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Preliminary communication

HYDROGEN TRANSFER REACTIONS CATALYZED BY CATIONIC RHODIUM(I) COMPLEXES

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Summary

Hydrogen transfer from isopropanol to various ketones such as cyclohexanone, 4-t-butylcyclohexanone and acetophenone are catalyzed by cationic rhodium(I) complexes of the type $[Rh(Diene)L_2]^+$ (Diene = 1,5-cyclooctadiene (COD) or norbornadiene (NBD); L_2 or L = mono- or bi-dentate phosphine ligands). The results indicate higher activities for complexes containing chelating ligands.

The reduction of unsaturated substrates by hydrogen transfer from various sources such as alcohols, amides, ethers, and olefins, is receiving increasing interest [1]. The reactions are catalysed by a variety of complexes of rhodium [2]. ruthenium [3] and iridium [4], and the highest catalytic activities were found for complexes containing chelating ligands such as bipyridine or phenanthroline derivatives [5]. The catalytic activity of rhodium(I) cationic complexes with phosphine ligands of the type $[Rh(Diene)L_2]^+$ was not investigated, although the system di-1,5-cyclooctadienedichlororhodium—monodentate aminophosphines was found to be active in hydrogen transfer reactions [6]. We have found that the complexes $[Rh(Diene)L_2]^+$ [Diene = 1,5-cyclooctadiene or norbornadiene; L or L_2 = $P(C_6H_5)_3$, $PCH_3(C_6H_5)_2$, $P(CH_3)_2C_6H_5$, $PCH_2C_6H_5(C_6H_5)_2$, $(C_6H_5)_2P(CH_2)_2$-$P(C_6H_5)_2$ (DPE), *cis*-$(C_6H_5)_2P(CH)_2P(C_6H_5)_2$ (DPET) and (+)DIOP)] catalyse hydrogen transfer to ketones from the isopropanol used as solvent to give the corresponding alcohols in quantitative yield (Table 1). Good catalytic activity requires the presence of KOH (Runs 1—4, Table 1), but a KOH/catalyst ratio larger than five appears to have little effect on the activity (Runs 1, 2, 8, 9, 13 and 14, Table 1). Of the complexes we have studied, $[Rh(COD)(DPE)]^+$ seems to be the most active, and its activity is similar to that of the $(4,7\text{-}Me_2Phen)$ derivative, which is probably the best known rhodium catalyst for hydrogen transfer (Table 2).

The catalysts are activated before the addition of ketones by refluxing them in i-PrOH in the presence of KOH (see reaction conditions in Table 1). During this time a colour change occurs and the catalytic species is formed. Much lower activ-

TABLE 1

REDUCTION OF KETONES

Conditions. Reactions were carried out in refluxing i-PrOH (50 ml) under nitrogen. Catalyst concentrations, 2×10^{-4}—1×10^{-3} *M*. Reaction time 1 h. Activation times: 15 min for 4-t-butylcyclohexanone, 30 min in other cases. Substrate/catalyst ratio: *a*, 1900; *b*, 648; c, during the reaction a water-soluble product is precipitated. In the presence of KOH alone in i-PrOH negligible reaction occurs under these conditions.

Run	Catalyst	KOH/catalyst	Conversion (%)	
A. Substrate: Cyclohexanone[a]				
1	$[\mathrm{Rh(COD)(DPE)}]^+$	10	99 (0.5 h)	
2	$[\mathrm{Rh(COD)(DPE)}]^+$	5	100	
3	$[\mathrm{Rh(COD)(DPE)}]^+$	2	87	
4	$[\mathrm{Rh(COD)(DPE)}]^+$	0	0	
5	$[\mathrm{Rh(NBD)(DPE)}]^+$	10	100	
6	$[\mathrm{Rh(COD)(DPET)}]^+$	10	19 (1.5 h)	
7	$[\mathrm{Rh(NBD)(PPh_3)_2}]^+$	10	19	
8	$[\mathrm{Rh(NBD)(PMe_2Ph)_2}]^+$	80	18	
9	$[\mathrm{Rh(NBD)(PMe_2Ph)_2}]^+$	10	10	
10	$[\mathrm{Rh(NBD)(PMePh_2)_2}]^+$	10	4[c]	
11	$[\mathrm{Rh(NBD)(PCH_2PhPh_2)_2}]^+$	10	10[c]	
12	$[\mathrm{Rh(COD)(+)DIOP}]^+$	10	22	
B. Substrate: 4-t-Butylcyclohexanone[b]				
13	$[\mathrm{Rh(COD)(DPE)}]^+$	30	99.5	74
14	$[\mathrm{Rh(COD)(DPE)}]^+$	5	99.5	74
15	$[\mathrm{Rh(COD)(DPE)}]^+$	3.5	94	75
16	$[\mathrm{Rh(COD)(DPE)}]^+$	2	14	85
C. Substrate: Methylphenylketone[b]				
17	$[\mathrm{Rh(COD)(DPE)}]^+$	5	81	
18	$[\mathrm{Rh(COD)(DPE)}]^+$	2	0[a]	
19	$[\mathrm{Rh(COD)(DPE)}]^+$	5	16[a]	

TABLE 2

REDUCTION OF CYCLOHEXANONE

Catalyst	Substrate/catalyst	Conversion (%)	Time (h)	Reference
$\mathrm{IrCl_3(DMSO)}$	300	97	72	7
$\mathrm{RhCl_3PPh_3}$	400	85	1	6
$[\mathrm{Rh(4,7\text{-}Me_2Phen)_2Cl_2}]^+$	5000	85	1	5
$[\mathrm{Rh(COD)(DPE)}]^+$	1900	99	0.5	this work

ities are found if monodentate phosphines are used as ligands, and this is an important feature, even though it is not always the case, since *cis*-$\mathrm{Ph_2P(CH)_2PPh_2}$ gives results similar to those obtained with monodentate phosphines. In our view to obtain high catalytic activity a strongly bound bidentate ligand is probably required. $[\mathrm{Rh(COD)(DPE)}]^+$ readily catalyses the reduction of 4-t-butylcyclohexanone to give a mixture of *cis* and *trans* alcohols, in a ratio which is slightly dependent on KOH concentration (Runs 13—15, Table 1), indicating possible kinetic control on the reaction. Complexes having bidentate chiral ligands are also effective as hydrogen transfer catalysts, and asymmetric reductions using prochiral ketones are now being studied.

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