

A novel efficient route for preparation of chiral β -hydroxycarboxylic acid: Asymmetric hydration of unsaturated carboxylic acids catalyzed by heterobimetallic complex wool–palladium–cobalt

Si-Qian Wang^{a,b}, Zi-Wei Wang^a, Lin-Chun Yang^a, Jin-long Dong^a, Cai-Qin Chi^b, Dan-Ni Sui^a,
Yong-Zhao Wang^a, Jian-Guo Ren^{a,*}, Mei-Yu Hung^b, Ying-Yan Jiang^b

^a College of Chemistry and Chemical Engineering, ShanXi University, Taiyuan 030006, China

^b Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

Received 18 February 2006; received in revised form 23 August 2006; accepted 24 August 2006

Available online 30 August 2006

Dedicated to Professor Y.Y. Jiang on the occasion of his 80th birthday.

Abstract

A new bio-polymer heterobimetallic complex wool–Pd–Co is found to be a novel efficient catalyst for asymmetric hydration of unsaturated carboxylic acids with high enantioselectivity by simple and clean process under mild conditions. Chemical and optical yields are affected by some parameters, such as the (Pd + Co) content in wool–Pd–Co, the Co/Pd molar ratio, reaction time, reaction temperature and amount of water. After five-time use of the complex, the chemical and optical yields of the products show no significant changes. Obviously, the methods provide an alternative way to produce chiral β -hydroxycarboxylic acids.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Chiral β -hydroxycarboxylic acid; Asymmetric hydration; Unsaturated carboxylic acids; Heterobimetallic complex; Wool–palladium–cobalt

1. Introduction

Many organic acids can be obtained by fermentation or by incomplete oxidation of the corresponding primary alcohols. The latter method is an old and established way to produce different acids, such as acetic or gluconic acids, in an industrial scale and it may also be used to produce aliphatic acids employed as natural flavors or chiral intermediates [1]. Regio- and enantioselective oxidation of diols can afford hydroxycarboxylic acids, such as α -methyl- β -hydroxypropanoic acid, to be used as chiral building blocks [2]. Although the production of carboxylic acids by microbial means is very attractive, its industrial application is still severely hampered by the low productivity compared with conventional chemical methods and by the difficulties concerned with product isolation [3].

Enantioselective functionalization of olefins constitutes among the most exciting challenges in modern synthetic chemistry to provide various chiral units [4], among which palladium-catalyzed asymmetric Wacker process has proven to be one of the most versatile methods for functionalization of alkenes (adding water or ethanol to alkene). In this field, Murahashi and co-workers have done a lot of pioneering work on chiral intramolecular Wacker-type oxidation cyclization and asymmetric acetalization of alkenes [5]. A mechanistic study of the reaction revealed that the chiral center of the product is created by *trans*-oxypalladation and 1,2-stereoselective hydride migration [6]. Uozumi [7] and Arai [8] also revisited and advanced the reaction of Wacker-type oxidation and oxidative cyclization. Furthermore, the palladium-catalyzed asymmetric hydrosilylation of alkenes have been also recognized to be a potent variant of the enantioselective Wacker process for functionalization of alkenes [9]. However, most methods usually involved oxidation steps using oxidants such as H_2O_2 , *t*-BuOOH and O_2 . The less developed competing reaction is the protonolysis of the σ -alkyl bond on palladium to give the addition product rather

* Corresponding author. Tel.: +86 351 7010588.

E-mail address: renjg@sxu.edu.cn (J.-G. Ren).

than oxidation product [10]. That is, when water is the nucleophile, alcohols are generated directly from alkenes (hydration). Since our first description of an effective asymmetric hydration of allyl alcohol catalyzed by polysulfostyrene–gelatin–cobalt (PSS–GE–Co) [11], we have been striving for new catalytic systems, such as wool–Pd [12] and silica-supported–casein–cobalt (SiO₂–CS–Co) [13], to obtain different optical alcohols. These chiral ligands, wool, CS and GE, are very cheap, abundant in nature. Directly green catalytic asymmetric hydration with water as benign reagent under mild conditions is another feature.

We continued to be interested in exploiting novel readily available alkenes in the synthesis of chiral alcohols. In the course of our study on the hydration of unsaturated polyesters, we firstly have a need to attempt the hydration of some unsaturated carboxylic acids. We used above catalytic systems to catalyze asymmetric hydration of these compounds with much less satisfactory results. In view of our successful research on using wool as an elegant chiral ligand [11,14] and the fact that interesting catalytic systems that contain two kinds of bimetallic center within one catalyst promote many reactions with high chemoselectivity and/or enantioselectivity [15,16], we were prompted to design heterobimetallic complex wool–palladium–cobalt (wool–Pd–Co) to promote the hydration. Although we speculate that the development of a directly catalytic asymmetric hydration might be feasible, our initial concerns were dominated by the possibility that our heterobimetallic asymmetric catalysts would be ineffective at promoting hydration reactions due to existence of carboxylic acid group in these alkene compounds. We have found that hydration reactions of the desired type proceeded smoothly using wool–Pd–Co as catalyst. In this paper, we firstly report our successful findings in using bio-polymer heterobimetallic complex wool–Pd–Co as novel efficient catalyst for the asymmetric hydration of unsaturated acids with water as benign reagent in a very simple, mild and facile workup under mild conditions.

To the best of our knowledge, this is the first method reporting the asymmetric hydration of unsaturated carboxylic acids catalyzed by heterobimetallic complex wool–Pd–Co.

2. Results and discussion

In order to clarify the molecular interaction of Pd and Co in palladium chloride and cobalt chloride with –NH–CO–, –NH₂, –SO₃H, and –S–S– groups in wool ligand, the X-ray photoelectron spectroscopy (XPS) was examined. Table 1 shows XPS data for wool–Pd–Co, wool, PdCl₂ and CoCl₂. It can be seen that there are two oxidation states of Pd, Pd (0) and Pd (II), in wool–Pd–Co complex (Scheme 1). Probably, a part of PdCl₂ was converted to Pd (0) during the preparation of wool–Pd–Co complex. The difference of Co (II)_{2p₃} binding energies between CoCl₂ and wool–Pd–Co is 0.9 eV. There are two kinds of nitrogen containing group, –NH–CO– and –NH₂, in wool, and their N_{1s} binding energies are different. Such data in wool–Pd–Co are also different from those in wool. The difference of N_{1s} binding energies between –NH–CO– in wool and –NH–CO– in wool–Pd–Co is 1.3 eV, and that between –NH₂ in wool and –NH₂ in wool–Pd–Co is 1.1 eV. There are

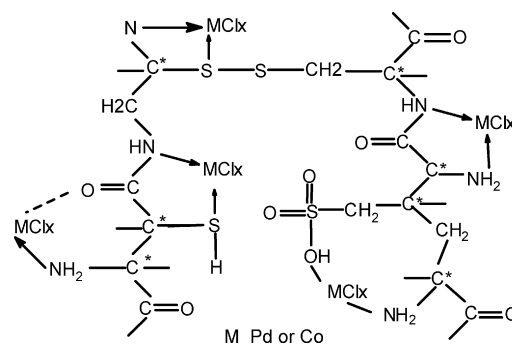
Table 1

X-ray photoelectron spectroscopy (XPS) data for wool–Pd–Co, wool, CoCl₂ and PdCl₂

| XPS peak | Binding energy (eV) | | | |
|------------------------------------|---------------------|-------|-------------------|-------------------|
| | Wool–Pd–Co | Wool | PdCl ₂ | CoCl ₂ |
| Pd(0) _{3d_{5/2}} | 336.2 | | | |
| Pd(II) _{3d_{5/2}} | 337.5 | | 337.8 | |
| Co(II) _{2p₃} | 781.4 | | | 782.3 |
| N _{1s} –NH–CO– | 401.3 | 400.0 | | |
| –NH ₂ | 399.9 | 398.8 | | |
| S _{2p} –SO ₃ H | 168.0 | 167.8 | | |
| –SH | 161.9 | 163.6 | | |
| –S–S– | 163.7 | 164.8 | | |
| O _{1s} | 532.2 | 531.7 | | |

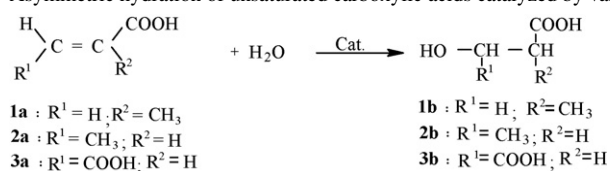
three kinds of S containing group, –SO₃H, –SH and –S–S–, in wool, and their S_{2p} binding energies are different. Such data in wool–Pd–Co are also different from those in wool. The difference of S_{2p} binding energy between –SO₃H in wool and –SO₃H in wool–Pd–Co is 0.2 eV, that between –SH in wool and –SH in wool–Pd–Co is 1.7 eV and that between –S–S– in wool and –S–S– in wool–Pd–Co is 1.1 eV. The difference of O_{1s} binding energy between wool and wool–Pd–Co is only 0.5 eV. These results show that coordination or ionic bonds are formed by the connection of N atoms (in –NH–CO– and –NH₂) and S atoms (in –SH and –S–S–) with Pd atoms in the wool–Pd–Co complex. Only a small amount of O atom is considered to form the complex.

The catalytic activity of various kinds of catalysts was first investigated in the asymmetric hydration of 2-methylacrylic acid (**1a**) as model (Table 2). When the direct catalytic asymmetric hydration of **1a** with 0.10 g wool–Pd (0.05 mmol/g) was carried out in the presence of 0.02 g oxalic acid at 90 °C for 20 h, we only obtained the desired product (*S*)-(+)- α -methyl- β -hydroxypropanoic acid (**1b**) in 51.7% yield and with 61.2% e.e. (entry 3). The use of wool–Co was found to be also ineffective, affording **1b** in 4.0% yield and 11.2% e.e. (entry 2). Much to our surprise and interest, however, both chemical and optical yields were greatly changed when the second metal (Fe, Co, Ni, Cu, Zn, Mn) is added into the complex. The three contiguous bimetallic complexes, wool–Pd–Fe [17], wool–Pd–Co, and wool–Pd–Ni, were all active catalysts for asymmetric hydration of **1a** (entries 4–6). Among these bimetallic complexes (entries



Scheme 1. The structure of wool–Pd–Co.

Table 2
Asymmetric hydration of unsaturated carboxylic acids catalyzed by various kinds of catalysts^a



| Entry | Catalyst | Substrate | Product ^b | Yield ^c (%) | [α] _D ²⁰ (°) | Optical yield ^d (% e.e.) | Absolute configuration ^e |
|-----------------|---|-----------|----------------------|------------------------|------------------------------------|-------------------------------------|-------------------------------------|
| 1 | PdCl ₂ or CoCl ₂ | 1a | 1b | <5 | | | |
| 2 | Wool–CoCl ₂ | 1a | 1b | 4.0 | +1.42 | 11.2 | S |
| 3 | Wool–PdCl ₂ | 1a | 1b | 51.7 | +7.78 | 61.2 | S |
| 4 | Wool–PdCl ₂ –CoCl ₂ | 1a | 1b | 84.3 | +11.77 | 92.5 | S |
| 5 | Wool–PdCl ₂ –FeCl ₃ | 1a | 1b | 72.5 | +8.92 | 70.1 | S |
| 6 | Wool–PdCl ₂ –NiCl ₂ | 1a | 1b | 75.6 | +10.34 | 81.3 | S |
| 7 | Wool–PdCl ₂ –CuCl ₂ | 1a | 1b | 53.8 | +8.17 | 64.2 | S |
| 8 | Wool–PdCl ₂ –ZnCl ₂ | 1a | 1b | 66.4 | +7.27 | 57.2 | S |
| 9 | Wool–PdCl ₂ –MnCl ₂ | 1a | 1b | 42.1 | +4.68 | 36.8 | S |
| 10 ^f | Wool–PdCl ₂ –CoCl ₂ | 1a | 1b | 43.5 | +6.58 | 51.7 | S |
| 11 | Wool–PdCl ₂ –CoCl ₂ | 2a | 2b | 81.2 | +9.71 | 94.3 | S |
| 12 ^g | Wool–PdCl ₂ –CoCl ₂ | 3a | 3b | 62.1 | +23.69 | 83.5 | R |

^a Reaction conditions: 0.10 g catalyst (0.05 mmol Pd, 0.15 mmol Co or Fe or Ni or Cu or Zn), 2.00 mmol α-methylacrylic acid, 5.0 ml 1-butanol, 2.0 ml water, 0.01 g hydroquinone, 90 °C, 0.02 g oxalic acid, 1 atm. N₂, 20 h.

^b All the products were determined by ¹H NMR.

^c Referred to GC yield.

^d Enantiomer excess were calculated on the basis of reported values for specific rotation of pure enantiomers: (*S*)-(+)-α-methyl-β-hydroxypropanoic acid (**1b**) [α]_D²⁰ + 12.72° (c 12.5, EtOH) [18]; (*S*)-(+)-3-hydroxybutyric acid (**2b**) [α]_D²⁰ + 10.3° (c 6, H₂O) [19]; (*R*)-(+)-α-hydroxybutanedioic acid (**3b**) [α]_D²⁰ + 28.4° (c 5.5, Py) [20].

^e Determined by the sign of optical rotation.

^f Adding no hydroquinone.

^g Reaction time 28 h.

4–9), wool–Pd–Co had the highest activity with 84.3% yield and 92.5% e.e. at 90 °C, Co/Pd molar ratio, 3/1 (entry 4). So the catalytic behavior of wool–Pd–Co has been researched in detail.

Table 3 shows that changing the Co/Pd molar ratio in wool–Pd–Co complex had remarkable effects on the yield and optical yield. The reason can be explained by synergistic action. The addition reaction requires a reasonable activation match between the C=C and O–H (in H₂O) bonds via interaction with the active site of the catalyst. Cobalt in heterobimetallic

Table 3
Influence of Co/Pd molar ratio on asymmetric hydration of **1a**^a

| Co/Pd molar ratio | α-Methyl-β-hydroxypropanoic acid | | | |
|-------------------|----------------------------------|------------------------------------|-------------------|------------------------|
| | Yield (%) | [α] _D ²⁰ (°) | Optical yield (%) | Absolute configuration |
| 1/0 ^b | 4.0 | +1.42 | 11.2 | S |
| 0/1 ^c | 51.7 | +7.78 | 61.2 | S |
| 1/1 | 71.5 | +9.87 | 77.6 | S |
| 2/1 | 80.7 | +11.01 | 86.3 | S |
| 5/2 | 81.2 | +11.50 | 90.4 | S |
| 3/1 | 84.3 | +11.77 | 92.5 | S |
| 7/2 | 71.3 | +10.20 | 80.2 | S |
| 4/1 | 79.3 | +10.76 | 84.6 | S |

^a Reaction conditions: 0.10 g wool–Pd–Co [(Pd+Co), 0.20 mmol/g], 2.00 mmol α-methylacrylic acid, 5.0 ml 1-butanol, 2.0 ml water, 0.01 g hydroquinone, 0.02 g oxalic acid, 1 atm N₂, 90 °C, 20 h.

^b Monometallic complex, wool–Co.

^c Monometallic complex, wool–Pd.

wool–Pd–Co complex acted as a promoter of Pd to grasp more electrophilic oxygen (H₂O, –COOH) tending to accumulate on the surface of the catalyst wool–Pd–Co, which enhanced the probability of attack on the C=C bond of **1a** by H₂O. Thus, on increasing the molar ratio from 1/1 to 4/1, catalytic ability increase initially, 71.5% yield and 77.6% e.e. at the Co/Pd molar ratio 1/1, then at the appropriate molar ratio (Co/Pd, 3/1), Pd and Co worked together well as two concordant partners to realize the most harmonious match of C=C and O–H (in H₂O) bond activation. However, an obvious decline in catalytic performance occurred after further increase in the Co/Pd molar ratio (Co/Pd > 3/1) as result of decrease in coordinative unsaturation of the central metal Pd [21]: 79.3% yield and 84.6% e.e. were obtained at the Co/Pd molar ratio of 4/1.

The influence of the (Pd + Co) content in wool–Pd–Co complex on the asymmetric hydration of **1a** is given in Table 4. The product yield of **1a** was 84.1–85.0% when the (Pd + Co) content was over 0.18 mol/g, but the optical yield increased from 68.7% to 92.5% e.e. when the (Pd + Co) content increased from 0.10 to 0.20 mmol/g, then it decreased to 89.2% e.e. at the (Pd + Co) content of 0.25 mmol/g. From Table 4, it is clear that the (Pd + Co) content plays an important role in this reaction. Low (Pd + Co) contents cannot activate the substrate adequately and high (Pd + Co) contents will cover the active centers of the wool–Pd–Co complex, causing the decrease in the optical yield. So 0.20 mmol/g (Pd + Co) content was appropriate.

The influence of reaction temperature on the reaction catalyzed by wool–Pd–Co has been also investigated (Fig. 1). It

Table 4
Influence of (Pd + Co) content on asymmetric hydration of **1a**^a

| (Pd + Co) content | α -Methyl- β -hydroxypropanoic acid | | | |
|-------------------|--|-----------------------|-------------------|------------------------|
| | Yield (%) | $[\alpha]_D^{20}$ (°) | Optical yield (%) | Absolute configuration |
| 0.10 | 42.7 | +8.74 | 68.7 | S |
| 0.15 | 72.3 | +8.94 | 70.3 | S |
| 0.18 | 84.1 | +10.38 | 81.6 | S |
| 0.20 | 84.3 | +11.77 | 92.5 | S |
| 0.25 | 85.0 | +11.35 | 89.2 | S |

^a Reaction conditions: 0.10 g wool-Pd-Co (Pd/Co 1/3), 2.00 mmol α -methylacrylic acid, 5.0 ml 1-butanol, 2.0 ml water, 0.01 g hydroquinone, 0.02 g oxalic acid, 1 atm N₂, 90 °C, 20 h.

can be seen that the product yield increased from 54.3% to 86.7% with increasing reaction temperature from 60 to 90 °C at 20 h. But very interestingly, optical yields keeping higher at the specific range of temperature (80–90 °C) evidently came down beyond the limitation of the temperature. The decrease in the stereoselectivity was rightly due to the transformation easily caused by the alteration of the configuration in active centers when the temperature increased further. The optimum reaction temperature was 90 °C, with 84.3% yield and 92.5% e.e.

Fig. 2 shows the influence of the reaction time on the asymmetric hydration of **1a**. It can be seen that, the reaction time was critical to optical selectivity. The suitable time for this reaction was 20 h. The curve, which represents the product yield, climbed up from 8 to 20 h, the other curve, which represents the optical yield climbed up first, reached its peak 92.5% e.e. at 20 h and then decreased. With the reaction time prolonged, the product yield increased obviously, but the optically active product would convert to a racemic mixture.

Table 5 shows the influence of the amount of water on the asymmetric hydration of **1a**. The selectivity and yield of **1b** were relatively sensitive to the amount of water and 1-butanol. The optimum ratio was 2/5 ml (H₂O/C₄H₉OH). Lower selectivity and yield were observed with further decreasing ratio to 1/6 ml (H₂O/C₄H₉OH). It is obvious that, a suitable ratio of water/1-butanol was necessary for this catalytic reaction. The

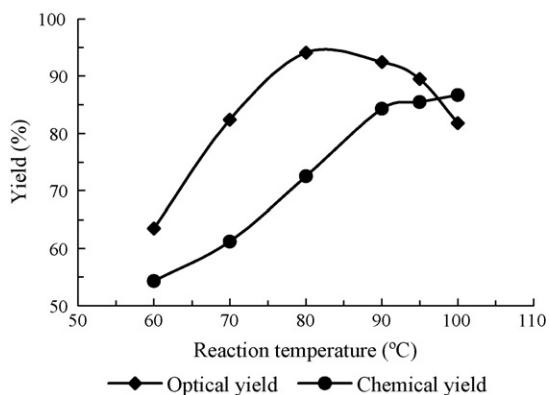


Fig. 1. Influence of reaction temperature on the asymmetric hydration of **1a**. Reaction on conditions: 0.10 g wool-Pd-Co [(Pd + Co), 0.20 mmol/g, Co/Pd 3/1], 2 mmol α -methylacrylic acid, 5.0 ml 1-butanol, 2.0 ml water, 0.01 g hydroquinone, 0.02 g oxalic acid, 1 atm N₂, 20 h.

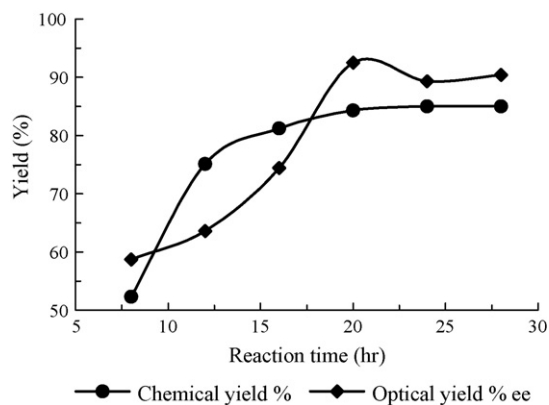


Fig. 2. Influence of reaction time on the asymmetric hydration of **1a**. Reaction conditions: 0.10 g wool-Pd-Co [(Pd + Co), 0.20 mmol/g, Co/Pd 3/1], 2.00 mmol α -methylacrylic acid, 5.0 ml 1-butanol, 2.0 ml water, 0.01 g hydroquinone, 0.02 g oxalic acid, 1 atm N₂, 90 °C.

optimum water/1-butanol ratio can more efficiently strengthen the swelling effect of the ligand wool and make the structure of the catalyst loosen which is beneficial for the diffusion of molecules to the active center.

Neither of the precursor, PdCl₂, CoCl₂, or the wool support alone, and the mechanical mixture of wool, PdCl₂, and CoCl₂ could catalyze the asymmetric hydration of **1a** to **1b** (Table 1, entry 1). Moreover, in the absence of hydroquinone, the yield of **1b** was very low (Table 1, entry 10), probably due to the formation of dimers/oligomers deactivating the catalyst [22]. The wool-Pd-Co was a versatile catalyst for the asymmetric hydration of other unsaturated acids such as *trans*-2-butenoic acid (**2a**) to (*S*)-(+)-3-hydroxybutyric acid (**2b**) and *trans*-2-butenedioic acid (**3a**) to (*R*)-(+)- α -hydroxybutanedioic acid (**3b**) (entry 11, 12). The optical yields of **2b** and **3b** reached 94.3% e.e. and 83.5% e.e. selectively.

In order to investigate the reuse stability of the complex catalyst, 2-methylacrylic acid asymmetric hydration was examined (Table 6). After each reaction, the catalyst was separated from the solution by filtration, washed with ethanol and dried under vacuum, then added as the catalyst to the next batch of reaction. It can be seen that after five-time use of the wool-Pd-Co com-

Table 5
Influence of ratio of water to 1-butanol on the hydration of **1a** catalyzed by wool-Pd-Co^a

| Water/butanol (ml/ml) | α -Methyl- β -hydroxypropanoic acid | | | |
|-----------------------|--|-----------------------|-------------------|------------------------|
| | Yield (%) | $[\alpha]_D^{20}$ (°) | Optical yield (%) | Absolute configuration |
| 7/0 | 54.6 | +6.00 | 47.2 | S |
| 6/1 | 62.4 | +6.55 | 51.5 | S |
| 5/2 | 67.3 | +7.78 | 61.2 | S |
| 4/3 | 75.1 | +9.44 | 74.2 | S |
| 2/5 | 84.3 | +11.77 | 92.5 | S |
| 3/4 | 84.1 | +10.48 | 82.4 | S |
| 2/5 | 76.3 | +9.31 | 73.2 | S |
| 1/6 | 50.2 | +8.08 | 63.5 | S |

^a Reaction conditions: 0.10 g wool-Pd-Co [(Pd + Co), 0.20 mmol/g, Pd/Co 1/3], 2.00 mmol α -methylacrylic acid, 0.01 g hydroquinone, 0.02 g oxalic acid, 1 atm N₂, 90 °C, 20 h.

Table 6
Recycling of wool–Pd–Co in the asymmetric hydration of 2-methylacrylic acid^a

| Run | α -Methyl- β -hydroxypropanoic acid | | | |
|-----|--|-----------------------|-------------------|------------------------|
| | Yield (%) | $[\alpha]_D^{20}$ (°) | Optical yield (%) | Absolute configuration |
| 1 | 84.3 | +11.77 | 92.5 | S |
| 2 | 84.0 | +11.73 | 92.2 | S |
| 3 | 83.5 | +11.66 | 91.7 | S |
| 4 | 83.1 | +11.58 | 91.0 | S |
| 5 | 82.7 | +11.47 | 90.2 | S |
| 6 | 71.3 | +10.72 | 84.3 | S |

^a Reaction conditions are identical to those in Table 2.

plex, the chemical and optical yields of the products show no significant changes.

In summary, the present work has provided a novel effective green methodology for the preparation of chiral β -hydroxycarboxylic acids, versatile reagents for organic syntheses, in excellent enantioselectivity. Moreover, the simple and cleaner procedure, mild reaction conditions, high stability and recovery rate of chiral catalyst will make this catalytic system an attractive and useful alternative to the existing methods involving expensive enzyme system or microbial means [23] with low productivity and complicated processing. We believe this methodology will find important application in industry.

3. Experimental

3.1. General

All starting materials and reagents were obtained from commercial suppliers and were used without further purification. Melting points were determined on an electrothermal melting point apparatus and uncorrected. ¹H NMR spectra were recorded at 300 MHz in CDCl₃. Chemical shifts (δ) for ¹H NMR were recorded in ppm downfield relative to the internal standard tetramethyl-silane (TMS). The progress of the reaction, composition and yield of the hydration products were analyzed on a Shanghai 103 Gas chromatograph (GC) using a 1-m steel column of SE-30 on silica (80–100 mesh; dinitrogen as carrier gas). Optical rotations were measured with a Shanghai WZZ-1S digital polarimeter. Enantiomeric excess were determined by HPLC (CHIRALPK AD, OD, AS). XPS was recorded on an ESCALABZOI-XL photoelectron spectrometer. Binding energy was referred to C_{1s} (285.0 eV). All spectral data of products were in accordance with those reported in literature [24].

3.2. Preparation of wool–Pd–Co complex catalyst

Common commercial white wool was washed with distilled water and ethanol, and then cut with scissors to very short pieces.

Several samples of wool–Pd–Co complex with different contents were prepared by the reaction of a definite amount of wool pieces with PdCl₂·2H₂O and CoCl₂·6H₂O in ethanol solution. For example, in order to obtain a sample of 0.20 mmol/g (Pd+Co) in wool–Pd–Co complex, 1.00 g of wool pieces,

0.05 mmol PdCl₂·2H₂O and 0.15 mmol CoCl₂·6H₂O and 10 ml ethanol were placed in a 50 ml flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was stirred and heated to reflux for about 10 h under nitrogen atmosphere to cause white wool pieces to become gray and the solution to become colorless and transparent. Then, the product was filtered, washed with ethanol and dried to give about 1.00 g of gray pieces (wool–Pd–Co).

3.3. Hydration of alkenes

The hydration reaction was carried out under an atmospheric pressure of nitrogen. For example, 0.10 g wool–Pd–Co [(Pd+Co), 0.20 mmol/g, Pd/Co 1/3], 2.00 mmol α -methylacrylic acid, 5.0 ml 1-butanol, 2.0 ml water 0.02 g oxalic acid and 0.01 g of hydroquinone, were placed in a 50 ml flask equipped with magnetic stirrer and a reflux condenser. The hydration was carried out at 90 °C under 1 atm N₂. The progress of the reaction, composition and yield of the hydration products were analyzed on GC. After 20 h, the reaction mixture was cooled and filtered in order to separate and recover the catalyst. The filtrate was extracted with chloroform (3 × 10 ml) and the combined organic layers were washed with brine (10 ml) and dried over Na₂SO₄. Analysis of the product solution by GC indicated 84.3% yield. The solvent was removed under reduced pressure and products were further purified by column chromatography (silica gel, ethyl acetate/hexane = 3/10) to yield an analytically pure sample α -methyl- β -hydroxypropanoic acid (1.69 mmol) as yellow oil for ¹H NMR assay. ¹H NMR (300 MHz, CDCl₃, δ ppm): 1.28 (d, *J* = 6.9 Hz, 3H), 2.41–2.52 (m, 2H), 4.18–4.25 (m, 1H), 7.79 (br s, 1H).

Acknowledgements

We are grateful to the Center for Physicochemical Analysis Measurement, Institute of Chemistry, the Chinese Academy of Sciences. We also acknowledge Professor Fen Liu, Liang-Zhong Zhao and Hongwen Ma for their helpful measurements and discussion during the preparation of this paper.

References

- [1] H.G. Davies, R.H. Green, D.R. Kelly, S.M. Roberts, in: A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), *Oxidation Reactions, in Biotransformations in Preparative Organic Chemistry*, Academic Press, London, 1989, p. 157.
- [2] H. Ohta, H. Tetsukawa, N. Noto, *J. Org. Chem.* 47 (1982) 2400.
- [3] A.S. Kertes, C.J. King, *Biotechnol. Bioeng.* 28 (1986) 269.
- [4] For reviews, see;
 - (a) R. Noyori, M. Kitamura, in: B. Scheffold (Ed.), *Modern Synthetic Methods*, vol. 5, Springer-Verlag, Berlin, 1989, p. 115;
 - (b) J.D. Morrison, *Asymmetric Synthesis*, vol. 1–5, Academic Press, London, 1983–1985;
 - (c) C.M. Crudden, D. Edwards, *Eur. J. Org. Chem.* (2003) 4695.
- [5] For typical catalytic asymmetric intramolecular Wacker-type oxidation cyclization of alkenes, see;
 - (a) T. Hosokawa, T. Uno, S. Inui, S.-I. Murahashi, *J. Am. Chem. Soc.* 103 (1981) 2318;
 - (b) T. Hosokawa, C. Okuda, S.-I. Murahashi, *J. Org. Chem.* 50 (1985) 1282;

- (c) T. Hosokawa, T. Yamanaka, S.-I. Murahashi, *J. Chem. Soc. Chem. Commun.* (1993) 117.
- [6] (a) T. Hosokawa, T. Yamanaka, M. Itotani, S.-I. Murahashi, *J. Org. Chem.* 60 (1995) 6159;
(b) T. Hosokawa, S.-I. Murahashi, *Acc. Chem. Soc.* 23 (1990) 49;
(c) T. Hosokawa, T. Ohta, S. Kanayama, S.-I. Murahashi, *J. Org. Chem.* 52 (1987) 1758.
- [7] (a) Y. Uozumi, K. Kato, T. Hayashi, *J. Am. Chem. Soc.* 119 (1997) 5063;
(b) Y. Uozumi, K. Kato, T. Hayashi, *J. Org. Chem.* 63 (1998) 5071;
(c) Y. Uozumi, K. Kyota, K. Kato, M. Ogasawara, T. Hayashi, *J. Org. Chem.* 64 (1999) 1620.
- [8] M.A. Arai, M. Kuraishi, T. Arai, H. Sasai, *J. Am. Chem. Soc.* 123 (2001) 2907.
- [9] For reviews on the hydrosilylation of olefins, see;
(a) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, 1994;
(b) H. Nishiyama, K. Itoh, in: I. Ojima (Ed.), *Catalytic Asymmetric Synthesis*, Wiley-VCH, New York, 2000, p. 111;
(c) T. Hayashi, in: S.-I. Murahashi, S.G. Davies (Eds.), *Transition Metal Catalysed Reactions*, Blackwell Science, 1999.
- [10] K.J. Miller, T.T. Kitagawa, M.M. Abu-Omar, *Organometallics* 20 (2001) 4403.
- [11] X. Zhang, Y.J. Li, M.Y. Huang, Y.Y. Jiang, *Polym. Adv. Technol.* 13 (2002) 305.
- [12] L. Xue, B. Jia, L. Tang, X.F. Ji, M.Y. Huang, Y.Y. Jiang, *Polym. Adv. Technol.* 15 (2004) 346.
- [13] L. Xue, D.J. Zhou, L. Tang, X.F. Ji, M.Y. Huang, Y.Y. Jiang, *React. Polym.* 58 (2004) 117–121.
- [14] (a) J.H. Miao, J.H. Yang, L.Y. Chen, B.X. Tu, M.Y. Huang, Y.Y. Jiang, *Polym. Adv. Technol.* 15 (2004) 221;
(b) M. He, D.Q. Zhou, H.L. Ge, M.Y. Huang, Y.Y. Jiang, *Polym. Adv. Technol.* 14 (2003) 273;
(c) M.Y. Yin, G.L. Yuan, M.Y. Huang, Y.Y. Jiang, *J. Mol. Catal. A: Chem.* 147 (1999) 89;
(d) G.L. Yuan, M.Y. Yin, M.Y. Huang, Y.Y. Jiang, *Polym. Adv. Technol.* 10 (1999) 1.
- [15] For reviews on heterobimetallic asymmetric catalyst, see;
(a) M. Shibasaki, N. Yoshikawa, *Chem. Rev.* 102 (2002) 2187;
(b) M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1236;
(c) M. Shibasaki, M. Kanai, *Chem. Pharm. Bull.* 49 (2001) 511;
(d) H. Steinhagen, G. Helmchen, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 2339;
(e) M. Shibasaki, M. Kanai, K. Funabashi, *Chem. Commun.* (2002) 1989.
- [16] Our some successful examples on heterobimetallic catalysts, see;
(a) X.T. Yang, J.X. Tian, M.Y. Huang, Y.Y. Jiang, *Makromol. Chem. Rapid Commun.* 14 (1993) 485;
(b) C.W. Chen, M.Y. Huang, Y.Y. Jiang, *Makromol. Chem. Rapid Commun.* 15 (1994) 587;
(c) L.M. Tang, M.Y. Huang, Y.Y. Jiang, *React. Polym.* 23 (1994) 119;
(d) X. Zhang, B. Han, M.Y. Huang, Y.Y. Jiang, *Polym. Adv. Technol.* 12 (2001) 693;
(e) B.W. Mao, J.F. Wu, M.Y. Huang, Y.Y. Jiang, *Polym. Adv. Technol.* 13 (2002) 301.
- [17] Hydration of some alkenes catalyzed by wool–Pd–Fe has also been investigated, but their optical activities haven't been investigated, see;
B. Jia, X. Yang, Y.Y. Huang, Y.Y. Jiang, *React. Polym.* 57 (2003) 163.
- [18] J.I.G. Cadogan, S.V. Ley, G. Pattenden, *Dictionary of Organic Compounds*, 6th ed., Chapman & Hall, 1996, p. 3728.
- [19] J.I.G. Cadogan, S.V. Ley, G. Pattenden, *Dictionary of Organic Compounds*, 6th ed., Chapman & Hall, 1996, p. 3599.
- [20] J.I.G. Cadogan, S.V. Ley, G. Pattenden, *Dictionary of Organic Compounds*, 6th ed., Chapman & Hall, 1996, p. 4103.
- [21] The effects of coordinative unsaturation of the central metal on catalytic activity, see;
Y. Iwasawa, *Tailored Metal Catalysis*, D. Reidel, Dordrecht, 1986, p. 87.
- [22] H. Zhang, S.M. Mahaiyani, M.M. Sharma, T. Sridhar, *Chem. Eng. Sci.* 57 (2002) 315.
- [23] (a) H. Ohta, H. Tetsukawa, N. Noto, *J. Org. Chem.* 47 (1982) 2400;
(b) T. Shigeno, A. Katayama, T. Nakahara, *Biosci. Biotech. Biochem.* 56 (1992) 320;
(c) R. Gandolfi, P. Nitti, M. Rollini, F. Molinari, *J. Mol. Catal. B: Enzym.* 17 (2002) 235;
(d) R.N. Patel, *Stereoselective Biocatalysis*, Marcel Dekker, Inc., New York, 2000, p. 347.
- [24] (a) P.J. Maure, M.J. Miller, *J. Am. Chem. Soc.* 105 (1983) 240;
(b) S. Henrot, M. Larcheveque, Y. Petit, *Synth. Commun.* 16 (1986) 183;
(c) N. Choy, P. Ma, S. Masamune, *Tetrahedron Lett.* 22 (1981) 3555.