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REDUCTION OF KETONES VIA HYDROGEN TRANSFER REACTIONS CATALYZED BY RHODIUM(I) COMPLEXES

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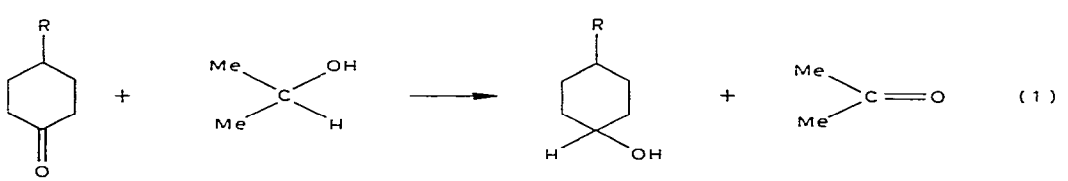
Summary

The reduction of ketones such as cyclohexanone or 4-t-butylcyclohexanone by hydrogen transfer from isopropanol is catalyzed by cationic rhodium complexes of the type $[Rh(diene)P_2]^+$ (diene = 1,5-cyclooctadiene or norbornadiene; P or P_2 = mono or bidentate phosphine ligands) or by neutral Wilkinson's type compounds. Complexes containing chelating ligands show the highest activities.

Introduction

The hydrogen transfer reaction is receiving growing interest and has recently been reviewed [1]. The reaction is catalyzed by several transition metal complexes, including those of rhodium [2,3], ruthenium [4] and iridium [5], containing a wide variety of ligands, and ethers, olefins, amides and alcohols have all been used as the source of hydrogen. The more complex systems of rhodium- or iridium-tin chloride [6] have been used to catalyze the homogeneous dehydrogenation of isopropanol to acetone with hydrogen evolution [6], and the same systems were used to transfer hydrogen to ketones [7]. In a preliminary report [2] we described hydrogen transfer reaction from isopropanol (i-PrOH) to cyclohexanone and to 4-t-butylcyclohexanone catalyzed by cationic rhodium(I) complexes of the type $[Rh(diene)P_2]^+$ (eq. 1).



(1)

R = H or t-butyl

In this paper we report a full study of the above reaction using as catalysts rhodium(I) complexes prepared in situ by reactions of $[Rh(diene)Cl]_2$ and phosphine ligands P, or cationic rhodium(I) compounds $[Rh(diene)P_2]^+$ (diene = 1,5-cyclooctadiene (COD) or norbornadiene (NBD), P or P_2 = PPh_3, $PMePh_2$, PMe_2Ph, PCH_2PhPh_2, $Ph_2PCH_2PPh_2$ (DPM), $Ph_2P(CH_2)_2PPh_2$ (DPE), $Ph_2P(CH_2)_3PPh_2$ (DPP), $Ph_2P(CH_2)_4PPh_2$ (DPB), *cis*-$Ph_2P(CH)_2PPh_2$ (DPET) and (+)DIOP).

Results and discussion

Rhodium complexes of the type $[Rh(diene)P_2]^+$ catalyze the reduction of ketones in refluxing isopropanol in the presence of KOH according to equation 1.

Table 1 summarizes the conversion values obtained with the various catalysts used. The complexes $[Rh(diene)P_2]^+$ are activated by refluxing them for 30 minutes in isopropanol in the presence of KOH under argon. During this time a colour change occurs and the active species is formed. The KOH appears to play a crucial role in this process, and the activity of the catalyst depends markedly on the concentration of this base in the solution (Tables 1 and 3, runs 1—4).

We also carried out the reaction in the presence of hydrogen, but there was no significant change in the catalytic activity of the system. Generally speaking $[Rh(diene)P_2]^+$ reacts with molecular hydrogen in alcohols, particularly in methanol in which it gives a *trans*-biphosphine dihydride $[RhP_2H_2(CH_3OH)_2]^+$ [8,9]. This is in contrast with the behaviour of the corresponding bis(diphenylphosphino)ethane complex which under identical conditions absorbs only 2 equivalents of hydrogen to form the methanol complex $[Rh(P\text{-}P)(CH_3OH)_2]^+$

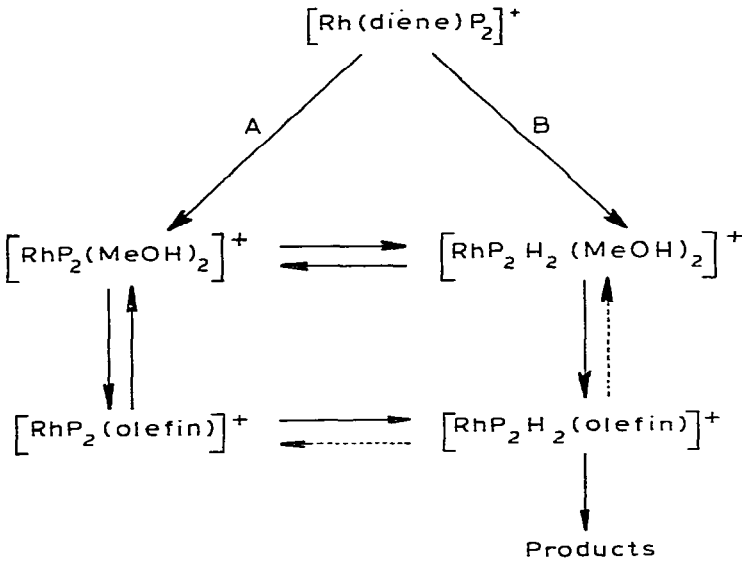
TABLE 1

REDUCTION OF CYCLOHEXANONE [a]

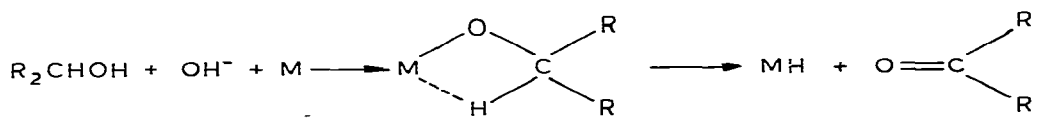
Run.	Catalyst	[KOH]/[Rh]	Conversion %
1	$[Rh(COD)DPE]^+$	10	90
2	$[Rh(COD)DPE]^+$	5	66
3	$[Rh(COD)DPE]^+$	2	47
4	$[Rh(COD)DPE]^+$	0	0
5	$[Rh(NBD)DPE]^+$	10	84
6	$[Rh(COD)DPP]^+$	10	17
7	$[Rh(COD)DPB]^+$	10	5
8	$[Rh(COD)DPET]^+$	10	4
9	$[Rh(COD)DIOP]^+$	10	8
10	$[Rh(NBD)(PPh_3)_2]^+$	10	15
11	$[Rh(NBD)(PMe_2Ph)_2]^+$	80	18 (1 h)
12	$[Rh(NBD)(PMe_2Ph)_2]^+$	10	10 (1 h)
13	$[Rh(NBD)(PMePh_2)_2]^+$	10	4 (1 h)
14	$[Rh(NBD)(PCH_2PhPh_2)_2]^+$	10	10 (1 h)

[a] Conditions: Reactions were carried out in refluxing i-PrOH (50 ml) under argon. Catalyst concentration 4×10^{-4} *M*. Reaction time 15 minutes. Activation time 30 minutes. [Substrate]/[catalyst] = 1900. In the absence of catalyst negligible reaction occurs under these conditions.

[8]. The chelating phosphine cannot form a *trans*-biphosphine dihydride species, and this factor may be responsible for the change in the course of the reaction. Hydrogenation in CH_3OH catalyzed by cationic rhodium(I) complexes could proceed as follows:



Route A is thought to be followed when the catalysts contain chelating phosphines, but monodentate phosphine complexes are thought to follow path B [10,11]. Replacement of the π acceptor ligand diene by two alcohol molecules will increase the basicity of the metal and by destabilizing the square planar state enhance the tendency for attachment of additional ligands [12]. This effect might be greater if the RO^- ligand is coordinated to the metal in a reactive intermediate. The catalytic activity in the hydrogen transfer is enhanced by the presence of KOH [13], and depends on the KOH concentration (cf. Tables 1 and 3). Alcoholic KOH is a widely used reducing agent in, for example, the synthesis of hydridocarbonyl complexes of a large variety of transition metals [14].



We believe that a similar process occurs during the activation time in our catalytic system, to form a metal-hydride species.

From the results reported in Table 1, $[Rh(COD)DPE]^+$ appears to be the best catalyst examined in this study, and its activity is similar to that of the 4,7-Me_2Phen derivative, which is probably the most active rhodium catalyst so far reported for hydrogen transfer reactions (Table 2).

The activity depends on the nature of the phosphine used, and follows the order DPE > DPP $\simeq$ PPh_3 > DPB $\simeq$ DIOP $\simeq$ DPET > PMe_2Ph > PCH_2PhPh_2 > $PMePh_2$. Thus in general higher activities are obtained if bidentate ligands are

TABLE 2
REDUCTION OF CYCLOHEXANONE

Catalyst	[substrate[/[catalyst]	Conversion (%)	Time (h)	Reference
$IrCl_3(DMSO)_3$	300	97	72	15
$RhCl(PPh_3)_3$	1900	59	0.25	this work
$[Rh(4,7\text{-}Me_2Phen)\ Cl_2]^+$	5000	85	1	5
$[Rh(COD)\ DPE]^+$	1900	90	0.25	this work

used. The catalytic activity is also dependent on the number of carbon atoms (n) in $Ph_2P(CH_2)_nPPh_2$, decreasing with increasing n. This could be related to steric effects and/or to possible differences in stability along the series. Cationic rhodium(I) complexes also catalyze the reduction of 4-t-butylcyclohexanone, and the activity roughly depends on the number of carbon atoms (n): DPE > DPP > DPB > DPET. The mixture of *cis* and *trans* alcohols obtained is not too far from the equilibrium composition, which is in the range 77—81% of the *trans* isomer [16].

The *cis*—*trans* isomer ratio appears to be slightly dependent on the KOH concentration (Table 3 runs 1—4) indicating a possible kinetic control of the reaction.

In Table 4 are listed the catalytic activities for hydrogen transfer from i-PrOH to cyclohexanone catalysed by Wilkinson's type complexes prepared in situ from $[Rh(COD)Cl]_2$ and various phosphines. The results are compared with those obtained using $RhCl(PPh_3)_3$, which we found to have rather higher activity than previously reported, although the experimental conditions are different [17]. In contrast with the results obtained with cationic complexes (Tables 1 and 3), in our studies the most active catalysts were found to be those involving the monodentate phosphine PPh_3 (Table 4 runs 9—12). With this ligand the maximum activity is reached at P/Rh ratio of 2 or 3, and these values are very close to those obtained with $RhCl(PPh_3)_3$. (Table 4).

As already pointed out, bidentate phosphines behave differently. Upon increasing the P/Rh ratio the catalytic activity rapidly decreases, and this is

TABLE 3
REDUCTION OF 4-*t*-BUTYLCYCLOHEXANONE [a]

Run.	Catalyst	[KOH]/Rh]	Conversion (%)	*trans* isomer (%)
1	$[Rh(COD)DPE]^+$	30	98	74
2	$[Rh(COD)DPE]^+$	5	97	75
3	$[Rh(COD)DPE]^+$	3.5	73	75
4	$[Rh(COD)DPE]^+$	2	10	85
5	$[Rh(NBD)DPE]^+$	10	98	67
6	$[Rh(COD)DPP]^+$	10	78	76
7	$[Rh(COD)DPB]^+$	10	33	69
8	$[Rh(COD)DPET]^+$	10	18	76

[a] Conditions: Reactions were carried out as reported in Table 1. Reaction time 30 minutes. [Substrate]/[catalyst] = 648. Catalyst concentration 1×10^{-3} *M* (runs 1—4) or 4×10^{-4} *M* (runs 5—8).

TABLE 4

REDUCTION OF CYCLOHEXANONE [a]

Run.	Ligand	[P]/[Rh]	Conversion (%)
1	DPE	1	12
2	DPE	2	19
3	DPE	3	3
4	DPE	4	3
5	DPM	2	12
6	DPP	2	24
7	DPB	2	17
8	DPET	2	6
9	PPh_3	2	55
10	PPh_3	3	56
11	PPh_3	4	25
12 [b]	$RhCl(PPh_3)_3$	—	59

[a] Conditions: Reactions were carried out as reported in Table 1. Catalysts prepared in situ from $[Rh(COD)Cl]_2$ (2×10^{-4} *M*). [Substrate]/[Rhodium] = 1900. [KOH]/[Rhodium] = 10. Reaction time 15 minutes.
[b] $RhCl(PPh_3)_3$ was used as catalyst.

probably related to the greater difficulty of forming the active species under these conditions.

Experimental section

Chemicals

Isopropanol was distilled over CaO before use and stored under an inert atmosphere. Cyclohexanone was purified by distillation under reduced pressure. 4-t-butylcyclohexanone was recrystallized from methanol and used in isopropanol solution. $[Rh(diene)Cl]_2$ [18], [Rh(diene)acac] [19] (diene = norbornadiene (NBD) and 1,5-cyclooctadiene (COD)), $[Rh(NBD)P_2]$ ClO_4 [20] (P = PPh_3, PMe_2Ph, $PMePh_2$ and PCH_2PhPh_2) and $RhCl(PPh_3)_3$ [21] were prepared by published methods. Complexes with the bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ (n = 2, 3 or 4), $Ph_2P(CH)_2PPh_2$ and (+)DIOP were prepared by extension of previously reported syntheses [20—22].

Procedure

All experiments were carried out under argon in refluxing isopropanol with magnetic stirring. The equipment consisted of a 100 ml three-necked round bottom flask fitted with a refrigerator and gas inlet and outlet. The reagents were added as follows: a solution of $[Rh(diene)P_2]^+$ in isopropanol was refluxed for 15 minutes, and then aqueous KOH: was added from a syringe through a serum cap. The resulting solution was refluxed for 30 minutes (activation time), during which the colour turned from red to orange brown, and at this point the substrate was injected into the reaction vessel. The samples were withdrawn at appropriate intervals and analyzed by GLC with a DANI 3400 apparatus equipped with a thermal conductivity detector and helium as carrier gas, using a 2 m steel column, 6 mm in diameter, filled with 60/80 mesh Chromosorb AW with 10% Carbowax 20 M.

Acknowledgments

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References

1 a). B.R. James, Advan. Organometal. Chem., 17 (1979) 319; b) I.S. Kolomnikov, V.P. Kukolev and M.E. Vol'pin, Russ. Chem. Rev., 43 (1974) 399; c) G. Brieger and T.J. Nestrick, Chem. Rev., 74 (1974) 567.
2 R. Spogliarich, G. Zassinovich, G. Mestroni and M. Graziani, J. Organometal. Chem., 179 (1979) C45.
3 C. Masters, A.A. Kiffen and J.P. Visser, J. Amer. Chem. Soc., 98 (1976) 1357.
4 Y. Sasson and J. Blum, J. Org. Chem. 40 (1975) 1887.
5 G. Zassinovich, G. Mestroni and A. Camus, J. Organometal. Chem., 168 (1979) C37.
6 H.B. Charman, J. Chem. Soc. B, (1969) 629; ibid., (1970) 584.
7 J. Kaspar, F. Benedetti, G. Zassinovich, G. Mestroni and M. Graziani. XIII National Meeting on Inorganic Chemistry. Trieste 1979. Paper L2.
8 J.M. Brown, P.A. Chaloner and P.N. Nicholson, J. Chem. Soc. Chem. Commun., (1978) 646.
9 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 98 (1976) 2134, 2145.
10 J. Halpern, D.P. Riley, A.S. Chau and J.J. Pluth, J. Amer. Chem. Soc., 99 (1977) 8055.
11 J.M. Brown and P.A. Chaloner, J. Chem. Soc. Chem. Commun., (1978) 321.
12 L. Vaska and M.F. Werneke, An. New York Acad. Sci., 172 (1972) 546.
13 C. Fragale, M. Gargano and M. Rossi, J. Mol. Catal., 5 (1979) 65.
14 J. Chatt and B.L. Shaw, J. Chem. Soc., (1962) 5073.
15 M. Gullotti, R. Ugo and S. Colonna, J. Chem. Soc., (1971) 2652.
16 E.L. Eliel and R.S. Ro, J. Amer. Chem. Soc., 79 (1957) 5992.
17 P. Svoboda and J. Hetflejs, Coll. Czech. Chem. Commun., 42 (1977) 2177.
18 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
19 R. Cramer, J. Amer. Chem. Soc., 86 (1964) 217.
20 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 93 (1971) 2397.
21 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
22 B. Denise and G. Pannetier, J. Organometal. Chem., 63 (1973) 423.