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CATALYTIC TRANSFER HYDROGENATION BY CATIONIC RHODIUM(I) COMPLEXES

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Summary

Complexes formed by adding Group Vb ligands to $[Rh(NBD)_2]ClO_4$ in the presence of potassium hydroxide catalyze hydrogen transfer from isopropanol to acetophenone, cyclohexene and other unsaturated substrates. The catalytic activity depends upon the nature of the mono- or bidentate nitrogen- or phosphorus-donor ligands. $[Rh(NBD)\{P(p\text{-}MeOC_6H_4)_3\}_2]ClO_4$ catalyses the selective reduction of hexyne or diolefins.

Introduction

Some of the numerous known rhodium(I) diolefin complexes react with hydrogen to give species which are active homogeneous catalysts [1]. Moreover, cationic species of the type $[Rh(diolefin)L_2]^+$ (with L_2 = bipyridine, phenantroline or phosphine type ligands) are active catalysts in alkaline media for the transfer of hydrogen from isopropanol to ketones [2—4].

In the present paper we report the results of a study of hydrogen transfer from isopropanol to cyclohexene, acetophenone and other unsaturated substrates, catalyzed by cationic rhodium(I) norbornadiene complexes formed by the addition of Group Vb ligands to $[Rh(NBD)_2]ClO_4$ (NBD = 2,5-norbornadiene) [5—6]. The following ligands were used: *o*-chlorobenzonitrile (Clbzn), *p*-methoxybenzonitrile (MeObzn), malononitrile (maln), succinonitrile (sucn), phthalonitrile (phtaln), *o*-phenylenediamine (phedn), 1,2-diphenylethylenediamine (stien), 2,*N*,*N*′-triphenylethylenediamine (tpen), aniline ($PhNH_2$), *p*-toluidine ($MePhNH_2$), 1,10-phenantroline (phen), 2,2′-diquinolyl (diquin), 6-methylquinoline (Mequin), 2,4-dimethylquinoline (Me_2quin), 4,7-dichloroquinoline (Cl_2quin), bis(diphenylphosphino)methane (dpm), bis(1,2-diphenylphosphino)-ethane (dpe), bis(1,3-diphenylphosphino)propane (dpp), bis(1,4-diphenylphosphino)butane (dpb), *cis*-bis(1,2-diphenylphosphino)ethylene (dpet), triarylphosphines, triarylarsines and triphenylstibine.

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Results and discussion

The results of the catalytic hydrogen transfer from isopropanol to acetophenone and cyclohexene, in the presence of potassium hydroxide, are presented in Table 1. The results can be rationalized in terms of the properties of the species obtained by treating $[Rh(NBD)_2]ClO_4$ with the different ligands [6].

i) Monodentate nitrile, arsine and stibine ligands

The (2/1 or 1/1) reaction of these ligands with $[Rh(NBD)_2]ClO_4$ does not give rise to the displacement of the diolefin, but leads to the formation of pentacoordinated species of the type $[Rh(NBD)_2L]ClO_4$ [6], which are very poor catalysts. Thus, after 1 h the conversion is not more than 10% for L = nitrile, and is practically nil for L = AsR_3 or $SbPh_3$.

ii) Monodentate phosphines and bidentate N or P ligands

The reaction of $[Rh(NBD)_2]ClO_4$ with 2 L (or L-L) gives rise to the displacement of one mole of diolefin and to formation of the catalyst precursors

TABLE 1

REDUCTION OF ACETOPHENONE AND CYCLOHEXENE WITH CATALYTIC SYSTEMS OF THE TYPE $[Rh(NBD)_2]ClO_4 + nL$

n	L	Conversion (%) after one hour	
		acetophenone	cyclohexene
2	Clbzn	8	0.5
1	Clbzn	8	0.5
2	MeObzn	10	7
2	$AsPh_3$	0	0
2	As(*p*-$MeC_6H_4)_3$	0	0
2	As(*m*-$MeC_6H_4)_3$	0	0
2	$SbPh_3$	0	0
2	PPh_3	72	46
1	PPh_3	40	67
1	dpm	64	31
1	dpe	54	44
1/2	dpe	28	46
1	dpp	60	32
1	dpb	56	15
1	dpet	66	25
1	maln	2	0
1	sucn	36	7
1	phtaln	71	5
1	phedn	56	8
1	stien	80	6
1	tpen	22	7
1	phen	41	0
1	diquin	16	0
2	$PhNH_2$	0	25
2	$MePhNH_2$	2	34
2	Cl_2quin	0	1
2	Mequin	7	42
2	Me_2quin	11	83

TABLE 2

HYDROGEN TRANSFER REACTIONS CATALYSED BY $[Rh(NBD)\{(p\text{-}RC_6H_4)_3\}_2]ClO_4$ COMPLEXES

$P(p\text{-}RC_6H_4)_3$	Conversion (%) after one hour			
	1-hexene	cyclohexene	styrene	acetophenone
$P(p\text{-}MeOC_6H_4)_3$	100	40	23	73
PPh_3	36	46	29	72
$P(p\text{-}FC_6H_4)_3$	32	10	4	31

$[Rh(NBD)L_2]ClO_4$ * or $[Rh(NBD)(L\text{-}L)]ClO_4$ [6—8].

The results of the hydrogen transfer reactions show that acetophenone is generally more efficiently reduced than cyclohexene, the difference being especially noteworthy for bidentate nitrogen-donor ligands. The tests, which were carried out with the system $[Rh(NBD)_2]ClO_4 + PPh_3$ (which leads to species of the type $[Rh(NBD)(PPh_3)(solvent)]^+$ [6]), show an inversion of the reduction capacity, cyclohexene being more rapidly reduced than acetophenone; a similar behaviour was observed for the $[Rh(NBD)_2]ClO_4$ + 1/2 dpe system. On the other hand, in a recent and detailed study [4] of rhodium/diphosphine complexes, it was observed that the catalytic activity in the reduction of ketones decreases if the P/Rh ratio diverges from 2/1.

iii) Monodentate nitrogen donor ligands of amine or quinoline types

In these systems the end product of the reaction may be $[Rh(NBD)L_2]^+$, though species of the type $[Rh(NBD)L(solvent)]^+$ must also be taken into account [6]. Studies of their catalytic activity reveal a higher conversion for cyclohexene than for acetophenone, in contrast with that found for systems of the type $[Rh(NBD)L_2]ClO_4$ (L = mono- or bidentate phosphines and bidentate nitrogen donor ligands), and analogously to that observed for $[Rh(NBD)(PPh_3)(solvent)]^+$, but in this case the differences are larger. These results seem to indicate that during the catalytic cycle one ligand remains coordinated to the rhodium atom.

iv) The conversions which are observed for systems containing only one type of ligand suggest that the activity decreases with decreasing basicity of the ligand. Thus, after one hour of reaction the extent of conversion of cyclohexene decreases in the sequences: i) Me_2quin (83) > Mequin (42) > Cl_2quin (1); ii) $MePhNH_2$ (34) > $PhNH_2$ (25); iii) MeObzn (7) > Clbzn (0.5); iv) triarylphosphines (Table 2). A positive effect of the basicity of the triarylphosphine ligands has previously been observed in the hydrogen transfer from dioxane to cyclopentene for the systems 1/2 $[RhCl(cyclooctene)_2]_2$ + 2 $P(RC_6H_4)_3$ [12], as well as in the hydrogenation of monoolefins by molecular hydrogen for complexes of the type $[Rh(diolefin)\{P(RC_6H_4)_3\}_2]ClO_4$ [10]. Since selective hydrogenations of diolefins and alkynes have been observed for this type of cationic complexes [10,13], we tested the selectivity of the hydrogen transfer

* Similar results were obtained by using as catalyst complexes of the type $[Rh(NBD)L_2]ClO_4$, synthesised by conventional methods [7—11].

TABLE 3

REDUCTION OF SOME UNSATURATED SUBSTRATES WITH CATIONIC RHODIUM(I) COMPLEXES

Catalyst	Substrate	Products after one hour (%)
$[Rh(NBD)\{P(p\text{-}MeOC_6H_4)_3\}_2]ClO_4$	3-hexyne	3-hexyne(66), hexene(33) [a, b], hexane (1)
	1,5-cyclooctadiene	cyclooctadiene (67) [c], cyclooctene (33) [d], cyclooctane (0.5)
	2,5-norbornadiene	2,5-norbornadiene (76), norbornene (17), norbornane (7)
	2-methyl-1,3-butadiene	2-methyl-1,3-butadiene (94), 2-methylbutene(6) [e], 2-methylbutane (0)
	acetophenone (50%) + cyclohexene (50%)	acetophenone (17), 1-phenylethanol (33), cyclohexene (44), cyclohexane (6)
	3-hexyne (60%) + cyclohexene (40%)	3-hexyne (36), hexene (23) [a], hexane (1), cyclohexene (40)
	1,5-cyclooctadiene (50%) + cyclooctene (50%)	1,3-cyclooctadiene (2), cyclooctene (92), cyclooctane (6)
$[Rh(NBD)_2]ClO_4$ + dpet	acetophenone (50%) + cyclohexene (50%)	acetophenone (10), 1-phenylethanol (40), cyclohexene (47), cyclohexane (3)
	1,5-cyclooctadiene (50%) + cyclooctene (50%)	cyclooctadiene (36) [f], cyclooctene (62), cyclooctane (2)
$[Rh(NBD)_2]ClO_4$ + phtaln	acetophenone (50%) + cyclohexene (50%)	acetophenone (7), 1-phenylethanol (43), cyclohexene (47), cyclohexane (3)
$[Rh(NBD)_2]ClO_4$ + 2 Me_2quin	acetophenone (50%) + cyclohexene (50%)	acetophenone (46), 1-phenylethanol (4), cyclohexene (46), cyclohexane (4)

[a] Internal isomers, mainly. [b] 42% after 2 h. [c] 1,5-COD (21%), 1,4-COD (15%), 1,3-COD (31%). [d] 55% after 2 h. [e] 2-methyl-2-butene (4%), 2-methyl-1-butene (2%). [f] 1,5-COD (1%), 1,4-COD (2%), 1.3-COD (33%).

for the complex $[Rh(NBD)\{P(p\text{-}MeOC_6H_4)_3\}_2]ClO_4$, and the results are listed in Table 3.

The observed selectivity for the corresponding monoenes is generally in the range 70—90% (defined as monoalkene/monoalkene + alkane ratio) though transfer is much slower than in hydrogenations by molecular hydrogen. The selectivity is possibly due to the displacement of the monoene formed by reduction of the corresponding diolefin or alkyne. Competitive reduction tests for acetophenone/cyclohexene, 3-hexyne/cyclohexene, and 1,5-cyclooctadiene/cyclooctene with the mentioned catalyst, or with other catalyst systems (see Table 3) generally show a preferential reduction of acetophenone to 1-phenylethanol and of 3-hexyne and 1,5-cyclooctadiene to the corresponding monoenes.

Whereas hydrogenation with cationic complexes of the type $[Rh(diolefin)L_2]ClO_4$ by molecular hydrogen can be carried out at room temperature, the transfer reaction requires to somewhat higher temperatures, which are probably necessary for the formation of an intermediate hydride from the coordinated iso-propoxide which must be formed in the basic media used:

$$Rh{-}OCHMe_2 \rightarrow H{-}Rh \leftarrow O{=}CMe_2$$

Such abstraction of the hydrogen from alkoxides is well known, and is especially favoured by the more basic ligands [14]. The observed high isomerization in the hydrogen transfer to 1-hexene or 1,5-cyclooctadiene might be due to the presence of an intermediate hydride. We have observed for some complexes containing N or P donor ligands that while molecular hydrogen cannot hydrogenate acetophenone in the absence of KOH, in its presence hydrogenation occurs even at room temperature ($P(H_2)$ = 1 atm).

Experimental

Most of the commercial reagents were purified and distilled before use. All the olefins, diolefins and alkynes were deperoxidized by percolation through active neutral alumina grade I, and the absence of peroxides confirmed by the Fe^{2+}/SCN^- reaction. The complexes $[Rh(NBD)\{P(p\text{-}MeOC_6H_4)_3\}_2]ClO_4$ and $[Rh(NBD)_2]ClO_4$, were prepared by published methods [5,11].

The transfer hydrogenation reactions were carried out under argon in refluxing isopropanol with magnetic stirring. The equipment consisted of a 50 ml round bottom flask, fitted with a refrigerator and provided with a serum cap.

The catalysts were prepared in situ by adding 0.04 mmol of L (0.02 mmol of L-L) to an isopropanol solution (8 ml) of $[Rh(NBD)_2]ClO_4$ (0.02 mmol) under argon (in some reactions $[Rh(NBD)L_2]ClO_4$ complexes were used). Then, a solution of 0.1 mmol of KOH in 1 ml of isopropanol was added. The resulting solution was refluxed for 1 h (preactivation time) and 2 mmol of the substrate in 1 ml of isopropanol was injected. Samples of the reaction were withdrawn every 30 min and analyzed by GLC.

The analysis were carried out with a Perkin-Elmer 3920-B apparatus connected to a Perkin-Elmer M-2 calculating integrator. The products of the hydrogen transfer reactions to acetophenone, styrene and to 1,5-cyclooctadiene, were separated with FFAP on a Chromosorb G HP 80/100 mesh column (3.6 m × 1/8 in); those of 2,5-norbornadiene with dinonyl phtalate (20%) on Chromosorb P 80/100 mesh (4 m × 1/8 in); and those of the other substrates with β,β'-oxydipropionitrile (15%) on Chromosorb W 80/100 mesh (4 m × 1/8 in) connected to the last one in serie.

During the preactivation a change in colour and often a precipitate were noted. At the end of the reaction it was possible to separate by centrifugation either a brown-greenish precipitate (nitrile, chelating amine and phosphine derivatives) or a red precipitate (quinolines and monodentate amine derivatives). All these precipitates were sparingly soluble in isopropanol and very soluble in water. Sometimes (with quinolines and with monodentate amine derivatives) a very little amount of a black precipitate insoluble in all solvents, was also found and was suspected of being metallic rhodium.

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