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HYDROGENATION OF KETONES AND OLEFINS VIA HYDROGEN TRANSFER CATALYZED BY RHODIUM AND IRIDIUM PHOSPHINE COMPLEXES

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Summary

The reduction of ketones and olefins by hydrogen transfer from isopropanol is catalyzed by tertiary phosphine complexes of rhodium and iridium. The influence of the nature of the ligands and of the reaction conditions on the catalytic activity has been investigated. The reduction of the carbonyl group in the presence of olefins is also reported.

Introduction

The hydrogen transfer reaction catalyzed by Group VIII transition metal catalysts [1,2] with a variety of ligands having nitrogen [3] or phosphorous [4] donor atoms has been used to reduce several types of organic substrates such as olefins or ketones. Phosphine complexes of molybdenum [5] have also been found to be active catalysts for the transfer hydrogenation of ketones, and those of zirconium [6] for 1,3-cyclohexadiene disproportionation.

Rhodium and iridium complexes have been investigated as catalysts using ionic [3,4,7,8] or in situ [9] systems for the reduction of non-prochiral and prochiral ketones to the corresponding alcohols. In this paper we describe a detailed study of the behaviour of phosphine-rhodium and -iridium complexes in the hydrogen transfer from isopropanol to ketones and olefins.

Results and discussion

We studied the reduction of ketones and olefins via hydrogen transfer from isopropanol using as procatalysts the "in situ" systems formed from [Rh(cyclooctene)Cl]$_2$, [Rh(1,5-cyclooctadiene)Cl]$_2$, or [Ir(1,5-cyclooctadiene)Cl]$_2$ and various tertiary phosphines, e.g. PPh_3, P(*p*-MePh)$_3$, P(*p*-MeOPh)$_3$, P(*o*-MePh)$_3$, P(*o*-MeOPh)$_3$, PCy_3, PBu^t_3, PCy_2Ph, $PCyPh_2$, $PMePh_2$, PMe_2Ph, or bidentate phosphines of the type $R_2PCH_2CH_2PR_2$ (R = phenyl: DPE; R = ethyl: DEPE; R = methyl: DMPE) in the presence of KOH. Table 1 shows the results obtained using

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TABLE 1

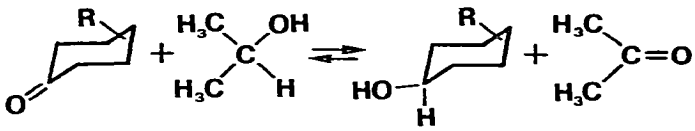
REDUCTION OF 4-t-BUTYLCYCLOHEXANONE CATALYZED BY [Rh(1,5-cyclooctadiene)Cl]$_2$ + nL SYSTEMS AT 83°C IN ISOPROPANOL

Run	L	L/Rh	Reaction time	Conversion (*cis* isomer) (%)		
				5 min	120 min	180 min
1.	PPh_3	2		97(77) [a]		
2.	PPh_3	4		29(55)	83(70)	93(74)
3.	P(*p*-MePh)$_3$	2		99(73)		
4.	P(*p*-MePh)$_3$	4		29(58)	92(69)	98(74)
5.	P(*p*-MeOPh)$_3$	2		98(71) [a]		
6.	P(*p*-MeOPh)$_3$	4		41(57)	87(65)	98(69)
7.	P(*o*-MePh)$_3$)	2		13(69)	83(77)	93(78)
8.	P(*o*-MePh)$_3$	4		13(68)	88(72)	95(72)
9.	P(*o*-MePh)$_3$	8		12(60)	82(67)	93(72)
10.	P(*o*-MePh)$_3$	14		12(48)	67(51)	81(52)
11.	P(*o*-MePh)$_3$	20		11(48)	65(46)	81(46)
12.	P(*o*-MePh)$_3$	50		9(45)	51(50)	69(46)
13.	P(*o*-MePh)$_3$	100		3(38)	14(44)	26(37)
14.	P(*o*-MeOPh)$_3$	2		6(61)	56(63)	80(68) [b]
15.	P(*o*-MeOPh)$_3$	4		8(48)	34(48)	52(48) [b]
16.	P(*o*-MeOPh)$_3$	8			9(48)	14(46) [b]
17.	PCy_3	2		45(48)	98(55)	
18.	PCy_3	4		39(50)	97(55)	
19.	PCy_3	20		24(56)	58(54)	
20.	PCy_2Ph	2		99(70) [c]		
21.	PCy_2Ph	4		99(70) [c]		
22.	PCy_2Ph	20		72(69)	99(77) [d]	
23.	$PCyPh_2$	2		49(70)	90(72) [d]	
24.	$PCyPh_2$	4		83(71)	98(80) [d]	
25.	$PCyPh_2$	8		19(71)	94(81)	
26.	$PCyPh_2$	20		11(70)	60(80)	74(79)
27.	PMe_2Ph	2		19(35)	97(30)	
28.	PMe_2Ph	4		10(48)	37(37)	77(27)
29.	$PMePh_2$	2		12(42)	97(36)	
30.	$PMePh_2$	4		9(52)	19(55)	97(35) [b]
31.	PBu^t_3	2		15(48)	56(56)	64(55)
32.	PBu^t_3	4		22(49)	77(51)	86(49)
33.	DPE	1		99(42) [e]		
34.	DEPE	1		9(43)	76(48)	
35.	DMPE	1		18(40)	95(40)	

[a] Reaction time 8 min. [b] 240 min. [c] 2 min. [d] 30 min. [e] 15 min. Activation time 30 min; substrate/catalyst = 450; KOH/catalyst = 10 in every run.

the [Rh(1,5-cyclooctadiene)Cl]$_2$-phosphine system as procatalyst for the reduction of 4-t-butylcyclohexanone to the corresponding mixture of *cis* and *trans* alcohols (eq. 1).

The catalytic activity depends on the nature of the phosphine, and falls in the following sequences: PCy_2Ph > P(*p*-MePh)$_3$ ~ P(*p*-MeOPh)$_3$ ~ PPh_3 > $PCyPh_2$ > PCy_3 ~ PMe_2Ph ~ $PMePh_2$ > P(*o*-MePh)$_3$ > PBu^t_3 > P(*o*-MeOPh)$_3$ and DPE > DMPE > DEPE. Neither the electronic nor steric [10] properties of the ligands can



(1)

(R = 4-t-butyl)

account for this trend, and the reaction rate is apparently determined by a combination of these two and/or other parameters. The catalytic activity also depends on the activation time (see Table 2), during which the precursor forms the catalytic species in the presence of the added base. We think that after this time the unsaturated ligand is lost to give a phosphine-rhodium (or -iridium) compound. The same reaction is in fact much faster when cyclooctene is used as ligand in the place of 1,5-cyclooctadiene (see Table 3, runs 1 and 2), as the former is more easily removed than the latter. Moreover, $Rh(PPh_3)_3Cl$ in the presence of one equivalent of PPh_3 (P/Rh = 4) reduces 4-t-butylcyclohexanone in 98% yield in 5 min with a selectivity of 77% towards the *cis* isomer. These results are consistent with the hypothesis that during the activation time the olefin is released (may be hydrogenated) and that the active species formed is a phosphine-rhodium (or -iridium) complex. The use of a cationic complex as procatalyst does not seem to influence the catalytic activity, since $[Rh(1,5\text{-cyclooctadiene})(PPh_3)_2]^+PF_6^-$ reduces 4-t-butylcyclohexanone with comparable reaction time and selectivity. With bulky ligands such as P(*o*-MePh)$_3$ or P(*o*-MeOPh)$_3$ there are no appreciable differences between the Rh-1,5-cyclooctadiene and the Rh-cyclooctene systems (compare runs 3 and 4, Table 3 with runs 8 and 15, Table 1). This behaviour suggests that steric effects may also play an important role in determining the catalytic activity of these complexes, and leading to different products or following different reaction paths, depending on the nature of the phosphine. It is known, for example, that $[Rh(cyclooctene)Cl]_2$ reacts with PCy_3 at 20°C in toluene to give, together with other compounds, the monohydride $HRhCl_2(PCy_3)_2$ [11], and the three-coordinated iridium and rhodium complexes $M(PCy_3)_2Cl$ have been reported [11,12]. Moreover, the chemistry of the system

TABLE 2

REDUCTION OF 4-t-BUTYLCYCLOHEXANONE CATALYZED BY $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ + *n*L SYSTEMS AT 83°C IN ISOPROPANOL USING DIFFERENT ACTIVATION TIMES [a]

Run	L	Activation time (min)	Conversion (*cis* isomer) (%)	Reaction time (min)
1	PPh_3	30	93(74)	180
2	PPh_3	120	97(78)	120
3	PPh_3	180	98(78)	15
4	PPh_3	240	95(78)	15
5	$PMePh_2$	30	97(35)	240
6	$PMePh_2$	180	92(35)	30

[a] L/RH = 4; substrate/catalyst = 450; KOH/catalyst = 10.

TABLE 3

REDUCTION OF 4-t-BUTYLCYCLOHEXANONE CATALYZED BY $[Rh(cyclooctene)_2Cl]_2 + nL$ SYSTEMS AT 83°C IN ISOPROPANOL [a]

Run	L	Conversion (*cis* isomer) (%)	Reaction time (min)
1	PPh_3	96(79)	15
2	P(*p*-MePh)$_3$	99(74)	5
3	P(*o*-MePh)$_3$	94(57)	240
4	P(*o*-MeOPh)$_3$	42(34)	240

[a] Activation time 30 min. L/Rh = 4; substrate/catalyst = 450; KOH/catalyst = 10.

Ir^I/PCy_3 is complicated by dehydrogenation of the cyclohexyl ring [11], and it is possible that some of the other phosphines we used give rise to interfering side reactions.

Increase in the ligand/metal ratio generally lowers the catalytic activity (Table 1), and this is taken as an indication that tertiary phosphines can compete with the hydrogen donor and/or acceptor for the vacant coordination site [13]. However, we obtained some peculiar results; e.g. with a bulky phosphine such as P(*o*-MePh)$_3$, the catalytic activity remains practically constant on varying the P/Rh ratio and only with an unusually high excess of ligand is a substantial decrease observed (Table 1, runs 7–13). In the reduction of olefins by hydrogen transfer from dioxane catalyzed by $Rh(PPh_3)_3Cl$, the addition of an excess of PPh_3 has no effect on the rate [14]. It was assumed that in this case dioxane coordinates are so strongly that it replace PPh_3 even in the presence of large amount of ligand. Under our reaction conditions, the steric requirements of the phosphines minimize the competition between the bulky ligand and the smaller donor and/or acceptor molecule for a vacant site, and only when a large excess of phosphine is used is the reaction slowed down. Table 4 shows the results obtained in the reduction of 4-t-butylcyclohexanone catalyzed by the Ir^I/PR_3 system. They parallel those for the rhodium system, but the reaction is slower and the selectivity poorer. The *cis/trans* ratio found for 4-t-butylcyclohexanol

TABLE 4

REDUCTION OF 4-t-BUTYLCYCLOHEXANONE CATALYZED BY $[Ir(1,5\text{-cyclooctadiene})Cl]_2 + nL$ SYSTEMS AT 83°C IN ISOPROPANOL

Run	L	L/Ir	Conversion (*cis* isomer) (%)		
			Reaction time 5 min	60 min	240 min
1	PPh_3	2	23(38)	56(27)	75(21) [a]
2	P(*o*-MePh)$_3$	2	5(48)	14(56)	34(54)
3	PCy_2Ph	2	65(40)	97(39) [b]	
4	$PCyPh_2$	2	8(27)	30(24)	74(28)
5	$PMePh_2$	2	11(39)	55(24)	79(22)
6	DPE	1	29(41)	55(39)	90(39)

[a] Reaction time 120 min. [b] 30 min; substrate/catalyst = 450; KOH/catalyst = 10. Activation time 30 min.

is also rather dependent on the ligand used, the axial isomer yield ranging from a minimum value of 21% to a maximum of 81% (see Tables); however, it is usually higher than that expected for the thermodynamic equilibrium (about 20% in *cis* isomer) [15]. The stereoselectivity also changes on varying the procatalyst, the

TABLE 5

REDUCTION OF VARIOUS SUBSTRATES CATALYZED BY [M(1,5-cyclooctadiene)Cl]$_2$ + nL IN ISOPROPANOL AT 83°C [a]

Run	L	M	Substrate	Products (conversion (*cis* isomer)) (%)
1 [b]	PPh_3	Rh	4-t-butylcyclohexanone	4-t-butylcyclohexanol (87, (64)); reaction time 180 min
2 [b]	PPh_3	Rh	cyclohexene	cyclohexane (9); reaction time 180 min
3 [b]	PPh_3	Rh	cyclohexene (50%) 4-t-butylcyclohexanone (50%)	cyclohexane (1), cyclohexene (49), 4-t-butylcyclohexanol (8, (51)), 4-t-butylcyclohexanone (42); reaction time 180 min
4	PPh_3	Rh	5-hexen-2-one	2-hexanone (8), 2-hexanol (3.5); reaction time 300 min
5	PPh_3	Rh	2-hexanone	2-hexanol (97); reaction time 10 min
6	PPh_3	Rh	5-methyl-5-hexen-2-one	5-methyl-2-hexanone (20.5), 5-methyl-5-hexen-2-ol (16), 5-methyl-2-hexanol (12), other products (9); reaction time 300 min
7	PPh_3	Rh	6-methyl-5-hepten-2-one	6-methyl-2-heptanone (5), 6-methyl-5-hepten-2-ol (15), other products (2); reaction time 300 min
8 [b]	PCy_2Ph	Rh	4-t-butylcyclohexanone	4-t-butylcyclohexanol (91, (58)); reaction time 210 min
9 [b]	PCy_2Ph	Rh	4-t-butylcyclohexanone (50%), cyclohexene (50%)	4-t-butylcyclohexanol (16, (63)), 4-t-butyl-cyclohexanone (34), cyclohexene (33), cyclohexane (17); reaction time 180 min
10	PCy_2Ph	Rh	1-methylcyclohexene	methylcyclohexane (5.5); reaction time 180 min
11	PCy_2Ph	Rh	3-methylcyclohexene	methylcyclohexane (30), 1-methyl-cyclohexene (60); reaction time 420 min
12 [b]	PPh_3	Ir	4-t-butylcyclohexanone (50%), cyclohexene (50%)	4-t-butylcyclohexanol (26, (17)), 4-t-butyl-cyclohexanone (24), cyclohexene (50); reaction time 300 min
13	PPh_3	Ir	5-methyl-5-hexen-2 one	no reaction in 300 min
14	PPh_3	Ir	6-methyl-5-hepten-2 one	no reaction in 300 min

[a] L/M = 2; activation time 30 min; substrate/catalyst = 450; KOH/catalyst = 10. [b] T 50°C, activation time 120 min.

reaction time and the P/Rh ratio, and this result could be related to the existence of an equilibrium between several catalytic species with different selectivities.

Iridium-based catalysts are often more selective than their rhodium analogues; for instance, the Ir^{III}/Sn^{II} system catalyzes the hydrogen transfer from isopropanol to 4-t-butylcyclohexanone to give up to 95% of *cis* isomer in the reduction product [16]. From our results, however, it is apparent that this trend is not always found.

Only few compounds have been found to catalyze the selective reduction of the carbonyl function. In particular Henbest's system converts α,β-unsaturated aldehydes to unsaturated alcohols [17], while $[Rh(bipy)_2]^+$ catalyzes the selective hydrogenation of ketones in the presence of carbon–carbon double bonds [18]. We have tried to carry out the selective reduction of the carbonyl group via hydrogen transfer catalyzed by the system Rh or Ir/PR_3, using mixtures of ketones and olefins or unsaturated ketones as substrates (Table 5). 4-t-Butylcyclohexanone is easily reduced to the corresponding alcohol in high yield in the presence of rhodium/PPh_3, but cyclohexene is poorly hydrogenated under the same experimental conditions (Table 5, runs 1,2). The overall catalytic activity is lowered when a mixture of olefin and ketone is used, even though an alcohol/alkane ratio of 8 is observed (Table 5, run 3). The iridium system reduces the ketone selectively, leaving unchanged cyclohexene (Table 5, run 12), but again the reaction rate drops when the olefin is also present.

We believe that this effect is probably related to the good coordination ability of cyclohexene, which competes efficiently with the ketone. For comparison, the $[Rh(norbornadiene)_2]^+$/*cis*-1,2-bis(diphenylphosphino)ethylene system reduces acetophenone to 1-phenylethanol in the presence of cyclohexene to give an alcohol/alkane ratio of about 13 [7].

Using 5-hexen-2-one as substrate and rhodium/PPh_3 as catalyst, no unsaturated alcohol is formed, while 5-methyl-5-hexene-2-one yields an (unsaturated alcohol)/(saturated ketone + saturated alcohol) ratio of 0.5. This value rises to 3 in the case of 6-methyl-5-hepten-2-one, and this can be attributed to the better coordinating ability of terminal olefins with respect to internal ones (Table 5, runs 4,6,7). The iridium catalyst appears to be more promising, even though no reaction occurs with unsaturated ketones (Table 5, runs 12, 13 and 14); better results might be obtained by changing the reaction conditions.

Experimental section

Chemicals

Isopropanol was distilled over CaO before use and stored under an inert atmosphere. 4-t-Butylcyclohexanone was recrystallized from isopropanol. Cyclohexene was purified by distillation in vacuo over sodium, the other substrates were distilled under reduced pressure. $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ [19], $[Rh(cyclooctene)_2Cl]_2$ [20], $Rh(PPh_3)_3Cl$ [21], $[Rh(1,5\text{-cyclooctadiene})(PPh_3)_2]PF_6$ [22] and $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ [23] were prepared using published methods.

Procedure

All the reactions were carried out in isopropanol under argon with magnetic stirring, using a three-necked vessel fitted with a gas inlet and a refrigerator. The reagents were added as follows: the catalyst precursor (2×10^{-5} mol) was dissolved

in 50 ml of deareated isopropanol, the system brought to reflux (or thermostatted at 50°C), and after 15 min aqueous KOH was injected through a serum cap. The "activation time" started from the addition of the base, in the presence of which the solution usually got darker (orange-brown), but sometimes remained yellow, depending on the system used. After this time (30 min or more) the substrate(s) was (were) added. The reaction was monitored by GLC, using a DANI 3400 apparatus equipped with a thermal conductivity detector, helium as carrier gas, and a Carbowax 20 M column.

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