



An efficiently cobalt-catalyzed carbonylative approach to phenylacetic acid derivatives



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ARTICLE INFO

Article history:

Received 12 March 2013

Received in revised form 18 June 2013

Accepted 24 June 2013

Available online 29 June 2013

Keywords:

Cobalt complex

Carbonylation

Phenylacetic acid derivatives

Scale-up experiment

Theoretical computation

ABSTRACT

A highly efficient cobalt-catalyzed carbonylative approach to phenylacetic acid derivatives under one atmosphere pressure is reported. This methodology represents a useful extension of benzimidazole used as ligand in metal catalysis, and the catalytic mechanism has been proved by computer simulation. Notably, this new cobalt precatalyst, which promotes the carbonylation reaction dramatically and has already been used for scale-up experiment of phenylacetic acid derivatives.

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1. Introduction

Phenylacetic acid derivatives are fundamental building blocks of a wide number of pharmaceutical compounds,¹ such as diclofenac, carbenicillin, vancomycin, or ibuprofen, and display significant biological activity (Fig. 1). Thus far, carbonylation reaction was recognized as the best approach to phenylacetic acid derivatives.² Unfortunately, the majority of the effective catalysts are precious metal complexes.³ These catalysts are limited in their substrate

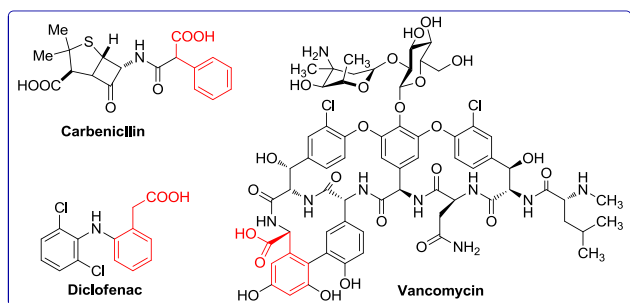


Fig. 1. Sampling of pharmaceuticals containing the phenylacetic acid core.

scope and often require forcing conditions. At present, the study of carbonylation reaction in a mild, broad manner, using efficient and low-cost catalysis represents a major challenge in the field.⁴

Previously reports indicated that cobalt seems to be an appropriate substitute for precious metal in this reaction.⁵ It is well known that various electron rich ligands have been proved usefully to enhance the catalytic activity by increasing the electron density of the metal center for carbonylation.⁶ Especially, benzimidazole derivatives are the electron rich ligand, and play important roles in maintaining the dimensionality of the structure and providing supramolecular recognition sites for π - π aromatic stacking interactions.⁷ Based on these properties, we have selected Co as the metal center and 2-(1*H*-benzimidazol-2-yl) benzoic acid as the ligand, gained an excellent cobalt catalyst $\text{Co}(\text{L1})_2(\text{H}_2\text{O})_2$ (**Cat.1**, CCDC: 922827), the structure of the crystal is shown in Fig. 2.

This unprecedented and ideal Co-catalyst not only shows great activity in the carbonylation of benzyl chlorides with carbon monoxide to generate phenylacetic acids under facile conditions, and also offers a wide application prospect due to its significantly lower cost, wider substrate scope, and greater commercial availability, when compared to previously reported methods.

2. Result and discussion

The catalytic performance of a series of transition metal complexes was investigated in the carbonylation of benzyl chloride (Table 1, entries 1–18). The data demonstrated that several ligands

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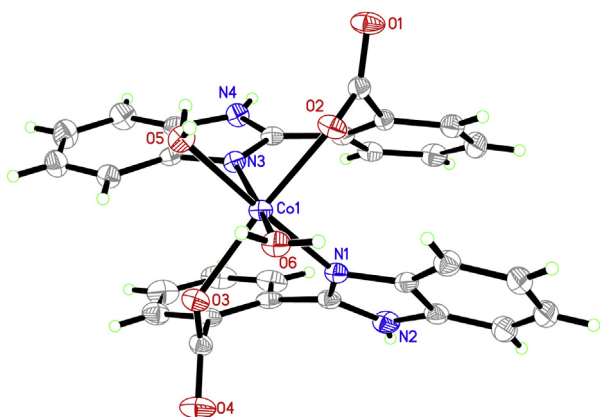


Fig. 2. X-ray crystal structure of $\text{Co}(\text{L}1)_2(\text{H}_2\text{O})_2$.

Table 1
Results of various cobalt catalysts in the carbonylation^a

Entry	Catalyst	Yield (%)
1	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0
2	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	33
3	$\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	30
4	$\text{Co}_2(\text{CO})_8$	47
5	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{ben}^b$	20
6	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{pic}^b$	42
7	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{bipy}^b$	35
8	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{PPh}_3$	33
9	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{L}1^c$	60
10	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{L}2^c$	48
11	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{L}3^c$	40
12	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{L}4^c$	41
13	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{L}5^c$	42
14	$\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}/\text{L}1$	0
15	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}/\text{L}1$	0
16	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}/\text{L}1$	21
17	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{L}1$	0
18	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{L}1$	19

^a Reaction conditions: catalyst (0.5 mmol), benzyl chloride (10 mmol), CO (1 atm), NaOH (15 mL, 15%), in 20 mL *n*-Butyl alcohol at 60 °C for 22 h.

^b ben=benzimidazole; pic=picolinic acid; bipy=2,2'-dipyridyl.

^c L1=2-(1*H*-benzimidazol-2-yl) benzoic acid. L2=2-(1*H*-benzimidazol-2-yl) phenol. L3=2-(1-(pyridin-2-ylmethyl)-1*H*-benzo[d]imidazol-2-yl) aniline. L4=2-(1*H*-benzo[d]imidazol-2-yl)-*N*-(pyridin-2-ylmethyl) aniline. L5=*N*-(pyridin-2-ylmethyl)-2-(1-(pyridin-2-ylmethyl)-1*H*-benzo[d]imidazol-2-yl) aniline.

are applicable for this transformation. Notably, benzimidazole based cobalt catalyst **Cat.1** showed superior activity in the series of complexes (Table 1, entry 9). And compared with our previous work⁸ using the benzothiazole Co catalyst, which could hardly get expected products, the introduction of benzimidazole ligand promoted the carbonylation reaction dramatically.

In order to further optimize the reaction conditions, **Cat.1** was chosen as the standard catalyst owing to its highly efficient and reaction conditions. Screen of various solvents revealed that *n*-Butyl alcohol was the most effective one for the transformation (Table 2, entries 1–5). Later on, the reaction temperature was varied as well, and 60 °C was found to be optimal (Table 2, entries 5–9). In addition, the reaction was significantly improved by using phase transfer catalyst TBAI that affords the product in excellent yield of 84% (Table 2, entries 10–12). Finally, variation the kind and concentration of the base led to inferior results than initial 15% concentration of NaOH (Table 2, entries 13–19). Consequently, **Cat.1** (5 mol %), CO (0.1 MPa), NaOH (15 mL, 15%), PTC (TBAI) in

Table 2
Optimization of the reaction conditions^a

Entry	Solvents	<i>T</i> (°C)	PTC	Base	Yield (%)
1	Dioxane	60	No PTC	15% NaOH	12
2	Toluene	60	No PTC	15% NaOH	35
3	Xylene	60	No PTC	15% NaOH	45
4	Methanol	60	No PTC	15% NaOH	0
5	<i>n</i> -Butyl alcohol	60	No PTC	15% NaOH	53
6	<i>n</i> -Butyl alcohol	40	No PTC	15% NaOH	0
7	<i>n</i> -Butyl alcohol	50	No PTC	15% NaOH	50
8	<i>n</i> -Butyl alcohol	70	No PTC	15% NaOH	38
9	<i>n</i> -Butyl alcohol	80	No PTC	15% NaOH	0
10	<i>n</i> -Butyl alcohol	60	TBAB	15% NaOH	65
11	<i>n</i> -Butyl alcohol	60	PEG-400	15% NaOH	70
12	<i>n</i> -Butyl alcohol	60	TBAI	15% NaOH	84
13	<i>n</i> -Butyl alcohol	60	TBAI	15% KOH	83
14	<i>n</i> -Butyl alcohol	60	TBAI	15% K_2CO_3	0
15	<i>n</i> -Butyl alcohol	60	TBAI	15% Na_2CO_3	0
16	<i>n</i> -Butyl alcohol	60	TBAI	15% NaHCO_3	0
17	<i>n</i> -Butyl alcohol	60	TBAI	5% NaOH	0
18	<i>n</i> -Butyl alcohol	60	TBAI	10% NaOH	32
19	<i>n</i> -Butyl alcohol	60	TBAI	20% NaOH	7

^a Reaction conditions: catalyst (0.5 mmol), benzyl chloride (10 mmol), CO (1 atm), in solvent (20 mL) for 22 h.

n-Butyl alcohol at 60 °C was chosen as the standard reaction conditions.

Under the optimized reaction conditions, the reaction scope was explored and the results were summarized in Table 3. The data showed that the catalytic protocol allowed good functional group tolerance. A great number of substituted benzyl chlorides can participate well in this new protocol. Benzyl chloride with methyl,

Table 3
Synthesis of various substituted phenylacetic acid catalyzed by the new catalyst^a

Entry	Benzyl chlorides 1	Phenylacetic acids 2	Yield (%)
1	1a	2a	84
2	1b	2b	88
3	1c	2c	85
4	1d	2d	82
5	1e	2e	86
6	1f	2f	82
7	1g	2g	84
8	1h	2h	71
9	1i	2i	80
10	1j	2j	85

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