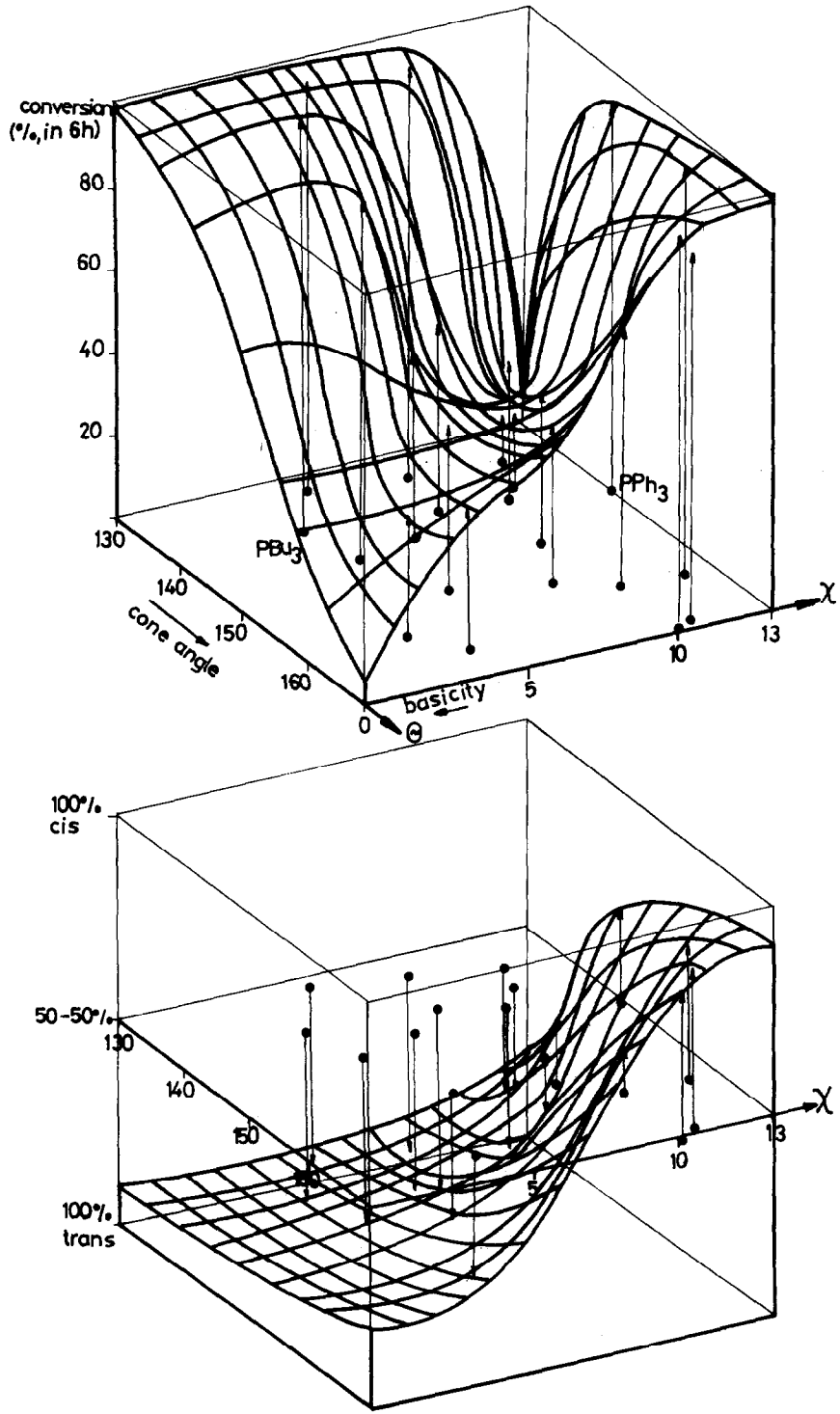


Fig. 2. Hydrogenation of 4-t-butylcyclohexanone with $[Rh(NBD)Cl]_2 + PR_3 + Et_3N$ catalytic systems (Rh/P/N = 1/3/5)
Reaction conditions: 50°C, 1 bar H_2; 1 mmol ketone and 0.05 mmol Rh in 5 ml benzene/ methanol (3/7).

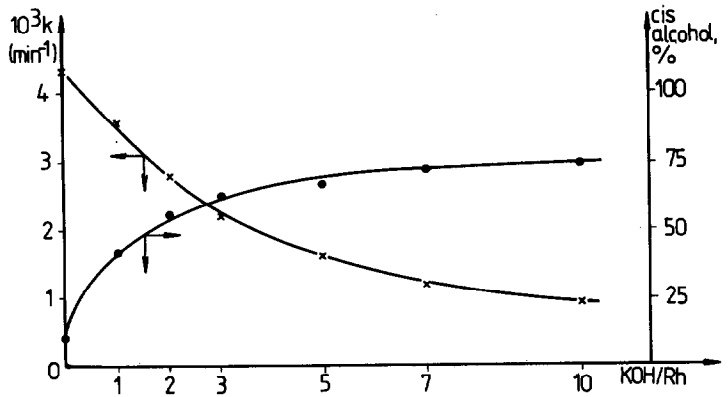


Fig. 3. Hydrogenation of 4-t-butylcyclohexanone with $[Rh(NBD)Cl]_2 + PBu_3 + KOH$ catalytic system (Rh/P = 1/3).

converted by strong bases into a catalyst which gives the *cis* alcohol as the main product. Under such conditions equilibrium 1 is more strongly shifted to the right, and Rh^I monohydrido species become the predominant catalytic species even in the case of aliphatic (basic) phosphines. In accord with this $HRh(PBu_3)_4$ (prepared separately [10]) also gives mainly the *cis* alcohol (Table 1).

We also investigated the variation in the catalytic properties of systems made in situ as the structure of phosphines was changed. For characterization of the phosphines we used Tolman's electronic (χ) and steric (θ) parameters [11] (Table 4). 4-t-Butylcyclohexanone served as a model substrate. Two catalytic systems were investigated:

$[Rh(NBD)Cl]_2 + PR_3$ (Rh/P = 1/2.2) and

$[Rh(NBD)Cl]_2 + PR_3 + Et_3N$ (Rh/P/N = 1/3/5)

In the absence of Et_3N, high reaction rates and consequently high conversions were obtained, and formation of the thermodynamically more stable isomer was preferred in the case of phosphines of high basicity and low bulk. In other cases only a very slow reaction was observed (Fig. 1); these diagrams show the structure, activity and structure, selectivity relationships of the Rh^{III} dihydride catalysts.

In presence of Et_3N (Fig. 2) active catalysts (Rh^I monohydrides) are also formed from ligands of low basicity and greater steric hindrance but there is a "transitional area" in which the Rh^{III} dihydride complexes are no longer active but the Rh^I monohydrides are not yet formed. The very characteristic change of stereoselectivity reflects the change of the dominating catalytic species in these solutions.

The ratio of monohydrido to dihydrido derivatives can obviously be regulated by changing not only the nature but also the quantity of the base. Thus with a $[Rh(NBD)Cl]_2 + PBu_3 + KOH$ catalyst system, increasing the amount of base increases the relative amount of the *cis* isomer to 73% (Fig. 3).

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