Pergamon

Tetrahedron Letters 40 (1999) 8897–8900

TETRAHEDRON
LETTERS

Direct conversion of benzyl alcohol to ketone by polymer-supported Rh catalyst

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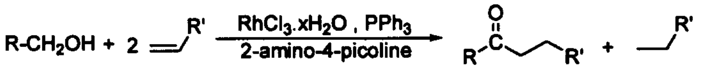
Received 30 August 1999; revised 27 September 1999; accepted 1 October 1999

Abstract

Benzyl alcohol reacted with 1-alkene to give the corresponding ketone by in situ generated polystyrene-based rhodium catalyst. The catalytic activity of this polymer-supported rhodium catalyst has not been reduced after reusing it four times. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: catalysis; ketones; rhodium; rhodium compounds; supported reagents/reactions.

Aldehydic C–H bond activation by transition metal catalyst has been utilized for the direct synthesis of ketone: hydroacylation.[1] Chelation-assisted hydroacylation with 2-aminopyridine derivative was devised in order to evade the decarbonylation frequently occurring in hydroacylation.[2] Recently, this type of hydroacylation has been further developed to the direct conversion of benzyl alcohol and 1-alkene to ketone (Eq. 1).[3]



(1)

These homogeneous catalytic systems, comprising of the precious rhodium, cannot be reused because no simple separation method for them exists. There are, however, several separation methods for a homogeneous catalyst enabling its further use.[4] One of them involves the polymer-supported catalyst which is the immobilized homogeneous catalytic species.[5] In this report, in situ generated polymer-supported rhodium catalysts were used as the reusable catalyst in the direct conversion of benzyl alcohol to ketone.

Benzyl alcohol (**1a**, 0.36 mmol) reacted with 1-hexene (**2a**, 3.6 mmol) in the presence of $RhCl_3 \cdot xH_2O$ (**3a**, 0.018 mmol), polystyrene-based diphenylphosphine (**4**, 0.054 mmol), and PPh_3 (0.018 mmol) with cocatalyst 2-amino-4-picoline (**5**, 0.36 mmol) in toluene at 130°C for 72 h (Table 1, entry 1).

After the reaction, the solution phase was decanted and the solid phase was washed with benzene 5–6 times.[6] The solution was concentrated in vacuo, and it was further purified by column-chromatography

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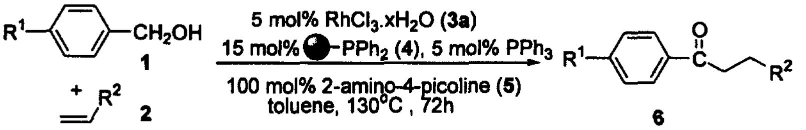
PII: S0040-4039(99)01907-3

Table 1
Direct conversion of **1** and **2** to **6** by in situ generated polymer-supported rhodium catalyst



Entry	Reactants		product	Yields of Product 6[a]			
	1(R¹)	2(R²)		1st	2nd	3rd	4th
1	H- (**1a**)	n-C_4H_9-(**2a**)	**6a**	69%	72%	71%	71%
2	F- (**1b**)		**6b**	75%	77%	74%	70%
3	CH_3- (**1c**)		**6c**	67%	66%	63%	60%
4	CF_3- (**1d**)		**6d**	70%	73%	72%[b]	68%[c]
5	CH_3O-(**1e**)		**6e**	61%[d]	68%[e]	59%[f]	58%[f]
6	H- (**1a**)	t-C_4H_9- (**2b**)	**6f**	50%	52%	52%	48%
7	F- (**1b**)		**6g**	53%	55%	53%	48%

[a] The polystyrene-based diphenylphosphine rhodium catalyst generated *in-situ* from **3** and **4** was reused, and **5** and PPh_3 removed on decant and washing operation were readded on each run. [b,c] Additional 3% yield of Tischenko type ester was obtained. [d] Additional 20% yield of 4-methoxybenzylamine was isolated. [e,f] 2% And 8% yield of 4-methoxybenzylamine was also obtained.

to give heptanophenone in a 69% yield.[7] After the same amounts of **1a**, **2a**, **5** and PPh_3 were added to the precipitate, in situ generated polymer-supported rhodium catalyst, the reaction was carried out under the previous reaction conditions to give a 72% isolated yield of **6a**. The third and fourth uses of the recovered polymer-supported rhodium catalyst both afforded 71% isolated yields of **6a**. The activity of the recovered catalyst did not decrease, even after three uses. Benzyl alcohols bearing various substituents were applied in this reaction. The electron-withdrawing substituents such as the fluoro- (**1b**) and trifluoromethyl- (**1d**) groups (entries 2 and 4) lead to better yields of ketone **6b** and **6d** than do the electron-donating substituents like the methyl (**1c**) and methoxy (**1e**) groups (entries 3 and 5). In these reactions, the first use of the catalyst afforded a lower yield of ketone **6** than did the second use. The reason must be that PPh_3 is partly used for the synthesis of Rh(I) species from Rh(III) when the first polystyrene-based diphenylphosphine Rh(I) complex is generated.[8] When the reaction was carried out with the sterically hindered olefin, 3,3-dimethylbutene (**2b**), the corresponding ketone **6f** was obtained in a 50% yield (entry 6), which is a lower yield than the reaction with **2a**. This can be explained by the fact that the polymer-supported rhodium catalyst is very sensitive to the steric hindrance of substrate olefins due to the difficult binding of the congested polymer-bound rhodium metal center.

This polymer-based Rh(I) catalyst was also generated in situ by the ligand-exchange reaction of Rh(I) complexes with **4**. Catalytic activities were examined, as shown in Table 2.

When $(PPh_3)_3RhCl$ was used, the catalytic activity dramatically decreased after the first use: 75% in the first use, 32% in the second, and 19% in the third (Table 2, entry 1). In this reaction, the rhodium catalyst might not be impregnated to **4**, and the real catalytic species of the first run must be $(Ph_3P)_3RhCl$, which is soluble in solvent and is washed away on decanting and washing. This type of leaching was also observed with $[(C_2H_4)_2RhCl]_2$ catalyst in the isolated yield of **6a** (entry 3). When $[(C_8H_{14})_2RhCl]_2$ with PPh_3 was used as the catalyst precursor, the catalytic activity did not decrease with repeated use in the yield of **6a**: 83% in the first use, 81% in the second, and 81% in the third (entry 5). This result implies

Table 2
Catalytic activity for various catalytic systems generated from **3** and **4**

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[\text{100 mol\% }\mathbf{5}\text{, toluene, 130°C, 72h}]{\text{M(}\mathbf{3}\text{, catalyst), 15 mol\% ●-PPh}_2\text{(}\mathbf{4}\text{)}} \mathbf{6a}$$

Entry	M (catalyst)	additive	Yields of Product **6a**[a]		
			1st	2nd	3rd
1	$(Ph_3P)_3RhCl$ (**3b**)	PPh_3 (5 mol%)	73%	32%	19%
2	$(Ph_3P)_3RhCl$ (**3b**)		61%	30%	21%
3	$[(C_2H_4)_2RhCl]_2$ (**3c**)	PPh_3 (5 mol%)	90%	50%	54%
4	$[(C_2H_4)_2RhCl]_2$ (**3c**)		76%	66%	44%
5	$[(C_8H_{14})_2RhCl]_2$ (**3d**)	PPh_3 (5 mol%)	83%	81%	81%
6	$[(C_8H_{14})_2RhCl]_2$ (**3d**)		34%	12%	15%
7	$RhCl_3 \cdot xH_2O$ (**3a**)	PPh_3 (5 mol%)	69%	72%	71%
8	$RhCl_3 \cdot xH_2O$ (**3a**)		42%	39%	32%

[a] The polystyrene-based rhodium catalyst generated *in-situ* from **3** and **4** was reused, and **5** and PPh_3 removed by decanting and washing operation were readded on each run.

that the in situ generated polymer-supported catalyst is fairly stable. Additional PPh_3 is important for the catalytic activity in this reaction since exclusive polystyrene-based diphenylphosphine rhodium catalyst may not undergo facile reductive elimination due to the difficult dissociation–coordination process of polymer-bound phosphine around the metal center.

In conclusion, polymer-supported rhodium complexes, generated in situ by ligand-exchange reaction, were utilized for the direct synthesis of benzyl alcohol to ketone. The catalytic activity of the recovered catalyst did not decrease after several uses.

Acknowledgements

This research was supported by the Korea Science and Engineering Foundation (Grant No. 97-05-01-3) and the Ministry of Education (BSRI-97-3422).

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6. Experimental procedure: A mixture of 17.6 mg **4** (purchased from Aldrich Chemical Co., polystyrene cross-linked with 2% DVB, 3 mmol P/g resin), 3.8 mg **3a**, 38.9 mg **5**, 4.7 mg PPh_3, 303 mg **2a**, and 38.9 mg **1a** was dissolved in 100

mg toluene in a screw-capped vial, and stirred at 130°C for 72 h. After the reaction, the solution was decanted and washed with benzene six times. The solvent evaporated and the resulting adduct was purified by column-chromatography (hexane:ethylacetate=5:2) to give 47.2 mg **6a** (69%) and 1.8 mg PPh$_3$. To the solid phase remaining in the vial, 38.9 mg **1a**, 38.9 mg **5**, PPh$_3$ (1.8 mg: amount of the removed PPh$_3$ on decanting and washing at the first run) and 303 mg **2a** were added. The reaction was carried out under the previous reaction conditions to give 49.2 mg **6a** (72%).

7. When the reaction was carried out with benzaldehyde instead of **1a**, no reaction occurred.
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