A New Catalyst for Hydrogen Transfer Hydrogenation of Acetophenone

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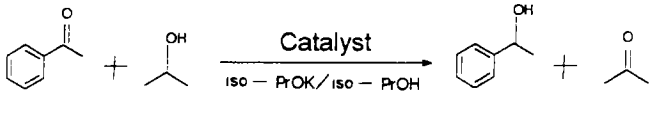
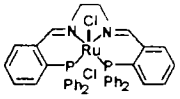
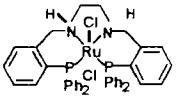
Abstract: A new C_2-symmetric diamine/diphosphine Ruthenium (II) complex, $RuCl_2P_2N_2H_4$, was used as an excellent catalyst to carry out the catalytic hydrogen transfer reduction of acetophenone. The conversion of acetophenone to 2-phenylethanol was up to 99% under the following reaction conditions: substrate:Ru:$(CH_3)_2CHOK$ = 200:1:12; reaction temperature of 65 ℃; reaction time of 2 h; normal pressure. A hydride transfer mechanism was also discussed.

Optically active secondary alcohols are important intermediates in the synthesis of a variety of physiologically active pharmaceuticals[1]. Although well-known chiral catalysts such as L-DIOP-Rh (I) and BINAP-Ru (II) can effectively catalyze the asymmetric hydrogen transfer hydrogenation of ketones with functional groups, the hydrogen transfer hydrogenation of simple aromatic ketones is still difficult to be realized[2]. We have successfully used ruthenium complexes with biphosphine or amino phosphine ligands, designed and synthesized by our laboratory, as the catalyst to effectively catalyze the hydrogenation of some functional alkene, but the same catalyst hardly had any activity in the hydrogenation of acetophenone even under the conditions of 100 ℃ and 5.0 MPa hydrogen pressure[3-5]. In the present work, a new catalytic system was designed to successfully carry out the hydrogen transfer hydrogenation of acetophenone.

In an potassium isopropoxide /isopropyl alcohol (iso-PrOK/iso-PrOH) solution, by using iso-PrOH as the hydrogen donor and the Ru (II) complexes possessing tetradentate $P_2(NH)_2$ ligands, such as $RuCl_2P_2N_2$ (I) or $RuCl_2P_2N_2H_4$ (II), as the catalyst , the hydrogen transfer hydrogenation of acetophenone was performed at the reaction temperature of 40-65 ℃ and normal pressure.



Catalyst  : 

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Experimental

$RuCl_2P_2N_2$ and $RuCl_2P_2N_2H_4$ were synthesized according to the reference [3] and [6], respectively. Their IR and NMR spectra were measured with PE-Spectroy 2000 IR and Varian Unity-5000 NMR Spectrometers, respectively. iso-PrOH was refluxed with calcium hydride to remove the micro amount of water. Dichloromethane was dried by anhydrous sodium sulfate before use iso-PrOK solution was prepared by putting metal potassium into iso-PrOH and its concentration was determined by the acid-base titration method.

All hydrogen transfer hydrogenation experiments were carried out under nitrogen atmosphere. The catalyst and 5.0 ml of dichloromethane were added into the reaction tube, after shaking and dissolving the catalyst, 20.0 ml of iso-PrOH was added and mixed, then acetophenone and 0.100 mol/L iso-PrOK/isoPrOH solution were seqentially added. Finally, the reaction was performed under the test conditions. The reaction products were analyzed by gas chromatography (column: 10% XE-60/Chromosorb W-HP, 2 m), and the relative molar response was calculated in terms of the effective carbon number method.

Results and discussion

Comparison of the catalytic character of different Ru complexes

The catalytic character of different Ru complexes on the hydrogen transfer hydrogenation of acetophenone were investigated and the results were listed in Table 1. It can be seen that $RuCl_2P_2N_2$ (I) and $RuCl_2P_2N_2H_4$ (II) display very high catalytic activity.

Table 1. Catalytic character of different Ru complexes for the hydrogen transfer hydrogenation of acetophenone

Catalysts	Acetophenone : Catalyst : iso-PrOK (Molar ratio)	Time (h)	Conversion (%)
$RuCl_3 \cdot 3H_2O$	200 : 1 : 8	8.0	<1
$Ru(OAc)_2(Ph_3P)_2$	200 : 1 : 12	9.0	<1
$Ru(OAc)_2(dppm)_2$	200 : 1 : 12	7.5	3.5
$Ru(OAc)_2(dppe)_2$	200 : 1 : 12	8.0	2.0
$RuCl_2(Ph_3P)_2$	200 : 1 : 12	6.5	4.1
$Ru_3(CO)_{12}$	200 : 1 : 12	7.5	5.7
$RuCl_2P_2N_2$	200 : 1 : 12	1.5	89.2
		2.0	93.5
$RuCl_2P_2N_2H_4$	200 : 1 : 12	1.5	98.8
		2.0	>99.0

Reaction conditions: catalyst, 0.01 mmol; acetophenone, 2.0 mmol; temperature, 65 ℃; CH_2Cl_2 (5.0 ml)/iso-PrOH (20.0 ml).

Effect of iso-PrOK concentration on the activity of catalyst

The catalyst did not display the activity on the hydrogen transfer hydrogenation in the absence of iso-PrOK. However, the catalytic activity increased with the increase of the iso-PrOK concentration. When the molar ratio of catalyst to iso-PrOK reached 1:12 and the reaction underwent for 2 h, the conversion of acetophenone to 2-phenylethanol was up to 99%. For different molar ratios of catalyst to iso-PrOK, the variation of conversion with the reaction time had similar patterns, the conversion sharply increased at the initial stage and then leveled off with the increase of reaction time.

Effect of reaction temperature and substrate concentration

The research results showed that the catalytic activity was severely affected by the reaction temperature. The reaction rate and the conversion of acetophenone to 2-phenylethanol steeply rose with the increase of temperature. When the molar ratio of acetophenone:$RuCl_2P_2N_2H_4$:iso-PrOK was 200:1:10, the conversion approahed 96% after reacting for 3 h at 65 ℃, but was only about 23% after reacting for 8 h at 40 ℃.

When the molar ratio of acetophenone to catalyst was raised from 100:1 to 400:1 and other experimental conditions kept constant, the conversion was only decreased from 98.1% to 83.2%, which means the catalyst can still be used to systems with higher substrate concentration.

Study on the mechanism

Hydrogen transfer hydrogenation are generally conducted by either a hydride way or direct hydrogen transfer[7]. The later involves the process in which both the hydrogen donor and the substrate are bound on the active centre of the catalyst. For the catalyst, $RuCl_2P_2N_2H_4$, used in this work, a direct hydrogen transfer way is difficult to be realized since the catalyst has the configuration with saturated coordination. Based on the fact that the catalyst has no activity in the absence of iso-PrOk and the catalytic activity increases with the increase of iso-PrOK concentration, we consider iso-PrOK may play a role of promoting the formation of Ru-hydride and suggest that the mechanism be as follows: firstly, iso-PrO^- attacks the central atom Ru and replaces the ligand Cl^- to form a Ru- iso-PrO^- intermediate, then transfers its active H atom to the central atom Ru to form an active Ru-H species, and finally the intramolecular hydrogen transfer takes place, leading to the formation of 2-phenylethanol. After the release of the reaction product, iso-PrO^- complexes with the central atom Ru to form Ru- iso-PrO^- again. This cycle repeats again and again to carry out the hydrogen transfer reaction.

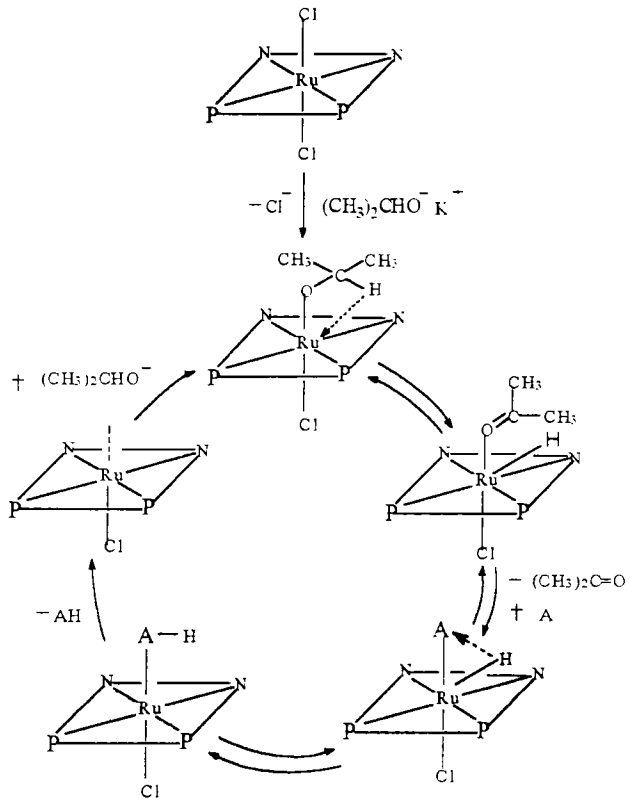

Fig.1 Mechanism of the hydrogen transfer hydrogenation of acetophenone catalyzed by $RuCl_2P_2N_2H_4$. A= Acetophenone, AH = 2-phenylethanol.

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